ABSTRACT BOOK

13TH HELLENIC POLYMER SOCIETY INTERNATIONAL CONFERENCE

12 – 16 December 2021

Live Virtual Event

ABSTRACT BOOK

13^{TH} HELLENIC POLYMER SOCIETY
INTERNATIONAL CONFERENCE
12 – 16 December 2021

INVITED LECTURES

SYNTHESIS, MOLECULAR CHARACTERIZATION AND PHASE BEHAVIOUR OF MIKTOARM STAR COPOLYMERS OF THE ABN=2,3 AND BAN=2,3 SEQUENCES WHERE A IS POLYSTYRENE AND B IS POLY(DIMETHYLSILOXANE)

George Liontos[1], Gkreti-Maria Manesi[1], Ioannis Moutsios, Dimitrios Moschovas, Alexei Piryazev[2], Egor Bersenev[2], Dimitri Ivanov[2], Apostolos Avgeropoulos

[1] Department of Materials Science Engineering, University of Ioannina, Ioannina, Greece
[2] Faculty of Chemistry, Lomonosov Moscow State University, Moscow, Russia

Various novel nanostructures in bulk and thin films can be obtained employing miktoarm star copolymers due to enhanced physical properties, rendering them materials of choice for several applications. The self-assembly of the above mentioned miktoarm stars in thin films is of major importance since they may be possibly utilized in nanotechnology, considering the extensive exploitation of PDMS-based polymers in similar applications. Utilizing anionic polymerization in combination with chlorosilane chemistry novel monodispersed miktoarm star copolymers with varying volume fractions of the $PS(PDMS)_{2,3}$ and $PDMS(PS)_{2,3}$ types were synthesized. All manipulations took place according to the high standards of anionic polymerization leading to well-defined polymers, exhibiting molecular and compositional homogeneity, verified by several molecular characterization techniques such as size exclusion chromatography, vapour pressure/membrane osmometry and proton nuclear magnetic resonance spectroscopy techniques. The thermal characterization was accomplished through differential scanning calorimetry where the two distinctive T_gs at values similar to the respective homopolymers verified the potential microphase separation of the miktoarm star copolymers. The structural behaviour of all miktoarm star copolymers in bulk was studied through transmission electron microscopy and small angle X-ray scattering experiments in order to determine the potential impact on the structure/properties relationship due to the additional arms as well as the different architectures [$PS(PDMS)_{2,3}$ *vs*. $PDMS(PS)_{2,3}$]. Higher flexibility of the PDMS chains, attributed to the increased bond angle in the inorganic backbone chain when compared to the stiffer amorphous PS components and the topological constrains imposed by the complex architecture hold a key role in the final adopted morphology. Apart from the χN product, the obtained nanostructures are affected by the curvature due to the overcrowding effect considering the flexibility of the multiple PDMS arms in the PS-core related copolymers and the stiffness of the PS chains for the PDMS-core miktoarm stars as well as the PS volume fraction.

NEXT GENERATION MULTIBLOCK COPOLYMERS WITH CONCURRENT CONTROL OVER SEQUENCE AND DISPERSITY

Athina Anastasaki

Laboratory of Polymeric Materials, Department of Materials ETH Zurich, HCI G523 8093 Zurich, Switzerland

Controlling monomer sequence in synthetic macromolecules is a major challenge in polymer science and the order of building blocks has already been demonstrated to determine macromolecular folding, self-assembly and fundamental polymer properties. Dispersity is another key parameter in material design, with both low and high dispersity polymers displaying unique properties and functions. However, synthetic approaches that can simultaneously control both sequence and dispersity remain experimentally unattainable. In this talk I will introduce and discuss a simple, one pot, and rapid strategy which enables the synthesis of sequence-controlled multiblocks with on demand control over dispersity while maintaining high livingness, excellent agreement between theoretical and experimental molecular weights and quantitative yields. Key to our approach is the regulation in chain transfer agent activity during controlled radical polymerization that allows the preparation of multiblocks with gradually ascending (?=1.16 →1.60), descending (?=1.66 →1.22), alternating low and high dispersity values (?=1.17 →1.61 →1.24 →1.70 →1.26) or any combination thereof. The enormous potential of our methodology will be further demonstrated through the impressive synthesis of highly ordered pentablock, octablock and decablock copolymers yielding the first generation of multiblocks with concurrent control over both sequence and dispersity.

DESIGN OF WATER-SOLUBLE COPOLYMERS FOR THE DEVELOPMENT OF FUNCTIONAL COATINGS

Georgios Bokias

Department of Chemistry, University of Patras, GR-26504, Patras, Greece

Copolymerization of monomers bearing reactive groups, such as glycidyl methacrylate (GMA) or vinylbenzylchloride (VBC) with functional comonomers is an interesting route to design water-based functional materials and coatings. In fact, the covalent modification of surfaces, as well as the preparation of self-standing films or stable coatings, may be achieved through the reaction of the epoxide group of GMA or the -CH_2Cl group of VBC with adequate reactive groups, such as amines, hydroxyl or carboxyl groups. Apart reactive units, suitable comonomers can be incorporated in the copolymer design, in order to introduce desirable functionalities. Here, we will focus on anionic or cationic comonomers, aiming at two applications. The fist case is the development of antimicrobial coatings based on quaternary ammonium compounds, with potential use in diverse applications, including antifouling applications and air purification systems. The second case is based on cationic copolymers, aiming at the charge inversion of the surface of cotton fabrics. Such a charge inversion is desirable for a controllable, more environmentally-friendly and effective dyeing process of cotton, using reactive dyes.

REVISITING ENTANGLED POLYMER DYNAMICS: NETWORKS AND LOOPS

Dimitrios Vlassopoulos

Iesl, Forth

The invention of the tube model and associated developments of predictive tools for entangled polymer dynamics represent arguably one of the most significant advances in polymer science in the last 50 years. The main macromolecular feature of linear and branched polymers is the presence of free ends which mediate the segmental orientation and tube escape. Recent advances identify the importance of the absence of free ends for the case of ring polymers, where entanglements are manifested as a self-similar stress relaxation modulus rather than the classic rubbery plateau of linear or branched polymers. Here, we discuss two important consequences of the loopy conformation of rings on polymer dynamics: (i) in strong flows which are relevant to processing, rings exhibit distinct features: weaker shear thinning compared to their linear counterparts and stronger strain hardening and unique extension-rate thickening in elongational flows due to interlocking. (ii) adding ring polymers to linear matrices significantly alters the viscoelastic response of the latter, represents a new path for macromolecular reinforcement and constraint release. These results offer new insights into the fundamental mechanisms of polymer dynamics, but also the understanding of biological function (e.g. chromosome territories).

The presented selected results reflect a longstanding international collaboration with T. Chang, M. Kaliva, G. Sakellariou, P. Lutz, N. Hadjichristidis, T. Ge, M. Rubinstein, A. Y. Grosberg, T. O’Connor, G. S. Grest, Q. Huang, O. Hassager, W. Wang, D. Parisi, S. Costanzo, K. Peponaki.

LIGAND-SPECIFIC X-RAY NANO-CONTRAST AGENTS FOR ENHANCEMENT OF BREAST CANCER DETECTION

Kalyan Ramesh[1] Yuzgen Wang[2], Mary Ruscjkowski[2] , Manos Gkikas[1]

[1] University of Massachusetts Lowell, Department of Chemistry, Lowell, Massachusetts 01854, U.S.A.

[2] University of Massachusetts Medical School, Department of Radiology, Worcester, Massachusetts 01605, U.S.A.

X-ray-computed tomography (CT) is considered one of the powerful diagnostic techniques for preclinical and clinical studies due to deep tissue penetration, high resolution, cost effectiveness, rapid scan times and patient comfort. Non-invasive disease detection with pronounced signal enhancement at the site of injury is a great challenge in medicine and allows for detection in early stages. Designing polymer-stabilized metallic nanoparticle (NP) contrast probes for spectral CT imaging that can be statistically discriminated from biological fluids, tissue, and bone (a property that is impossible to achieve with conventional CT), and are empowered by *molecular recognition*, align towards that direction. Although X-ray contrast with high-Z metals has been successfully shown in cells and small animals, the probes usually focus on intravenous imaging with fast clearance, while there are only few cases reporting *disease-targeting NPs* with *prolonged imaging* capabilities. We have established a Team (UML/UMMS) to develop ***ligand-specific X-ray contrast probes based on molecular recognition for breast cancer***, aiming to achieve early disease diagnosis and enhanced detection, at low NP dosages. Our approach combines ***targeting specificity*** with ***photon-counting spectral CT (PCD-CT),*** a state-of-the-art form of spectral CT that allows for visualization of tissue composition based on intensity of signal, which is dictated by *atomic number and density of contrast materials*, and thus is enhanced by metallic NPs. ***Au offers significant advantages towards materials differentiation since its K-edge is 81 vs. 4 keV of Ca, while its density is 19.6 vs. 1.6 g/mL of Ca***. Since X-ray absorption is highly dependent on K-edge and density of materials, we synthesize Au-based nano-contrast agents with high affinity for breast cancer cells and high retention, low toxicity, and CT contrast comparable/higher to FDA-approved iodinated molecules. Our materials are tested *in vitro* and *in vivo* with breast cancer animal models.

ARYL ETHER FREE ION SOLVATING BLEND MEMBRANES FOR ALKALINE WATER ELECTROLYSIS

Valadoula Deimede[1], Maria Makrygianni[1], Stefania Aivali[1], Yifan Xia[2], Mikkel Rykaer Kraglund[3], David Aili[2]

[1] *Chemistry Department, University of Patras, Patras, Greece*
[2] *Energy Conversion and Storage, Technical University of Denmark, Kgs. Lyngby, Denmark*
[3] *Energy Conversion and Storage, Technical University of Denmark,Kgs. Lyngby, Denmark*

Alkaline water electrolysis is a long known technology for hydrogen production via water splitting into hydrogen and oxygen using electrical energy. Hydrogen has been currently recognized as the only viable solution to store multi GW of electrical energy from intermittent renewable energy sources and is essential for the decarbonisation of the transportation and industrial sector.

A new series of aryl-ether free main backbone copolymers containing ion-solvating side PEO and isatin groups (P(IB-PEO)) were prepared via superacid-catalyzed polyhydroxyalkylation (Figure 1) to be used as ion-solvating membranes for alkaline water electrolysis. High molecular weight ion solvating polymers were obtained and mechanically stable membranes were fabricated but their insufficient KOH doping led to low ionic conductivity. We therefore employed PBI, another ion-solvating polymer to develop a new blend system which mitigates the low ionic conductivity and affords good cell performance and good alkaline stability. A detailed physicochemical and alkaline stability investigation of the prepared PBI/PIS-PEO blend membranes was performed. In addition, the blended membranes were tested in an alkaline electrolyzer system.

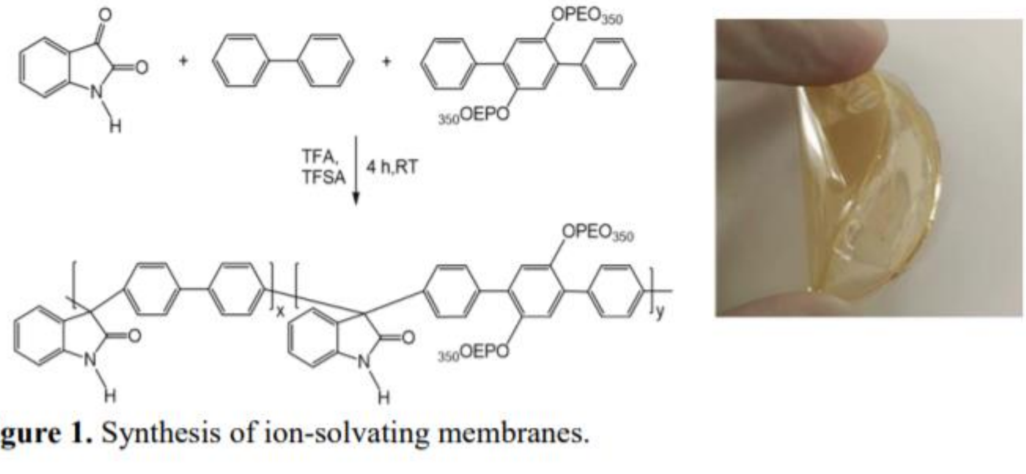


Figure 1. Synthesis of ion-solvating membranes.

Acknowledgements

This work was financially supported by the program NEXTAEC ("Materials for Next Generation Alkaline Electrolyzer", grant agreement no.862509) via the EU program for research and Innovation H2020.

THERMORESPONSIVE POLYMERS BASED ON POLY(L-LYSINE) GRAFTED BY NIPAM

Konstantinos Tsitsilianis[1], **Hermis Iatrou**[2], **Aggeliki Stamou**[3]

[1] *Depeartment of Chemical Enfineering, University of Patras, Patra, Greece*
[2] *Department of Chemistry, University of Athens*
[3] *Department of Chemical Engineering, University of Patras*

Thermoresponsive polymers exhibiting lower critical solution temperature (LCST) constitute an important class of macromolecules. The integration of these macromolecules to block-type segmented polymers, e.g., block copolymers or terpolymers of any macromolecular architecture (linear, star, graft etc.) can lead to pH/thermo-responsive "smart" self-assemblies that could be used as nano carriers and/or 3D networks (scaffolds) towards potential bio-applications.[1] In this presentation examples of such polymeric materials incorporated PNIPAM segments will be demonstrated. PNIPAM however is not entirely non-toxic and more importantly it is not biodegradable which render it not acceptable for real biomedical applications. To overcome this problem, we suggest a peptide-based polymer resulted by partial modification of Poly(L-lysine) (PLL) with NIPAM moieties via the free-catalyzed aza-Michael addition reaction at room temperature. The resulted PLL-g-NIPAM exhibited LCST-type thermosensitivity which can be tuned by the NIPAM content, incorporated in the macromolecule. Importantly, depending on the NIPAM content, the LCST is highly affected by pH and ionic strength.

ION MOBILITY IN PHOTOSENSITIVE POLYMERIC FILMS INCORPORATED AS DIELECTRICS IN ELECTRONIC DEVICES AND POTENTIAL APPLICATIONS

Charalampos Katsogridakis[1], Eleftherios Kapetanakis[2], Antonios M. Douvas[3], Kyriaki G. Papadokostaki[3], Dimitra Dimotikali[1], Pascal Normand[3], Panagiotis Argitis[3]

[1] School of Chemical Engineering, National Technical University of Athens
[2] Department of Electronic Engineering, Hellenic Mediterranean University
[3] Institute of Nanoscience and Nanotechnology, NCSR 'Demokritos'

Polymeric films are extensively investigated as components of devices in the area of organic electronics. The most attention is devoted to polymers that are proposed as semiconductors in devices such as organic light emitting devices, photovoltaics and field effect transistors. Nevertheless, the introduction of polymers as dielectrics has also attracted considerable attention. In one approach photosensitive polymeric films are employed as gate dielectrics of silicon transistors. Following irradiation, mobile ions can be generated inside the polymeric dielectric giving rise to dramatic changes in the transistor characteristics. Such an approach was presented by our group few years ago, where the incorporation of photosensitive sulfonium salts in the polymeric film was proposed as a route for developing radiation detectors [1].

In the current presentation the incorporation of photosensitive polymeric films as dielectrics in organic semiconductor devices and approaches towards the development of sensors or other analytical applications are discussed. The device architectures already explored include two-terminal [2] and three-terminal devices. The organic semiconductor used is p-type, and in particular p3HT (poly 3-hexyl thiophene), enabling the movement of the photosensitive sulfonium salt anions towards the organic semiconductor film at time domains suitable for the observation of changes in the electrical characteristics of the device. It has been shown that these changes are correlated to exposure dose, type of photosensitive salt, type of polymer matrix and processing conditions for the preparation of the polymeric dielectric. Possibilities for developing radiation sensors or for the investigation of ion mobility and reaction kinetics in polymeric films that could serve as photoresists will be presented. In addition, this investigation paves the way for developing organic semiconductor based chemical sensors for analyzing ionic species in solution.

1. E. Kapetanakis et al.,ACS Applied Materials & Interfaces, 05, 5667-5674, 2013.

2. E. Kapetanakis et al., Adv. Electron. Mater. 6, 2000238, 2020.

DESIGNING ALL-POLYMER NANOSTRUCTURED ELECTROLYTES FOR ENERGY STORAGE

Emmanouil Glynos

Department of Chemistry, University of Crete, Institute of Electronic Structure and Laser,
Foundation for Research and Technology – Hellas, Greece

Solid polymer electrolytes (SPEs) could be a real “game-changer” as they represent the ultimate solution to the safety issues associated with the use of flammable and toxic liquid electrolytes in commercial Li-ion batteries. Most importantly, SPEs hold the key for the realization of high energy-density Li-metal batteries, as they are chemical stable towards Li metal while their mechanical resistance could reduce, or even suppress Li dendrite formation and eliminate the associated safety hazards and the catastrophic failure of the battery. Despite the considerable research effort in SPEs, the development and realization of their potential has been hampered by the inability to design materials that possess simultaneously, high ionic conductivity, good mechanical properties, and cation transference number close to unity (i.e. single-ion solid polymer electrolytes). In this talk, we will present a new material platform based on the principles of macromolecular engineering/design that provides new opportunities for the synthesis of all-polymer nanostructured SPEs with properties to levels not accessible before by conventional linear polymer systems.

Acknowledgment: This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness and innovation, under the call RESEARCH –CREATE –INNOVATE (project code: T1EΔK-02576, MIS5033805)

PHOTO-SENSITIVE NANO-VEHICLES FOR DRUG DELIVERY

Maria Vamvakaki[1], Maria Psarrou[1], Theodore Manouras[1], Ioanna Peraki[2]

[1] Department of Materials Science and Technology, University of Crete, Heraklion, Greece and Institute of Electronic Structure and Laser (IESL), Foundation of Research and Technology-Hellas (FORTH), Crete, Heraklion, Greece

[2] Institute of Molecular Biology and Biotechnology, Foundation of Research and Technology-Hellas (IMBB-FORTH), Heraklion, Greece

Near-Infrared (NIR) light has emerged as a powerful tool for on demand drug release offering deep tissue penetration and minimum damage to healthy cells. NIR-sensitive nanocarriers reported to date employ upconverting nanoparticles or two-photon absorption processes.[1] Herein, a novel low-power, NIR-photoactivated drug release process is proposed, based on the encapsulation of two non-toxic organic molecules, a NIR-photosensitizer (NIR-PS) and a photoacid generator (PAG) which absorbs in the UV region, within the cores of acid-degradable PEG-*b*-polyacetal copolymer micelles. Degradation of the nanocarriers is induced by the acid-catalyzed cleavage of the acetal bonds, along the main chain of the polyacetal block, by acid molecules generated via an electron transfer process from the exited NIR-PS to the PAG.

The PEG-*b*-polyacetal copolymers were synthesized via a two-step process: first the acid-catalyzed polycondensation of 1,4-benzenedimethanol with divinyl ether, followed by end-capping with monohydroxy-terminated PEG at the vinyl chain ends.[2] Spherical micelles loaded with PAG/NIR-PS were prepared in water using NIR-PSs with appropriate HOMO-LUMO energy states to facilitate the electron transfer process. The proposed photoactivation mechanism was verified for three irradiation wavelengths, which correspond to the absorption maxima of the NIR-PS molecules, at 440, 510 and 808 nm, and the release of the cargo was monitored by measuring the absorption of the NIR-PS *vs* the irradiation time. Micelles loaded with the NIR-PS, PAG and the model anticancer drug, camptothecin, exhibited significant cytotoxicity (88%) following NIR irradiation, verifying the *in vitro* efficiency of the drug delivery system.

References

1. Karimi, M., et al. *J. Am. Chem. Soc.* **139,** 4584-4610, (2017).
2. Pasparakis, G., et al. *Nat. Commun.* **5,** 3623 (2014).

Acknowledgements

This research has been cofinanced by the European Maritime and Fisheries Fund (EMFF) of the European Union and Greek national funds through the Operational Program Fisheries and Maritime, under the call INNOVATION IN AQUACULTURE (MIS: 5029684).

PROTEIN-POLYMER NANOCARRIERS: DESIGN, SYNTHESIS AND APPLICATIONS

Kelly Velonia

Department of Materials Science and Technology, University of Crete, Heraklion, Crete, Greece

Proteins represent a unique class of biomaterials critical in all key processes of life. With the exception of PEGylated proteins, protein-based biomaterials remain largely understudied due to the instability and inherent immunogenicity of native proteins. A key approach toward protein-based biomaterials involves the synthesis well-defined protein-polymer conjugates which the conventional synthetic methodologies mostly fail to address. To this end, novel oxygen tolerant, controlled radical polymerization approaches that readily afford quantitative yields of well-defined protein-polymer conjugates will be discussed.[1,2,3] Following such approaches, diverse monomer classes including acrylates, methacrylates, styrenics and acrylamides can be utilized to produce a wide variety of bioconjugates within short periods of time (minutes to hours), in the absence of any additives or external deoxygenation procedures using no or low organic content media and ppm levels of copper.[1,2,3] Importantly, it will be shown that these new methodologies are compatible with multiple proteins and enzymes without damaging their secondary structure or catalytic profiles. To exemplify the robustness of these protocols, implementation under different light sources and reaction media as well as by the ability to tune polymer grafting through varying the reaction components will be presented. Special focus will be given to novel families of responsive and amphiphilic protein-polymer conjugates which were synthesized following these approaches in quantitative yields, forming hybrid nanostructures with a broad range of potential applications.[4]

References

1. Theodorou, A., Liarou, E., Haddleton, D.M., Stavrakaki, I. G., Skordalidis, P., Whitfield, R., Anastasaki, A., Velonia *Nat. Commun*. **2020**, *11*, 1486.
2. Theodorou, A., Mandriotis, P., Anastasaki, A. Velonia, K. *Polym. Chem*., **2021**, *12*, 2228-2235.
3. Theodorou, A., Gounaris, D., Voutyritsa, E., Andrikopoulos, N., Anastasaki, A., Velonia, K. **2021**, *submitted.*
4. Papadimitriou, L., Theodorou, A., Papageorgiou, M., Papagiannaki, A., Velonia, K., Ranella, A. **2021**, *submitted.*

Keywords: bioconjugates; protein polymer conjugates; biopolymers; nanoparticles; catalysis; delivery

TOPOLOGICAL INTERACTIONS IN MELTS OF RING POLYMERS AND THEIR EFFECT ON DYNAMIC AND RHEOLOGICAL PROPERTIES

Dimitrios G. Tsalikis[1], Vlasis G. Mavrantzas[2]

[1]Department of Chemical Engineering, University of Patras and FORTH-ICE/HT, GR 26504, Patras, Greece
[2]Particle Technology Laboratory, Department of Mechanical and Process Engineering, ETH Zürich, CH-8092 Zürich, Switzerland

Ring polymers lack chain ends, thus their physicochemical properties (structural, dynamic and conformational) can be very different from those of their linear counterparts. Experimentally, it has already been demonstrated through the seminal work of Kapnistos et al. [1] that pollution of ring melts with linear chains can dramatically influence their rheology. It is also true that synthesizing pure ring polymers in large quantities is quite challenging, thus we are in the need of microscopic insight from simulations. Synthetic ring polymers are also model systems for understanding the behavior of more complex ring structures in Nature. We mention, for example, DNA mini-circles and DNA plasmids that are essential to fundamental life processes, playing a key role in DNA replication and maintenance of circular genomes, DNA looping, the design of plasmid-based DNA vaccines and of biologically active macrocycles (such as drugs), even in cancer growth. Guided by all these challenges, our objective in this work is to demonstrate how we can make use of computer simulations in order to get a microscopic picture of conformational, dynamic and mostly topological properties of ring polymer melts, using as a model system ring polyethylene oxide (PEO) melts at $T = 413$ K where a wealth of experimental data exist in the literature regarding their structural and dynamic properties [2, 3]. We wish to compare quantitatively with experimental data and other simulation works (mostly using bead-spring chain models) and carry out a topological analysis based on geometric criteria (vector calculus) which can provide insight into possible topological interactions in such melts due to ring-ring and ring-linear threading events. We will focus on the crossover regime from Rouse to entangled and we will demonstrate that even present at low fractions, linear contamination can dramatically affect the characteristic time scales in the ring polymer melt, creating dynamic heterogeneity and delaying system orientational relaxation. This helped us propose a new model for the shear modulus of relaxation G(t) of a ring melt that can fit experimental data at long times (the so-called slow modes) quite remarkably. We will also present results from detailed nonequilibrium molecular dynamics simulations which reveal that ring polymers under strong shear flow undergo not only tumbling but also a tank-treading type of rotational motion wherein chain segments rotate along the deformed contour of the polymer.

References

[1] Kapnistos, M.; Lang, M.; Vlassopoulos, D.; Pyckhout-Hintzen, W.; Richter, D.; Cho, D.; Chang, T.; Rubinstein, M. Unexpected power-law stress relaxation of entangled ring polymers. *Nat. Mater.* **2008**, *7*, 997-1002.

[2] Gooßen, S.; Bràs, A. R.; Krutyeva, M.; Sharp, M.; Falus, P.; Feoktystov, A.; Gasser, U.; Pyckhout-Hintzen, W.; Wischnewski, A.; Richter, D. Molecular scale dynamics of large ring polymers. *Phys. Rev. Lett.* **2014**, *113*, 168302.

[3] Gooßen, S.; Krutyeva, M.; Sharp, M.; Feoktystov, A.; Allgaier, J.; Pyckhout-Hintzen, W.; Wischnewski, A.; Richter, D. Sensing polymer chain dynamics through ring topology: A neutron spin echo study. *Phys. Rev. Lett.* **2015**, *115*, 148302.

PREDICTION OF CROSSLINKING KINETICS AND VISCOELASTIC PROPERTIES OF TYRAMINE FUNCTIONALIZED HYALURONIC ACID CROSS-LINKABLE SOLUTIONS USING STOCHASTIC AND DETERMINISTIC COMPUTATIONAL METHODS

Filippos Karageorgos, **Costas Kiparissides**

Certh/Cperi & Auth

In the present study, advanced mechanistic and stochastic dynamic models are developed to describe the crosslinking kinetics of tyramine-modified Hyaluronic Acid (HA-Tyr) solutions mediated by horseradish peroxidase (HRP) - hydrogen peroxide (H_2O_2) initiation system. Two different modelling approaches, namely a deterministic model and a stochastic multi-dimensional Monte Carlo approach, are developed to quantify the effects of crosslinking conditions (e.g., polymer concentration, HRP and H_2O_2 concentrations) on the gelation onset time, evolution of molecular weight distribution of the cross-linkable polymer chains, sol and gel fractions. In the deterministic modelling approach, the method of moments is applied to derive a system of differential equations describing the conservation of all molecular species in the reactive system. This method can provide information on the dynamic evolution of all reactive species concentrations as well as the number and weight average molecular weights of the polymer chains. In the stochastic approach, two Monte Carlo (MC) models are presented, based on Gillespie's algorithm, to describe the dynamic evolution of a finite sample of cross-linkable polymer chains and calculate the evolution of molecular weight distribution of polymer chains in both the pre- and post-gelation regimes. The first MC model assumes that each polymer chain is characterized by three internal variables (i.e., degree of polymerization, the number of residual tyramine groups, and number of crosslinks). The second MC model includes an additional forth internal variable (i.e., the number of activated tyramine groups) to characterize a HA-Tyr polymer chain. The three derived models are validated using experimental measurements on crosslinking kinetics of a HA-Tyr system reported in the literature. Finally, it is shown that using the MC model predictions (number of crosslinks, etc.) the viscoelastic properties (i.e., the value of plateau storage modulus (G') and time required to reach the plateau value) can be predicted. Model predictions are successfully compared with reported experimental measurements on the evolution of viscoelastic properties of HA-Tyr cross-linkable system.

GREEN POLYMERIC MATERIALS FROM RENEWABLE RESOURCES: POLY(ALKYLENE 2,5-FURANDICARBOXYLATE)S

George Papageorgiou

Department of Chemistry, University of Ioannina, 45110, Ioannina, Greece

Concerns regarding depletion of fossil resources, disposal-related issues, and government policies, have led to growing interest in green, sustainable and safe environmentally-friendly plastic materials from renewable resources. The first approach towards green plastics is associated with the biorefinery concept, applying sustainable processes, and using biomass feedstocks. Renewable polymers are isolated from natural biopolymers or synthesized from biobased monomers. Carbohydrates such as cellulose, lignin, terpenes, proteins, and biopolyesters can be chemically modified. Thus, traditional (drop-in) monomers and platform chemicals from renewable resources can be synthesized, e.g. ethylene, propylene, or butadiene can be produced from bioethanol. Diols, such as ethylene glycol, 1,3-propanediol, 1,4-butanediol, and polyols, diacids, etc., are also available and traditional polymers, like polyethylene, polypropylene and poly(ethylene terephthalate) are considered biobased. In addition, novel biobased polymers have gained increasing interest. Organic acid monomers from biomass including glycolic, 3-hydroxypropionic, lactic, succinic, vanillic, and 2,5-furandicarboxylic acids, and important alcohol monomers such as isosorbide, xylitol, sorbitol, glycerol can be derived from sugars. Recent research has shown that synthetic polymers can be synthesized within living cells. Finally, green polymers can be produced by activating and polymerizing carbon dioxide. Poly(ethylene 2,5-furandicarboxylate) (PEF) is the biobased alternative to the 'giant' of the polymer industry poly(ethylene terephthalate) (PET). It can be synthesized from 2,5-furandicarboxylic acid (FDCA), which can be produced from 5-Hydroxymethyl-Furfural (HMF). 5-HMF is readily available from sugars like fructose. PEF shows higher gas barrier, thermal and mechanical properties compared to PET. The industrial production of PEF is associated with reduced non-renewable energy use, low carbon footprint and atom economy. In this work poly(alkylene 2,5-furandicarboxylate)s based on FDCA and a series of aliphatic diols or 1,4-cyclohexanedimethanol were synthesized and their thermal properties and crystallization were studied. Random copolymers were synthesized to increase biodegradability. Blends of PAFs were also studied, especially with terephthalic acid (TPA) polyesters.

ADSORPTION KINETICS OF *CIS*-1,4-POLYISOPRENE IN NANOPORES BY *IN SITU* NANODIELECTRIC SPECTROSCOPY

Chien-Hua Tu[1], **George Floudas**[1,2]

[1] *Max Planck Institute for Polymer Research, Mainz, Germany*

[2] *University of Ioannina, Dept. of Physics, Ioannina, Greece*

Herein we address the question of how macromolecules penetrate narrow pores relevant in several applications. In particular, we follow the polymer dynamics *in situ* at the chain length scale by studying the evolution of normal modes in the type A polymer (according to Stockmayer's classification) polyisoprene (PI) during imbibition in nanopores. The specific scientific question we address is, *if* and *how*, adsorption affects the imbibition kinetics of polymers. This question, despite of importance in the design of membranes/devices, has not been addressed so far. It requires precise measurements of polymer dynamics *during* flow. Herein we follow the details of polymer imbibition *in situ* by employing the *nanofluidic* method. The latter provides simultaneous access to (i) the kinetics of imbibition, (ii) the molecular dynamics and (iii) the viscosity experienced by the polymer during flow. Results show that polymer imbibition proceeds in two time-regimes with *higher* effective viscosity than in bulk. We discuss this finding with the help of a microscopic picture that considers the competition from an increasing number of chains entering the pores and a decreasing number of fluctuating chains with time. The latter provide unambiguous evidence for increasing adsorption sites during flow. In a second step we investigate the imbibition of PI blends in the same nanopores. We show that a homogeneous mixture composed of long and short PI chains phase separates on entering the pores by the different imbibition speeds of the respective chains and evaluate the dynamics at the chain length scale.

The work is supported by the by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the "First Call for H.F.R.I. Research Projects to support Faculty members and Researchers and the procurement of high-cost research equipment grant" (Project Number: 183).

TUNING COLLOIDAL GELS BY SHEAR: A PARADIGM TO MANIPULATE METASTABLE SOFT MATTER SYSTEMS

Georgios Petekidis

Department of Materials Science and Technology, University of Crete, Institut of Electronic Structure And Laser, Foundation for Research and Technology - (FORTH), Heraklion, Crete, Greece

Attractive colloids form out-of-equilibrium states such as colloidal gels and attractive glasses, which often exhibit strong thixotropy. Their mechanical properties are affected by pre-shear history and show a time evolution after nonlinear steady or oscillatory shear tests due to shear induced structural changes and subsequent restructuring and stress relaxation after shear cessation. Both in model and industrial systems such preshear protocols can be used to enable fine-tuning of the structure and mechanical properties. In fact such systems may be driven in different metastable states, possibly, not accessible via a thermodynamic route, i.e. changing interactions or volume fraction.

Here we present a variety of experiments (combining rheometry and confocal microscopy) and computer simulations on colloidal gels with different attraction strengths and volume fractions both for spherical or rod-like particles as building blocks. We follow microstructural changes at the single particle and the cluster level during yielding induced either by steady or by oscillatory shear. In the latter we distinguish between reversible and irreversible rearrangements of single particles (spheres or rods) or clusters as a function of strain amplitude and frequency, and relate them with the rheological response and final mechanical properties of the gel. We thus demonstrate how steady or oscillatory shear is able to tune the gel structure (both local density and orientational order) and how this is linked with the mechanical properties of the sample. These studies may be used as an example for potential use of external fields such as shear to manipulate of a more general class of metastable soft matter systems.

MOLECULAR MOBILITY IN SEMI-CRYSTALLINE POLYMER NANOCOMPOSITES: DISENTANGLING THE IMPACT OF NANOPARTICLES AND CRYSTALLINITY

Apostolos Kyritsis[1], Dimitrios Bikiaris[2], Panagiotis Klonos[1]

[1] Physics Department, National Technical University of Athens, Athens, Greece
[2] Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece

Polymer nanocomposites (PNCs) are intensively investigated during the last decades because they offer the possibility of developing materials with enhanced, or even new properties due to the presence of the nanoparticles (NPs) or the modification of the polymer matrix. It is widely accepted, that in semi-crystalline PNCs, the molecular mobility, which is one of the factors that control the PNC properties, is strongly affected by both the nanoparticles (NPs) and the crystalline domains. Taking into consideration that the presence of NPs modifies the crystalline domains, it is obvious that the prediction of the features of molecular mobility in semi-crystalline PNCs is not a trivial task.

In this work, we employ Broadband dielectric spectroscopy as the basic tool to study molecular mobility (local, segmental) in various semi-crystalline polyesters in conjunction with Differential scanning calorimetry studies on phase transitions and crystallinity. In particular, the investigation involves three categories of renewable/ecofriendly polyesters, the traditional polylactides, poly(ε-caprolactone) and, the more advanced, poly(alkylene furanoate)s. The polymers are reinforced by various inorganic NPs, differing in dimensionality (nanotubes, nanoplatelets, spherical nanoparticles) and surface chemistry, including modifications. Depending on the degree of interfacial interactions, the filler aspect ratio and the surface area, the segmental mobility (α relaxation) is either accelerated or retarded, while at the same time the number of mobile polymer segments mainly drops. However, the most dominant effects on mobility are the indirect ones, arising from the formation of crystals which generally slow down the dynamics and suppress the fraction of the mobile chain segments. The impact of the strength of polymer-NP interactions on the crystallization process, in terms of nucleation efficiency, crystal growth and crystallization kinetics, is also discussed.

METAL OXIDE/POLYMER NANOCOMPOSITES AND LITHOGRAPHIC PATTERNING

Margarita Chatzichristidi[1], **Eleni Makarona**[2]

[1] Laboratory of Industrial Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Zografou GR-15771, Greece
[2] Institute of Nanoscience and Nanotechnology, NCSR "Demokritos", Aghia Paraskevi GR-153 10, Greece

Polymer nanocomposites have emerged as a new powerful class of materials that can be used as the functional core of novel micro/nano-electronic devices [1]. Towards that goal, intense research effort has been focusing on the successful incorporation of nano-sized fillers into polymers with particular emphasis on their development and use as new resist materials or sensing elements [2,3]. On the other hand, metal oxide nanostructures and nanoarchitectures have been finding their way into a plethora of applications ranging from optoelectronic to sensing devices, catalysis and photovoltaics. Hydrothermal and solvothermal synthesis and growth techniques used for their production have gained significant popularity, since they are an inexpensive and relatively facile means to obtain -through tuning of simple parameters- 3-dimensional nanostructures characterized by structural complexity, hierarchy and multiple functionalities.

In this work, we will firstly present a relatively facile and cost-efficient approach for the creation of CuO/PMMA nanocomposites as a novel Electron Beam Lithography (EBL) resist material. The CuO nanofillers have been synthesized via a low-cost solution-based method, which offers a high degree of design versatility through simple key parameters. The produced nanocomposites were evaluated as positive tone EBL resists, while the studies were complemented by micro-X-ray fluorescence spectroscopy (µXRF) so as to investigate the miscibility of the nanofillers within the polymer matrix. The second part will discuss how optical lithography and hydrothermal techniques producing CuO and NiO nanoarchitectures can be merged to produce meaningful structures that can become the core elements of novel devices. Challenges and future perspectives will be discussed.

-

References:

A. 1.L. S. Schadler, L. C. Brinso & W. G. Sawyer, *JOM* **59**, 53 (2007)
B. 2.L. Merhari et al., *Microelectronics Engin.* 63, 391–403 (2002)
C. 3.S. Botsi et al., *Nano-Structures & Nano-Objects* **17**, 7 (2019)

MECHANISTIC STUDIES ON TYPE II BICHROMOPHORIC PHOTOINITIATOR SYSTEMS

Michael Siskos

Department of Chemistry, University of Ioannina, Section of Organic Chemistry and Biochemistry, University of Ioannina, Ioannina, 45110, Greece

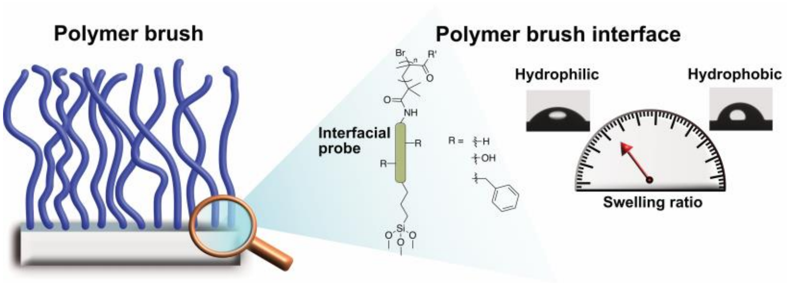
Photoinitiated radical polymerizations are usually carried out in the presence of a photoinitiator, which constitute the most crucial component of the photopolymerization system. It absorbs light and generates the active radicals to initiate the polymerization reaction. According to their radical generation mechanism, photoinitiators are divided into two main categories. The direct *a*-cleavage-type (Type I) and the hydrogen abstraction or electron transfer followed by proton transfer type (Type II) initiators. The typical type II photoinitiators are two-component photoinitiating systems, which usually are include an aromatic carbonyl molecule (aromatic ketones or structurally related compounds) and a coinitiator acting as hydrogen or electron/proton donor (e.g., a thiol or an amine). After triplet-state excitation, the aromatic ketone can abstract hydrogen from the co-initiators generated the reactive center on donor molecule which initiate the free radical polymerization process.

In this contribution, we synthesized, studied photophysically/photochemically and theoretically, type II bichromophoric photoinitiator systems which are proposed as an alternative class of high performance photoinitiators for the polymerization (scheme 1). The involved chemical mechanisms, the excited state processes are investigated by laser flash photolysis, UV-*vis*, fluorescence spectroscopy and steady state photolysis experiments. Finally, these studies are supported by DFT calculations.

POLYMER BRUSH SWELLING AND THE ROLE OF INTERFACIAL PHENOMENON

Kuljeet Kaur, Harm-Anton Klok

Polymer brushes consist of densely grafted polymer chains tethered to a surface. When swollen in a good solvent, they acquire a stretched chain conformation away from the substrate, which imparts them with unique properties. Swollen polymer brushes are suitable candidates for several functional surface applications such as adhesives, sensors, lubricants, and anti-biofouling coatings. However, solvent exposure can also result in instabilities in the polymer brush films leading to detachment or delamination. This is believed to be a result of hydrolysis of ester, amide, and, siloxane bonds at the brush-substrate interface that are amplified by solvent- induced stretching of polymer chains.[1,2] While the effects of polymer molecular weight and composition, grafting density, and nature of the solvent on the swelling of polymer brushes are well studied, the role of thebrush-substrate interface is less known, partly due to limited chemistries available for interfacial modification. In this talk, I will present a design of a library of probes that can be inserted at the polymer brush interface and allow for systematic modulation of interfacial properties. These probes impart hydrophilic or hydrophobic characteristic to the interface depending on the functional groups involved. I will show that the polymer brush swelling and degrafting is sensitive to chemical structure of the interfacial anchoring groups. Furthermore, I will discuss the scope of application of these probes in both hydrophobic and hydrophilic polymer brush systems, and how they can help us better understand the interfacial phenomenon in polymer brushes.



1 N. C. Ataman and H. A. Klok, *Macromolecules*, 2016, **49**, 9035–9047.
2 J. Wang and H. A. Klok, *Angew. Chemie - Int. Ed.*, 2019, **58**, 9989–9993.

WHAT LIMITS THE EFFICIENCY IN ORGANIC SOLAR CELLS AT NEGLIGIBLE ENERGY LEVEL OFFSETS?

Christos Chochos[1], Vasilis Gregoriou[2], Andrej Classen[3], Larry Lüer[3], Jonas Wortmann[3], Andres Osvet[3], Karen Forberich[3], Thomas Heumueller[3], Iain McCulloch[4], Christoph J. Brabec[3]

[1] *Institute of Chemical Biology, National Hellenic Research Foundation*
[2] *National Hellenic Research Foundation*
[3] *Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander University Erlangen-Nürnberg*
[4] *KAUST Solar Center (KSC), King Abdullah University of Science and Technology (KAUST)*

Introduction: Organic solar cells (OSC) utilize an energy level offset (E_{offset}) to generate free charge carriers. While a very small E_{offset} increases the open-circuit voltage, which is the key requirement to reach higher efficiencies, it typically yields poor charge generation. Thus, it raises the question of which factors limit OSCs with well-matched energy levels. Therefore, it is critical to quantify the factors limiting device operation at very small E_{offset}.

Methods: *Materials*: $PC_{70}BM$ was purchased from Solenne. ITIC was purchased from 1-Material. o-IDTBR was purchased from Flexink. eh-IDTBR was purchased from 1-Material. Y6 was purchased from Derthon OPV. WF3, WF3S, WF3F, WF3FS were synthesized in-house at Advent Technologies Inc.

Results: In this work, we address this question by investigating a representative number of blends consisting of conjugated polymers as the electron donors and non-fullerene materials as the electron acceptors, with offsets in their highest occupied molecular orbital energies (ΔE_{HOMO}) between 0 – 300 meV. At negligible ΔE_{HOMO} we detect ultra-slow exciton splitting with lifetimes up to 1300 ps, which reaches or even exceeds the pristine materials´ exciton lifetimes. This drastically limits charge generation, and we demonstrate a strong correlation between the exciton splitting efficiency and the external quantum efficiency (EQE). Based on these experimental findings, we postulate a very long exciton lifetime as the key parameter to maintain efficient device operation at negligible ΔE_{HOMO}.

References:

1. A. Classen, C. L. Chochos, L. Lüer, V. G. Gregoriou, J. Wortmann, A. Osvet, K. Forberich, I. McCulloch, T. Heumueller, C. J. Brabec, *Nat. Energy* **2020**, *5*, 711 - 719.
2. N. Gasparini, F. V. A. Camargo, S. Frühwald, T. Nagahara, A. Classen, S. Roland, A. Wadsworth, V. G. Gregoriou, C. L. Chochos, D. Neher, M. Salvador, D. Baran, I. McCulloch, A. Görling, L. Lüer, G. Cerullo, C. J. Brabec, *Nat. Commun.* **2021**, *12*, 1772.

CURRENT CHALLENGES IN POLYMER RECYCLING

Dimitrios S. Achilias

Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece ·

The two major challenges of humanity today are the fight against the pandemic and the protection of the environment. Concerning the latter, one of the great concerns is the successful management of plastic wastes and particularly plastic packaging. In 2020, from the collected post-consumer plastic packaging (17.8 million tones), 42% was recycled 39.5% was used for energy recovery and 18.5 % was landfiled. Most of the waste was recycled mechanically, and only very limited volumes (less than 0.1 million tonnes) were treated by chemical recycling processes (PlasticsEurope, 2020). To achieve the circular economy for plastics, zero landfilling is needed. Therefore, the amount of polymers recycled should be greatly increased. Europe is the leading area on regulations. In 2015, the European Commission adopted the Circular Economy Action Plan which included goals to increase the recycling of the packaging waste and to reduce the landfill by 2030 and a more detailed strategy was laid on 2018. The reduction of single-use plastic bags had already been targeted. These increasing regulations and bans against single-use plastics are increasing the demand for biodegradable plastics. However, what will be the impact of bioplastics in the recycling streams of conventional plastics is still under investigation. This is one of the current challenges in polymer recycling. Other, topics of great concern that will be discussed include, removal of additives from conventional plastics, such as brominated flame retardants from WEEE, ink or odours from plastic wastes, methods for the recycling of multilayer plastic packaging and method for converting post-industrial plastic scraps or end-of –lif waste into high quality raw material and therefore contribute to the circular economy.

POLYMER NANOCOMPOSITES: FROM STRUCTURE TO DYNAMICS AND PROPERTIES

Kiriaki Chrissopoulou

Institute of Electronic Structure and LaserFoundation for Research and Technology-Hellas,
Heraklion, Crete, Greece

Addition of nanosized inorganic materials in a polymeric matrix results to nanohybrids with optimized properties with respect to the initial components. Understanding the relationship between the physicochemical attributes of the nanofillers and the host matrix and the final properties of the hybrid is of great importance for the design of new materials with specific functionalities. [1]

In this work we investigate the morphology, chain conformations as well as the dynamics and the rheological properties of nanohybrids composed of poly(ethylene oxide)s, PEO, of different molecular weights and silica nanoparticles, SiO_2, of different sizes. The nanohybrids were synthesized by dispersing the SiO_2 nanoparticles in the PEO matrices in different compositions. The morphology and crystallization behavior were investigated with X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC). The crystallinity was found to be constant at hybrids with high polymer content whereas it decreased with further increase of the additive. The composition that this decrease starts as well as the way it decreases depends on a combined effect of the degree of the confinement and the chain adsorption capacity. [2] On the contrary, PEO dynamics in the presence of the nanoadditives, measured with Dielectric Spectroscopy, did not show any significant deviation from the respective behavior of the neat polymer. The rheological responce of these series of PEO/SiO_2 nanocomposites was investigated through oscillatory shear rheology measurements seeking to correlate the morphological changes to the rheological response of the materials in an attempt towards better understanding of the structure-properties relation.

Acknowledgements: This research has been co-financed by EU and Greek national funds (INGRECO MIS: 5030174, Action RESEARCH – CREATE - INNOVATE).

[1] Kumar, S. K.; Krishnamoorti, R. *Annu. Rev. Chem. Biol. Eng.* **1,** 37-58 (2010).

[2] Papananou, H.; Perivolari, E.; Chrissopoulou, K.; Anastasiadis, S. H. *Polymer* **157**, 111-121 (2018).

THE DISCOVERY X3 DSC AS A TOOL TO INCREASE PRODUCTIVITY IN A QC AS WELL AS IN AN R&D POLYMER LABORATORY

Els Verdonck, Daniël Roedolf

TA Instruments

The Discovery X3 DSC (Figure 1 and Reference 1) is a multi-sample differential scanning calorimeter allowing the simultaneous analysis of up to three samples.

It's based on Tzero technology for measuring heat flow (Reference 2). Including the thermal resistance and capacitance of the sample and reference sensors and heating rate imbalances in the measurement of heat flow largely improve the baseline and heat flow resolution of the DSC. The possibility to perform Modulated DSC is included (Reference 3).

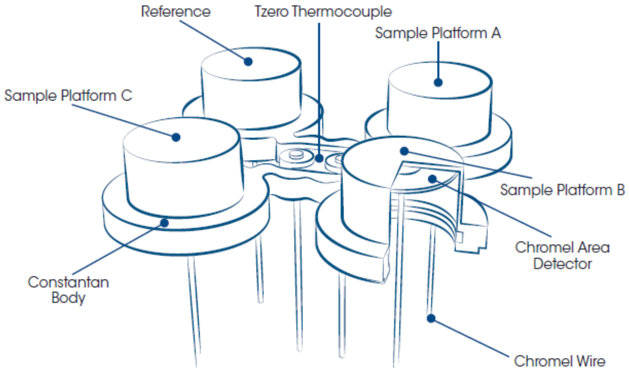


Figure 1. Schematics of the X3 multi-sensor DSC cell

The simultaneous measurement of three samples provides many advantages:

- real-time validation/verification of the data by testing a standard simultaneously with the samples

- 3 times faster generation of statistical datasets: this is important if one is looking at very weak heat flow effects near the limits of the instrumentation

- higher sample throughput

- less bench space and lower consumption of utilities (purge gas, liquid nitrogen for cooler) in comparison to 3 single units

Obviously, the higher throughput is important in a quality control environment where quick follow-up of the production line is important for product release. But in an R&D environment it can be at least equally important to permit the use of more in-depth methodologies that can provide better material characterization.

One example is the use of Modulated DSC, allowing the separation of overlapping heat flow events (Reference 4). Another example is the application of thermal fractionation techniques (SIST, SSA) to reveal subtle differences in molecular architecture (References 5 and 6). These methods have an increased test time with respect to typical DSC tests, and so the ability to run three samples simultaneously mitigates that time impact.

Some examples will be discussed:

- MDSC testing to provide information with respect to the freeze-drying process and stability of the lyophilised product
- MDSC to study compatibility in mixtures of API with excipients
- Thermal fractionation to study differences in crystallizable chain length for PE resins

References

1. US Patent 2020/0064209 A1
2. R.L. Danley, Thermochimica Acta 395 (2003) 201-208.
3. R.L. Danley, Thermochimica Acta 402 (2003) 91-98.
4. E. Verdonck, K. Schaap, L.C. Thomas, International Journal of Pharmaceutics 192 (1999) 3-20.
5. E. Verdonck, S. Heyez, TA300, DSC step annealing for fingerprinting molecular structure in PVDF.
6. P. Davies, TA439, Thermal fractionation techniques for polymer characterization – faster throughput with the Discovery X3 DSC.

ADVANCE YOUR POLYMER GPC CHARACTERISATION BY COMBINING MULTI-DETECTION TO HIGH RESOLUTION SEPARATION

Stefan Cairns

Product Technical Specialist at Malvern Panalytical

In this presentation we will discuss Waters' breakthrough technology the ACQUITY Advanced Polymer Chromatography (APC™), that provides SEC analyses of polymeric materials with higher resolution and higher speed than conventional SEC. The APC system has focused on conventional calibration, meaning it can only generate relative molecular weight information. However, the Malvern Panalytical OMNISEC REVEAL, containing refractive index (RI), UV-Vis photodiode array (UV), light scattering (LS), and differential viscometry detectors can give far more comprehensive details of the sample being studied. Here we present the combination of the Waters APC for high-resolution analysis, reduced run times, reduced solvent consumption and lower sample loading, with the OMNISEC REVEAL to give absolute molecular weight independent of the standard's chemistry and retention volume, compositional analysis of copolymers and, the intrinsic viscosity which when combined with molecular weight gives the Mark-Houwink plot and the ability to compare samples' structure.

ORAL PRESENTATIONS

OP01

COMPLEX STAR ARCHITECTURES OF WELL-DEFINED POLYETHYLENE-BASED CO/TERPOLYMERS

Konstantinos Ntetsikas[1], **George Zapsas**[1], **Panayiotis Bilalis**[1], **Yves Gnanou**[1],

Xueyan Feng[2], **Edwin L. Thomas**[2], **Nikos Hadjichristidis**[1]*

[1]Physical Sciences and Engineering Division, Polymer Synthesis Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia

[2]Department of Materials Science and NanoEngineering Rice University, Houston, TX 77030, USA

Polyethylene (PE)-based materials are essential in modern life, covering a broad spectrum of applications from commodity plastics (packaging, bottles) to precision-processed biomaterials (medical devices).[1] The development of new PE topologies will expand applications as the properties of the polymers are highly influenced by macromolecular architecture. In this work, well-defined (PE)-based 3-miktoarm star copolymers $(PI)_2PE$-OH, PI_2(PI′-*b*-PE)-OH and terpolymer PI_2(PS-*b*-PE)-OH (PI: polyisoprene, PS: polystyrene), bearing a functional group (–OH) at the PE chain-end, were synthesized by combining anionic polymerization, polyhomologation with the help of a "bridging" molecule, BF_3OEt_2.[2,3] 4-(Dichloromethylsilyl)diphenylethylene (DCMSDPE) was first synthesized and titrated with PILi to afford a "living" star, followed by linking reaction with BF_3OEt_2 (macroinitiator) and polyhomologation of dimethylsulfoxonium methylide (Figure). All intermediates and final products were characterized by high-temperature size exclusion chromatography (HT-SEC), proton nuclear magnetic resonance spectroscopy (^{1}H-NMR), and differential scanning calorimetry (DSC). The microdomain morphologies of the samples were evaluated by transmission electron microscopy (TEM), as well as small-angle (SAXS) and wide-angle x-ray scattering (WAXS) as a function of temperature.

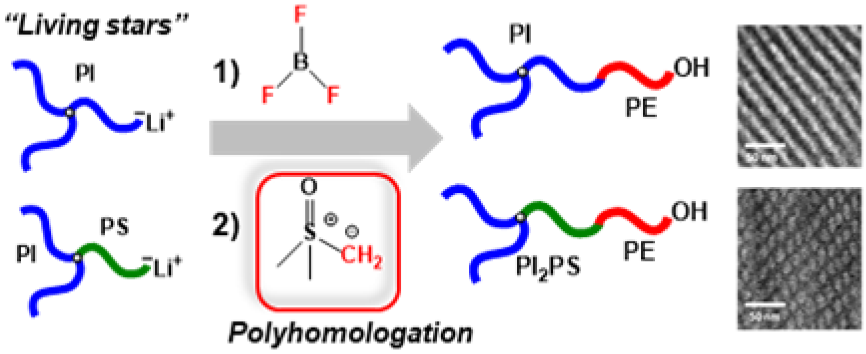


Figure. Schematic procedures for the synthesis of the PE-based miktoarm star co/terpolymers by the combination of anionic polymerization and polyhomologation.

References

1. Wang, D.; Zhang, Z.; Hadjichristidis, N. *Polym. Chem.* **2017**, *8*, 4062-4073.
2. Zapsas, G.; Ntetsikas, K.; Kim, J.; Bilalis, P.; Gnanou, Y.; Hadjichristidis, N. *Polym. Chem.* **2018**, *9*, 1061-1065.
3. Ntetsikas, K; Zapsas, G.; Bilalis, P.; Gnanou, Y.; Feng, X.; Thomas, E.L.; Hadjichristidis, N. *Macromolecules* **2020**, *53*, 4355-4365.

OP02

TRANSFORMER-INDUCED METAMORPHOSIS OF POLYMERIC NANOPARTICLE SHAPE AT ROOM TEMPERATURE

Kostas Parkatzidis, Nghia P. Truong, Athina Anastasaki

Laboratory of Polymeric Materials, Department of Materials, ETH Zurich

Controlled polymerizations have enabled the synthesis of a wide range of amphiphilic block copolymers which can form nanostructured materials with different shapes exhibiting distinct properties and performance.[1] Despite the importance of shape, current strategies that allow for the efficient morphological transformation are limited in polymer scope, often alter the chemical structure, operate at high temperatures, and can be fairly tedious and time-consuming. Herein we present a rapid and versatile morphological transformation strategy which operates at ambient temperature and without impairing the chemical structure of the resulting morphologies. By simply adding a small amount of a molecular transformer (i.e. small organic molecule) in an aqueous solution of polymeric nanoparticles, a rapid evolution to the next high-ordered morphology was observed within seconds, yielding a range of nanoparticles morphology from the same starting material. Significantly, this approach can be applied to nanoparticles produced by disparate block copolymers (i.e. with different cores and coronae) obtained by various synthesis techniques, including emulsion polymerization, polymerization-induced self-assembly and traditional solution self-assembly.[2]

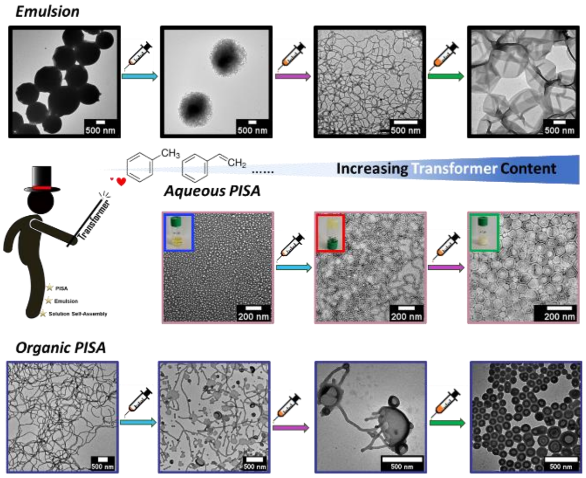


Figure 1: Transformer-Induced Metamorphosis of Polymeric Nanoparticle Shape at Room Temperature: application in nanoparticles obtained via emulsion polymerization, aqueous PISA and organic PISA

Refernces: [1]: K. Parkatzidis, H. S. Wang, N. P. Truong and A. Anastasaki, *Chem*, **2020**, 6, 1575–1588
[2]: K. Parkatzidis, N. P. Truong, M. Rolland, V. Lutz-Bueno, E. H. Pilkington, R. Mezzenga and A. Anastasaki, *Angew.Chem*., Just accepted.

OP03

POLY(VINYLIDENE FLUORIDE)/POLYMETHYLENE-BASED BLOCK COPOLYMERS AND TERPOLYMERS

G. Zapsas, Y. Patil, P. Bilalis, Y. Gnanou, N. Hadjichristidis

Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Kingdom of Saudi Arabia

In an attempt to correlate the properties of fluorinated with non-fluorinated segments, poly(vinylidene fluoride) (PVDF)-based block-copolymers is an acceptable approach in combining properties such as crystallinity, chemical, solubility, processability.[1] Dual crystalline diblock copolymers consisting of polymethylene (PM) and PVDF blocks as well as triblock terpolymers with polystyrene (PS) middle block were synthesized. For the synthesis, two/three different polymerization methods such as polyhomologation, atom transfer radical polymerization (ATRP), and iodine transfer polymerization (ITP) along with chain-end post polymerization reactions were employed.[2] Solid-state NMR spectroscopy revealed the characteristic peaks of all constituent blocks as covalently linked each other, while the controlling/living nature of all implemented polymerization methods was demonstrated among others and by gel permeation chromatography (GPC). Analysis based on differential scanning calorimetry (DSC), X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopies indicates the coexistence of α- and β-phase in diblock copolymers as well as β-and γ-phase in triblock terpolymers.[2]

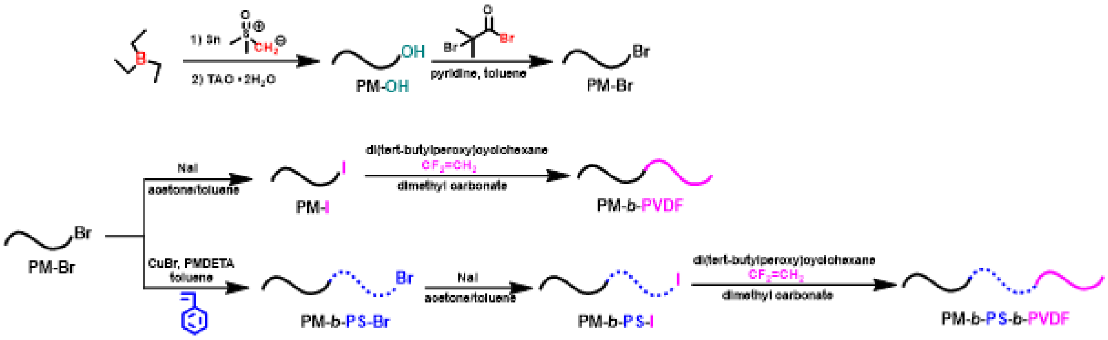


Figure. *Synthesis of PM-b-PVDF diblock copolymer and PM-b-PS-b-PVDF triblock terpolymer by subsequent polyhomologation/ITP or Polyhomologation/ATRP/ITP techniques, respectively.*

References

1. Ameduri B. Vinylidene Fluoride (VDF) to the Applications of VDF-Containing Polymers and Copolymers: Recent Developments and Future Trends. *Chem. Rev*. **2009**, *109*, 6632-6686.
2. Zapsas, G. Patil, Y.; Bilalis, P.; Gnanou, Y.; Hadjichristidis, N.; Poly(vinylidene fluoride)/Polymethylene-Based Block Copolymers and Terpolymers. *Macromolecules*, **2019**, *52*, 1976-1984.

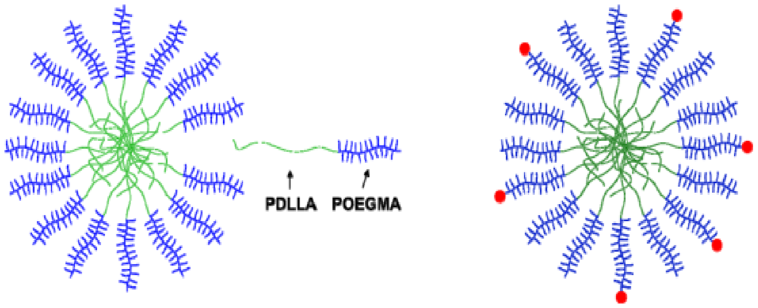
OP04

SYNTHESIS AND CHARACTERIZATION OF BIOTIN/FOLIC ACID FUNCTIONALIZED BIOCOMPATIBLE AND BIODEGRADABLE BLOCK COPOLYMERS. ENCAPSULATION OF HYDROPHOBIC DRUG MODEL COMPOUNDS IN MICELLES

Ioannis Choinopoulos, Nikos Karanikolopoulos, Marinos Pitsikalis

Industrial Chemistry Laboratory, Department of Chemistry, National & Kapodistrian
University of Athens, Panepistimiopolis Zografou, 15 771 Athens, Greece

Well-defined poly{DL-lactide-b-[oligo(ethylene glycol) methyl ether (meth)acrylate)]} (PDLLA-b-POEG[M]A) functional amphiphilic diblock copolymers were synthesized in different molecular weights. The synthetic procedure began with ring-opening polymerization of DL-lactide using n-decanol and stannous octoate as the initiating system and was followed by esterification reaction of the PDLLA hydroxyl end groups with 2-bromoisobutyryl bromide. Consequent atom transfer radical polymerization of OEG(M)A with the newly created bromoisobutyryl initiating site, and incorporation of biotin or folic acid at the POEGA chain ends using click chemistry provided the final copolymers. The products were characterized by NMR spectroscopy and SEC analysis. Micelles of the synthesized block copolymers were prepared and investigated by dynamic light scattering at 25^{o}C in aqueous solutions. The hydrophobic drug model compounds Nile red and pyrene were efficiently incorporated into the copolymer aggregates in aqueous solutions. High partition coefficient values were determined by fluorescence spectroscopy.



OP05

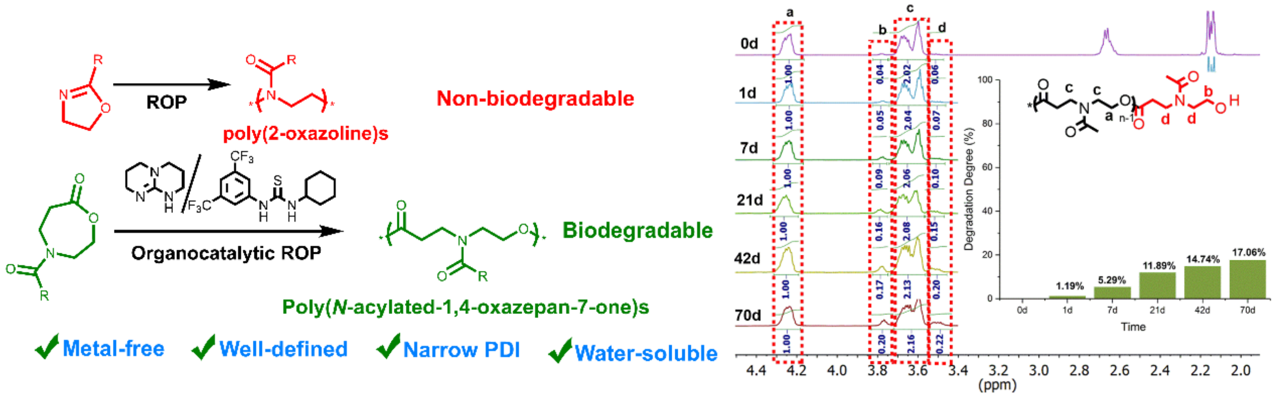
BIODEGRADABLE ALTERNATIVE TO POLY(2-OXAZOLINE) SYNTHESIZED BY ORGANOCATALYTIC RING-OPENING POLYMERIZATION OF N-ACYLATED-1,4-OXAZEPAN-7-ONE

Xin Wang, Nikos Hadjichristidis*

King Abdullah University of Science and Technology (KAUST), Physical Sciences and
Engineering Division, KAUST Catalysis Center, Polymer Synthesis Lab., Saudi Arabia

Poly(2-oxazoline), as a non-ionic water-soluble polymer containing polypeptide-isomeric structures, has attracted significant attention in various research fields.[1, 2] However, in general, poly(2-oxazoline)s are considered nonbiodegradable, as they lack hydrolytically sensitive bonds and bear tertiary amides that severely hinder the enzymatic degradation. When the nonbiodegradable poly(2-oxazoline)s are used for long-circulating drug delivery system, the high molecular weight poly(2-oxazoline)s will accumulate in the human body leading to toxic side effects.[3] Herein, we reported a biodegradable alternative to poly(2-oxazoline), which was synthesized by organocatalytic ring-opening polymerization (ROP) of *N*-acylated-1,4-oxazepan-7-one (OxP) (Figure 1).[4] The polymerizations were conducted in CH_2Cl_2 at room temperature with benzyl alcohol as initiator and TBD/TU (1,5,7-triazabicyclo[4.4.0]dec-5-ene/thiourea) as a binary organocatalyst. The synthesized polymers possess predictable molecular weights and narrow molecular weight distributions. Based on the DSC results, all synthesized polymers are amorphous and have adjustable glass transition temperatures (T_g: −2.90 to 43.75 °C) by changing the *N*-acylated substituent. In particular, *N*-acetyl substituted polymer is water-soluble. Compared with polycaprolactone, it degrades much faster in an aqueous phosphate buffer saline solution (pH = 7.4).

Figure 1: The synthesis of biodegradable poly(2-oxazoline) by organocatalytic ring-opening polymerization and its biodegradability.



References

1. Hoogenboom, R. *Angew. Chem. Int. Ed.* **2009,** 48, (43), 7978-7994.
2. Schlaad, H.; Diehl, C.; Gress, A.; Meyer, M.; Demirel, A. L.; Nur, Y.; Bertin, A. *Macromol. Rapid Commun.* **2010,** 31, (6), 511-525.
3. Sedlacek, O.; Monnery, B. D.; Filippov, S. K.; Hoogenboom, R.; Hruby, M. *Macromol. Rapid Commun.* **2012,** 33, (19), 1648-1662.
4. Wang, X.; Hadjichristidis, N. *ACS Macro Lett.* **2020,** 9, (4), 464-470.

OP06

VANILLIC ACID: A PROMISING MONOMER FOR BIOBASED AROMATIC POLYESTERS

**Alexandra Zamboulis[1], Eleftheria Xanthopoulou[2], Lazaros Papadopoulos[1],
Zoi Terzopoulou[1,2], George Z. Papageorgiou[2], Dimitrios N. Bikiaris[1]**

[1] Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece
[2] Department of Chemistry, University of Ioannina, Ioannina, Greece

For the last decades, fueled by environmental concerns combined with economic issues, the scientific community has been striving to develop sustainable, industrially viable, polymers. In this quest, the valorization of biomass is a key step,[1] and biobased candidates, such as poly(ethylene furanoate) (PEF) and poly(lactic acid) (PLA), have already emerged from carbohydrate sources. In parallel, the valorization of lignin, the second most abundant natural polymer and the richest renewable source of aromatic monomers, has attracted a lot of interest. Vanillin is the only commercially available lignin-derived monomer[2] and a promising starting monomer for the preparation of bio-based thermoplastic and thermoset polymers.[3] Herein, we will present the work of our research group on polyesters from vanillic acid, a monomer obtained from vanillin by oxidation.[4] Vanillic acid has been derivatized *via* a Williamson reaction to yield ω-hydroxyalkylene vanillic acids which have been further polymerized to afford alipharomatic polyesters bearing ether bonds. In parallel, copolymers with PEF have also been prepared. PEF, the most prominent member of the family of furandicarboxylate polyesters, is considered the renewable substitute of poly(ethylene terephthalate). Poly(ethylene furanoate)/poly(ethylene vanillate) copolymers were prepared to investigate how the presence of benzene moieties and ether linkages could affect the behavior and properties of PEF. The synthesis, structural characterization, thermal properties and crystallization behavior of these promising polymers will thus be presented.

OP07

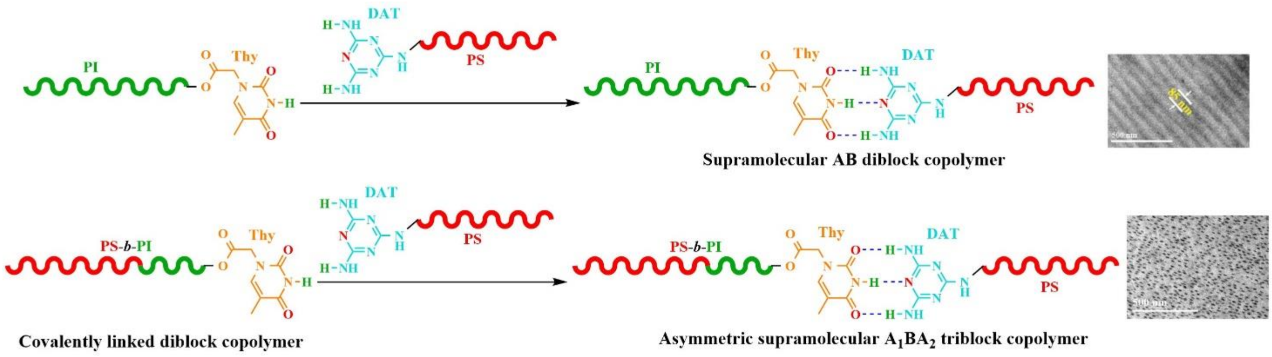
NON-COVALENT SUPRAMOLECULAR AB DIBLOCK AND ASYMMETRIC A1BA2 TRIBLOCK COPOLYMERS: SYNTHESIS AND MICROPHASE SEPARATION

Saibal Bhaumik[1], Konstantinos Ntetsikas[1], Wenpeng Shan[2],
Edwin Thomas[2], Nikos Hadjichristidis*,[1]

[1] Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia
[2] Materials Science and Engineering Department, Texas A & M University, College Station, TX 77843. USA

Block copolymers have undergone extraordinary evolution from simple surfactant materials to an expansive class of macromolecules. Self-assembly of block copolymers is considered an attractive means of generating varieties of nanostructures and patterning over a large area. One way towards complex supramolecular structures is to synthesize the suitable functional homopolymer or block copolymer precursors.[1] Many intermolecular interactions like π-π stacking, ionic interactions, metal-ligand interactions and hydrogen bonding can assist in building complex supramolecular architectures.[2] Reversibility, directionality and self-organization nature make hydrogen bonding one of the most common motifs to design and construct supramolecular polymers with complex macromolecular architecture. 2,6-Diaminotriazine (DAT) and thymine (Thy) are two of the most common triple hydrogen bonded systems for the construction of supramolecular structures.[3-4] In this work, supramolecular diblock (A-*sb*-B)[5] and asymmetric triblock (A_1-*b*-B-*sb*-A_2) copolymers were synthesized *via* non-covalent hydrogen bonding among well-defined thymine end-functionalized polyisoprene (PI-Thy) or polystyrene-*b*-polyisoprene (PS-*b*-PI-Thy) and diaminotriazine end-functionalized polystyrene (PS-DAT). The complementary DAT/Thy interaction resulted in the microphase separation of the supramolecular diblock (A-*sb*-B) and asymmetric triblock (A_1-*b*-B-*sb*-A_2) copolymer system. Detailed characterization of all functionalized homopolymers and covalently linked block copolymers was carried out *via* proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy, gel permeation chromatography (GPC), matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry and differential scanning calorimetry (DSC). The self-assembly process of supramolecular diblock (A-*sb*-B) and asymmetric triblock (A_1-*b*-B-*sb*-A_2) copolymers was evidenced by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) measurements.

Figure 1: General scheme for the synthesis of hydrogen-bonded diblock (A-*sb*-B) and asymmetric triblock (A_1-*b*-B-*sb*-A_2) copolymers and their corresponding TEM images.



References:

1. Yan, T.; Schröter, K.; Herbst, F.; Binder, W. H.; Thurn-Albrecht, T. *Macromolecules* **2014**, *47*, 2122-2130

2. Sherrington, D. C.; Taskinen, K. A. *Chem. Soc. Rev.,* **2001**, *30*, 83-93.

3. Cortese, J.; Soulie-Ziakovic, C.; Cloitre, M.; Tence-Girault, S.; Leibler, L. *J. Am. Chem. Soc.,* **2011**, *133*, 19672-19675.

4. Chen, S.; Binder, W. H. *Acc. Chem. Res.,* **2016**, *49*, 1409-1420.

5. Bhaumik, S.; Ntetsikas, K.; Hadjichristidis, N. *Macromolecules* **2020**, *53*, 6682-6689.

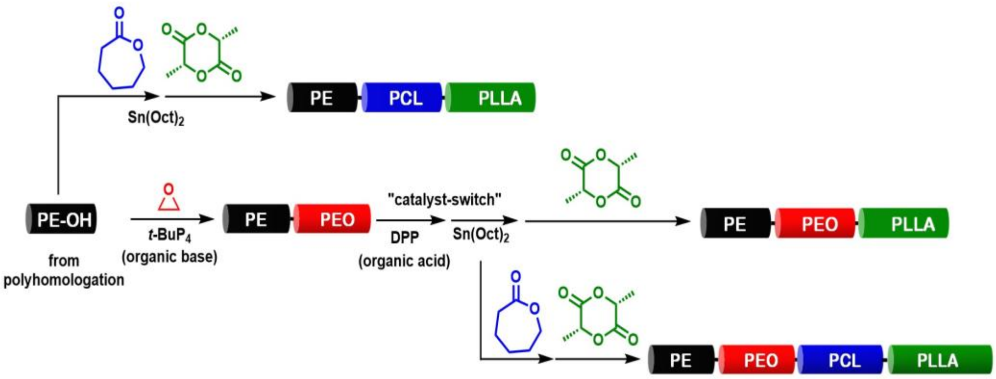
OP08

MULTICRYSTALLINE MULTIBLOCK POLYMERS VIA A COMBINATION OF POLYHOMOGATION, RING-OPENING POLYMERIZATION AND ORGANIC/METAL CATALYST-SWITCH

Viko Ladelta, George Zapsas, Nikos Hadjichristidis

KCC, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia. Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory, Saudi Arabia

Multicrystalline block polymers having three or more crystalline segments are essential materials for the advancement of physics in the field of crystallinity.[1] Due to the challenging synthetic procedure, only a few reports are available on the synthesis of tricrystalline triblock terpolymer,[2,3] while tetracrystalline tetrablock quarterpolymer has never been reported. Here, we report for the first time, tetracrystalline tetrablock quarterpolymer, polyethylene-*b*-poly(ethylene oxide)-*b*-poly(*ε*-caprolactone)-*b*-poly(*L*-lactide) (PE-*b*-PEO-*b*-PCL-*b*-PLLA).[4] Linear *ω*-hydroxyl PE, synthesized by polyhomologation, was used as the macroinitiator to initiate the ring-opening polymerization (ROP) of ethylene oxide (EO) catalyzed by phosphazene superbase t-BuP$_4$ (pK_a = 42.6) followed by neutralization of t-BuP$_4$ with diphenyl phosphate (DPP, pK_a = 3.88). Due to the poor solubility of PE at room temperature, the ROPs must be performed in toluene at 80 °C. At that condition, tin(II) 2-ethylhexanoate [Sn(Oct)$_2$] has to be used (organic/metal catalyst-switch) to promote the ROPs *ε*-caprolactone (CL) and *L*-lactide (LLA) from PE-*b*-PEO macroinitiator to avoid the formation of (*R,S)meso*-lactide monomeric units and affording tetracrystalline polymer. Two new tricrystalline triblock terpolymers, PE-*b*-PEO-*b*-PLLA (synthesized by organic/metal catalyst-switch strategy) and PE-*b*-PCL-*b*-PLLA (synthesized by a straightforward ROP), are also reported.[5] The structure of tri- and tetrablock terpolymer was characterized by 1D and 2D NMR spectroscopy as well as by gel permeation chromatography. Differential scanning calorimetry, X-ray diffraction, and solid-state NMR spectroscopies reveal the existence of four crystalline blocks.



Scheme. Schematic procedures for the synthesis of tetracrystalline tetrablock quarterpolymer by organic/metal-catalyst switch.

References:

1.R. V. Castillo and A. J. Müller, *Prog. Polym. Sci.*, 2009, **34**, 516-560.
2.B. Guillerm, V. Lemaur, B. Ernould, J. Cornil, R. Lazzaroni, J.-F. Gohy, P. Dubois and O. Coulembier, *RSC Advances*, 2014, **4**, 10028-10038.
3.M. Vivas, J. Contreras, F. López-Carrasquero, A. T. Lorenzo, M. L. Arnal, V. Balsamo, A. J. Müller, E. Laredo, H. Schmalz and V. Abetz, *Macromolecular Symposia*, 2006, **239**, 58-67.
4.V. Ladelta, G. Zapsas, E. Abou-hamad, Y. Gnanou, N. Hadjichristidis, *Angew. Chem. Int. Ed.*, 2019, **131**, 16413-16420.
5.V. Ladelta, G. Zapsas, Y. Gnanou, N. Hadjichristidis, *J. Pol. Sci., Part A: Polym. Chem.,* 2019, **57**, 2450–2456.

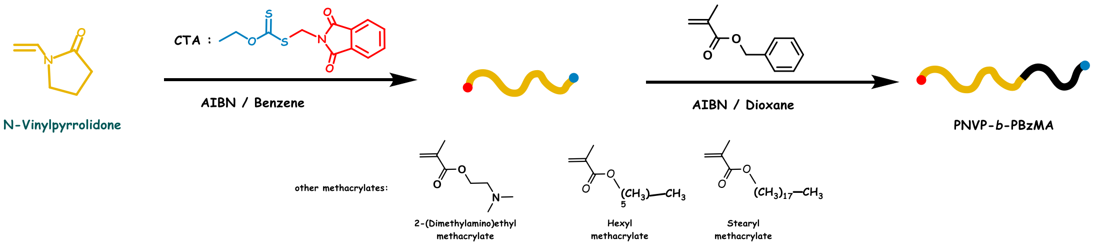
OP09

POLY(N-VINYLPYRROLIDONE) BASED AMPHIPHILIC BLOCK COPOLYMERS: SYNTHESIS VIA REVERSIBLE ADDITION-FRAGMENTATION CHAIN TRANSFER POLYMERIZATION, THERMAL PROPERTIES AND ASSOCIATION BEHAVIOR IN DILUTE SOLUTIONS

Nikoletta Roka, Marinos Pitsikalis

Industrial Chemistry Laboratrory, Department of Chemistry, National & Kapodistrian
University of Athens, Panepistimiopolis Zografou, Athens 157 71, Greece

Poly(N-vinylpyrrolidone) (PNVP) is an attractive polymer, industrially important due to its biocompatibility and biodegradability, low toxicity, high complexing ability and good film-forming characteristics. [1] PNVP can be efficiently polymerized via Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization. RAFT polymerization is a well-established method for providing living characteristics to conventional radical polymerization. [2] The advantages of RAFT include the facile processes under routine experimental conditions coupled with the tolerance of unprotected functionality in monomer and solvent. In this work, NVP based block copolymers with various methacrylates such as benzyl methacrylate, [3] 2-(dimethylamino)ethyl methacrylate, [4] stearyl methacrylate and hexyl methacrylate [5] were prepared by RAFT polymerization. Eventhough N-vinylpyrrolidone is a less active monomer compared to the methacrylates, both of them are successfully polymerized with the same Chain Transfer Agent. The synthesis was monitored by SEC and NMR. The glass-transition temperature values of the copolymers were measured by Differential Scanning Calorimetry and the thermal degradation behavior of the copolymers was investigated, compared to the respective homopolymers, by Thermogravimetric Analysis. Furthermore, the dilute solution properties of the copolymers were studied by Dynamic Light Scattering.



References:

1. P. Bilalis, et al., J. Polym. Sci. Part A: Polym. Chem. 44:1, 659 (2006)
2. S. Perrier, Macromolecules. 50:19, 7433 (2017)
3. N. Roka, J. Polym. Sci. Part A: Polym. Chem. 55, 3776 (2017)
4. N. Roka, J. Macromol. Sci. A. 55:3, 222 (2018)
5. E. Mitsoni, J Polym Res 26, 118 (2019).

Acknowledgements:

This research is co-financed by Greece and the European Union (European Social Fund-ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project “Strengthening Human Resources Research Potential via Doctorate Research” (MIS-5000432), implemented by the State Scholarships Foundation (IKY).

Ευρωπαϊκή Ένωση
European Social Fund

Operational Programme
Human Resources Development,
Education and Lifelong Learning
Co-financed by Greece and the European Union

ΕΣΠΑ
2014-2020
ανάπτυξη - εργασία - αλληλεγγύη

OP10

MODELING OF EXTRUSION FLOW INSTABILITIES OF POLYMER NANOCOMPOSITES: INFLUENCE OF FILLER AMOUNT

**Christos Georgantopoulos[1], Masood Khabazian[1], Ingo Naue[1], Andrea Causa[2],
Roland Kádár[3], Manfred Wilhelm[1]**

[1] Karlsruhe Institute of Technology (KIT), Institute for Chemical Technology and
Polymer Chemistry (ITCP), Karlsruhe, Germany
[2] Pirelli Tyre S.p.A., Milan, Italy
[3] Chalmers University of Technology, Department of Industrial and Materials Science,
Gothenburg, Sweden

Extrusion flow instabilities of commercial SBR rubber and model filled systems with silica are investigated by capillary rheology.[1,2,3] The extrusion flow instabilities of the compounds are investigated as a function of filler amount, keeping a constant ratio between the filler and the dispersing agent (silane) for all samples at 100 °C. This study uses the Wang *et al.*,[4] analytical model which correlates the spatial characteristic wavelength (λ) of the extrusion flow instabilities with the diameter of the die D, the swelling of the extrudate $D|$, sharkskin time periodicity, τ^* and the shear rate, γ.Hence, the spatial characteristic wavelength of the model filled systems are predicted. Furthermore, a geometry-dependent[5] correlation is used to predict the spatial characteristic wavelength (λ) of the extrusion ?ow instabilities from a round capillary die to a slit die and vice versa.

References

[1]S. G. Hatzikiriakos, *Progress in Polymer Science*, **2012**, 624, 37.
[2]M. M. Denn, *Annual Review Fluid Mechanics*, **2001**, 265, 33.
[3]S. G. Hatzikiriakos, K. Migler, *Polymer Processing Instabilities. Control and Understanding*, Marcel Dekker **2005**.
[4]S. Q. Wang, P. A. Drda, andY. W. Inn, *Journal of Rheology*, **1996**, 875, 40.
[5]C. K. Georgantopoulos, M. K. Esfahani, C. Botha, I. F. C. Naue, N. Dingenouts, A. Causa, R. Kádár, and M. Wilhelm, *Macromol. Mater. Eng.* **2021**, *306*, 2000801.

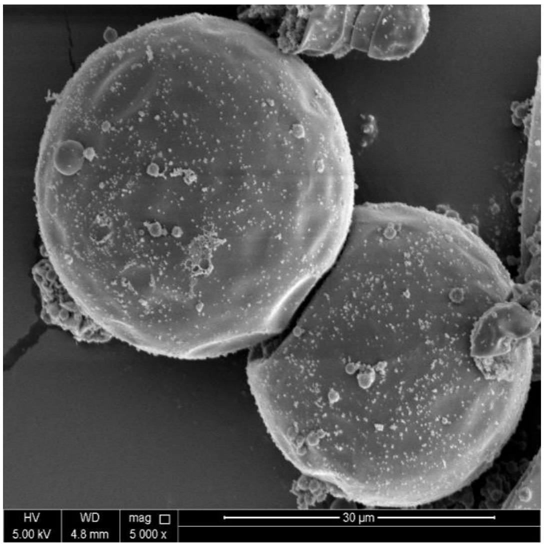
OP11

TAILOR-MADE EPOXY LOADED POLY(UREA-FORMALDEHYDE) MICROCAPSULES FOR SELF-HEALING COATINGS

Christos Zotiadis[1], Ioannis Patrikalos[1], Vasileia Loukaidou[1], Dimitrios Korres[1],
Antonis Karantonis[2], Stamatina Vouyiouka[1]

[1] Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zographou Campus, Athens, 157 80, Greece
[2] Laboratory of Physical Chemistry and Applied Electrochemistry, School of Chemical Engineering, National Technical University of Athens, Zographou Campus, Athens, 157 80, Greece

Self-healing technology can offer autonomous crack repair and increase the service lifetime of a protective coating for different industrial sectors, such as marine applications. Polymeric microcapsules containing healing agents can be used in that perspective and exhibit significant potential. The aim of the current work is to produce poly(urea-formaldehyde) microcapsules with an encapsulated epoxy resin *via* one stage *in situ* polymerization in an oil-water emulsion. The encapsulation process took place in a closed reaction vessel under mechanical agitation based on the work of Tzavidi et al. (Journal of Applied Polymer Science, 2020) The capsules were collected as free-flowing white powder after vacuum filtration, washing with acetone and drying in an oven (40 °C) for 24 h (Figure 1). The suggested system is designated for coating applications thus the microcapsules need to be smaller than 50 μm to allow them to be incorporated into the standard coating thickness, with high encapsulation efficiency values ??(> 70%) (ratio of encapsulated substance to microcapsule mass). The synthetic conditions varied and each process parameter was correlated to *in situ* polymerization mechanism. The most appropriate conditions were determined based on the microcapsule size distribution, encapsulation efficiency, surface morphology and thermal properties. Spherical microcapsules were obtained with a size ranging from 37 to 66 μm controlled during the emulsification stage and the encapsulation efficiency varied between 43-78 %. Finally, microcapsules were successfully dispersed in a paint and applied on a steel plate to demonstrate the self-healing properties of the respective coating using electrochemical impedance spectroscopy.


HV
5.00 kV
WD
4.8 mm
mag □
5 000 x
30 µm

OP12

NANOSTRUCTURED BIOMATERIALS BASED ON BIOPOLYMERS WITH POTENTIAL IN BIOMEDICAL AND FOOD SCIENCES

Aristeidis Papagiannopoulos

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece

Introduction: Soft nanomaterials formed by the co-assembly of proteins and polysaccharides are attractive for applications as nanocarriers of drugs and nutrients and as scaffolds for cell culture and tissue engineering, because they are biocompatible and nontoxic. In this talk the use of electrostatic interactions between proteins and polysaccharides to prepare nanoparticles and multilayers will be presented.

Methods: Several polysaccharides (e.g. xanthan, hyaluronic acid) and proteins (e,g, bovine serum albumin, fibrinogen) were used for the formation of thermally stabilized nanoparticles (Figure 1) and layer-by-layer deposited films. Characterization methods included light scattering and ATR-FTIR spectroscopy in solution and surface plasmon resonance in interface studies.

Results: It was proved that polysaccharide/protein nanoparticles stabilized by thermal treatment against pH changes are capable of encapsulating and preserving nutraceutical compounds. On the other hand, the prepared adsorbed polysaccharide/protein layers showed strong cooperative build-up and good biocompatibility and viability of cardiomyocytes.

Conclusions: These studies demonstrate that proteins act both as building blocks and nanocarriers inside multifunctional nanostructures. The prepared nanoparticles and multilayers can be used as a guide for other systems of polysaccharide/protein pairs and bioactive substances.

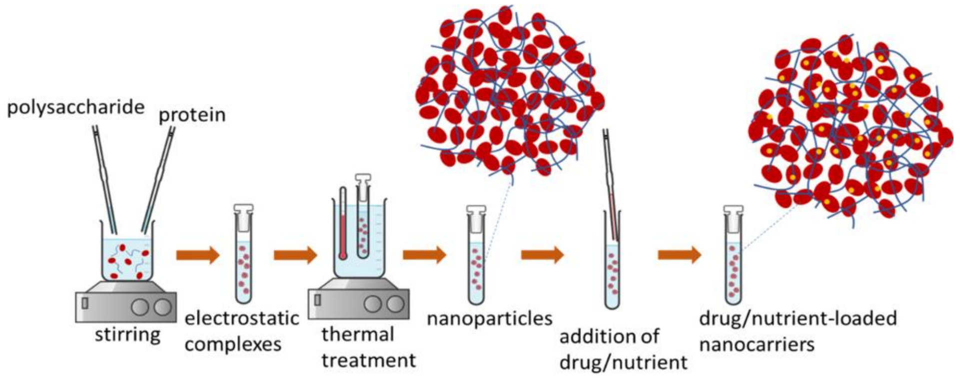


Figure 1: Schematic illustration of drug or nutrient-loaded thermally stabilized polysaccharide/protein nanoparticles

Acknowledgements: This research was partially supported by IKYDA 2020, an integrated action program between the Greek State Scholarship Foundation (I.K.Y.) and the German Academic Exchange Service (DAAD).

.

OP13

FLUORESCENT BIODEGRADABLE TRIBLOCK COPOLYMER MICELLES FOR SIMULTANEOUS ANTICANCER DRUG DELIVERY AND CELLULAR IMAGING

Bhagyashree Kulkarni,[1] Somayah Salah Qutub,[2] Viko Ladelta,[1] Niveen M. Khashab,[2,*] Nikos Hadjichristidis[1,*]

[1]Polymer Synthesis Laboratory, KAUST Catalysis Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia
[2]Smart Hybrid Materials (SHMs) Laboratory, Advanced Membranes and Porous Materials Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

The recent past has witnessed enormous interest in polymeric micelles that self-assemble in water from amphiphilic block copolymers for drug delivery application.[1] The PEG-*b*-PCL block copolymers are currently being investigated as a carrier in different drug delivery systems.[2] However, PEG-*b*-PCL is non-fluorescent, so these nanocarrier designs depend on encapsulated fluorescent drugs or fluorescent molecules to track intracellular drug delivery. Consequently, this approach does not provide direct information on the fate of the drug at the intracellular level.[3] Here, we report the one-pot sequential organocatalytic (*t*-BuP$_2$/TEB) ring-opening polymerization (ROP) of *ε*-caprolactone (CL) and ethylene oxide (EO) leading to two well-defined triblock copolymers, TPE-(PCL-*b*-PEO)$_2$ and TPE-(PEO-*b*-PCL)$_2$. These fluorescent copolymers self-assemble into micelles in water. The anticancer drugs doxorubicin and curcumin were encapsulated into the block copolymer micelles and exhibited sustained drug release over time. Confocal laser scanning microscopy analysis confirmed strong emission from TPE inside the cells, making it possible to use these systems for simultaneous drug delivery and cellular imaging.

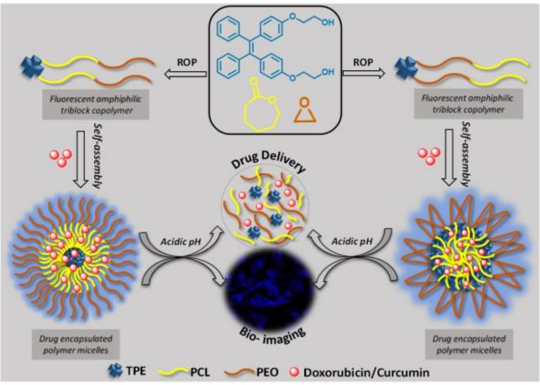


Figure 1: Schematic representation of fluorescent biodegradable triblock copolymer micelles for simultaneous anticancer drug delivery and cellular imaging application.

References

1. Cabral, H.; Miyata, K.; Osada, K.; Kataoka, K., Block Copolymer Micelles in Nanomedicine Applications. *Chem. Rev.* **2018,** *118* (14), 6844-68922.

2. Grossen, P.; Witzigmann, D.; Sieber, S.; Huwyler, J., PEG-PCL-based nanomedicines: A biodegradable drug delivery system and its application. *J Control Release* **2017,** *260*, 46-60.

3. Luk, B. T.; Zhang, L., Current advances in polymer-based nanotheranostics for cancer treatment and diagnosis. *ACS Appl Mater Interfaces* **2014,** *6* (24), 21859-73.

OP14

THERANOSTIC NANOPARTICLES BASED ON PEO-POLYACETAL DIBLOCK COPOLYMERS FOR DRUG DELIVERY

Theodore Manouras[1,2] , **Maria Vamvakaki**[1,2]

[1] Department of Materials Science and Technology, University of Crete, Crete,Greece
[2]Insitute of Electronic Structure and Laser, Foundation of Research and Technology- Hellas

Keywords: Theranostic nanoparticles, polyacetal, multisensitive polymer, ultrasound sensitive, photosensitive, redox sensitive

Introduction: Modern nanoparticle-based drug delivery systems are considered a promising therapeutic platform because of their potential to enhance the efficacy of drugs in anticancer and antiviral therapy. Besides their therapeutic action, modern nanoparticulate materials have been also used in biomedical imaging allowing drug targeting and the assessment of the therapeutic effect. Modern nanomedicine combines the above two actions in a single entity known as theranostic nanoparticles, which allow simultaneous diagnosis of the disease site, drug delivery to cure the disease and monitoring of the drug response [1-3].

Methodology: The block copolymer was synthesized via a two-step polycondensation reaction (figure 1), in the first step nitrobenzenedimethanol, hydroxyethyldisulfide, butyne diol and cyclohexyl divinyl ether were added in equimolar amounts with 1% PPTS. Next, for the synthesis of the block copolymer, 5 kDa monohydroxy terminated PEG was added to the preview's solution along with 1% PPTS. The block copolymer was isolated after precipitation and fractionation in hexanes. The quad-stimulus mediated degradation of the polymers either by UV (365 nm) photolysis or ultrasound (1 MHz) irradiation or in REDOX environment or by acidolysis at mildly acidic pH (ca. 5.2) was monitored using gel permeation chromatography. Micelles loaded with the model drug camptothecin (CPT) were prepared in aqueous medium and the ability of this micelles to serve as MRI contrast agents was evaluated using NMR. Furthermore, the release of the model drug CPT under the aforementioned stimuli was calculated using UV-Vis.

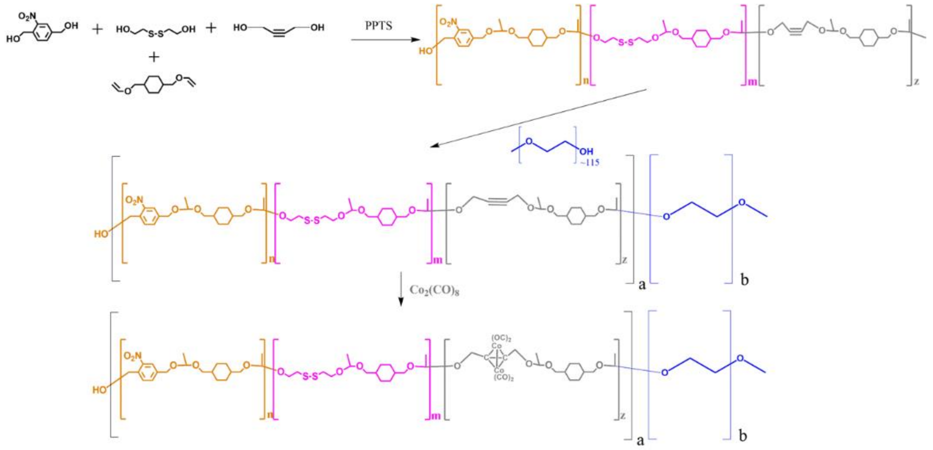


Figure 1: Synthetic procedure of the Polyacetal-PEO diblock copolymer.

Discussion: Polyacetals have a well-established hydrolysis profile under the mildly acidic conditions (pH 5.5) found in the late endosome. In an effort to introduce red-shifted photolability on the backbone of the polymer in the visible, nitrobenzene comonomers were used (figure 1). Furthermore, we introduced disulfide bonds in the main chain of the polyacetal block which are redox labile. Ultrasound irradiation of the PEO-Polyacetal block copolymer has resulted in its degradation by the direct breaking of the acetal bonds. The polymer formed spherical nanoparticles in water with mean diameter of 130 nm determined by dynamic light scattering. The morphology of the nanoparticles was examined by SEM microscopy which confirmed their spherical shape and their relatively uniform size distribution. After 3 h of light irradiation (365nm) of 7 h ultrasound irradiation of the micelles at pH 7.4, 90 % release of the CPT was achieved (figure 2a). Conversely, the drug release rate was more pronounced when the pH was lowered to 5.2 (figure 2b). Furthermore, 60 h treatment of the nanoparticles with the reducing agent dithiothreitol has resulted in 50% and 70% release of the CPT at 7.4 and 5.2 pH, respectively (figure 2).

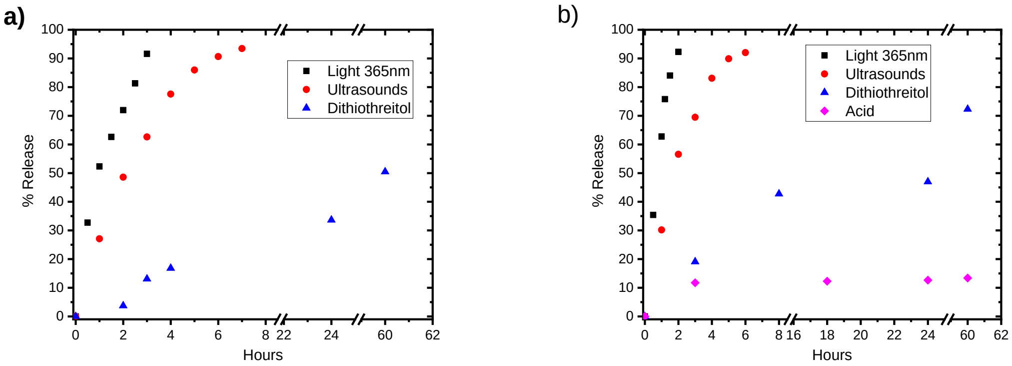


Figure 2: CPT release from the NPs upon the application of several stimuli.

Conclusions: We have developed a new multi-responsive polymer that responds individually to four different stimuli, while also exhibiting a super-paramagnetic behavior, and demonstrate its potential in the development of "smart" nanocarriers with ideal properties as contrast agents for MRI.

Acknowledgements

This research is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project "Reinforcement of Postdoctoral Researchers - 2nd Cycle" (MIS-5033021), implemented by the State Scholarships Foundation (IKY).

Ευρωπαϊκή Ένωση
European Social Fund

Operational Programme
Human Resources Development,
Education and Lifelong Learning
Co-financed by Greece and the European Union

ΕΣΠΑ
2014-2020
ανάπτυξη - εργασία - αλληλεγγύη

References

[1] G. Pasparakis, T. Manouras, P. Argitis and M. Vamvakaki "Photodegradable Polymers for Biotechnological Applications" Macromolecular Rapid Communications, vol. 33, pp. 183-198, 2012.

[2] G. Pasparakis, T. Manouras, A. Selimis, M. Vamvakaki and P. Argitis "Laser-Induced Cell Detachment and Patterning with Photodegradable Polymer Substrates" Angewandte Chemie International Edition, vol. 50, pp. 4142-4145, 2011.

[3] G. Pasparakis, T. Manouras, M. Vamvakaki and P. Argitis "Harnessing photochemical internalization with dual degradable nanoparticles for combinatorial photo-chemotherapy" Nature Comm., vol. 5, pp. 3623, 2014.

OP15

STRUCTURE AND THERMAL STABILITY OF ROP AND RM6 PROTEINS VIA ALL-ATOM MOLECULAR DYNAMICS SIMULATIONS

Maria Arnittali[1,2,*], **Anastassia N. Rissanou**[1,2], **and Vagelis Harmandaris**[1,2,3]

[1]Institute of Applied and Computational Mathematics (IACM), Foundation for Research and Technology Hellas, (FORTH), IACM/FORTH, FR-71110 Heraklion, Greece
[2]Department of Mathematics and Applied Mathematics, University of Crete, GR-71409, Heraklion, Crete, Greece
[3]Computation-based Science and Technology Research Center, The Cyprus Institute, Nicosia 2121, Cyprus

In the field of nanotechnology, functional materials at the nanometer scale is an ultimate challenge. Nature provides with peptides and proteins a major source of inspiration for the engineering of responsive, protein-based nanomaterials for medical and biotechnology applications. In this aspect, detailed understanding of how amino acid sequences of proteins dictate their structures and physicochemical properties, is a main challenge. For example, the thermal stability of natural proteins is generally limited to a narrow range of temperatures outside of this proteins frequently denature. An extension of this temperature range could be achieved through the introduction of mutations of stabilizing agents, making proteins more suitable for biotechnology or biomedical applications. To address the above challenges nowadays, mathematical and computational methods, such as molecular dynamics (MD) simulations are being applied for the study of proteins. MD generates a trajectory by numerical integration of classical equations of motion that contain all the dynamical information. In this work, we explore in atomic detail how a protein mutation can cause major changes in its physical properties, like its structural stability. Two proteins are studied: the dimeric RNA-binding ColE1 Repressor of Primer (Rop) protein that is a paradigm of a highly regular 4-α-helical bundle, and its loopless mutation (RM6) are used as our models[1]. A comprehensive investigation of the thermal stability of both proteins is performed through atomistic MD simulations at three different temperatures in water[1]. The detailed analysis, that is performed based on key structural parameters, such as α-helix dimensional properties, Ramachandran plot and pair correlation functions, reveals RM6 as more thermostable than Rop protein. Deviations from native structures are detected mostly in tails and loop regions and the most flexible residues are indicated.

1. Arnittali, M.; Rissanou, A. N.; Amprazi, M.; Kokkinidis, M.; Harmandaris, V. *Int. J. Mol. Sci.* **2021**, *22* (11), 5931.

OP16

pH/THERMO-RESPONSIVE SODIUM ALGINATE-BASED INJECTABLE HYDROGELS: ENRICHMENT OF RESPONSIVENESS BY BORONIC ACID CONJUGATIONS AND/OR Ca2+ Cations

Sofia - Falia Saravanou, Fotoula Kounelaki, Vasilis Alexandris, George Pasparakis, Constantinos Tsitsilianis

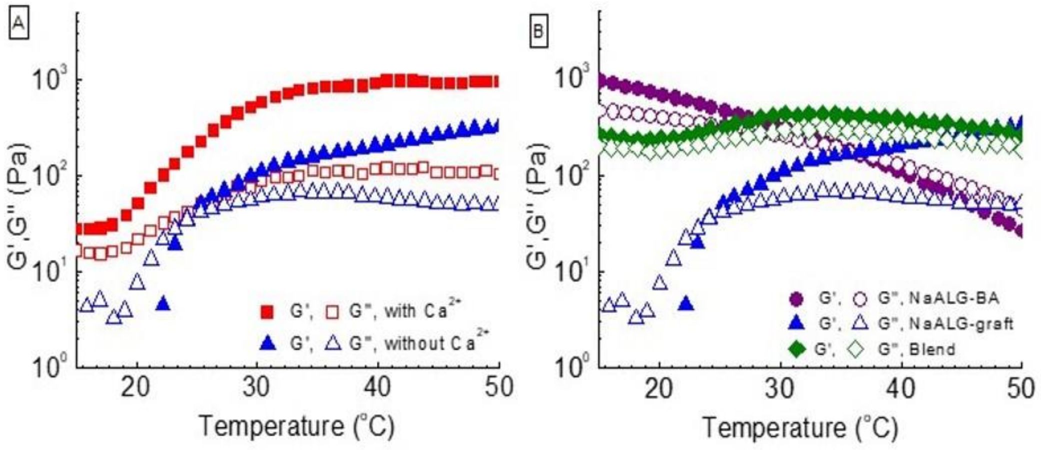
Department of Chemical Engineering, University of Patras, Patra, Greece

We present recent developments in self-healable, pH/thermo-responsive sodium alginate-based hydrogels. Graft copolymers of alginate, bearing thermo-sensitive side chains of the copolymer poly(N-isopropylacrylamide-co-N-tertiary-butyl-acrylamide), (NaALG-g-P(NIPAM-co-NtBAM)) with tunable sol-gel transition and gelation temperature controlled by the NtBAM content.[1] Herein we present two novel directions towards hydrogels with enriched properties, either by introducing boronic acid functionalization or simple addition of Ca^{2+} cations.

In the first direction, the [NaALG-g-P(NIPAM-co-NtBAM)] gelator formed a weak 3D network at low temperatures due to the interactions of Ca^{2+} cations with carboxylate moieties compared with the calcium-free formulation (Figure A). By heating above a critical temperature, the storage modulus G' increased due to the hydrophobic associations of the copolymer side chains. Thus, the presence of Ca^{2+} shifted the behavior from sol-to-gel to weak-to-strong gel. The transition properties could also be tuned by the Ca^{2+} content.

In the second approach, aqueous polymer blends of NaALG-BA and NaALG-g-P(NIPAM-co-NtBAM) (1:1) were found to form stronger gels at physiological pH due to boronate-diol ester formation, while G' increased progressively by increasing the temperature from 20 ^{o}C to 37 ^{o}C, because of the hydrophobic interactions of the PNIPAM-co-NtBAM moieties. However, the thermo-thickening effect was weakened due to the thermo-thinning behavior of NaALG-BA component (Figure B). The system is highly versatile owing to the pH sensitivity of the boronate-diol ester bonds and the possibility to induce de-crosslinking by simple addition of glucose molecules.

Both systems exhibit shear-responsiveness as well, which provides injectability even for the soft gels formed at low temperatures. The rich behaviour of these systems, namely pH, temperature, shear, and glucose sensitivity renders them interesting candidates for bioapplications (e.g., cell/tissue growth regeneration, scaffold fabrication etc.).


A
10^3
10^2
10^1
10^0
G',G'' (Pa)
20
30
40
50
Temperature (°C)
G', G'', with Ca2+
G', G'', without Ca2+
B
G', G'', NaALG-BA
G', G'', NaALG-graft
G', G'', Blend

OP17

MECHANICAL PROPERTIES OF PMMA RESIN COMPOSITES FOR INTERIM FIXED PROSTHESES REINFORCED WITH CALCIUM β-PYROPHOSPHATE

Iouliana Chrysafi[1], Eleana Kontonasaki[2], Antonios Anastasiou[3], George Vourlias[1], Evangelia Vouvoudi[4], Dimitris Bikiaris[4]

[1] Physics Department, Aristotle University of Thessaloniki, Thessaloniki, Greece
[2] Dentistry Department, Aristotle University of Thessaloniki, Thessaloniki, Greece
[3] Chemical Engineering and Analytical Science, University of Manchester, Manchester, UK
[4] Chemistry Department, Aristotle University of Thessaloniki, Thessaloniki, Greece

Introduction: Temporary dental restorations are removable restorations that can completely replace human denture for a short period of time. PMMA is widely used in Dentistry due to its biocompatibility and convenient properties. Calcium *β*-pyrophosphate (*β*-$Ca_2P_20_7$, *β*-CPP) is a promising inorganic material for dental applications and especially for tooth enamel restorations. The aim of this study was the investigation of the mechanical properties of a PMMA resin reinforced with *β*-CPP, for interim dental restorations in certain conditions and compositions.

Methods: A self-polymerized PMMA dental resin of two ingredients, named "mega TRIMM" (Mega dental® manufacturer, Germany), for interim restorations was used in all experiments. Calcium *β*-pyrophosphate ($Ca_2P_2O_7$) was produced in laboratory by sintering brushite at 800 °C The polymeric PMMA matrix was prepared by mixing the two ingredients, the powder and the liquid, in 5:3 ratio, for 30 s. The *β*-CPP powder was pre-weighted in order to get 0.25%, 0.5%, 0.75%, 1%, 2%, 3%, 4% and 5% w/w *β*-CPP content in relation to PMMA powder. The evaluation of the reinforcing impact of the inorganic filler was conducted through the study of other mechanical parameters in 3-point bending test for flexural strength and DMA recordings for storage modulus (E′), loss modulus (E′′) and loss factor (tan*δ*), along with the T_g temperature.

Results: The flexural characteristics of a reinforced material are often affected by interactions between the filler and the matrix of the composite. Although no coupling agent was used in the present study to achieve chemical bonds, the composites did not fail during test, and the load was transferred due to the high contact area between PMMA and *β*-CPP. The reduction in flexural strength observed for the composites with *β*-CPP concentrations higher than 0.75 wt% could be associated with inhomogeneous dispersion of *β*-CPP particles, which increased by increasing the *β*-CPP content. As for T_gs, are located at 120–130 °C, with no variations for the different proportions.

Conclusion: the addition of *β*-CPP in PMMA resins in appropriate proportions can increase the mechanical properties of the material, improving the overall clinical performance of interim restorations

OP18

HYBRID CHITOSAN-BASED FILMS EXHIBITING A STRONG ANTIMICROBIAL ACTION UNDER VISIBLE-LIGHT IRRADIATION AND STIMULI-RENEWABLE PROPERTIES

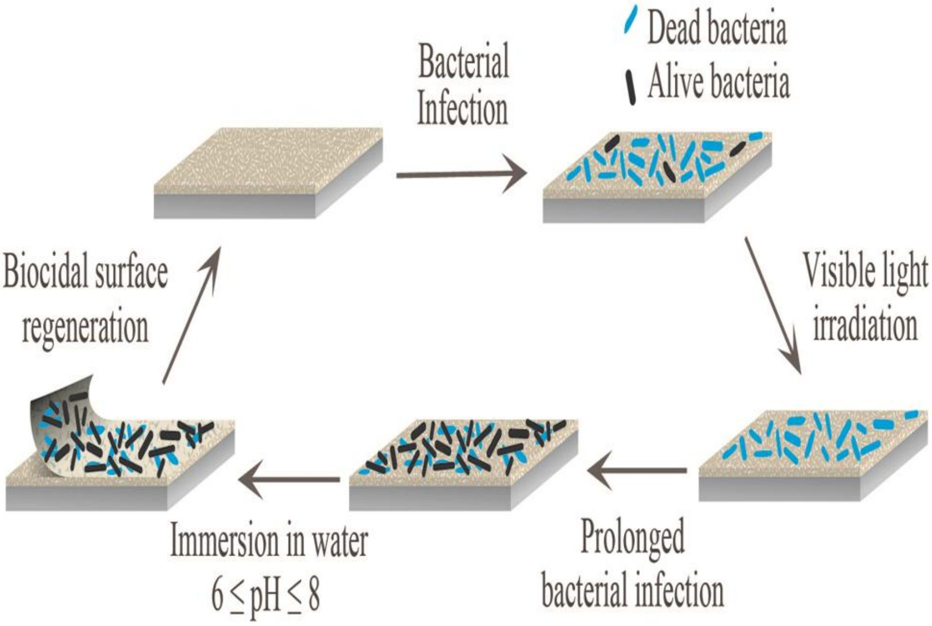
Theodore Manouras[1], Evangelia Vasilaki[1], Eleftherios Koufakis[1], Ioanna Peraki[2], Maria Vamvakaki[1]

[1] Department of Materials Science and Technology, University of Crete, Heraklion 700 13, Crete, Greece & Institute of Electronic Structure and Laser, Foundation for Research and Technology–Hellas, Heraklion 700 13, Crete, Greece
[2] Institute of Molecular Biology and Biotechnology, Foundation for Research and Technology–Hellas, 700 13 Heraklion, Crete, Greece

Hybrid, polymer-inorganic, films, exhibiting an effective antimicrobial action and stimuli-renewable properties were developed [1]. The films were prepared using a chitosan derivative bearing permanent quaternary ammonium salt (QAS) groups along the polymer chains and TiO_2 nanoparticles, modified with reduced graphene oxide (rGO) to shift their photoactivity in the visible light regime. An acid-degradable, acetal-based crosslinker was synthesised and used to cross-link the polymer chains forming stable hybrid films on glass substrates. The surface of the films exhibited an effective biocidal activity in the dark, against both Gram-positive and Gram-negative bacteria, assigned to the biocidal QAS sites, and a pronounced biocidal action upon visible light irradiation, due to the synergistic antimicrobial effect of the QAS moieties and the rGO modified TiO_2 nanoparticles. The stimuli-renewal behaviour of the pH-polishable films was verified by the gradual decrease of the film thickness upon immersion in neutral and slightly acidic aqueous media, attributed to the hydrolysis of the acetal-based crosslinker. Importantly, the hybrid films exhibited a high biocompatibility against mammalian cells, and retained their effective antimicrobial action after self-polishing. The proposed approach underlines the development of highly functional polymer-based coatings, exhibiting durable bactericidal activity for prolonged use in advanced applications.

Acknowledgements*: This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH–CREATE–INNOVATE (project code:T1EDK-01499).*

[1] T. Manouras, E. Koufakis, E. Vasilaki, I. Peraki, M. Vamvakaki, *ACS Appl. Mater. Interfaces* **2021**, *13*, 17183.


Dead bacteria
Alive bacteria
Bacterial Infection
Visible light irradiation
Prolonged bacterial infection
Immersion in water 6 ≤ pH ≤ 8
Biocidal surface regeneration

OP19

MISCIBILITY STUDY OF MODIFIED WITH VANILLIN CHITOSAN BLENDS AND THEIR APPLICATION IN 3D PRINTING

Georgia Michailidou, Dimitrios Bikiaris

Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece

Chitin, the second most abundant natural polysaccharide after cellulose, is derived from certain fungi as well as from the exoskeleton of certain arthropods and crustaceans. Chitosan (CS), the deacetylated derivative of chitin, is a biocompatible, biodegradable and non-toxic material. Owed to its favorable characteristics along with its feasibility of forming films, nanoparticles and sponges, it has been utilized in many pharmaceutical and biomedical applications. Furthermore, derivatization of CS with various monomers as well as combination of various polymers with neat CS for the formation of blends, are exceptional techniques for the preparation of new materials with ameliorated physicochemical properties. Vanillin as a biobased monomer, has been vastly utilized in many areas due to its pleasant flavor, its antioxidant and antimicrobial activity. Nowadays, research is focused on the application of CS in 3D printing procedure. In this study CS was modified with vanillin (VACS) through a Schiff-based reaction. CS/VACS blends were prepared in ratios 90/10-10/90 while their miscibility along with the synergic interaction was examined. Inks designed for 3D printing were prepared and their printing accuracy was evaluated. The new material was assessed through FT-IR and ^{1}H-NMR and results revealed the successful derivatization of the polysaccharide. When designing inks for 3D printing applications, high viscosity values and shear thinning behavior are prerequisite for a uniform extrusion process. Viscosity measurements showed the miscibility of the prepared blends while the synergic interaction index (SI) was calculated, revealing the interactions among the polymeric materials. The extensive interactions between CS and VACS materials lead to highly viscous inks capable of maintaining their structure after 3D printing procedure. These results render the CS/VACS blends promising materials for 3D printing applications.

OP20

CAPILLARY FLOW OF IONOMERS AND THEIR CORRESPONDING COPOLYMERS: EFFECTS OF IONIC AND HYDROGEN BONDING ASSOCIATIONS

Tanja Tomkovic[1], Evan Mitsoulis[2]

[1] Department of Chemical and Biological Engineering, UBC
[2] School of Mining Engineering and Metallurgy, NTUA

Using a parallel plate rheometer equipped with a partitioned plate, and an extensional fixture (SER), a full rheological characterization of several commercial ionomers and their corresponding copolymers has been carried out including the determination of the linear viscoelastic moduli, the damping function and the tensile stress growth coefficient (extensional viscosity). The experimental rheological data have been fitted to a viscoelastic model (K-BKZ). Capillary flow simulations have been carried out to determine the effects of ionic and hydrogen bonding associations on the entry pressure (indication of extensional rheological effects), corner vortex length and strength as well as on the flow patterns formed due to these strong associations.

OP21

MOLECULAR SIMULATIONS OF MULTI-PROCESS AGING OF POLYMER GLASSES: CURRENT STATUS AND PERSPECTIVES

Georgios Vogiatzis[1], Lambèrt van Breemen[2], Markus Hütter[2], Doros Theodorou[1]

[1] Materials Science and Engineering, School of Chemical Engineering, National Technical University of Athens, Athens, Greece
[2] Mechanical Engineering, Eindhoven University of Technology

While the aging of polymer glasses is putting a burden on the long-term functionality of products made out of them, a bottom-up (i.e., molecular-level based) understanding of the parallel aging mechanisms acting is still missing. Since aging mechanisms affect the polymer at the molecular scale, investigation of the change in macroscale properties using atomistically-detailed molecular simulations can provide crucial insights into the processes of physical and chemical aging (e.g., exposure of polymers to aggressive chemicals), as well as UV-induced degradation. By introducing a two-level approach to the treatment of aging, i.e., discerning between individual low-level events and collective phenomena, we have set up a unified description of the time-evolution of a physically aging specimen exposed to reactive chemicals. The first results have been encouraging, i.e., the prediction, from atomistic simulations, of the time-scales of the subglass relaxations of polystyrene and the calculation of diffusivity of reactant polymers within a polymer matrix. However, the goals of incorporating chemical reactions and irradiation-induced degradation are still challenging.

OP22

CLUSTERS OF FREE VOLUME ACCESSIBLE TO SMALL PENETRANTS AND THEIR CONNECTIVITY IN POLYMER NANOCOMPOSITES CONTAINING CARBON NANOTUBES THROUGH A GEOMETRIC ANALYSIS

Panagiotis Mermigkis[1], Vlasis Mavrantzas[2]

[1] Department of Chemical Engineering, University of Patras, & Forth/Ice-Ht,
[2]Department Of Mechanical and Process Engineering, Eth Zurich

Using Delaunay tessellation of space into tetrahedra and Monte Carlo integration [1-2], we have carried out a geometric analysis of clusters of free volume accessible to small penetrants in model carbon nanotube-atactic poly(methyl-methacrylate) (CNT-PMMA) nanocomposites and have analyzed their connectivity [3]. Configurations for the geometric analysis were borrowed from molecular dynamics simulations at higher temperatures and subsequent cooling of selected, thoroughly equilibrated microstructures. The geometric analysis provides direct information for the unoccupied and accessible (to several hard sphere penetrants) volume of the nanocomposites analyzed, as well as the size and shape of the cavities formed. This allowed us to study the dependence of unoccupied and accessible volume on the penetrant size, the temperature, the loading of the matrix in CNTs and the diameter of the CNTs. Nanocomposites containing CNTs with a small diameter were found to contain very few but large cavities of accessible volume to large penetrants, all of which being located inside the CNTs. Nanocomposites containing CNTs with a large diameter, on the other hand, were found to be characterized by small clusters of accessible volume to small penetrants such as water, since these CNTs are fully penetrated by PMMA chains. Overall, a polymer matrix containing CNTs offers larger cavities of accessible volume to water molecules. However, the clusters in the PMMA domains right next to CNT faces are fewer and smaller, or even absent. This might be critical for the transition of a penetrant like a water molecule from a CNT to the PMMA region and vice versa, leading to slower diffusive motion in the nanocomposite than the desired one.

[1] M. Greenfield and D.N. Theodorou, *Macromolecules* **1993**, *26*, 5461−5472.
[2] E. Voyiatzis, M.C. Bo?hm, F. Mu?ller-Plathe, *Comput. Phys. Commun.* **2015**, *196*, 247−254.
[3] P.G. Mermigkis and V.G. Mavrantzas, *Macromolecules* **2020**, *53*, 9563−9583.

OP23

SELF-ASSEMBLY OF AMPHIPHILIC POLYMER CONETWORKS IN THE BULK VIA DISSIPATIVE PARTICLE DYNAMICS SIMULATIONS

Dimitrios G. Tsalikis[1], Yuji Higuchi[2], Mihai Ciobanu[3], Costas S. Patrickios[3]

[1] Department of Chemical Engineering, University of Patras & FORTH ICE/HT
[2] Institute for Solid State Physics, The University of Tokyo
[3] Department of Chemistry, University of Cyprus

Amphiphilic polymer conetworks (APCN) represent a relatively new polymer architecture where the constituent chains are chemically cross-linked, comprising both hydrophilic and hydrophobic units. This unique class of materials has attracted the interest of the polymer community over the last years due to their unique ability to self-assemble, assuming different morphologies by varying the monomer composition, in both aqueous environments and in bulk. In this work, our goal is to model their morphological behavior in bulk to improve our understanding of these networks at the molecular level and facilitate the design of next-generation APCNs

We carried out dissipative particle dynamics (DPD) simulations on APCNs of four-armed star diblocks varying the monomer composition. The chain ends were connected to tetrafunctional cross-links, and the initial configurations were mapped onto a diamond lattice geometry. The corresponding bulk (uncross-linked) systems were also simulated for comparison.

The DPD methodology was validated by comparing our simulation predictions for the morphology with those from established theoretical mean-field models for systems in the bulk. [1] The DPD simulation results had the same phase behavior as those from the theoretical models predicting four different structures: spheres, cylinders, gyroid, and lamellae, modifying the monomer composition. In the case of the APCNs, the situation changed. Due to the presence of cross-links, the demixing in the macroscopic scale was hindered, in sharp contrast to the behavior of the uncross-linked melts. The resulting structures often assumed bicontinuous morphologies in agreement with experimental measurements.[2]

We have presented mesoscopic simulation results for the morphology of APCNs. This work paves the way for establishing a novel understanding of the assumed APCN morphologies and their impact on the resulting (e.g., mechanical) properties of this intriguing class of materials.

[1] M. W. Matsen, M. Schick, Macromolecules 1994, 27, 6761-6767
[2] C. Fodor et al., RSC Adv. 2017, 7, 6827-6834.

OP24

POLYBUTADIENE COPOLYMERS VIA ATOMISTIC AND SYSTEMATIC COARSE GRAINED SIMULATIONS

Anastassia Rissanou[1], Antonis Chazirakis[1], Vagelis Harmandaris[1,2]

[1] Institute of Applied and Computational Mathematics (IACM), Foundation for Research
and Technology Hellas, (FORTH), IACM/FORTH, FR-71110 Heraklion, Greece;
Department of Mathematics and Applied Mathematics, University of Crete, GR-71409,
Heraklion, Crete, Greece
[2] Computation-based Science and Technology Research Center, The Cyprus Institute,
Nicosia 2121, Cyprus

The systematic coarse graining of polymeric systems is a usual route in order to extend the range of spatiotemporal scales and systems accessible to molecular simulations. Here we present a hierarchical bottom-up methodology in order to obtain coarse-grained (CG) models for copolymers, derived from more than one species of monomers, via detailed atomistic simulations.[1] In the proposed scheme each monomer type is represented as a different CG particle. The effective CG interactions are obtained via a dual stage multi-component iterative Boltzmann inversion (IBI) optimization scheme, in which the same component terms of the CG model are obtained from homopolymer simulations, whereas the interactions between different CG type particle (mixed terms of the CG model) from the simulation of a single copolymer, of symmetric composition of the different microstructures. As an example, the proposed optimization scheme is applied on polybutadiene (PB) copolymers consist of cis-1,4, trans-1,4 and vinyl-1,2 isomers. The derived CG PB copolymer model is examined with respect its transferability across molecular weight and the copolymer composition. In addition, using the newly derived CG model various PB copolymers across a broad range of cis-1,4, trans-1,4 and vinyl-1,2 compositions are examined. Structural and dynamic properties of PB copolymers are presented, via the detailed atomistic and the systematic CG simulations, for various compositions. The effect of the vinyl-1,2 component in conformational properties of PB copolymer melts is particularly emphasized, due to the different local packing imposed by side groups. The predicted results are compared against theoretical predictions and composition mixing rules are used to predict the properties of the PB copolymers.

This work is supported by the Goodyear Tire and Rubber Company.

[1] A. Rissanou, A. Chazirakis, M. Doxastakis, P. Polinska, C. Burkhart, V. Harmandaris, to be submitted (2021).

OP25

INDIVIDUAL CONTRIBUTIONS OF ADSORBED AND FREE CHAINS TO MICROSCOPIC DYNAMICS OF UNENTANGLED POLY(ETHYLENE GLYCOL)/SILICA NANOCOMPOSITE MELTS AND THE IMPORTANT ROLE OF END GROUPS: THEORY AND SIMULATION

Emmanuel Skountzos[1], Dimitrios Tsalikis[1,2], Pavlos Stephanou[1], Vlasis Mavrantzas[1,2]

[1]Chemical Engineering Department, Cyprus University of Technology, Cyprus

[2]Foundation For Research and Technology Hellas/ Institute of Chemical Engineering Sciences, Greece

Polymer nanocomposites comprise a class of nanostructured materials where nanosized particles are embedded in a host polymer matrix in order to improve its properties. Several issues remain unresolved, and one of them is the dynamic behavior of the host matrix, and how it depends on the chemistry of polymer's terminal units.

We employed molecular dynamics (MD) simulations to study poly(ethylene glycol) (PEG) melts filled with spherical silica nanoparticles. Two different matrices were examined: hydroxyl-terminated and methoxy-terminated PEG. Information from these MD simulations is used as input into our newly-developed theoretical model, based on the Rouse theory for polymer chains adsorbed by one or both of their ends onto the nanoparticle.

The MD simulations reveal significant differences in the structural and dynamic properties of the PEG/silica nanocomposites studied for different PEG's terminal groups (hydroxyl versus methoxy), originating from the different ways that polymer chains adsorb on the silica surface: hydroxyl-terminated PEG chains are adsorbed by their ends giving rise to a brush-like structure, whereas methoxy-terminated ones are adsorbed equally probably along their entire contour, thus resulting in better packing of adsorbed segments. Due to the dense interfacial layer that develops in both cases, the diffusive behavior of free chains is also affected (it slows down compared to that in the corresponding pure PEG melt), especially in the nanocomposite where PEG chains are terminated with hydroxyl groups. Direct comparison of simulation and theoretical predictions with previously reported experimental data in the literature for the dynamic structure factor [1] for the same systems under the same thermodynamic conditions reveals excellent agreement.

MD simulations were combined with theoretical modelling in order to accurately describe the microscopic dynamics of PEG/silica nanocomposites revealing also the differences when switching polymer's terminal units from hydroxyl to methyl groups. Excellent description of practically the full spectrum of dynamic properties of the two nanocomposites examined was found, judging from the very favorable comparison with the experimental data [1].

[1] T. Glomann et al. *Phys. Rev. Lett.* **2013**, 110, 178001.

OP26

PATCHY-LIKE MIKTO-ARM STAR POLYMERS: ATOMISTIC STUDY OF SOFT BUILDING BLOCKS

Petra Bacova[1], Dimitris G. Mintis[2], Eirini Gkolfi [3], Vagelis Harmandaris[2,3]

[1] Institute of Applied and Computational Mathematics, Foundation for Research and Technology - Hellas, Crete, Greece
[2] Computation-Based Science and Technology Research Center, The Cyprus Institute, Cyprus
[3] Department of Mathematics and Applied Mathematics, University of Crete, Crete

Patchy-like particles represent a family of nanostructured building blocks with multiple segregated regions. By tuning the character and the spatial distribution of these regions, patchy nanoparticles can be used as versatile building units for the design of self-assembled macro-objects. Asymmetric nanostructured objects are achieved by the soft and directional interactions that arise between the patchy regions. Recently, we showed that a single-molecule 32-arm star composed of alternately connected poly(ethylene oxide) and polystyrene arms (PS/PEO stars) nanosegregates into a patchy-like particle in an unfavorable environment for both components [1].

Here, we present an atomistic simulation study of multiple-star systems consisting of PS/PEO mikto-arm stars with a patchy-like morphology [2]. In contrast to the commonly used multi-compartment nano-objects, e.g., mixed hairy particles, the mikto-arm stars are penetrable and intramolecularly nanosegregated. Consequently, the patches are fully interconnected when incorporated into a self-assembled structure. By varying the number of stars in the system, we aim to examine systematically the directional segregation of the star-like building blocks. The individual stars preserve their morphology and shape when they link into a multi-star macromolecular object. We analyse various patterns and types of mutual orientation of the particles. Our results represent the first evidence that the mikto-arm stars can be used as building blocks with the patchy-like morphology in the macromolecular design and reveal possible attachment of these particles in the assembly.

[1] Bacová, P.; Glynos, E.; Anastasiadis, S.H.; Harmandaris, V. Nanostructuring Single-Molecule Polymeric Nanoparticles via Macromolecular Architecture. ACS Nano 2019, 13, 2439–2449.
[2] Bacová, P.; Mintis, D. G.; Gkolfi, E.; Harmandaris, V. Mikto-Arm Stars as Soft-Patchy Particles: From Building Blocks to Mesoscopic Structures. Polymers 2021, 13(7), 1114

OP27

BIOPOLYMER BASED ORGANIC/INORGANIC HYBRID NANOPARTICLES RELEVANT TO BIOIMAGING APPLICATIONS

Maria Karayianni, Stergios Pispas

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation

Introduction: The latest developments in cancer treatment aim to combine therapy and diagnostic imaging, in an attempt to maximize specificity and efficacy [1]. Additional benefits arise by utilizing multifunctional nanoparticles as carriers of bioactive compounds. Biological macromolecules are ideal candidates for these applications, because of their intrinsic biocompatibility, biodegradability, and nontoxicity. Apart from linear biopolymers like chondroitin sulphate (CS), of particular interest is glycogen (Glyc) which is a highly branched polysaccharide of glucose, structured into roughly spherical nanoparticles [2].

Methods: In this work we investigate the interaction of Glyc with CoFe2O4 magnetic nanoparticles (MNPs) and CS with Gd or Eu metal ions, towards the development of biocompatible nanostructures that can serve as bioimaging modalities. Dynamic and electrophoretic light scattering along with cryo-TEM measurements elucidated the properties of the resulting formulations. Magnetophoretic behavior was monitored using a UV-Vis spectrophotometer and a neodymium permanent magnet, while fluorescence spectroscopy probed the optical properties of Eu. Moreover, the bio-applicability of the nanostructures i.e., stability, interaction with biological media (FBS) and drug-loading capacity was also examined.

Results: The solution behavior, size, effective charge and stability of the nanoparticles proved to be dependent on their component ratio, whereas their structure is rather loose. The Glyc/MNPs complexes exhibit a relatively slow response to the magnetic field, while the photoluminescence of the CS/Eu complexes is proportional to the Eu concentration.

Conclusions: Overall, the developed hybrid nanostructures feature innate biocompatibility, are suitable for blood circulation, respond to external stimuli (magnetic field or light), and can be loaded with drugs. All these properties give them great potential as novel theranostic nanocarriers.

References

[1] P. Mi, F. Wang, N. Nishiyama, and H. Cabral, Macromol. Biosci., 2017, 17(1), 1600305.

[2] Q. A. Besford, F. Cavalieri, and F. Caruso, Adv. Mater., 2020, 32(18), 1904625.

OP28

SYNTHESIS OF DOUBLE RESPONSIVE NANOPARTICLES FOR ENCAPSULATION AND DELIVERY OF DOXORUBICIN

Dimitrios Skourtis, Dimitra Stavroulaki, Iro Kyroglou, Hermis Iatrou

Chemistry Department, National and Kapodistrian University of Athens, Athens, Greece

Introduction: Stimuli-responsive nanocarriers have received considerable attention as potential drug delivery vehicles, because they have expressed many benefits for cancer therapy due to the minimization of serious side effects, resulting in improved therapeutic efficacy. For this reason, a series of hybrid polypeptide terpolymers containing poly(ethylene oxide) (PEO), poly(L-Cysteine) (PCys) and poly(L-Histidine) (PHis) were synthesized through a ring opening polymerization process (ROP) of the corresponding N-carboxy anhydrides of a-amino acids using an amine-terminated PEO as macroinitiator. These amphiphilic terpolymers possess the ability to self-assemble in aqueous media and form vesicular nanostructures, comprised of an outer hydrophilic corona of PEO chains, and a pH- and redox- responsive core based on PHis and PCys. PCys has the ability to form disulfide bonds and acts as a crosslinking and stabilizing agent for the NPs. The crosslinking topology of PCys was also studied on the efficiency of encapsulation of the anticancer drug doxorubicin (DOX). The redox-responsiveness of PCys was investigated in the presence of the reductive tripeptide of glutathione (GSH), showing efficient cleavage of the disulfide bonds.

Methods: High vacuum techniques were employed for the synthesis of the polymeric materials. Size exclusion chromatography, FTIR and NMR spectroscopy were used for the characterization of the polymers. Z-potential, Static and Dynamic light scattering and TEM were used for the characterization of the nanoconstructs.

Results: The study showed that DOX was effectively encapsulated in the core of the nanostructures and released in a pH- and redox- triggered manner, as in vitro release studies revealed.

Conclusions: Finally, in vitro cytotoxicity assay of the DOX-loaded nanoparticles against three different breast cancer cell lines showed that the nanocarriers exhibited comparable activity to DOX, rendering these novel double-responsive nanoparticles very promising materials for drug delivery applications.

OP29

FUNCTIONAL PH-RESPONSIVE POLYESTERS FOR TISSUE ENGINEERING APPLICATIONS

Maria Kaliva, Stella Afroditi Mountaki, Konstantinos Loukelis,
Maria Chatzinikolaidou, Maria Vamvakaki

Department of Materials Science and Technology, University of Crete, Crete, Greece

Main chain polyesters have been extensively investigated as promising biomaterials for tissue engineering applications due to their biodegradability and biocompatibility. However, the most commonly used polyesters lack specific functionalities which confer additional physicochemical and biological properties. In this work, we present the synthesis of pH-responsive main chain polyesters bearing alkene/carboxylic acid pendant groups and investigate their potential for use in tissue engineering [1]. The synthesis of the pH-responsive polyesters involved the condensation copolymerization of a vinyl functionalized diol with a diacid chloride, followed by a photo-induced thiol-ene click reaction to attach carboxylic acid side-groups along the polyester chain. Two different mercaptocarboxylic acids were employed, allowing to vary the alkyl chain length of the polymer side groups, while the degree of modification of the alkene side groups the polymer was adjusted at 50, 80, and 100 mol% by varying the irradiation time during the thiol-ene click reaction. The synthesized polyesters exhibited a pH-responsive behavior with tunable solubility in aqueous media as a function of the degree of ionization of the carboxylic acid moieties. Next, the polyesters containing the carboxylic acid/alkene moieties were employed to form cross-linked polymer films on glass slides by chemically linking their vinyl side groups using 2,2-dimethoxy-2-phenylacetophenone as the photo-initiator. The biocompatibility of the cross-linked polyester films was evaluated in L929 fibroblast cultures and showed that the cell viability, proliferation, and adhesion were promoted on the polymer surface bearing the shorter alkyl chain length side groups and the higher content of carboxylic acid functionalities.

References

1. Mountaki, S.A.; Kaliva, M.; Loukelis, K.; Chatzinikolaidou, M.; Vamvakaki, M. *Polymers* **2021**, *13*, 1636.

Acknowledgments: This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code: T1EDK-04052).

OP30

EFFECTS OF NANOMETER CONFINEMENT ON THE SELF-ASSEMBLY AND DYNAMICS OF POLY(Γ-BENZYL-L-GLUTAMATE) HOMOPOLYMERS AND ITS COPOLYMERS WITH POLYISOBUTELENE

Marianna Spyridakou[1], Manos Gkikas[2], Martin Steinhart[3], George Floudas[1],[4]

[1] Department of Physics, University of Ioannina, Ioannina, Greece
[2] Department of Chemistry, University of Lowell, Massachusetts, Lowell
[3] Institut für Chemie neuer Materialien, Universität Osnabrück, D-49069 Osnabrück, Germany
[4] University Research Center of Ioannina (URCI) - Institute of Materials Science and Computing, Ioannina, Greece

Synthetic polypeptides play an important role in biomedical sciences because of their exceptional similarity to proteins. The control of their secondary structure and dynamics, especially under confinement, is a challenge for biological applications. Poly(*γ*-benzyl-L-glutamate), a model rigid-rod polymer,[1-3] was studied as a homopolypeptide and as a copolymer with the flexible polyisobutelene (PBLG-*b*-PIB), and investigated in the bulk and under nanometer confinement in aloumina pores with diameters from 400 nm to 40 nm. Confinement affects the persistence length of their secondary structure (α-helices), as well as the coherence length of the hexagonal packing of the helices. A comparison is made on the self-assembly and dynamics of PBLG polymerized directly from the aloumina pore walls[4] and of PBLG infiltrated from the solution state. A reduction in the glass temperature was found in both cases but the reduction was more severe in the former case. The infiltration method affects also the self-assembly and produces less ordered chain configurations. Infiltration from the solution forces the polypeptide to "break" the ideal helices as it enters the pores. In the copolymers PBLG-*b*-PIB, phase mixing of the two blocks reduces the persistence length of the polypeptide secondary structure, whereas nanometer confinement further destabilizes the α-helices and their hexagonal packing. Inevitably, phase mixing and confinement reduce the PBLG order. Such effects should be considered when biomacromolecules are entering narrow pores.

[1] Block, H. Gordon and Breach Science Publishers, 1983.

[2] Floudas, G.; Spiess, H.W. *Macromol. Rapid Commum.* 2009, 30, 278-298.

[3] Papadopoulos, P.; Floudas, G.; Klok, H.-A.; Schnell, I.; Pakula, T. *Biomacromolecules* 2004, *5*, 81.

[4] Duran, H.; Gitsas, A.; Floudas, G.; Mondeshki, M.; Steinhart, M.; Knoll, W. *Macromolecules* 2009, 42, 2881-2885.

OP31

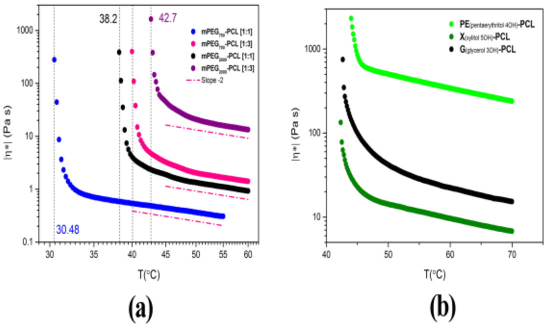
AMPHIPHILIC COPOLYMERS BASED ON POLY(E-CAPROLACTONE) WITH TUNABLE PROPERTIES FOR CONTROLLED RELEASE FORMULATIONS OF THE ANTICANCER DRUG PACLITAXEL

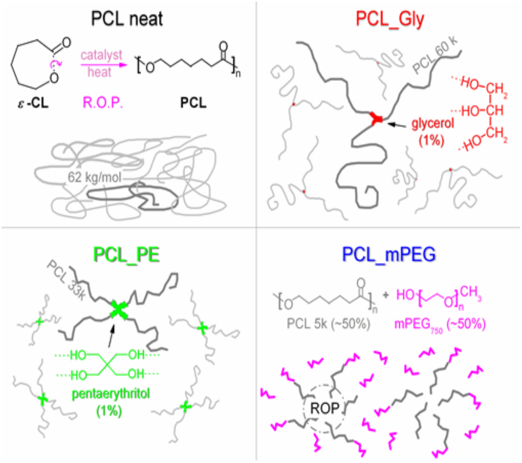
Evi Christodoulou[1], Alexandra Zamboulis[1], Panagiotis Klonos[2], Maria Kasimatis[3], Hermis Iatrou[3], Dimitrios N. Bikiaris[1]

[1] Department of Chemistry, Laboratory of Polymer Chemistry and Technology, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Greece
[2] Department of Physics, National Technical University of Athens (NTUA), Zografou Campus, 15780, Athens, Greece
[3] Department of Chemistry, University of Athens, Panepistimiopolis, Zografou, Athens 15771, Greece

Biodegradable aliphatic polyesters have already found use in a variety of biomedical, pharmaceutical, agricultural and industrial applications. Polycaprolactone (PCL) is a semi-crystalline aliphatic polyester of great significance, particularly in pharmaceutical technology (as a drug carrier matrix or coating material) and tissue engineering, due to its biodegradability, biocompatibility, high flexibility, and low glass transition temperature and melting point. Regarding drug delivery applications, it is commonly known that drug release is severely affected by several parameters, including the glass transition and melting point, the degree of crystallinity and the biodegradation rate of the employed polyesters. Thus, it has been of major interest to tune these properties by the synthesis of either copolyesters using suitable comonomers or polymer (nano)composites.

In the present study, a series of random linear and star-shaped copolymers of different architecture has been prepared *via* ring-opening polymerization of ε-caprolactone with methoxy-poly(ethylene glycol) and three multi-functional alcohols, respectively (**Scheme 1**). Their synthesis was confirmed by NMR and FTIR spectroscopy, while for the structure-properties characterization a combination of complementary techniques has been performed, i.e. GPC, XRD, DSC and rheology measurements (**Figure 1**). Their cytotoxicity has been also tested *in vitro*, demonstrating good biocompatibility for all materials. The synthesized copolymers were then used to fabricate nanoparticles by the oil-in-water emulsion-solvent evaporation technique. The chemotherapeutic agent Paclitaxel (PTX) has been employed as the model drug. The prepared NPs were studied for their size, morphology, and drug loading capacity. The *in vitro* drug release profiles showed enhanced Paclitaxel dissolution rates against neat PCL nanoparticles (presumably due to the hydrophilic segments attached onto the caprolactone backbone), as well as a controlled release behavior in all cases.





Acknowledgements: *The authors wish to acknowledge co-funding of this research by European Union-European Regional Development Fund and Greek Ministry of Education, Research and Religions/EYDE-ETAK through program EPANEK 2014-2020/Action “EREVNO-DIMIOURGO-KAINOTOMO” (project T1EΔK-01612).*

OP32

BIO-BASED THERMOSETTING EPOXY COMPOSITES UTILIZING KRAFT LIGNIN

Christina Pappa, **Konstantinos Triantafyllidis**

Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece

Lignin is a phenolic biopolymer and one of the three main structural components of lignocellulosic biomass, representing also the most abundant natural source of aromatics and phenolics. Even though technical lignins, like Kraft (a side product of pulp and paper industry), are versatile resources being characterized by highly aromaticity and hydroxylated surface, they are underutilized in the currently biorefinery schemes and are being used for in-house production of heat and energy. However, in the last decades the potential of Kraft lignin has been exploited towards the production of new bio-based polymers or as bio-based additive in polymer blends and composites. Epoxy resins have been studied for both the above options, i.e. by replacing petroleum based BPA by lignin derived phenolic analogues or by using lignin as a reactive additive in the bulk epoxy polymer with or without various pre-treatments, e.g., mechanical/chemical modifications (glycidylation, etc.).In this work, Kraft lignin was utilized towards the production of lignin-based epoxy composites. Kraft lignin was used as received or after chemical or mechanical treatment. Epoxy blends were prepared using commercial epoxy resin, i.e., diglycidyl ether of bisphenol A (DGEBA) and Jeffamines D-230 (glassy system) and D-2000 (rubbery system) as curing agents resulting in glassy and rubbery lignin/epoxy composites. The utilization of Kraft lignin was successful in both glassy and rubbery epoxy composite systems. In the rubbery lignin/epoxy composites, up to a 34% replacement was achieved leading to improved stress, stiffness and strain before break. The glassy epoxy composites containing initial kraft lignin and all treated lignins as additives exhibited increased strength and stiffness at low loadings (3 wt.%). This research work was supported by the Hellenic Foundation for Research and Innovation (HFRI) under the HFRI PhD Fellowship grant (Fellowship Number: 967)

OP33

ION TRANSPORT IN POLYMERIZED IONIC LIQUIDS

**<u>Achilleas Pipertzis[1]</u>, George Papamokos[1], Markus Mühlinghaus[2,3], Oskar Sachnik[2,3],
Markus Mezger[4], Ullrich Scherf[2,3], George Floudas[1]**

[1] Department of Physics, University of Ioannina, P. O. Box 1186, 451 10 Ioannina,
Greece
[2] Department of Macromolecular Chemistry, Bergische Universität Wuppertal
[3]Wuppertal Center for Smart Materials and Systems (cm@s), Gauss-Str. 20, D-42119
Wuppertal, Germany
[4] Max Planck Institute for Polymer Research, 55128 Mainz, Germany

Mixed ionic and electronic conductors have great interest for Li-ion batteries.[1] Herein, the ion transport in imidazolium based Polymerized Ionic Liquids (PILs) bearing a π-conjugated polythiophene backbone with four different side-chain lengths [n = 4, 6, 8 and 10] and seven different counteranions ($[Br]^-$, $[BF_4]^-$, $[ClO_4]^-$, $[PF_6]^-$, $[Picrate]^-$, $[TFSI]^-$, and $[B(Ph)_4]^-$) were studied.[2] The combination of DFT calculations with X-ray scattering and dielectric measurements of ion conduction revealed that cation-anion complexation strongly influences the backbone dynamics (T_g) and the associated ionic conductivity. Pressure dependence of ionic conductivity showed that ion conduction is facilitated by local anion jumps and a simple "stick and jump" model can account for the enhanced ion conductivity for anions with intermediate size. In the second part, diblock copolymer electrolytes based on a π-conjugated polyfluorene (PF) backbone were synthesized comprising grafted nanodomains of a PIL and of a solid polymer electrolyte (SPE).[3] The former consists of an imidazolium PIL with a $[Br]^-$ counteranion and the latter of short EO chains doped with LiTFSI. It was revealed that local jumps of $[Li]^+$ ($[Br]^-$) ions in the SPE (PIL) nanophase have the major (minor) contribution to the ionic conductivity.

[1] Patel, S. N.; Javier, A. E.; Stone, G. M.; Mullin, S. A.; Balsara, N. P. Simultaneous Electronic and Ionic Conduction in a Block Copolymer: Applications in Lithium Battery Electrodes. *Angew. Chem., Int. Ed.* **2011**, *50*, 9848−9851.

[2] Pipertzis, A.; Papamokos, G.; Mu?hlinghaus, M.; Mezger, M.; Scherf, U.; Floudas, G. What Determines the Glass Temperature and dc-Conductivity in Imidazolium − Polymerized Ionic Liquids with a Polythiophene Backbone? *Macromolecules* **2020**, *53*, 3535−3550.

[3] Pipertzis, A.; Papamokos, G.; Sachnik, O.; Allard, S.; Scherf, U.; Floudas, G. Ionic Conductivity in Polyfluorene-Based Diblock Copolymers Comprising Nanodomains of a Polymerized Ionic Liquid and a Solid Polymer Electrolyte Doped with LiTFSI. *Macromolecules* **2021**, *54*, 4257-4268.

OP34

DYNAMICS OF POLYMER SOLUTION THIN LIQUID FILMS

Emmanouil Chatzigiannakis, Jan Vermant

Materials, Department of Materials, Soft Materials group, ETH Zurich

Introduction: Film dynamics control many processes in multiphase soft materials, such as emulsions, foams, antibubbles, and polymer blends.

Methods: Using the dynamic thin film balance technique [1] we study the drainage and rupture of thin liquid films consisting of polymer solutions. The variation of the capillary pressure that drives film thinning allows us to control the ratio of the two competing timescales involved in coalescence, i.e. that of drainage and rupture.

Results: Depending on the value of the capillary number and the degree of confinement, different stabilisation mechanisms are observed. For low capillary numbers, the lifetime of the films was the highest for the highly concentrated, narrowly-distributed, low molecular weight polymers. In contrast, at high capillary numbers, the flow-induced concentration differences in the film resulted in lateral osmotic stresses, which caused a dynamic stabilisation of the films. Phenomena such as cyclic dimple formation, vortices, and dimple recoil were observed. The factors which lead to enhanced lifetime of the films as a consequence of these flow instabilities can be used to either stabilise foams or prevent foam formation [2]. The rupture of the films occurs through the evolution of thickness fluctuations, the characteristics of which were measured experimentally. The effect of such fluctuations in the coalescence time becomes gradually less important as drainage intensifies. The criteria for the rupture were extended from equilibrium [3] to draining films [4] and distinct regimes for the character of coalescence were proposed.

Conclusions: Our results show the complexity in the dynamics of "simple" polymer solution films and provide clear guidelines for formulations containing polymers as additives.

[1] E. Chatzigiannakis, et al., Soft Matter, 2020, 16, 9410.
[2] E. Chatzigiannakis and J. Vermant, Soft Matter, 2021, 17, 4790.
[3] A. Vrij, Disc Far Soc, 1966, 42,23.
[4] E. Chatzigiannakis and J. Vermant, PRL, 2020, 125, 158001

OP35

EFFECT OF CONFINEMENT ON THE DYNAMICS OF 1-PROPANOL AND OTHER MONOHYDROXY ALCOHOLS

<u>Antonela Ananiadou</u>[1], George Papamokos[1], Martin Steinhart[2], George Floudas[1,3]

[1] Department of Physics, University of Ioannina, P.O. Box 1186, 451 10 Ioannina, Greece
[2] Institut für Chemie neuer Materialien, Universität Osnabrück, D-49069 Osnabrück, Germany
[3] University Research Center of Ioannina (URCI) - Institute of Materials Science and Computing, Ioannina, Greece

Hydrogen Bonds (HBs) are present in several physical, chemical, and biological processes.[1] Monohydroxy alcohols (MHAs) can easily be supercooled allowing the study of HBs by changing their chemical structure. In dielectric loss curves of MHAs, beyond the relaxations expected from glass-forming systems (β- and α-processes), there exists a process (known as "Debye") with dielectric strength that depends strongly on the molecular architecture, temperature and pressure reflecting supramolecular HB assemblies.[2,3] In this study, we investigate the effect of confinement on the dynamics of three MHAs (1-propanol, 2-ethyl-1-hexanol and 4-methyl-3-heptanol) differing in their chemical structure.[4] First, we employ DFT calculations in bulk 1-propanol to obtain the energetics of linear and ring-like associations composed of up to 5 repeat units. The results show that the ring structures with a low dipole moment (~ 2 D) are energetically preferred. On the other hand, the long-lived *metastable* linear associations have a dipole moment of 2.18 D per repeat unit. The confining media were nanoporous alumina templates with pore diameters from 400 nm to 20 nm. We find that, irrespective of the molecular architecture, all dynamic processes speed-up under confinement. The freezing temperatures for the α and Debye-like processes follow the pore size dependence: $T_{\alpha,D}=T_{\alpha,D}(bulk)-A/d^{1/2}$, where d is the pore diameter. Furthermore, the slow Debye process in 1-propanol turns non-Debye in 2-ethyl-1-hexanol and 4-methyl-3-heptanol. Lastly, we studied the effect of surface treatment of alumina nanopores. Silanization of alumina pore walls only partially recovers the bulk-like dynamic behavior.

References

(1) R. Böhmer, C. Gainaru, R. Richert, Physics Report. **545**, 125-195 (2014).
(2) F. X. Hassion, R. H. Cole, J. Chem. Phys. **23**, 1756 (1955).
(3) C. Gainaru, R. Meier, S. Schildmann, C. Lederle, W. Hiller, E. A. Rössler, R. Böhmer, Phys. Rev. Lett. **105**, 258303 (2010).
(4) A. Ananiadou, G. Papamokos, M. Steinhart, G. Floudas, in preparation (2021).

OP36

SYNERGISTIC EFFECTS OF HUMIDITY AND TEMPERATURE ON THE RHEOLOGY OF SUPRAMOLECULAR ORGANOGELATORS

Emmanouil Vereroudakis[1,2], Daniele Parisi[2], Dimitris Vlassopoulos[2,3]

[1] University of Vienna, Faculty of Physics 71110 Heraklion, Crete, Greece
[2] Institute of Electronic Structure and Laser, Foundation for Research and Technology – Hellas, Greece
[3] Department of Materials Science and Technology, University of Crete,Crete, Greece

It was recently shown that the self-assembly and the viscoelastic properties of organogelators can be affected by the presence of trace amount of water in alkanes[1,2]. The water molecules interact with the supramolecular moieties and participate in the self-assembly process, affecting the overall properties of the material[3]. In this work, we investigate the effects of these interactions on the nonlinear shear response of a supramolecular polymer based on hydrogen bonding. We find that depending on temperature and degree of relative humidity the system can behave in two different ways. When the temperature is low (< 20°C) and/or the relative humidity high (>60%) the system exhibits the typical response of strain softening and shear thinning coupled with shear banding at larger shear rates exhibited typically by living linear wormlike micelles. On the other hand, when the temperature is high (>30°C) and/or the relative humidity low.

We are thankful to N. J. Van Zee, E.W. Meijer and L. Bouteillier for the collaboration and many helpful discussions.

References

(1) Louhichi, A. et al, *J. Rheol.* **2017**, *61* (6), 1173–1182.
(2) Van Zee N.J. et al, *Nature* **2018**, *558* (7708), 100–103.
(3) Vereroudakis, E. *Viscoelastic Properties of Supramolecular Gels Based on Hydrogen Bonding.* Master's Thesis, University of Crete, Greece, 2020.

OP37

LAYERS OF DISTINCT MOBILITY IN DENSELY GRAFTED DENDRIMER ARBORESCENT POLYMER HYBRIDS

Panagiotis Kardasis[1], Nikolaos Kalafatakis[2,3], Mario Gauthier[4], Dimitris Vlassopoulos[2], George Floudas[1,4]

[1] Department of Physics, University of Ioannina, Ioannina, Greece
[2] Institute of Electronic Structure and Laser, Foundation for Research and Technology (FORTH), Crete, Greece
[3] Department of Materials Science & Technology, University of Crete, Crete, Greece
[4] Department of Chemistry, Institute for Polymer Research y, University of Waterloo, Waterloo, Canada
[4] University Research Center of Ioannina (URCI)—Institute of Materials Science and Computing, Ioannina, Greece

A series of multiarm stars of 1,4–Polybutadiene melts (dendrimer-arborescent hybrids) of extreme functionality, (f) and small arm molar mass were studied using dielectric spectroscopy, differential scanning calorimetry and rheology. In particular, a series of stars with 929, 1110 and 2830 side chains, with arm length of 1.5 kg.mol^{-1} and 5 kg.mol^{-1} behave as jammed colloids and show *distinct* layers of segmental mobility [1]. Three mobility layers were identified, comprising outer, intermediate and core segments all with Vogel-Fulcher-Tammann temperature dependence. Functionality affected even the dynamics of those segments located in the outer layer that showed slower dynamics and higher fragility as compared to linear chains. We show that intermediate and core segments have different power law dependencies on functionality (as $f^{-1.3}$ and $f^{-2.0}$, respectively). The corresponding glass temperatures increase as $f^{1/2}$, in qualitative agreement with the results from a recent simulation [2]. Our findings pave the way for further progress in this field by reconsidering previous theoretical treatments based on a single friction coefficient in hybrid nanoparticles such as densely grafted stars.

- [1] P. Kardasis, N. Kalafatakis, M. Gauthier, D. Vlassopoulos and G. Floudas, *Physical Review Letter*, 126, 207802 (2021).
- [2] J. Fan, H. Emamy, A. Chremos, J. F. Douglas, and F. W. Starr, *J. Chem. Phys.* 152, 054904 (2020).

OP38

PROCESSABLE AROMATIC POLYETHERS CONTAINING CONJUGATED CHROMOPHORES OR METALLOCOMPLEXES WITH CONTROLLABLE LIGHT EMISSION FOR LARGE AREA PLEDS

K. Andrikopoulos, S. Aivali, C. Anastasopoulos, A. K. Andreopoulou, J. K. Kallitsis

[1]Chemistry Department, University of Patras, Rio-Patras, GR26504 Patras, Greece
[2]Foundation for Research and Technology Hellas/Institute of Chemical Engineering Sciences (FORTH/ICE-HT), Platani Str., Patras, GR26504, Greece

Organic and polymeric light emitting diodes are promising candidates for lighting applications due to their high processability, simple construction and large area applications. Our previous approach toward soluble film forming polymers with controllable light emission, was based on combinations of conjugated semiconducting units with flexible aliphatic spacers resulting in aromatic aliphatic polyethers that emitted throughout the visible spectrum.[1-4] More recently, unique aromatic polyethers have been created bearing a vast number of conjugated semiconducting units using high temperature polycondensations. This methodology afforded high polymerization yields and versatility in the co-chromophores' ratio within the polymeric backbone. In addition, bis-tridentate iridium(III) complexes have been incorporated along the aromatic polyether backbones affording processable polymeric and co-polymeric metallocomplexes achieving broad and controllable luminescence.[5] Notably, changes of the comonomers' type and ratio led to fine tuning of the emitted light color. All aromatic polyether combine processability with high molecular weights and excellent film forming properties. Thus materials with enhanced solubility in common organic non-volatile, non-chlorinated solvents have been developed allowing their deposition and printing from solution.

Acknowledgements: This research has been co-financed by EPAnEK RESEARCH–CREATE–INNOVATE 2014-2020, project code: Apollon-T1EDK-01039 "Printed OLEDs for Intelligent, Efficient & Tunable solid-state lighting devices in Large Scale".

References

1] F.D.Konstandakopoulou, et.al J. Polym. Sci. Polym. Chem. 37, 3826 (1999).
2] F.D. Konstandakopoulou, et.al. Chem. Mater. 12, 2957 (2000).
3] M. Gioti, et.al. Phys. Status Solidi RRL, 1800419 (2018).
4] M. Gioti, et.al. Materials Today: Proceedings In press 2021.
5] K. Andrikopoulos, et.al. Polymers 12, 2976 (2020).

OP39

CONJUGATED POLYMER NANOPARTICLES AS POTENTIAL THERANOSTIC AGENTS OF BREAST CANCER

Panagiota Koralli[1], Spyridon Tsikalakis[2], Maria Goulielmaki[1], Stella Arelaki[3], Janina Müller,[2,4] Alkmini D. Nega[5], Friederike Herbst[3], Claudia R. Ball[6], Vasilis G. Gregoriou[7], Antonia Dimitrakopoulou-Strauss[5], Stefan Wiemann[2], Christos L. Chochos[1]

[1] Institute of Chemical Biology, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, Athens, 11635, Greece

[2] Division of Molecular Genome Analysis, German Cancer Research Center (DKFZ), Im Neuenheimer Feld 580, 69120, Heidelberg, Germany

[3] Translational Functional Cancer Genomics, National Center for Tumor Diseases (NCT) Heidelberg and German Cancer Research Center (DKFZ), 69120 Heidelberg, Germany

[4] Faculty of Biosciences, University of Heidelberg, Im Neuenheimer Feld 234, 69120, Heidelberg, Germany

[5] Clinical Cooperation Unit Nuclear Medicine, German Cancer Research Center, 69120 Heidelberg, Germany

[6] Translational Medical Oncology, National Center for Tumor Diseases (NCT) Dresden and German Cancer Research Center (DKFZ) Heidelberg, 01307 Dresden, Germany

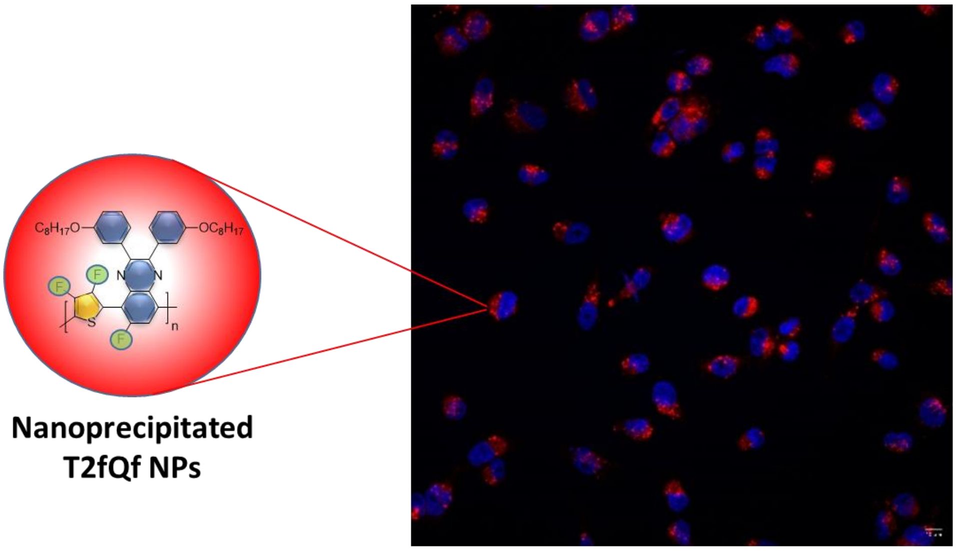
[7] National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, Athens, 11635, Greece

Keywords: polymer dyes, bioimaging, conjugated polymers, nanoparticles, breast cancer, cytotoxicity

Introduction: Conjugated polymer nanoparticles (CPNs) have emerged as a new promising class of cancer theranostic agents due to their unique optoelectronic properties. In this study, nanoprecipitated and encapsulated aqueous CPNs were formulated consisting of thiophene–quinoxaline type conjugated polymers varying as regards the number of the fluorine atoms (three versus four) on the repeat unit. The obtained CPNs were systematically examined in terms of cytotoxicity and intracellular uptake in two different malignant human breast cell lines compared with a non-malignant epithelial cell line, whilst their ability to be used as potential cancer theranostic agents was evaluated.

Methods : To examine the cytotoxic effects of the CPNs on the cells depending on their preparation method, cell proliferation and late apoptotic cell numbers were evaluated. Confocal fluorescence microscopy and flow cytometry investigated the CPNs' ability to be introduced to the cells and their potential application for intracellular imaging protocols. Moreover, to evaluate the potential therapeutic response of CPNs, we compared the cell proliferation and apoptosis results with those induced by the antibiotic staurosporine.

Discussion: The obtained results for the *in vitro* cell viability and cytotoxicity tests revealed that both the nanoprecipitated and the encapsulated T2fQ2f CPNs, as well as the nanoprecipitated T2fQf could potentially be used as FR/NIR fluorescent bioimaging dyes. However, FACS analysis and confocal microscopy confirmed that only the nanoprecipitated T2fQf CPNs could enter into the triple-negative, highly aggressive breast cancer cells with high efficacy and, to a lesser extent into the luminal type-A cells. Interestingly, we observed that these specific CPNs trigger apoptosis in cancer cells, and not in normal-like cells, making them an attractive candidate for further therapeutic intervention.



Nanoprecipitated T2fQf NPs

Fluorescence Image of MDA-MB-231 breast cancer cells with T2fQf NPs

Scheme 1: Structure (left) and representative capture of cellular uptake (right) of T2fQf CPNs by confocal fluorescence microscopy. Merged confocal fluorescence images of cell nuclei (Hoechst/blue) and CPNs (red) were acquired after 24 h treatment of MDA-MB-231 cells with 0.176 mg/mL of nanoprecipitated T2fQf.

Conclusion: In this study, we presented one of the limited studies on the rational design of CPNs for specific biological purposes. The obtained results exhibit the potential of the CPNs to be used for bioimaging applications, as well as the putative therapeutic potential of the nanoprecipitated T2fQf CPNs.

Acknowledgement: Part of this research is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project “Reinforcement of Postdoctoral Researchers - 2nd Cycle” (MIS-5033021), implemented by the State Scholarships Foundation (IKY).

References:

1. **P. Koralli**, A. D. Nega, L.E. Vagiaki, A. Pavlou, M. Siskos, A. Dimitrakopoulou-Strauss, V. G. Gregoriou and C. L. Chochos "***New Conjugated Polymer Nanoparticles with High Photoluminescence Quantum Yields for Far-red and Near Infrared Fluorescence Bioimaging***", Mater. Chem. Front., 2020, 4 (8), 2357-2369 (*https://doi.org/10.1039/D0QM00195C*)
2. **P. Koralli**, S. Tsikalakis, M. Goulielmaki, S. Arelaki, J. Müller, A. Nega, F. Herbst, C. Baul, V. Gregoriou, A. Dimitrakopoulou-Strauss, S. Wiemann, C. Chochos, "***Rational Design of Aqueous Conjugated Polymer Nanoparticles as Potential Theranostic Agents of Breast Cancer***", Mater. Chem. Front. 2021, (*https://doi.org/10.1039/D1QM00479D*)

OP40

AGING ASSESSMENT OF EVERYDAY-USED POLYMERS UNDER UV-B EXPOSURE: AN INSIGHT INTO PHYSICOCHEMICAL ALTERATIONS AND MICROPLASTICS' FORMATION

Nina Maria Ainali [1,2], Dimitrios N. Bikiaris [1], Dimitra A. Lambropoulou [2,3]

[1] Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece
[2] Laboratory of Environmental Pollution Control, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece
[3] Center for Interdisciplinary Research and Innovation (CIRI-AUTH), Balkan Center, Thessaloniki, GR-57001, Greece

Microplastics (plastic items with size <5 mm) are mainly formed by the degradation of plastic wastes under the action of several physicochemical mechanisms in the environment, and they are characterized as emerging pollutants which attract global attention. Nevertheless, research on the aging characteristics and mechanism of microplastics' formation is limited. In the framework of the present study, to ameliorate understanding of plastics' aging under UV exposure and how microplastics are formed, some widely used polymers covering a wide spectrum of applications, including polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET), polyamide (PA), poly(methyl methacrylate) (PMMA) and polycarbonate (PC) in the form of thin sheets, were exposed to UV-B radiation at 280 nm (25 °C, relative humidity 50%). After exposure, the films were removed from the UV-chamber (after 5, 10, 20, 30, 45 and 60 days of radiation) and photodamage was examined by using Fourier-Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), X-Ray Diffraction (XRD) and Pyrolysis − Gas Chromatography / Mass Spectrometry (Py-GC/MS). According to FTIR, the formation of new carbonyl, vinyl, and hydroxyl groups was confirmed, while XRD and DSC measurements boosted the evident effect of UV irradiation in their crystalline and thermal properties. The mechanism of plastic deterioration properties throughout UV exposure was studied by Py-GC/MS, confirming that compounds with low molecular weights are formed, following an increasing tendency as the exposure period increases. SEM micrographs depicted the considerable morphological alterations at the irradiated samples. Py-GC/MS results also proved the differentiation at peak areas of the pyrolytic marker compounds of the currently explored polymers in microplastic analysis, imposing thus a notable impact on the reliability of microplastics' quantification in real samples. All these alterations, accompanied by mechanical properties deterioration proves significantly that UV irradiation leads to reduction of plastics properties whereas gradual fragility leads to microplastic formation.

Acknowledgments

This work was supported by the Greek Ministry of Development and Investments (General Secretariat for Research and Technology) through the research project "Intergovernmental International Scientific and Technological Innovation-Cooperation.

Joint declaration of Science and Technology Cooperation between China and Greece" with the topic "Development of monitoring and removal strategies of emerging micro-pollutants in wastewaters" (Grant no: T7ΔKI-00220) and it is gratefully acknowledged.

OP41

STIMULI-RESPONSIVE PHOTONIC LIQUID MARBLES BASED ON HYDROXYPROPYL CELLULOSE

Manos Anyfantakis[1], Venkata S. R. Jampani[2], Rijeesh Kizhakidathazhath[1],
Bernard P. Binks[3], Jan P. F. Lagerwall[1]

[1] Department of Physics & Materials Science, University of Luxembourg
[2] Department of Condensed Matter Physics, Jozef Stefan Institute
[3] Department of Chemistry and Biochemistry, University of Hull

Liquid marbles (LMs), liquid drops coated by solvophobic particles, represent a unique platform for transporting liquids across substrates with no leakage. Beyond this, the potential of LMs to serve as “mini-reactors” for preparing new materials has been exploited very little and mostly for conventional chemical reactions. Here, we exploit LMs as miniature platforms for programming the self-assembly of the bioderived polymer hydroxypropyl cellulose (HPC), into a cholesteric liquid crystal with tailored structural coloration.

Short-pitch cholesteric phases form in aqueous HPC solutions above a critical polymer concentration. At sufficiently high concentrations, the helical pitch assumes submicrometre values and the material displays structural coloration. Considering this, we prepare LMs of HPC solutions in the biphasic regime, where an isotropic and a cholesteric phase coexist, and by immersing the LMs in a solvent with poor water miscibility, we slowly extract the desired water amount. This allows the chains to self-organize into a cholesteric structure, the pitch of which is tuned by programming the final concentration in the LM. We thus make LMs with selective Bragg reflection tailored to be anywhere in the visible. The LM optical response is sensitive to various external stimuli. For instance, LMs respond with color changes detectable by eye, to temperature changes, the presence of toxic chemicals in their environment, and mechanical compression [1].

From a scientific perspective, the presented concept highlights the advantages of using LMs as a well-controlled experimental platform for inducing, monitoring, and controlling the cholesteric self-assembly of bio-derived polymers; this may improve our understanding of the LC self-assembly of bio-sourced nanomaterials. From a more practical viewpoint, it showcases the potential of LMs as responsive photonic soft objects that may be useful for developing sustainably produced, multifunctional sensing and photonic devices.

Reference

[1] M. Anyfantakis, et al., Angew.Chem. Int. Ed., 59, 19260 (2020)

OP42

CONTROLLING THE SUPRAMOLECULAR SELF-ASSEMBLY OF NUCLEOBASE-CONTAINING BLOCK COPOLYMER NANOSTRUCTURES

Spyridon Varlas,[1, 2] **Jeffrey C. Foster,**[2] **Marjolaine Thomas,**[2] **Zan Hua,**[3, 4]
Rachel K. OReilly[2]

[1]Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, United Kingdom
[2]Department of Chemistry, University of Birmingham, Birmingham, B15 2TT, United Kingdom
[3]Department of Chemistry, University of Warwick, Coventry, CV4 7AL, United Kingdom
[4]Biomass Molecular Engineering Centre, Anhui Agricultural University, Hefei, Anhui, China

The solution self-assembly of amphiphilic block copolymers has facilitated the preparation of a wide variety of nano-objects of diverse morphology. Nucleobase-containing block copolymers and their nanostructures have been extensively studied for their ability to mimic DNA and for their specific and complementary hydrogen-bonding interactions. Recently, our group has reported a novel supramolecular self-assembly process for tuneable growth of well-defined anisotropic worm-like micelles from isotropic spherical micelle seeds, based on H-bonding interactions between complementary adenine (A)- and thymine (T)-containing block copolymers. Based on our initial study, the universal character of this hierarchical self-assembly mechanism has been further extended herein toward transforming nucleobase-containing block copolymer vesicles, prepared *via* aqueous reversible addition-fragmentation chain-transfer (RAFT)-mediated polymerization-induced self-assembly (PISA), as well as core–shell bottlebrush polymers (BBPs) synthesized *via* a combination of ring-opening metathesis polymerization (ROMP) and RAFT polymerization, following a “grafting-from” approach. In both cases, unique higher-order morphologies could be accessed and their characteristics could be precisely tuned by controlling the degree of polymerization and molar ratio of complementary A- and T-functionalized copolymers. Overall, our work highlights the potential of nucleobase-containing block copolymer nano-objects as platforms for understanding fundamental self-assembly processes and their future application in catalysis, sensing, and nanomedicine.

OP43

NOVEL CONDUCTING TRIMERS FOR IN VIVO ELECTRONIC FUNCTIONALIZATION OF TISSUES

Daniele Mantione[1], Emin Istif[1], Gwennael Dufil[2], Lorenzo Vallan[1], Daniela Parker[2], Eleni Stavrinidou[2], Eleni Pavlopoulou[1,3]

[1]Laboratoire de Chimie des Polymères Organiques, Université de Bordeaux, Bordeaux INP, CNRS, France
[2]Laboratory of Organic Electronics, Linköping University, Sweden
[3]Institute of Electronic Structure and Laser, Foundation for Research and Technology – Hellas, 71110 Heraklion Crete, Greece

Electronic materials that can self-organize in-vivo and form functional components along the tissue of interest can result in seamless integration of the bioelectronic interface. We have designed and synthesized three new trimers based on 3,4-ethylenedioxythiophene (EDOT) and thiophene that can be used as conducting building blocks in bioelectronics. The trimers comprise an EDOT-thiophene-EDOT or an all-EDOT backbone and are functionalized by the addition of side groups that bear anionic or cationic moieties. Functionalizing the side groups with anions or cations proves to be an efficient way to tailor the doping level, as well as the oxidation potential, which consequently affects the polymerization kinetics. In addition, we successfully performed the chemical, electrochemical and enzymatic (in physiological pH) in vitro polymerization of the three trimers. Furthermore, the trimers were efficiently polymerized in vivo along the roots of living plants due to the presence of native peroxidase enzymes. The localization of the resulting polymer in the roots depends on the trimers structure. This work not only offers to the bioelectronics community a set of new water-soluble EDOT-based materials for interfacing living tissue, that complements nicely the currently used ETE-S trimer, but, most importantly, paves the way for rational design of electronic materials that can self-organize in vivo for spatially-controlled electronic functionalization of living tissue.

OP44

SYNTHESIS OF MODEL CYCLIC POLYMERS VIA EFFICIENT ETHERIFICATION-BASED BIMOLECULAR RING-CLOSURE STRATEGY

Sandeep Kumar Sharma, Konstantinos Ntetsikas, Viko Ladelta, Saibal Bhaumik, Nikos Hadjichristidis*

Polymer Synthesis Laboratory, Physical Sciences and Engineering Division, KAUST Catalysis Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia

The synthesis of cyclic polymers on a large scale is a challenging task for polymer scientists due to the requirement of ultra-high dilution conditions.[1,2] In this work, we demonstrate a very simple and straightforward method to prepare cyclic polymers with moderate dilution and up to a 1 gram scale. We have used a bimolecular ring-closure strategy by employing the simple and well-known Williamson etherification reaction in the presence of solvent/non solvent combination. In this way, various polystyrene (PS) and polyethylene glycol (PEG) cyclic homopolymers were synthesized. The linear *α,ω*-dihydroxyl PS precursors (HO-PS-OH) were synthesized via anionic polymerization using high vacuum techniques and post-polymerization reaction (deprotection of *α-tert*-butyldimethylsilyl group). The cyclization was carried out through a Williamson etherification reaction among the dihydroxyl- functionalized polymers and two different linking agents [1,4-bis(bromomethyl)benzene and 2,6-bis(bromomethyl)pyridine] in moderate dilution (Figure 1). The synthesized linear and cyclic homopolymers were fully characterized using various analytical techniques such as size exclusion chromatography (SEC), matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS), and differential scanning calorimetry (DSC). Detailed nuclear magnetic resonance (NMR) spectroscopy studies were also performed to obtain complete structural information of the synthesized polymers.

References

1.F. M. Haque and S. M. Grayson, *Nat. Chem.* **2020**, *12*, 433-444.
2.T. Josse, J. De Winter, P. Gerbaux and O. Coulembier, *Angew. Chem. Int.l Ed.* **2016**, *55*, 13944-13958.

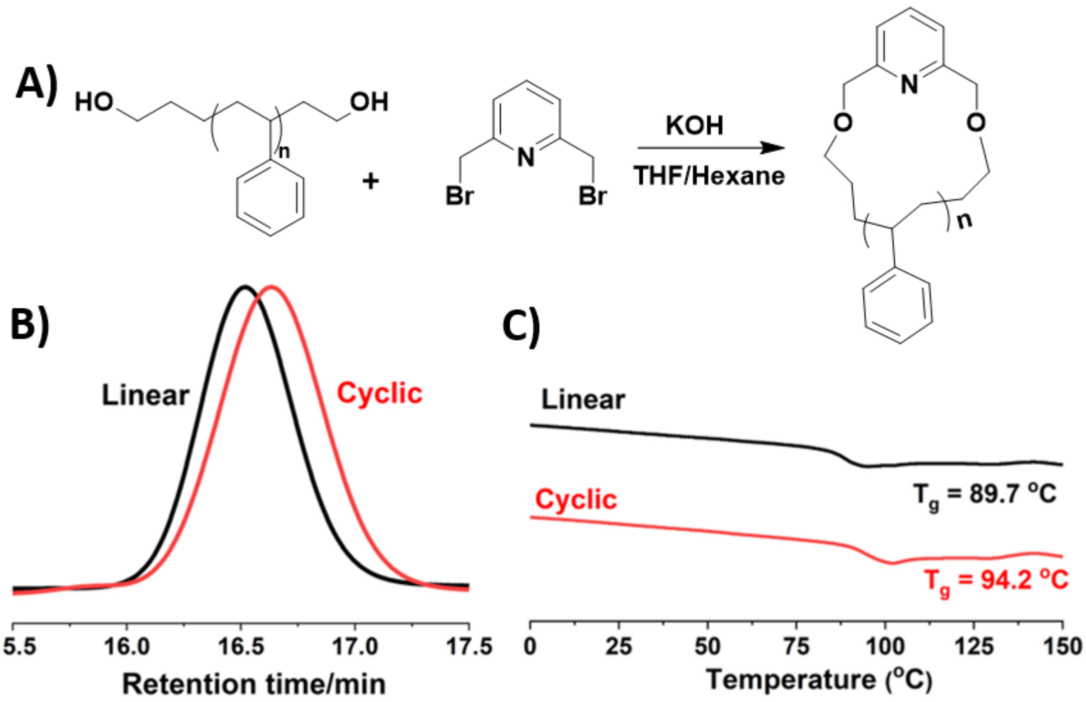


Figure 1. A) General reaction for the synthesis of cyclic PS, B) SEC traces of the linear precursor and the corresponding cyclic PS, C) DSC traces of the linear and the corresponding cyclic PS.

OP45

BIOLOGICAL CELL KILLING INDUCED BY ANISOTROPIC MAGNETIC POLYMERSOME ROTATION UNDER LOW FREQUENCY ALTERNATING MAGNETIC FIELD

Diana Kazaryan, Olivier Sandre, Frédéric Peruch

Laboratoire de Chimie des Polymères Organiques (LCPO), Université de Bordeaux /
CNRS / Bordeaux INP

This project aims at combining the properties of polymersomes as drug delivery systems as well as the magnetic properties of superparamagnetic iron oxide nanoparticles (SPIONS) in order to force mechanical disruption of cell membranes, under the application of a low frequency magnetic field (LF), inducing cell death.

A triblock copolymer consisting of PEG-*b*-PTMC-*b*-PI, synthesized via a combination of ring opening polymerization (ROP) and post-polymerization modification techniques, is being self-assembled into vesicles. SPIONS are embedded in the hydrophobic membrane and induce morphological changes of the polymersomes, under the application of a static magnetic field, by aggregating in a straight line and forcing a deformation which results in anisotropic nanoparticles.

Permanent deformation is induced by UV cross-linking of the hydrophobic membrane while under the magnetic field. Such“ellipsoid” like polymersomes will be introduced into cells at a higher rate than isotropic polymersomes. Finally cell death will be accomplished by application of a LF magnetic field, forcing the polymersomes to rotate with a magnetic torque and distort cell membranes, resulting in cell death.

Various characterization techniques were employed during the synthesis of the copolymers as well as to establish the embedding of the SPIONS and the final formation of the vesicles. Some of those are size exclusion chromatography (SEC), proton nuclear magnetic resonance (NMR) and transmission electron microscopy (TEM).

OP46

CHARACTERISATION AND PYROLYSIS OF THE PLASTIC FRACTION FROM WASTE ELECTRIC AND ELECTRONIC EQUIPMENT (WEEE)

Maria Anna Charitopoulou[1], Lambrini Papadopoulou[2], Dimitris Achilias[1]

[1] Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece
[2] Department of Mineralogy-Petrology-Economic Geology, Aristotle University of Thessaloniki, Thessaloniki, Greece

Waste electric and electronic equipment (WEEE) has increased enormously because of the rapid expansion and consumption of electronic devices and their short lifespan. Recycling of WEEE is challenging, due to the presence of various materials including glass, metals and plastics (~30% of WEEE). Pyrolysis is an environmentally friendly method, since secondary valuable materials or monomers can be recovered. In this work various plastic fractions coming from WEEE, including televisions, computers, printers, remote controls (for TV and DVD), were collected, reduced in size and analysed by various techniques. The plastic parts retrieved from the mentioned devices were manually shredded using hand cutting tools in order to reduce their size and were then subjected to FTIR measurements so as to identify the polymers that were present in each device. Since plastics from WEEE frequently contain brominated flame retardants (BFR), samples from each device were analysed by XRF measurements, with the aim of identifying the possible presence of bromine (in case they were flame retarded). Their degradation behaviour was investigated by Evolved Gas Analysis (EGA), during which samples were heated from 100 to 700 °C with a rate of 20 °C/min, under satisfactory vacuum. Single Shot Analysis was also applied, using a pyrolyser coupled with a Gas Chromatographer/Mass Spectrometer, for the determination of pyrolysis products, after pyrolysis at the maximum degradation temperature that was received from EGA. From EGA analysis it was found that the thermal degradation of the samples in most cases followed a one-step mechanism; however, in some samples two maximum peaks were received. From Single Shot Analysis it was revealed that most samples mainly consisted of styrenic polymers, such as ABS, HIPS, etc. while some of them were blends of ABS/PC. These results were in accordance with those obtained from FTIR.

The research work was supported by the Hellenic Foundation for Research and Innovation (HFRI) under the HFRI PhD Fellowship grant (Fellowship Number: ..853...).

OP47

PREPARATION AND CHARACTERIZATION OF POLYSILOXANE-MULTIWALLED CARBON NANOTUBE NANOCOMPOSITES FOR POTENTIAL SENSORING APPLICATIONS

Panayiotis Ketikis[1], Achilleas Syrmos[1], Panagiotis Klonos[2], Apostolos Kyritsis[2], Petroula A. Tarantili[1*]

[1]Polymer Technology Lab., School of Chemical Engineering, National Technical University of Athens, Heroon Polytechniou 9, Zografou, 15780 Athens, Greece
[2]Department of Physics, School of Applied Mathematical and Physical Sciences, National Technical University of Athens, Heroon Polytechniou 9, Zografou, 15780 Athens, Greece

Composites based on carbon nanotubes and poly(dimethylsiloxane) PDMS, have shown some impressive features with respect to their mechanical and electrical properties, which made them suitable materials for sensors applications. In this work, composites of PDMS filled with multiwalled nanotubes (MWCNT) were prepared by solution mixing in tetrahydrofuran (THF), with the assistance of sonication, in order to achieve adequate dispersion. DSC measurements revealed a decrease in crystallization temperature (T_c) of the elastomeric matrix at low CNTs content (0.05 & 0.1 phr) and an increase at higher loadings (0.2-1 phr), whereas the crystallinity of PDMS matrix was decreased at all the examined filler loadings. The thermal degradation of the investigated composites started at lower temperatures but the completion of the process shifted to higher values, as it was confirmed by thermal degradation analysis (TGA). Impressive enhancement of the tensile strength was recorded, especially in specimens with higher CNT's content. The modulus of elasticity was also improved by the addition of nanofiller, reaching an increase of 48 %, for composites with 1 phr CNT content. Swelling after immersion in toluene was decreased up to 23.7% in the case of composites with 1 phr CNT content, in comparison with pure PDMS specimens. Characterization of composites with dielectric spectroscopy revealed that the percolation threshold was reached at very low CNT's loading, more specifically in the range of 0.02 to 0.05 phr. The increase of CNT?s content in the composites led to increased conductivity up to a level, where saturation was reached. Based on the results of this work, it seemed that solution mixing using sonication led to MWCNT's/PDMS composites with improved mechanical performance and electrical conductivity even at very low filler loadings.

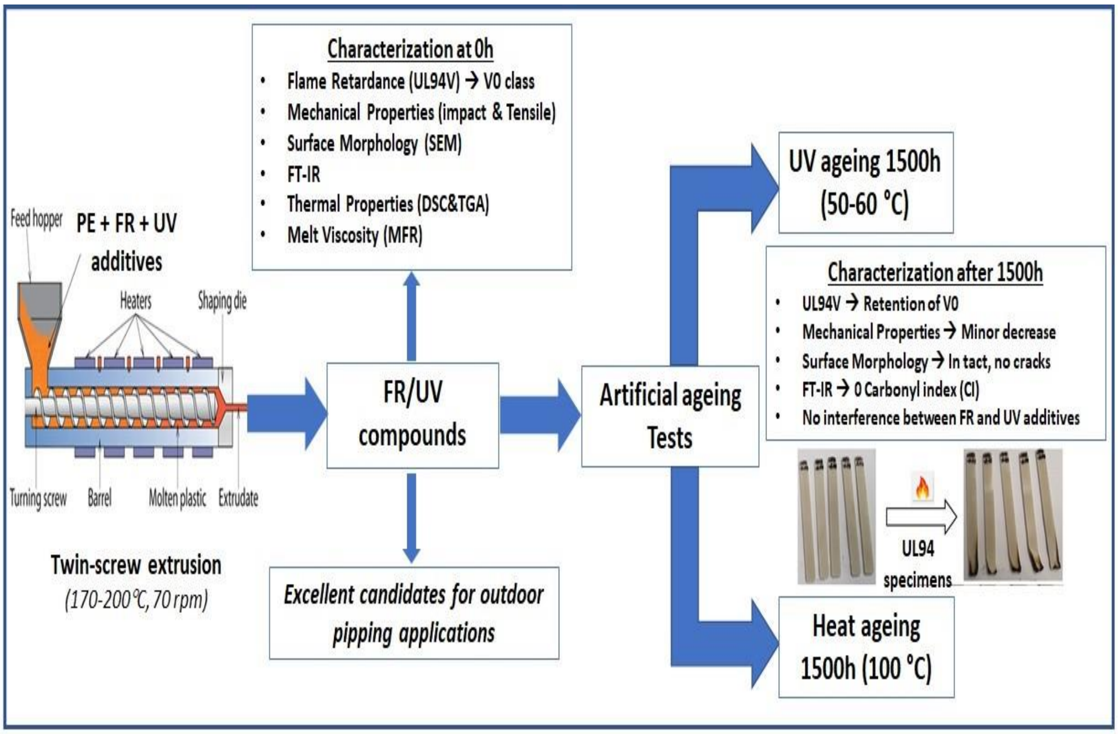
OP48

WEATHERING RESISTANT FLAME RETARDED POLYETHYLENE COMPOUNDS FOR OUTDOOR APPLICATIONS

**Athanasios Porfyris[1], Stamatina Vouyiouka[1], Adriaan Luyt[2], Dimitrios Korres[1],
Sarah Malik[2], Soumia Gasmi[2], Michael Grosshauser[3], Rudolf Pfaendner[3],
Constantine Papaspyrides[1]**

[1] Lab of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zographou Campus, Athens, 157 80, Greece
[2] Center For Advance Materials, Qatar University, Qatar
[3] Plastics Division, Fraunhofer Institute for Structural Durability and System Reliability LBF

This work focuses on the development of different novel, tailor-made polyolefin formulations exhibiting both low flammability and high weathering resistance, so as to provide value-added polyethylene grades with extended service lifetime. Two low-density (LDPE) and one linear low-density (LLDPE) polyethylene grades were modified via melt compounding with an additive system comprising: (a) a nitrogen-phosphorous intumescent system for flame retardance and (b) a hindered amine light stabilizer and a benzophenone-type UV absorber for UV/heat stabilization, at a total loading of 30–35 wt%. The target was to reach V0 classification in UL94V flammability tests, while to a large extent maintaining the mechanical properties, such as, tensile and impact strength of the investigated polymers, thus ensuring that the additives do not interfere significantly with the material quality. Subsequently, the compounds were subjected to separate artificial UV and heat aging at 100°C for 1500 h; the formulations showed good flame retardance, even after prolonged artificial weathering, but there was an observable, although acceptable, decrease in the mechanical properties. Nevertheless, all the results show that the developed polyethylene compounds are very promising for outdoor applications, such as, irrigation piping and profiles, where long-term weathering stability is important, and where flame retardance is important for safety during storage.



Characterization at 0h

- Flame Retardance (UL94V) → V0 class
- Mechanical Properties (impact & Tensile)
- Surface Morphology (SEM)
- FT-IR
- Thermal Properties (DSC&TGA)
- Melt Viscosity (MFR)

Characterization after 1500h

- UL94V → Retention of V0
- Mechanical Properties → Minor decrease
- Surface Morphology → In tact, no cracks
- FT-IR → 0 Carbonyl index (CI)
- No interference between FR and UV additives

Excellent candidates for outdoor pipping applications

OP49

DEVELOPMENT OF SUPERHYDROPHOBIC AND WATER REPELLENT POLYMER COATINGS

Fanourios Krasanakis [1], Thaleia Michaela Chatzaki [1,2], Kiriaki Chrissopoulou [1], Spiros H. Anastasiadis[1,2]

[1]Institute of Electronic Structure and Laser, Foundation for Research and Technology, Hellas, Heraklion Crete, Greece
[2]Department of Chemistry, University of Crete, Heraklion Crete, Greece

Superhydrophobic and water - repellent coatings have attracted a lot of attention due to their wide range of applications. In this work, nanohybrid coatings were developed on Low Density Polyethylene (LDPE) flexible surfaces to enhance their hydrophobicity. The coatings consisted of hydrophobic polymers of different chemistry and suitable inorganic nanoparticles, imparting both low surface energy and the appropriate roughness to the substrate. The surface properties were examined both for the neat and for the coated surfaces; in the latter case the effect of the concentration of the polymer in its initial aqueous dispersion/solution as well as the polymer/inorganic nanoparticles composition was investigated. Contact angle (CA) and contact angle hysteresis (CAH) measurements revealed the optimal cases, that the surface exhibits a superhydrophobic ($CA>150°$) and water - repellent behaviour ($CAH<5°$), as shown in Figure 1. The thermal stability of the obtained surfaces was examined as well, and it was found that their properties remain unchanged with the same contact angles and roll off angles even after annealing at 90°C. Furthermore, the optical and thermal properties of the coated substrates were evaluated and it was found that the transmittance and the thermal transitions of the LDPE remain unaffected by the presence of the coating. These coatings, because of their low roll off angles and their antidust properties, can be ideal candidates for greenhouses applications.

Acknowledgements: This research has been co-financed by EU and Greek national funds (INGRECO MIS: 5030174, Action RESEARCH – CREATE - INNOVATE).

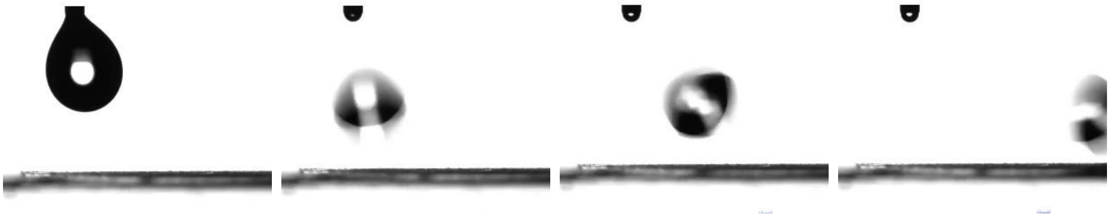


Figure 1: *Water repellency of coated LDPE substrate.*

OP50

NEW ASPECTS ON THE DIRECT SOLID STATE POLYCONDENSATION (DSSP) OF ALIPHATIC NYLON SALTS: THE CASE OF HEXAMETHYLENE DIAMMONIUM DODECANOATE

Angeliki D. Mytara, Athanasios D. Porfyris, Stamatina N. Vouyiouka,
Constantine D. Papaspyrides

Lab of Polymer Technology, School of Chemical Engineering,School of Chemical Engineering, National Technical University of Athens, Zographou Campus, Athens, 157 80, Greece

The Direct Solid State Polycondensation (DSSP) of aliphatic polyamide salts presents significant practical interest, but remains unexploited due to problems arising from solid melt transition (SMT). In this work, the DSSP of hexamethylene diammonium dodecanoate (PA 612 salt) was investigated, shifting the focus to reactor design being the main issue for influencing DSSP kinetics.

Two grades of PA 612 polyamide salt were used as monomers for DSSP, one fossil-based and one partly bio-based. The reaction temperature window for the DSSP experiments was chosen at 160 °C, 165 °C, 168 °C and 170 °C (19-29 °C below monomers' melting point). Reaction was examined both at the microscale (in a TGA chamber), as well at the laboratory scale *via* two different reactors, a commercial cylindrical autoclave (R1) and a novel reactor designed by authors' group (R2). The two reactors were compared in terms of bypassing SMT phenomena and the effect of the critical reaction parameters was examined.

Microscale experiments showed that samples polymerized at 170 °C have fallen completely in the melt state, proving that 168 °C is the upper limit for the successful performance of DSSP.

Turning to laboratory scale results, when tested under the same experimental conditions, SMT occurred in R1, while R2 proved successful in maintaining the solid state during the reaction. After testing different time-temperature profiles in R2, the synthesis of PA 612 was verified for all runs (M_n = 1300-5300 g mol^{-1}), while the imbalance between amine and carboxyl end-groups was minimized at 165 °C for the fossil-based grade.

Finally, a real DSSP process was demonstrated, starting from PA 612 salt crystals and ending with PA 612 particles, involving two isothermal steps, while correcting amine content in between.

Therefore, DSSP was successfully applied for the first time in literature on an Aliphatic Nylon Salt, namely Hexamethylene Diammonium Dodecanoate.

OP51

THERMAL CHARACTERIZATION OF POLYMERS IN NON STANDARD (HIGH PRESSURE, LARGE VOLUME, IN SOLUTION…) CONDITIONS

P. Alafasou

e- POSTERS

RECENT DEVELOPMENTS IN POLYMER SYNTHESIS AND CHARACTERIZATION METHODS

eP01

TEOS-BASED SUPERHYDROPHOBIC COATING FOR THE PROTECTION OF STONE-BUILT CULTURAL HERITAGE

Fotios Adamopoulos[1], Evangelia Vouvoudi[1], Dimitris Achilias[1],
Ioannis Karapanagiotis[2]
[1] Chemistry Department, Aristotle University of Thessaloniki, Thessaloniki, Greece
[2] Management and Conservation of Ecclesiastical Cultural Heritage Objects, University Ecclesiastical Academy of Thessaloniki, Thessaloniki, Greece

Introduction: Alkoxysilanes are widely applied materials for stone consolidation and protection, mainly due to their low viscosity, which allows the materials to penetrate deep into the interior of the stones, forming polysiloxane networks. The introduction of a polyfluoronated silane, FAS, in the recipe induced superhydrophobic and water-repellent properties to the TEOS-based material. Superhydrophobicity and water repellency were evidenced by the large static (CA > 170°) and low sliding (SA < 5°) contact angles of water drops on the coated marble surface.

Methods: Three drops of distilled water were placed at three different spots on coated substrates. Static (CA) and sliding (SA) contact angles were measured using an optical tensiometer apparatus (Attension Theta, Gothenburg, Sweden). For the measurements of the SAs, the tilt rate was adjusted to 1°/s.

Results: Superhydrophobicity and water repellency were obtained on every coated material, as evidenced by the extremely large CA (>160°) and low SA (<7°). Consequently, the TEOS-FAS coating could be applied on a large variety of materials to induce extreme, non-wetting properties. The coating deposition method did not affect the wetting properties of the coating surface. CA and SA of water drops varied roughly within the same range on coatings that were deposited on marble using brush, the spraying system, and the dip coating method. The largest amount of TEOS-FAS was deposited on marble by the dip coating method, followed by brush and finally spray deposition. Likewise, a major difference could be seen in the uptakes of TEOS-FAS deposited by brush and spray. However, CA and SA on the marble specimens coated by the three deposition methods varied within only 171.5–173.0° and 2.3–4.7°, respectively

Conclusion: It was shown that the new material can be used to treat marble, whereas the deposition method does affect the wetting properties.

eP02

IDENTIFYING THE ORIGIN OF AGED VARNISHES FOR THE PROPER RESTORATION OF OLD PAINTINGS USING SPECTROSCOPIC AND SPECTROMETRIC TECHNICS.

Eleni Kargioti[1], Evangelia Vouvoudi[1], Christina Nannou[2], Dimitris Bikiaris[1], Dimitra Lambropoulou[1]

[1] Chemistry Department, Aristotle University of Thessaloniki, Thessaloniki, Greece
[2] Centre for Interdisciplinary Research and Innovation, Thessaloniki, Greece

Introduction: The lifespan of a painting depends heavily on the environment where is stored and exposed, since environmental conditions (temperature, relative humidity, light, contaminants) play a major role in the preservation status of a work of art. Over time, layered materials are exposed to the above conditions for countless consecutive days or change environments at regular time intervals due to their transport, exposure, or storage. The aim of restoration is to bring the project as close as possible to its original situation without losing its authentic elements. The removal of the aged protective layer of the varnish is an extremely delicate process and entails risks, since it is a non-reversible operation.

Methods: Six paintings dated back to 19th century were studied. The traces of varnishes were extracted by scratching a scalpel manually and carefully. FT-IR recordings, Py-GC/MS chronograms and LC–Orbitrap MS/MS chromatograms and spectra were equipped for detailed analysis concerning the ingredients analysis for varnishes.

Results: It was identified through FT-IR that all samples consisted of natural resins and synthetic resins were excluded after comparison with spectra of standard synthetic resins. Py-GC/MS was used to detect the fatty acids of the drying oils in all samples, some of the characteristic substances of the triterpenic resins in some of them and substances from the deposition layer of some works. Then, analyses were performed with the Q Exactive Orbitrap LC–MS, which was used in order to find and identify the substances in the resinous part by finding characteristic substances such as linseed oil, turpentine, mastic and dammar resins or essential oils. Note that it cannot be stated precisely whether there is a second triterpenic resin in paintings TIT2000.272 and TIT2000.025 or not. The presence of nicotine in T?T2001.006 and T?T2000.025 artworks implies their exhibition in home conditions for several years.

Conclusion: regarding the solubility of the varnishes in order to safely remove them of the works of art, it was concluded that the oxidized varnish was removed with ethanol - white spirit 2:1 solution, with the use of cotton swabs. The process was executed manually by an experienced conservator.

eP03

(PDMAEMA)X(POEGMA)Y MIKTO-ARM STAR-SHAPED COPOLYMERS VIA RAFT POLYMERIZATION AND THEIR HYDROPHOBIC MODIFICATIONS TOWARDS AMPHIPHILIC STAR COPOLYMERS

Martha Kafetzi, Stergios Pispas

Theoretical And Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece

Star polymers are an important family of polymers with unique macromolecular topological structures and distinctive solution properties compared to their linear analogues. Moreover, they are appealing materials, applicable in biomedicine for diagnostic and therapeutic purposes. RAFT polymerization is a highly standing synthetic approach that allows the controllable preparation of well-defined star polymers. We report on the synthesis of $(PDMAEMA)_x(POEGMA)_y$ double hydrophilic star polymers by employing the "arm-first" RAFT approach. Firstly, PDMAEMA and POEGMA homopolymers (the arms) were prepared by RAFT and the star copolymer was formed through the polymerization of EGDM that comprises the star core, in the presence of the PDMAEMA and POEGMA arms. Two different star copolymers in terms of composition, molecular weight and arm number were obtained. They were molecularly characterized by SEC, ^{1}H-NMR, LS and ATR-FTIR. Subsequently, the iodohexane and iodododecane agents were used to partially modify the star-shaped copolymers, in order to deliver amphiphilic star copolymers where groups of long hydrophobic chains are randomly distributed along the arms. The modification was confirmed by ^{1}H-NMR. As a result, nanoscale assemblies of star copolymers with hydrophobic inner regions protected by hydrophilic segments were formed in aqueous media, being sensitive to morphological alterations induced by pH and temperature variations, as evidenced by light scattering techniques. When iodododecane was used as the modification agent, the resulting nanostructures respond to pH and temperature changes more abruptly and aggregates of higher mass and smaller dimensions appear.

Acknowledgements: The research work was supported by the Hellenic Foundation for Research and Innovation (HFRI) under the HFRI PhD Fellowship grant (Fellowship Number: 799).

ePO4

A GREEN ENZYME-BASED PROCESS FOR THE PRODUCTION OF POLY(BUTYLENE SUCCINATE)

C.I. Gkountela, D.M. Korres, S.N. Vouyiouka*

Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Greece

Enzymatic polymerization is a sustainable route, forming products free of chemical catalyst residues. Sustainability is reinforced when bio-based and biodegradable polymers are formed, such as poly(butylene succinate) (PBS). Herein, biocatalysis is applied to prepare PBS prepolymers and then post-polymerization in the vicinity of PBS melting point (T_m) is used to upgrade thermal properties and molecular weight.

Stoichiometric amounts of diethyl succinate and 1,4-butanediol were used, and Novozym 435 was added (10 wt%). Solution and solvent-free polymerization systems were studied while the reactions occurred for 24 h at 40°C - 60°C. The formed polyesters were collected as colorless powders.

The chemical structure of the PBS grades was verified via ^{1}HNMR. The achieved process yield was 25-60% and the number-average molecular weight 1000 - 2800 g/mol (Fig. 1). A promising PBS prepolymer (isooctane, 50°C) was scaled up and submitted to a two-step post-polymerization. The aim was to fine-tune the reaction temperature to reach increased polymerization rate with minimum material loss (e.g. oligomers sublimation). The most appropriate conditions were defined (2 h at 80°C, 8 h at 90°C) and resulted in PBS of T_m equal to 104°C, mass fraction crystallinity 70% (Fig. 2) and weight-average molecular weight of 4500 g/mol, free of metal catalyst residues.

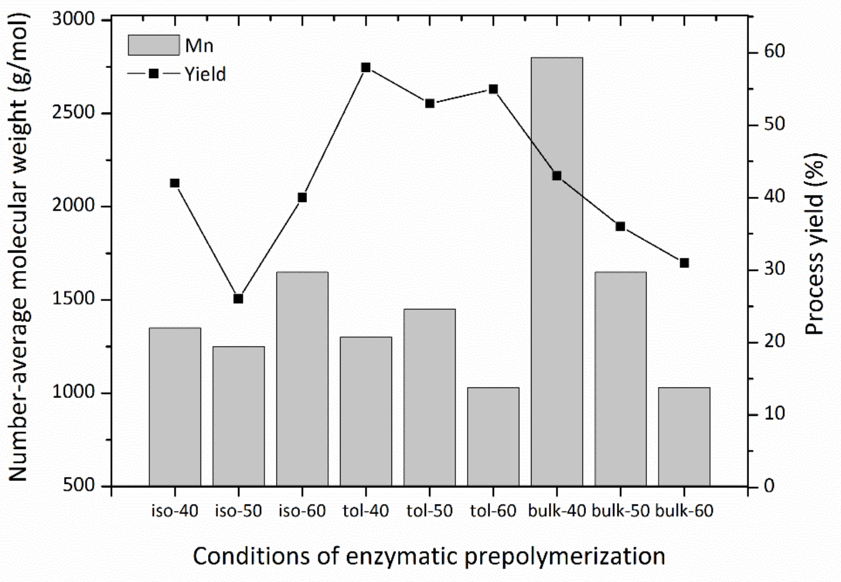


Figure 2. Process yield and ^{1}HNMR-based number-average molecular weight ($\overline{M_n}$) for PBS prepolymers enzymatically synthesized under different conditions (solvent-temperature). *Iso: isooctane, Tol: toluene.*

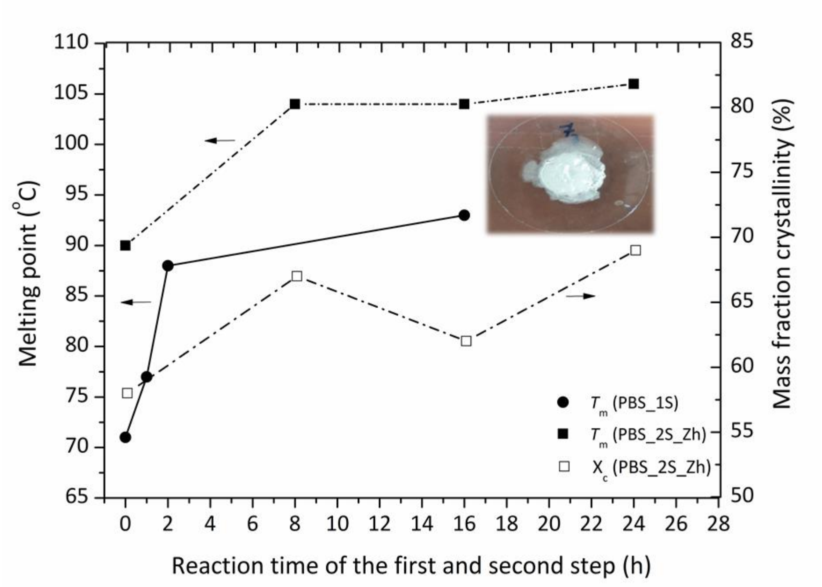


Figure 3. Melting points of PBS_1S and PBS_2S_Zh. Mass fraction crystallinities of PBS_2S_Zh. *PBS_YS_Zh, where Y: Number of steps, Z: Reaction time in the 2nd step (h).*

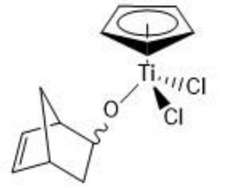
eP05

SYNTHESIS AND CHARACTERIZATION OF COMPLEX MACROMOLECULAR ARCHITECTURES EMPLOYING STATISTICAL AND BLOCK COPOLYMERS BASED ON POLYISOCYANATES WITH FUNCTIONAL END GROUPS AND/OR SIDE CHAINS. INVESTIGATION OF THEIR THERMAL AND OPTICAL PROPERTIES

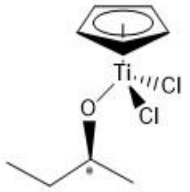
Dimitra Mantzara, Maria Panteli, Aikaterini Katara, Ioannis Choinopoulos,
Marinos Pitsikalis

Industrial Chemistry Laboratory, Department of Chemistry, National & Kapodistrian
University of Athens, Panepistimiopolis Zografou, 15 771 Athens, Greece

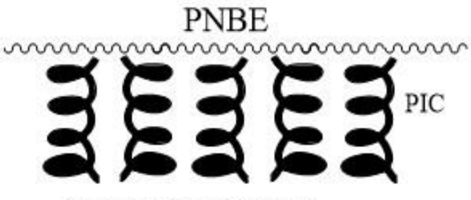
Well-defined statistical and block copolymers of hexyl isocyanate and a) 2-chloroethyl isocyanate, b) 2-phenylethyl isocyanate, c) 3-(triethoxysilyl)propyl isocyanate were synthesized employing titanium complexes as initiators. (S)-2-butyl or 5-norbonenyl end groups have been incorporated in the polymeric chains through the appropriate titanium initiator complex. Subsequent polymerization of the norbornenyl functionalized copolymers with Grubbs catalysts led to complex macromolecular architectures known as bottlebrushes. Enantiomeric (S)-2-butyl end group induced the synthesis of one-handed helical copolymers and their optical properties were investigated using cyclic dichroism spectroscopy. Copolymers with 3-(triethoxysilyl)propyl isocyanate units were hydrolyzed providing star-like architectures. The linear copolymers and the complex architectures were characterized by nuclear magnetic resonance spectroscopy and size exclusion chromatography, and their thermal properties were investigated.



norbornenyl initiator



enantiomeric initiator



bottlebrush architecture

star architecture

ePO6

SYNTHESIS OF A WELL-DEFINED SINGLE-ION MIKTOARM STAR COPOLYMER

Christos Pantazidis,[1,3] **Emmanouil Glynos**,[1,2] **Georgios Sakellariou**[3]

[1]Institute of Electronic Structure and Laser, Foundation for Research and Technology−Hellas, P.O. Box 1385, 71110 Heraklion, Crete GR, Greece
[2]Department of Materials Science & Technology, University of Crete, 71003 Heraklion, Greece
[3]Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, Zografou, 15771 Athens, Greece

Single lithium-ion solid polymer electrolytes (SLI-SPEs) have been extensively researched for their potential use in lithium-ion battery applications. Morphology has a significant impact on the properties of such materials thus, reliable synthetic protocols are needed for different macromolecular architectures. In this work, we report the synthesis and molecular characterization of a miktoarm star copolymer star consisting of poly(ethylene oxide), PEO, and poly(lithium 4-styrenesulfonyl trifluoromethylsulfonyl imide), PSTFSILi, arms and a poly(divinylbenzene), PDVB, core. Initially, a PEO-NMP macroinitiator was synthesized. The “arm-first” method, was employed to produce a PEO star with 22 arms, $(PEO)_{22}$, with a spacious PDVB core, bearing active NMP initiation sites. Subsequent polymerization of the STFSIK monomer (“in-out” method), followed by ion exchange using LiCl, produced a well-defined $(PEO)_{22}(PSTFSILi)_{22}$ miktoarm star, with the crystallization behavior of the PEO segments totally suppressed, as the result of the interactions/complexation of the Li^+ with the PEO arms.

eP07

SYNTHESIS AND CHARACTERIZATION OF THE NOVEL NE-9-FLUORENYLMETHOXYCARBONYL-L-LYSINE N-CARBOXY ANHYDRIDE. SYNTHESIS OF BRANCHED POLYPEPTIDE

Pandora Thimi, Hermis Iatroy

National and Kapodistrian University of Athens Department of Chemistry, Athens, Greece

In this poster the synthesis and characterization of the novel monomer N^{ε}-9-Fluorenylmethoxycarbonyl-l-Lysine *N*-carboxy anhydride (N^{ε}-Fmoc-l-Lysine NCA), as well as the Poly(l-Lysine)$_{78}$–*block*–[Poly(l-Lysine)$_{10}$–*graf*t–Poly(l-Histidine)$_{15}$] block-graft copolypeptide, are presented. The synthesis of the graft copolypeptide was conducted via ring-opening polymerization (ROP) of the N^{ε}-Boc-l-Lysine NCA while using *n*-hexylamine as the initiator, followed by the polymerization of N^{ε}-Fmoc-l-Lysine NCA. The last block was selectively deprotected under basic conditions, and the resulting *ε*-amines were used as the initiating species for the ROP of N^{im}-Trityl-l-Histidine NCA. Finally, the *Boc*- and *Trt*- groups were deprotected by TFA. In order to achieve the synthesis of well-defined polymers, ensure the purity of the solvents and therefore the purity of the whole system so to avoid non controlled polymerization and termination reactions, high vacuum techniques were applied. The characterization of the polymer in order to confirm the successful synthesis as well as to define its molecular characteristics was carried out by Size Exclusion Chromatography, Proton Nuclear Magnetic Resonance and Infrared Spectroscopy. Finally, Dynamic Light Scattering, ζ-potential, and Circular Dichroism measurements were used in order to investigate the ability of the polypeptide to self-assemble in different conditions. This monomer opens avenues for the synthesis of polypeptides with complex macromolecular architectures that can define the aggregation behavior, and, therefore, can lead to the synthesis of “smart” stimuli-responsive nanocarriers for controlled drug delivery applications.

ePO8

STATISTICAL COPOLYMERS OF N-VINYLPYRROLIDONE AND ISOBORNYL METHACRYLATE: SYNTHESIS VIA FREE RADICAL AND RAFT POLYMERIZATION, CHARACTERIZATION, REACTIVITY RATIOS AND THERMAL PROPERTIES

Philippos Kontoes-Georgoudakis, Olga Kokkorogianni, Maria Athanasopoulou, Nikolaos Polizos and Marinos Pitsikalis*

Industrial Chemistry Laboratory, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece

The synthesis of statistical copolymers of N-vinylpyrrolidone (NVP) with isobornyl methacrylate (IBMA) was conducted by free radical and reversible addition-fragmentation chain transfer (RAFT) polymerization. The reactivity ratios were estimated using the Finemann-Ross, inverted Fineman-Ross, Kelen-Tüdos, extended Kelen-Tüdos and Barson-Fenn graphical methods, along with the computer program COPOINT, modified to both the terminal and the penultimate models. According to COPOINT the reactivity ratios were found to be equal to 0.292 for NVP and 2.673 for IBMA for conventional radical polymerization, whereas for RAFT polymerization and for the penultimate model the following reactivity ratios were obtained: r11 = 4.466, r22 = 0, r21 = 14.830, and r12 = 0 (1 stands for NVP and 2 for IBMA). In all cases, the NVP reactivity ratio was significantly lower than that of IBMA. Structural parameters of the copolymers were obtained by calculating the dyad sequence fractions and the mean sequence length. The thermal properties of the copolymers were studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and differential thermogravimetry (DTG). The results were compared with those of the respective homopolymers.

ePO9

INVESTIGATION OF HIGH-χ BLOCK COPOLYMERS WITH LINEAR OR COMPLEX ARCHITECTURE

Polyxeni P. Angelopoulou, Maria-Malvina Stathouraki, Georgios Sakellariou

Department of Chemistry, National and Kapodistrian University of Athens, Athens, Greece

The synthesis of linear (A-*b*-B) and miktoarm star (AB_n, n=2,3) block copolymers with high Flory-Huggins interaction parameter, χ, is described. Anionic polymerization, chlorosilane chemistry and high-vacuum techniques were utilized, to yield monodisperse copolymers with precisely tuned molecular characteristics. The microphase separation of block copolymers with high-χ values allows for well-ordered, distinct, nanodomains even for chains with particularly low molar masses. This, in turn, can lead to ultra-small nanostructures scaling to the sub-10-nm regime. Such remarkably small, periodically ordered structures hold great promise in several fields like nanolithography, nanomembranes or as nanotemplates for various applications. Macromolecular architecture can strongly affect the microphase separation process of block copolymers. Particularly, for miktoarm star copolymers it is known that the phase diagram can be strongly shifted, providing an extra means for tuning obtained morphology of nanostructures. Not much work has been done in the microphase separation of high-χ copolymers with complex architecture, mainly due to synthetic challenges especially in this kind of samples. In this work, we investigate both high-χ miktoarm star copolymers of the $AB_{2,3}$ type and their topological linear isomers, A-*b*-B. Different molecular weights and compositions are examined, to make comparisons between different architectures and highlight the potential of utilizing complex macromolecular architecture of high-χ copolymers to create nanostructures with miniaturized dimensions. The block copolymers synthesized were characterized by Nuclear Magnetic Resonance Spectroscopy (NMR), Size Exclusion Chromatography (SEC) and Small-Angle X-Ray Scattering (SAXS).

eP10

HYPERBRANCED POLYMERS/GRAPHENE OXIDE NANOCOMPOSITES: EFFECT OF GO DEGREE OF OXIDATION

Ioannis Karnis [1,2], Fanourios Krasanakis [1], Anastasia N. Rissanou [1],
Konstantinos Karatasos [3], Kiriaki Chrissopoulou [1]

[1]Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas, Heraklion, Crete, Greece
[2]Department of Chemistry, University of Crete, Heraklion Crete, Greece
[3] Department of Chemical Engineering, Aristotle University of Thessaloniki, Greece

Polymer nanocomposites have been a point of interest for the research community due to the significant enhancement of properties they exhibit which are key aspects for their industrial use. In this work, polymer nanocomposites consisting of Hyperbranched Polymers (HBPs) of varying molecular weight and number of functional groups and Graphene Oxide (GO) of varying degree of oxidation were developed. The change in the degree of oxidation of the nanoadditives was achieved by changing either the oxidation time or the mass of the oxidation medium. In order to quantify the changes, X-Ray Photoelectron Spectroscopy (XPS), X-Ray diffraction (XRD), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were utilized. The mass of the oxidant was proved to be the critical parameter to change the degree of oxidation and thus the hydrophilicity of GO whereas the oxidation time did not affect the results. Following the successful oxidation, GOs with different hydrophilicity were mixed with three generations of the Boltorn Hyperbranched Polymers (HBPs) in a series of concentrations. The structure of the resulting nanohybrids was investigated by XRD, whereas their properties and thermal stability were characterized by DSC, TGA, FTIR and Raman Spectroscopies. For both the GO additives and the nanocomposite materials, computational models were developed to predict their properties, compare with the experimental results and interpret their overall behavior. This research has been co-financed by Greece and EU (POLYGRAPH, MIS: 5050562).

eP11

COPOLYMERIZATION STUDIES OF VINYL ETHERS EMPLOYING ACTIVATED METALLOCENE COMPLEXES AS CATIONIC INITIATORS. CHEMICAL MODIFICATION OF THE COPOLYMERS FOR THE SYNTHESIS OF GRAFT COPOLYMERS

Stavros Zouganelis, Ioannis Choinopoulos, Marinos Pitsikalis

Industrial Chemistry Laboratory, Department of Chemistry, National & Kapodistrian
University of Athens, Athens, Greece

Poly(vinyl ethers) are a class of polymers with a wide variety of applications, such as adhesives, surface coatings and chemical processing. [1] Among these polymers poly(2-chloroethyl vinyl ether) is a very useful intermediate product, since the chlorine atom can be substituted by other groups, thus offering the possibility to prepare functionalized and more complex architectures. [2] Poly(ε-caprolactone) and poly(L-lactide) are highly compatible polymers with various industrial uses, including packaging, films and fibers. [3] In this work, butyl vinyl ether and 2-chloroethyl vinyl ether were copolymerized using an activated cationic zirconocene complex as cationic initiator. The reactivity ratios were estimated using several methods and the structural parameters of the copolymers were obtained by calculating the dyad sequence fractions and the mean sequence length.

The resulting polymers were then chemically modified by various methods leading to the synthesis of graft copolymers. Graft copolymers bearing poly(vinyl ethers) as backbone and either poly(ε-caprolactone) or poly(L-Lactide) as branches were synthesized after substituting the chlorine groups of the poly(vinyl ethers) into azide groups (grafting onto method) or hydroxide groups (grafting from method). Additionally, the hydroxy group poly(vinyl ethers) were reacted with an appropriate acyl bromide to form ATRP initiating groups, which were then used to polymerize N,N-Dimethylaminoethyl methacrylate. The methacrylate containing graft copolymers were also reacted with a phospholane in order to introduce zwitterions to the final polymers. SEC, IR and NMR were employed to monitor the reaction sequence and characterize the products. Finally, the properties of these graft copolymers were studied with Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Circular Dichroism (CD) and Dynamic/Static Light Scattering (DLS/SLS). This synthetic route offers a general approach for the synthesis of amphiphilic or amorphous-crystalline graft copolymers with unique solution and solid state properties.

1. E. Batagianni, Journal of Macromolecular Science, Part A, **53:3**, 140 (2016)
2. O. Confortini, Macromol. Chem. Phys., **208**, 1871 (2007)
3. S. Penczek, Macromol. Symp., **201**, 261 (2003)

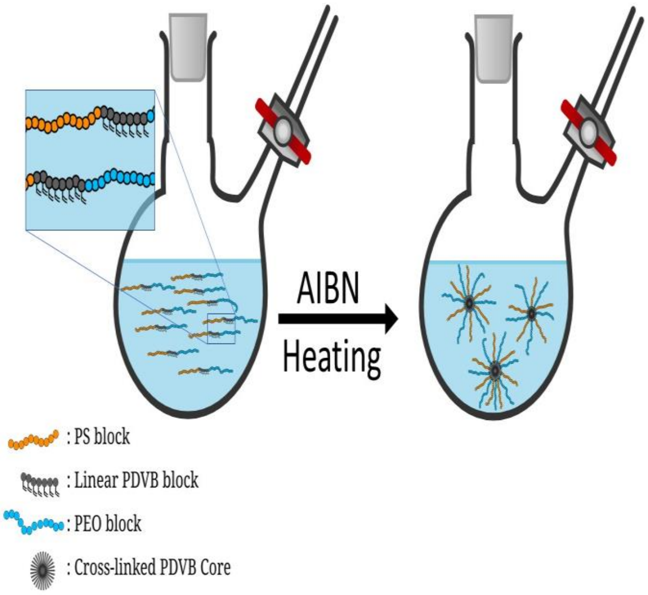
eP12

CONTROLLED BLOCK-POLYMERIZATION OF STYRENE, DIVINYLBENZENE AND ETHYLENE OXIDE. INTERMOLECULAR CROSS-LINKING TOWARDS WELL-DEFINED MIKTOARM COPOLYMER STARS

Emmanouil Mygiakis[1], **Emmanouil Glynos**[2], **Georgios Sakellariou***[1]

[1] Department of Chemistry, National and Kapodistrian University of Athens,
Panepistimiopolis Zografou, 15771 Athens, Greece
[2] Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1385, 71110 Heraklion, Crete GR, Greece

A novel approach for the synthesis of miktoarm copolymer stars with divinylbenzene cross-linked core, via anionic polymerization is reported. This synthetic route gives access to polymers, characterized by low dispersity values and improved structural homogeneity for both arm species. Specifically, miktoarm copolymer stars of A_nB_n type, with cross-linked divinylbenzene (DVB) core and arms of polystyrene (PS) and poly(ethylene oxide) (PEO), are synthesized via anionic polymerization and sequential monomer addition, employing high vacuum techniques. Analytically, the first step involves the synthesis of a triblock terpolymer PS-*b*-PDVB-*b*-PEO. Then, in the presence of a free radical initiator the pending vinyl groups of the middle DVB block cross-link intermolecularly, leading to the final miktoarm copolymer star. The novelty of the proposed synthetic route, lies in the potassium alkoxide *co*-initiator, which is responsible for the controlled polymerization of both DVB and EO in one pot, without the need for end group modification between the two steps. Concerning the final polymer, there are numerous benefits advancing from this synthetic protocol, such as the control of the molecular characteristics of both arms, as well as the easily confirmed structural integrity of the precursor triblock which is inherited to the resulting miktoarm star. For comparison reasons, another batch of (PS)(PEO) miktoarm copolymers was synthesized, following the “in-out” synthetic route. For this reason, styrene was polymerized using *s*-BuLi, which is used as macroinitiator for the polymerization / cross-linking of DVB, resulting PS star with DVB cross-linked core. With the addition of EO, in the presence of p4 *t*-Bu phosphazene base, PEO arms are polymerized, initiating from the core’s active cites outwards.


AIBN
Heating
: PS block
: Linear PDVB block
: PEO block
: Cross-linked PDVB Core

eP13

TRIPLE-STIMULI RESPONSIVE SPIROPYRAN-BASED TRIBLOCK COPOLYMERS

Dimitrios Gounaris Nikolaidis[1], **Maria Vamvakaki**[2]

[1] Department of Chemistry, University of Crete, Crete, Greece
[2] Department of Materials Science and Technology and Institute of Electronic Structure and Laser, University of Crete and Foundation of Research and Technology-Hellas, Crete, Greece

Light-responsive polymers have attracted great attention for use in various applications due to their spatiotemporally controlled response. Photo-responsive polymer micelles have been proposed as nanocarriers to encapsulate hydrophobic molecules within their cores and release them in response to light irradiation.[1] In this work, multifunctional, stimuli-responsive block copolymers were synthesized via reversible addition fragmentation chain transfer polymerization. The well-defined triblock copolymers comprise a hydrophobic poly(spiropyran methacrylate) block, a pH- and T-responsive poly(2-(dimethylamino)ethyl methacrylate) middle block and a hydrophilic poly(ethylene glycol) third block, and can self-assemble, to form spherical micelles, in water. The core of the micelles exhibits a temperature-, pH- and light-responsive behavior, whereas the shell is responsive to the solution pH and temperature. Following UV light irradiation, the hydrophobic spiropyran (SP) moieties in the micellar cores isomerize to their hydrophilic merocyanine (MC) counterparts, leading to the disruption of the micellar structures (Figure 1a), whereas, visible light irradiation of the latter sample induces the MC-to-SP isomerization and the reformation of the spherical micelles. More interestingly, 3 days after UV irradiation the sample revealed the formation of elongated rod-like particles (Figure 1b), which grow further to form helical ribbons after 7 days in the dark (Figure 1c). Work is in progress to further understand and exploit the adjustable polymorphism of the self-assembled structures formed by the newly developed polymers.

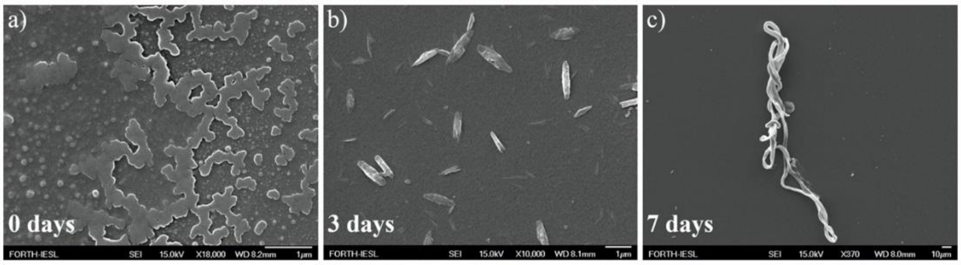


Figure 1: SEM images of the triblock copolymer (a) 0 h, (b) 3 days and (c) 7 days after UV irradiation.

References

1. Falireas, P.G. and Vamvakaki, M. *Macromolecules* **51**, 6848 (2018).

Acknowledgments: This project has received funding from the European Union's Horizon 2020 research and innovation programme H2020-FETOPEN-1-2016-2017 under grant agreement No 737071 (ULTRACHIRAL)

eP14

MELT RHEOLOGY OF SINGLE - CHAIN NANOPARTICLES AND THEIR BLENDS WITH LINEAR HOMOPOLYMERS

Christina Pyromali[1,2], Nikolaos Patelis[3], Emmanouil Glynos[1,2], Georgios Sakellariou[3], Dimitris Vlassopoulos[1,2]

[1] FORTH, Institute of Electronic Structure & Laser, Heraklion 71110, Crete, Greece &

[2]Department of Materials Science and Technology, University of Crete, Heraklion 71110, Crete, Greece
[3]Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, 15771, Athens, Greece

Single – chain nanoparticles (SCNPs) have received attention recently as models for soft colloids and promising candidates in a number of biological and industrial applications. We present a systematic experimental study of the linear viscoelastic properties of polystyrene (PS) SCNPs with the aim to understand the interplay of the polymeric/colloidal dynamics as function of the molecular design parameters. Well-defined SCNPs are synthesized from the linear precursor through the intramolecular cross-linking in a benzene ring-opening reaction under dilute conditions. Intramolecular self-confinement restricts the degrees of freedom of chains forming loops, suppressing the extend and magnitude of plateau modulus in comparison to linear precursor which is an entangled polymer. Increasing the fraction of crosslinker (CrF) at constant molecular weight of the parent polymer (~60k) leads to more internal crosslinks that increase the moduli and delay the (self-similar) stress relaxation. Larger precursor molar mass slows down the dynamics because of the increase in the number of larger loops that promotes the creation of multiloop domains and loops interlocking. The dynamics of SCNPs have been also explored in blends with linear chains showing a consistent increase of the viscosity in the low fraction regime. This is attributed to threading of loops by linear chains similarly to ring-linear blends. More rigid globular SCNPs appear to act as fillers increasing locally the entanglement density. These results provide insights into molecular tailoring of viscoelastic properties of such polymeric materials and mixtures.

eP15

SYNTHESIS AND CHARACTERIZATION OF POLY(DMAEMA-co-LMA-co-OEGMA) TERPOLYMERS

Maria Tomara, Dimitris Selianitis, Stergios Pispas

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, 11635 Athens, Greece

Amphiphilic statistical copolymers are of great interest due to their ability to self-assemble into nanoparticles when inserted in aqueous media, which makes them particularly attractive in industrial level and very useful as drug and gene carriers[2].

In the current study, we report on the synthesis of five novel statistical terpolymers of the type poly(2-dimethylamino ethyl methacrylate-co-lauryl methacrylate-co-oligo ethyl methacrylate) having different compositions via RAFT polymerization.

The PDMAEMA homopolymer is a double-responsive polymer, towards pH and temperature with a pKa[3] of around 7.0 and LCST[3] 32-53 ^oC. PDMAEMA due to the protonation of its amino groups at pH range below neutral, behaves as a cationic polyelectrolyte. Such properties are expected to be found also in statistical copolymers of DMAEMA monomer.

By using dynamic light scattering (DLS) it was observed that the terpolymers form large aggregates in aqueous solution, regardless of the chemical composition and temperature, when the DMAEMA amino group is fully protonated at low pH. When partial or total deprotonation of the amino groups takes place, nanoparticles of very small dimensions and mass appeared, while tending to increase in size and mass as solution temperature increases. Solution ionic strength also affects the structure of copolymers in aqueous solutions resulting in the formation of larger aggregates by increasing NaCl concentration.

References

2. Li Longyu, Raghupathi Kishore, Song Cunfeng, Prasad Priyaa, Thayumanavan S., 2014, *Self-assembly of random copolymers. Chem. Commun., 50(88), 13417–13432*
3. Pepa Cotanda, Daniel B. Wright, Martin Tyler, Rachel K. O'Reilly, 2013, *Polymer Chemistry, 51(16), 3333-3338*

eP16

SYNTHESIS AND CHARACTERIZATION OF MACROMOLECULAR BRUSHES AS SOLID POLYMER ELECTROLYTES IN LITHIUM-ION ELECTROCHEMICAL CELLS

Christos Zisis, Marinos Pitsikalis

Department of Chemistry, National and Kapodistrian University of Athens, Athens, Greece

The ever-increasing demands for new sources of energy is accompanied for novel, safe and efficient ways to store and transfer energy. Our work is focused in synthesizing and studying the properties of solid polymer electrolytes based on poly(ethylene oxide) (PEO), a polyether that shows great conductivity in the amorphous state, in conjunction with polymers that can provide decent mechanical support. Towards this direction advanced synthetic techniques, such as anionic and ring opening metathesis polymerization (ROMP) were employed to produce complex, “brush” like macromolecular architectures that have been proven to show unique effects in reducing the degree of crystallinity of PEO and improving the mechanical properties of the samples. Linear poly(ethylene oxide), poly(styrene oxide) (PStO) and poly(styrene) (PS) with norbornene-end groups were synthesized and were further used to produce macromolecular brushes via ROMP applying suitable Grubbs catalysts. The products were characterized by Size exclusion Chromatography (SEC), NMR spectroscopy, Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). The effect of the macromolecular structure on the crystallinity of PEO and the mechanical properties of the samples were examined.

eP17

AGGREGATION STUDY OF APHIPHILICK BLOCK COPOLYMERS FEATURING A SURFACE LIGAND

Panagiotis Christakopoulos, Hermis Iatrou

Chemistry Department, National and Kapodistrian University of Athens, Athens, Greece

Amphiphilic block copolymers have been used widely as drug delivery systems, due to their ability to encapsulate medical substances. Moreover, many works have been published, about drug delivery systems bearing a target group, in order to achieve greater selectivity against the problematic area. For this purpose, we have synthesized the amphiphilic block copolymer polyethylene glycol -*b*- poly(L-Histidine) (PEG-PHis), featuring the 18β-glycyrrhetinic acid (GA) as a targeting group. GA has been proved to be an efficient target group against tumor cells. Furthermore, PHis due to its ability to respond in different pH environments can be used in polymeric drug delivery systems. Considering these features, we studied the aggregation of these polymers, to determine the capability of been used as drug delivery systems.

eP18

SYNTHESIS OF STAR AND BLOCK COPOLYMERS BASED ON POLY(N-VINYLPYRROLIDONE) THROUGH REVERSIBLE ADDITION FRAGMENTATION CHAIN TRANSFER POLYMERIZATION (RAFT)

Olga Kokkorogianni, Marinos Pitsikalis

Chemistry Department, National and Kapodistrian University of Athens, Athens, Greece

The synthesis of complex architectures of poly(N-vinylpyrrolidone) through various routes has been extensively explored. Both syntheses of PNVP star-shaped homopolymers were based on the arm first strategy, hence the pre-prepared branch was later either conjugated on a multifunctional core or cross-linked using a difunctional monomer as the core. In the latter course Divinylbenzene (DVB) was employed as the cross-linker following the synthesis of the arm of PNVP. In addition to the synthesis of star-shaped homopolymers of PNVP we employed tris(2-aminoethyl)amine as the multifunctional core, on which the PNVP arm was conjugated via an amide bond formation. Finally, PS-b-PNVP along with PEO-b-PNVP copolymers were synthesized, making use of Reversible Addition Fragmentation Chain Transfer (RAFT), polymerization. To begin with, the synthesis of a polystyrene and a poly(ethylene oxide) macro-RAFT agent took place, which were later used for the block co-polymerization of N-vinylpyrrolidone. All the aforementioned materials were characterized structurally and molecularly by Gel Permeation Chromatography (GPC), Nuclear Magnetic Resonance Spectroscopy (NMR) and Static Light Scattering (SLS).

References:

1) McDowall, L., Chen, G. & Stenzel, M. H. Macromolecular Rapid Communications 29, 1666-1671 (2008).

Acknowledgments: Financial Support from the Special Account for Research Grants, in the context of “Stavros Tsakyrakis” Scholarships.

ePl19

SYNTHESIS OF POLY(N-HEXYL ISOCYANATE) AND POLY(Β-BENZYL L-ASPARTATE) BLOCK COPOLYMER, VIA COMBINATION OF COORDINATION AND RING OPENING POLYMERIZATION

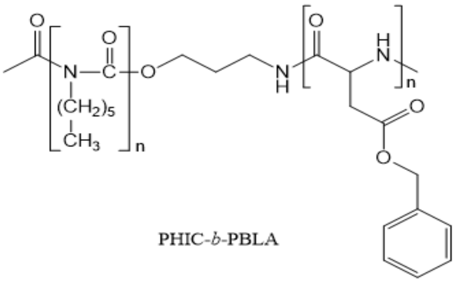
Evangelos Apostolakis, Ioannis Choinopoulos, Marinos Pitsikalis

Industrial Chemistry Laboratory, Department of Chemistry, National & Kapodistrian University of Athens, Athens, Greece

In this work, the synthesis and characterization of the block copolymer (PHIC-*b*-PBLA) is exploited, where PHIC is poly(n-hexyl isocyanate) and PBLA is poly(β-benzyl L-aspartate). The n-hexyl isocyanate was initially polymerized via the coordination polymerization technique using (half-)titanocene alkoxy complexes bearing suitable ligand with protected amino-group.

The protected amine ligand of (half-)titanocene alkoxy complexes is finally located as end-group of the poly(n-hexyl isocyanate) chain. After deprotection this amine moiety may serve as initiator promoting the ring opening polymerization of the N-carboxy anhydrite of L-aspartic acid β-benzyl ester to form the desired block copolymer (PHIC-*b*-PBLA).

The synthesized polymers were thereafter characterized by various methods, such as size exclusion chromatography (SEC), for the study of their molecular characteristics, nuclear magnetic resonance spectroscopy (NMR) to determine their composition, infrared spectroscopy (IR) which helps monitor the conversion of N-carboxy anhydride monomer to polymer (PBLA), differential scanning calorimetry (DSC) to calculate the glass transition temperatures (T_g) and melting temperature (T_m) and thermogravimetric analysis (TGA) in order to study their thermal degradation.



PHIC-*b*-PBLA

eP20

AMPHIPHILIC POLYMER CONETWORKS BASED ON POLY(L-ALANINE) AND FOUR-ARMED POLY(ETHYLENE GLYCOL) STARS: SYNTHESIS AND CHARACTERIZATION

Demetris Apostolides[1], Costas Patrickios[1], Takamasa Sakai[2], Hermis Iatrou[3], Maria Kassimatis[3]

[1] Department of Chemistry, University of Cyprus, 1 University Avenue, 2109 Aglanjia, Nicosia, Cyprus
[2] Bioengineering Department, The University of Tokyo, Tokyo, Japan
[3] Department of Chemistry, National and Kapodistrian University of Athens, Athens, Greece

Amphiphilic polymer conetworks (APCNs) have attracted the attention of many researchers, due to their unique properties and applicability in various fields [1]. APCNs are three-dimensional cross-linked materials consisting of hydrophilic and hydrophobic segments connected with covalent bonds, having the ability to swell in non-polar solvents, and, also, in water. In an aqueous medium, the APCNs nanophase separate leading to the formation of nanoscale sized domains of different morphologies. An important feature of this kind of networks is their higher mechanical strength, compared to the conventional hydrogels, due to the hydrophobic domains acting as energy dissipation centers [2].

Herein, we prepared model APCNs cross-linked *via* the reversible acylhydrazone bonds, combining a linear bis-telechelic hydrophobic *L*-alanine homopolymer having two acylhydrazide terminal groups, with a hydrophilic tetra-telechelic ethylene glycol homopolymer star having four terminal benzaldehyde groups in a non-selective solvent. Initially, on the one hand, the terminal primary amine groups of the hydrophobic homopolymer were transformed to protected benzaacylhydrazide groups through an amidation reaction, before their de-protection with hydrazine hydrate. On the other hand, the terminal hydroxyl groups of the hydrophilic homopolymer were transformed to benzaldehyde groups through an etherification reaction. The formation times of the APCNs were examined with rheology and tube inversion experiments, whereas their degrees of swelling were investigated in selective and non-selective solvents. The mechanical strength of the as-prepared APCNs, as well as the mechanical strength of the swollen APCNs was evaluated with compression and rheology experiments. In addition, small-angle neutron scattering measurements were performed to study the self-assembly of the polymer chains.

References

[1] C. S. Patrickios, Amphiphilic Polymer Co-networks: Synthesis, Properties, Modelling, and Applications, **2020**, Royal Society of Chemistry, London, United Kingdom.

[2] H. Kamata, Y. Akagi, Y. K. Kariya, U. Chang, T. Sakai, *Science* **2014**, *343*, 873-875.

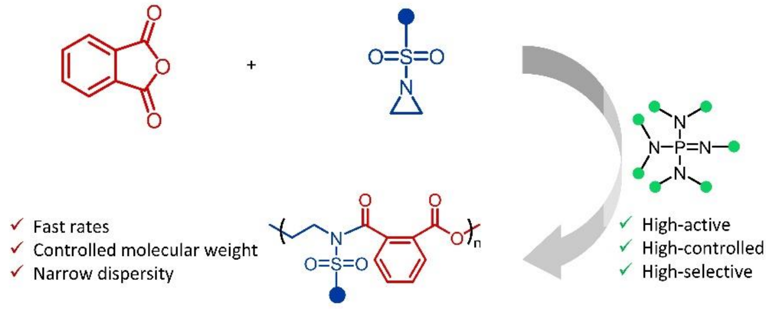
ePP21

CONTROLLED POLY(ESTER AMIDE) VIA ORGANOCATALYTIC SEQUENCE-SELECTIVE RING-OPENING COPOLYMERIZATION OF N-SULFONYL AZIRIDINES AND CYCLIC ANHYDRIDES

Jiaxi Xu and Nikos Hadjichristidis*

King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia
Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory

Poly(ester amide)s, combining the biodegradability and biocompatibility of polyesters with the excellent thermal and mechanical properties of polyamides, have gained an increasing impact in various field.[1, 2] Unfortunately, the poly(ester amide)s with high-controlled molecular weight and narrow distribution were rarely reported. Herein, we reported a new synthetic methodology of poly(ester amide)s from sequence-selective ring-opening alternating copolymerization of *N*-sulfonyl aziridines with cyclic anhydrides. Simple phosphazenes organocatalysts promoted a high-active, high-controlled, and high-selective copolymerization progress without any competitive side reactions (zwitterionic mechanism and exchange transacylations). The block copolymers of poly(ester amide)s and polyamine were prepared in one-pot. The structure of homo- and block copolymers were characterized by NMR spectroscopy, FTIR spectrum, MALDI-ToF MS spectrum, and gel permeation chromatography. Differential scanning calorimetry and thermogravimetric analysis reveal the thermal properties of the poly(ester amide)s.



Scheme. Phosphazenes catalyzed ring-opening alternating copolymerization of *N*-sulfonyl aziridines and cyclic anhydrides.

References:

1. A. C. Fonseca, M. H. Gil and P. N. Simões, *Prog. Polym. Sci.*, 2014, **39**, 1291-1311.
2. P. Ranganathan, C.-W. Chen, S.-P. Rwei, Y.-H. Lee and S. K. Ramaraj, *Polym. Degrad. Stabil.* , 2020, **181**, 109323.

eP22

OXYGEN-TOLERANT SYNTHESIS OF GIANT AMPHIPHILES VIA CUAAC AND THIOL-YNE POST-FUNCTIONALIZATION

E. Voutyritsa, A. Theodorou, Ch. Gryparis, K. Velonia

Laboratory of Synthetic Biomaterials Department of Materials Science and Technology
University of Crete, Crete, Greece

Bioconjugates, presenting enhanced characteristics such as improved stability, biocompatibility and solubility as compared to the parent proteins, are considered as ideal functional biomaterials with numerous potential industrial applications such as molecular sensors, switches or drug delivery systems.[1] Click chemistry is an ideal option for the synthesis of protein-polymer conjugates containing two building blocks in a facile, selective and high-yielding way.[2] However, conventional polymerization protocols are reported to occur under harsh reaction conditions, including deoxygenation of the reaction.[2] Herein, taking advantage of the recently introduced oxygen tolerant, photoinduced and fast RDRP grafting *from* approach for the synthesis of protein-polymer conjugates by Velonia and collaborators,[3] we present a new study, in which chemically addressable biohybrids are synthesized in quantitative yields. Additionally, we present the post-modification of these functional bioconjugates produced via copper mediated CRP *via* CuAAC and thiol-yne click chemistry leading to the formation of giant amphiphiles in quantitative yields either in a sequential or in a one-pot method. This new approach expands the pool of bioconjugates that can be readily synthesized. The synthetic approach as well as the self-organization and activity of the bioconjugates will be presented.

1. R. Duncan, *Nat. Rev. Drug Discovery*, **2003**, *2*, 347.
2. a) L. Zhang, Y. Zhang, J. Cheng, L. Wang, X. Wang, M. Zhang, Y. Gao, J. Hu, X. Zhang, J. Lü, G. Li, R. Tai and H. Fang, *Sci. Rep.*, **2017**, *7*, 10176. b) E. Daskalaki, B. Le Droumaguet, D. Gerard and K. Velonia, *Chem. Commun*., **2012**, *48*, 1586.
3. a) A. Theodorou, E. Liarou, D. M. Haddleton, I. G. Stavrakaki, P. Skordalidis, R. Whitfield, A. Anastasaki and K. Velonia, *Nat Commun*, **2020**, *11*, 1486; b) A. Theodorou, P. Mandriotis, A. Anastasaki, K. Velonia, *Polym. Chem.*, **2021**, *12*, 2228.

eP23

SELF ASSEMBLY OF LOW MOLECULAR WEIGHT ASYMMETRIC LINEAR TRIBLOCK TERPOLYMERS: HOW LOW CAN WE GO?

Ch. Miskaki [1], I. Moutsios [1], G.-M. Manesi [1], K. Artopoiadis [1], C.-Y. Chang [2], E. A. Bersenev [3,4], D. Moschovas [1,3], M.Karabela [1], N.E. Zafeiropoulos [1], D. A. Ivanov [3,4,5], R.-M. Ho[2], A. Avgeropoulos[1,3*]

[1]Department of Materials Science Engineering, University of Ioannina, University Campus- Dourouti, 45110 Ioannina, Greece.
[2]Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan
[3]Faculty of Chemistry, Lomonosov Moscow State University (MSU), GSP-1, 1-3 Leninskiye Gory, 119991 Moscow, Russia
[4]Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, 142432 Moscow, Russia
[5]Institut de Sciences des Matériaux de Mulhouse–IS2M, CNRS UMR7361, 15 Jean Starcky, 68057 Mulhouse, France

Linear triblock terpolymers have attracted great scientific interest due to the well-defined three-phase morphologies they obtain which are often unattainable by diblock copolymer systems, attributed to the third chemically different block, rendering them as potential candidates for advanced applications. Sequential anionic polymerization under high vacuum conditions was employed, in order to synthesize novel, extremely low total number average molecular weight triblock terpolymers of the PS-*b*-$PB_{1,4}$-*b*-PDMS and the $PB_{1,4}$-*b*-PS-*b*-PDMS type, where PS corresponds to polystyrene, PDMS to poly(dimethylsiloxane) and $PB_{1,4}$ to high 1,4-microstructure poly(butadiene). The aim of this work is twofold: (a) to examine the self-assembly capability in such systems and (b) to examine the potential microphase separation when the elastomeric $PB_{1,4}$ block is either the first block or the middle block, respectively. The molecular characterization was accomplished via size exclusion chromatography, vapor pressure osmometry and proton nuclear magnetic resonance spectroscopy in order to verify the molecular characteristics of all precursors, intermediate diblock copolymers and final linear triblock terpolymers. In addition, differential scanning calorimetry experiments were carried out in order to verify the existence of the characteristic glass transition temperatures (T_g) for each segment. The morphological characterization of all samples was achieved via transmission electron microscopy and small angle X-ray scattering. Furthermore, the structure/properties relationship of such triblock terpolymers in bulk was determined for the first time, leading to dimensions as low as 16 nm. The self-assembly in thin films may possibly lead to sub-10 nm periodicities enabling the use of such materials in nanotechnology and nanopatterning.

Acknowledgements

C.M., I.M., G.-M.M., K.A., D.M. and A.A. would like to acknowledge the Network of Research Supporting Laboratories at the University of Ioannina for letting them use the Electron Microscopy Facility and the Nuclear Magnetic Resonance Spectroscopy Center. The National Synchrotron Radiation Research Center (NSRRC) is also acknowledged for its assistance in the Synchrotron SAXS experiments.

Funding

A.A., D.M., D.A.I. and E.A.B. acknowledge financial support from the Ministry of Science and Higher Education of the Russian Federation within State Contract 075-15-2019-1889. D.A.I. and E.A.B. performed their work in accordance with State Task No. AA 19-119101590029-0. The research work was partially supported by the Hellenic Foundation for Research and Innovation (HFRI), under the HFRI PhD Fellowship grant (fellowship no. 1651) for G.-M.M. The research work was partially supported by the Hellenic Foundation for Research and Innovation (HFRI), under the HFRI PhD Fellowship grant (fellowship no. 1650) for I.M. The research work was also supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.), under the "First Call for H.F.R.I. Research Projects to support Faculty members and Researchers and the procurement of high-cost research equipment grant" (Project Number: 3970, acronym: NANOPOLYBRUSH)

H.F.R.I.
Hellenic Foundation for
Research & Innovation
NANOPOLYBRUSH

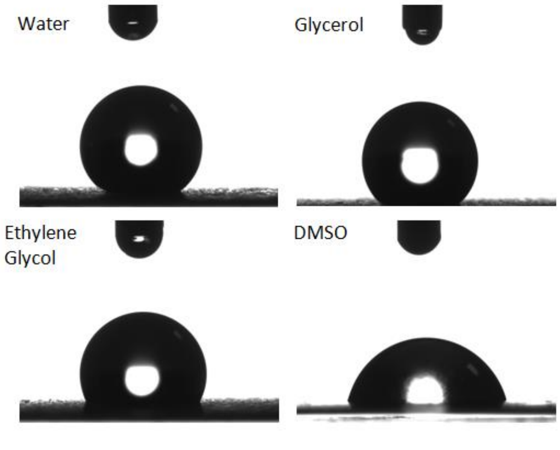
eP24

ALTERING THE SURFACE PROPERTIES OF FLEXIBLE SUBSTRATES BY UTILIZING NANOSTRUCTURED COATINGS

Thaleia - Michaela Chatzaki[1,2], Fanourios Krasanakis[1], Kiriaki Chrissopoulou[1] and Spiros H. Anastasiadis[1,2]

[1] Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Heraklion Crete, Greece
[2] Department of Chemistry, University of Crete, Heraklion Crete, Greece

In recent years, the development of amphiphobic surfaces has attracted considerable interest due to their broad range of applications. Simultaneously, the properties of polymers can be tuned by the incorporation of nanoadditives in a polymer matrix, forming a composite material. In this study, we report on the development of oleophobic nanocomposite coatings, utilizing nanoparticles of different size added in a low surface energy polymer. The coatings were deposited on Low Density Polyethylene (LDPE) substrates appropriately modified by Corona treatment. The surface properties of the films were evaluated via Contact Angle (CA) measurements, indicating they highly depend on the kind of polymer matrix (silane/siloxane mixture, fluoropolymer), its concentration in aqueous solution, as well as on the content and size of the incorporated inorganic nanoparticles. Moreover, the CA values were affected by each solvent's surface tension (Glycerol, Ethylene Glycol and Dimethyl Sulfoxide), with none of them surpassing that of water (Figure). The surface topology and roughness of the coatings were studied by Scanning Electron Microscopy (SEM) providing complementary information towards the interpretation of the results. The coated films exhibited the same transmittance and thermal properties as the original ones, as proven by UV-Vis spectroscopy and Differential Scanning Calorimetry (DSC), respectively, making them potential candidates in applications for the coverage of greenhouses.



Acknowledgements: This research has been co-financed by EU and Greek national funds (INGRECO MIS: 5030174, Action RESEARCH – CREATE - INNOVATE).

eP25

INTERACTIONS, MORPHOLOGY, AND THERMAL PROPERTIES OF ALL-POLYMER NANOCOMPOSITES MATERIALS COMPOSED OF MIKTO-ARM COPOLYMER STAR/LINEAR POLYMER BLENDS

Georgia Nikolakakou,[1,2] Georgia Giannadaki, [1,2] Lampros Papoutsakis,[1,2]
Alkmini D. Nega,[4] Georgios Sakellariou,[4] Spiros H. Anastasiadis[1,2],
Emmanouil Glynos[1,3]

[1] Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1385, 711 10 Heraklion, Crete, Greece
[2] Department of Chemistry, University of Crete, P.O. Box 2208, 710 03 Heraklion, Crete, Greece
[3] Department of Materials Science and Technology, University of Crete, P.O. Box 2208, 710 03, Heraklion, Crete, Greece
[4] Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografrou, 15 771 Athens, Greece

One of the most demanding challenges in the nanocomposite area is the ability to control nanoparticle spatial distribution within a polymer matrix. This is a critical issue since it is currently accepted, that a specific nanoparticle dispersion state is necessary to optimize desired properties of polymer nanocomposites[1]. Recent theoretical[2] and experimental[1] works are instructive about how entropic and enthalpic interactions between polymer-tethered nanoparticles and a polymer host may be used to control the dispersion state of NPs in the polymer host. Here, in order to take advantage of both developments, we utilized stiff/rigid nanostructured polymer particles as additives to liquid poly(ethylene oxide), PEO, for the synthesis of all-polymer nanocomposite systems with controlled morphologies. The nanoparticles composed of high functionality mikto-arm copolymer stars, in which *n* polystyrene (PS) arms complement *n* poly(methyl methacrylate) (PMMA) arms, $(PS)_n(PMMA)_n$. We show that when the lengths of the PMMA arms are comparable with that of the PS arms, bicontinuous nanostructured materials with highly interconnected, interpenetrating percolating domains within the oligomeric PEO are formed, while the polymer nanoparticles are homogeneously dispersed in the PEO matrix when the PMMA arms are longer than that of the PS arms. The final morphology is the result of two competing interactions: (i) inter-molecular attractions between the PS, which promote aggregation, as they are immiscible with the oligomeric PEO, and (ii) the favorable enthalpic interactions of the PMMA arm with the oligomeric PEO host that promote particle dispersion. We show that both the interfacial interactions between the PEO host and the mikto-arm stars and the dispersion state drive the crystallization behavior of the PEO within the nano-structured materials.

References

1. Kumar, S. K., Jouault, N., Benicewicz, B. & Neely, T. Nanocomposites with polymer grafted nanoparticles. *Macromolecules* **46,** 3199–3214 (2013).

2. Borukhov, I. & Leibler, L. Enthalpic stabilization of brush-coated particles in a polymer melt. *Macromolecules* **35,** 5171–5182 (2002).

Ευρωπαϊκή Ένωση

ΕΛΛΗΝΙΚΗ ΔΗΜΟΚΡΑΤΙΑ
ΥΠΟΥΡΓΕΙΟ
ΑΝΑΠΤΥΞΗΣ ΚΑΙ ΕΠΕΝΔΥΣΕΩΝ

ΕΠΑνΕΚ 2014-2020
ΕΠΙΧΕΙΡΗΣΙΑΚΟ ΠΡΟΓΡΑΜΜΑ
ΑΝΤΑΓΩΝΙΣΤΙΚΟΤΗΤΑ
ΕΠΙΧΕΙΡΗΜΑΤΙΚΟΤΗΤΑ
ΚΑΙΝΟΤΟΜΙΑ

ΕΣΠΑ
2014-2020

Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

eP26

EXPLORING “SOFT-NATURE” DIENE-SILOXANE ELASTOMERS

Ioannis Moutsios[1,*], Gkreti-Maria Manesi[1], Konstantina Tsitoni[1], Cheng-Yen Chang[2], Rong-Ming Ho[2], Apostolos Avgeropoulos[1]

[1]Department of Materials Science and Engineering, University of Ioannina, University Campus, Ioannina 45110, Greece

[2]Department of Chemical Engineering, National Ching Hua University, Hsinchu, 30013, Taiwan, R.O.C

Semi-organic polymers and especially siloxane-based copolymers have gained a worldwide interest due to their unique properties and their direct and indisputable application in the field of nanotechnology. Combining two soft nature polymeric segments such as: $PB_{1,2}$: high ~1,2 microstructure poly(butadiene) and PDMS: poly(dimethylsiloxane), prominent results have been retrieved, giving rise to new studies in flexible nanoelectronics. Copolymers of the $PB_{1,2}$-*b*-PDMS type, with different molecular weights and volume fraction ratios, have been synthesized through anionic polymerization under high vacuum techniques, exhibiting low dispersity indices and well-ordered morphologies when studied in bulk. Molecular and structural characterization methods were conducted through size exclusion chromatography (SEC), membrane osmometry (MO) and proton nuclear magnetic resonance spectroscopy (^{1}H-NMR). Differential scanning calorimetry (DSC) measurements were carried out in order to thermally characterize all the synthesized diblock copolymers. The morphological characterization was accomplished *via* transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS). Despite the soft elastomeric and viscoelastic nature of $PB_{1,2}$ and PDMS segment respectively, the intrinsic chemical incompatibility between the polymeric segments, results in high Flory-Huggins parameter χ, a fact that is verified from the different morphologies obtained by TEM studies. The different molecular weights and volume fraction ratios of the synthesized samples, led to either gyroid phases or symmetric tilt grain boundary morphologies.

Acknowledgements: The research work was funded by the Hellenic Foundation for Research and Innovation (HFRI), under the HFRI PhD Fellowship Grant (Fellowship Number 1650).

ePP27

SYNTHESIS AND SELF-ASSEMBLY BEHAVIOR OF LINEAR AND NON-LINEAR STAR BLOCK COPOLYMERS

Gkreti-Maria Manesi,[1,*] Ioannis Moutsios[1], Cheng- Yen Chang[2], Rong-Ming Ho[2], Apostolos Avgeropoulos[1]

[1]Department of Materials Science and Engineering, University of Ioannina, University Campus, Ioannina 45110, Greece

[2]Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan, R.O.C

Block copolymers self-assembly has been rendered a method of choice for current nanotechnology-related applications in areas as diverse as electronics, photonics, etc. Complex architecture star block copolymers have attracted considerable attention and now hold a key role in fabricating nanostructures exhibiting feature sizes as small as 10 nm. Polystyrene-*b*-poly(dimethylsiloxane) linear and star block copolymer systems have been extensively studied in the literature due to the exquisite properties they exhibit, the high χ values and the ability to self-assemble in well-ordered nanodomains. The synthesis of PS-*b*-PDMS diblock copolymer arms was achieved employing anionic polymerization under high vacuum techniques and subsequently, chlorosilane chemistry was utilized for the synthesis of star block copolymers with various arm numbers [$(\text{PS-}b\text{-PDMS})_{2,3,4,6}$]. All linear and star shaped materials were molecularly characterized through size exclusion chromatography, vapour pressure/membrane osmometry and proton nuclear magnetic resonance spectroscopy, in order to determine the total number average molecular weights, the dispersity indices as well as the volume fraction of each block. The thermal transitions were specified through differential scanning calorimetry, indicating the absence of mixing, since the corresponding values were almost identical with those of the relative homopolymers. The bulk phase behaviour and the architecture effect on the obtained morphologies were studied through transmission electron microscopy and small angle X-ray scattering.

Acknowledgments: The research work was supported by the Hellenic Foundation for Research and Innovation (HFRI), under the HFRI PhD Fellowship grant (fellowship no. 1651).

ePP28

ASSOCIATING POLYMERS AND SELF-ASSEMBLIES UNDER HIGH PRESSURE

N. A. Burger[1,2*], A. Mavromanolakis[1], G. Meier[3], K. Ntetsikas[4], N. Hadjichristidis[4], L. Bouteiller[5], B. Loppinet[1], D. Vlassopoulos[1,2]

[1]Foundation for Research & Technology Hellas (FORTH), Institute for Electronic Structure & Laser, Heraklion 70013, Greece
[2]University of Crete, Department of Materials Science & Technology, Heraklion 70013, Greece
[3]Forschungszentrum Jülich, Institute of Complex Systems (ICS-3), Jülich 52425, Germany
[4]King Abdullah University of Science and Technology, Thuwal 23955, Saudi Arabia
[5]Sorbonne Université, CNRS, IPCM, Equipe Chimie des Polymères, Paris 75005, France

An experimental methodology to investigate the dynamics and frequency dependent linear viscoelasticity of solutions of complex polymeric assemblies at high pressures (reaching 1 kbar) is presented. A dynamic light scattering (DLS) approach was combined with a high-pressure stainless-steel chamber consisting of 6 optical windows to perform measurements at three different scattering angles. Nitrogen gas was the pressure transmitting medium. We report results with two systems. (i) We established the dynamic state diagram of a supramolecular polymer based on hydrogen-bonding (EHUT) in apolar solvents cyclohexane and dodecane, which forms two supramolecules structures, tubes and filaments. Pressure was found to stabilize the tubes. (ii) Telechelic star polymers of different functionality (3,16) and block copolymer arms, associate in selective solvents for the inner block and form clusters at low concentrations. High pressure yielded a significant decrease of hydrodynamic radius of the clusters, whereas at high temperatures and pressures they broke-up and only single stars existed in solution. These examples indicate the important role of pressure on both structure and dynamics of associating supramolecular systems and call for further investigations into this virtually unexplored regime.

ePP29

POLYMER CRYSTALLIZATION IN THE PRESENCE OF INORGANIC NANOPARTICLES

Georgia Markozanne[1,2], Antigonos Theodorakis[1,2], Kiriaki Chrissopoulou[1],
Spiros H. Anastasiadis[1,2]

[1]Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (FORTH), Heraklion Crete, Greece

[2]Department of Chemistry, University of Crete, Heraklion Crete, Greece

In this work, the thermal behavior of poly(ethylene oxide), PEO, upon the incorporation of SiO_2 nanoparticles (NPs) was investigated. More specifically, SiO_2 NPs of three different sizes,NP_{67} (SNOWTEX ZL, R= 67nm), $NP_{18.5}$ (LUDOX AS40, R = 18.5 nm) and NP_7 (LUDOX LS, R = 7 nm) were embedded into PEO (MW =300,000 g/mol), in various ratios, and the thermal properties of the composites were evaluated, in terms of the total crystallinity as well as of the critical temperatures of melting (T_m), crystallization (T_c), glass transition (T_g) and thermal decomposition (T_d), via Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). According to DSC measurements, both the number of thermal transitions and the respective temperatures were affected by the composition and the size of the NPs. For nanohybrids with high PEO composition the total crystallinity and the critical temperature values remained relatively constant. However, when the ratio of NPs is increased, additional transitions were observed, with lower T_m and T_c, whereas the total crystallinity and T_g (where distinguished) were decreased as well. On the other hand, the T_d of the systems remained relatively constant, as proved by TGA measurements. Our findings imply that the thermal stability of the polymer is not affected by the presence of SiO_2 NPs. The results are compared with nanohybrids with the same kind of nanoparticles and a PEO polymer of lower molecular weight to investigate the effect of confinement on the obtained results.

Acknowledgements: This research has been co-financed by EU and Greek national funds (INGRECO MIS: 5030174, Action RESEARCH – CREATE - INNOVATE).

eP30

APPLICATION OF ALTERNATIVE AND ECO-FRIENDLY METHODS TO ESTIMATE COPOLYMER COMPOSITION IN LAB SCALE MICROBIALLY PRODUCED PHBVS BY RAMAN SPECTROSCOPY AND DIFFERENTIAL SCANNING CALORIMETRY

Panagiotis Tsaousis[1], Elianta Kora[1,2], Giannis Penloglou[3], Kostas S. Andrikopoulos[1,4], Ioanna Ntaikou[1], Christos T. Chasapis[5], George Voyiatzis[1], Gerasimos Lyberatos[1,6], Costas Kiparissides[7,8]

[1] Foundation for Research and Technology-Hellas, Institute of Chemical Engineering Sciences, (FORTH/ICE-HT), Stadiou Str. Platani, GR-265 04 Patras, Greece
[2] Department of Environmental Engineering, University of Patras, 2 Seferi st., GR 30100, Agrinio, Greece
[3] Chemical Process and Energy Resources Institute (CPERI), Centre for Research and Technology Hellas (CERTH), Thermi, Thessaloniki, 57001, Greece
[4] Department of Physics, University of Patras, GR 26500, Patras, Greece
[5] NMR facility, Instrumental Analysis Laboratory, School of Natural Sciences, University of Patras, GR 26500, Patras, Greece
[6] School of Chemical Engineering, National Technical University of Athens, Zografou Campus, GR 15780, Athens, Greece
[7] Chemical Process and Energy Resources Institute (CPERI), Centre for Research and Technology Hellas (CERTH), Thermi, Thessaloniki, 57001, Greece

[8]Department of Chemical Engineering, Aristotle University of Thessaloniki (AUTH), Thessaloniki, 54124, Greece

Polyhydroxyalkanoates (PHAs) are a category of biological polymers synthesized and stored in the cytoplasm of various microorganisms as a source of energy in environments of nutrient limitation. These high molecular weight polyesters, being fully biodegradable, provide a great alternative to conventional plastics and when produced from renewable sources can contribute to the goal of a circular economy. Since polyhydroxybutyrate P(3HB), the pure homopolymer of this category, is quite unstable around the melting temperature, its processing via conventional thermal processing techniques is largely inhibited. Thus, the challenging intracellular copolymerization poses the most efficient method to depress the melting point, as predicted by the theories of random copolymer statistics. The production of PHAs was established with a Pure Microbial Culture for the case of P(3HB) homopolymer and a Mixed Microbial Culture for the case of P(3HB-co-3HV) copolymers of different 3-Hydroxy Valerate Content (3HV content). In the present work, the copolymer composition was intensively studied by comparing fittings from vibrational peaks in a series of micro Raman spectra alongside implementing thermal protocols established with Differential Scanning Calorimetry (DSC) and data extrapolations in order to estimate the Equilibrium Melting Temperature (T_m^o) of these Lab Scale produced polyesters. The results were then compared with reference materials

and published data. By implementing the aforementioned protocols, the P(3HB-co-3HV), produced by the Mixed Microbial Culture contained 3-Hydroxy Valerate Content, was estimated, ranging from 2.5 to 6 % (mol) and Equilibrium Melting Temperatures from 183 to 178 ^{o}C, whereas the T_m^o of P(3HB) was estimated as 198 ^{o}C.

Combining the non-Destructive Raman with the popular DSC technique, a quick and efficient method is developed as an alternative to the traditional methods, without the necessity of pyrolyzing the materials or dissolving them in harmful solvents. The project “Wastes-to-Biopolymers” is implemented under the “Action for the Strategic Development on the Research and Technological Sector”, funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and European Regional Development Funds (project code: T1EDK-02822).

eP31

DEVELOPMENT OF FUNCTIONAL MATERIALS SURFACES

Franceska Gojda, [1, 2] **Lampros Papoutsakis,** [1] **Michael Loulakis,** [1] **Stelios Tzortzakis** [1, 3]
Kiriaki Chrissopoulou, [1] **Spiros H. Anastasiadis**[1, 4]

[1] Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Heraklion Crete, Greece
[2] Department of Physics, University of Crete, Heraklion Crete, Greece
[3]Department of Materials Science and Technology, University of Crete, Heraklion Crete, Greece
[4] Department of Chemistry, University of Crete, Heraklion Crete, Greece

The development of a superhydrophobic and in certain cases water repellent surface is reported utilizing a simple, fast and economical way that needs minimum demands regarding the necessary equipment and methods. The material used was a smooth Ti6Al4V metal alloy that is widely utilized in several applications however its surface is considered hydrophilic. The surface of the material was initially irradiated by a femtosecond (fs) laser, without following a specific pattern, in order to acquire the necessary roughness. Following the irradiation, the effect of different parameters like temperature, pressure as well as residence time under heating or vacuum on the surface properties was investigated and the results were compared to the respective ones of a smooth surface. Contact angle and contact angle hysteresis measurements were performed to evaluate the wetting properties. The surface morphology was imaged by scanning electron microscopy (SEM) whereas the surface chemical composition was evaluated by energy dispersive X-Ray spectroscopy (EDS). A just-irradiated surface exhibits superhydrophillic behavior, nevertheless its residence in an oven at different temperatures results in an alteration of its surface characteristics and in the manifestation of a hydrophobic behavior especially for temperatures higher than 120°. A similar effect was observed in the case that an irradiated surface was placed in a vacuum chamber (pressure 10^{-2} mbar); after a minimum of 3 hours the surface was converted to a superhydrophobic one, which additionally possessed water repellent properties, exhibiting very high contact angle and very low contact angle hysteresis. The observed behavior can be understood if one considers the change in the surface morphology and surface chemical composition.

Acknowledgements: This research has been financed by FEMTOSURF, the European Union’s Horizon 2020 research and innovation program under grant agreement No 825512.

eP32

EFFECT OF CONFINEMENT ON POLYMER CRYSTALLIZATION AND DYNAMICS IN POLY(ETHYLENEOXIDE)/NANOCLAY NACRE-MIMETIC NANOCOMPOSITES

Anthi Sapouna[1], Maximilian Röhrl[2], Josef Breu[2], George Floudas[1],[3]

[1] Department of Physics, University of Ioannina, P.O. Box 1186, 451 10 Ioannina, Greece
[2] Bavarian Polymer Institute and Department of Chemistry, University of Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany
[3] University Research Center of Ioannina (URCI) - Institute of Materials Science and Computing, Ioannina, Greece

We investigate the effect of polymer molecular weight (and thus the presence of entanglements) on PEG crystallization and dynamics over a wide composition range. For this reason, we employ two series with different molar mass: Mn~1000 g?mol^{-1} (unentangled) and one with Mn~20000 g?mol^{-1} (entangled), with different Hectorite content from 0 to 90 %. We employ DSC, SAXS and WAXS for the phase state and POM for analyzing the PEG crystallization kinetics. SAXS results show the presence of crystalline PEG with a domain spacing of ~7 nm and ~25 nm for PEG molar mass of 1000 g·mol^{-1} and 20000 g·mol^{-1}, respectively, in the composites with low PEG content ((4) and one at high temperatures replace the heterogeneous of PEG. In addition, DSC established the phase diagram of the nanocomposites. POM identified the influence of hectorite on the nucleation density, growth rate and equilibrium melting temperature on PEG crystals. Nacre combines high stiffness and toughness with a tailored biopolymer. Nacre-mimetic nanocomposites(1,2) are based on a hard phase (composed from synthesis high aspect ratio nanoclays) and a sift phase (polymeric) aiming at advanced materials properties, including high barrier materials against oxygen with enhanced mechanical properties. Here, we employ PEG as the soft phase and nanoclay nacre-mimetics based on sodium fluorohectorite(2,3).

References

(1) E. Giannelis, Adv. Mater. (**1996)**, 8, No. 1
(2) C. Habel, J. Maiz, J. L. Olmedo-Martínez, J. V. Lopez, J. Breu, A. J. Müller, Polymer 202 **(2020)** 122734
(3) D. Gournis, G. Floudas, Chem. Mater. 2004, 16, 1686-1692
(4) Y. Suzuki, H. Duran, M. Steinhart, H.-J. Butt, G. Floudas, Soft Matter, 2013, 9, 2621

ePP33

SYNTHESIS AND STUDY OF WELL-DEFINED SINGLE CHAIN POLYSTYRENE NANOPARTICLES IN SOLUTION AND BULK

Nikolaos Patelis[1], Panagiotis Klonos[2], Emmanouil Glynos[3], Apostolos Kyritsis[2], Georgios Sakellariou[1]

[1] Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, 15771, Athens, Greece
[2] Department of Physics, National Technical University of Athens (NTUA), Zografou Campus, 15780, Athens, Greece
[3] Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1385, Heraklion, Crete, 711 10, Greece

Single chain nanoparticles (SCNPs) are well-defined polymeric systems, with regard to their size and arrangement of functional groups, synthesized through intramolecular collapse of single polymer chains. The ability to synthesize SCNPs with irreversible or reversible intra-chain bonding, as well as their similarity with nature's biomacromolecules (intrinsic disordered proteins), opens a very large field for their utilization? in solution as catalytic nanoreactors, sensors, as drug delivery vehicles in nanomedicine and bulk, in the development of the so-called "all-polymer" nanocomposites. Up to now, experimental and molecular simulation studies have revealed the morphology and dynamics of these nanostructures, mainly in solution. Herein, a series of well-defined polystyrene SCNPs with variable molecular weights (M_n) and crosslinker fraction (*CrF*) were synthesized following standard synthetic protocol. Size exclusion chromatography (SEC), ^{1}H-NMR, dynamic light scattering (DLS) and viscometry were employed for the molecular and structural characterization of these nanomaterials. The molecular dynamics of polystyrene (PS) SCNPs in the melt were investigated by employing Broadband Dielectric Spectroscopy (BDS), and differential scanning calorimetry (DSC). For the first time a dynamic "*phase diagram*" has been proposed for PS SCNPs, where the *CrF* and M_n of the linear precursor define the formation of loose, dense, or rigid SCNP, in terms of the activation of only the segmental PS chain α process, both α and β^* or only the local-like β^* process. The results of this study indicate that size characteristics and crosslinking density in PS SCNPs determine in a large extent their dynamics in the melt and it is expected that they will also affect significantly the dynamics in "all-polymer" nanocomposites.

eP34

CALORIMETRIC AND DIELECTRIC STUDIES ON POLY-(LAURYL METHACRYLATE)-co-POLY-(OLIGO ETHYLENE GLYCOL METHACRYLATE) (PLMA-co-POEGMA) RANDOM COPOLYMERS

Olga Vassiliadou[1], Anastasia Mpalafouti[2], Stergios Pispas[2], Apostolos Kyritsis[1]

[1] Department of Physics, National Technical University of Athens, Athens, Greece
[2] Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece

Significant progress has been made in recent years in the design and synthesis of a variety of amphiphilic block and random copolymers consisting of two or more covalently connected macromolecular chains with different hydrophobicity.

In the present work we study poly-(lauryl methacrylate)-co-poly-(oligo ethylene glycol methacrylate) (PLMA-co-POEGMA) amphiphilic random copolymers with two different weight ratios: 31/69 and 48/52. The copolymers are synthesized by reversible addition-fragmentation chain transfer (RAFT) copolymerization.

We employ Differential Scanning Calorimetry (DSC) and Broadband Dielectric Spectroscopy (BDS) techniques in order to investigate comparatively the thermal transitions and molecular dynamics of PLMA and POEGMA homopolymers as well as of PLMA-co-POEGMA copolymers in the solid state.

Our aim here is to investigate whether the crystallization of the one component of the copolymer can be affected by the presence of the other and therefore, how the combination of hydrophilic and hydrophobic moieties in this particular architecture of brush copolymers can cause microphase separation.

Our thermal measurements on PLMA and POEGMA reveal that the two semi-crystalline homopolymers undergo the glass transition in the same approximately temperature range. In the copolymers, the crystallization/melting of POEGMA phase is much more affected than PLMA.

BDS, in addition, provides evidence that support the calorimetric results concerning the phase separation and sheds light on the local dielectric relaxation mechanisms of the two components of the copolymers.

eP35

EFFECT OF STAR ARCHITECTURE ON THE DYNAMICS OF 1,4-CIS-POLYISOPRENE UNDER NANOMETER CONFINEMENT

Panagiotis Kardasis,[1] **Angelos Oikonomopoulos,**[2] **Georgios Sakellariou,**[2]
Martin Steinhart,[3] **George Floudas**[1,4]

[1]Department of Physics, University of Ioannina, 45110 Ioannina, Greece
[2]Department of Chemistry, National and Kapodistrian University of Athens, 15771 Athens, Greece
[3]Institut für Chemie neuer Materialien, Universitat Osnabrück, D-49069 Osnabrück, Germany
[4] University Research Center of Ioannina (URCI) - Institute of Materials Science and Computing, 45110 Ioannina, Greece

The dynamics of a series of *cis*-1,4-polyisoprene stars located inside nanoporous alumina was investigated as a function of functionality, *f*, ($2 \leq f \leq 64$), arm molar mass, *M* ($2.6 \leq M \leq 13.5$ kg·mol^{-1}) and degree of confinement ($0.01 \leq 2R_g/d \leq 0.6$; R_g, is the radius of gyration and, *d,* is the pore diameter) by dielectric spectroscopy.[1] In the bulk, dielectric spectroscopy revealed broadening of the chain modes with increasing functionality. In addition, a slower dielectric process was found in the vicinity of the soft-colloidal process identified earlier by rheology. The latter associates with the cooperative reorganization of the stars and involves rotational and translational motions. The effect of confinement on the dynamics of stars was stronger than for linear chains.[2,3] First, the dielectric strength of the normal modes was reduced in the stars and, second, the chain dynamics were slower. The reduced dielectric strength was employed as a measure of the thickness of the interfacial layer. Based on the dielectric strength, we can account for possible arm star configurations in the vicinity of the pore walls. The slower chain dynamics reflect the increased entanglement density near the pore walls due to extra topological constraints imposed by the adsorbed arms.[4] Functionalization of the pore walls restored partially the dielectric strength of the chain modes. Overall, star-shaped polymers are more prone to adsorption effects when confined in nanopores as compared to linear chains.

[1] P. Kardasis, A. Oikonomopoulos, G. Sakellariou, M. Steinhart, G. Floudas, *Macromolecules* (submitted)

[2] C. Politidis et. al., *Macromolecules* 2019, 52, 4185–4195.

[3] Chien-Hua Tu et. al., *Phys. Rev. Lett.,*125, 127802 (2020)

[4] M. Krutyeva et. al., *Phys. Rev. Lett.,* 110, 108303 (2013)

eP36

NON-DEBYE SEGMENTAL RELAXATION OF POLY-N-VINYL-CARBAZOLE IN DILUTE SOLUTION

P. Siafarika[1,*], C. Kouderis[1] and A. G. Kalampounias[1,2]

[1]Department of Chemistry, University of Ioannina, Ioannina, GR-45110, Greece
[2]University Research Center of Ioannina (URCI), Institute of Materials Science and Computing, Ioannina, Greece

Ultrasonic relaxation spectroscopy is widely considered as an effective tool in the study of conformational changes or rotational isomerism. In this work, we used this spectroscopic technique to elucidate the conformational changes taking place in dilute poly-N-vinyl-carbazole polymer solutions. Poly-N-vinyl-carbazole, as its name indicates, is a vinyl-type polymer. It can be produced by radical polymerization of vinyl-carbazole monomers with the presence of Ziegler-Natta catalyst or a radical starter, for example azobisisobutyronitrile [1]. Ultrasonic absorption measurements performed in a dilute solution of poly-N-vinyl-carbazole with 1,2-dichloro-ethane used as solvent. The frequency and the temperature range of the measurements were from 1 to 50 MHz and from 10 to 45°C with increments of 5°C, respectively. The experimental findings were compared with theoretical molecular mechanics calculations. From the ultrasonic absorption results it was concluded that a single relaxation process takes place in the solution, which is associated with segmental motions of the polymer chain. The results were found not to follow a Debye-type distribution function. The relaxation frequency value of this process was estimated and found close to the corresponding frequencies of other vinyl-type polymers. Furthermore, thermodynamic properties were also calculated from the temperature-dependence of the acoustic parameters. Specifically, the activation enthalpy and enthalpy difference of segmental motion were estimated equal to $\Delta H^*=3.64 \pm 0.16$ kcal/mol and $\Delta H^0=10.20 \pm 0.24$ kcal/mol, respectively. An additional confirmation of the proposed process resulted from the molecular mechanics calculations on polymeric chains with low number of monomeric units. The enthalpy differences exhibit a slight deviation from the experimental value, but the theoretical activation energies deviate monotonically, when monomeric units added [2].

References

[1] G. Wypych, *Handbook of Polymers* (Elsevier, Ontario, Canada, 2016).

[2] P. Siafarika, C. Kouderis, A. G. Kalampounias, Molecular Physics, 119 (2020), 1.

eP37

PROTON-TRANSFER AND ROTATIONAL-ISOMERIC EQUILIBRIA IN POLY-VINYL-ALCOHOL AQUEOUS SOLUTIONS BY MEANS OF ULTRASONIC RELAXATION SPECTROSCOPY

C. Kouderis[1], **P. Siafarika**[1], **and A. G. Kalampounias**[1,2,*]

[1]Department of Chemistry, University of Ioannina, Ioannina, GR-45110, Greece
[2]University Research Center of Ioannina (URCI), Institute of Materials Science and Computing, Ioannina, Greece

The Polyvinyl Alcohol is a vinyl polymer which is produced by the hydrolysis of polyvinyl acetate. It is soluble in water and non-soluble in most organic solvents. It is a biodegradable polymer and has low toxicity [1]. In this study we attempt to make a detailed temperature and concentration dependent ultrasonic relaxation study in aqueous polyvinyl alcohol solutions as a function of frequency under isobaric conditions at a frequency range 700kHz - 50MHz. We selected the transmission method in order to determine the properties of the polymer solution as the best tool for this frequency range [2]. We utilized the Cole-Cole distribution function in order to fit our experimental results [3]. We found two relaxation processes that occur in our frequency domain. One in the low frequency domain and one in the high frequency domain. The first relaxation mechanism was assigned to segmental motion of the polymer chain and the later relaxation prosses to proton transfer reaction. By utilizing Eyring's theory, the activation enthalpy of the low- and high-frequency relaxation were found equal to $\Delta H_1^*=4.50 \pm 0.18$ kcal/mol and $\Delta H_2^*=19.74 \pm 0.75$ kcal/mol, respectively. The experimental results were complemented with molecular mechanics calculations performed in parallel. The comparison between the experimental data and the outcome of the theoretical calculations evidenced that the length of the relaxing element in a PVA polymer chain is between 5-8 monomers in agreement with what is expected for vinyl-polymers and established the local segmental motions of the PVA polymer chains in the solution.

References

[1] C. A. Finch, Polyvinylalcohol, J. Wiley and Sons, Londoon and New York (1973).

[2] A. Abu-Bakr, R. A. Pethrick, J. Emery, Polymer, 23 (1982) 1446.

[3] M. A. Cochran, P. B. Jones, A. M. North and R. A. Pethrick, J. Chem. Soc. Faraday II, 68 (1972) 1719.

ePP38

SUB-ROUSE DYNAMICS IN POLY(ISOBUTELENE) (PIB) AS A FUNCTION OF MOLAR MASS

Marianna Spyridakou[1], Manos Gkikas[2], Kai L. Ngai[3], George Floudas[1,4]

[1] Department of Physics, University of Ioannina, Ioannina, Greece
[2] Department of Chemistry, University of Lowell, Massachusetts, Lowell
[3] Dipartimento di Fisica, CNR-IPCF, Università di Pisa, Pisa, Italy
[4] University Research Center of Ioannina (URCI) - Institute of Materials Science and Computing, Ioannina, Greece

Poly(isobutelene) (PIB) has a symmetric chemical structure but several characteristics that deviate from the "ordinary" behavior of structurally similar polymers.[1-4] PIB despite its weak dipole moment has dielectrically active modes in the glassy state, at the segmental level and a slower process described earlier as sub-Rouse.[3-5] The glass temperature has a molar mass dependence that can be approximated by the Fox-Flory equation, whereas the fragility parameter is independent of molar mass within the broader range of molar masses investigated herein. Rheology provided access to the terminal times that were found to scale approximately as $\tau_{\text{term}} \sim M^{3.2}$. The molar mass dependence of the slower dielectric process was studied here for the first time. It shows a very weak molar mass dependence ($\tau_{\text{sub-Rouse}}/\tau_{\text{SM}} \sim M0.1$) that is distinctly different from the Rouse and terminal dynamics. Hence the (sub-Rouse) mode has a lengthscale intermediate to the statistical segment length ($b \sim 1.25$ nm) and the length of an entanglement strand (the latter can be estimated from the occupied volume of an entanglement strand as $V_e^{1/3} \sim 2.3$ nm)[6].

1. Ngai, K.L.; Plazek, D.J. *Rubber Chem. Technol.* **1995**, 68, 376-434.
2. Richter, D.; Arbe, A.; Colmenero, J.; Monkenbusch, M.; Farago, B.; Faust, R. *Macromolecules* **1998**, 31, 1133-1143.
3. Plazek, D.J.; Chay, L.-C.; Ngai, K.L.; Roland, C.M. *Macromolecules* **1995**, 28, 6432-6436.
4. Santangelo, P.G.; Ngai, K.L.; Roland, C.M. *Macromolecules* **1993**, 26, 2682-2687.
5. Paluch, M.; Pawlus, S.; Sokolov, A.P.; Ngai, K.L. *Macromolecules* **2010**, 43, 3103-3106.
6. Fetters, Lohse, Colby. Ch. 25 of Physical Properties of Polymers Handbook (J. E. Mark, editor) AIP Press, Woodbury, NY (**1996**).

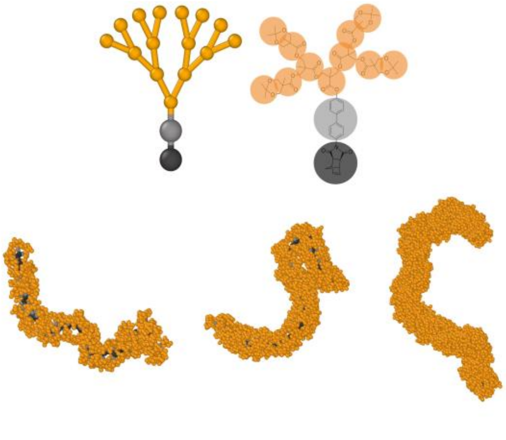
ePᴾ39

COARSE-GRAINED MOLECULAR DYNAMICS SIMULATIONS OF DENDRONIZED POLYMERS

<u>Emmanouil Vereroudakis</u>[1], Emanuele Locatelli[2], Christos Likos[1]

[1] Faculty of Physics, University of Vienna, Vienna, Austria
[2] Institute for Theoretical Physics, Technical University of Vienna, Vienna, Austria

Dendronized polymers (denpols) belong to the general category of thick polymers which includes molecules such as bottlebrushes. Denpols comprise a linear backbone grafted with dendritic side-chains. The dendritic side-chains give rise to molecular thickness which can be controlled by tuning the generation. Such increase of size of the side-chains will also affect the rigidity of the backbone. In this work we seek to achieve a first step in the coarse-graining process of such a largely complex system. We employ bead-spring molecular dynamics simulations to study the effect increasing generation and degree of polymerization on the conformation of denpols, seeking to reproduce earlier experimental results. We find that our moderately coarse-grained approach can capture the experimental behaviour and can still be described by well-known worm-like chain models. These findings may serve as a stepping-stone into largely coarse-grained models of such complex polymeric architectures that might allow examination of the behaviour of such systems under concentrated or melt conditions.



eP40

RENEWABLE POLY(ALKYLENE FURANOATE)-BASED NANOCOMPOSITES – INTERFACIAL INTERACTIONS, MOLECULAR MOBILITY AND CRYSTALLIZATION

Panagiotis Klonos[1], Lazaros Papadopoulos[2], Apostolos Kyritsis, Dimitrios Bikiaris[2]

[1] Physics Department, National Technical University of Athens, Athens, Greece
[2] Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece

Poly(*n*-alkylene furanoate)s, PnAFs, form a new class of renewable polyesters that have attracted much interest envisaging wide ranges of applications, also, in the modern frame of green and circular economy demands. We have synthesized and investigated many series of nanocomposites, NCs, based on PnAFs (with *n*=2-6) filled by low amounts of various nano-inclusions, furthermore, differing in morphology, dimensions and surface chemistry (e.g., nanotubes, nanographene, nanoclays, nanosilica). The final goal is the manipulation / tuning of the materials mechanical and small molecules (gas) permeation performance which is strongly connected with the segments' mobility and PnAF's crystallinity, the latter being initially slow and weak. The main experimental tools employed are broadband dielectric spectroscopy (BDS) and differential scanning calorimetry (DSC), supplemented by polarized light microscopy, infrared spectroscopy and X-ray diffraction. The crucial factors that favor nucleation and enhance the polymer chains diffusion were found the monomer alkylene length (*n*), the overall PnAF chain length (molar mass), which mainly drops in the NCs due to the *in-situ* preparation route, and the presence of filler-polymer interfacial interactions. In addition to the filler aspect ratio and/or surface area, for weak or strong interfacial interactions, crystallization and segments mobility are mainly accelerated or decelerated, respectively. As expected, the strongest impact on mobility is that of crystallization, moreover, the alternations in the semi-crystalline morphology, that may either impose constraints of induce spatial confinement effects. Also, models involving free volume localized changes have been successfully applied in rationalizing the overall effects. Local dynamics of PnAFs is, interestingly, found to depend on the overall chain mobility and to sense the early stages of the overall matrix changes (glass transition, cold crystallization). This has been marked within our work to be a common effect in polyesters in the cases of local relaxations originating from segment motions (dipoles) on the polymer backbone.

eP41

THERMAL CONDUCTIVITY IN POLYMER NANOCOMPOSITES

Sokratis Tegopoulos[1], Panagiotis Klonos[1], Dimitrios Bikiaris[2], Evagelia Kontou[3], Apostolos Kyritsis[1]

[1] Department of Physics, National Technical University of Athens, Zografou Campus, 15780, Athens, Greece
[2] Department of Chemistry, Laboratory of Polymer Chemistry and Technology, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Greece
[3] Mechanics Department, National Technical University of Athens, Zografou Campus, 15780, Athens, Greece

It is well known that nanoparticles (NPs) can modify a number of properties in polymer nanocomposites (PNCs), such as mechanical performance and thermal behavior. What is of great interest and has not been extensively studied yet, is the indirect effect of NPs, through the fraction of the polymer that is located at the surfaces of the filler NPs, resulting in formation of the so called interfacial rigid amorphous fraction (RAFfiller). The interfacial polymer is considered immobile, as it shows no contribution to calorimetric glass transition in general, and may affect the final PNC properties. In the case of semicrystalline PNCs, an additional contribution to RAF exists near the crystals, i.e., RAFcrystal. In this context, we study two series of PNCs based on amorphous styrene-butadiene rubber (SBR) and semicrystalline linear low-density polyethylene (PE) matrices, filled with carbon nanotubes (CNTs).

The focus of our study is on the effects (direct/indirect) of CNTs on thermal diffusivity α and thermal conductivity λ, that were determined by Laser Flash Analysis technique (LFA). Measurements were carried out at various temperatures. We have also employed calorimetry and dielectric spectroscopy, as supplementary methods, in order to correlate the results of LFA with RAF, crystalline fraction (CF) and electrical conductivity (σ), and to shed light on the transport processes in PNCs.

Combining the various results, we show, for the first time that, interestingly, despite the presence of the well dispersed thermally conductive NPs, α of the matrix decreases with the increase in RAFfiller, whereas increases systematically with RAFcrystal.

We propose that these opposite trends originate from the qualitative differences in the structure of the RAFs (i.e., disorded RAFfiller vs. ordered-like RAFcrystal), that control the thermal transport processes within each matrix. More recently, we have successfully checked this scenario in polylactide-based PNCs, amorphous and semicrystalline, reinforced with CNTs and graphene oxide.

ePP42

CHITOSAN NANOPARTICLES BY ELECTROSTATIC INTERACTIONS WITH MULTIFUNCTIONAL ACIDS

Angeliki Chroni [1], Dimitris Selianitis[1], Maria-Despoina Charavgi[1], Maria Karayianni[1], Aristeidis Papagiannopoulos[1], Stergios Pispas [1], Despina Tsiriva [2], Lazaros Laskaridis [2]

[1]Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation,
48 Vassileos Constantinou Avenue, 11635 Athens, Greece

[2]Phytorgan S.A., 6 Perivoias & Xrisappou, 14564 Nea Kifissia, Greece

Presenting author e-mail: angelikechrone@gmail.com

Chitosan (CS) is an abundant cationic natural biopolymer derived simply by alkaline N-deacetylation of chitin. It is biocompatible, non-toxic, has antimicrobial properties and acts as a phytostimulator (Elicitor), inducing plant defense mechanisms and preparing them for impending attack by bacteria, fungi and viruses. [1] The purpose of this work was to prepare chitosan nanoparticles (CS-NPs) by non-covalent crosslinking, due to electrostatic interaction and / or hydrogen bonds, using three multifactional molecules that act as crosslinkers. Bare CS-NPs were synthesized at various concentrations of CS for each crosslinker and at different crosslinker / CS mixing ratios (2% w/w, 5% w/w, 10% w/w and 15% w/w) using the following protocols. The first protocol was related to the direct addition of the crosslinker in the CS solution, while the second protocol regards the gradual addition of the crosslinking agent. The crosslinkers used were phytic acid (PA), tannic acid (TA) and tripolyphosphate (TPP). CS-NPs were studied by dynamic and electrophoretic light scattering techniques (DLS, ELS), to determine the hydrodynamic radius (R_h) and size polydispersity index (PDI), surface charge and detect possible changes in the scattered light intensity.

References

[1] Xing, K., et al. Agron. Sustain. Dev. 2015, 35, 569-588.

Acknowledgements: This work is co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE - INNOVATE (project code: T2EDK-02113).

ePa43

BIOBASED POLYMYRCENE: EFFECT OF BRANCHING ON THE DYNAMICS AS A FUNCTION OF TEMPERATURE AND PRESSURE

Ioannis Tzourtzouklis [1], **Christoph Hahn** [2] **Holger Frey** [2] **and George Floudas** [1,3,4]

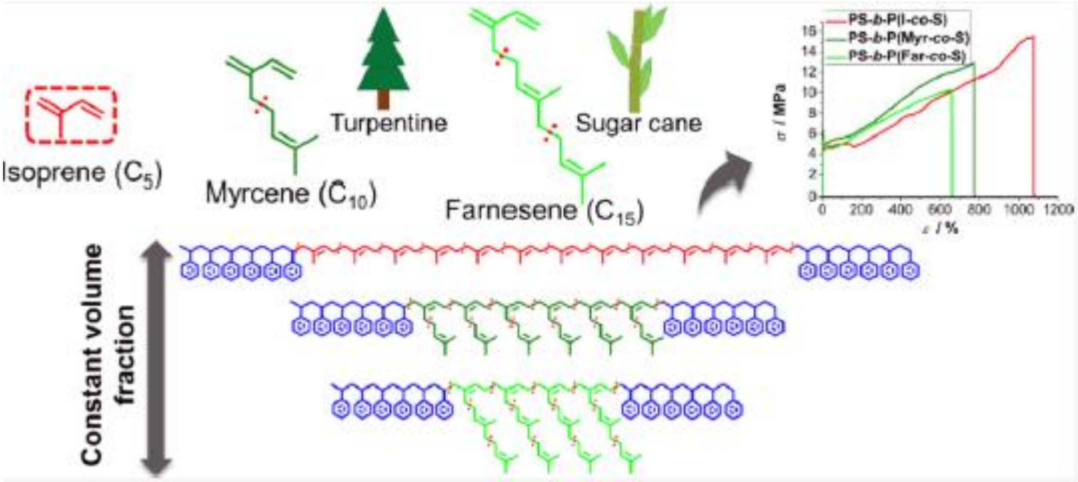
[1]Department of Physics, University of Ioannina, 45110 Ioannina, Greece
[2]Institute of Organic Chemistry, Johannes Gutenberg, Duesbergweg 10-14,55128 Mainz, Germany
[3]Max Planck Institute for Polymer Research, D-55128 Mainz, Germany
[4]University Research Center of Ioannina (URCI)—Institute of Materials Science and Computing, 45110 Ioannina, Greece

Limited fossil feedstock along with the environmentally adverse effects of petrochemical products, have increased the necessity of finding sustainable alternatives to replace the petroleum-based 1,3-diene monomers butadiene and isoprene (which are commercially used for the synthesis of thermoplastic elastomers)[1]. Such alternatives are Farnesene and Myrcene, simple monoterpenes found in essential oil of various plants (wild thyme, bay, cannabis, etc.)[2]. Herein, we examine the dynamics of polymyrcene using Dielectric Spectroscopy (DS) as a function of temperature and pressure for a range of molar masses. Polymyrcene (PMyr) is structurally akin to polyisoprene (PI), but unlike PI it has a branched structure[1]. We are interested in the changes of the branched structure on the segmental and normal mode dynamics as well as in possible changes of the entanglement molar mass. To this end, we combine DS with rheology. As expected, in DS the dynamics of PMyr reflect the normal and segmental mode (as with PI and PF) but with different relative dielectric strength. The latter mode is more sensitive to *T* and *P* variations, implying a higher apparent activation volume for the segmental mode. Additionally, shape parameters of the two modes remain unchanged under variation of *T* and *P.* The glass temperature (T_g) of PMyr is approximately 5 K lower than in PI due to the internal plasticization effect. The entanglement molar mass could be estimated from the terminal relaxation times as extracted from the dielectric and rheology experiments.

[1] Wahlen, C.; Blankenburg, J.; von Tiedemann; Ewald, J.; Sajkiewicz, P.; Axel H.; Müller, E.; Floudas, G.; Frey, H. Tapered Multiblock Copolymers Based on Farnesene and Styrene: Impact of Biobased Polydiene Architectures on Material Properties. *Macromolecules* **2020** *53* (*23*), 10397-10408.

[2] Sarkar, P.; Bhowmick, A.K. Synthesis, characterization and properties of a biobased elastomer: polymyrcene. *RSC Adv*. **2014**, *4*, 61343.

[3] Tzourtzouklis, I.; Hahn, C.; Frey, H.; Floudas, G. Biobased Polymyrcene: Effect of branching on the dynamics as a function of Temperature and Pressure. (Under preparation)



ePP44

NANO-ASSEMBLIES FROM AMPHIPHILIC PnBA-b-POEGA COPOLYMERS AS DRUG NANOCARRIERS: STRUCTURE AND DRUG–POLYMER INTERACTIONS

Angeliki Chroni[1], Thomas Mavromoustakos[2], Stergios Pispas[1]

[1] Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation,
48 Vassileos Constantinou Avenue, 11635 Athens, Greece
[2] Department of Chemistry, National and Kapodistrian University of Athens,
Panepistimioupolis, 15771 Zografou, Greece

Nano-drug delivery systems have received significant attention in the last few decades, endowing drugs with increased stability and water solubility, prolonging the cycle time, enhancing the uptake rate of target cells, reducing enzyme degradation, and controlling the release of the drug.[1] Amphiphilic block copolymers (AmBCs) have been the workhorse of pharmaceutical nanotechnology in recent years towards the design of drug-loaded block copolymer nanocarriers for the demanding treatment of crucial diseases. Highly stable drug nanocarriers were successfully developed by encapsulating losartan potassium (LSR) into two amphiphilic poly(n-butyl acrylate)-block-poly(oligo(ethylene glycol) methyl ether acrylate) (PnBA-b-POEGA) copolymers with different molecular weights of PnBA. Based on dynamic light scattering (DLS), the $PnBA_{30}$-b-$POEGA_{70}$ and $PnBA_{27}$-b-$POEGA_{73}$ (where the subscripts denote wt.% composition of the components) copolymers formed micelles of 10 nm and 24 nm in water. The LSR-loaded PnBA-b-POEGA nanocarriers presented increased size and greater mass compared to empty micelles, implying the successful loading of LSR. A thorough nuclear magnetic resonance (NMR) characterization, by 2D-NOESY experiments, of the LSR-loaded PnBA-b-POEGA nanocarriers evidenced strong intermolecular interactions between the biphenyl ring and the butyl chain of LSR with the methylene signals of PnBA. The highest hydrophobicity of the $PnBA_{27}$-b-$POEGA_{73}$ micelles contributed to an efficient encapsulation of LSR into the micelles exhibiting a greater value of %EE compared to $PnBA_{30}$-b-$POEGA_{70}$ nanocarriers. Ultrasound release profiles of LSR signified that a great amount of the encapsulated LSR is strongly attached to both $PnBA_{30}$-b-$POEGA_{70}$ and $PnBA_{27}$-b-$POEGA_{73}$ micelles.

References

[1] Cabral, H.; Miyata, K.; Osada, K.; Kataoka, K. Chem. Rev. 2018, 118, 6844–6892.

eP45

DERIVATION OF SIMPLE QUALITATIVE MODEL TO PREDICT SPATIAL CHARACTERISTICS OF EXTRUSION FLOW INSTABILITIES

Christos Georgantopoulos[1], Masood Khabazian[1], Ingo Naue[1], Andrea Causa[2], Roland Kádár[3], Manfred Wilhelm[1]

[1] Karlsruhe Institute of Technology (KIT), Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe, Germany
[2] Pirelli Tyre S.p.A., Milan, Italy
[3] Chalmers University of Technology, Department of Industrial and Materials Science, Gothenburg, Sweden

The extrusion flow instabilities[1] of a commercial polybutadiene (PBD) sample are investigated as a function of different die geometries. Qualitative models[2,3,4] are used to fit the experimental data for the spatial characteristic wavelength (λ) of extrusion flow instabilities. A new qualitative model for slit die geometry (rectangular cross-section) is derived based on the theoretical concept of the "two layers" extrudate and the force balance at the die exit region. Correlation between the ratio of the extensional and shear stresses at the die exit area and the characteristic dimension, height H and diameter D, of the dies is presented.

References

[1]S. G. Hatzikiriakos, *Progress in Polymer Science*, 2012, 624, 37.
[2]J. R. Barone, N. Plucktaveesak, S. Q. Wang, *J. Rheol.* **1998**, *42*, 813.
[3]Y. W. Inn, R. J. Fisher, M. T. Shaw, *Rheol. Acta* **1998**, *37*, 573
[4]C. K. Georgantopoulos, M. K. Esfahani, C. Botha, I. F. C. Naue, N. Dingenouts, A. Causa, R. Kádár, and M. Wilhelm, *Macromol. Mater. Eng.* **2021**, *306*, 2000801.

eP46

ANNULAR POISEUILLE FLOW OF A BINGHAM PLASTIC WITH WALL SLIP

Georgios C. Georgiou, Evgenios Gryparis

Department of Mathematics and Statistics, University of Cyprus, Nicosia, Cyprus

We consider the annular Poiseuille flow of Bingham plastics with wall slip. First the analytical solution is derived for the case where different Navier-slip conditions are applied at the two cylinders. A sliding regime is observed initially as the imposed pressure gradient is increased and the material eventually yields near the two walls. If different slip laws apply at the two walls, an intermediate semi-sliding regime is observed where the material yields only near the wall corresponding to weaker slip and the unyielded core slides at the other wall. Next, we consider the case where slip occurs above a critical wall shear stress, the slip yield stress, which is taken to be less than the yield stress. Different flow regimes are observed depending on the relative values of the slip yield stress and the yield stress and the radii ratio. Closed form solutions are provided for all cases and the effects of wall slip on the flow curve are discussed. The results are compared with available theoretical and experimental results in the literature.

eP47

POLY(UREA – FORMALDEHYDE) MICROCAPSULES FOR SELF-LUBRICATING APPLICATIONS

Christos Zotiadis, Athanasios Porfyris, Dimitrios Korres, Stamatina Vouyiouka

Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zographou Campus, Athens, 157 80, Greece

Moving parts of all mechanical systems need to be lubricated for the efficient operation of the system. The effectiveness and stability of lubrication are crucial for improving reliability and lifetime of manufactured products, also reducing wastes of natural resources and energy. Introducing microcapsules containing lubricant into the surface of moving parts, significantly improves anti-friction properties and wear resistance. When the surface is subjected to friction, the microcapsules are ruptured and the encapsulated lubricants are released onto the surface, forming a boundary lubrication film that significantly reduces the friction coefficient and wear rate. The aim of the current work is to produce poly(urea-formaldehyde) microcapsules with an encapsulated lubricating oil to be used in metal coating produced *via* thermal spraying. Poly(urea-formaldehyde) microcapsules preparation was carried out by one stage *in situ* polymerization in an oil-water emulsion. The encapsulation process took place in a closed reaction vessel under mechanical agitation based on the work of Tzavidi et al. (Journal of Applied Polymer Science, 2020). The capsules were collected as free-flowing white powder after vacuum filtration, washing with hexane and drying at room temperature for 24 h. Spherical microcapsules were obtained with a size ranging from 57 to 88 μm, high encapsulation efficiency (up to 79 %) and increased thermal stability ($T_{d5\%} > 210\ ^{O}C$).

This research has been co?financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code: T2EDK-01883).

Co-financed by Greece and the European Union

eP48

EFFECT OF HUMIDITY LEVEL ON THE THERMAL AND MECHANICAL PROPERTIES OF POLY(VINYL ALCOHOL) AND POLY(VINYL PYRROLIDONE) BLEND FILMS

Petros Oikonomou, Merope Sanopoulou, Kyriaki Papadokostaki

Inst. Nanoscience and Nanotechnology, NCSR Demokritos, 15310 Ag. Paraskevi,
Athens, Greece

Blending of hydrophilic, water soluble polymers is an easy, environmentally friendly, non-toxic method to produce new materials for use in several applications such as food packaging, agricultural, humidity sensing and various biomedical applications (drug delivery systems, wound dressings, tissue engineering, biosensors etc.). In this study, blends of PVA and PVP in the form of films, were prepared by aqueous solutions casting. Thermally annealed films with compositions covering the whole range between the two parent polymers were used. The T_g and PVA crystallinity of the blends was investigated by DSC measurements and the compositional dependence of the T_g of the blends was fitted to the Couchman-Karasz equation, with physically meaningful fitting parameters. The blend films were also equilibrated at four different humidities, and the effect of increasing humidity levels on the degree of hydration, the thermal and tensile mechanical properties was studied. A linear relation between weight fraction of absorbed water at a specific external humidity and the composition of the blend was observed. The depression of the T_g of each blend with increasing amounts of absorbed water, was also analyzed by the Couchman-Karasz equation, leading to a useful linear relation between the composition of the blend and the minimum amount of water absorbed needed to transform the initially glassy material to a rubber. For all blend compositions, the Young modulus of hydrated samples suffers a sharp drop of approximately one order of magnitude when the degree of hydration was sufficient to transform the initially dry, glassy films to rubbery materials.

Acknowledgment: This work was supported by two projects (MIS 5002567 and 5002772) funded by the Operational Programme “Competitiveness, Entrepreneurship and Innovation” (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

References

1. Konidari M. V., Papadokostaki K. G., Sanopoulou M., J. Appl. Polym. Sci. 2011, 120, 3381
2. Oikonomou P., Sanopoulou M., Papadokostaki K.G., Ind. Eng. Chem. Res. 2021, 60, 14203

eP49

DESIGN AND DEVELOPMENT OF NEW CONJUCATED POLYMERS FOR APPLICATIONS IN ORGANIC PHOTOVOLTAIC DEVICES

Athanasios Katsouras[1], Christos L. Chochos [2], Apostolos Avgeropoulos[1]

[1]Department of Materials Science Engineering, University of Ioannina, Ioannina 45110, Greece

[2]Institute of Chemical Biology, National Hellenic Research Foundation, Athens, Greece*

Conjugated polymers represent one of the most important class of materials for the fabrication of many optoelectronic applications, such as light emitting diodes, field effect transistors, organic photovoltaics, sensors, etc. In this work, our studies were focused on donor-acceptor (D-A) conjugated polymers containing indacenodithiophene (IDT) and indacenodithienothiophene (IDTT) moieties as electron donating units and various electron withdrawing building blocks, such as:

1. Thienopyrrolodione (code names: XPL1-XPL6)
2. Thiadiazine and thiadiazinone (code name: Π1-Π8)
3. Quinoxaline monomers (code name: K1-K3).
4. Benzothiadiazole monomer (code name: CTL1-CTL6).

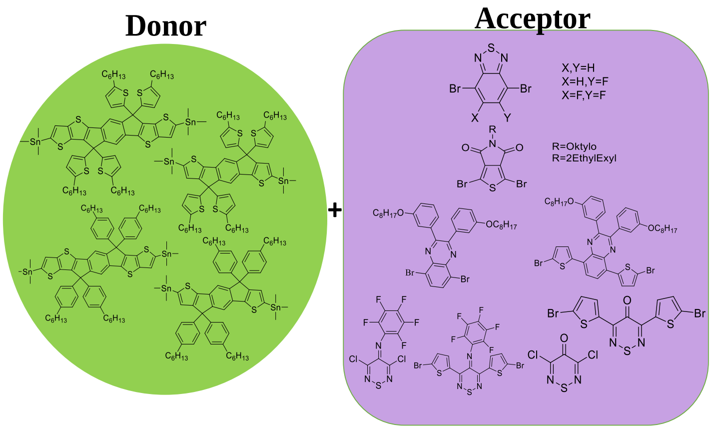


Fig. 1: *Chemical structures of the monomers used as donors and acceptors*

These polymers were employed as electron donor materials in bulk heterojunction solar cells and the devices were characterized in terms of photovoltaic performance and stability. Useful structure-properties-performance correlations have been achieved and they will be presented.

References:

1. ***A. Katsouras***, N. Gasparini, C. Koulogiannis, M. Spanos, T. Ameri, C. J. Brabec, C. L. Chochos and A. Avgeropoulos, ***Macromol. Rapid Comm.,*** **2015**, *36*, 1778-1797.
2. Chochos C. L., Kalogirou A. S., Ye T., Tatsi E., **Katsouras A.,** Zisimou G. A., Gregoriou V. G., Avgeropoulos A., Koutentis P. A., ***J. Mater. Chem. C ,*** **2018**, *6,* 3658
3. Chochos, C. L., Singh, R., Kim, K., Gasparini. N., **Katsouras. A**., Kulshreshtha. C., Gregoriou. V. G., Keivanidis. P. E., Ameri. T., Brabec. C. J., Cho. K., Avgeropoulos. A., ***Adv. Funct. Mater.*** **2016**, 26, 1840
4. Christos C. L., Leclerc N., Gasparini N., Zimmerman N., Tatsi E., **Katsouras A**., Moschovas D., Serpetzoglou E., Konidakis I., Fall S., Leveque P., Heiser T., Spanos M., Gregoriou V. G, Stratakis E., Ameri T., Brabec C. J., Avgeropoulos.A., ***J. Mater. Chem. A,*** **2017**, 5, 25064

ePS0

INTEGRATING MULTI-FUNCTIONALITY IN Fe3O4/BaTiO3/EPOXY RESIN HYBRID NANOCOMPOSITES

Anastasios C. Patsidis[1], Sevasti Gioti[1], Aikaterini Sanida[1], George Mathioudakis[2],
Nikolaos Petropoulos[3], Athanasios Kanapitsas[3], Christos Tsonos[3],
Thanasis Spiliotis[4], Georgios C. Psarras[1]

[1] Smart Materials & Nanodielectrics Laboratory, Department Of Materials Science,
School Of Natural Sciences, University Of Patras, Patras 26504, Greece
[2] Institute of Chemical Engineering Sciences (ICE-HT), Foundation for Research &
Technology-Hellas (FORTH), Stadiou Str., Platani, P.O.Box 1414, GR-26504 Patras, Hellas
[3] PHYSICS, University of Thessaly, Lamia, Greece
[4] Institute of Nanoscience and Nanotechnology, NCSR "Demokritos", Aghia Paraskevi,
Athens 15310, Greece

Modern global society exhibits a continuously increasing demand for new high-tech products, equipment and services, the performance of which requires the development of novel and advanced engineering materials. Materials play a key-role in the whole range of technological applications, related to transportation, energy, electrical and electronic applications, mechanical engineering, structural performance, biomedical applications, sports industry, and others.

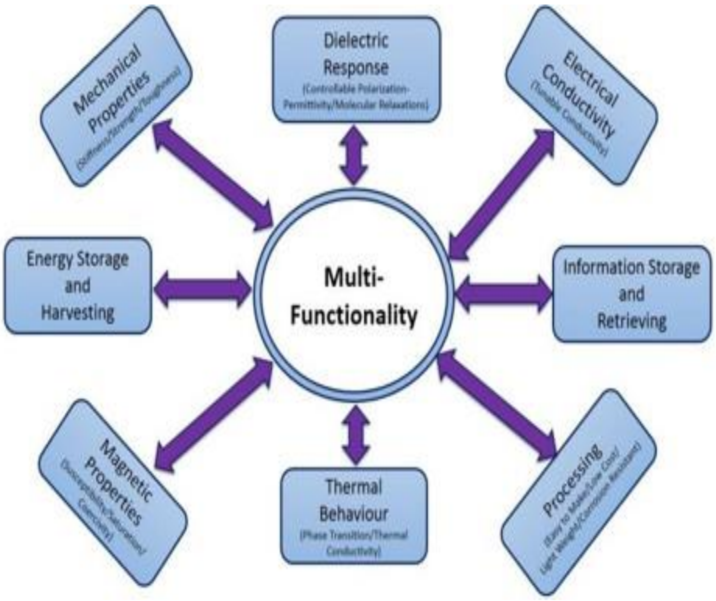
Multifunctionality is the combination of various desirable properties in a material or materials' system, aiming to develop a single material/system exhibiting all necessary responses under various loading conditions at service. Mechanical sustainability, suitable thermal response, tunable electric conductivity, variable electric polarization and dielectric permittivity, magnetic properties, thermally induced phase changes could be parts of the overall multifunctional behaviour, Figure 1.

Figure 1: Schematic representation of materials' multifunctionality.

The challenge of the study is the development of a material/device being able to execute several functions (such as variable polarization, tunable dielectric response, adjustable conductivity, varying magnetic performance, energy storage and others), while being easy to make, light weight, cost effective exhibiting at the same time possessing structural integrity and suitable thermal response.

The under study nanodielectric materials are polymer matrix nanocomposites, reinforced with: (i) ferroelectric/polar oxides ($BaTiO_3$), and (ii) ferromagnetic (Fe_3O_4) nanoparticles.

Acknowledgements: The research work was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the “First Call for H.F.R.I. Research Projects to support Faculty members and Researchers and the procurement of high-cost research equipment grant” (Project Number:2850).



eP51

Fe3O4/MWCNTs/EPOXY NANOCOMPOSITES: DEVELOPMENT, THERMO-MECHANICAL AND MAGNETO-DIELECTRIC BEHAVIOUR

Sevasti Gioti[1], Aikaterini Sanida[1], Georgios Mathioudaki[2], Thanassis Speliotis[3], Anastasios Patsidis[1], Georgios Psarras[1]

[1] Smart Materials & Nanodielectrics Laboratory, Department of Materials Science, University of Patras, 26504, Patras
[2] Institute of Chemical Engineering Sciences (ICE-HT), Foundation for Research & Technology-Hellas (FORTH), Stadiou Str., Platani, P.O.Box 1414, GR-26504 Patras
[3] Institute of Nanoscience and Nanotechnology, NCSR “Demokritos”, Aghia Paraskevi, Athens 15310

Materials having tunable electrical and magnetic properties are promising candidates for advanced technological applications in microwave communication devices, electronic devices, energy storing systems etc. Ferrites can be also applied as inductors, magnetic field sensors, switched-mode power supplies, and ferromagnetic insulators in electrical circuits. Magnetite nanoparticles (Fe_3O_4) are the most popular nanoferrites. Such magneto-dielectric materials must exhibit not only a high relative dielectric permittivity but also the appropriate mechanical properties. In addition, the weight, shape-flexibility, and ease of processing of the material are also key factors for their application. For this reason many recent research efforts are focused on polymer hybrid nanocomposites with magnetic and semiconductive or conductive inclusions. The addition of carbon nanoparticles to polymer magneto-nanocomposites makes possible the increase of conductivity of the composites at a very low filling concentration, achieving homogeneity in a larger extent than in the case of microcomposites. The magneto-dielectric and mechanical behaviour of polymer nanocomposites can be tailored by simply controlling the type and amount of the nanofiller. In this work hybrid polymer nanocomposites reinforced with ferromagnetic (Fe_3O_4) nanoparticles and multiwalled carbon nanotubes (MWCNTs) were fabricated and studied, in terms of the type and amount of the filler content. Specimens’ morphology was examined by means of X-ray Diffraction spectra and Electron Microscopy, mechanical properties were studied under static and dynamic conditions electrical and magnetic response were investigated via Broadband Dielectric Spectroscopy and Vibrating Sample Magnometer.

Acknowledgements: The research work was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the “First Call for H.F.R.I. Research Projects to support Faculty members and Researchers and the procurement of high-cost research equipment grant” (Project Number: 2850).

ePS52

THERMOMECHANICAL BEHAVIOR OF POLYVINYLIDENE FLUORIDE(PVDF)-GRAPHENE NANOCOMPOSITES

Aikaterini Giallousi, Anastasios C. Patsidis, Georgios C. Psarras

Smart Materials & Nanodielectrics Laboratory, Department of Materials Science,
School of Natural Sciences, University Of Patras, Patras 26504, Greece

Polymer matrix nanocomposites are considered as the new frontiers of materials science [1]. Nanocomposites are developed by dispersing a small amount of nanoinclusions within a polymer matrix. Graphene appears to be an ideal filler, because of its superior mechanical, electrical and thermal properties, which lead to high-performance multifunctional nanocomposites.

In this study, the thermal and dynamic mechanical behavior of polyvinylidene fluoride (PVDF) systems reinforced with graphene nanoplatelets (GnP) is investigated. PVDF is a technologically important polymer with a complex structure including five distinct crystalline phases [2]. The nanocomposites' response is examined by employing the techniques of Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). The results of DSC, indicated that the addition of graphene into the PVDF matrix promotes an increase of crystallization temperature (Tc), while glass transition temperature (Tg) remains practically unaffected. Furthermore, DMA measurements showed that the nanocomposites exhibit significant increase in Storage Modulus compared to the neat PVDF.

Figure 1. Storage modulus versus temperature varying the GnP content in PVDF.

References

[1] G.C. Psarras, Nanographite-polymer composites, p.647-673, in "Carbon Nanomaterials Sourcebook: Nanoparticles, Nanocapsules, Nanofibers, Nanoporous Structures and Nanocomposites", K.D. Sattler eds., Taylor & Francis, 2016.

[2] C. Tsonos, H. Zois, A. Kanapitsas, N. Soin, E. Siores, G.D. Peppas, E.C. Pyrgioti, A. Sanida, S.G. Stavropoulos, G.C. Psarras, Polyvinylidene fluoride/magnetite nanocomposites: Dielectric and thermal response, Journal of Physics and Chemistry of Solids, 129, p.378–386, 2019.

eP53

DEVELOPMENT, CHARACTERIZATION AND FUNCTIONALITY OF EPOXY RESIN/ GRAPHENE NANOCOMPOSITE SYSTEMS

Spyridon Vrettas, Anastasios C. Patsidis, Georgios C. Psarras

Smart Materials & Nanodielectrics Laboratory, Department of Materials Science,
University of Patras, 26504, Patras, Hellas (Greece)

Science has always been the key to the growth of technology. New technological advances aiming to fulfill social needs, require novel materials with enhanced performance [1,2]. Nanocomposites constitute a new, rapidly growing, domain in materials science. These materials offer the ability to combine the properties of nanoinclusions with the properties of polymer matrices, addressing a wide range of applications. In this research, graphite nanoplatelets were embedded in an epoxy resin. Graphene is considered to be one of the most promising materials of the 21st century. It has excellent mechanical, electrical and thermal properties. On the other hand, epoxy resin is a thermosetting polymer that is commonly known for its insulating properties [2].

The main purpose of this study was the development of nanocomposites with different concentrations of graphene and the investigation of the materials' dielectric and thermomechanical response. Dielectric tests were made via the Broadband Dielectric Spectroscopy in the frequency range of 10^{-1}–10^{7} Hz and over the temperature range of 30-160°C. The results showed an increase in permittivity as composites become more conductive. Furthermore, at higher temperatures dipoles move easier, resulting to even higher permittivity. The presence of two dielectric relaxations were also revealed, α-relaxation and β-relaxation.

Thermomechanical tests were made by means of Dynamic Mechanical Analysis for all systems over the range of 30-160 °C with a rate of 5 °C/min to explore the viscoelastic behavior of the composites. Storage modulus increases with filler content until a certain temperature and then decreases passing from glassy to elastomeric state.

[1] K. Friedrich. Routes for achieving multifunctionality in reinforced polymers and composite structures in Multifunctionality of Polymer Composites, K. Friedrich and U. Breuer eds. Elsevier, 2015.

[2] G.C. Psarras, Nanographite-polymer composites, p.647-673, in "Carbon Nanomaterials Sourcebook: Nanoparticles, Nanocapsules, Nanofibers, Nanoporous Structures and Nanocomposites", K.D. Sattler eds., Taylor & Francis, 2016.

eP54

DIELECTRIC BEHAVIOR OF POLYOXYMETHYLENE/POLYURETHANE/FLUOROHECTORITE TERNARY NANOCOMPOSITES

<u>Andrea Duka</u>, Anastasios C. Patsidis, Georgios C. Psarras

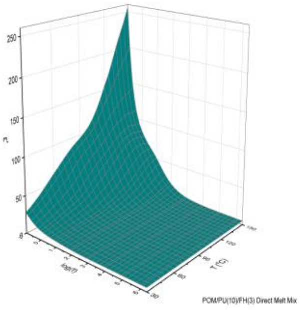
Smart Materials & Nanodielectrics Laboratory, Department of Materials Science,
School of Natural Sciences, University of Patras, Patras 26504, Greece

Polymer matrix nanocomposites remain on the spotlight of the scientific research, because of their superior properties. By employing layered silicates, as reinforcing phase, the surface area-to-volume ratio increases compared to the particle-like inclusions, thus greater interfacial area is exhibited for the same filler content [1,2].

In this work the dielectric behavior of Polyoxymethylene (POM)/Polyurethane (PU)/Fluorohectorite (FH) nanocomposites is studied. POM/PU/FH nanocomposites were prepared by two methods: (a) direct melt compounding (DM) and (b) melt compounding using a masterbatch containing both PU and FH (MB) [2].

The dielectric measurements were accomplished via Broadband Dielectric Spectroscopy in a wide frequency and temperature range.

Electrical conductivity and dielectric permittivity enhance with temperature. The dielectric response of specimens reveals relaxation processes such as, α-relaxation, β-relaxation, and the phenomenon of interfacial polarization due to the accumulation of charges at the interfaces.



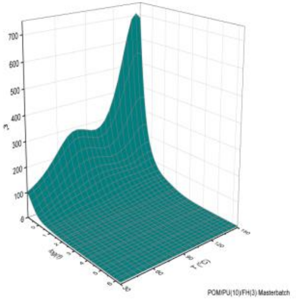


Figure 1. Real part of permittivity versus temperature and frequency for the POM/PU(10)/FH(3) nanocomposite produced via DM.

Figure 2. Real part of permittivity versus temperature and frequency for the POM/PU(10)/FH(3) nanocomposite produced via MB.

References

[1] S. Siengchin, T. N. Abraham, J. Karger-Kocsis, Mechanics of Composite Materials, 44(5), 495-504, 2008.

[2] G. N. Tomara, P. K. Karahaliou, G. C. Psarras, S. N. Georga, C. A. Krontiras, S. Siengchin, J. Karger-Kocsis, European Polymer Journal, 95, 304-313, 2017.

eP55

RECYCLING HDPE FOR THE SYNTHESIS OF ECOFRIENDLY WOOD/PLASTIC COMPOSITE PRODUCTS

Nikolaos D. Bikiaris[1], Georgia Michailidou[1], Iouliana Chrysafi[2],
Theopoula Asimakidou[2], Alexandra Zamboulis[1]

[1] Department of Chemistry, Laboratory of Polymer Chemistry and Technology, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece
[2] School of Physics, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece

High-Density Polyethylene (HDPE) is one of the most popular plastics due to its many advantages such as its low cost, easy processing, light weight, high chemical resistance and durability. However, these last properties also contribute to its low degradability and its accumulation in the environment. In recent years, due to the inability for proper waste management resulting in severe environmental pollution, coupled with the dwindling crude oil resources, emphasis is given on more sustainable materials and processes. This translates, on one hand, in the production of polymers from renewable monomers and, on the other hand, in efforts invested towards recycling. In this context, the recycling of HDPE and the valorization of recycled HDPE has attracted a lot of interest.

In the present study, HDPE was thermally recycled and the properties of the recycled HDPE obtained are investigated. The structural studies were performed by infra-red spectroscopy (ATR) and X-ray diffraction (XRD), while the thermal behavior of recycled HDPE was characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Finally, the mechanical properties were examined by tensile experiments. It was concluded that the thermal recycling of HDPE did not deteriorate the properties of HDPE and only slightly its physical appearance. This recycled HDPE is therefore appropriate to be further combined with biomass from agricultural waste, for the preparation of wood plastic composite products with a low-environmental impact.

Acknowledgements: This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH-CREATE-INNOVATE (project code: T2EDK – 00008).

ePP56

COMBINING POLYLACTIDE WITH POLYPEPTIDES FOR MATERIALS APPLICABLE IN THE TREATMENT OF PERIODONTITIS

Pandora Thimi, Ioannis Choinopoulos, Vassilios Roussis, Efstathia Ioannou, Hermis Iatrou

Laboratory of Industrial Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Zografou GR-15771, Greece

Periodontitis, characterized by the destruction of periodontal ligament and alveolar bone, is a microbiologically induced inflammation of periodontium that constitutes the principal cause of teeth loss in adults. Treatment methods that arrest the evolution of the inflammatory process and in a way stagnate further attachment loss are used frequently as a first-step procedure. These involve improvement of oral hygiene and management of all predisposing factors that contribute to plaque retention. However, the ultimate goal of reestablishing tooth functionality is achieved by periodontal regeneration procedures that try to restore the periodontal apparatus to its initial state. These include, among others, guided tissue regeneration (GTR) membranes that act as a physical barrier isolating the fast-growing epithelium and providing adequate time and space for the periodontal ligament cells and osteoblasts to proliferate and counter effect attachment loss. The major drawback of the currently available GTR membranes is the low predictability of attachment and bone gains. The aim is to develop tri-layer hybrid multifunctional, biocompatible and biodegradable electrospun barrier membranes that will enhance bone and periodontal ligament regeneration, preventing epithelial cells growth and protecting the surrounding environment from anaerobic bacterial pathogens. The designed membranes will consist of three layers: a) an outer layer of hydrophobic biodegradable polymers to provide the overall mechanical strength to the membrane, blocking also the epithelial cells from reaching the periodontal ligament region, b) a middle layer of electrospun amphiphilic calcium polyaspartate di-block co-polymers to support bone regeneration, constantly releasing calcium ions, and c) an inner layer of electrospun marine sulfated polysaccharides chemically bonded and/or loaded with antibacterial agents to promote periodontal ligament regeneration, inhibiting the undesired growth of anaerobic pathogens.

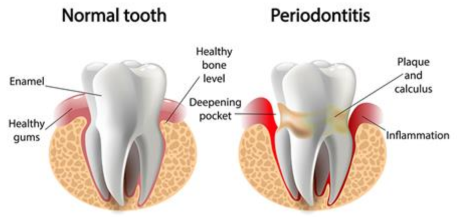
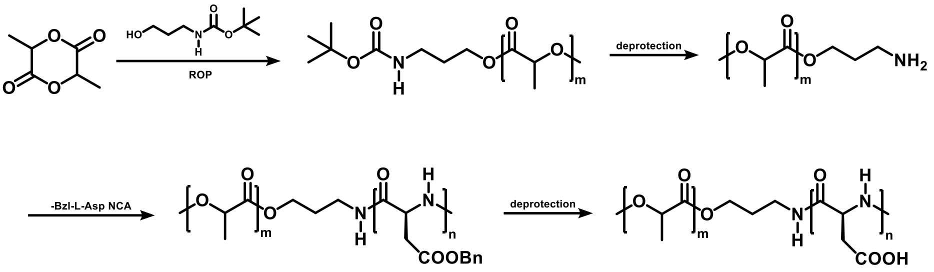


Figure 4: Periodontitis



Scheme 1: Synthesis of polymeric material

Acknowledgments:

The research has been co-financed by the European Union (European Social Fund- ESF) and Greek national funds through the Operational Program EPANEK – Research Funding Program ΤΙΕΔΚ-02499.

Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

eP57

SELF-HEALING pH- AND ENZYME STIMULI-RESPONSIVE HYDROGELS FOR TARGETED DELIVERY OF GEMCITABINE TO TREAT PANCREATIC CANCER

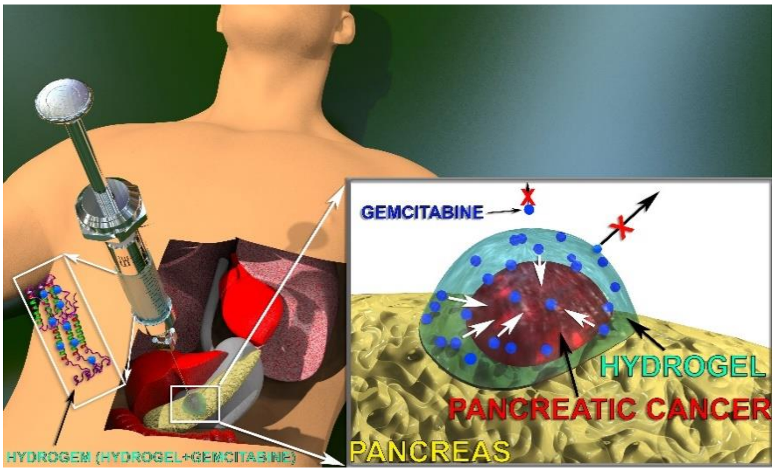
Hermis Iatrou*[,1], **Panayiotis Bilalis,**[1] **Dimitrios Skoulas,**[1] **Anastasis Karatzas,**[1]
John Marakis,[2] **Athanasios Stamogiannos,**[3] **Chrisida Tsimblouli,**[4] **Evangelia Sereti,**[4]
Efstratios Stratikos,[3] **Konstantinos Dimas**[4] **, Dimitris Vlassopoulos**[2]

[1]University of Athens, Department of Chemistry, Panepistimiopolis, Zografou, 15771, Athens, Greece
[2]FORTH, Institute for Electronic Structure and Laser, Heraklion 71110, Greece and Department of Materials Science & Technology, University of Crete, Heraklion 71003, Greece
[3]National Centre for Scientific Research Demokritos, Patriarhou Gregoriou and Neapoleos 27, Agia Paraskevi 15341, Athens, Greece.
[4]Department of Pharmacology, Faculty of Medicine, University of Thessaly, Larissa, Greece

A novel, multifunctional hydrogel that exhibits a unique set of properties for the effective treatment of pancreatic cancer (PC) is presented. The material is comprised of a pentablock terpolypeptide of the type PLys-*b*-(PHIS-*co*-PBLG)-PLys-*b*-(PHIS-*co*-PBLG)-*b*-PLys which is a non-cytotoxic polymer. It can be implanted via the least invasive route and selectively delivers gemcitabine to efficiently treat PC. Simply mixing the novel terpolypeptide with an aqueous solution of gemcitabine within a syringe results in the facile formation of a hydrogel that has the ability to become liquid under the shear rate of the plunger. Upon injection in the vicinity of cancer tissue, it immediately reforms into a hydrogel due to the unique combination of its macromolecular architecture and secondary structure. Due to its pH responsiveness, the hydrogel only melts close to PC, thus the drug can be delivered directionally towards the cancerous rather than healthy tissues in a targeted, controlled and sustained manner. The efficacy of the hydrogel was tested *in-vivo* on human to mouse xenografts using the drug gemcitabine. It was found that the efficacy of the hydrogel loaded with only 40% of the drug delivered in one dose, was equally or slightly better to the peritumoral injection of 100% of the free drug delivered in two doses, the typical chemotherapy used in clinics so far. This results suggest that the hydrogel can direct the delivery of the encapsulated drug effectively in the tumor tissue. Enzymes lead to its biodegradation, avoiding removal by resection of the polymeric carrier after cargo delivery. The unique properties of the hydrogel formed can be predetermined through its molecular characteristics, rendering it a promising modular material for many biological applications.

Reference:

1. P. Bilalis, D. Skoulas, A. Karatzas, J. Marakis, A. Stamogiannos, C. Tsimblouli, E. Sereti, E. Stratikos, K. Dimas, D. Vlassopoulos, and H. Iatrou Biomacromolecules, 19 (9), pp 3840–3852 (2018).


GEMCITABINE
HYDROGEL
PANCREATIC CANCER
PANCREAS
HYDROGEM (HYDROGEL+GEMCITABINE)

eP58

RENEWABLE UNSATURATED POLYESTER RESINS BASED ON ADIPIC ACID

Alexandra Zamboulis[1], Lazaros Papadopoulos[1], Christina Kyriakou Tziamtzi[2], Nikolaos Athanasopoulos[3], Stavros Tsompanidis[3], Konstantinos Chrissafis[2], Dimitrios N. Bikiaris[1]

[1] Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124, Thessaloniki, Greece
[2] School of Physics, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece
[3] Phee, 17 Kolokotroni Str., Rio, Patras, GR-26504, Tel: 2613023239, www.phee.gr

In today's society, plastics have a major role in our lives. However, the low biodegradability of plastics in combination with our inability for proper waste management has led to the accumulation of waste causing serious environmental problems. In addition, crude oil's price is fluctuating and its resources are steadily decreasing. All these issues have drawn attention to the production of polymers from renewable resources, the so-called bio-based polymers.

Among others, unsaturated polyester resins (UPRs) are one of the most used polymer classes, due to their simple processing and the variety of fields of application. UPRs are linear polycondensation products based on unsaturated and saturated acids/anhydrides and diols or oxides. The unsaturation in the backbone provides sites for reaction with unsaturated monomers using free-radical initiators, thereby leading to the formation of a three-dimensional network. A UPR consists of an unsaturated polymer matrix that is then mixed with an unsaturated monomer called reactive diluent; after a thermally or UV induced curing a cross-linked network is obtained.

The aim of this work is the production of novel unsaturated polyester resins based on adipic acid with poly(ethylene glycol). Adipic acid is a biobased dicarboxylic acid monomer with a huge market and environmental potential. The resins were synthesized and further subjected to curing. Several characterization methods were utilized to examine physicochemical properties of the materials.

Acknowledgement

This research has been co-funded by the European Regional Development Fund (ERDF) and Greek national funds through the Operational Program "Competitiveness, Entrepreneurship and Innovation", EPAnEK 2014-2020, under the call "Aquaculture"-"Industrial materials"-"Open innovation in culture" as well as by private funds (project code T6YBP-00006).

ePS9

LONG-ACTING INJECTABLE FORMULATIONS OF PALIPERIDONE PALMITATE BASED ON BIOCOMPATIBLE POLY(ALKYLENE SUCCINATE) MICROSPHERES

Rizos D. Bikiaris , Evi Christodoulou [1], Maria Kasimatis [2], Hermis Iatrou [2],
Nikolaos Nikolaidis [1]

[1] Department of Chemistry, Laboratory of Polymer Chemistry and Technology, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Greece
[2] Department of Chemistry, University of Athens, Panepistimiopolis, Zografou, Athens 15771, Greece

Biodegradable polymeric microsparticles are currently the strategy for long-term delivery of active pharmaceutical ingredients (APIs) due to their unique properties, such as the maintenance of the therapeutic concentration of the API in plasma for longer periods of time by controlling its release, and the ease of encapsulating either hydrophilic or hydrophobic drugs. Hydrolytically labile aliphatic polyesters have attracted attention for the development of such controlled-release drug delivery systems, combining biocompatibility, renewability and tunable properties (i.e. mechanical, physicochemical, degradation rates etc.)

In the present study, the preparation of five poly(alkylene succinate)-based microspheres (PESu, PBSu, PHSu, POSu, PDeSu) for the sustained release of the antipsychotic agent paliperidone palmitate (PDP) is, for the first time, evaluated. The biocompatible aliphatic polyesters derived from succinic acid and different aliphatic diols were synthesized by a typical two-stage melt-polycondensation method and characterized by a combination of techniques. The microsphere formulations were then developed using oil-in-water emulsification/solvent evaporation method and thoroughly investigated by SEM, FT-IR (**Figure 1**), XRD, DSC and in terms of cytotoxicity and dissolution rates (**Figure 2**).

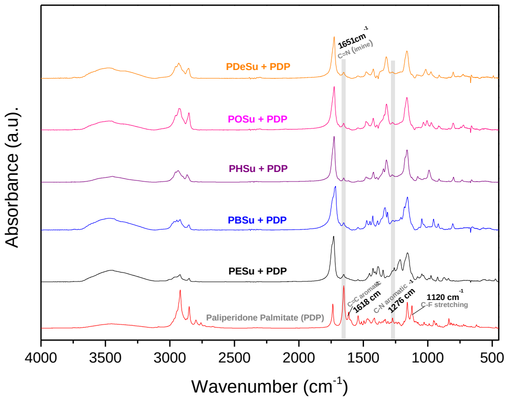


Figure 1. FTIR spectra of neat Paliperidone Palmitate API and the fabricated PDP-loaded microspheres.

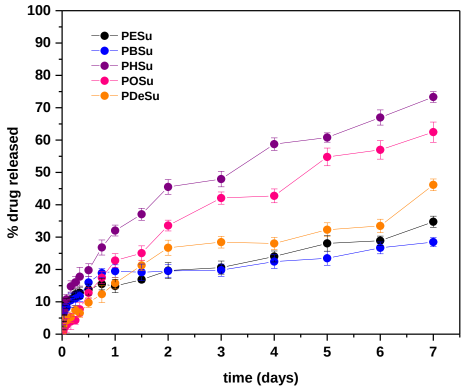


Figure 2. *In vitro* release profiles of Paliperidone Palmitate from the prepared microspheres for 7 days.

All prepared copolymers were of semi-crystalline nature, and their melting points and degradation rates varied based on the diol type used. PDP was amorphously dispersed within the polymeric microspheres leading to enhanced dissolution rates during the API release.

eP60

DEVELOPMENT, CHARACTERIZATION AND IN VITRO EVALUATION OF CHITOSAN-FISH GELATIN-GLYCEROL HYDROGEL MEMBRANES FOR WOUND HEALING APPLICATIONS

**Andreas Karydis-Messinis[1], Dimitrios Moschovas[1], Maria Markou[2], Carol Murphy[2],
Anastasios Vasileiadis[3], Apostolos Avgeropoulos[1],
Nikolaos Evangelos Zafeiropoulos[1]**

[1] Materials Science and Engineering, University of Ioannina, Ioannina, Greece
[2] Department of Biomedical Research, Foundation for Research & Technology-Hellas (FORTH), Institute of Molecular Biology and Biotechology (IMBB), Greece
[3] Department of Biological Applications & Technology, University of Ioannina, Ioannina, Greece

The mortality of patients suffering from large surface burns (70% of total body surface area) and the high cost of wound management / care, render the development of patches through simple and economical synthetic routes, imperative.

The natural polymers chitosan and fish gelatin were used for the development of hydrogel membranes, while the use of glycerol was found to be pivotal for the overall improvement of the materials' properties. The hydrogel membranes were synthesized through a solution casting-evaporation method. To further improve some of the properties, heat treatment was performed, leading to materials with enhanced characteristics (reduction of the degradation rate and improvement of cell proliferation). The materials synthesized in the present study were characterized by infrared (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM). Water absorption and degradation rate studies were also conducted. In addition, antibiotic (tetracycline hydrochloride) was incorporated into the hydrogels to enhance antimicrobial properties. Finally, in vitro endothelial cell colonization tests were carried out on hydrogels with the aim of firstly studying the presence of a cytotoxic agent and then study the cell adhesion and proliferation on the hydrogel membranes. The results of the inhibition zone (antimicrobial tests), the cell attachment and proliferation (in vitro endothelial cell colonization tests) as well as the easy application of the patches (swollen or dry) in various body parts and the cost-effective preparation method, indicate that the hydrogel membranes could be potential biomaterials in wound healing/care applications (protection against bacteria, providing a moist environment etc.).

Ευρωπαϊκή Ένωση
Ευρωπαϊκό Κοινωνικό Ταμείο

Επιχειρησιακό Πρόγραμμα
Ανάπτυξη Ανθρώπινου Δυναμικού,
Εκπαίδευση και Διά Βίου Μάθηση
Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

ΕΣΠΑ
2014-2020
ανάπτυξη - εργασία - αλληλεγγύη

eP61

H-[P(OEGMA-co-LMA)] : NOVEL HYPERBRANCHED RANDOM AMPHIPHILIC COPOLYMERS AS SELF-ASSEMBLED NANOCARRIERS FOR DRUG DELIVERY AND BIO-IMAGING APPLICATIONS

Anastasia Balafouti, Stergios Pispas

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation,
Athens, Greece

Over the last years, amphiphilic copolymers have attracted significant research interest, since they find potential applications in targeted drug delivery, nanomedicines and many other fields. This is mostly due to their ability to self-assemble into nanostructures in aqueous media. The copolymers molecular architecture and composition are the main influences to their self assembling behavior.

In our study, innovative amphiphilic hyperbranched random copolymers, namely H-[poly (ethylene glycol) methyl ether methacrylate-co- lauryl methacrylate] (H-[P(OEGMA-co-LMA)]), with variable hydrophobic content, were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. The divinyl monomer, ethylene glycol dimethacrylate (EGDMA) was used as a branching agent. Molecular characterization by size exclusion chromatography (SEC) and proton nuclear magnetic resonance (1H-NMR) spectroscopy indicated the success of the polymerization, whereas self-assembling behavior in aqueous media was investigated by light scattering techniques and fluorescence spectroscopy. In addition, the model hydrophobic drug, curcumin, known for its intrinsic fluorescence properties, was used in order to investigate the H-[P(OEGMA-co-LMA)] copolymers drug encapsulation ability. Curcumin was successfully loaded into the polymeric nanoparticles, as confirmed by dynamic light scattering, UV-Vis and fluorescence spectroscopy. Interestingly, curcumin incorporation contributes to more structurally defined self assembly, consisting of small size nanoparticles (

Overall results signify that the biocompatible H-[P(OEGMA-co-LMA)] nanostructures could potentially serve as nanocarrier systems for drug delivery and bio-imaging applications.

eP62

THE BINDING KINETICS OF A MULTILAYER FILM COMPOSED OF ALTERNATING PROTEIN-POLYSACCHARIDE LAYERS AND ITS RESPONSIVENESS ON PH CHANGES

Nikolitsa Katsenou[1], Nikolaos Spiliopoulos[1], Dimitris Anastassopoulos[1],
Aristeidis Papagiannopoulos[2], Chris Toprakcioglu[1]

[1] Department of Physics, University of Patras, Patras 26504 Greece
[2] Theoretical and Physical Chemistry InstituteNational Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, Athens, 11635, Greece

Introduction: In this work, we use the anionic polysaccharide chondroitin sulfate (CS) and the globular protein bovine serum albumin (BSA) to prepare polysaccharide-protein multilayers (PPMLs). Bovine serum albumin is one of the most important blood proteins due its ability to bind with organic and inorganic molecules and transport various substances in the blood. Chondroitin sulfate is a highly sulfated polysaccharide that is normally found in cartilage around joints in the human skeleton and it can bind to a large variety of proteins. Polyelectrolyte multilayers are investigated for applications in drug-carrying blood contacting biomaterials, cell growth, functional biomedical supports and antibacterial coatings while polysaccharides play a central role as nontoxic, biocompatible and natural polyelectrolytes.

Methods: The binding kinetics of PPMLs is examined with Surface Plasmon Resonance Spectroscopy, a powerful tool, to study biomolecular interactions since it is able to rapidly monitor any dynamic process in real time, within a fluid environment. The binding kinetics describe how fast and strong is the interaction of the two biomolecules to each other. The measurement of SPR shift, during layer formation, gives information about the surface concentration of the biomolecules.

Results: A multilayer film is formed at pH=4, from alternating BSA/CS layers based on the electrostatic interaction between the macromolecules. During the formation of PPMLs the binding rate of molecules is investigated. The stability of the alternating multilayer is examined by changing the ph to neutral. As both the protein and the polysaccharide are negatively charged on pH=7, the system is disassembled.

Conclusions: Preliminary results show that albumin binding rate is an order of magnitude faster than chondroitin. Experiments are designed and performed for all stages of adsorption of the alternating layers in order to reach safe conclusions.

eP63

PREPARATION OF POLY (LACTIC ACID)/POLY (ETHYLENE ADIPATE) BLENDS AS DRUG DELIVERY SYSTEM VIA ELECTROSPINNING TECHNIQUE

Maria Lazaridou, Christina Samiotaki, Dimitrios N. Bikiaris

Laboratory of Chemistry and Technology of Polymers and Dyes, Chemistry Department,
Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece

Poly (lactic acid) is a highly biocompatible and biodegradable polyester that has concentrated a lot of interest in the last few decades. However, despite its unique properties and characteristics, this polyester requires a long time for its biodegradation to be completed and so it tends to be combined with other biodegradable polymers. This can happen through copolymerization or with the synthesis of polymeric mixtures.

Transdermal drug delivery is a process that even though has many advantages over other routes of administration such as oral or injectable, it presents the great requirement of skipping the skin in order to introduce the active substance inside the body. To serve this type of administration, transdermal patches have been made of various polymers such as chitosan and hyaluronic acid, but without much success due to various factors such as their crystallization behavior and the degree of degradation.

On this work, poly (lactic acid)/poly (ethylene adipate) blends were prepared with solvent casting method in different ratios (90/10, 80/20, 70/30, 60/40 and 50/50) in order to examine the impact of poly (ethylene adipate) on the characteristic properties of poly (lactic acid) (such as the biodegradion rate). The ratio with the best mechanical property was chosen for fabrication of transdermal patches via electrospinning process.

Both poly (ethylene adipate) and the mixtures were characterized by Fourier-transform infrared spectroscopy, X-ray diffraction, differential scanning calorimetry (DSC), viscosity, tensile test and enzymatic hydrolysis. The ratio 80/20 PLA/PEAd was then used to fabricate transdermal patches from nanofibers, utilizing electrospinning technique with aim to release the antibacterial drug levofloxacin over an appropriate, prolonged period. Nanofibers have been extensively studied in terms of crystallinity, morphology, release rate of the active substance in vitro and morphology.

eP64

PRODUCTION OF (NANO)CELLULOSE FROM AGRICULTURAL AND LIGNOCELLULOSIC BIOMASS

Eleni Psochia, Antigoni Margellou, Konstantinos Triantafyllidis

Department of Chemistry, Aristotle University of Thessaloniki, GR-54124, Thessaloniki, Greece

The growing environmental awareness along with the demand for replacing petrochemical resources with green and renewable feedstock, have centered the scientific interest on the use of biodegradable, biomass-derived polymers and composites. Cellulose is one of the three main structural components of lignocellulosic biomass and the most abundant natural polymer, which exhibits exceptional properties with numerous applications. Particular attention has been drawn to nanocellulose, which can be produced from cellulose either with mechanical or with chemical treatments, resulting in cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs), respectively. Its interesting features like, low density, relatively high surface area, biodegradability, biocompatibility, high elastic modulus and crystallinity have led to the utilization of nanocellulose as polymer additive in various industrial applications such as in packaging, biomedicine, tissue engineering, drug delivery systems, nanoelectronics or adhesives. In this work, cellulose was obtained from different agricultural wastes such as olive and poplar pruning and wheat straw, which were fractionated by various hydrothermal pretreatments with different reaction solvents, based on state-of-the-art biorefinery approaches. The isolated cellulose was further converted to cellulose nanoparticles and CNFs using sonication and high shear blending and to CNCs with acid hydrolysis method. Nanocellulose materials were also produced from commercial microcrystalline cellulose, for comparison reasons. All the prepared celluloses were characterized as to their structure by Fourier Infrared Spectroscopy (FT-IR) and their crystallinity by X-ray Diffraction (XRD) while their thermal behaviour was studied by Thermogravimetric Analysis (TGA). The nanoparticles' size was determined by Dynamic Light Scattering technique (DLS) and their surface area by N_2 sorption (Brunauer–Emmett–Teller method). Finally, their morphology was investigated by Scanning Electron Microscopy (SEM). The results demonstrate the successful production of highly crystalline CNFs and CNCs with increased surface area and promising thermal properties, highlighting the dynamic potential of biomass utilization to high added value products through biorefinery pathways.

This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation (EPAnEK 2014-2020), under «Special Actions "Aquaculture" - "Industrial Materials" - "Open Innovation In Culture"» (project code: T6YBP-00341).

eP65

pH-SENSITIVE NANOGATES BASED ON POLY(L-HISTIDINE) FOR CONTROLLED DRUG RELEASE FROM PEGYLATED MESOPOROUS SILICA NANOPARTICLES

Foteini Arfara, Hermis Iatrou

Department of Chemistry, National and Kapodistrian University of Athens, Athens, Greece

The design and synthesis of novel poly(ethylene oxide) and poly(L-histidine) grafted mesoporous silica nanoparticles (MSNs) by the grafting to method and a surface-initiated ring-opening polymerization process (ROP) is reported. Using PEG-silanes chains in order to graft poly(ethylene oxide) on the outer surface and APTES to introduce primary amino groups on the MSN outer surface that work as a ROP initiators, the nanoparticles acquired stealth properties and were decorated with a uniform pH-sensitive poly(L-histidine) (PHis) shell. The method applied for the MSN functionalization, guaranteed that there were not grafted PEO and PHis chains inside the MSNs' nanochannels. The successful grafting of the PEO and PHis chains was confirmed by FT-IR spectroscopy, TEM, SEM and TGA. Dynamic light scattering (DLS) and zeta potential analysis were used to reveal the pH-responsive nature of the polypeptide-gated mesoporous silica nanoparticles. Brunauer-Emmett-Teller and Barrett-Joyner-Halenda analysis were applied in order to determine the surface area and pore size of the nanoparticles. Overall, the described materials are promising candidates as nanocarriers for potential drug delivery applications.

ePB66

SYNTHESIS AND CHARACTERIZATION OF PH- AND REDOX-RESPONSIVE POLY(ETHYLENE OXIDE)-B-POLY(HISTIDINE-CO-CYSTEINE) TERPOLYMERS

Iro Kyroglou, Hermis Iatrou

Department of Chemistry, National and Kapodistrian University of Athens, Athens, Greece

In this poster the synthesis of a series of hybrid double-stimuli-responsive polypeptide terpolymers of the type $mPEO_{227}$-*b*-P(His_x-*co*-Cys_y) with two different rates (of 13% and 29%) by mole% in cysteine content is presented. The synthesis of the polymers was accomplished through ring opening polymerization of the corresponding protected N-carboxy anhydrides (monomers) using amine end-functionalized poly(ethylene oxide) ($mPEO_{227}$- NH_2) as a macroinitiator. High vacuum techniques were used for the synthesis of N-carboxy anhydrides, for the purification of solvents and for the isolation of well-defined polymers, ensuring high purity in the system and the absence of impurities that could lead to uncontrolled polymerization processes. The amphiphilic terpolymers synthesized have the ability to self-organize in aqueous solutions and form micelle-like structures on a nanoscale. The outer hydrophilic corona of the nanostructures consists of PEO chains and the pH-responsive core from PHis and PCys, which was used as a hydrophobic component but also as a cross-linking agent. The successful synthesis of the polymers was confirmed by extensive molecular characterization and techniques were used to study the dependence of the secondary structure of the polypeptides on pH and temperature, the ability to self-organize and the size of the synthesized nanoparticles. The ultimate goal is to create stable and stimuli-responsive to cancerous environments nanostructures, which will be used in targeted and controlled drug release applications in cancerous tissues.

eP67

SYNTHESIS AND CHARACTERIZATION OF NOVEL HYDROGEN PEROXIDE RESPONSIVE MEMBRANES FROM AMPHIPHILIC ABA TRIBLOCK COPOLYMERS FOR THE DEVELOPMENT OF BIOSENSORS COUPLED WITH SMARTPHONES

Papadopoulos G.[1], Moutsios I.[1], Tzianni E.[2] Moschovas D.[1], Prodromidis M.[2], Avgeropoulos A[1].

[1]Department of Materials Science Engineering, University of Ioannina, University Campus-Dourouti, 45110. Ioannina, Greece
[2]Department of Chemistry, University of Ioannina, University Campus-Dourouti, 45110 Ioannina, Greece

Medical diagnostic smartphone-aided operation devices constitute an ever-growing scientific field due to their small size, light weight, low power consumption and ability to provide reliable clinical measurements at home. The synthesis of amphiphilic ABA triblock copolymers using poly(ε-caprolactone) (PCL) as the core block and poly(ethylene glycol) (PEG) as the side blocks (PEG-*b*-PCL-*b*-PEG), containing aromatic peroxalate ester as linkage at the junction points was accomplished through ring opening polymerization in combination with esterification reactions. The synthesized triblock copolymers were molecularly characterized through Size Exclusion Chromatography (SEC), Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR), Infrared Spectroscopy (IR) and thermally characterized through Differential Scanning Calorimetry (DSC). Different number average molecular weight triblock copolymers were synthesized in order to control the porous size and a variety of volume fraction ratios of the hydrophobic (PCL) to the hydrophilic (PEG) polymer chains were prepared, in order to control the membranes hydrophobicity as well as their degradation rate. The hydrophobicity of all final membranes was calculated through Contact Angle measurements and the porosity was measured through Scanning Electron Microscopy (SEM). The aim of the scientific project was to synthesize a novel type of membranes for medical diagnostic devices (biosensors), able to provide reliable clinical measurements for detecting H_2O_2 as a product of more than 150 oxidase enzymatic activities. The synthesis of responsive copolymer membranes with controlled hydrophobicity, porosity, thickness and the existence of aromatic peroxalate ester as linkage at the junction points that can be oxidized, when stimulated by H_2O_2, to an unstable intermediate able to be degraded to carbon dioxide resulting in the membrane cleavage.

Acnolegment: The scientific work was supported by NSRF 2014-2020

Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

eP68

INFLUENCE OF THE CRYSTALLIZATION TEMPERATURE AND FILLER CONTENT ON THE PHYSICAL PROPERTIES OF POLY(L-LACTIC ACID)/TITANIUM DIOXIDE BIONANOCOMPOSITES

Aimilia Barmpaki[1], Evangelia Zavvou[1], Emmanouela Mystiridou[2], Ioannis Iliopoulos[3], Panagiota Karahaliou[1], Panagiotis Svarnas[4], Stavroula Georga[1], Christoforos Krontiras[1]

[1] Department of Physics, University of Patras, 26504 Patras, Greece
[2] Department of Materials Science, University of Patras, 26504 Patras, Greece
[3] Department of Geology, University of Patras, 26504 Patras, Greece
[4] Department of Electrical & Computer Engineering, University of Patras, 26504 Patras, Greece

Bionanocomposites are an effective approach for the enhancement of the physical properties of biopolymers towards food packaging applications [1]. Poly(L-lactic acid) (PLLA) is extensively employed as the matrix in bionanocomposites with a variety of nanofillers. Titanium dioxide (TiO_2), a non-toxic, inert and low-cost inorganic nanoinclusion, is an excellent candidate for the production of nanocomposites [2]. In this work, the influence of the crystallization temperature (T_C) on the thermal properties of PLLA is investigated in a wide range of crystallization temperatures [3]. Considering these results, PLLA/TiO_2 bionanocomposites were prepared in a twin-screw extruder and isothermally crystallized at T_C=85°C and 130°C, where the two most common crystal structures α′ and α of PLLA are formed, respectively [4]. The morphological characterization of all bionanocomposites through Scanning Electron Microscopy revealed good dispersion of the nanoparticles within the polymer matrix. Comparison of the X-ray Diffraction results of samples crystallized at 85°C and 130°C manifests the transformation of α′ to α crystalline phases [5]. The glass transition temperature is independent of the TiO_2 content, while melting behavior is strongly affected by the crystallization temperature, as suggested by Differential Scanning Calorimetry studies. Thermogravimetric Analysis reveals an improved thermal stability of nanocomposites upon increasing filler content [6]. The crystallization process was monitored via Polarizing Optical Microscopy, where the characteristic spherulitic textures were observed. Finally, contact angle and surface energy measurements suggest that the wettability of the bionanocomposites remains practically independent with increasing TiO_2 content.

Acknowledgements: Authors acknowledge Dr. V. Drakopoulos for the SEM experiments and Prof. A. Ladavos and Asst. Prof. A. Giannakas for the use of the twin screw extruder. The present work was financially supported by the «Andreas Mentzelopoulos Foundation».

References

[1] Rhim J.-W. et al., Progress in Polymer Science 38, 1629– 1652, 2013.
[2] Kaseem M. et al. Materials 12, 3659, 2019.
[3] Zavvou E.E et al. to be publised
[4] Di Lorenzo M.L. & Androsch R., Polym. Int. 68, 320-334, 2019.
[5] Zavvou E.E. et al., Mod Concept Material Sci. 3(5), 2021, MCMS. MS.ID.000572.
[6] Li W. et al., Polymers 22, 1170, 2017.

ePANEL69

NANOPARTICLES FEATURING GOLD NANOSHELLS THROUGH HYBRID POLY(L-HISTIDINE) POLYMERS, THEIR NIR ABSORBANCE AND MOLECULAR CHARACTERISTICS

Varvara Athanasiou[1], Dimitra Stavroulaki[1], Foteini Arfara[1], Dimitrios Kabras[1], Ioannis Kleideris[1], Niki Roumelioti[1], Panagiota G. Fragouli[2], Georgios Patias[3], David Haddleton[3], Hermis Iatrou[1]

[1] Department of Chemistry, Industrial Chemistry Laboratory, National and Kapodistrian University of Athens, Athens, Greece
[2] DIDPE, Dyeing, Finishing, Dyestuffs and Advanced Polymers Laboratory, University of West Attica, Athens, Greece
[3] Department of Chemistry, University of Warwick, Coventry, United Kingdom

A novel simple synthesis of hybrid nanoparticles containing goldnanoshells (AuNSs) that absorb at near-infrared (NIR) is reported. Hybrid copolypeptides, i.e., Poly(ethylene oxide)-*b*-poly(L-histidine), poly(ethylene oxide)-*b*-poly(L-histidine)-*b*-poly(L-phenylalanine) and poly(ethylene oxide)-*b*-poly(L-histidine)-*b*-poly(γ-benzyl-L-glutamate), were utilized.

The addition of $HAuCl_4$, followed by heating, resulted in the reduction of the Au ion by poly(L-histidine) (PHis) and the deposition of gold nanoparticles only at the PHis layer; thus, a nanoshell within the preformed spherical nanoparticles (NPs)—initially formed by the self-assembly of the amphiphilic hybrid polypeptides in water—was created. These NPs are composed of a PEO shell, a Phis layer containing the nanoshell and a PPhe or PBLG core.

A shift of the absorption peak corresponding to longitudinal surface plasmon resonance to NIR wavelengths was achieved, as the optical properties of the goldnanoshells can be fine-tuned to absorb at a specific wavelength by controlling the AuNS thickness and core diameter. Size and morphology of Au NPs were examined by TEM and DLS techniques. Studies on the temperature increase of a NPs solution irradiated by a low radiation laser at 808 nm showed the ability of NPs to induce thermal cell ablation.

Our novel biocompatible polymeric nanoparticles featuring AuNSs with a peak optical absorption in the NIR are biomaterials valuable not only for molecular imaging but also for photothermal therapy.

eP70

DEVELOPMENT OF NEW AQUEOUS CONJUGATED POLYMER NANOPARTICLES FOR BIOIMAGING AS FLUORESCENT PROBES

Aristea Pavlou[1,2,3], Athanasios Katsouras[2,4], Markou Maria[2], Alkmini Negka[5], Sofia Bellou[2], Andriana Schiza[1], Panagiota Koralli[1], Antonia Dimitrakopoulou-Strauss[5], Vassilis G. Gregoriou[6], Michael G. Siskos[3], Theodore Fotsis[2], Apostolos Avgeropoulos[4], Carol Murphy[2], Christos L. Chochos[1]

[1]Institute of Chemical Biology, National Hellenic Research Foundation, Athens, Greece
[2]Department of Biomedical Research, Institute of Molecular Biology and Biotechnology, Foundation for Research and Technology-Hellas (FORTH), Ioannina, Greece
[3]Department of Chemistry, Section of Organic Chemistry and Biochemistry, University of Ioannina, Ioannina, Greece
[4]Department of Materials Science Engineering, University of Ioannina, Ioannina, Greece
[5]Clinical Cooperation Unit Nuclear Medicine, German Cancer Research Center, Heidelberg, Germany
[6]National Hellenic Research Foundation, Athens, Greece

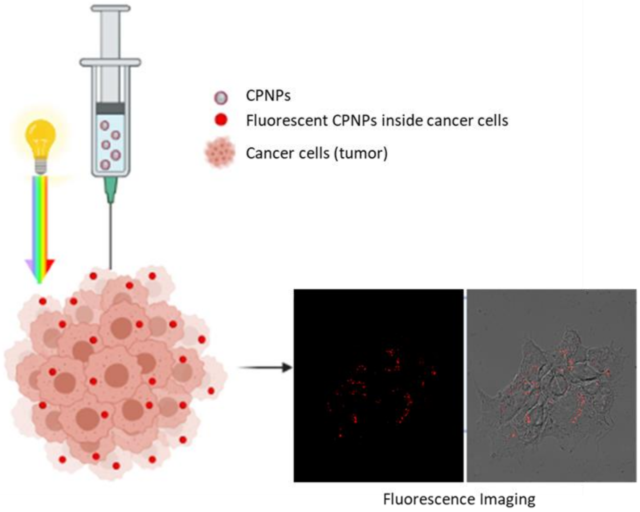
Keywords: conjugated polymers, aqueous nanoparticles, optical bioimaging

Introduction: π-Conjugated Polymers (CPs) due to their unique optical and therapeutic properties have emerged as the next generation cancer theranostic nanomaterials. However, due to their hydrophobic nature, CPs are not water soluble thereby limiting their applications. Strategies such as nanoprecipitation to prepare conjugated polymer nanoparticles (CPNPs) have overcome this limitation and CPNPs can be resuspended in aqueous solutions, thereby allowing their addition to cell culture media and cellular uptake. In this study we present the preparation of new aqueous CPNPs for use as fluorescent contrast agents in cultured cells.

Methods: Alternating conjugated polymers were synthesized via metal catalyzed aromatic cross coupling Stille polymerization reaction. All polymers were analyzed via GPC, 1H-, 13C-NMR, UV-Vis and fluorescence spectroscopy. The formations of NPs were carried out via nanoprecipitation. The shape of the NPs was investigated with Atomic Force Microscopy while Dynamic Light Scattering was exploited to elucidate the NPs size. In vitro experiments were performed to study the behavior of the CPNPs as contrast agents in HCT-116 and HUVEC cell lines. The experiments presented address CPNPs toxicity, cellular uptake, endocytic pathway and intracellular localistaion.

Results: We synthesized 3 donor-acceptor (D-A) CPs. In all CPs the thienopyrroledione was maintained fixed as the electron withdrawing unit. For The first electron donating units, in the first one thienyl substituted benzodiathiaphene was used, whereas tetraphenyl or tetrathienyl substituted-indacenodithiophene were employed on the second and third CPs, respectively. These three CPs have absorbance between 570-590nm in THF and exhibit high quantum yields of ~30-40%. CPNPs of 90-100nm were prepared and have similar optical properties and lower, but efficient, fluorescence quantum yields compared to the CPs. The CPNPs are internalised by cultured cells, maintain their fluorescence and do not exhibit any toxicity. The CPNPs particle size, combined with the good fluorescent properties inside the cells, qualifies them to be ideal probes for fluorescence imaging.

Conclusion: In conclusion, the 3 CPNPs generated in this study show good optical behavior, cellular uptake and low toxicity. In particular, the third CPNP stands out, exhibiting strong fluorescent signal, very good cellular uptake and no cell toxicity and can be further investigated as a possible nanocarrier.



Scheme 1: General display of CPNPs inside cancer cells after excitation. (cited by BioRender.com)

eP71

FUNCTIONAL BIODEGRADABLE POLYESTERS WITH AN UPPER CRITICAL SOLUTION TEMPERATURE IN WATER

Maria Karouzou[1], Maria Kaliva[1,2], Maria Vamvakaki[1,2]

[1] Department of Materials Science and Tecnology, University of Crete, Crete, Greece
[2] Institute of Electronic Structure and Laser, Foundation of Research and Technology-Hellas, Crete, Greece

Thermo-responsive polymers have attracted great attention for use in biomedical applications, including controlled drug delivery, tissue engineering and others. Thermo-responsive polymers are classified into two main types: polymers which phase separate in water upon heating, and are characterized by a lower critical solution temperature (LCST) and those which become soluble when increasing the solution temperature, and display the so-called upper critical solution temperature (UCST). UCST-type polymers are much less studied compared to their LCST counterparts[1], whereas UCST-type, biodegradable polymers are scarce in the literature[2].

In the present work, we have synthesized main chain biodegradable polyesters bearing ionizable primary amine side groups, which exhibit a UCST in water in the presence of hydrophobic counterions. The polymers were synthesized by the polycondensation of a vinyl functionalized diol with a diacid chloride, followed by the post-polymerization modification of the alkene side groups of the polymer with cysteamine hydrochloride using photo-induced thiol-ene click chemistry. The functional polyesters exhibited pH responsive properties in aqueous solution and a thermo-responsive behavior in the presence of tetrafluoroborate anions which act as counterions to the charged amino groups. The cloud point temperature (T_c) was tuned between 2 and 52 °C, following a linear dependence on the salt concentration, whereas it first increased and then decreased when varying the polymer concentration at a constant salt content, which was attributed to intra- and/or inter-molecular ionic interactions.

The tunable transition temperature and excellent biodegradability of these novel smart polyesters render them promising biomaterials for use in drug delivery applications.

References

1. Gandhi, A., Paul, A., Sen, S. O. & Sen, K. K. *Asian Journal of Pharmaceutical Sciences* **10**, 99–107 (2015).
2. Zhu, S., Wen, L., Xiao, Y. & Lang, M. *Polym. Chem.* **11**, 5173–5180 (2020).

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme H2020-FETOPEN-1-2016-2017 under grant agreement No 737071 (ULTRACHIRAL).

eP72

RESPONSIVE 3D-PRINTED POLYESTER SCAFFOLDS FOR TISSUE-ENGINEERING APPLICATIONS

Stella Afroditi Mountaki[1,2], Maria Kaliva[2,3], Konstantinos Loukelis[2,3]
Maria Chatzinikolaidou[2,3], Maria Vamvakaki[2,3]

[1] Department of Chemistry, University of Crete, Crete, Greece
[2]Institute of Electronic Structure and Laser (Iesl) Foundation for Research and Technology – Hellas (Forth)

[3] Department of Materials Science and Technology, University of Crete, Crete, Greece

In the recent years, three-dimensional printing (3D-printing) has received great attention, which has led to a vast progress in the available technologies and materials. So far, 3D-printing via additive manufacturing is considered as the most promising technique for use in regenerative medicine and tissue engineering, as it allows to prepare complex constructs, resembling the native tissues and organs. However, despite the significant developments in the design and functionalization of biomaterials to address challenges encountered in drug delivery, device integration and tissue replacement, their diversity in 3D-printing applications is still limited due to the required combination of printing fidelity with biological function. The reported 3D-printable biomaterials include polymers and hydrogels, ceramics, composites, and others. Synthetic aliphatic polyesters are considered as excellent biomaterial candidates due to their combined biocompatibility, biodegradability and printability. However, they lack specific functional groups that will confer responsive bioactive properties. Herein we present a novel responsive polyester-based composite biomaterial, used to fabricate 3D printed scaffolds for potential tissue engineering applications. More specifically, a main chain polyester, bearing pH-sensitive carboxylic acid pendant groups, was blended with laponite, a bioactive nanosilicate clay, to obtain a composite biomaterial, used to fabricate 3D scaffolds via the extrusion-based 3D-printing method.

References

1. Guvendiren, M.; Molde, J.; Soares, R. M. D.; Kohn, J. *ACS Biomater. Sci. Eng.* **2016**, 2, 1679.
2. Griffith, L. G. *Acta Biomater.* **2000**, 48, 263.
3. Mountaki, S. A.; Kaliva, M.; Loukelis, K.; Chatzinikolaidou, M. ; and Vamvakaki, M. *Polymers* **2021**, 13, 1.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation program H2020-FETOPEN-1-2016-2017 under grant agreement No 737071 (ULTRACHIRAL).

eP73

MOLECULAR DYNAMICS SIMULATION OF THE FORMATION OF POLYCATION-BASED DNA COMPLEXES INTENDED FOR GENE DELIVERY APPLICATIONS

Terpsichori Alexiou[1], Vlasis Mavrantzas[2], Dimitris Mintis[2]

[1] Chemical Engineering, Cyprus University of Technology, Cyprus
[2] Chemical Engineering, University of Patras, Patras, Greece

Introduction: Complexes formed from DNA and polycations are of particular interest because of their potential use in gene therapy,[1] and some representative synthetic non-viral vectors based on this approach have made use of polycations such as poly(ethylene imine) (PEI), polylysine (PLL), polyamidoamine dendrimers (PAMAM) and poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA).[2] Despite experimental progress, there remains a lack of understanding of the structure and formation of DNA-polycation complexes at an atomistic scale.

Methods: In order to improve the fundamental understanding of the structure and formation of DNA-polycation complexes at an atomistic scale, we have performed rigorous, atomistic MD simulations for the investigation of the microscopic mechanisms of complexation formed between a model polycation consisting of PDMAEMA chains[3,4] with a moderate polymerization degree (e.g., N=25) and a series of relatively short double stranded DNA chains (e.g., number of base pairs equal to 24)..

Results: The effects of varying base sequence and DNA architecture (linear & cyclic duplexes) have been investigated. Special emphasis is placed into the investigation of the effect of N/P ratio (stoichiometric ratio of polycation amine groups to DNA phosphate groups; varied by increasing polycation concentration) on structural and thermodynamic aspects of the PDMAEMA−DNA complexation process.

Conclusions: In the case of the short and stiff cyclic DNA molecules (DNA minicircles) studied here, a topologically induced increase in the local charge density per volume unit leads to a substantial increase in the number of complexation sites (DNA-polycation contact points). Importantly, among the base sequences studied, adenine-thymine (AT)-rich DNA sequences are prone to decomplexation events, due to base-specific variations of the hydrogen bond network formed between DNA and polycation in the major and minor grooves.

The outcomes of this study are expected to shed more light into the underlying microscopic mechanisms that dictate potential DNA base-specific or DNA architecture-dependent effects on the complexation process.

eP74

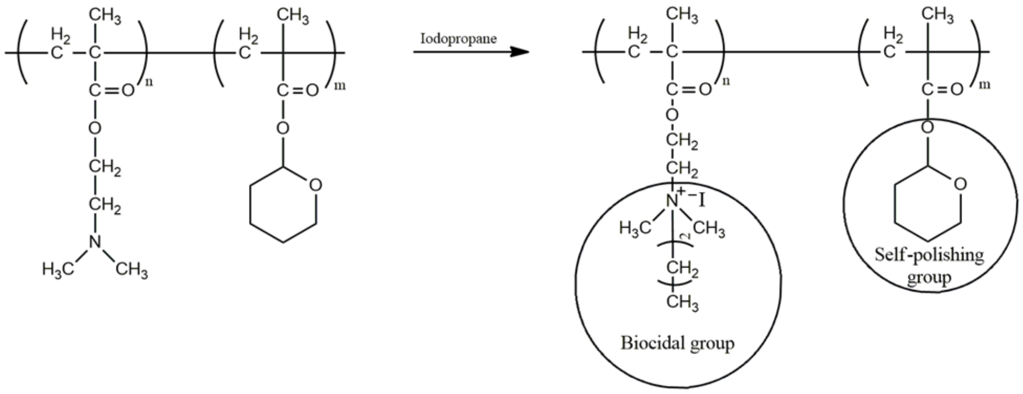
SELF-ASSEMBLED PDMAEMA-B-PTHPMA DIBLOCK COPOLYMERS COMPRISING BIOCIDAL AND SELF-POLISHING PROPERTIES

Theodore Manouras[1,4], Apostolos Vagias[2], Eleftherios Koufakis[1,4], Peter Müller-Buschbaum[2], Spiros Anastasiadis[3,4], Maria Vamvakaki[1,4]

[1] Department of Materials Science and Technology, University of Crete, Crete, Greece
[2] Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München and Fachgebiet Physik weicher Materie/Lehrstuhl für Funktionelle Materialien, Physik Department, Technische Universität München
[3] Department of Chemistry, University of Crete, Crete, Greece
[4]Insitute of Electronic Structure and Laser, Foundation of Research and Technology-Hellas

Antimicrobial surfaces that prevent biofouling from any type of microorganism are attractive in inhibiting the spread of microbial infections. Such surfaces either repel microbes, so they cannot attach to the surface, or kill microbes in the vicinity of the surface. Such contact-active antimicrobial surfaces can be realized by tethering antimicrobial polymers onto a given substrate. Biocidal surfaces are continuously being developed for a plethora of applications spanning from biomedical tools, packaging management, marine technology and navigation.

In this work, we demonstrate the development of new unexplored polymeric materials exhibiting controllable biocidal properties in the solid state. These polymers comprise environmental-friendly biocidal species and can self-organize into nanostructured films with controlled self-polishing and biocidal features. Amphiphilic diblock copolymers containing hydrophobic and hydrolyzable tetrahydropyranyl methacrylate (THPMA) units and hydrophilic 2-(dimethylamino)ethyl methacrylate (DMAEMA) moieties were synthesized by group transfer polymerization (GTP) and were characterized by gel permeation chromatography (GPC) and proton nuclear magnetic resonance spectroscopy. These symmetric diblock copolymers in the solid state are self-assembled into lamellae structures in parallel to the substrate as verified by independent X-ray reflectivity (XRR) and Grazing incidence small angle X-ray scattering (GISAXS) measurements. Propyl iodide was used for the quaternization of the DMAEMA units in order to introduce the cationic biocidal groups (see Figure 1). The self-polishing behavior of the quaternized diblock copolymer thin films in aqueous media, over a period of about 1 year, was periodically monitored by ellipsometry. Furthermore, the quaternized block copolymer thin films exhibited good antimicrobial properties against both Gram-positive and Gram-negative bacteria.



Acknowledgment

This research has been co-financed by the European Maritime and Fisheries Fund (EMFF) of the European Union and Greek national funds through the Operational Program Fisheries and Maritime, under the call INNOVATION IN AQUACULTURE (MIS: 5029684)

Ευρωπαϊκή Ένωση
European Social Fund

Operational Programme
Fisheries and Maritime
Co-financed by Greece and the European Union

ΕΣΠΑ
2014-2020
ανάπτυξη - εργασία - αλληλεγγύη

eP75

FERMENTATIVE PRODUCTION OF BIOPOLYMERS FOR ADIPOGENESIS, MYOGENESIS AND BONE FORMATION

Eleni Chatzilakou, Olga Tsave, Christos Chatzidoukas

Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece

Introduction: Metal alloys have been used extensively as medical implants, however, various data correlating metal traces with the development of immune-related adverse events have emerged safety concerns. Consequently, biodegradable and biocompatible polymers are more than ever used in bioengineering to produce medical devices and implants. The aim of this study was the production of three biomedically promising Polyhydroalkanoates (PHAs), namely poly-hydroxybutyrate (PHB), poly-hydroxybutyrate-co-valerate (PHBV) and poly-hydroxyoctanoate (PHO), followed by the complete characterization of their properties prior to assessing their biological profile.

Methods: Biopolymer synthesis was performed in a lab-scale bioreactor, employing established fed-batch cultivation protocols. *Pseudomonas putida* and *Azohydromonas lata* were cultivated to acquire PHO and PHB, PHBV, respectively. Complete characterization of the formatted biopolymeric scaffolds' physical-chemical and mechanical properties was performed using several techniques (SEM, Tensile-Compressive Strength testing, etc.). Moreover, three cell lines, namely 3T3-L1, SaOs-2 and C2C12 were examined. All cell lines were seeded in appropriate culture plates coated with the PHAs and assessed for cell adhesion, toxicity, proliferation and differentiation. Cell adhesion, viability and proliferation were determined by colorimetric and luminescence assays. Successful differentiation was confirmed by Oil-red-O staining for 3T3-L1, whereas C2C12 were differentiated until mature myotubes were observed via SEM.

Results and Conclusions: Polymer recovery techniques were implemented to obtain sufficient amounts of biopolymers with minimum implication at their molecular properties. The mechanical and physicochemical measurements indicated that the produced biomaterials are suitable for tissue engineering applications. The film formation study led to the optimization of the applied protocol, acquiring homogeneous/unfissured films for biomimetic purposes. Scaffolds exhibited successful cell adhesion for all cell lines tested. Regular examination of cell morphology indicated no aberration from the healthy state whereas no reduction in cell viability was observed. Cell differentiation was successful in all cases examined. Concisely, PHB, PHBV and PHO stand as valuable candidates to meet the demanding tissue engineering requirements.

ePJ76

POLYPEPTIDE SYNTHESIS USING THE NOVEL MACRO-INIATOR GLYCYRRHETINIC ACID WITH AMINO ENDING GROUPS TO TARGET CANCER CELLS

Ioanna Stavropoulou, Hermis Iatrou

Industrial Chemistry Laboratory, Department Of Chemistry, National & Kapodistrian University Of Athens, Greece

The aim of the current research is to synthesize a novel macro-initiator containing glycyrrhetinic acid and an amine ending group capable of polymerization.

In that manner, for the first time, a homopolymer of sarcosine was synthesized by this macro-initiator. Why use glycyrrhetinic acid, though? Glycyrrhetinic acid has the ability to target liver cancer cells so it can be used in the future as an agent to selectively deliver anti-cancer drugs. For the synthesis of the macro-initiator inert atmosphere was used but for the polymer synthesis high vacuum techniques were required. The monomers were polymerized by ring-opening polymerization.

The purity of the macro-initiator was determined by infrared and nuclear magnetic resonance spectroscopy. The successful synthesis of the polymers was also determined by infrared and nuclear magnetic resonance spectroscopy, size exclusion chromatography and UV-Vis.

To conclude glycyrrhetinic acid proves to be an important asset for selective drug delivery to cancer cells. Polymeric micelles consisting of polypeptides enhance this behaviour making them more effective and less toxic to the human organism

ePrivate77

THE CHARACTERIZATION OF THE HEATING PROPERTIES OF BIO-BRIQUETTES OF COAL AND CORN COB

Issie Ikelle

Department of Industrial Chemistry, Ebonyi State University Abakaliki, Pmb 053, Nigeria, West-Africa

In this work, smokeless briquettes of various compositions were produced using coal and corn cob, starch was used as the binder while $Ca(OH_2)$ was the desulphurizing agent. The briquettes were produced mechanically using a manual briquetting machine with force and compression pressure of 276.36 N and 31.67 N/m^2 respectively. The briquettes were produced in the following ratio of mixtures; coal and corn cob 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100 respectively. The proximate analysis of the raw coal had the following values ash content 10.12 ± 0.023%, moisture content 3.25 ± 0.021%, volatile matter 20.12 ± 0.017%, fixed carbon 66.51 ± 0.013% and calorific value 29573.13 ± 0.014 kJ/kg. The raw corn cob sample showed ash content 12.56 ± 0.012%, moisture content 7.03 ± 0.015%, volatile matter 39.21 ± 0.016%, fixed carbon 41.2 ± 0.021% and calorific value 27277.84 ± 0.013 kJ/kg. The prepared briquettes were sun dried for seven days, subjected to various tests to assess their fuel quality. Of the briquettes produced, the 60% coal: 40% rice husk briquette showed the following values; ash content 20.46%, fixed carbon 37.47%, moisture content 3.38%, density 0.323 g/cm^3, volatile matter 38.69%, porosity index 62.88%, calorific value 23057.21 kJ/kg, water boiling test 2.69 minutes, burning time 19.69 minutes, ignition time 32.52 seconds and compressive strength 14.13 N/mm^3. The briquette showed improved properties with regards to combustible property of the bio-briquettes when compared to the other briquettes produced with the same binder but different compositions. The work also showed that biomass could be useful for heating purposes rather than open incineration.

eP78

A BIOBASED APPROACH FOR NEW ADHESIVES IN THE WOOD INDUSTRY

**Ioanna Koumentakou[1], Lazaros Papadopoulos[1], Labrini Malletzidou[2],
Charles Markessini[3], Electra Papadopoulou[3], Kostantinos Chrissafis[2],
Dimitrios Bikiaris[1]**

[1] Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece
[2] Solid State Physics Section, Physics Department, Aristotle University of Thessaloniki, Thessaloniki, Greece
[3] CHIMAR HELLAS SA

Unsaturated polyester resins (UPRs) are linear polycondensation products based on unsaturated and saturated acids/anhydrides and diols or oxides. The unsaturation in the backbone provides sites for reaction with vinyl monomers using free-radical initiators, thereby leading to the formation of a three-dimensional network. Unsaturated polyester resins (UPRs) have been known for many years. The production of UPRs started in the 1930s. Polyester resins, because of their versatility and low cost, are widely used throughout the world. UPRs are, along with polyurethanes, the most important cross-linkable polymeric materials. In recent years, due to the increased environmental pollution levels, research focuses on the production of polymers from renewable monomers, the so-called biobased polymers. Succinic acid is a dicarboxylic acid which is a new biobased monomer with a huge market and environmental potential.

This work was based on the production of UPRs from succinic acid. Succinic acid, ethylene glycol and maleic anhydride were used to prepare unsaturated polyester resins. The physicochemical properties of the prepared resins were examined with ^{1}H NMR, FTIR and TGA.

Acknowledgement: *This research has been co?financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code:T1EDK-01413).*

eP79

FULLY BIO-BASED PLASTICS VIA SOLVENT FREE MODIFICATION OF POLYSACCHARIDES

**Athanasios Porfyris[1], Constantine Papaspyrides[1], Natnael Behabtu[2],
Christian Lenges[3], Alexander Kopatsis[3]**

[1] Lab of Polymer Technology, School of Chemical Engineering,School of Chemical Engineering, National Technical University of Athens, Zographou Campus, Athens, 157 80, Greece
[2] Nutrition & Biosciences, IFF
[3] Health & Biosciences, Engineered Polysacharides Venture, IFF

Plastic materials are widely used for food packaging but sustainability and circularity issues are inherent with this application. The goal of our work is the synthesis of new materials, which could be used in the packaging sector while being abundant in nature, such the polysaccharides. In this case, it is predicted that the cost will be very suppressed together with the pertinent carbon footprint. In particular, the nature-identical engineered polysaccharide, α-(1,3) glucan, produced by the enzymatic polymerization of sucrose, was chemically modified by acylation with succinic anhydride. This modification reaction was initially performed at the micro-scale in a TGA reactor to access a range of reaction conditions and to study the mechanism of the reaction. Subsequently, the best performing conditions were reproduced at the larger laboratory scale. The reaction products were characterized via coupled TGA/DSC analysis, FT-IR spectroscopy, solution viscosity and pH determination. The acylation path resulted in partially modifying the polysaccharide, by altering its behavior in terms of thermal properties and solubility. The acylation in a solvent free approach was found promising for the development of novel, potentially melt-processable and fully bio-based and biodegradable ester compounds.

α-(1,3) glucan/DMSO

α-(1,3) glucan/SA uncatalyzed

α-(1,3) glucan/SA catalyzed

eP80

3D-PRINTED CHITOSAN/GELATIN/COLLAGEN DRESSING FOR WOUND HEALING

Nina Maria Ainali [1], Artemis Palamidi [1], Ioanna Koumentakou [1], Zoe Terzopoulou [1], Anna Michopoulou [2], Dimitrios N. Bikiaris [1]

[1] Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
[2] Biohellenika Biotechnology Company, Leoforos Georgikis Scholis 65, 555 35, Thessaloniki, Greece

Skin is the largest organ of the body, critical to the survival of the organism through acting as a barrier to the external environment. As a result, skin injuries require effective treatment to prevent morbidity or mortality. Over the past years, significant progress has been made in growth and tissue regeneration. 3D printing technique has shown great potential assisting and promoting the wound healing process. In this context, the 3D printed structures present pre-determined pore sizes which aid material exchange, cell attachment and migration, and thus, allow better tissue regeneration after injury. The current research reports on 3D-printed films comprising chitosan (CS), gelatin (Gel) and collagen (Col) as potential bioadhesive dressings for wound healing purposes. The successful synthesis of hydrogels was confirmed by FTIR spectroscopy, their crystallinity was analyzed by XRD, whereas water swelling and stability capacity were also investigated. This work was based on the production of hydrogels with different ratios of CS, Gel and Col. The printability of hydrogels was studied, changing the parameters of 3D printer (needle size, pressure and temperature). The material which presented the optimal printability was used to fabricate dressings with different porosity. The 3D printed porous patches were cross-linked with the aid of ammonia gas, NaOH/EtOH and KOH solutions.

Acknowledgement

The author wishes to acknowledge co-funding of this research by European Union-European Regional Development Fund and Greek Ministry of Education, Research and Religions/EYDE-ETAK through program EPANEK 2014-2020/Action “EREVNO-DIMIOURGO-KAINOTOMO” (project T1EΔK-03798).

eP81

LIGHT- AND ACID-INDUCED MAIN-CHAIN SCISSION OF A POLYACYLHYDRAZONE-DOXORUBICIN PRODRUG

Maria Psarrou,[1] Martha Georgia Kothri[2] and Maria Vamvakaki[1,3]

[1]Department of Materials Science and Technology, University of Crete, Vasilika Vouton 700 13 Heraklion, Crete, Greece
[2]Department of Medicine, University of Crete, Vasilika Vouton 700 13 Heraklion, Crete, Greece
[3]Institute of Electronic Structure and Laser, Foundation of Research and Technology-Hellas, Vasilika Vouton 700 13 Heraklion, Crete, Greece

Stimuli-degradable polymers have attracted significant scientific attention for use in various applications in the fields of nano- and bio-technology.[1] Among other stimuli, light in particular, offers unique advantages including its spatiotemporal control and the tunability of the irradiation wavelength and dose. As a result, photo-degradable polymers have been proposed for the development of nanocarriers for drug delivery, as photoresists for 2D and 3D patterning, as recyclable plastics, and others.[2] In this work, a new family of main-chain, photo-scissionable polymers based on hydrophilic polyacylhydrazones is reported.[3] The step-growth copolymerization of adipic acid (AA) dihydrazide with dibenzaldehyde terminated poly(ethylene glycol), under mild acidic conditions, was employed to afford hydrophilic P(EG-*alt*-AA) alternating copolymers. The main-chain photo-degradation of the copolymers upon light irradiation at $\lambda = 254$ nm and at a very low power density of 0.1 mW/cm^2 was studied by size excluzion chromatography and proton nuclear magnetic resonance and UV-visible spectroscopies. Next, the hydrophobic anticancer drug, doxorubicin (DOX), was linked to the hydrazide end-groups of the polymer via acylhydrazone linkages, to produce an amphiphilic P(EG-*alt*-AA)-DOX prodrug. The polymer-drug conjugate self-assembled in aqueous media to form spherical nanoparticles evidenced by scanning and trasmission electron microscopies. Irradiation of the self-assembled nanostructure solution resulted in the photolysis of the acylhydrazone bonds along the polymer chains, causing the disruption of the nanoparticles and the release of the DOX molecules. The synergistic effect of acidic pH and light irradiation on the disruption of the self-assembled prodrug nanostructures, due to the combined photo- and acido-lysis of the acylhydrazone bonds, was also investigated.

References

1 X. Hu, Y. Zhang, Z. Xie, X. Jing, A. Bellotti and Z. Gu, *Biomacromolecules*, 2017, **18**, 649–673.

2 C. Zhu, C. Ninh and C. J. Bettinger, *Biomacromolecules*, 2014, **15**, 3474.

3 M. Psarrou, M. G. Kothri and M. Vamvakaki, *Polymers*, 2021, **13**, 2461.

Acknowledgments

This project has received funding from the European Union’s Horizon 2020 research and innovation programme H2020-FETOPEN-1-2016-2017 under grant agreement No 737071 (ULTRACHIRAL).

eP82

3D-PRINTED ANTI-INFLAMMATORY & ANTIBACTERIAL PATCHES FOR CHRONIC WOUND HEALING

**Alexandra Zamboulis[1], Ioanna Koumentakou[1], Zoe Terzopoulou[1],
Anna Michopoulou[2], Dimitrios N. Bikiaris[1]**

[1] Laboratory of Polymer Chemistry and Technology, Chemistry Department, Aristotle University of Thessaloniki, Thessaloniki, Greece
[2] Biohellenika Biotechnology Company

A wound is a disruption of the continuous structure of skin, caused by trauma or burn, or as a result of a medical condition. Skin provides protection against external harmful agents and plays a pivotal role in the maintenance of the body homeostasis. Wound healing is a complex process including various factors and the role of a wound dressing is to create a favorable environment to support healing, with an aesthetically satisfactory result. When the normal process of healing is interrupted, chronic wounds may occur. Open wounds present a high risk for fluid loss, inflammation, bacterial colonization, and infection that can lead to sepsis. As a result, the control of inflammation and cell regeneration are crucial for effective healing.

In the present study, hydrogels based on chitosan (CS), gelatin (Gel) and poly(vinyl alcohol) (PVA) were developed and scaffolds were 3D-printed for wound dressing applications. 3D printing allows the preparation of scaffolds with well-defined architectures and tailored properties (size, shape, microstructure, etc.), opening new possibilities for personalized medical treatment. CS is a non-toxic, biocompatible and biodegradable polymer, exhibiting intrinsic antimicrobial properties. Gel was selected to improve the printability of CS and the tissue repair capacity of dressing due to its cell adhesion, migration, and proliferation ability. The hydrogel was reinforced with PVA to improve the mechanical properties of the dressings. Herein, the preparation of CS, Gel and PVA scaffolds by pneumatic extrusion 3D printing will be discussed. Post-printing physical crosslinking with ammonia vapors, NaOH/EtOH and KOH solutions were tested to further stabilize the produced scaffolds. The physicochemical properties of the prepared 3D-printed scaffolds were examined with FTIR and XRD. The water swelling ratio and stability were also assessed.

Acknowledgement: The authors wish to acknowledge co-funding of this research by the European Union-European Regional Development Fund and the Greek Ministry of Education, Research and Religions/EYDE-ETAK through program EPANEK 2014-2020/Action “EREVNO-DIMIOURGO-KAINOTOMO” (project T1EΔK-03798).

ePS83

USING XANTHAN-BASED POLYSACCHARIDE/PROTEIN NANOPARTICLES TO ENCAPSULATE AND PRESERVE CURCUMIN

Aristeidis Papagiannopoulos[1], Aggeliki Sklapani[2]

[1] Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece
[2] Physics Department, National Technical University of Athens, Athens, Greece

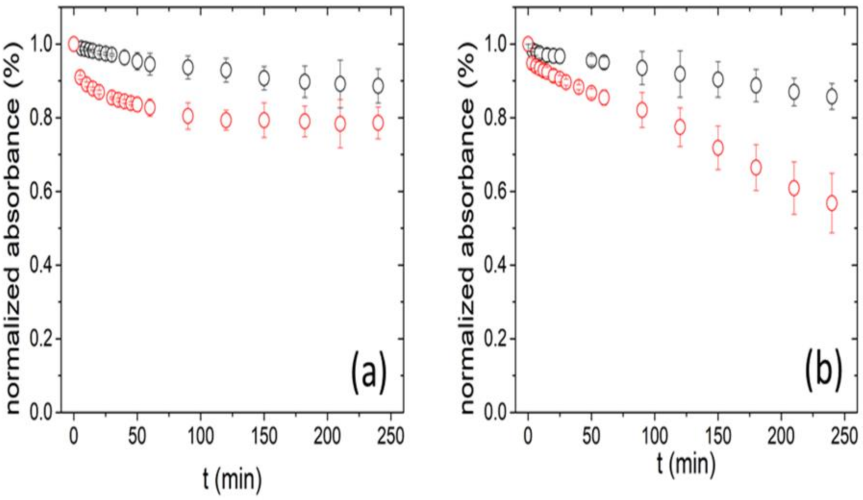
Introduction: Nanoparticles (NPs) that are based on proteins are attractive as nanocarriers of nutrients and drugs owing to their biodegradability, biocompatibility, metabolizability and nontoxicity. Curcumin (CUR) is a beneficial nutraceutical however it has extremely low solubility in water and poor bioavailability. Xanthan gum (XG) is a high molar mass anionic polysaccharide which is customarily used in food and pharmaceutical industry, nevertheless has not yet tested in polysaccharide-protein NPs for bioactive substances' delivery. Bovine serum albumin (BSA) has been already applied in NPs to encapsulate hydrophobic compounds.

Methods: We apply our recently established protocols of electrostatic polysaccharide-protein complexation and thermal treatment to prepare XG-BSA NPs that are resistant to disintegration upon pH changes. The NPs are studied by light scattering, the protein conformation by ATR-FTIR spectroscopy and the structure of CUR by UV-Vis spectroscopy.

Results: The NPs have well defined hydrodynamic radii distribution (50-200 nm) and inherit the surface hydrophobicity and the pH-tunable surface charge of BSA. They are able to encapsulate curcumin and preserve its conjugated diene structure against degradation at neutral pH (Figure 1).

Conclusions: This investigation motivates the use of XG for the preparation of protein nanocarriers of bioactive substances.

Figure 1: Curcumin's absorbance at 425 nm (UV-Vis) free in solution (red) or encapsulated in XG-BSA NPs (black) at pH 5 (a) and pH 7 (b).


normalized absorbance (%)
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
t (min)
(a)
normalized absorbance (%)
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
t (min)
(b)

ePP84

DETERMINATION OF PROTEIN STRUCTURE AND DYNAMICS BY COMBINING MOLECULAR SIMULATIONS WITH EXPERIMENTAL DATA

Faidon Brotzakis, **Peter G. Bolhuis**[2], **Michele Vendruscolo**[1]

[1]Chemistry Department, University of Cambridge, Cambridge, UK
[2]HIMS, University of Amsterdam, Amsterdam, Netherlands

Molecular simulations have been instrumental in identifying the structure-function relationships of biomolecules in the atomic level as well as providing a means for structure based drug discovery, thereby explaining and guiding experimental findings. The increase in computational power, the new physics and machine-learning-based algorithms is significantly driving the boost in the field and gives access to addressing biomolecular phenomena of increasing length and timescales. However, molecular simulations are delimited by the accuracy of the sampling and of the molecular mechanics forcefield they use.

In this talk I will discuss two examples where we simultaneously address the sampling problem in terms of enhanced sampling methods and the forcefield problem, by injecting experimental data into the simulation. This enables as to accurately model protein dynamics and reveal key mechanistic components such as transient states often eluding experimental resolution, that are further used to guide experiments. A) Devise a maximum entropy based method that incorporates rate constants experimental data into molecular simulations in order to accurately determine protein folding transition state configurations[1]. B) Incorporate experimental Cryo-EM data to enhanced-sampling-based molecular simulations as restraints, in order to accurately capture the free energy landscape that reveals potentially druggable cryptic binding sites in a SARS-CoV-2 spike protein [2].C) Devise a forcefield optimization algorithm that targets experimental kinetics and ameliorates stable and transition state configurations.

[1]Z. F. Brotzakis, M. Vendruscolo, and P. G. Bolhuis, Proceedings of the National Academy of Sciences 118, e2012423118 (2021).
[2] F. Brotzakis, T. Lohr, and M. Vendruscolo, ChemRxiv,(2020), 10.26434/chemrxiv.13222073.v1.
[3] F. Brotzakis, M. Vendruscolo and P. G. Bolhuis (in prep) 2021

ePS5

THERMO-MECHANICAL PROPERTIES OF PLA CONTAINING INORGANIC FILLERS

Olga Thoda, George Vekinis

Institute of Nanoscience and Nanotechnology, National Center for Scientific Research
“Demokritos”, Athens, Greece

PLA is a thermoplastic, aliphatic, semi-crystalline polyester with excellent strength and modulus, but with unfortunately low impact strength and low heat deflection temperature. In this work four types of powder fillers were studied: blast furnace slag waste, spinel $MgAl_2O_4$ nanopowder produced by Solution Combustion Synthesis (SCS), cellulose and glass bubbles, aiming at reduce density and environmental benefits. The experimental results of the derived composites with the 4 tested powders are presented. In the series of blast furnace slag waste experiments four different PLA composites were synthesized by changing the filler's concentration in the PLA matrix (5, 10, 15, 20wt%). In the case of the spinel-based composites, the as-produced spinel was added to the PLA matrix in four concentrations (2, 3, 4, 6%) in order to produce 4 different composites. When cellulose was employed as filler, 1, 2, and 3% of the filler was added to produce 3 different composites, while in the case of glass bubbles the applied concentration was 0.5, 1, and 2%. The as-synthesized samples were tested in heat deflection temperature tests, creep resistance tests, 3-point flexural tests, SEM/EDX analysis, X-Ray diffraction analysis and Hertzian compression tests. Despite the fact that the slag waste was easily incorporated in the PLA matrix, the as-synthesized composites characteristics were not satisfactory. The effect of the spinel addition is the stiffening of the composite, at least if filler wetting and dispersion are efficiently accomplished. In the cases of glass bubbles and spinel as fillers in small concentrations (1% and 2% respectively), the heat deflection temperature was improved from 55°C to 60°C. Taking all the results into consideration, the addition of small concentrations (2-3%) of $MgAl_2O_4$ spinel as filler gives decreased strength but provides substantial benefits in terms of toughening and creep resistance.

eP86

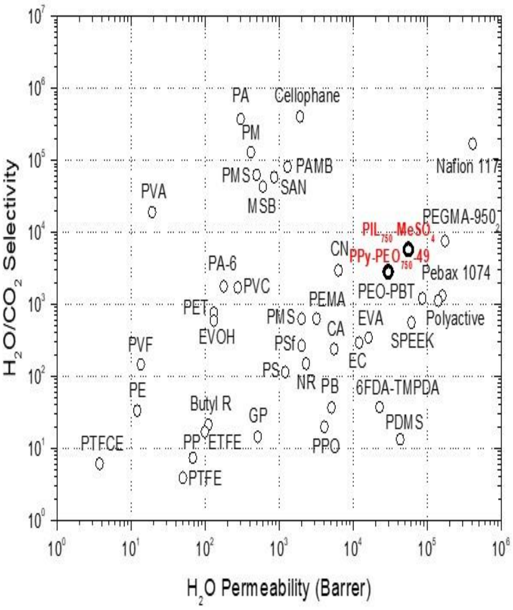
DEVELOPMENT OF POLY(ETHYLENE OXIDE) BASED COPOLYMER MEMBRANES FOR EFFICIENT GAS/VAPOR SEPARATION

Alkistis Ioannidi[1], Dionysios Vroulias[2], Joannis Kallitsis[1], Theophilos Ioannides[2]
Valadoula Deimede[1]

[1] Chemistry Department, University of Patras, Patras, Greece
[2] Institute of Chemical Engineering Sciences (FORTH/ICE-HT), Foundation for Research and Technology-Hellas

Poly(ethylene oxide) (PEO)-based membranes have raised attention to CO_2-related gas separations due to their high CO_2 selectivity. Nevertheless, the fabrication of such membranes is quite challenging as PEO suffers from poor film forming ability and high crystallization tendency, which restricts gas transport. In this work, a new series of aromatic polyethers bearing flexible PEO side chains and their corresponding ionic analogues PILs were prepared to be evaluated as CO_2 and water selective membranes. The presence of PEO groups supports both high CO_2 solubility and high water permeability stemming from their hydrophilic nature. The prepared membranes were mechanically and thermally robust, completely amorphous even for high PEO contents and formed flexible membranes. The effect of PEO content as well as the effect of the counteranion of the prepared PILs on the gas (CO_2, CH_4, H_2, N_2) and water vapor separation performance was studied in details (Figure 1).

Acknowledgements: This work was supported by: (i) the project “Bioconversion of lignite power plant emissions to fuels and fine chemicals (BIOMEK)” (project code T1EDK-00279) which is implemented under the “EPAnEK 2014-2020 Operational Programme”, funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).




Precursor PEO_{750}


PIL_{750}-$MeSO_4$

ePP87

DESIGN OF MICROCAPSULES AS POTENTIAL SELF-HEALING ADDITIVES FOR WATER BASED POLYURETHANES

Efterpi Avdeliodi[1], Amaia Soto Beobide[1],[2], George A. Voyiatzis[1],[2], Athena Fidelli[3], Poppy Krassa[3], Georgios Bokias[1], Joannis K. Kallitsis[1]

[1] Department of Chemistry, University of Patras, GR-26504, Patras, Greece
[2] FORTH/ICE-HT, Stadiou Street, P.O. Box 1414, GR-26504, Rio-Patras, Greece
[3] Megara Resins Anastassios Fanis S.A., Vathi Avlidas, GR-34100 Evia, Greece

Self-healing coatings have attracted a great research interest during the last decade.[1] In many cases, the self-healing of the matrix is achieved through the dispersion of adequately designed microcapsules, containing an active self-healing substance in the core.[2, 3] In this work, a new type of polyurethane-based microcapsules were synthesized, which are consisted of a composite shell and a liquid core containing isophorone diisocyanate (IPDI) as the self–healing substance. The microcapsules were synthesized via interfacial polymerization in an oil-in-water emulsion, where the organic phase contains IPDI and a second more active isocyanate monomer, while the aqueous phase consists a diamine compound. The active isocyanate mixture reacts with the diamine compound at the interphase to form the polyurethane shell, while IPDI is encapsulated in the microcapsule core. It is found that the size and shape of the microcapsules is controlled by the reaction conditions and the reactants ratio. The microcapsules were characterized with different techniques and subsequently were incorporated into polyurethane coatings, in order to evaluate potential self-healing abilities.

References

[1] Song, M.-M. et al. (2019) Soft Matter, 15, 6615-6625
[2] Attaei, M. et al. (2018) Polymers, 10(8), 825-835
[3] Ma, Y. et al. (2019) Advanced Powder Technology, 30(10), 1995-2002

Acknowledgements: This research has been cofinanced by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code:T2EΔK-00307 “Synthesis of waterborne polyurethane dispersions with encapsulation of micro/nano structures for ecological self-healing coatings”)

European Union
European Regional
Development Fund

HELLENIC REPUBLIC
MINISTRY OF
DEVELOPMENT AND INVESTMENTS
SPECIAL SECRETARIAT FOR
ERDF & CF PROGRAMMES
MANAGING AUTHORITY OF EPAnEK

EPAnEK 2014-2020
OPERATIONAL PROGRAMME
COMPETITIVENESS
ENTREPRENEURSHIP
INNOVATION

ΕΣΠΑ
2014-2020
ανάπτυξη - εργασία - αλληλεγγύη
Partnership Agreement
2014 - 2020

Co-financed by Greece and the European Union

eP88

THE EFFECT OF FILLER LOADING ON THE THERMAL PROPERTIES OF GRAPHITE-REINFORCED SILANE CROSSLINKED HIGH-DENSITY POLYETHYLENE

Maria Lazaridou[1], Dimitra Kourtidou[2], Dimitrios N. Bikiaris[1],
Konstantinos Chrissafis[2]

[1] School of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece
[2] School of Physics, Aristotle University of Thessaloniki, Thessaloniki, Greece

During the last decades, there has been a growing interest in polymer composites due to the significantly enhanced mechanical and thermal properties of such polymers caused by incorporating a small amount of a reinforcing filler. For this reason, carbon-based materials of different shapes in nano and micro scale have been proposed as multifunctional fillers to enhance the polymer matrices since they are characterized by outstanding mechanical performance, thermal and electrical conductivity. Crosslinked high-density polyethylene (PEX) composites with spherical graphite (SG) as a reinforcing filler are examined in the present study regarding their thermal properties. The neat PEX and its corresponding composites with various SG contents (0.5-5 wt.%) were prepared using the melt-compounding technique. Crosslinking was succeeded by immersing the prepared materials in a hot bath of 90°C temperature for 24 hours. The melting and crystallization behavior of neat PEX and PEX/SG composites was evaluated using the Differential Scanning Calorimetry technique (DSC). Additionally, the thermal stability of the prepared materials was studied by Thermogravimetric Analysis (TGA). Thermal diffusivity measurements were performed using Laser Flash Analysis (LFA) to calculate the thermal conductivity of the samples. Various models used to predict the thermal conductivity of composites materials were applied to the experimental data. Thermal conductivity measurements showed a significant improvement in the case of the PEX composites with increasing filler content (40.6% augmentation for 5 wt% SG), while the experimental data presented a good agreement with the Chauhan theoretical model for spherical particles.

ePP89

SYNTHESIS OF GLYCIDYL METHACRYLATE-BASED AMPHIPHILIC COPOLYMERS AND THEIR ORGANIZATION PROPERTIES IN AQUEOUS MEDIA

Ioanna Tzoumani[1], Zacharoula Iatridi[1], Amaia Soto Beobide[1,2], George A. Voyiatzis[2], Georgios Bokias[1], Joannis K. Kallitsis[1]

[1] Department of Chemistry, University of Patras, GR-26504, Patras, Greece
[2] FORTH/ICE-HT, Stadiou Street, P.O. Box 1414, GR-26504, Rio-Patras, Greece

Copolymerization of glycidyl methacrylate (GMA) with hydrophilic comonomers is an interesting route to prepare water-based functional materials[1]. Such copolymers have already been used for the modification of collagen derivatives, resulting in biofertilizers with controlled release[2].

In this work, a series of random GMA-based copolymers with a poly(ethylene glycol) methyl ether methacrylate (PEGMEMA) macromonomer or with a variety of monomers, including the anionic sodium styrene sulfonate (SSNa), the nonionic sparingly water-soluble 2-hydroxyethyl methacrylate (HEMA), as well as the hydrophobic monomers methyl methacrylate (MMA) and butyl acrylate (BA) were synthesized. Such polymeric structures combine the functionality of GMA with additional properties, like the at will control of hydrophilicity/hydrophobicity, responsiveness or Tg. The copolymers were characterized with ^{1}H NMR, GPC, ATR-FTIR, etc. Furthermore, the organization properties of the copolymers were explored in aqueous solution.

Such functional copolymers have been used as antifouling coatings[3] or as self-healing reagents[4], topics where the synthesized copolymers are also currently tested.

References

[1] Lainioti, G. Ch., et al., *Polymers*, **2016**, *8*, 190.
[2] Tzoumani, I., et al., *Materials*, **2019**, *12*, 4067.
[3] Druvari, D., et al., *ACS Appl. Mater. Interfaces*, **2016**, *8*, 35593.
[4] Davydovich, D., et al., *Nat. Commun.*, **2020**, *11*, 5743.

Acknowledgements: This research has been co?financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code:T2EΔK-00307 “Synthesis of waterborne polyurethane dispersions with encapsulation of micro/nano structures for ecological self-healing coatings”).

European Union
European Regional
Development Fund

HELLENIC REPUBLIC
MINISTRY OF
DEVELOPMENT AND INVESTMENTS
SPECIAL SECRETARIAT FOR
ERDF & CF PROGRAMMES
MANAGING AUTHORITY OF EPAnEK

EPAnEK 2014-2020
OPERATIONAL PROGRAMME
COMPETITIVENESS
ENTREPRENEURSHIP
INNOVATION

ΕΣΠΑ
2014-2020
ανάπτυξη - εργασία - αλληλεγγύη
Partnership Agreement
2014 - 2020

Co-financed by Greece and the European Union

eP90

BIOCIDAL WATER-BASED POLYMERIC COATINGS FOR AIR-CLEANING FILTERS

Denisa Druvari[1,3], Ioanna Tzoumani[1,2], Alexios Vlamis-Gardikas[1,2],
Georgios Bokias[1],[2], Iliana Tselenti[3], Joannis K. Kallitsis[1],[2]

[1] Department of Chemistry, University of Patras, GR-26504, Patras, Greece
[2] Department of Chemistry, University of Patras, GR-26504, Patras, Greece &
FORTH/ICE-HT, Stadiou Street, P.O. Box 1414, GR-26504, Rio-Patras, Greece
[3] Metricon SA, Athinon 65, Ag. Georgios, Rio GR-26504, tel. +30 261 099 3002,
info@metricon.gr

Global concern currently focuses on infectious diseases caused by airborne bacteria and viruses, since they can lead to serious effects on human health. Several technologies have been developed for air purification, such as air filtration, ultraviolet (UV)-C light or plasma air ionization. Filtration is the most interesting technology for removal of airborne particles since it offers a simple operation, low energy requirement, and low operating and investment cost. However, the airborne microorganisms may accumulate on air filters, which can become a secondary polluting source. Therefore, antimicrobial air filters are urgently required. This work demonstrates a facile and scalable fabrication approach for the development of new water-based, stable materials bearing biocidal groups, as potential antimicrobial coatings for air-cleaning filters[1]. The antimicrobial filters were successfully prepared through spray-coating of aqueous solutions based on biocidal copolymers. Taking advantage of our previous knowledge[2], two series of copolymers poly (4-vinyl benzyl trimethylammonium chloride-co-acrylic acid) P(VBCTMAM-co-AAx) and poly (cetyltrimethylammonium 4-styrenesulfonate-co-glycidyl methacrylate) P(SSAmC$_{16}$-co-GMAx) were combined in order to obtain polymeric materials that bear both covalently- and electrostatically-bound biocidal species. A thorough investigation was made to develop a novel green methodology for the synthesis of the copolymers P(VBCTMAM-co-AAx) and P(SSAmC$_{16}$-co-GMAx) under aqueous conditions[3]. The water-soluble copolymers also bear complementary reactive groups, such as AA and GMA which can lead to crosslinking reaction and therefore to stable coatings, with long-lasting activity for the air-filters. All these polymers presented strong antimicrobial activity (>99,9%) against *Staphylococcus aureus* and *Escherichia coli* in standard bacterial media.

References

[1] I. Tselenti, N. Bougioukos, D. Druvari, I. Tzoumani. Biocidal air-cleaning filters coated with organic biocidal materials. Greek patent application, Feb. 2021.
[2] D. Druvari et al. *ACS Applied Materials & Interfaces*, **2016**, *8*, 35593–35605.
[3] A. Tsagdi et al. *Molecules*, **2020**, *25*, 1678.

Acknowledgements

This research has been funded by the company Metricon SA.

eP91

FORMATION OF MICELLEPLEXES BETWEEN CATIONIC BLOCK COPOLYMER MICELLES AND DNA

Varvara Chrysostomou[1], Aleksander Forys[2], Barbara Trzebicka[2], Costas Demetzos[3], Stergios Pispas[1]

[1] Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece
[2] Centre of Polymer and Carbon Materials, Polish Academy of Sciences, Zabrze, Poland
[3] Pharmacy Department, Section of Pharmaceutical Technology, Department of Pharmacy, School of Health Sciences, National and Kapodistrian University of Athens, Greece

The delivery of nucleic acids to target cells for the treatment of several diseases, including inherited disorders, viral infections and cancer, at a genetic level is defined as gene therapy and it is being considered as a revolution in molecular medicine. A successful gene delivery strategy requires the design of effective gene transfer vectors that are able to target a specific tissue, protect nucleic acids from serum degradation, present high transfection efficiency and regulate gene expression without any immunogenic response. Gene delivery carriers can be divided into viral and non-viral vectors. Viral vectors present high transduction efficiency and specificity, but they are associated with several dangerous immunogenicity issues. Hence, research has been focused on the development and improvement of non-viral vectors. In this regard, amphiphilic block copolymers comprised of a cationic polyelectrolyte block have gained stupendous interest for their potential as non-viral vectors. They can electrostatically interact with nucleic acids, forming nanosized micelleplexes. In our previous work, we reported the synthesis and self-assembly behavior of the quaternized poly(2-(dimethyl amino ethyl methacrylate)-*b*-poly(lauryl methacrylate) (QPDMAEMA-*b*-PLMA) amphiphilic polyelectrolyte copolymers. Herein, we aim to investigate the ability of these copolymers to interact with linear DNA of different molar masses by forming stable micelleplexes, for their potent application as non-viral vectors for nucleic acids delivery. Micelleplexes were formed at various N/P ratios, through the electrostatic interaction of the positive charged nitrogen (N) of QPDMAEMA quaternary amino group with the negatively phosphate (P) groups of DNA. The successful complexation of QPDMAEMA-*b*-PLMA with DNAs and the formation of stable micelleplexes at various N/P ratios were confirmed by implementing several techniques for physicochemical and morphological characterization, including Light Scattering, UV/Vis, Fluorescence Spectroscopy and Cryo-TEM.

(Acknowledgements: The research work was supported by the Hellenic Foundation for Research and Innovation (HFRI) under the HFRI PhD Fellowship grant (Fellowship Number: 907).)

eP92

SYNTHESIS, SELF-ORGANIZATION AND EMULSIFYING / FOAMING CAPABILITY OF 2-ACRYLAMIDO-2-METHYL-1-PROPANESULFONIC ACID (AMPSA)-BASED AMPHIPHILIC COPOLYMERS

Zacharoula Iatridi[1,2], Christina Ntente[1,2], Maria Theodoropoulou[2],
Georgios Bokias[1,2], Christos Tsakiroglou[2]

[1] Department of Chemistry, University of Patras, GR-26504, Patras, Greece
[2] FORTH/ICE-HT, Stadiou Street, P.O. Box 1414, GR-26504, Rio-Patras, Greece

Amphiphilic water-soluble polymers are a class of polymers that have attracted great scientific interest during the last decades. Their ability to self-organize into various structures in solution allows them to be used as nanocarriers, emulsifiers or rheology modifiers, and can find application in several fields like nanomedicine, sensing, etc [1,2].

In the present work, amphiphilic polyelectrolytes of the hydrophilic, anionic unit 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA), with hydrophobic units bearing alkyl groups such as dodecyl chains, were synthesized through free radical polymerization (FRP). In addition, the synthesis of polymer-coated nanoparticles (PNPs) was attempted through post-grafting or FRP on inorganic nanoparticles. The above materials were characterized by techniques like ^{1}H NMR, acid-base titration, TGA analysis and ATR-FTIR. Moreover, their self-organization behavior was explored in aqueous media. Their capability to be used as emulsifying and foaming agents for the stabilization of Pickering oil-in-water emulsions and nitrogen-in-water foams was investigated through macroscopic inspection and microscopic analysis of oil drops and gas bubbles, measurements of dynamic and static interfacial and surface tensions with pendant drop and Du Nouy Ring method, respectively. Changes caused on the wettability of the water/oil/solid surface were monitored by measuring the contact angle. Such systems could be promising candidates for enhanced oil recovery processes [3,4].

References

[1] Palao-Suay, R., et al. *Prog. Polym. Sci.*, **2016**, *53*, 207.
[2] Wang, F., et al. *Mater. Chem. Front.*, **2019**, *3*, 356.
[3] ShamsiJazeyi, H., et al. *J. Appl. Polym. Sci.*, **2014**, *131*, *15*, 40576.
[4] Corredor, L. M., et al. *Adv. Colloid Interface Sci.*, **2019**, *272*, 102018.

Acknowledgements: The research project was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the “1st Call for H.F.R.I. Research Projects to support Faculty members and Researchers and the procurement of high-cost research equipment” (Project Number: HFRI-FM17-361, acronym: EOR-PNP).

eP93

EVALUATION OF SHELF LIFE OF LOW DENSITY POLYETHYLENE (LDPE) FILMS WITH ENCAPSULATED ANTIMICROBIAL SUBSTANCES FOR APPLICATION IN MEDICAL WASTE MANAGEMENT

Marina Stramarkou[1], Sofia Papadaki[1], Ioanna Thanassoulia [2], Magdalini Krokida[1]

[1] School of Chemical Engineering, National Technical University of Athens, Athens, Greece
[2] Achaika Plastics S.A

Introduction: In recent years, there is an increasing demand for better management of waste from healthcare activity with high microbial load, potentially hazardous to human health, since it can create an extensive outbreak of infection.

Methods: In this perspective, the development of innovative bags with antimicrobial action to collect medical waste and litter in order to neutralize the contained microbes and make the waste safer for public health was performed in our study. Specifically, Oregano Essential Oil (OEO) and organic extract of citrus bioflavonoids (Flavomix) with antimicrobial activity were encapsulated in low density polyethylene (LDPE) through extrusion. The aim of the present study is the evaluation of the shelf life of the produced films, as well as, the examination of the controlled release of the encapsulated compounds. In this context, the films were stored under controlled conditions of temperature- radiation (20°C-darkness and 45°C-light) and humidity (relative humidity-RH 35, 70 and 95%) for 60 days, in order to determine the effect of storage parameters in the release of the encapsulated antimicrobial agents over time.

Results: The 60-days analysis exhibited that elevated temperature (45°C) and humidity (95% RH) values led to reduced encapsulation efficiency, reaching 84% in the case of Flavomix, whereas in moderate temperature (20 °C) the shelf life of the films is prolonged.

Conclusions: Finally, the produced films have the potential to be applied in medical waste and the gradual release of the antimicrobial agents will ensure the elimination of contained microbes.

Acknowledgements: The work was co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH– CREATE – INNOVATE (project code T2EΔK-04762).

eP94

CONTROL OF WETTING AND FRICTION PROPERTIES ON FLUORINATED ETHYLENE PROPYLENE SURFACES USING PLASMA MICRO-NANOTEXTURING

Kosmas Ellinas, Evangelos Gogolides

Institute of Nanoscience and Nanotechnology (Inn), NCSR Demokritos, Athens, Greece

Fluoro-containing polymers have attracted a lot of interest due to their hydrophobic nature, which enables a number of functionalities (i.e. low friction, self-cleaning, etc.). Fluorinated ethylene propylene (FEP) is a copolymer of hexafluoropropylene and tetrafluoroethylene, in contrast to polytetrafluoroethylene (PTFE) it is melt-processable using injection molding and it is highly transparent and resistant to sunlight. In this work, we transform fluorinated ethylene propylene **(**FEP) surfaces to superhydrophobic using two different plasma reactors (Inductively coupled reactor and reactive ion etcher) and different etching conditions and we probe their friction properties against water using a tilting stage. In particularly, we demonstrate wetting control of FEP surfaces with water static contact angle ranging from 95^{o} to 156^{o} and hysteresis ranging from 20^{o} down to 1^{o}. Video analysis of drops moving on different FEP surfaces show that water drops face reduced friction when etching time increases so that a hierarchical morphology is created. This is achieved using both plasma reactors, whereas the optimum performance is observed for the 10 min etched surface in a inductively coupled plasma reactor in which friction becomes 0.2 μN.

eP95

LARGE-AREA MEMBRANE DEVELOPMENT OF OPTIMIZED, SCALED-UP AND HIGHLY DOPABLE POLYMER ELECTROLYTES FOR HIGH TEMPERATURE PEM FUEL CELLS

G. Charalampopoulos, Ch. Anastasopoulos, A.K. Andreopoulou, J.K. Kallitsis

1) Chemistry Department, University of Patras, Rio-Patras, GR26504 Patras, Greece

2) Foundation for Research and Technology Hellas/Institute of Chemical Engineering Sciences (FORTH/ICE-HT), Platani Str., Patras, GR26504, Greece

Polymer electrolyte membranes for High Temperature PEM fuel Cells based on acid doped basic polymers have led to increased operation temperature of PEM Fuel Cells even above 180°C resulting thus in simplified systems able to use reformate hydrogen as fuel feed. Our efforts have long concentrated on the development of polymers bearing basic main chain pyridine [1] or quinoline groups[2], to ensure strong interactions with the strong acid proton carrier. Thus, a large number of copolymers has been created of different architectures and chemical composition that afforded highly dopable and robust PEMs which led to extended operation temperatures even above 200°C.[1,2] Recently, monitoring of interactions between the basic groups and phosphoric acid or water molecules has attracted attention as a pathway to design optimized polymer structures.[3] Working in this direction, various difunctional polymerizable monomers are combined under different ratios affording polymer electrolytes of distinct chemical variations. Strong dependencies of their properties and function are realized upon the exact chemical structure of the polymer electrolyte. Main emphasis is given on understanding the mechanism of interaction of impregnated membranes with water and phosphoric acid, as well as the effect of structure on their ability to retain phosphoric acid under diverse conditions. Through this exhaustive study, the factors decisively affecting the doped membranes properties are enlightened aiming to elucidate the key parameters for increased lifetime and efficiency of the HT-PEMFCs.

Acknowledgements: Financed by EPAnEK RESEARCH–CREATE–INNOVATE 2014-2020 through the project «Autonomous cogeneration system from renewable sources "fuel cell / H2O electrolysis / H2 storage"-Solar2Hyp (T2EΔK-01877/MIS 5072495)»

References

1) “Pyridine Containing Aromatic Polyether Membranes” J.K Kallitsis, A.K Andreopoulou, M. Daletou, S. Neophytides, Chapter 5/Part I in “High Temperature Polymer Electrolyte Fuel Cells - Approaches, Status and Perspectives”, Springer International Publishing, **2016.**

2) K. Kallitsis et.al. J. Power Sources **2018**, *379*, 144–154.

3) A.S. Lee et.al. J. Mater. Chem. A. **2019**, 7, 9867–9876.

eP96

FEASIBILITY OF SOLID-STATE POLYMERIZATION AS AN ALTERNATIVE ROUTE TO SYNTHESIZE FOSSIL- AND BIO-BASED VITRIMERS FROM COMMERCIALLY AVAILABLE POLYESTERS

Christos Panagiotopoulos, Athanasios Porfyris, Dimitrios Korres,
Stamatina Vouyiouka

School of Chemical Engineering, National Technical University of Athens, Zographou Campus, 157 80 Athens, Greece

Vitrimers constitute a very new class of smart polymeric materials (cited also as recyclable thermosets) in which topological rearrangement of the dynamic network is thermally stimulated by associative exchange reactions, while keeping the number of the bonds and crosslink density constant. Solid-state polymerization (SSP) was herein studied for the synthesis of fossil- and bio-based vitrimers from commercial engineering polyesters, such as poly(butylene terephthalate) (PBT) and stereocomplex poly(lactic acid) (scPLA), both expected to greatly extend their range of applications as vitrimers. A two-step process was followed; the first step involved alcoholysis reactions and the incorporation of glycerol in the polymer chains. The second step comprised transesterification reactions in the solid state in the presence of zinc(II) catalyst, resulting in the formation of a dynamic crosslinked network with glycerol moieties serving as the crosslinkers. The appropriate SSP conditions were found to be 3 h at 180 ^{o}C (in the case of PBT) and 160 ^{o}C (in the case of scPLA) under N_2 flow (0.5 L/min) to reach high vitrimer insolubility and melt strength (especially in the case of PBT), while increasing the glycerol concentration improved further their properties. Glass transition temperature (T_g) was almost tripled in PBT-based vitrimers compared to initial thermoplastic, whereas the melting point (T_m) was slightly decreased for both polyesters, due to the loss of symmetry perfection under the influence of the crosslinks.

This work was made possible by the "Basic Research Programme, NTUA, PEVE 2020 NTUA" [PEVE0050] of the National Technical University of Athens and is gratefully acknowledged.

eP97

POLY(E-CAPROLACTONE)-CO-POLY(2-HYDROXYETHYL METHACRYLATE) FOR THE REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTIONS

Vasiliki Iliadou[1], Pavlos Efthymiopoulos[1], Alexandra Zamboulis[2], Nikolaos Bikiaris[2], Georgios Maliaris[1], George Kyzas[1]

[1]Department of Chemistry, International Hellenic University, Kavala 65404, Greece
[2]Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece

Water contamination with organic pollutants through various anthropogenic activities poses a serious threat to public health and the environment. Synthetic dyes, for example, are persistent and bioaccumulative substances which not only cause the aesthetic degradation of water bodies but can also have diverse effects on all forms of life. Therefore, the efficient removal of such noxious compounds from industrial and domestic wastewater effluents is a crucial issue. Among the available methods for this purpose, adsorption is probably the most promising due to its high efficiency, inexpensiveness, operation simplicity and large-scale applicability. Polymeric adsorbents have recently attracted great attention as promising wastewater decolorization agents. Their major advantage over traditional adsorbents is the ease of their functionalization with various groups. Thus, the utilization of tailor-made polymeric adsorbents towards targeted dyes is possible. In this study, we employed poly(ε-caprolactone)-co-poly(2-hydroxyethyl methacrylate) (PCL-co-PHEMA) (Figure 1) as a novel copolymer adsorbent for the removal of the water-soluble cationic dye Methylene blue (MB) from its aqueous solutions. The effect of solution pH, contact time and initial dye concentration on the adsorption of MB were investigated by batch experiments. The final concentration of MB was determined by spectrophotometry at a wavelength of 663nm. The optimum pH of adsorption was found to be alkaline.

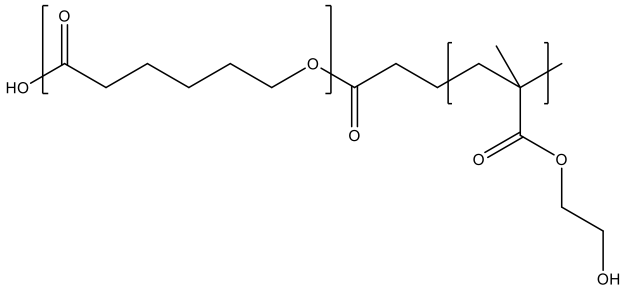


Figure 1. Chemical structure of Poly(ε-caprolactone)-*co*-poly(2-hydroxyethyl methacrylate)

Acknowledgements: This research was funded by the Greek Ministry of Development and Investments (General Secretariat for Research and Technology) through the research project “Research-Create-Innovate”, with the topic “Development of an integration methodology for the treatment of micropollutants in wastewaters and leachates coupling adsorption, advanced oxidation processes and membrane technology” (Grant no: T2EDK-04066).

ePt98

DEVELOPMENT, ELECTRICAL AND MECHANICAL CHARACTERIZATION OF BORON CARBIDE/EPOXY RESIN NANOCOMPOSITES

Theodore G. Velmachos, **Georgios C. Psarras**

Smart Materials & Nanodielectrics Laboratory, Department of Materials Science,
School of Natural Sciences, University Of Patras, Patras 26504, Greece

Nanodielectric composite materials with polymer matrices combine the high dielectric constant of filler nanoparticles with the high dielectric strength of polymers, thus resulting in technologically advanced materials [1,2].

In this study, a set of specimens were manufactured, using commercially available materials, varying the filler's (boron carbide) concentration. Samples were characterized using Broadband Dielectric Spectroscopy (0.1 Hz–1 MHz and 30^{o}C–200^{o}C range) and Dynamic Mechanical Analysis (1 Hz and 30^{o}C–140^{o}C range).

Higher filler content results in higher permittivity values as evident in studied plots. In addition, three distinct relaxation mechanisms have been identified and the energy storage capabilities of the nanocomposites has also been examined. Storage modulus increases with boron carbide concentration, as shown by the DMA analysis.

In conclusion, epoxy resin/boron carbide nanocomposites were successfully manufactured and tested via BDS and DMA techniques. Information about the specimens' properties were extracted, and three relaxation mechanisms were identified and studied.

[1] M. F. Fréchette, M. L. Trudeau, H. D. Alamdari, S. Boily, "Introductory remarks on nanodielectrics," IEEE Trans. Dielectr. Electr. Insul., 11(5), 808–818, 2004.

[2] G. C. Psarras, "Nanodielectrics: An emerging sector of polymer nanocomposites," Express Polym. Lett., 2(7), 460, 2008.

This research is co-financed by Greece and the European Union (European Social Fund-ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project "Strengthening Human Resources Research Potential via Doctorate Research" (MIS-5000432), implemented by the State Scholarships Foundation (IKY)

Ευρωπαϊκή Ένωση
European Social Fund

Operational Programme
Human Resources Development,
Education and Lifelong Learning

Co-financed by Greece and the European Union

ΕΣΠΑ
2014-2020
ανάπτυξη - εργασία - αλληλεγγύη

eP99

COATING POROUS PVDF-HFP MEMBRANES WITH SUPERHYDROPHOBIC NANOPARTICLES IMPROVES MEMBRANE DISTILLATION PERFORMANCE

Ioannis Tournis, Dimitris Tsiourvas, Zili Sideratou, Andreas Sapalidis

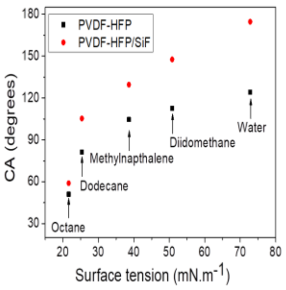
Institute of Nanoscience and Nanotechnology, NCSR “Demokritos”, Aghia Paraskevi,
Athens 15310, Greece

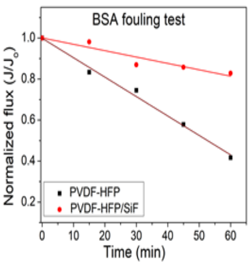
Climate change and water pollution presents one of the major global challenges. Therefore, the development of emerging water treatment technologies is crucial to address water scarcity and water purification. To this end, membrane technology, such as membrane distillation (MD), has received significant scientific and technological attention. Polymeric membranes are currently the most widely used membranes for water treatment due to their enhanced structural properties and relatively low cost compared to inorganic membranes [1]. The aim of this study is to improve the properties of porous polymeric membranes (PVDF-HFP) by introducing superhydrophobic fluorinated silica (SiF) nanoparticles [2] as a top coating. The produced SiF nanoparticles were characterized by a variety of techniques, such as SEM, EDS, AFM and TEM, while the characterization of the nanocomposite polymeric membranes was performed employing SEM, and contact angle (CA), liquid entry pressure of water (LEP) and bubble point (BuP) measurements. Additionally, the evaluation of the membranes was performed by investigating the anti-fouling performance of the membranes using bovine serum albumin (BSA) as model fouling agent and the wetting resistance of them by measuring the contact angle of different surface tension liquids. The results showed that, compared to the unmodified PVDF-HPF membrane, the SiF nanoparticles endow to the membrane superhydrophobic (CA>170^o) and oleophobic properties. Direct contact membrane distillation experiments proved the increase of the permeate flux and the enhanced anti-fouling properties of the nanocomposite membrane. The results indicate that the developed nanocomposite membranes exhibit improved overall performance aiming to tackle critical issues of membrane distillation process.

References

[1] L. Y. Ng, A.W. Mohammad, C.P. Leo and N.Hilal, *Desalination* 308, 15–33, 2013.

[2] C. Kyrou, D. Tsiourvas, S. Kralj, and I. Lelidis, *J. Mol. Liq.* 298, 111984, 2020.


PVDF-HFP
PVDF-HFP/SiF
CA (degrees)
180
150
120
90
60
30
Octane
Dodecane
Methylnapthalene
Diidomethane
Water
20
30
40
50
60
70
80
Surface tension (mN.m-1)


BSA fouling test
Normalized flux (J/J$_o$)
1.0
0.8
0.6
0.4
0.2
PVDF-HFP
PVDF-HFP/SiF
0
10
20
30
40
50
60
Time (min)

eP100

INTRINSIC CANCER THERAPEUTIC PROPERTIES OF CONJUGATED POLYMER NANOPARTICLES

Alkmini Negka[1], Panagiota Koralli[2], Maria Goulielmaki[2], Lida Evmorfia Vagiaki[2],
Aristea Pavlou[2], Giannis N. Antoniou[3], Panagiotis E. Keivanidis[3], Dimitris Moschovas[4],
Apostolos Avgeropoulos[4], Vassiliki Papadimitriou[2], Vassilis Zoumpourlis[2],
Antonia Dimitrakopoulou-Strauss[1], Vasilis G. Gregoriou[5],
Christos L. Chochos[2]

[1] Clinical Cooperation Unit Nuclear Medicine, German Cancer Research Center (DKFZ), Heidelberg, Germany
[2] Institute of Chemical Biology, National Hellenic Research Foundation, Athens, Greece
[3] Department of Mechanical Engineering and Materials Science and Engineering, Cyprus University of Technology, Cyprus
[4] Department of Materials Science Engineering, University of Ioannina, Ioannina, Greece
[5]National Hellenic Research Foundation

Introduction: π–conjugated polymers, in particular in the form of nanoparticles (CNPs), have emerged as nanomaterials for optical imaging and cancer therapy due to their distinct advantages[1]. More specifically, the nanoparticles have find plethora of biological applications by taking advantage of their fluorescence and photoacoustic[2] properties and their efficiency in photodynamic[3] and photothermal[4] therapy. However, biocompatible CNPs are rare and their use resulting in long-term toxicity[5] in the living organism. In this contribution, was manifested for the first time, the physical low cytotoxicity in normal cells and the anticancer effect of novel CPNs.

Methods: The conjugated polymers were synthesized via Stille coupling polymerization reaction. The molecular and structural characterization were determined via GPC in chloroform ($CHCl_3$) and 1H-, 13C- NMR, respectively. The optical properties were studied by UV-Vis and fluorescence spectroscopy. The NPs' formation was carried out via nanoprecipitation method and their shape and size was investigated by SEM and DLS In vitro and iv-vivo experiments were performed to study the cytotoxicity of the NPs in in selected normal and cancer cell lines (WJ-MSC, HCT116, and WM164) and in mice.

Results: Two donor-acceptor-donor (D-A-D) conjugated polymers based on bithiophene as the electron donating segment and thiadiazolequinoxaline substituted with phenyl and methyl groups as the electron deficient unit were synthesized (BTTDQ-Ph and BTTDQ-Me). The resulting NPs were approximately 60nm, compatible in size for biological applications, and stable in aqueous solution. The in vitro results showed that neither of the newly synthesized CPNs affects stem cell viability, even when administered in higher concentrations. On the contrary, a remarkable effect on cancer cell viability was recorded. Consequently, SCID mice bearing WM164 xenografts were treated with both BTTDQs, and a significant attenuation of tumor growth was observed. The respective mechanisms that orchestrate the observed anticancer effects were studied thoroughly and it was demonstrated that the activation of reactive oxygen species is the dominant mechanism.

eP101

LOW-CYTOTOXICITY CONJUGATED POLYMER NANOPARTICLES AS PHOTOACOUSTIC CONTRAST AGENTS IN NIR-II REGION

Andriana Schiza[1,2], Alkmini Negka[3], Maria Goulielmaki[1], Katerina Mavronasou,[1] Panagiota Koralli[1], Aristea Pavlou,[1] Vasssilis Zoumpourlis,[1] Antonia Dimitrakopoulou-Strauss,[3] Vassilis G. Gregoriou,[4] Christos L. Chochos*[1]

[1]Institute of Chemical Biology, National Hellenic Research Foundation, Athens, Greece
[2]Department of Chemistry, Section of Industrial Chemistry, National and Kapodistrian University of Athens, Greece
[3]Clinical Cooperation Unit Nuclear Medicine, German Cancer Research Center, Heidelberg, Germany
[4]National Hellenic Research Foundation, Athens, Greece

Keywords: conjugated polymer nanoparticles, NIR-I photoacoustic imaging, cytotoxicity

Introduction-The development of new nanomaterials for NIR photoacoustic bioimaging has identified as a “hot” topic of research. The NIR is an ideal region for imaging as the naturally components of the body do not absorb in this window.1 Furthermore, nanoparticles with sizes ≤100 nm can efficiently accumulate into tumors and prolong the circulation time.2 Our goal was based on the production of non-toxic conjugated polymer nanoparticles with proper sizes that absorb in NIR in order to be used as photoacoustic contrast agents in biological applications.3

Methods-The conjugated polymer (IDTTDQ-Th) contains two alternating building blocks, the thiadiazoloquinoxaline and the indacenodithiophene both substituted (Fig.1a). After the composition, we characterized the polymer via 1H-, 13C-NMR in CDCl3 and UV-Vis. The average molecular weights per number and weight and the dispersity were measured through gel permission chromatography in chloroform. The nanoparticles were prepared via encapsulated method, utilizing the FDA-approved amphiphilic polymer poly(ethylene glycol) methyl ether-block-poly(lactide- co-glycolide) (m-PEG-PLGA) (Fig.1b). The size and the zeta potential of CPNs were determined by Dynamic Light Scattering and their morphology by TEM. Photoacoustic measurements were occurred. Wharton's Jelly-Derived Mesenchymal Stem Cells were studied to estimate the cell viability and cytotoxicity.

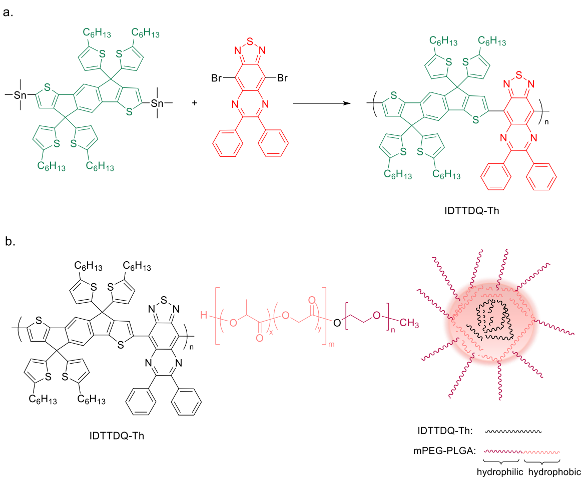


Fig.1 (a) Polymerization through Stille Reaction (b) Preparation of Nanoparticles in aqueous media

Results-The IDTTDQ-Th was synthesized via cross coupling Stille reaction. Then, the nanoparticles were produced though encapsulation, using variable ratios per weight between IDTTDQ-Th and m-PEG-PLGA (from 1/10 to 1/50). We prepared spherical nanoparticles with sizes ≈100nm and intensive colors (Fig.2a). The photoacoustic measurements indicated the 1/30 as more effective with higher signal in ≈900nm, using indocyanine green, an FDA-approved dye as control (Fig.2b). Coming up to the best ratio, we evaluated the cell viability and cytotoxicity in Wharton's Jelly- Derived Mesenchymal Stem Cell's. The results showed low cytotoxicity at 48h and 72h after the administration (Fig.2c-2d).

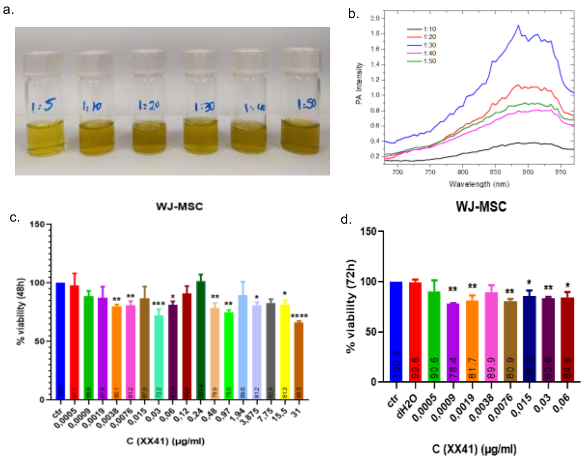


Fig.2 (a) Illustration of the different samples (b) Photoacoustic intensity as a function of wavelength for the five ratios (c),(d) Cytotoxicity studies in various concentrations of conjugated polymer at 48 h and 72 h.

Conclusion-CPNs with different ratios per weight between IDTTDQ and m-PEG-PLGA were produced in order to be studied as imaging agents. The CPNs had spherical shape and sizes ≈100 nm. The ratio 1/30 exhibited high photoacoustic signals, good cell viability and low cytotoxicity at 48h and 72h after the administration.

Reference:

1. Ding D., Liu J., Feng G., Li K., Hu Y, Liu B., Small., 2013, 9 (18), 3093-3102.
2. Hobbs S.K., Monsky W.L., Yuan F., Roberts, W.G., Griffith L., Torchilin V.P., Jain R.K., Proc. Natl. Acad. Sci., 1998, 95 (8), 4607-4612.
3. Xu M., Wang L. V., Rev. Sci. Instrum., 2006, 77, 041101.

eP102

COPPER/EPOXY MULTILAYERED COMPOSITE SYSTEMS: DEVELOPMENT, PROPERTIES AND FUNCTIONALITY

Sevasti Gioti, Anastasios C. Patsidis, Georgios C. Psarras

Smart Materials & Nanodielectrics Laboratory, Department of Materials Science,
School of Natural Sciences, University of Patras, Patras 26504, Greece

The development and study of epoxy based multilayered composites employing metal particles as reinforcement is a new research area in the field of composites. This type of composites can be used as structural materials and, at the same time, as devices for storing and harvesting energy, while they can exhibit optimum thermomechanical behavior and electrical properties [1-2].

In this study, composites consisted of an epoxy resin as matrix and copper particles, as reinforcement were produced, varying the filler content. Furthermore, two-layer and three-layer copper particles/epoxy laminated composites were prepared varying the infused layer order. The morphology of systems was investigated via Scanning Electron Microscopy, while thermomechanical properties were examined via Dynamic Mechanical Analysis. The electrical characterization under AC conditions was conducted via Broadband Dielectric Spectroscopy, while conductivity and energy storage/harvesting were studied under DC conditions.

Results have shown that dielectric permittivity, conductivity, and energy density are increasing with the increase of the number of purred layers. Similar behavior is observed in thermomechanical characterization. However, the overall optimum performance is displayed by the copper/epoxy particulate composite.

Figure 1: Real part of dielectric permittivity versus temperature at 0.1 Hz.

[1] G. C. Manika, G. C. Psarras, Energy storage and harvesting in BaTiO3/epoxy nanodielectrics. High Voltage, 1, (2016), p. 151–157.

[2] S. Gioti, S. G. Stavropoulos, A. Sanida, G. C. Psarras, A comparative study on the thermomechanical and electrical properties of carbide/or graphite/epoxy?reinforced composites. Journal of Thermal Analysis and Calorimetry, 142 (2020), p.1649-1657.

eP103

ARE POLYDIENES SOLUTIONS PHOTOREACTIVE?

Thanasis Bogris, Benoit Loppinet

Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH)

Solutions of polydienes present spectacular unanticipated response to irradiation by mild power (mW) red laser light. A local variation of refractive index forms which itself affects the light propagation (providing a case of nonlinear propagation). Most solutions respond with a local increase of refractive index (RI) as a result of local change of composition. It leads to self focusing. But solutions in certain solvent show local decrease of RI and defocusing. Large differences in refractive index of the constituents (typically 0.1 RIU) provide for large change of RI.

It would obviously be of great interest to identify the physico-chemical origin and mechanism of the observed responses. I will show that crosslink accompanied by increase of polymer concentration is a plausible scenario for the RI local increase. We have accumulated experimental evidences of relevance of photochemistry and free radical chemistry. They include EPR signals showing presence of free radicals during the irradiation, IR and Raman spectroscopy showing clear modification or alteration of vibrational spectra with in particular a clear appearance of hydroxyl group, strong influence of the O2 content on the kinetics.
I will show how self written wave guide property can be used to create optical fiber interconnect .
I will discuss how the concept of photoreactive polymer solutions could be generalized to other solutions.

eP104

ADSORPTION OF PHARMACEUTICALS ONTO VIRGIN AND AGED BIOBASED MICROPLASTICS

Dimitris Kalaronis[1], Nina Maria Ainali[1], Eleni Evgenidou[1,2], George Z. Kyzas[3], Dimitrios N. Bikiaris[4], Dimitra A. Lambropoulou[1,6]

[1] Laboratory of Environmental Pollution, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece

[2] Center for Interdisciplinary Research and Innovation, Balkan Center, Thessaloniki, Greece

[3] Department of Chemistry, International Hellenic University, Kavala, Greece

[4] Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece

[6] Center for Interdisciplinary Research and Innovation, Balkan Center, Thessaloniki, Greece

As microplastics (MPs) can be defined as the polymeric fragments with size < 5 mm. MPs can adsorb organic and inorganic pollutants onto their surface and transfer them to the Ecosystems. Regarding the latter, biobased and biodegradable polymer PLA, and four pharmaceuticals (Diclofenac, Ketoprofen, Valsartan, and Trimethoprim) were chosen with aim to monitor their adsorption onto PLA MPs surface. PLA particles were milled in size < 2 mm and separated into three categories: (i) Virgin PLA-MPs, (ii) UV-irradiated MPs and (iii) solar-aged MPs. A stock solution of the selected pharmaceuticals was prepared using an initial concentration of 10 mg/L for each compound. The experiments were carried out into a bath with continuous stirring (200 rpm) and constant temperature at 25 °C. For monitoring the pharmaceuticals' adsorption on PLA surface, four different types of experiments were carried out: (i) selection of optimal pH, (ii) kinetics of reaction, (iii) isotherms, and (iv) different initial concentration of pharmaceuticals. The adsorption results were analyzed using chromatographic techniques like LC-MS. The adsorption of the selected compounds is ranged in various values depending on the type of the drug. However, > 50% adsorption was observed in most of the cases, while higher percentages were noticed in pH=2 and by solar-aged microplastics. Regarding the adsorption kinetics, all materials adsorbed a significant amount of pollutants, however the faster kinetics was achieved by UV-irradiated MPs, with a range of adsorption between 30-81% in most of the cases, which was reached greatly in 90 minutes of adsorption. To sum up, PLA MPs can adsorb and transfer common pharmaceuticals compounds on their surface and especially, aged-MPs can increase their adsorption ability, rising the concerns about Ecosystems.

Acknowledgments: This work has been done after financial support received from the Greek Ministry of Development and Investments (General Secretariat for Research and

Technology) through the research project “Intergovernmental International Scientific and Technological Innovation-Cooperation. Joint declaration of Science and Technology Cooperation between China and Greece” with the topic “Development of monitoring and removal strategies of emerging micro-pollutants in wastewaters” (Grant no: T7ΔΚ?-00220) and it is gratefully acknowledged.

ePI05

FLUOROPOLYMERS APPLICATION IN BIO-FUNCTIONAL SURFACES CREATION VIA LITHOGRAPHY

P. Petrou[1], C. Gkioka[2], M. Chatzichristidi[2], A. Nika[2], F. Machairioti[1,2]

[1] Immunoassay/Immunosensors Lab, INRaSTES, NCSR Demokritos, Aghia Paraskevi, Greece
[2] Industrial Chemistry Laboratory, Department of Chemistry, National and Kapodistrian University of Athens, Athens, Greece

A critical aspect to the development of micro- and nanoscale arrays and biosensors is the ability to immobilize biomolecules onto a surface with high resolution. The chemistry and the topography of the patterned surfaces can also be used to control the size and the structure of cells attached to them, thus affecting cell behavior [1].

Patterning techniques using optical lithography and electron beam lithography are not suitable methods for such applications since they are using harsh solvents that are not bio-compatible, leading to denaturation of biomolecules. To overcome this obstacle, fluorinated photoresists that can be developed with biomolecule friendly solvents (hydrofluoroethers) have been proposed [2].

In this work, fluorinated homopolymers and copolymers were synthesized by free radical polymerization and evaluated as photoresists for biomolecules patterning. The main idea was to create patterned surfaces with high (more than 20 degrees) hydrophilicity change between exposed and non-exposed areas. Fluoropolymers that lose their fluoro atoms in the presence of acid or/and amine were the first candidates. Thus, novel 4-vinylbenzyl glycidyl ether-co-pentafluophenyl methacylate copolymars were synthesized and their response to UV irradiation in the presence of a photoacid generator was evaluated especially in terms of hydrophilicity change. Amongst the different copolymers, those undergoing the highest hydrophilicity change presented also the highest contrast in terms of biomolecules immobilization capacity.

The findings of this work are expected to provide a new surface patterning method using optical lithography applicable in biosensors and cell patterning.

References:

A. 1.R.S. Kane et al., *Biomaterials* **20**, 2363-2376 (1999)
B. 2.K. M. Midthun et al., *Biomacromolecules* **14**, 993-1002 (2013)

Acknowledgements

This research is co-financed by Greece and the European Union (European Social Fund-ESF) through the Operational Programme "Human Resources Development, Education and Lifelong Learning 2014-2020" in the context of the project "Bio-functional surfaces of fluoropolymers via lithography techniques" (MIS: 5048147).

Ευρωπαϊκή Ένωση
European Social Fund

Operational Programme
Human Resources Development,
Education and Lifelong Learning
Co-financed by Greece and the European Union

ΕΣΠΑ
2014-2020
ανάπτυξη - εργασία - αλληλεγγύη

eP106

DEVELOPMENT OF CHIRAL HELICENE-BASED CONJUGATED POLYMERS OF HIGH MOLECULAR WEIGHTS AND PROCESSABLE IN COMMON ORGANIC SOLVENTS FOR THE FIRST TIME

Clement Gedeon[1,2], Vasilis Gregoriou[1,3], Jeanne Crassous[2], Christos Chochos[1,3]

[1] ADVENT Technologies, Patras Science Park, Patras, Greece
[2]Université de Rennes 1, Rennes, France
[3]National Hellenic Research Foundation (NHRF), Athens, Greece

Keywords: π-Conjugated Polymers, Chirality, Chiral Polymer, Helicene, Self-Assembly

Introduction: Helicenic molecules have drawn considerable attention in the recent years due to their excellent chiroptical properties.1 However, these molecules are complicated to synthesize, thus slowing down their development. In addition, their poor solubility, which is translated by a complex processability, have excluded them from the polymer field. In fact, only two attempts have been reported for their use in polymers, which resulted in the formation of small oligomers.2-3

Methods: New conjugated polymers were synthesized using a metal catalyst (Pd) for the aromatic cross coupling Stille polymerization reaction. The average molecular weights per number and weight and the dispersity of the polymers were determined by size exclusion chromatography in high temperatures. Thin films of polymers were obtained *via* spin-coating, and then annealed under vacuum. All polymers were analysed via 1H-, 13C-NMR, and for UV-Vis and fluorescence spectroscopy, both before and after the thermal annealing.

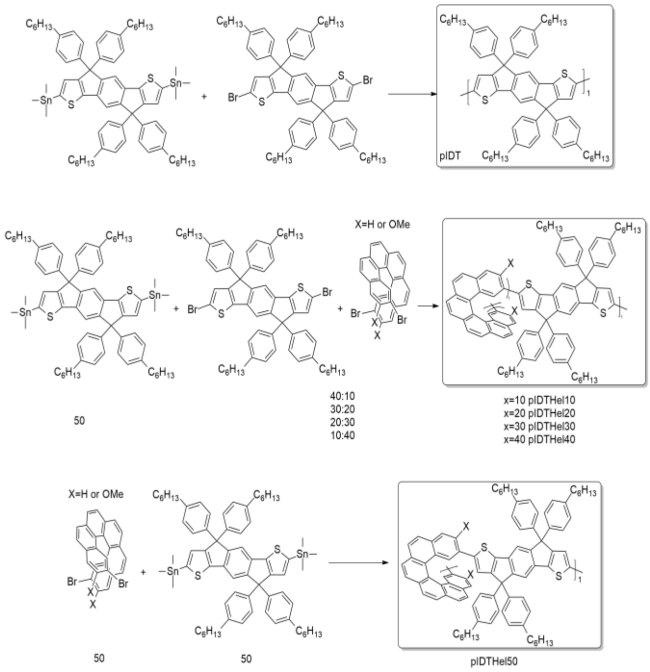
Results: We synthesized a range of new helicene-indacenodithiophene (Hel-IDT) polymers with a decreasing number of solubilizing IDT units. Starting from 10% of the poorly soluble dibromohexahelicene, we increased this amount to 50%. Thus, we were able to probe the influence of the helicene moiety on the molecular weight as well as the optoelectronical properties. OPVs and OLED devices based on these polymers were made, thus demonstrating the processability of the hexahelicene as a new building block for conjugated polymers. Finally, Transmission Electronic Microscopy was performed in order to investigate the supramolecular arrangement of the polymers, which plays an important role on the macro-scale properties.

References

[1] Crassous J. Circularly polarized luminescence in helicene and helicenoid derivatives. Circularly Polarized Luminescence of Isolated Small Organic Molecules, Springer Singapore, pp.53-97, **2020**

[2] Yashima *et al.*, *Polym. Chem.*, **2014**, 5, 4909-4914

[3] Crassous J. *et al.*, *Front. Chem.*, **2020**, 8:237., doi: 10.3389/fchem.2020.00237



ePl07

PROPERTIES OF POLYBUTADIENE MELTS ADSORBED IN ALUMINA VIA ATOMISTIC SIMULATIONS PARAMETRIZED ON DENSITY FUNCTIONAL THEORY CALCULATIONS

Nikolaos Patsalidis[1], Georgios Papamokos[2], George Floudas[2,3],
Vangelis Harmandaris[1,4,5], Alireza Foroozani Behbahani[4,5]

[1] Computation-based Science and Technology Research Center, The Cyprus Institute, Cyprus
[2] Department of Physics, University of Ioannina, Ioannina, Greece
[3] University Research Center of Ioannina (URCI)—Institute of Materials Science and Computing, Ioannina, Greece
[4] Department of Mathematics and Applied Mathematics, University of Crete, Crete
[5]Institute of Applied and Computational Mathematics (IACM), Foundation for Research and Technology Hellas, (FORTH), IACM/FORTH

The properties of polymeric nanostructured materials involving a solid phase are typically determined by the presence of polymer/solid interfaces. Polymer chains in interfaces are characterized by a very broad range of characteristic time (from fs up to sec) and length (from Å up to several nm) scales. Here, we study such systems via a new hierarchical multi-stage simulation methodology, involving ab-initio calculations and atomistic simulations of polybutadiene (PB)/alumina interfacial systems. First, density functional theory (DFT) calculations of a single butadiene monomer adsorbed on alumina surface are performed. A detailed scan of the interaction energy between butadiene and alumina is applied in order to get the equilibrium configuration and the interaction between butadiene and alumina as a function of the butadiene/alumina distance. Moreover, in the DFT calculations alumina was simulated both as a cluster and as a periodic surface. In the second stage, a detailed (classical) atomistic force field is obtained for the butadiene/alumina interaction by machine learning (ML) algorithms using proper functional forms (e.g. Morse) to fit the DFT data. We deal with challenges of obtaining well-distributed data from DFT calculations and at the same time performing multi-parameter fitting while we are increasing the dataset by using non-optimal (intermediate) configurations. The last stage of the proposed hierarchical simulation approach concerns the prediction of the properties of PB/Alumina interfaces at the atomic level, using the new classical atomistic force field. We study the structure, conformations and dynamics of polymer chains as a function of distance from the alumina substrate.

eP108

STRUCTURAL AND DYNAMICAL PROPERTIES OF HYBRID POLYMER NANOCOMPOSITES SYSTEMS THROUGH ATOMISTIC MOLECULAR DYNAMICS SIMULATIONS

Albert John Power[1], Ioannis N. Remediakis[2,3], Vagelis Harmandaris[1,4,5]

[1] Mathematics and Applied Mathematics, University of Crete
[2] Department of Materials Science and Technology, University of Crete

[3]Institute of Electronic Structure and Laser, Foundation for Research and Technology – Hellas, Greece
[4]Institute of Applied and Computational Mathematics (IACM), Foundation for Research and Technology-Hellas (FORTH), Heraklion, Crete, Greece

[5]Computation-based Science and Technology Research Center, The Cyprus Institute, Nicosia 2121, Cyprus

The study of polymer-based nanocomposites (PNC) with metal nanoparticles is an intense research area that has attracted growing scientific and technological interest. In this work we investigate the behavior of hybrid polyethylene (PE)/gold (Au) nanoparticle (NP) systems at the molecular level by using classical atomistic simulations. We examine the properties of polymer chains in PNCs with bare Au NPs or functionalized Au NPs.

Ten different model systems are considered, including two different monodisperse PE matrices; one consists of chains with 22 monomers and the other one with 100 monomers. Two different gold NPs with Wulff construction were modeled: one with diameter of 25 Å and one with 50 Å. Both of the grafted gold nanoparticles have a diameter of 5 nm. The first one has 20 monomers per chain and the other one 62 monomers per chain. The grafting density is 0.67 chains per square nm.

Structural, conformational, and dynamical properties of the chains were analyzed and compared to the behavior of the bulk PE system. Local structural and conformational features were analyzed at the level of both individual segments (atoms or bonds) and entire chains. Orientational relaxation of PE chains in the hybrid systems at the segmental and terminal level was quantified through the time autocorrelation function of the second Legendre polynomial. Translational segmental and center of masses dynamics of PE chains were examined by calculating the average mean-square displacement. We found that structural and dynamical properties of the polymers show big changes near the Au NPs. At the vicinity of the bare Au NPs a dense layer of polymer atoms appears. For the case of the core/shell NPs the anchors change polymer's behavior/properties and especially the density profile. Dynamics become slower close to the Au NP and terminal relaxation time decreases with the distance from the Au NP.

eP109

SYNTHESIS, REACTION KINETICS AND CHARACTERIZATION OF INNOVATIVE THERMO-RESPONSIVE NANOCOMPOSITES BASED ON BIOCOMPATIBLE OLIGO-ETHYLENE GLYCOL ACRYLATES (POEGA)

Ioannis Tsagkalias, Dimitris Achilias

Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece,
Laboratory of Organic Chemical Technology

The field of "smart" polymers with the ability to respond to external stimuli through changes in their physicochemical properties has developed very significantly in recent years. Radical polymerization normally concerns vinyl monomers with at least one double bond in their structure. Polymerization of these monomers leads to a significant heat release due to the addition reaction to the double bond. Amongst thermochemical methods, the most commonly employed one for measuring polymerization kinetics is differential scanning calorimetry (DSC). It offers the benefit of continuous monitoring of the variation of the reaction rate, which allows the estimation and identification of specific phenomena taking place during polymerization (such as diffusion controlled, besides chemical reactions).

The polymerization enthalpy and conversion were estimated by integrating the area between the DSC curves and the baseline established by extrapolation from the trace produced after complete polymerization (invariable heat produced during the reaction).

The objective of this research is to implement the methodology employed previously for HEMA, for a different acrylic now monomer, 2-hydroxyethyl acrylate (HEA). Similar to HEMA, this acrylate displays hydrogen bonding responsible for such properties as its high boiling point and water solubility.

This research is co-financed by Greece and the European Union (European Social Fund-ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project “Reinforcement of Postdoctoral Researchers - 2nd Cycle” (MIS-5033021), implemented by the State Scholarships Foundation (IKY).

eP110

ON THE ROLE OF MOLECULAR ARCHITECTURE IN POLYMER SIZE AND DIFFUSION: THE CASE OF RING AND LINEAR POLY(ETHYLENE OXIDE) CHAINS IN AQUEOUS SOLUTIONS

Dimitrios G. Tsalikis[1], Terpsichori S. Alexiou[1], Panagiotis V. Alatas[1],
Vlasis G. Mavrantzas[2]

[1] Department of Chemical Engineering, University of Patras
[2] Department of Chemical Engineering & Department of Mechanical and Process Engineering, University of Patras, and ETH-Zurich

Ring polymers is a special category of macromolecules that lack chain ends, thus they cannot be reliably described by established molecular theories. Therefore, and despite recent advances in the field, several issues remain open, including (e.g.) their conformation and diffusive behavior in solution as a function of their molecular weight (MW) and concentration.

We have resorted to molecular dynamics (MD) simulations to study model aqueous solutions of ring and linear poly(ethylene oxide) (PEO) with MW both below and well above the characteristic entanglement MW of linear PEO over a broad range of polymer concentrations c (wt. %).

Conformational and diffusion properties of PEO chains were analyzed in terms of their mean square radius of gyration $<R^2_g>$ and of their center-of-mass diffusion coefficient Ds, respectively. For low concentrations (c < 10%), the dimensions of both architectures were found to be concentration-independent. For higher concentrations (c > 10%), the $<R2g>$ value decreased with increasing concentration following a power law of the form c^{-b}. For linear PEO, the exponent b was found to be practically unaffected by the MW, whereas for ring PEO b decreased with decreasing molecular length. At that region, the chain diffusivity decreased with concentration c as $D_S^{-0.4 \pm 0.05}$. Increasing further the polymer concentration was found to cause a steeper decrease in Ds, with the scaling exponents decreasing quickly with decreasing molecular length for both architectures. Our findings have been compared with theoretical predictions and experimental data.[1]

Our MD simulations showed that in the dilute regime, the conformation and diffusivity of the PEO chains are practically molecular topology independent. In the semi-dilute regime, on the other hand, molecular topology starts to bear a distinct effect on the conformation and dynamics of the two different molecular geometries.

References: [1] D.G. Tsalikis et al. *Macrom. Theory Simul.* **2020**, 29, 2000016.

eP111

MODELING NON-EQUILIBRIUM DYNAMICS OF COARSE-GRAINED MOLECULAR SYSTEMS

Georgia Baxevani [1,], Evangelia Kalligiannaki [2], Vagelis Harmandaris [1,2,3]

[1] Department of Mathematics and Applied Mathematics, University of Crete, Heraklion, Greece,
[2] Institute of Applied and Computational Mathematics, Foundation for Research and Technology Hellas, Heraklion, Greece
[3] Computation-Based Science and Technology Research, Center, The Cyprus Institute, 2121 Nicosia, Cyprus

In recent years, the development of coarse-grained models for studying large-scale physicochemical processes that cannot be practically studied with atomically detailed molecular dynamics simulations is an active research field. Defining the new effective coarse-grained system, which reduces the dimensionality, means finding the model which best represents the reference system both in structure and dynamic properties.

In the present work, we estimate the dynamics of coarse-grained models at non-equilibrium conditions. The non-equilibrium systems considered are generated by applying a constant external driving field to a classical fluid initially at equilibrium. We propose parametrized stochastic dynamics for non-equilibrium. We infer the model parameters based on applying a path-space variational inference method to systems with non-equilibrium steady-states. In practice, we approximate dynamical observables, i.e., quantities that are averaged over the path distribution, and obtain optimized coarse-grained models for non-equilibrium systems.

Towards this end, we implement non-equilibrium molecular dynamics simulations at the atomistic scale. By extracting the data from the detailed atomistic simulations corresponding to a non-equilibrium steady-state of the systems, we calculate transport coefficients of interest. The methodology is illustrated for water molecular system.

eP112

CONFORMATION AND DYNAMICS OF SHORT LINEAR AND RING DNA MOLECULES IN THE CROSS-OVER FROM THE DILUTE TO THE SEMI-DILUTE SOLUTION REGIME: INSIGHTS FROM ATOMISTIC MOLECULAR DYNAMICS SIMULATIONS

Terpsichori Alexiou[1,2], Dimitrios Tsalikis[2], Pavlos Stephanou[1], Vlasis Mavrantzas[2]

[1] Chemical Engineering, Cyprus University of Technology, Cyprus
[2] Chemical Engineering, University of Patras, Patras, Greece

Introduction: In addition to their great importance for cellular biological processes, frequently occurring *in vivo* in a crowded environment, concentrated solutions of moderately short (length less than 250bp) DNA molecules, are also becoming highly relevant to a variety of novel oligonucleotide-based biotechnological applications. The objective of the work presented here is to explore high fidelity, large scale molecular simulations as a tool for understanding the structural and dynamic properties of solvated linear and circular DNA molecules and how these are influenced by parameters such as concentration, varying from the very dilute to the semi-dilute regime, and molecular length.

Methods: To this end, we have performed detailed atomistic molecular dynamics (MD) simulations of aqueous solutions of short linear DNA and circular DNA duplexes (the latter also called minicircles, amenable to detailed atomistic simulations). Last generation force fields of the AMBER family have been implemented, taking into account the most recent PARMBSC1 modifications specifically developed for DNA.[1-3]

Results: Special emphasis is placed on the estimation of the zero-shear rate viscosity, as well as the rotational and translational components of the self-diffusion coefficient of linear DNA, which are calculated and compared to relevant experimental data obtained via dynamic light scattering and nuclear magnetic resonance, as well as to theoretical models.

Conclusions: In the case of the linear DNA duplexes studied here, very good agreement is observed compared to the relevant experimental data in the limit of very dilute concentrations, as well as to theoretical models developed for rod-like molecules. Importantly, concentration effects in the dilute regime are clarified, reconciling earlier conflicting experimental data. Ultrashort and very stiff 30 bp minicircles exhibit an unexpectedly pronounced degree of anisotropic diffusion, a phenomenon that is attenuated as the molecular length increases due to the emergence of out-of-plane bending motions.

eP113

BIOADHESION OF POLYMERIC FORMULATIONS TO BIOLOGICAL SURFACES: MULTISCALE MODELING AND COMPUTATIONAL METHODS

Stefania Serpetsi[1], Costas Kiparissides[1,2]

[1]Centre for Research and Technology Hellas - CERTH / Chemical Process and Energy Resources Institute CPERI
[2] Aristotle University of Thessaloniki, Thessaloniki, Greece

With the diverse and increasing number of bioadhesive material applications, the development of polymeric materials with controllable and well-tuned adhesive properties has attracted great interest by both the scientific research community and biomedical industry. It is well accepted that the bioadhesive performance of polymers can be adjusted by controlling the molecular properties (i.e., molecular weight distribution, chemical character of structural monomer units, copolymer composition, presence of functional groups, etc.), physicochemical, mechanical and viscoelastic properties, surface's wettability, nanostructure, and so forth. Thus, the numerous performance criteria that need to be satisfied for effective polymer bioadhesion reflect the complexities of optimal selection of a polymeric formulation. Irrespectively of the polymer physical form, an optimal bioadhesive polymeric formulation should be characterized by rheological synergy with the target tissue, controllable wetting behavior, rapid swelling in aqueous media (determined by the target tissue), selective adhesiveness to the target tissue, and prolonged residence at the target site. The elucidation of the bioadhesion mechanisms and quantification of the bioadhesive properties of polymers under different environmental conditions have paved the way to the rational design of novel bioadhesive materials via the development of advanced multiscale computational mathematical models. The present modeling approaches can be broadly classified into: (i) local material models, (ii) local interface models and (iii) effective models. The local material models describe the stress-strain behavior of the bioadhesive layer due to local viscoelastic and fracturing effects. The local interface models describe the local traction-separation behavior at the polymer-tissue interface related to strong or weak molecular bonds, electrostatic interactions, phenomenological fracture and debonding mechanisms. Finally, the effective adhesion models predict the effective debonding and bonding at a global level, for instance, in the form of global load-displacement curves. In the present work, the benefits arising from the coupling of the different bioadhesive models are discussed by considering the durability of adhesive joints under nonlinear mechanical forces.

eP114

MICELLIZATION THROUGH COMPLEXATION OF OPPOSITELY CHARGED DIBLOCK COPOLYMERS: EFFECTS OF COMPOSITION, POLYMER ARCHITECTURE AND SALT OF DIFFERENT VALENCY

Christos Gioldasis[1], Leonidas Gergidis[2], Costas Vlahos[1]

[1] Chemistry Department, University of Ioannina, Ioannina, Greece
[2] Department of Materials Science and Engineering, University of Ioannina, Ioannina, Greece

The structural and electrical characteristics of polyelectrolyte complex micelles (PCMs) formed by mixing of oppositely charged double hydrophilic copolymers are studied by means of molecular dynamics simulations. In mixtures of linear diblock copolymers we found that the preferential aggregation number N_p of PCMs is a universal function of the ratio $\gamma_\pm$ of the total positive to total negative charges of the mixture. The addition of divalent salts ions induces a secondary micellization. In mixtures of copolymers bearing a common neutral thermoresponsive block, micelles with contracted corona consisting of thermoresponsive blocks and complex polyelectrolyte core are formed at low salt concentration and temperature far away the biphasic regime. At high salt concentration and temperature in the biphasic regime, reversed micelles are obtained. In equimolar mixtures of linear copolymers with miktoarm stars we found that N_p of PCMs decreases as the number of charged branches of miktoarm copolymer increases. The shape of micelles progressively changes from spherical to worm-like with the increase of number of branches of miktoarm copolymers. Our findings are in full agreement with existing experimental and theoretical predictions and provides new and additional insights.

eP115

STRUCTURAL AND DYNAMICAL BEHAVIOR OF STAR-SHAPED POLYSTYRENE AND POLY(ETHYLENE-OXIDE) MELTS, THROUGH ATOMISTIC MOLECULAR DYNAMICS SIMULATIONS

Eirini Gkolfi[1,2], **Petra Bačová**[2], **Vagelis Harmandaris**[1,2,3]

[1] Department of Mathematics and Applied Mathematics, University of Crete

[2] Institute of Applied and Computational Mathematics (IACM), Foundation for Research and Technology-Hellas (FORTH), Heraklion, Crete, Greece
[3] Computation-based Science and Technology Research Center, The Cyprus Institute, Nicosia 2121, Cyprus

Star polymers have been used as model systems for more complex architectures of industrial relevance due to their relatively simple and well-defined structure. As a consequence of their internal morphology, namely of the internal packing of arms in the molecule, their structural and dynamical behavior ranges from linear-like to coloidal-like, as the number of arms, f, increasing. In this talk we present a computational study of un-entangled poly(ethylene oxide) and polystyrene star polymer melts. We employ atomistic molecular dynamics simulations to study chemistry-dependent properties of two dissimilar polymers, differing in flexibility and glass transition temperature. The used method captures all atomistic details, accounting for local packing, specific interactions and/or stiffness of the polymers. We also developed a specific protocol for the equilibration and the analysis of the polymeric melts. Then we analyze the atomistic simulation data to quantifiy the shape and size characteristics of the star polymers and confronted them with widely used theoretical predictions. Furthermore, taking advantage of our atomistic representation, we implemented a challenging grid-based algorithm for estimating the free volume in the systems, a quantity directly related to the permeability of the material. Finally, dynamical heterogeneities of the segments along the arms were investigated, highlighting the effect of chemistry. The current work, to the best of our knowledge, represents the first attempt to describe the behavior of star polymer melts as a function of the number of arms in full atomistic detail. Our results on structural and dynamical properties are related to the packing and cooperative motion of the molecules. Thus, we obtain a molecular-level understanding of the behavior of star-shaped polymers, while at the same time we provide additional information to the experimental techniques and mesoscopic (coarse-grained) simulation models, aiming, in this way, to predict structure-dynamics relations in polymeric materials with complex branch-like architectures.

eP116

EMPLOYING BIOBASED MONOMERS TO DEVELOP ADHESIVES FOR THE WOOD INDUSTRY

Lazaros Papadopoulos[1], Electra Papadopoulou[2], Lamprini Malentzidou[1], Konstantinos Chrissafis[1], Charles Markessini[2], Dimitrios Bikiaris[1]

[1] Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece
[2] CHIMAR HELLAS SA

Unsaturated polyester resins (UPRs) are a polymer class asserting a position among the greatest achievements of polymer industry. Their simple processing and the variety of fields of application are the reasons they are considered a breakthrough since the 1930s, when they were firstly produced industrially, and they remained relevant to this day among other cross-linkable materials. In general, UPRs consist of a polymeric matrix with unsaturated double bonds and via radical polymerization they are combined with unsaturated monomers to create a cross-linked network

In recent years, due to the inability for proper waste management and the uncertainty surrounding crude oil in terms of price and availability, emphasis is given in the production of polymers from renewable monomers, the so-called bio-based polymers. So, a demand for bio-based UPRs was also created. A bio-based UPR should meet criteria for low cost, hazardless raw materials, no biodegradability and a performance equal or superior to the materials currently in use, in order to maintain sustainability in the chemical industry

In this work, UPRs partially based on biobased monomers were prepared. Succinic acid, ethylene glycol and maleic anhydride were used to prepare unsaturated polyester chains. Acrylic acid was used as the reactive diluent, and the cross-linking was made through thermal curing. The physicochemical properties of the prepared materials were examined with ^{1}H NMR, FTIR, DSC and TGA. From ^{1}H NMR and FTIR the successful synthesis of the materials was confirmed. With DSC measurements, parameters of the cross-linking reaction were examined and TGA was used to investigate the thermal stability of the cross-linked materials.

Acknowledgement

This research has been co?financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code:T1EDK-01413).

eP117

DYEING PROPERTIES OF CURCUMIN POWDER ON SYNTHETIC OR NATURAL FIBERS AND THEIR ANTIMICROBIAL ENHANCEMENT

Smaro Lykidou, Meropi Pashou, Evangelia Vouvoudi, Nikos Nikolaidis

Chemistry Department, Aristotle University of Thessaloniki, Thessaloniki, Greece

Introduction: a growing interest in the use of natural dyes in textile applications has been noticed, thus Cotton, wool, polyester and polyamide fabrics have been dyed with the aqueous extract of curcumin, attempting to replace synthetic colourants with natural ones. Certain properties that have been attributed to curcumin in pharmacological studies have demonstrated that curcumin used in traditional medicine possess antibacterial, anti-inflammatory, antifungal activities which may be transferred to fabrics or textiles as well of certain applications.

Methods: Cotton, wool, polyamide and polyester fabrics were dyed in curcumin bath with a depth of dyeing 2% o.w.f. Wool, polyamide and polyesters were dyed at pH=4 at 60, 98 and 130 ^oC for polyester, 60 and 98 ^oC for wool and polyamide. Cotton fabrics were also dyed at 60 and 98 ^oC using NaCl at 20 g/L as electrolyte. All dyeing processes were carried out without mordants into aqueous baths in the presence of dispersing agent.

Results: It was found that curcumin has high coloristic power on both natural and synthetic substrates offering dark yellow shades. The wash fastness tolerance on all substrates was excellent classifying curcumin as a "universal natural dye" being able to effectively dye both natural and synthetic fibres, and thus possibly replacing the synthetic and sometimes toxic and allergenic synthetic dyes. it can be stated that curcumin-dyed cotton, polyamide and polyester fabrics presented a strong bacteriostatic activity against *S. aureus*. This can be possibly attributed to the presence of phenolic groups present in curcumin that have been found to be responsible for antimicrobial activity The excellent wash fastness results obtained indicate thatcurcumin is strongly attached to the substartes involved, showing high affinity and that the natural colourant is not superficially adsorbed on them but penetrates inside the fibres well.

Conclusion: It was found that its antioxidant and antibacterial behaviour is considerable too, providing useful characteristics to the substrates applied.

eP118

MULTI-RESPONSIVE P(OEGMA-co-DIPAEMA) HYPERBRANCHED COPOLYMERS VIA RAFT POLYMERIZATION

Dimitris Selianitis, Stergios Pispas

Institute of Theoretical and Physical Chemistry, National Hellenic Research Foundation

Hyperbranched polymers are macromolecules with a high degree of polymerization, which, like dendrimers, are characterized by macromolecular topologies similar to that of a tree and by a large number of internal/external functional groups. Herein, we report on the synthesis of novel poly(oligo (ethylene glycol) methyl ether methacrylate)-co-poly(2-(diisopropylamino) ethyl methacrylate), P(OEGMA-co-DIPAEMA), hyperbranched copolymers via RAFT polymerization, utilizing EGDM as the branching agent. The homopolymer of 2-(diisopropylamino) ethyl methacrylate (PDIPAEMA) is a double-responsive polymer, towards pH and temperature with a pKa of around 6.2[1] and Tcp ca. 28oC[2]. PDIPAEMA becomes a water-soluble polymer due to the protonation of its amino groups at pH range below neutral, where it behaves as a cationic polyelectrolyte.[3] By using static light scattering it was possible to determine the molecular weights of all hyperbranched copolymers as evidence for the branched macromolecular structures resulting from the synthetic procedures followed. From DLS results, it was observed that the copolymers form large aggregates in aqueous solutions, regardless of the chemical composition and temperature, when the amino groups of DIPAEMA are fully protonated at low pH. In contrast, when partial or total deprotonation of the amino groups takes place, nanoparticles of very small dimensions and mass appeared, while tending to increase in size and mass as solution temperature increases. Solution ionic strength also affects the structure of copolymers in aqueous solutions resulting in the formation of larger aggregates by increasing NaCl concentration.

eP119

DEVELOPMENT OF PROCESS - MOLECULAR STRUCTURE – END-USE POLYMER PROPERTY RELATIONSHIPS USING BIG DATA-DRIVEN COMPUTATIONAL METHODS

Maria Bloutsou[1], Costas Kiparissides[1,2]

[1]Centre for Research and Technology Hellas - CERTH / Chemical Process and Energy Resources Institute CPERI
[2] Aristotle University of Thessaloniki, Thessaloniki, Greece

The linear-low density polyethylene (LLDPE) production is expected to grow significantly owing to its unique end-use properties such as high tensile strength, high impact resistance, and flexibility. The properties of LLDPE makes it suitable for applications in packaging, agriculture, building-construction, and healthcare. By 2025, the LLDPE production is expected to rise to more than 56 million tons. LLDPE is produced by copolymerization of ethylene with butane or hexene and octene, using Ziegler-Natta catalysts. Several companies have developed and are licensing gas-phase technologies for production of LLDPE including the Univation's Unipol, the Innovene G (Ineos), the LyondellBasell's Spheriline , and the Borstar process of Borealis. All of them are based on the same principle of using a fluidized-bed gas-phase reactor, although the operating mode and conditions differ among the different processes.

The end-use properties of LLDPE depend on the operating mode and conditions in the FBR, the resin macromolecular architecture, and processing conditions, all of which can be related via the application of polymer reaction engineering, polymer science, and polymer processing fundamentals. However, gaps in these theories limit their use, particularly in developing new LLDPE grades with a desired performance. Machine learning methods including regression techniques (e.g., multivariate statistics, Projection to Latent Structures (PLS), etc.) and Neural Networks can address the present limitations of fundamental modeling methods and identify the underlying relationships between process conditions-macromolecular structure–end-use polymer properties. In this presentation, regression and neural networks data-driven methods are applied to establish the relationships between the process operating conditions in a gas-phase LLDPE FBR – macromolecular architecture (i.e., molecular weight distribution from GPC curves; peak maxima, widths, and separation distances for TREF copolymer composition, etc.) - processing conditions - end-use properties (e.g., tensile tests, tear tests, impact tests, puncture tests, environmental stress crack resistance, etc.) of commercial LLDPE grades.

eP120

TENSILE PROPERTIES AND MICROMECHANICAL MODELING FOR THE ELASTIC MODULUS PREDICTION OF GRAPHITE REINFORCED SILANE CROSSLINKED HIGH-DENSITY POLYETHYLENE

Dimitra Kourtidou[1], Zoi Terzopoulou[2], Dimitrios Bikiaris[2], Konstantinos Chrissafis[1]

[1] Department of Physics, Aristotle University of Thessaloniki, Thessaloniki, Greece
[2] Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece

During the last decades, polyolefins such as polyethylene and polypropylene have been commonly used as piping materials to replace metallic systems due to their lower weight, superior resistance to corrosion, abrasion and chemical attack. Crosslinked polyethylene is commonly used in domestic pipework systems for hot and cold water applications. In this work, crosslinked high-density polyethylene (PEX) composites with spherical graphite (SG) as a reinforcing filler are examined in terms of their mechanical properties. The melt-compounding technique was used to prepare the PEX composites with various SG contents (0.5-5 wt.%). Crosslinking was complete by immersing the prepared materials in a hot bath of 90^{o}C temperature for 24 hours. Tensile tests were conducted to evaluate the tensile properties of neat PEX and its corresponding composites, while the morphology of each specimen's fracture surface was examined using the Scanning Electron Microscopy technique(SEM). Tensile tests results indicate that the elastic modulus of PEX composites increased with increasing SG content (23.6% augmentation for 5 wt% SG). Various micro-mechanical models for composites' elastic behavior were applied to the experimental data. The Takayanagi I two-phase model for low concentrations of SG, and the Takayanagi II two-phase model for higher filler content presented a satisfactory agreement with the elastic modulus of PEX composites suggested that the stress transfer is more efficient in the PEX composites with filler content 1 wt% and below. In contrast, for filler concentrations 2.5 wt% and above, the stress transfer across planes containing the tensile stress is weaker.

Acknowledgements

This research has been co?financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH–CREATE–INNOVATE (project code: T1EDK- 02611).

eP121

TOWARDS SUSTAINABILITY: SYNTHESIS AND CHARACTERIZATION OF NOVEL ADIPIC ACID-BASED UNSATURATED POLYESTER RESINS

Eleftheria Xanthopoulou[1,2], Lazaros Papadopoulos[1,2], Alexandra Zamboulis[1], Christina Kyriakou- Tziamtzi[3], Nikolaos Athanasopoulos[4], Stavros Tsompanidis[4], Electra Papadopoulou[5], Konstantinos Chrissafis[3], Dimitrios N. Bikiaris[1,2]

[1] Department of Chemistry, Aristotle University of Thessaloniki, GR-54124, Thessaloniki, Greece
[2]Chemistry Department, University of Ioannina, P.O. Box 1186, GR-45110, Ioannina, Greece
[3] Physics Department, Aristotle University of Thessaloniki, GR-54124, Thessaloniki, Greece
[4] Phee, 17 Kolokotroni Str., Rio, Patras, GR-26504
[5] CHIMAR HELLAS SA, 15km National Road Thessaloniki-Polygyros, GR-57001 Thessaloniki, Greece

The growing environmental concerns over the excessive emissions of greenhouse gases and the accumulation of synthetic plastics in terrestrial and aqueous recipients have driven the public, academic and industrial awareness towards the production of novel bio-based polymeric materials. Within this frame, unsaturated polyester resins (UPRs) constitute one of the most important polymer classes, thanks to their wide range of processing temperatures, and subsequently, their numerous applications. In general, UPRs are formed by the polycondensation reaction between unsaturated and saturated acids or anhydrides and diols or oxides. The final properties of the resin are mainly affected by the choice and proportion of the starting materials and the unsaturated comonomer, which enables the formation of a three-dimensional network at the sites of unsaturation in the polyester backbone, after a thermally or UV-induced curing, using free-radical initiators. Herein, novel unsaturated polyester resins based on adipic acid, a biobased dicarboxylic acid with a great environmental potential, were prepared. The selected diols, ethylene (EG) or poly(ethylene glycol) (PEG200) were combined with maleic anhydride at several molar ratios for the synthesis of resins and two different reactive diluents, acrylic acid and styrene, were used at the curing stage. Characterization of the synthesized resins was conducted by various complementary techniques, such as carboxyl- and hydroxyl- end-group analysis, nuclear magnetic resonance spectroscopy (NMR) and Fourier-transformed infra-red spectroscopy (FTIR), confirming the success of the polymerization reaction. Furthermore, thermogravimetric analysis was performed to access the thermal behavior of the prepared products, before and after the curing stage. As revealed, by increasing the cross-linking density better thermal stability was achieved. Concerning reactive diluents, acrylic acid resulted in more thermally stable cured products in the case of poly(ethylene glycol)-containing

resins, while styrene appeared to have the same effect on the ethylene glycol-including ones.

Acknowledgements

This research has been co-funded by the European Regional Development Fund (ERDF) and Greek national funds through the Operational Program "Competitiveness, Entrepreneurship and Innovation", EPAnEK 2014-2020, under the call "Aquaculture"-"Industrial materials"-"Open innovation in culture" as well as by private funds (project T6YBP-00006).

eP122

CHARACTERIZATION OF OLIVE-TREE DERIVED BIOMASS FOR SUSTAINABLE WOOD-BASED PANELS

Georgia Michailidou[1], Theopoula Asimakidou[2], Electra Papadopoulou[3], Panagiotis Nakos[3], Konstantinos Chrissafis[2], Dimitrios Bikiaris[1]

[1] Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece
[2] Solid State Physics Section, Physics Department, Aristotle University of Thessaloniki, Thessaloniki, Greece
[3] CHIMAR HELLAS SA, 15 km Nationalroad Thessaloniki-Polygyros, 57001 Thermi, Thessaloniki, Greece

At the dawn of the 21st century, consumers are in demand of more environment friendly products and this demand spans from more ecological cars to greener packaging materials and garments made of recycled fibers. In the field of furniture and interior constructions, this trend is expressed by a turn towards wood-based products instead of plastic. More sustainable products can be manufactured if wood is replaced by lignocellulosic materials recovered from agricultural wastes. In this context, the present project focuses on the valorization of wastes from the exploitation of olives and olive trees, *i.e.* small branches of olive trees, olive leaves and olive-pomace. The olive branches will be used to replace virgin wood for particleboard production, while the leaves and olive pomace will be incorporated in adhesive mixtures for plywood panels. In parallel, these wastes will be subjected to extraction processes, in order to use the extractable compounds for other value-added applications. The in-depth physicochemical characterization of these agricultural wastes, before and after extraction, to determine their characteristics, the impact of extraction and their suitability for the manufacture of greener particleboards and plywood will be presented in the present communication. Indeed, chemical composition was determined by infra-red spectroscopy and X-ray diffraction analysis, thermal stability was measured by thermogravimetric analysis, morphology was studied by scanning electron microscopy and swelling experiments in water were performed. Overall, the behavior of the biomass derived from agricultural wastes was found appropriate and their use in particleboards and plywood will be further implemented.

Acknowledgements: This research has been co-funded by the European Regional Development Fund (ERDF) and Greek national funds through the Operational Program "Competitiveness, Entrepreneurship and Innovation", EPAnEK 2014-2020, under the call

"Aquaculture"-"Industrial materials"-"Open innovation in culture" (project T6YBP-00161).

eP123

CONTROLLING THE SEPARATION OF GRAPHENE OXIDE SHEETS IN AQUEOUS POLYMER NANOCOMPOSITE SYSTEMS

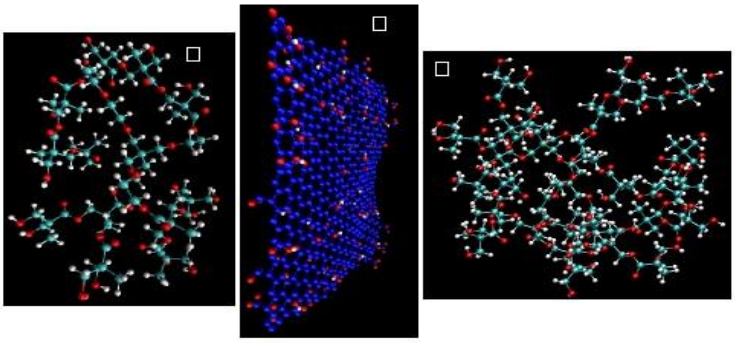
Anastassia Rissanou[1], Ioannis Karnis,[1,2] Fanourios Krasanakis,[1] Kiriaki Chrissopoulou,[1] Kostas Karatasos[3]

[1]Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Heraklion Crete, Greece
[2]Department of Chemistry, University of Crete, Heraklion Crete, Greece
[3]Chemical Engineering Department, Aristotle University of Thessaloniki, Thessaloniki, Greece

Graphene-based nanocomposite membranes are considered among the most promising materials for nanofiltration purposes, including water purification and desalination[1]. However, there are many challenges to address before commercialization become possible. Apart from issues related to thermal and mechanical stability, selectivity of the membranes to different pollutants (e.g, wastewater products, heavy metals etc) appears to be crucial for the optimization of their performance. To this end we have studied systems comprised by Graphene Oxide (GO) nanosheets and hyperbranched molecules of different generations, to assess the role of different parameters such as the size and the number of functional groups of the polymer, the oxidation pattern of the GO sheets and the polymer concentration, in those morphological details of the formed membranes which essentially control their selectivity. We have employed fully atomistic molecular dynamic simulations, using also input from relevant experimental studies. It was found that variation of the aforementioned parameters was essential towards the control of structural properties, which are directly associated with the selectivity performance of these systems.

This research has been co-financed by Greece and EU (POLYGRAPH, MIS: 5050562)

Y. C. Woo, S.-H. Kim, H. K. Shon and L. D. Tijing, in *Current Trends andFuture Developments on (Bio-) Membranes*, eds. A. Basile, E. Curcio and Inamuddin, Elsevier, 2019, DOI: https://doi.org/10.1016/B978-0-12-813551-8.00028-0, pp. xxv-xlvi.



eP124

POLY (ETHYLENE TEREPHTHALATE) CARBON-BASED NANOCOMPOSITES: A CRYSTALLIZATION AND MOLECULAR ORIENTATION STUDY OF TWISTED FILAMENT YARNS FOR POTENTIAL APPLICATION IN PROTECTIVE TEXTILES

V. F. Alexiou[1], G. A. Voyiatzis[2], G. N. Mathioudakis[2], K. S. Andrikopoulos [1],
I. Kizlaridis [3], V. Polychronos [4], Ch. Fragkogiannis [5], A. Soto Beobide Soto Beobide [2]

[1] Department of Physics, School of Natural Sciences, University of Patras, Patras, Greece
[2] Forth/Ice-Ht, Stadiou Str, Rio-Patras, Greece
[3] Department of Industrial Design and Production Engineering, West Attica University,Greece
[4] Nafpaktos Textile Industry SA
[5] Department of Materials Science, University of Patras, Patra, Greece

The aim of this study lies on the development of flexible smart lightweight textiles for military and civil protection applications. The ultimate goal is the improvement of the current technology and the development of protective clothing (body armors, uniforms, undergarments and gloves) in order to provide greater protection as well as lighter and more flexible clothes. Due to their remarkable physical properties, such as high aspect ratio and excellent mechanical strength, carbon nanotubes (CNTs) are regarded as ideal reinforcing fillers in high performance polymer nanocomposites.[1] The influence of CNTs is apparent on the crystallization and the orientation of the composite upon processing, since these parameters impact on the final mechanical properties of the nanocomposite yarns.[2] In cooperation with Souris SA (GR) and ZM Makina Tekstil (TR), fully oriented multiwall carbon nanotubes (MWCNTs) reinforced polyethylene terephthalate (PET) yarns have been industrially prepared by melt-extrusion. These yarns were further weaved according to different fabric motifs and several layers of these fabrics were stitched together. In the present study, these protective panels have been assessed at the molecular level by several methods before and after ballistic and stab resistance tests, performed at AITEX (ES). More precisely, microscopic (e.g. SEM) and spectroscopic (e.g. polarized micro-Raman) methods have be applied to both “visualize” and identify the effect of the resistance tests at all level of layered protective textile panels. The corresponding structural changes could be further correlated, *via* modeling, with mechanisms related to the response of the materials to the bullet and knife impact, thereby acting as a feedback towards the optimization of the related production processes.

- [1]Dresselhaus MS, Dresselhaus G and Avouris P. Carbon nanotubes: synthesis, properties and applications. Berlin: Springer-Verlag, (2001).
- [2]Alexiou V., Mathioudakis G., Andrikopoulos K., Soto Beobide A. and Voyiatzis G. A., *Polymers* ,**12**, 2626 (2020).

Acknowledgment: This research has been financed by the European Union- European Regional Development Fund under the Action "Promotion of Translational Research Projects for Small and Medium Enterprises - Year 2018", which is part of the Operational Program "Western Greece 2014-2020 (MIS 5032900-PROTECT).

eP125

NANOCOMPOSITE POLYPROPYLENE DRAWN FIBERS WITH VARIOUS INORGANIC FILLERS

Costas Tsioptsias[1], Kontstantinos Leontiadis[1], Evangelos Tzimpilis[1], Kontstantinos Karatasos[1], Costas Panayiotou[1], Ioannis Tsivintzelis[1]

[1] Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece

Polypropylene (PP) is one of the most popular thermoplastics, while almost one third of its production is related to polymer fibers. The enhancement of mechanical and thermal properties of PP fibers is mainly performed using two routes, i.e. drawing, which induces the alignment of polymer chains in the drawing direction, and the introduction of (nano) fillers in the polymer matrix.

In this study, composite drawn PP fibers were prepared using four different fillers, i.e. talc, attapulgite, wollastonite and single wall carbon nanotubes (SWNT), and two additives, i.e. a phenolic type antioxidant and PP grafted with maleic anhydride (PP-g-MA) as compatibilizer. The mechanical and thermal properties of the obtained fibers were investigated using tensile tests, differential scanning calorimetry and thermogravimetric analysis, while the interactions of additives with the polymer matrix were studied using FTIR spectroscopy.

Composites with attapulgite showed the poorest mechanical properties, while for the rest of the fillers optimization was carried out, based on the Box-Behnken design of experiments (DoE) method and using the draw ratio, the filler and the compatibilizer content as design variables. The results revealed that the draw ratio is the most important factor for the enhancement of tensile strength followed by the filler content. A linear relationship between draw ratio and tensile strength, until a maximum value, was observed. However, in some cases, the surface response analysis revealed nonlinear correlations between design and response. It was found that this nonlinearity arises from multiple and competitive effects between the various additives. More specifically, it was found that in some cases the used antioxidant acts also as weak PP-filler compatibilizer, while the used compatibilizer (PP grafted with maleic anhydride) facilitated the dispersion of the antioxidant and, thus, promoted the thermal protection of the polymer PP properties during the extrusion thermal treatment. Finally, it was observed that the composites with needle-like fillers (wollastonite and SWCNT), without the use of PP-g-MA as compatibilizer, yielded the best results, This observation is, probably, related to their geometry, since it has been reported that during drawing the needle-like particles with high aspect ratio align along the axis of PP chain alignment.

Acknowledgements: Plastika Kritis S.A. are gratefully acknowledged for the kind supply of the used masterbatches, and Thrace NonWovens & Geosynthetics for the fruitful discussions on the results.

This research has been co?financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call INDUSTRIAL MATERIALS (project code: T6YBP-00035).

eP126

PHYSICOCHEMICAL CHARACTERIZATION OF CATIONICALLY MODIFIED COTTON TEXTILES BY BIFUNCTIONAL POLYMERS FOR ECOFRIENDLY IMPROVEMENT OF THEIR DYEING AFFINITY

Konstantinos Papapetros[1,3], Konstantinos Andrikopoulos[2,3], Labrini Sygellou[3],
Loukia Tsimpouki[4], Charalampos Anastasopoulos[4], Georgios Bokias[4],
Joannis Kallitsis[4], Amaia Soto-Beobide[3], George Voyiatzis[3]

[1] Department of Chemical Engineering, University of Patras, Patras, GR-265 04, Greece
[2] Department of Physics, University of Patras, Patras, GR-265 04, Greece
[3] Institute of Chemical Engineering Sciences (ICE-HT) & Foundation for Research & Technology-Hellas (FORTH, Stadiou Str., Rio-Patras, GR-265 04, Greece,
[4] Department of Chemistry, University of Patras, Patras, GR-265 04, Greece

Cotton is one of the predominant raw materials in the textile industry. One of the most demanding procedures for the textile industry is dyeing of cotton fabrics with reactive dyes since traditional dyeing processing leads to substantial economic and environmental impacts. Through cationic modification of the cotton surface, dyeing affinity can be significantly improved, while the discharge of a highly colored and saline dyebath is avoided. In fact, in traditional dyeing processes high electrolyte concentrations, such as sodium chloride, are needed to overcome the repulsive forces between the negative charges of cellulose fibers surface and the similarly charged reactive dyes.

Within this context, the present study focuses on the water-based modification of cotton fabrics with adequately designed bifunctional water-soluble copolymers, aiming at a) the covalent attachment of the polymer on the fabric surface and b) the charge inversion of cotton fabrics' surface, allowing for a highly effective dyeing process, bypassing the use of electrolytes. The modification of cotton with a series of water-soluble cationic copolymers and the dyeing of the thus-modified cotton fabrics through water-based procedures under alkaline conditions at ambient temperature without the use of electrolytes were followed by a variety of physicochemical and surface techniques. Molecular characterization of the modified fabrics achieved by application of Raman spectroscopy, molecular characterization of the dye-polymer subsystems by using ATR-IR spectroscopy, as well as XPS spectroscopy revealed the physicochemical processes associated with the modification and dyeing of cotton fabrics.

The results have shown that by using specific bifunctional copolymers, the dyeing affinity of cotton textiles was increased, by achieving chemical bonding between the cotton substrate and the copolymer, prior to the electrostatic attraction of the anionic dye molecule by the polymer cationic site.

Acknowledgement: This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH–CREATE–INNOVATE (project code: T1EDK- 03073)»

eP127

ANTIBACTERIAL POLYMER COATINGS ON FLEXIBLE SUBSTRATES

**Nikolaos Konios[1], Maria Kaliva[1], Eleni Ouranou[2], Dimosthenis Chochlakis[2],
Anna Psaroulaki[2], Maria Vamvakaki[1]**

[1] Department of Materials Science and Technology, University of Crete, Crete, Greece
[2] Department of Medicine, University of Crete, Crete, Greece

Bacterial infections in food comprise a major threat for public health. Ensuring food safety has always been a challenge and therefore, intensive research has been devoted to successfully control microbial growth in food packaging [1]. Recent scientific advances involve the coating of common food packaging materials, including polyethylene and polypropylene, with antimicrobial, non-toxic polymers [2,3]. In the present work, water-soluble natural polymer derivatives were employed to coat flexible food packaging films, and confer them contact-active, antibacterial properties [4]. The coatings, with thickness in the micrometer range, were prepared using Mayer rods, whereas their stability and adhesion onto the substrate was achieved using a crosslinker to chemically link the polymer chains among them and onto the substrate. Fourier Transform Infrared Spectroscopy and Field-Emission Scanning Electron Microscopy verified that both coatings were stable and remained intact onto the polyethylene films after one month immersion in water. The coated films presented enhanced antibacterial activity against a range of food-related bacteria, including *Escherichia Coli, Lysteria Monocytogenes* and *Staphylococcus Aureus*. Notably, the coatings increased the oxygen and water vapour barrier properties of the polyethylene films, without affecting their mechanical strength. The above results suggest that the developed coatings are promising for use in active food packaging technologies.

References

1. Harrison, L.M.; Balan, K.V.; Babu, U.S. *Nutrients* **2013,** 5, 1801.
2. Theapsak, S.; Watthanaphanit, A.; Rujiravanit, R. *ACS Appl. Mater. Interfaces* **2012,** 4, 2474.
3. Amri F.; Husseinsyah S.; Hussin K. *Compos. - A: Appl. Sci. Manuf.* **2013,** 46, 89.
4. Manouras, T.; Koufakis, E.; Vasilaki, E.; Peraki, I.; Vamvakaki, M. *ACS Appl. Mater. Interfaces* **2021**, *13,* 17183

Acknowledgments: This research has been co?financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code: T1EDK-04052).

eP128

CHARACTERIZATION AND SELF-HEALING PROPERTIES OF PUDS INCORPORATING GO AND HYDROPHILIC CLAYS

Evangelia Giannakaki[1,2], Antigonos Theodorakis[1,2] , Minas M. Stylianakis [1],
Athina Fidelli[3], Poppy Krassa[3], Kiriaki Chrissopoulou [1] , Spiros H. Anastasiadis [1,2]

[1]Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas Heraklion Crete, Greece
[2]Department of Chemistry, University of Crete, Heraklion Crete, Greece
[3]Megara Resins, Anastassios Fanis, S.A. Megara, Greece

In the last decade, waterborne polyurethanes (WBPUDs) have dominated against the traditional solvent-based ones towards the development of environmentally friendly coatings, plasticizers, adhesives and so on [1,2,3]. Their versatile properties in terms of soft and hard segments tunability, thermal stability, high flexibility, strong adhesion, mechanical stability and self-healing, mainly due to host–guest interactions and the presence of hydrogen bonds, attracted the interest of many researchers who focused on their improvement through chemical modification, doping etc. Graphene derivatives are widely used to reinforce the properties of WBPUDs, concerning on the mechanical, thermal and self-healing ones [4,5]. In this frame, graphene oxide (GO) synthesized by a modified Hummers method, and a hydrophilic clay of the structure Na^+MMT were incorporated within the polyurethane matrix to develop nanocomposites in different compositions [6]. It should be noted that polyurethane dispersions based on different polycarbonate and polyether polyols were used as the host material. Finally, the prepared nanocomposites were thoroughly characterized through conventional spectroscopic, microscopic, surface and thermal analysis techniques, as well.

Acknowledgements: This research has been supported by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH CREATE INNOVATE (SELFNANOPUD, MIS: 5067612).

References

[1] T. Wan, D. Chen. J Mater. Sci., 2017, 52, 197.
[2] J.V. Nardeli, C.S. Fugivara, E.R.P., Pinto, W.L. Polito, Y. Messaddeq, S. José Lima Ribeiro, A.V. Benedetti. Polymers, 2019, 11, 1890.
[3] L. Xia, J. Shi, K. Wu, M. Lu. React. Funct. Pol., 2020, 148, 104482.
[4] X. Luo, Y. Wu, M. Guo, X. Yang, L. Xie, J. Lai, Z. Li, H. Zhou. J. Appl. Polym. Sci., 2021, 138, e50827.
[5] T. Wan, D. Chen. Prog. Org. Coatings, 2018, 121, 73.
[6] F. Alizadegan, S. M. Mirabedini, S. Pazokifard, S. G. Moghadam, R. Farnood, Prog. Org. Coatings, 2018, 123

eP129

IMPACT OF INORGANIC NANOADDITIVES ON THE PROPERTIES OF POLYURETHANE DISPERSIONS

Evangelia Giannakaki [1,2], **Ioanna Karamitrou** [1,2], **Minas M. Stylianakis** [1], **Athina Fidelli**[3], **Poppy Krassa**[3], **Kiriaki Chrissopoulou** [1] , **Spiros H. Anastasiadis** [1,2]

[1]Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Heraklion Crete, Greece
[2]Department of Chemistry, University of Crete, GR-71003 Heraklion Crete, Greece
[3]Megara Resins, Anastassios Fanis, S.A. Megara, Greece

The incorporation of inorganic nanoparticles (NPs) within a polymeric matrix in various concentrations is a common strategy to adjust the properties of the prepared nanocomposites [1-4]. In addition, the overall behavior of the nanohybrids is strongly influenced by the kind and/or the size of the additives. In the current work, silica (SiO_2) NPs of different size have been incorporated within three waterborne polyurethanes (WBPUDs) in various concentrations. More specifically, LUDOX (LS, R=7 nm) and SNOWTEX (ZL, R=67 nm) SiO_2 NPs were added at different compositions, covering the whole possible range of polymer/inorganic. All WBPUDs were prepared according to the prepolymer method, using isophorone diisocyanate (IPDI), poly(ether-ester) polyol (NCO/OH ~ 1.4), dimethylo propionic acid (DMPA), ethylene diamine (EDA) and triethylamine (TEA), as neutralizing agent. The first one consists of pure polyurethane, while the second and the third are hybrid ones, that have been modified with alkyd and/or acrylic groups, respectively. The dispersion of the NPs as well as the properties of the resulting nanocomposites were investigated by spectroscopic, microscopic and thermal analysis techniques and the behavior was compared with the respective one of the pristine polymers. The effect of the nanohybrid composition, the NPs size as well as the PUDs/NPs interactions on the measured properties were evaluated.

Acknowledgements: This research has been supported by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH CREATE INNOVATE (SELFNANOPUD, MIS: 5067612).

References

[1] V. Mittal, Macrom. Mater. Eng. 2014, 299, 906.

[2] H. Papananou, E. Perivolari, K. Chrissopoulou, S. H. Anastasiadis, Polymer 2018, 157, 111.

[3] R. Behnam, H. Roghani-Mamaqani, M. Salami-Kalajahi. J. Therm. Anal. Calorim. 2019, 135, 3311.

[4] H. Shirvani, S. Maghami, A. Pournaghshband Isfahani, M. Sadeghi. Membranes 2019, 9, 82.

eP130

MACROCYCLIC SELF-ASSEMBLED CAGES TO ROTAXANES CONSISTING OF FUNCTIONALIZED BODIPY-DYES FOR LIGHT-HARVESTING AND CONTROLLED ENERGY TRANSFER

Theodora Menidiati[1] , Adelajda Shahu[1], Vyron Sotirios Petrakis[1],George Pistolis*,[2]

[1]National and Kapodistrian University of Athens , Department of Chemistry
, Panepistimiopolis Zografou, 157 84, Greece

*Molecular Engineering of Photofunctional Supramolecular Nanostructures. Institute of Nanosciences and Nanotechnology N.C.S.R. “Demokritos”, Ag. Paraskevi, 15310, Athens, Greece

Precise donor–acceptor supramolecular synthesis and in particular coordination-driven self-assembly provides a sophisticated and time-saving way to construct compact and stiff metallosupramolecular architectures with well-defined shape and size [1]. When the metal atom is coordinated directly to the electronically conjugated backbone of a fluorophore, it is observed that the excitation decays nonradiatively to the ground state. Our team has outreached the obstacle of fluorescence quenching of the local emissive state of the organic fluorescent ligand by engineering its connection topology with the metal center to form [2+2] rhomboidal [2] and [6+6] hexagonal [3] macro cyclic host nanoarchitectures.
The current work is focused on the construction of 3D metallosupramolecular cages and their threaded architectures (Rotaxanes) onto a suitable polymeric chain via self-assembly with a naked Pd(II) or Pt(II) center of suitable chromophoric building blocks bearing the well known BODIPY dyes (*Figure 1*).

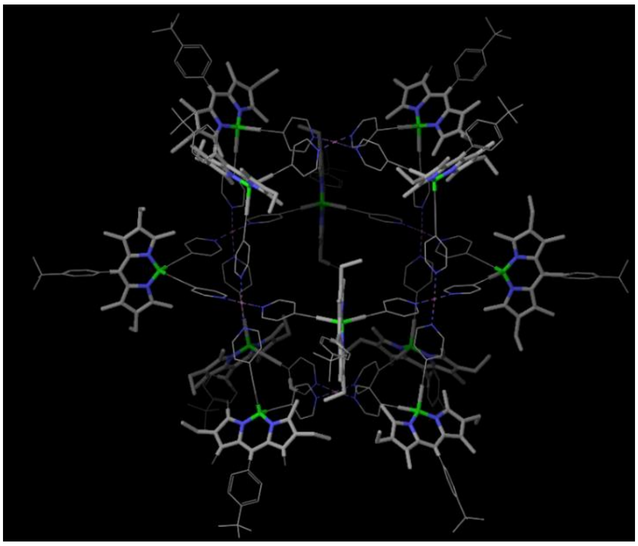


Figure 1: Schematic representation of the self-assembled M_6L_{12} polyhedron.
M: Pd(II), or Pt(II)
L: BODIPY dye functionalized at the meso position with a phenyl-*tert*-butyl group

1. A. Kaloudi-Chantzea, N. Karakostas, C. P. Raptopoulou, V. Psycharis, E. Saridakis, J. Griebel, R. Hermann and G. Pistolis*, J. Am. Chem. Soc.* 132 (2010) 16327–16329
2. A. Kaloudi-Chantzea, N. Karakostas, F. Pitterl, C. P. Raptopoulou, N. Glezos and G. Pistolis, *Chem. Commun.* 48 (2012) 12213-12215
3. Xuzhou Yan , Timothy R. Cook , Pi Wang , Feihe Huang and Peter J. Stang , *Nature Chem.* 7 , (2015) 342-348
4. Zhixuan Zhou , Cory E. Hauke , Bo Song , Xiaopeng Li , Peter J. Stang and Timothy R. Cook , *J. Am. Chem. Soc.*,141, 8, (2019) 3717–3722

eP131

STIMULI-RESPONSIVE POLYPEPTIDE HYDROGELS FOR TARGETED DRUG DELIVERY AGAINST PANCREATIC CANCER

Maria Kasimati[1], Panagiota G. Fragouli[2], Hermis Iatrou[1]

[1]Industrial Chemistry Laboratory, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece

[2]University of West Attica, DIDPE, Laboratory of Dyeing, Finishing, Dyestuffs and Advanced Polymers, 250 Thivon Street, 12244 Athens, Greece

Injectable hydrogels constitute a very promising system, in order to achieve effective and selective delivery of chemotherapeutic drugs to cancer cells. The drug carrier should present multiple functions, so as to implant the formulation into the body without surgical operation, to prolong the drug release kinetics from the hydrogels, and to expand the type of drugs which can be delivered. The only materials that can be organized at such a hierarchical level, besides natural proteins, are polypeptides especially due to their sensitive stimuli response. Most of these systems take advantage of the higher temperature and lower pH of the malignant tissue. Thus, the polymer-drug mixture, when injected it is transformed from liquid to hydrogel within the tissue, and releases the drug slowly in a controlled manner. Polypeptides are composed of repeating amino acids, connected by an amide bond and they adopt the 3D structures found in natural proteins, such as α-helices and β-sheets. In this work, a series of different polypeptide hydrogels containing poly-histidine, poly-lysine, poly-sarcosine and poly-L-glutamic acid have been synthesized. For this reason, the Ring Opening Polymerization of the N-Carboxyanhydrides of the corresponding amino acids was contacted. Hydrophobic poly-histidine provides pH and temperature responsiveness in the hydrogel, which in combination with the hydrophilic blocks of the poly-lysine and poly-sarcosine, results in an effective drug delivery system. In addition, hydrophobic poly-L-glutamic acid, plays a vital role on the effective encapsulation of the anticancer drug, into the hydrogel network. Size exclusion chromatography, proton nuclear magnetic resonance and infrared spectroscopy were employed for the characterization of the synthesized polypeptides. Circular dichroism was carried out to study the correlation between the secondary structure, pH and temperature. All these techniques demonstrate the promising properties of these well-defined materials.

eP132

SQUARED PLGA MICROPLATES AS INJECTABLE DEPOT FOR THE MANAGEMENT OF POST-TRAUMATIC OSTEOARTHRITIS

Agnese Fragassi[1], Martina Di Francesco[1], Sean K. Bedingfield[2], Juan M. Colazo[2], Valentina Di Francesco[1], Fang Yu[2], Miguel Ferreira[1], Daniele Di Mascolo[1], Craig Duvall[2], Paolo Decuzzi[1]

[1]Fondazione Istituto Italiano di Tecnologia, Italy
[2]Vanderbilt University, Tennessee

Introduction: Osteoarthritis (OA) is a chronic inflammatory joint disease that affects population across all ages. It is caused by progressive breakdown of joint cartilage and underlying bone, resulting in joint pain, function loss and, eventually, permanent disability. To date, there is no disease-modifying drug available to reverse the progression of the OA and conventional therapies are solely palliative, providing only a temporary relief from the symptoms.

Methods: In that light, a top-down strategy was used for synthetizing squared-poly (D,L-lactide-co-glycolide) (PLGA) microPlates (µPLs) [1, 2] for prolonged release of anti-inflammatory molecules, such as Dexamethasone (DEX) and matrix metalloproteinase 13 (MMP-13) RNA interference nanoparticles (siMMP13-NPs). A full characterization of the physical-chemical, mechanical and pharmacological properties of both formulations was performed. Also, their therapeutic efficacy was assessed in vivo in a mechanically-induced OA mouse model (PTOA).

Results: µPLs showed an edge length of 20 µm and a height of 10 µm. (**Figure 1**b) They displayed a Young Modulus of about 3.1 ± 0.9 MPa, similar to the cartilage one. In addition, µPLs provided a sustained release of DEX and siMMP13-NPs in biologically relevant volumes. DEX-loaded µPLs decreased inflammation in vitro on LPS-stimulated chondrocytes (ATDC5) and in vivo on PTOA mouse model (Figure 1c) At the same time, siMMP13-NPs loaded µPLs provided both in vitro and in vivo gene silencing, reaching 70% of gene silencing efficiency after 4 weeks in the same animal model (**Figure 1**d,e).

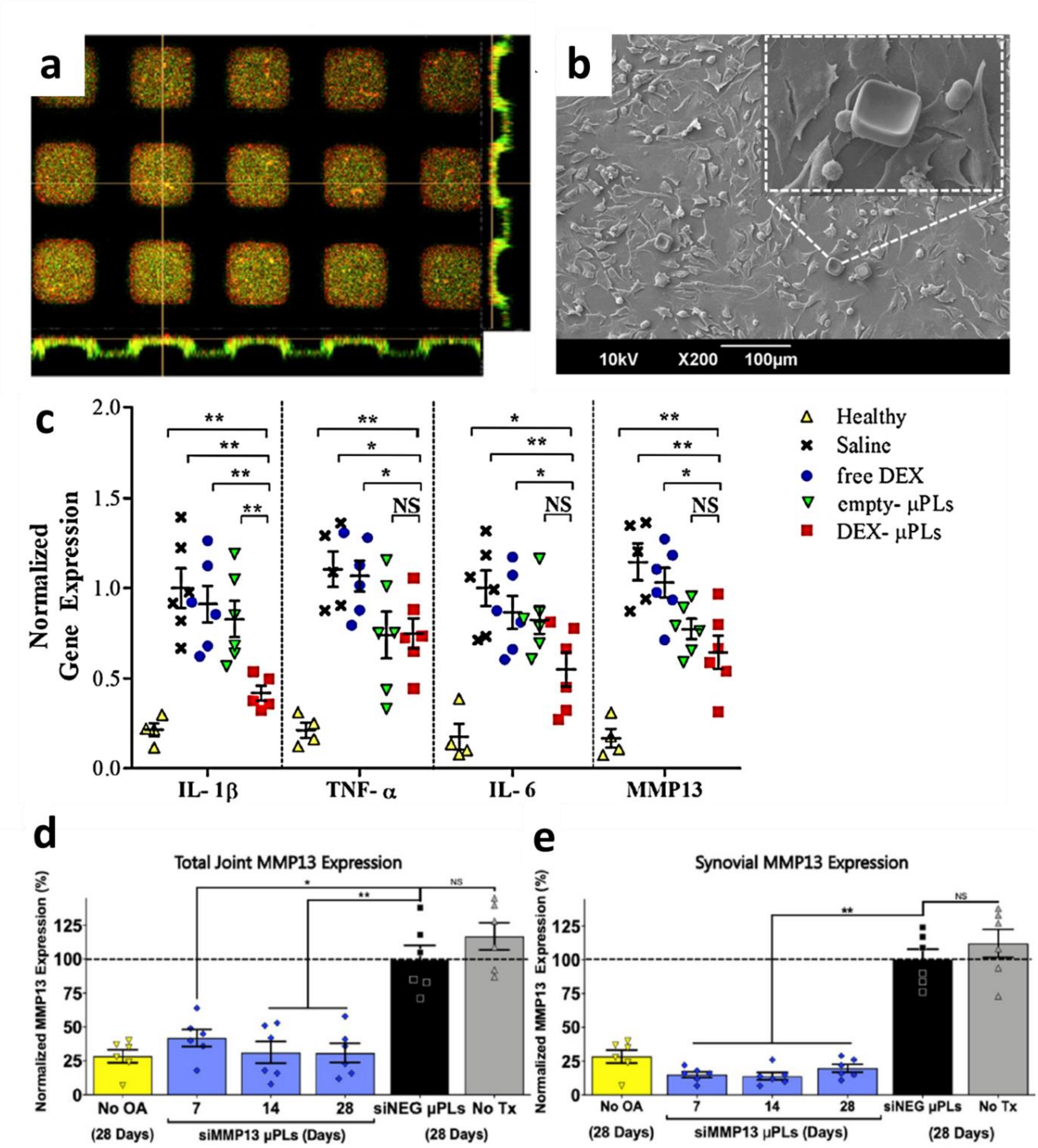


Figure 1. a. False-color SEM image of a µPL (red) deposited and not internalized over a layer chondrocytes (green). **b.** Confocal microscopy image of the PVA template containing Cy5-siNPs (red) dispersed within PLGA paste (curcumin, CURC, only added for these images to enable PLGA visualization as yellow-green fluorescence). **c.** In vivo expression of IL-1β, TNF-α, IL-6, and MMP-13 measured by TaqMan qPCR (for each treatment groups n = 6, while for the healthy group n = 4). **d.** MMP13 gene expression in combined cartilage over time after a single siMMP13-µPL treatment in mouse PTOA model. **e**. MMP13 gene expression in medial synovial tissue alone over time after a single siMMP13-µPL treatment in mouse PTOA model.

Conclusions: In conclusion, μPLs can effectively act as intra-articular depots for the local treatment of OA, to reduce inflammation and pain and to improve mechanical properties of the OA-affected joint.

References

[1] M. Di Francesco, S.K. Bedingfield, V. Di Francesco, J.M. Colazo, F. Yu, L. Ceseracciu, E. Bellotti, D. Di Mascolo, M. Ferreira, L. E. Himmel, C. Duvall, and P. Decuzzi. *ACS Appl. Mater. Interfaces* **2021**, 13, 27, 31379–31392.

[2] S.K. Bedingfield, J.M Colazo, M. Di Francesco, F. Yu, D.D. Liu, V. Di Francesco, L. E. Himmel, M. K. Gupta, H.Cho, K. A. Hasty, P. Decuzzi, and C.L. Duvall. *ACS Nano,* In press.

eP133

REGENERATING THE DIABETIC HEART AND KIDNEY BY USING STRESS-SPECIFIC THYROID HORMONE NANOCARRIERS

Skourtis Dimitris, Maria Kasimati, Hermis Iatrou

Industrial Chemistry Laboratory, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece

Diabetic cardiomyopathy (DC) and diabetic nephropathy (DN) are two major complications of diabetes that account for more than two thirds of deaths in the diabetic population. The primary hallmarks of these conditions are cell dedifferentiation, hypertrophy and maladaptive proliferation through the reactivation of classic developmental pathways. Preclinical and early clinical studies have indicated that thyroid hormone (TH) treatment could be a potential strategy for reversing or preventing this maladaptive recapitulation of organ development. However, there is a major obstacle to translating this strategy into clinical practice: the high doses of TH that are needed to induce tissue repair and regeneration may cause several adverse effects. To maximize the therapeutic efficacy of TH, and minimize its adverse effects, we aim to develop innovative nanoparticle-based drug delivery systems that will be able to target and deliver L-triiodothyronine (T3) to diabetes-injured cells in order to restore cardiac and renal function and hopefully regenerate damaged tissue. Using nanotechnology we develop injectable modified PEG-PBLG NPs, that will be functionalized with a Transient Receptor Potential Cation Channel Subfamily C Member 6 (TRPC6)-specific inhibitor – to specifically target stressed cells – and loaded with T3. For this reason, Ring Opening Polymerization was conducted to synthesize PEG-PBLG copolymer and a series of modifications followed in order to encapsulate T3 in the next stage. Size exclusion chromatography, proton nuclear magnetic resonance and infrared spectroscopy were employed for the characterization of the synthesized copolymer and dynamic light scattering and circular dichroism for the study of the properties of the corresponding nanoparticles.

eP134

OPTIMIZED PROCESS OF PLA PRODUCTION FROM FOOD WASTE

E. Voutyritsa,[1] C. I. M. Baltzaki,[1] A. Theodorou,[1] C. Gryparis[1], A. Maragkaki[2], C. Tsobanidis[3], T. Manios[2] , K. Velonia[1]

[1] *Department of Materials Science and Technology, University of Crete, University Campus Voutes, 70013 Heraklion, Crete, Greece*

[2] *Department of Agriculture, Hellenic Mediterranean University, Estavromenos, 71410 Heraklion, Crete, Greece*

[3] *ENVIROPLAN SA, 23 Perikleous & Iras Str, 15344 Gerakas Athens, Greece*

The society is facing tremendous challenge due to the extensive use of petrol based plastics and the huge amount of disposal which can be environmentally harmful,[1] thus requiring special treatment in order to eliminate their negative effect. If global food loss and waste could be annually considered as a whole country, then it would be the third-largest CO_2 emitter (after the US and China, according to FAO, 2013). Apart from prevention and reduction through education and policy, advanced technology also plays a crucial role in order to facilitate recycling in food waste management. In the past decades, many research groups have described the conversion of different kinds of food waste including molasses, bakery waste, water waste, and sugar cane into value-added products, such as lactic acid. Lactic acid (2-hydroxypropanoic acid), is an organic compound widely used in food, pharmaceutical and chemical industry, which can be polymerized to form biodegradable and compostable polylactic acid (PLA), a potential substitute for petroleum-derived plastics. The present study particularly focuses on the optimization of PLA production from food-waste material[2] for the development of a scalable synthetic process. More specifically, a sequence consisting of fermentations to convert endogenous D, L-lactic acid from mashed foods to optically pure L-lactic acid, followed by purification of L-lactic acid by ammonium lactate esterification and hydrolysis of the isolated ester was utilized for monomer isolation, while a azeotropic polycondensation was developed in order to achieve the ultimate goal, which is the optimization of bioplastic production with respect to energy consumption. The yields and limitations of this process will be discussed.

This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH -CREATE - INNOVATE (project code: T1EDK-02746).

References

1. Jambeck, J. R.; Geyer, R.; Wilcox, C.; Siegler, T. R.; Perryman, M.; Andrady, A.; Narayan, R.; Law, K. L. *Science*, **2015**, 347, 768-771.
2. Sakai, K.; Taniguchi, M.; Miura, S.; Ohara, H.; Matsumoto, T.; Shirai, Y. *J. Ind. Eco*l. **2003**, *7*, 63-74.

Keywords*: Waste management, L-Lactic acid, fermentation, bioplastic*