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University of Ioannina

Department of Materials Science & Engineering

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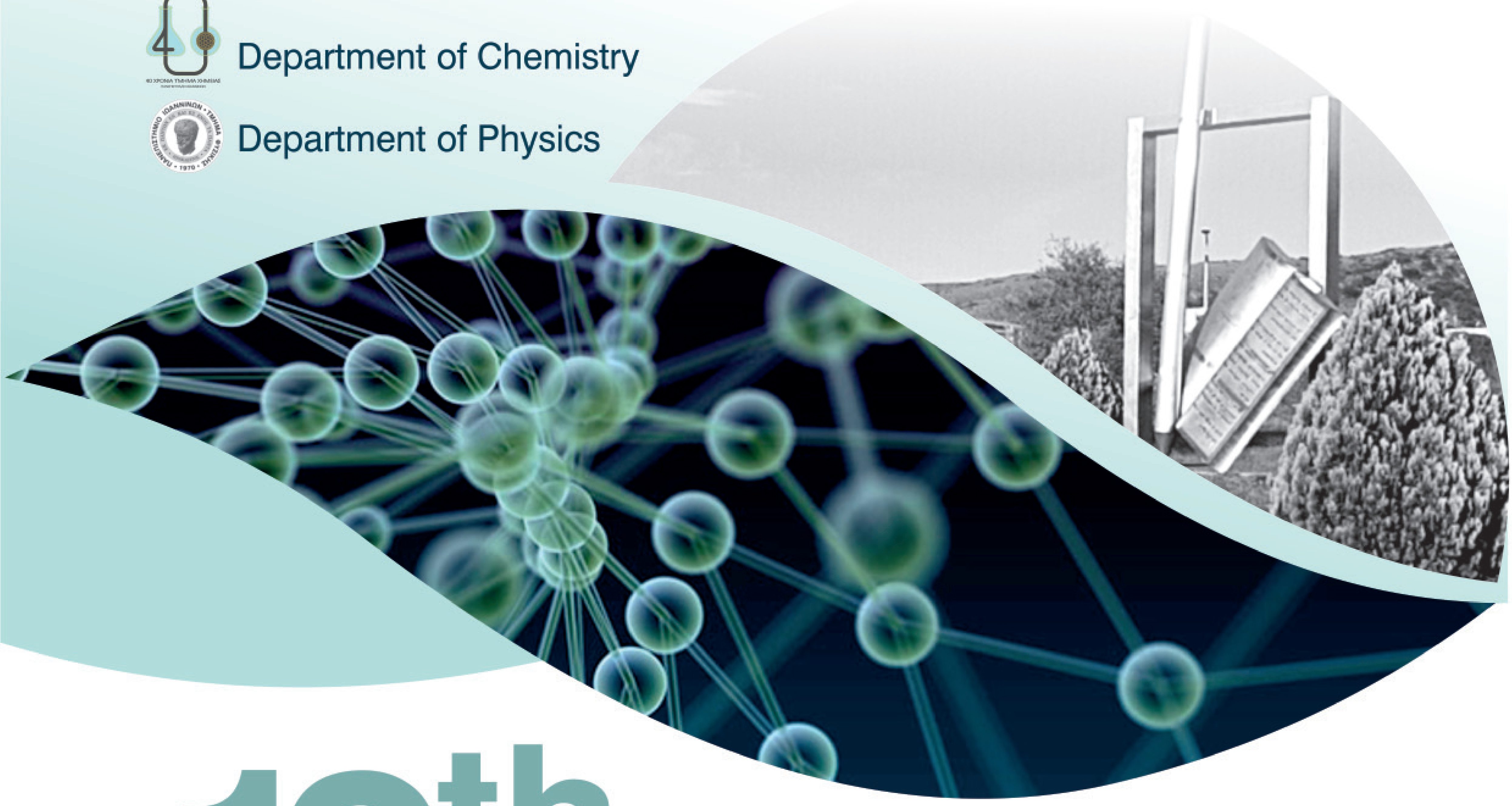
Department of Physics

Under the auspices:
Hellenic Polymer Society

European Polymer Federation



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“Georgios Mylonas”

ABSTRACT BOOK

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Recent Developments in Polymer Synthesis and Characterization Methods

PLENARY ORAL

RING-BASED MACROMOLECULAR ARCHITECTURES: THEIR IMPORTANCE IN POLYMER PHYSICS

Nikos Hadjichristidis
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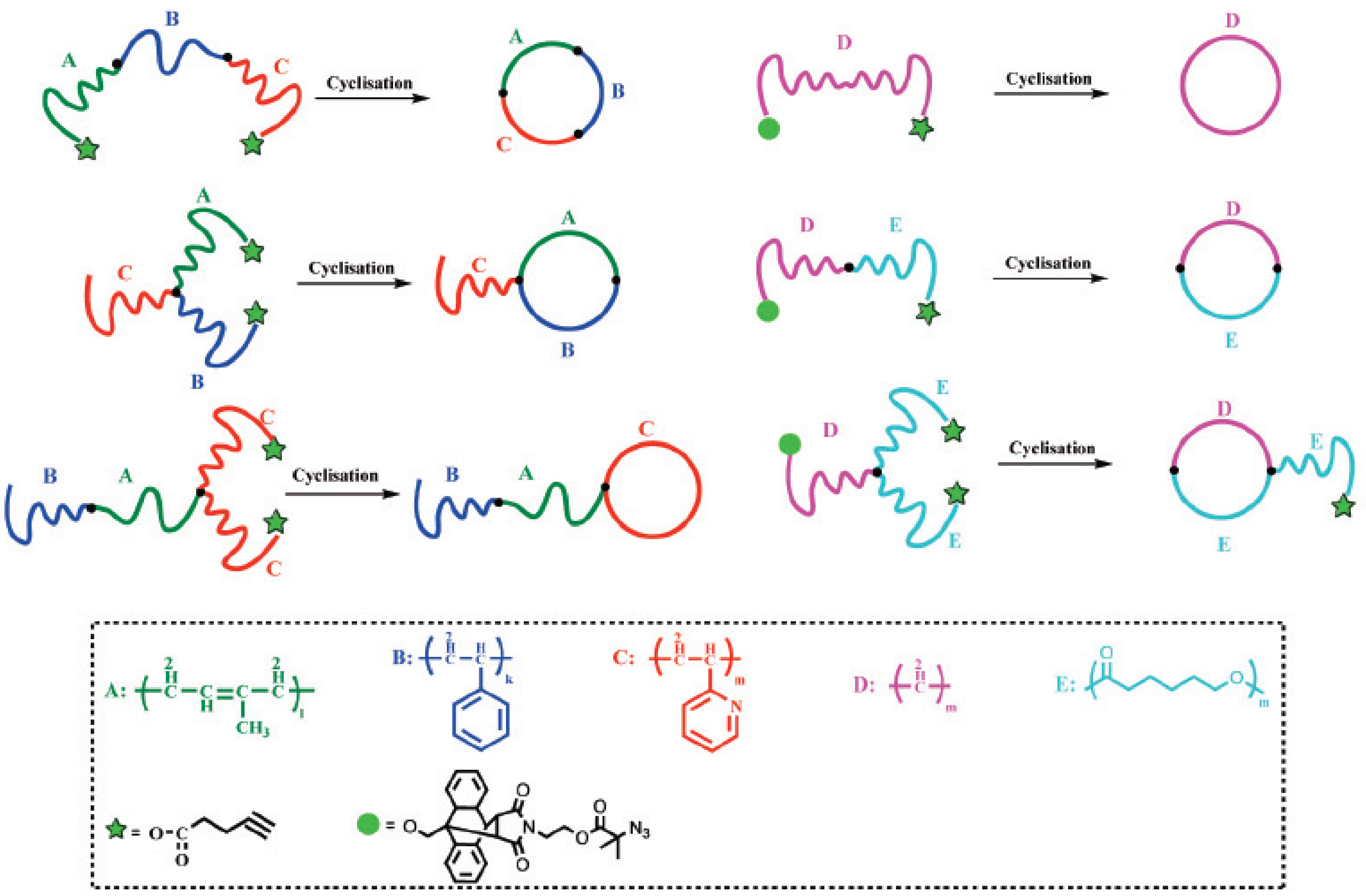
A straightforward strategy for the synthesis of ring-based homo/co/terpolymers of styrene, isoprene and 2-vinyl pyridine, will be discussed. The general approach involves the synthesis of the corresponding OH-terminated precursors (linear and star), transformation of the OH to alkyne groups, by esterification with pentynoic acid and subsequent intramolecular ring closure using Glaser coupling under high dilution conditions[1]. In addition, by combining polyhomologation[2], Diels-Alder and "click" chemistry, we were able to synthesize polyethylene-based ring and tadpole homo/copolymers[3,4]. Representative examples are given in Scheme 1.

The first exploratory TEM results showed the tremendous influence of the cyclic structure on the microphase separation of co/terpolymers[1,5]



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PLENARY ORAL

ANIONIC COPOLYMERIZATION OF CO_2 WITH EPOXIDES AS A NEW APPROACH FOR THE SYNTHESIS OF POLYCARBONATES

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Carbon dioxide (CO_2) is an abundant, inexpensive, and non-toxic renewable C1 feedstock that is only used in a limited number of product-yielding reactions due to its low reactivity. After the discovery by Inoue *et al.* of the copolymerization of CO_2 and epoxides by diethyl zinc [1] a number of efficient transition metal catalysts functioning by coordinative chemistry have been developed: in the latter case the polymerization occurs by co-ordination of the epoxide monomer, followed by successive insertions of epoxides and CO_2 until a transfer reaction takes place producing aliphatic polycarbonate chains. [2-5]

In the present lecture we will show that CO_2 and epoxides can be copolymerized *anionically* using classical alkali metal *anionic* initiators or even metal-free *anionic* initiators, without resorting to transition metal-based coordinative chemistry used so far. This opens up new horizons for the utilization of CO_2 in its *anionic* copolymerization with epoxides: [6-7]

1) as perfectly defined polycarbonate telechelics can now be prepared for further use as precursors of polyurethanes,[6-7]

2) as very high molecular weight polycarbonates samples can be generated due to the “living” nature of the copolymerization,

3) as diblock and triblock copolymers can be easily obtained and thus thermoplastic elastomers generated by sequential addition of two different epoxides,

4) as various functional polycarbonates can be derived by copolymerizing under “living” conditions functional epoxides with CO_2 . [8]

So far CO_2 has been uniquely used in *anionic* polymerization for carbonation purpose of living carbanionic chains by R. Quirk[9]; we demonstrate here that it can be *anionically* copolymerized with epoxides, provided a Lewis acid is added to specifically activate the epoxide monomer.

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INVITED ORAL

DYNAMIC COVALENT POLYMER NETWORKS COMPRISING FOUR-ARMED STAR POLYMERS CROSS-LINKED WITH ACYLHYDRAZONE BONDS

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Dynamic covalent polymer networks (**DCPN**) represent a rapidly growing class of polymeric networks cross-linked *via* dynamic covalent bonds, and possessing the important properties of self-healing ability, reversibility, and injectability [1]. This lecture will provide an overview of our work on DCPNs consisting of four-armed star polymers end-linked through acylhydrazone bonds. A first study will focus on a hydrophilic poly(ethylene glycol) (PEG) system which could be formed from its components in totally aqueous media over the whole pH range (2.0 – 12.5), and gelation times strongly depending on pH [2]. A subsequent study will involve an amphiphilic DCPN system resulting from the combination of four-armed star homopolymers of PEG and poly(vinylidene fluoride) [3]. These materials could microphase separate in the bulk or in water, and could also be loaded with an ionic liquid to serve as gel polymer electrolytes. Finally, another amphiphilic DCPN system will be presented, composed of four-armed star block copolymers of PEG and poly(propylene glycol), capable of aqueous microphase separation with long-range order.

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INVITED ORAL

TRIBLOCK TERPOLYMERS BY RAFT POLYMERIZATION: SYNTHESIS AND SELF-ASSEMBLY

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Introduction: Triblock terpolymers present an interesting class of polymeric materials due to the formation of complex self-assembled nanostructures in solution and in the solid state, which may be utilized in several nano(bio)technological applications, including nanocarriers of bioactive compounds, nanotemplates and multifunctional films. So far RAFT polymerization has been rather scarcely utilized in the synthesis of triblock terpolymers.

Methods: Amphiphilic and pH and thermo-responsive triblock terpolymers of the types PDMAEMA-b-PLMA-b-POEGMA and PnBA-b-PNIPAM-b-PAA have been synthesized by RAFT polymerization, and molecularly characterized by SEC, NMR and FTIR spectroscopies. Their self-assembly and complexation properties towards lysozyme and DNA have been studied in aqueous media by DLS, SLS, ELS, SANS, TEM and fluorescence spectroscopy.

Results: Characterization results show that the synthetic schemes followed give well-defined triblock terpolymers with relatively narrow molecular weight distributions and predefined compositions and molecular weights. The terpolymers self-assemble in micellar aggregates with their structure and properties being influenced mainly by solution pH, temperature and ionic strength, as a result of the presence of selected responsive and functional blocks. The PDMAEMA-b-PLMA-b-POEGMA terpolymers can act as compaction agents for DNA, whereas PnBA-b-PNIPAM-b-PAA terpolymers can complex with lysozyme, followed by modulation of their thermoresponsive behavior.

Conclusions: Well-defined triblock copolymers with determined sequences of blocks have been synthesized by RAFT methodologies. The terpolymers self-assemble into supramolecular aggregates in aqueous media as a result of the physicochemical parameters of the medium. The terpolymer can act as carriers of nucleic acids and proteins and may find application in drug delivery protocols.

INVITED ORAL

METALLOCENE-MEDIATED CATIONIC POLYMERIZATION OF VINYL ETHERS. A NEW ROUTE FOR THE SYNTHESIS OF STATISTICAL, BLOCK AND GRAFT COPOLYMERS

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The cationic polymerization of ethyl, *n*-butyl, *iso*-butyl and chloroethyl vinyl ether, EVE, BVE, iBVE and CEVE respectivelyη^5-cyclopentadienyl)dimethyl hafnium, Cp_2HfMe_2, or bis(η^5-cyclopentadienyl)dimethyl zirconium, Cp_2ZrMe_2 in combination with either tris(pentafluorophenyl)borate, $B(C_6F_5)_3$, or tetrakis(pentafluorophenyl)borate dimethylanilinum salt, $[B(C_6F_5)_4]^-[Me_2NHPh]^+$, as initiation systems. The evolution of polymer yield, molecular weight and molecular weight distribution with time was examined. In addition, the influence of the initiating system, the monomer and the reaction conditions on the control of the polymerization was studied. Furthermore, statistical copolymers of EVE with BVE were prepared employing Cp_2HfMe_2 and $[B(C_6F_5)_4]^-[Me_2NHPh]^+$ as the initiation system. The reactivity ratios were estimated using both linear graphical and non-linear methods. Structural parameters of the copolymers were obtained by calculating the dyad sequence fractions and the mean sequence length, which were derived using the monomer reactivity ratios. The glass transition temperatures, Tg, of the copolymers were measured by Differential Scanning Calorimetry, DSC, and the results were compared with predictions based on several theoretical models. The kinetics of thermal decomposition of the copolymers along with the respective homopolymers was studied by thermogravimetric analysis within the framework of the Ozawa-Flynn-Wall and Kissinger methodologies. Block copolymers of EVE with BVE and iBVE were synthesized and their micellization behavior was examined in organic selective solvents. Statistical copolymers of BVE and CEVE were synthesized and were employed as scaffolds for the synthesis of graft copolymers bearing poly(ε-caprolactone) or poly(L-lactide) branches by suitable click chemistry.

INVITED ORAL

COOPERATIVE RESPONSE OF TRIPLE-STIMULI SENSITIVE DIBLOCK COPOLYMERS

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Stimuli-responsive, amphiphilic diblock copolymers can self-assemble into different morphologies such as micelles, rods or vesicles in aqueous media. These self-assembled structures undergo reversible or irreversible physical and/or chemical transformations upon exerting external stimuli, such as pH, temperature, ionic strength and others. Of great scientific interest is the morphological reorganization of the self-assembled *nanostructures* driven by chemical or physical means [1-2]. Physical stimuli, such as light irradiation, are particularly attractive because they can be applied remotely and they allow spatiotemporal control, without introducing chemical impurities [3-6]. Research efforts over the last decade have focused on the synthesis and characterization of multi-responsive polymers using robust synthetic approaches, to create synthetic systems capable of responding to multiple stimuli in a controllable and predictable fashion [7]. Herein, triple stimuli-responsive block copolymers have been prepared via the sequential atom transfer radical polymerization (ATRP) of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and the in-house synthesized 1΄-(2-methacryloxyethyl)-3΄,3΄-dimethyl-6-nitrospiro-(2H-1-benzopyran-2,2΄-indoline) (SPMA) monomer [8]. The amphiphilic nature of the PDMAEMA-*b*-PSPMA diblock copolymers led to the formation of spherical micelles in water, comprising a hydrophobic PSPMA core and a hydrophilic PDMAEMA shell. The combination of the pH- and temperature-responsive character of PDMAEMA with the pH-, temperature- and light-sensitive properties of the PSPMA block has resulted in a complex responsive behavior of the copolymer micelles in aqueous solution, when applying three different external stimuli (i.e. light irradiation, pH and temperature). The cooperative response and structural reorganization of the polymeric nanostructures when applying simultaneously two different external stimuli, were studied.

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ORAL

SYNTHESIS AND CHARACTERIZATION OF SUPRAPOLYMERSOMIC STRUCTURES FROM WELL-DEFINED LINEAR PENTABLOCK QUINTOPOLYMERS

Panagiota G. Fragouli[1], **Nikos Hadjichristidis**[2], **Olli Ikkala**[3], **Nikolay Houbenov**[3],
Hermis Iatrou[4], **Johannes S. Haataja**[3], **Vladimir Aseyev**[5], **Rachid Sougrat**[2]
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Through controlled high-vacuum anionic polymerization well-defined model polymers with complex macromolecular architectures having the highest molecular weight, structural and compositional homogeneity can be achieved. Block copolymers allow progressively ever more complex self-assemblies upon involving increasing number of the constituent blocks, where the structures are determined by the block lengths, block-block and block-solvent interactions, interface curvatures, and molecular topologies. To recognize the microphase domains in the complex multiblock copolymer structures using electron microscopy, is stimulus as the number of staining agents and their selectivity is restricted.

Anionic polymerization high vacuum techniques were used to synthesize linear pentablock quintopolymers. Molecular characterization carried out by Size exclusion chromatography, Membrane Osmometry and Nuclear Magnetic Resonance. Differential Scanning Calorimetry was used for the characterization of the precursors and the final polymers. Dynamic Light Scattering and Transmission Electron Microscopy were used for the structure and properties of polymersomes.

The multiblock multicomponent polymers exhibited a high degree of molecular and compositional homogeneity. The first reported suprapolymersomic structures that pentablock quintopolymer self-assembled were asymmetric, proposing practically new methods of producing directional drug release through the asymmetric polymersome membranes.

The conjunction of polymer chemistry and supramolecular chemistry interactions is required to synthesize multiblock copolymers, highly complex macromolecular superstructures with controlled internal structures and hierarchical solution-based self-assemblies suitable for nanochemistry, encapsulation, and biological applications. Moreover, in our belief, in complex diseases, very sophisticated structures should be designed to encapsulate a significant quantity of drugs, bypass biological barriers to effectively and selectively deliver the drug to the desired pathological site.

ORAL

POLY(DIMETHYLAMINOETHYL METHACRYLATE)-B-POLY(HYDROXYPROPYL METHACRYLATE) COPOLYMERS: SYNTHESIS AND PH/THERMO-RESPONSIVE BEHAVIOR IN AQUEOUS SOLUTIONS

Theodore Sentoukas, Stergios Pispas
Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece

Introduction: Double thermoresponsive and pH responsive block copolymer systems have been at the center of attention due to their ability to self-assemble into discrete nanoscale formations at different temperatures and solution pH. In the present work, the synthesis and self-assembly properties in aqueous solutions of novel amphiphilic diblock copolymers composed of one hydrophilic, pH and temperature responsive poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) block and one weakly hydrophobic, thermoresponsive poly(hydroxypropyl methacrylate) (PHPMA) block, are reported.

Methods: The block copolymers were prepared by RAFT polymerization and were molecularly characterized by size exclusion chromatography, NMR and FTIR spectroscopies. The PDMAEMA blocks were quaternized with CH_3I, leading to QPDMAEMA-*b*-PHPMA amphiphilic polyelectrolyte-neutral block copolymers. Self-assembly studies on aqueous solutions were conducted using three solubilization protocols at different pHs, followed by light scattering measurements.

Results: PDMAEMA-*b*-PHPMA copolymers exhibit thermoresponsive behavior at all pHs. Zeta potential and fluorescence spectroscopy experiments revealed a great dependence of the aggregate surface charge and the intraggregate polymeric chain assembly on the solvent-exchange protocol utilized and the pH of the aqueous solution. Direct solubilization in aqueous media led to swollen aggregates, while solvent exchange protocols led to more hydrophobic aggregates. Regarding the block polyelectrolyte analogs, the QPDMAEMA-*b*-PHPMA solutions presented also thermoresponsiveness, but to a lesser extent.

Conclusions: These studies shed light on ways for manipulating structure formation of doubly thermoresponsive and pH responsive diblock copolymers. Their nanostructured aggregates show potential for utilization in drug delivery and/or protein/peptide and gene delivery.

POSTER 1.1

POLYMERIZATION KINETICS OF N-BUTYL METHACRYLATE IN THE PRESENCE OF GRAPHENE OXIDE PREPARED BY TWO DIFFERENT OXIDATION METHODS WITH OR WITHOUT FUNCTIONALIZATION

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Introduction: Graphene is a one-atom-thick, two-dimensional layer of sp bonded carbon atoms arranged in a honeycomb lattice. It is believed to be the “thinnest and strongest material known so far” and has recently attracted significant research interest because of its outstanding mechanical, thermal, optical, and electrical properties. Therefore, it has been used for the preparation of graphene-reinforced polymer nanocomposites.
Methods: Nanocomposite materials based on poly(butyl methacrylate) and either graphene oxide (GO) or functionalized graphene oxide (F-GO) were produced using the in situ bulk radical polymerization technique. It was found that the Hummers method results in a higher degree of oxidation, compared to the Staudenmaier, whereas F-GO was produced using a silane-modifying agent.
Results: Polymerization kinetics were studied both experimentally and theoretically, and it was found that the presence of hydroxyl groups in the surface of GO results in scavenging the primary initiator radicals, thus reducing the initiator efficiency and the reaction rate, whereas the number-average molecular weight of the polymer formed was increased. The presence of F-GO affected the polymerization kinetics in a different way resulting in partially grafted structures. The theoretical study included the addition of a phenomenological transfer to the polymer side-reaction to account for the polymerization occurring at the F-GO surface. A big variety of techniques such as HATR-FTIR, GPC, TGA, DSC and XRD were used to investigate the properties of the butyl methacrylate/graphene oxide nanocomposites.
Conclusions: Using of functionalized or not graphene oxide affects polymerization kinetics.

POSTER 1.2

SYNTHESIS AND MOLECULAR CHARACTERIZATION OF POLYSTYRENES CARRYING PENDANT TEMPO RADICALS

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Abstract:

A synthetic strategy taking advantage of well-studied chemical reactions was employed in order to produce poly(methylstyrene) chains with pending 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) groups. More specifically, a series of random copolymers of the difunctional monomer para-chloromethylstyrene and styrene of varying compositions and molecular weights were synthesized *via* free radical polymerization and nitroxide-mediated radical polymerization techniques. These polymer chains were then functionalized through the chloromethyl groups with several TEMPO-carrying moieties yielding a polystyrene derivative with side-groups of stable radicals. These polymer chains are known to exhibit interesting properties both in biochemical applications and in new technologies. The precursor polymers and the poly(methylstyrene-TEMPO) chains were characterized by Proton Nuclear Magnetic Resonance (^{1}H-NMR) spectroscopy, Size Exclusion Chromatography (and Fourier-Transform Infrared Spectroscopy).

KEY WORDS: *TEMPO, Chloromethyl styrene, nitroxide mediated polymerization*.

POSTER 1.3

SYNTHESIS AND CHARACTERIZATION OF NEW HIGH Tg BIOBASED COPOLYESTERS FROM ISOSORBIDE, 1,6-HEXANEDIOL AND 2,5-FURANDICARBOXYLIC ACID

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In recent years, a significantly rising interest has been to develop a more sustainable bio-based economy, due to the rapid oil feedstock depletion, the increase of petrochemicals price and the emission of greenhouse gasses. Thus, extensive research efforts were focused on the production of eco-friendly polymeric materials from renewable resources, which can substitute those derived through petrochemical ways. Biomass is a renewable resource to produce value added products, such as bio-based polymers used in various fields. Isosorbide and 2,5-furandicarboxylic acid derived from sugars and polysaccharides, are two of the most promising chemicals. Specifically, in the present study, relative copolyesters based on poly(isosorbidefuranoate) (PIsF) and poly(1,6-hexanediol furanoate) (PHdF) were synthesized and their properties were examined. The copolyesters were produced via melt polycondensation, using dimethyl-2,5-furan dicarboxylate ester (DMFD), 1,6-hexanediol (1,6-HD) and isosorbide (Is), in different proportions. The successful synthesis was confirmed with Nuclear Magnetic Resonance spectroscopy (^{1}H-NMR) and Infrared spectroscopy (FTIR). Their molecular weights were estimated from Intrinsic Viscosity (IV) and end groups analysis. Via X-ray Diffraction (XRD) was assessed their solid-state, and their thermal properties were determined with Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). As was found from NMR in all case random copolymers have been prepared. From XRD and DSC studies it was found that copolyesters with high isosorbide ratios are amorphous and show beneficial high T_g values, while they can crystallize only in case of high 1,6-hexanediol furanoate content. All materials exhibit high thermal stability, since they degrade at temperatures higher than 300°C.

POSTER 1.4

ASSOCIATION EFFECTS OF END-FUNCTIONALIZED POLYMERS INTERACTING THROUGH HYDROGEN BONDS

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Three different series of very low molecular weight ω-functionalized homopolymers PS-OH and diblock copolymers PS-b-PI-OH and PI-b-PS-OH, where PS is polystyrene and PI is polyisoprene, were synthesized by living anionic polymerization techniques. Samples of different molecular weights, and/or compositions where obtained. Through the end-hydroxyl group the functional unit 2-ureido-4-pyrimidone (UPy) was introduced in each sample. The UPy-group is strongly dimerized in a self-complementary array of four cooperative hydrogen bonds.

This new class of supramolecular, non-covalent polymers (in this case with hydrogen bonds) is promising as their properties can be manipulated upon changing the experimental conditions (temperature, solvent, shear forces and concentration). (SEC) and ^{1}H-NMR were carried out to verify the existence of these ω-functionalized polymers. Atomic force microscopy (AFM), dynamic light scattering (DLS) and viscometry were carried out and revealed that the above mentioned polymers, do not only form dimers, but also create different populations of nanostructures and networks. Other experimental techniques, such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and rheology, confirm the strong effect of the non-covalent bonds.

The polar UPy-groups are responsible for this complex aggregation behavior in non polar solvents due to the formation of self-complementary hydrogen bonds. This behavior is even more pronounced due to the low molecular weight of the polymeric chains. As a result, the ω-functionalized polymers can self assemble into large aggregates of a variety of sizes.

POSTER 1.5

The 1-phenyltetrazole-5-thiyl Radical in the Photopolymerization of MMA

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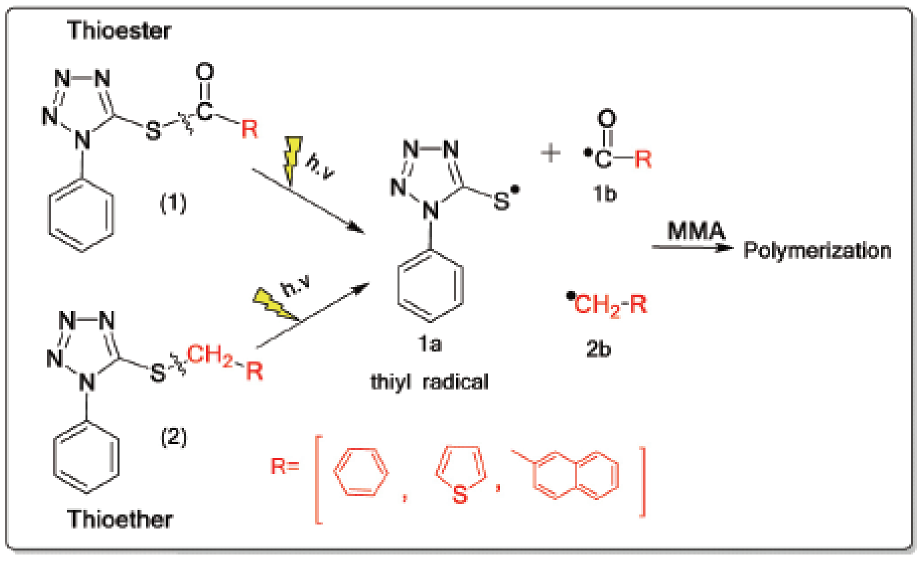
The free-radical photopolymerization (FRP) has gained practical importance in the industrial field during the past decades.[1] During this time a variety of different radicals are clearly recognized as powerful polymerization initiating agents. So, searching for new radicals having enhanced or specific properties is *a task* of outstanding interest. It is also well known, that the key for the radical formation is the photoinitiator (PI). The free radical photoinitiators fall in two categories: *the direct photofragmentating **(Type I)** initiators* and *the hydrogen-abstracting type **(Type II)** initiators*. In the last case a co-initiator are used. From the other point, the ***sulfur centered radicals*** (thiyl radicals)[2-3] have two main advantages in the polymerization process, the high reactivity toward a large set of monomer double bonds and the low sensitivity to atmospheric oxygen. These types of radicals would be formed through sulfur containing PI, which are designed as cleavable compounds or through a co-initiator with an aromatic ketone.



In the present report, we are synthesized some new *novel photocleavage photoinitiators* (***type I***) based on **thioester** and **thioether** derivatives (Scheme). The **1-phenyltetrazole-5-thiyl radical**, a very reactive sulfur centered radical,[2] had chosen as the initiating radical species and for this reason constitute a part of the photodissociative photoinitiator molecule. This radical was also formed photochemically by use of a ***type II*** photoinitiator which is based on some fluorenone derivatives and the corresponding thiol as co-initiator.[4] The methylmetacrylate (MMA) monomer was used in all photopolymerization experiments.

For this study we have used techniques such as ^{1}H- and ^{13}C-NMR, FT-IR, mass spectroscopy, UV-visible and fluorescence spectroscopy, laser flash photolysis (LFP) (*ns-timescale*) and product analysis. Finally, all these studies were supported by *ab initio* and DFT calculations.

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POSTER 1.6

RAFT SYNTHESIS AND SELF-ASSEMBLY OF AMPHIPHILIC BLOCK COPOLYMERS BASED ON POLY(n-BUTYL ACRYLATE)

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Introduction: Amphiphilic block copolymers demonstrate a unique ability to self-assemble in aqueous solutions, forming well-defined polymeric micelles, which allows their utilization as drug and gene nanocarriers. Five well defined block copolymers consisting of a common hydrophobic poly(n-butyl acrylate) (PnBA) block, and a different hydrophilic block, i.e. poly(oligoethylene glycol acrylate) (POEGA) and poly(2-dimethylaminoethyl acrylate) (PDMAEA) respectively, were synthesized and studied in aqueous media.

Methods: PnBA-b-POEGA and PnBA-b-PDMAEA block copolymers with different compositions were synthesized via RAFT polymerization. Their molecular weight (M_w), the polydispersity index (M_w/M_n) and their chemical composition, were determined by SEC and ^{1}H-NMR. Aqueous solutions of the block copolymers were investigated by DLS and SLS, and critical micelle concentration (CMC), was determined by fluorescence spectroscopy.

Results: The synthetic scheme followed for each copolymer system, resulted in well-defined diblocks having narrow molecular weight distributions and the desired compositions. DLS and SLS measurements have shown the formation of spherical aggregates in water. Results on the PnBA-b-PDMAEA diblock, indicate significant shrinkage of the aggregates at pH=3, probably indicating disaggregation in comparison to pH=7 solutions. All copolymers show low values of CMC in aqueous media, which depend on copolymer composition.

Conclusion: Amphiphilic PnBA-b-POEGA and PnBA-b-PDMAEA block copolymers were successfully synthesized using RAFT polymerization. In aqueous solutions, all copolymers form core/shell micelles, which either could be used as drug nanocarriers encapsulating hydrophobic drugs into the hydrophobic PnBA core or as gene delivery systems, where DNA/RNA could strongly bind with the PDMAEA corona.

POSTER 1.7

SYNTHESIS AND CHARACTERIZATION OF WELL-DEFINED SINGLE CHAIN POLYMER NANOPARTICLES THROUTH THERMAL CYCLOADDITION AND FRIEDEL-CRAFTS ALKYLATION REACTIONS

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Single-chain nanoparticles (SCNPs), unimolecular soft nano-objects consisting of individual polymer chains collapsed to a certain degree by means of intramolecular bonding, have attracted significant interest in recent years. Organic nanoparticles in a polymer matrix have been shown to influence both the mechanical and rheological properties of the nanocomposite material due to nanoscale effects. Herein, we present a facile and scalable method to synthesize well-defined single chain polystyrene nanoparticles through nitroxide-mediated polymerization and an intramolecular crosslinking reaction. Intramolecular thermal cycloaddition and Friedel-Crafts alkylation were employed for the synthesis of the nanoparticles. Size exclusion chromatography (SEC), light scattering and ^{1}H-NMR were employed for the molecular characterization of these polymer nanostructures.

SUBJECT AREA: Polymer chemistry, polymer characterization, nitroxide mediated polymerization.

KEY WORDS: Thermal cycloaddition, Friedel-Crafts alkylation, chloro methyl styrene (St), 4-vinyl benzocyclobutene (4-VBCB), intramolecular crosslink.

POSTER 1.8

SYNTHESIS OF NEW ECO-FRIENDLY COPOLYESTERS FROM FULLY RENEWABLE RESOURCES: POLY(Ɛ-CAPROLACTONE-CO-HEXAMETHYLENE 2,5-FURANDICARBOXYLATE)

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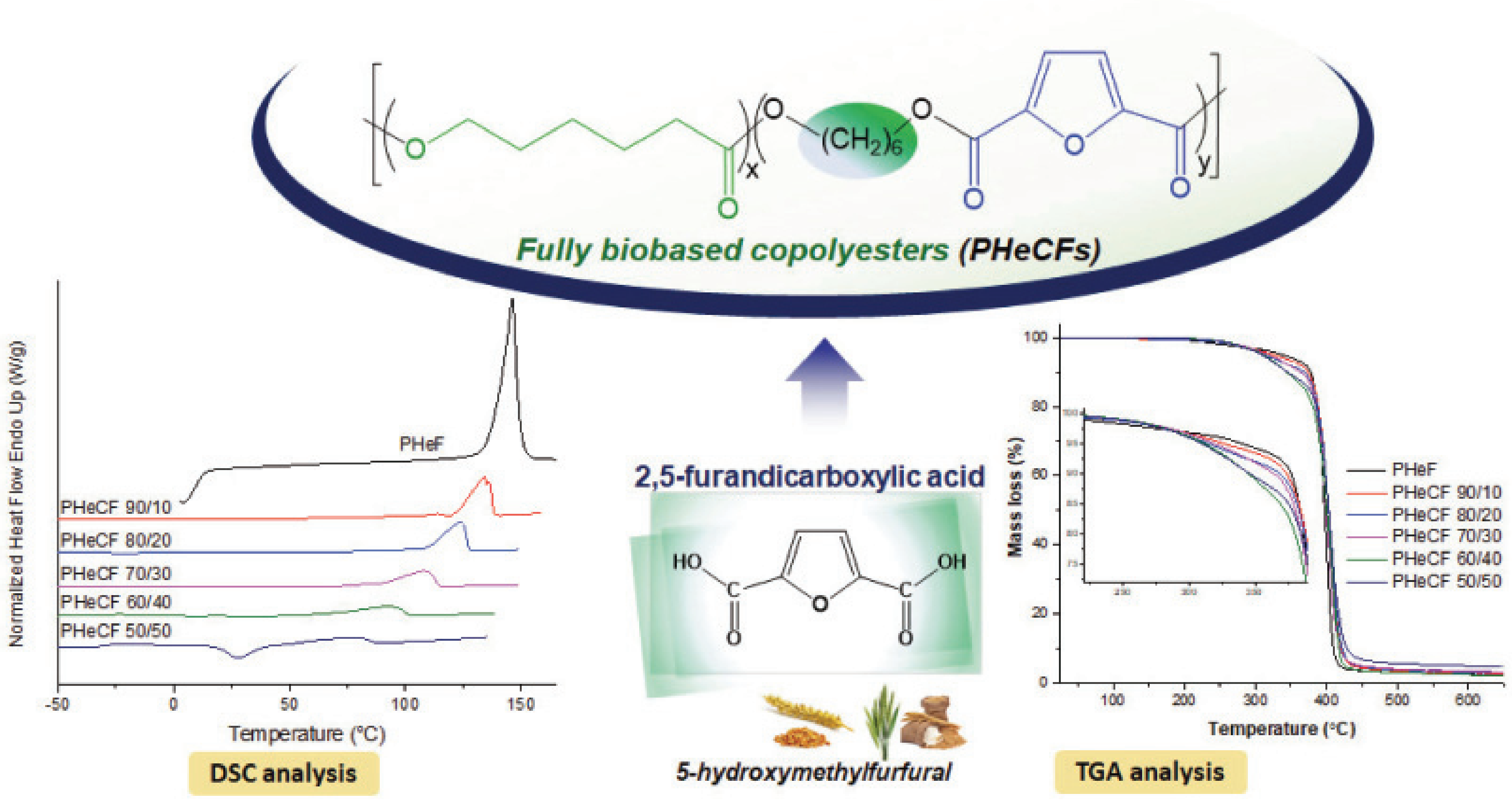
A new fully bio-based copolyesters series, poly(?-caprolactone-co-hexamethylene 2,5-furandicarboxylate) (PHeCFs), have been synthesized from dimethyl-2,5-dicarboxylate, ?-caprolactone (?-CL) and 1,6-hexanediol covering the compositions range of 10, 20, 30, 40 and 50 % ?-caprolactone content. The obtained copolymers, through a two-step melt polycondensation procedure and using stannous octoate as catalyst, were duly characterized in terms of chemical structure by ^{1}H and ^{13}C NMR to determine their compositions and sequence distribution and on the other hand in terms of thermal properties by using Differential Scanning Calorimeter (DSC), wide-angle X-ray diffraction (WAXD) and thermogravimetric analysis (TGA).

DSC results showed a crystalline behavior of PHeCFs, while their glass transition temperatures (T_g) ranging from -28.1 to 0 °C and their melting temperatures ranging from 76.3 to 134.1 °C steadily increased with the decrease of molar content of ?-CL in the prepared copolymer composition. The intrinsic viscosity values [η] (IV) were in the range of 0.23-0.27 dL/g. Thermogravimetric analysis (TGA) reveals an excellent thermal stability up to temperatures exceeding 310 °C for all prepared copolyesters. This study allowed to confirm that the homopolyester PHeF insertion into the prepared polymer backbone is distinctly effective in enhancing of T_g and T_m of synthesized materials.



POSTER 1.9

DIELECTRIC BEHAVIOR AND FUNCTIONALITY IN EPOXY RESIN/BARIUM OXIDE COPOSITE MATERIALS

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Introduction: Polymer matrix composites are used in a variety of applications, because of their ease production, low weight, low cost, thermomechanical, and electrical properties. In this study, nanocomposites of epoxy resin/barium oxide (BaO) nanoparticles were prepared and studied.

Methods: The electrical properties were investigated by means of Broadband Dielectric Spectroscopy (BDS) in a wide frequency and temperature range. Recorded relaxation phenomena include contributions from both the polymeric matrix and the presence of the reinforcing phase. Data were analyzed via the formalisms of dielectric permittivity, electric modulus and ac-conductivity.

Results: Three relaxation processes are revealed: (a) glass to rubber transition (α-mode), (b) re-arrangement of polar side groups (β-mode) and (c) interfacial polarization (IP) or Maxwell-Wagner-Sillars (MWS) effect.

Conclusions: Composites' permittivity increases with temperature and with the decrease of frequency. Permittivity diminishes with filler content, since BaO exhibit lower values of ε΄.

POSTER 1.10

SYNTHESIS AND CHARACTERIZATION OF WELL-DEFINED MIKTOARM STAR POLYMERS, (PS)n(PEO)n

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Miktoarm star-shaped copolymers of Poly(styrene)nPoly(ethylene oxide)n were synthesized through a novel synthetic strategy that gives easy access to complex macromolecular architectures, through a controlled polymerization and post polymerization cross-link of the difunctional monomer, divinylbenzene (DVB). This approach offers the advantage of controlled and well defined products to the already known difunctional monomer chemistry, resulting in a synthetic route that combines low-cost and easily accessible reagents with short reaction times compared to silane chemistry.

A series of linear triblock terpolymers, poly(styrene)-b-poly(divinylbenzene)-b-poly(ethylene oxide), were synthesized employing anionic polymerization via sequential monomer addition. Subsequently, the pending vinyl groups of the middle block were crosslinked, using AIBN as a free radical polymerization initiator, resulting in well-defined miktoarm star-shaped copolymers. Any residual unreacted linear triblock was easily removed by fractionation. These polymers were characterized with Size Exclusion Chromatography (SEC), Nuclear Magnetic Resonance Spectroscopy (NMR), Differential Scanning Calorimetry (DSC), Dynamic Light Scattering (DLS), Low Angle Light Scattering (LALS) and Viscometry.

POSTER 1.11

COMPLEX ARCHITECTURE ASYMMETRIC COPOLYMERS VIA ANIONIC POLYMERIZATION: SYNTHESIS, CHARACTERIZATION AND SELF-ASSEMBLY

Christos Ntaras[1], **Apostolos Avgeropoulos**[1], **Weichao Shi**[2], **Andrew L. Hamilton, Kris T. Delaney,**
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In this work we report the synthesis, characterization and properties of non-linear block copolymers prepared by anionic polymerization in order to show the well-defined microstructures adopted in bulk when these materials are studied morphologically. Very well ordered morphologies with minor defects and dislocations are evident.

The synthesis of linear asymmetric triblock copolymers of the ABA' type (A and A':PS, B:PI) and asymmetric miktoarm star-copolymer of the $A(BA')_n$ type (A and A':PS, B:PI) where n = 2 and 3 is reported via anionic polymerization and high vacuum techniques in combination with chlorosilane chemistry.[1] The linear triblock copolymers of the SIS' type were synthesized via sequential addition of the corresponding monomers. Details on the synthesis of all samples are already reported in the literature.[2,3]

Blending of these copolymers with homopolymer PS of various molecular weights and weight fraction concluded to the observation of a new thermodynamically stable, aperiodic "bricks and mortar" (B&M) cellular mesophase structure where PS comprises discrete hard "bricks" and PI the continuous soft "mortar".[4] The B&M phase lacks long-range positional order but exhibits quasi-long-range orientational order.

Furthermore, extremely asymmetric lamellar structures were obtained with up to 97 wt % polystyrene, remarkably leaving the poly(isoprene) layers intact at only 3 wt % with domain spacing tuned from 37 nm to over 300 nm when the miktoarm star block copolymer is blended with suitable molecular weight polystyrene homopolymers.[5,6]

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POSTER 1.12

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

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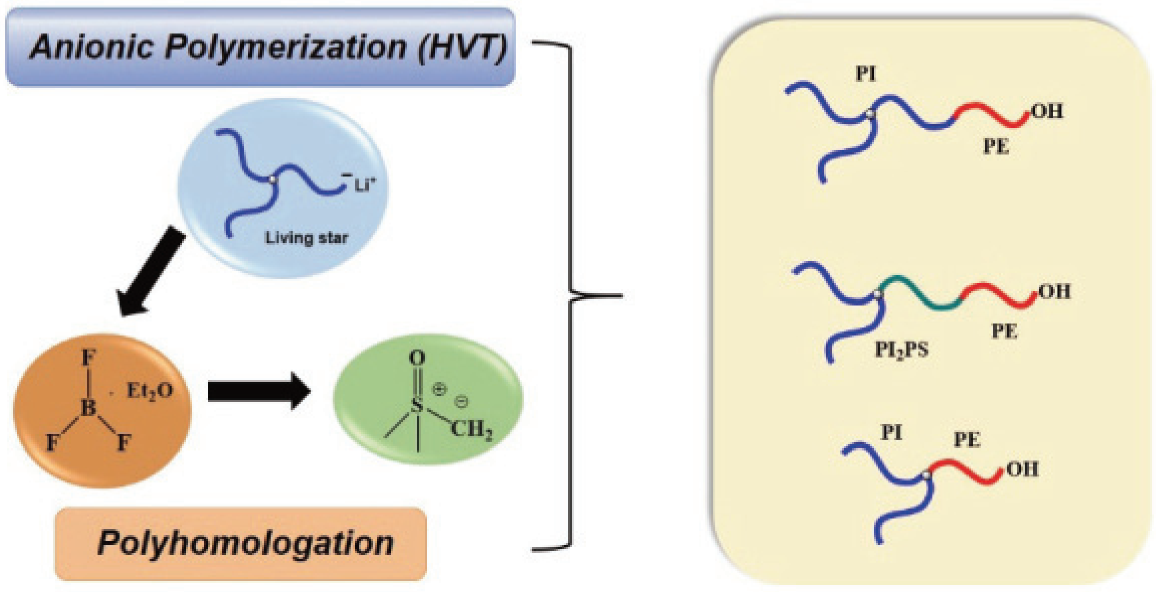
Polyethylene (PE)-based materials are very important in modern life, covering a wide spectrum of applications from commodity plastics (packaging, bottles) to precision-processed biomaterials (medical devices).[1] Developing new topologies will broaden the applications of thesematerials, r copolymers $(PI)_2$PE-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 (high vacuum techniques),ion and linking reaction with a “bridge” molecule, BF_3OEt_2. 4-(Dichloromethylsilyl)diphenylethylene (DCMSDPE) was first synthesized and linked with anionically prepared linear PI, through titration, to afford the “living” star precursors. Subsequently, boron-linked macroinitiators were prepared through linking reaction with BF_3OEt_2 for thepolyhomologation of dimethylsulfoxonium methylide[2] to produce novel PE-based miktoarm star polymers. All intermediates and final products were characterized by high temperature gel permeation chromatography (HT-GPC), proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) and differential scanning calorimetry (DSC). Preliminary studies were also performed through TEM measurements, indicating microphase separation.



POSTER 1.13

SYNTHESIS, MOLECULAR AND MORPHOLOGICAL CHARACTERIZATION OF LINEAR AND MIKTOARM POLYSTYRENE/POLYDIMETHYLSILOXANE COPOLYMERS

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Block copolymers composed of Polystyrene and Polydimethylsiloxane are well known for their nanolithography applications. Such materials are able to produce stable nanostructures through microphase separation.

The present research involves the synthesis and molecular characterization of linear diblock or triblock copolymers of the A-*b*-B or A-*b*-B-*b*-A type and miktoarm star copolymers of theA(B)$_{2,3}$ and B(A)$_{2,3}$ type, where A: polystyrene (PS) and B: polydimethylsiloxane (PDMS).

A series of linear diblock and triblock copolymers with same total molecular weight and different chemical compositions was synthesized by anionic polymerization along with sequential monomer addition. Anionic polymerization along with chlorosilane chemistry were employed for the synthesis of all the miktoarm star copolymers. All samples were characterized *via* size exclusion chromatography (SEC) and proton nuclear magnetic resonance spectroscopy (^{1}H-NMR), while transmission electron microscopy (TEM) was employed for the morphological characterization of the samples.

Our main goal is to understand the effect of macromolecular architecture at the microphase separation of these samples and to create a complete phase diagram for the polystyrene/polydimethylsiloxane copolymers.

POSTER 1.14

DOUBLE-HYDROPHILIC SEMI-INTERPENETRATING HYDROGELS WITH TUNABLE AND PREDICTABLE MECHANICAL PERFORMANCE

Georgia Papaparaskeva[1], Chrysovalantis Voutouri[1], Vasiliki Gkretsi[1,2], Mariliz Achilleos[1], Ivo Safarik[3,4], Kristyna Pospiskova[4], Triantafyllos Stylianopoulos[1] and Theodora Krasia-Christoforou[1]*

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Hydrogels are three dimensional (3-D) highly hydrated polymer structures that have attracted a lot of attention especially in the biomedical sciences field with regard to drug delivery and tissue engineering. One limitation of conventional hydrogels is that their mechanical properties are not ideal. Thus, the necessity for tuning as well as predicting the mechanical performance of hydrogels has led to the development of new synthetic methodologies in order to achieve this goal.

This study focuses on the synthesis and evaluation of the mechanical performance of double-hydrophilic semi-interpenetrating (semi-IPN) hydrogels consisting of a primary poly(2-(dimethylamino)ethyl methacrylate) (pDMAEMA) hydrogel and hydrophilic polyvinylpyrrolidone (PVP) linear chains introduced within the former as interlaced chains at various amounts [1]. 1,2-bis-(2-iodoethoxy)-ethane (BIEE) was introduced as a crosslinking agent, thus enabling the crosslinking step to take place at ambient conditions [1, 2]. Investigation of the mechanical performance of the water-swollen specimens under compressive loading conditions revealed that the materials' mechanical properties could be tuned by varying the amount of the linear PVP chains within the BIEE-crosslinked pDMAEMA hydrogel, with the hydrogels becoming more ductile upon increasing the linear PVP content. Most importantly, the mechanical properties of these materials could be predicted by using a non-linear hyperelastic constitutive equation. Finally, *in vitro* biocompatibility tests demonstrated absence of toxicity in cultured cells [1].

POSTER 1.15

SYNTHESIS AND CHARACTERIZATION OF WELL-DEFINED SINGLE CHAIN POLYSTYRENE NANOPARTICLES

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Single-chain nanoparticles (SCNPs), unimolecular soft nano-objects consisting of individual polymer chains collapsed to a certain degree by means of intramolecular bonding, have attracted significant interest in recent years. Organic nanoparticles in a polymer matrix have been shown to influence both the mechanical and rheological properties of the nanocomposite material due to nanoscale effects. Herein, we present a facile and scalable method to synthesize well-defined single chain polystyrene nanoparticles through nitroxide-mediated polymerization and an intramolecular crosslinking reaction. In addition, even more complex architectures, where one or two polystyrene chains are attached to the SCNPs, are presented. A series of nanoparticles with different dimensions as well as different percent of crosslinking has been synthesized. Size exclusion chromatography (SEC), ^{1}H-NMR, dynamic light scattering (DLS) and viscometry were employed for the molecular and structural characterization of these nanomaterials. Other experimental techniques, such as differential scanning calorimetry (DSC), rheology and dielectric spectroscopy are used in order to study the unique melt properties of these nanostructures.

POSTER 1.16

THIOESTERS AS TYPE I PHOTOINITIATORS: THE ROLE OF THE CHROMOPHORE

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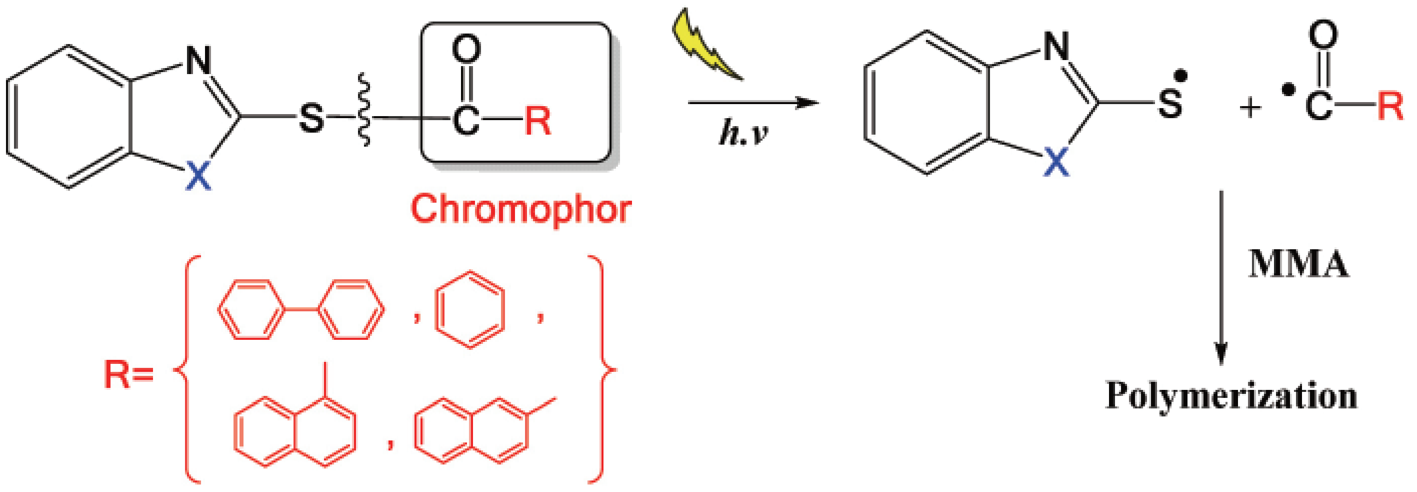
Photoinitiators are compounds that are specifically added to convert the absorbed light energy, UV or visible light into chemical energy in the form of initiating species (*free radicals or cations*).[1-4] Based on the mechanism by which initiating radicals are formed, photoinitiators are generally divided into two classes:

- ***Type I*** photoinitiators undergo a unimolecular bond cleavage upon irradiation to yield free radicals.
- ***Type II*** photoinitiators undergo a bimolecular reaction where the excited state of the photoinitiator interacts with a second molecule (which is called coinitiator) to generate free radicals.

This study focuses on the synthesis and testing of a series of novel *type I photoinitiators*. These compounds carry out as *a photodissociative bond* a **thioester group** and a *variety* of **chromophores.** The most important goal is to study *the key role* of the chromophore unit (the other part of the initiator) and their photophysical/photochemical properties. For this purpose, a number of techniques are used to characterize the molecules (^{1}H- and ^{13}C-NMR, FT-IR, mass spectroscopy), while for the photochemistry and the mechanistic studies the UV-visible spectroscopy, fluorescence, LFP at the level of nanoseconds (ns) are used. The whole study is also approached by quantum-mechanical calculations.



Scheme

The above scheme shows the photoinitiators (thioesters) that were studied and finally used for the photopolymerization of methylmethacrylate (MMA) and styrene monomers. One moiety of the molecule contains the mercaptobenzothiazole or mercaptobenzoxazole unit and the other moiety a series of different chromophores.

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POSTER 1.17

SYNTHESIS AND CHARACTERIZATION OF WELL-DEFINED RING POLYSTYRENES

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Herein, we report a facile and scalable synthesis of ring polystyrenes from their linear counterparts. A series of different molecular weights linear polystyrenes ranging from 23 to 110 Kg/mol was synthesized by anionic polymerization using high-vacuum techniques. A few units of 4-vinyl benzocyclobutene were polymerized at both ends of the linear polystyrenes. Cyclization reaction took place through the *o*-quinodimethane intermediates, at high dilution conditions and high temperature, under inert atmosphere. The intramolecular cyclization proceeded with good yield as monitored by the size exclusion chromatography analysis. Highly pure ring polystyrenes were obtained after the fractionation utilizing liquid chromatography at the critical condition (LCCC).

POSTER 1.18

PnBA-b-PNIPAM-b-PDMAEA pH- AND THERMO- RESPONSIVE TRIBLOCK TERPOLYMERS VIA RAFT POLYMERIZATION AND THEIR PROPERTIES IN AQUEOUS SOLUTIONS

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Introduction: Stimuli-responsive polymers are a new class of materials that exhibit reversible or irreversible changes in their chemical structures and/or physical properties, after the application of one or more external signals. In our work, we synthesized novel pH- and temperature- responsive PnBA-b-PNIPAM-b-PDMAEA amphiphilic triblock terpolymers and studied their properties in aqueous solutions.

Methods: The molecular weight and molecular weight distributions of the terpolymers were determined by SEC and their composition was determined by ^{1}H-NMR. Light scattering techniques (DLS, SLS, ELS) were utilized for the determination of mass, size, morphology and surface charge of the polymeric aggregates. Imaging of the terpolymer aggregates was achieved by TEM and AFM.

Results: PnBA-b-PNIPAM-b-PDMAEA triblocks were synthesized by RAFT polymerization. Methyl iodide (CH_3) was used in order to convert the PDMAEA tertiary amine groups into quaternary amine groups with permanent positive charges. In aqueous solutions, the triblocks self-assemble into micellar aggregates where PNIPAM and PDMAEA form the hydrophilic coronas and PnBA the hydrophobic cores. Significant changes are observed when variations of temperature and pH occur in the solution.

Conclusions: RAFT polymerization was successfully utilized for the synthesis of well-defined PnBA-b-PNIPAM-b-PDMAEA triblock terpolymers with different block ratios. The PDMAEA block was chemically modified in order to have permanent positive charge. In aqueous solutions, the terpolymers have been found to self-assemble into aggregates of micelles, showing also interesting structural changes with variation of solution temperature and pH.

POSTER 1.19

LINEAR AND STAR BLOCK COPOLYMERS WITH HIGH “FLORY-HUGGINS” (X) INTERACTION PARAMETER

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Panepistimiopolis Zografou, 15 771 Athens, Greece

We report herein the modular synthesis and lithographic potential of linear and star block copolymers with low molar mass and high “Flory-Huggins” interaction parameter. Anionic, Ring-Opening (ROP) and Controlled/Living Radical Polymerizations (CRP) were employed along with high vacuum techniques for the polymer synthesis. These block copolymers incorporate highly incompatible blocks, such as poly(l-lactide), poly(dimethylsiloxane) and poly(2-vinylpyridine) and are termed as “high X” polymers. Due to high incompatibility, low molar mass polymers allow for the formation of very small domain periods to be obtained. Size exclusion chromatography (SEC) light scattering and ^{1}H-NMR were employed for the molecular characterization of these polymers. Transmission electron microscopy (TEM) and small-angle X-ray scattering experiments (SAXS) were used to confirm the size and structure of the resulting nanomaterials.

POSTER 1.20

DOUBLE SEMI-CRYSTALLINE POLY(VINYLIDENE FLUORIDE)-BASED DIBLOCK CO- AND TRIBLOCK TER-POLYMERS

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Poly(vinylidene fluoride)-based block copolymers is difficult to prepare but quite advantageous owing to its satisfactory mechanical properties, excellent thermal stabilities and good chemical resistance. Their ability to self-assemble into well-ordered structures in solution and in bulk state can be used for the preparation of various nanostructured materials.[1] ck copolymers of poly(vinylidene fluoride) (PVDF) covalently linked with poly(ethylene) (PE) either PE-*b*-PS (polystyrene) were synthesized by the chain-extension strategy of two/three different polymerization methods respectively. We build upon a previous work which describes the Br → I exchange and the combination of two/three subsequent “living” and “pseudo-living” polymerization methods [polyhomologation, atom transfer radical polymerization (ATRP), iodine transfer polymerization (ITP)] reporting the synthesis of PE-*b*-PVDF and PE-*b*-PS-*b*-PVDF co/terpolymers respectively.[2] Morphology and self-assembly of these double-crystalline BCPs were investigated by transmission electron microscopy (TEM).

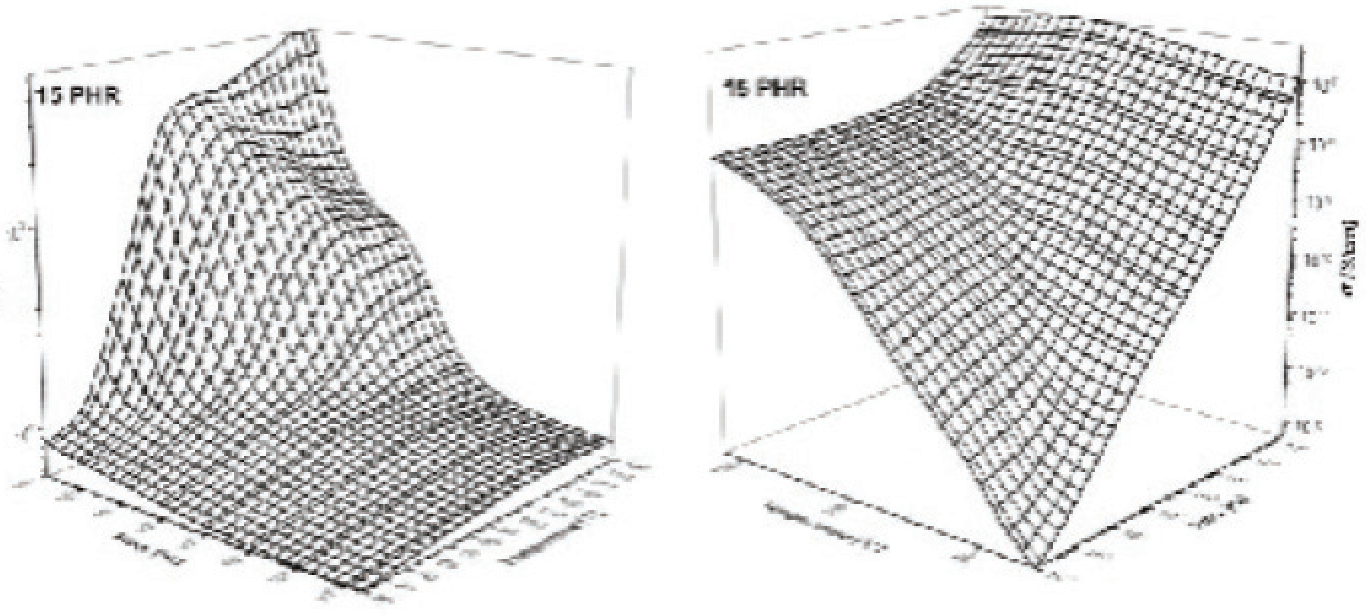

Figure 1. Variation of (a) real part of dielectric permittivity (ε΄) and (b) ac-conductivity (σ), for the 15 phr BaO nanocomposite as a function of frequency and temperature.

POSTER 1.21

METALLOCENE MEDIATED CATIONIC POLYMERIZATION OF VINYL ETHERS AND CHEMICAL MODIFICATION FOR THE SYNTHESIS OF GRAFT COPOLYMERS

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Poly(vinyl ethers) are a class of polymers with a wide variety of applications, such as adhesives, surface coatings and chemical processing. 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. Poly(ε-caprolactone) and poly(L-lactide) are highly compatible polymers with various industrial uses, including packaging, films and fibers. In this work, butyl vinyl ether and 2-chloroethyl vinyl ether were copolymerized using an activated cationic zirconocene complex as an initiator. The chlorine atoms of the resulting polymers were then substituted by azide groups after reaction with sodium azide. Poly(ε-caprolactone) and poly(L-Lactide) were synthesized using ring opening polymerization employing propargyl alcohol and stannous octate as the initiating system. The poly(vinyl ether) polymers and the poly(lactones) or poly(lactides) were consequently reacted through copper catalyzed click reaction, resulting in graft copolymers. SEC, IR and NMR were employed to monitor the reaction sequence and characterize the products. Finally, the thermal properties of these graft copolymers were studied with Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) and were compared with the responding properties of the original polymers. This synthetic route offers a general approach for the synthesis of amphiphilic or amorphous-crystalline graft copolymers with unique solution and solid state properties.

Polymer Physics

INVIDED ORAL

MULTI-FUNCTIONAL SURFACES WITH CONTROLLABLE WETTABILITY AND WATER ADHESION

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The design of multifunctional surfaces based on biomimetic structures has gained the interest of the scientific community. This is mainly due to potential applications like self-cleaning surfaces, microfluidics. nanomedicine and catalysis. Such biomimetic structures can be achieved by using “smart” coatings, which can respond to external stimuli, such as light, temperature, electric field, pH or solvent selectivity, onto appropriately structured substrates. Novel multifunctional surfaces have been developed, able to alter their wetting properties in response to temperature and/or pH as well as light illumination, by combining proper chemistry and surface micro/nano-structuring. For this purpose, dual scale micro/nano-roughened surfaces are prepared by irradiating Si wafers using ultrafast (femtosecond) laser under a reactive atmosphere; polymeric or inorganic coatings are subsequently introduced to provide the desired functionality. The combination of such hierarchical surfaces with a ZnO coating results in efficient photo-catalytic properties as well as reversible superhydrophobicity / superhydrophilicity in response to the light illumination. Utilization of end-functionalized polymer chains anchored onto the hierarchical surfaces can lead to surfaces that exhibit reversible and controllable wettability to temperature and/ or pH from the “parahydrophobic” behavior of natural plant leaves all the way to superhydrophilic properties in response to the external stimuli. Moreover, such surfaces can be seeded with human fibroblasts in order to examine the cellular response on both the surface roughness and the surface chemistry.

We acknowledge support of this work by the project “Materials and Processes for Energy and Environment Applications” (MIS 5002556) which 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 the European Union (European Regional Development Fund).

INVITED ORAL

WHAT CAN POLYMER SCIENCE LEARN FROM THE VIBRATION DYNAMICS OF POLYMER COLLOIDS?

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ABSTRACT

Polymer and colloids become mature sciences and many benefits are still ahead, just to mention polymer nanocomposites. The topic of the presentation was deliberately chosen to demonstrate how polymer colloid architecture can advance our understanding of polymer thermomechanical behavior in curved geometries at nanoscale. Two examples from polymer chains tethered on hard core(SiO_2)(aka "particle brush") [1-3] and polymer core-shell colloids[4] will be highlighted. The former assume different polymer density profile depending on the grafting density and degree of polymerization. The local anisotropy of the elastic parameters across the SiO_2/polymer (polystyrene, PS) besides tuning of the phononic band diagram impacts the elastic moduli of the ' one-component nanocomposite. At constant volume fraction, the modulus increase with decreasing high density due to enhanced interparticle interactions. In the second example, the particle vibration spectrum provides a direct observation of the polymer surface mobility beyond its glass transition and measures the nanoparticle shear modulus. [4] Covalently bonded or adsorbed thin shells allow engineering of the particle surface mobility and the glass transition temperature.

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INVITED ORAL

MONITORING CRYSTALLIZATION AND MELTING WITH MILLISECOND TIME RESOLUTION: IN-SITU COMBINATION OF MICRO-FOCUS X-RAY SCATTERING AND ULTRA-FAST SCANNING CHIP CALORIMETRY

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A custom-made fast scanning chip calorimeter (FSC) was designed and made compatible with the environment of the micro- and nano-focus X-ray beamlines such as the ID13 beamline at the ESRF (Grenoble) [1-2]. The advent of fast single-photon-counting X-ray detectors enabled *in-situ* coupling of the two techniques with a possibility of conducting continuous synchronous acquisition of the thermal and 2D X-ray scattering data with time exposures on the order of one millisecond. The practical aspects such as temperature and power calibration of the device as well as the possible X-ray beam damage will be discussed in the talk.

The designed setup was used to re-explore the thermal behavior of commodity semicrystalline polymers. In particular, the setup allowed monitoring the early stages of crystallization of HDPE in order to evaluate the morphology and exact supercooling at the crystal growth front. To this end, the lattice parameters of the crystals, which are younger than 5 milliseconds were measured during fast cooling ramps at heating rates faster than 1000 K/s. Also, the phenomenon of multiple melting, which constitutes one of the long-standing issues in polymer science, was revisited. In this case, even isothermally crystallized samples can exhibit several melting endotherms in the DSC heating traces. With the advent of FSC, it became possible to achieve much higher heating or cooling rates than in the classical DSC experiments. The use of such rates allows bypassing the recrystallization processes on heating and cooling and facilitates in-depth analysis of the thermal behavior. In the present work, by using heating and cooling rates much higher than the rates of recrystallization, the structural transformation corresponding to each of the observed thermal events was extracted from X-ray data analyzed in detail [3-4].

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INVITED ORAL

NONLINEAR SHEAR RHEOMETRY OF ENTANGLED POLYMERS

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Whereas the nonlinear shear response (such as shear thinning) is inherent in viscoelastic materials and has been studied experimentally and theoretically/computationally for over 50 years, it is not yet fully understood. We address some of the outstanding issues and discuss recent advances in rheometry which allow determining the viscosity and first and second normal stress differences in entangled polymer solutions and melts in unprecedentedly high Rouse-Weissenberg numbers, well into the stretching regime. We identify stretching and tumbling regimes, compare with current state-of-the-art modeling and simulations and, importantly, show the importance of macromolecular architecture by comparing the shear response of different macromolecular structures (linear, star, ring) with the same total molar mass.

ORAL

STRUCTURE AND DYNAMICS IN BIO-BASED POLYMER NANOCOMPOSITES

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Intercalated polymer / layered silicate nanohybrids offer a unique avenue to study the behavior of macromolecules under severe confinement, i.e., over dimensions comparable to their sizes. Moreover, the investigation of the polymer dynamics in the bulk and under confinement has attracted the scientific interest both because it greatly affects many of the macroscopic properties and because of the complexity it exhibits over many length- and time-scales. On the other side, biodegradable polymers have attracted considerable attention as green materials and biomaterials in pharmaceutical, medical, and biomedical applications. In the present work the structure, properties and dynamics of polyester polyols were investigated in the bulk and under severe confinement, when the polymer is intercalated within the galleries of natural hydrophilic sodium montmorillonite, Na^+-MMT. A series of linear biobased polyesters with hydroxyl end groups, were utilized and compared with the case of hyperbranched polymers of similar chemistry. The structure and thermal properties of all polymers and nanocomposites were studied by X-Ray Diffraction (XRD) and Differential Scanning Calorimetry (DSC), respectively. Their dynamics were studied by Broadband Dielectric Spectroscopy (BDS) in a wide range of temperatures. A significant effect of polymer architecture on the dynamical properties under confinement was observed.

This work was supported by the project "National Research Infrastructure on nanotechnology, advanced materials and micro/nanoelectronics "(MIS 5002772) 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 the European Union (European Regional Development Fund).

ORAL

TUNING POLYMER CRYSTALLINITY

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Controlling the crystallization behavior of semicrystalline polymers is of paramount importance since it largely determines their final properties. A way to affect crystallinity is via the addition of nanosized additives in the polymer matrix that are usually utilized to improve polymer properties. In this work, we demonstrate control of the degree of polymer crystallinity in poly(ethylene oxide) / silica, PEO / SiO_2, nanohybrids when nanoparticles of different sizes, i.e., smaller, comparable and larger than the polymer radius of gyration are utilized, introducing a varying degree of chain confinement. More importantly, tuning of the degree of crystallinity can be achieved when mixtures of silica nanoparticles of different sizes are introduced to enhance chain confinement and at the same time provide different adsorption capabilities. Polymer crystallinity can, indeed, be controlled by modifying the ratio of large to small nanoparticles for constant polymer concentration. Moreover, systems with zero crystallinity can be obtained for ternary systems where the fraction of large nanoparticle is kept constant and the ratio of the polymer versus small nanoparticles is varied. At the same time, in cases of severe confinement, the chain conformations are significantly altered compared to the corresponding in the bulk.

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ORAL

HIGH CONDUCTIVITY, HIGH MODULUS SOLID POLYMER ELECTROLYTES VIA MACROMOLECULAR ENGINEERING

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Many present-day batteries involve the presence of a liquid organic electrolyte that leads to safety issues associated with its flammable nature while its unstable nature with Li metal electrodes prohibits the development of high-energy storage cells. Solid polymer electrolytes (SPEs) could be a real “game-changer” as they hold the promise to solve the safety problems of liquid electrolytes and most importantly, they are compatible with Li metal anodes. Despite the considerable research effort, the primary challenge is the development of SPEs with good mechanical properties without sacrificing ionic-conductivity. In this talk, the use of novel polymer nanostructured nanoparticles will be introduced as additives to liquid electrolytes for the synthesis of SPEs that exhibit an unprecedented combination of high modulus and ionic conductivity. The nanoparticles are composed of high functionality mikto-arm star copolymers in which stiff insulating arms complement ion conducting arms. Because of their molecular design, these materials constitute the first example of all-polymer nanostructured materials where each and every building block is a nano-sized polymeric nanostructured “molecular material”. It will be demonstrated that the final/desired morphology and phase dimensions of the SPEs may be precisely controlled as is encrypted within the macromolecular characteristics and the chemical composition of the “nanoparticles”. As the synthesis of high performance SPEs has been the subject in a wide variety of electrochemical devices, this approach may significantly contribute to other applications, beyond lithium metal batteries, such as anion exchange membranes for fuel cells, efficient active layers in dye-sensitized solar cells, and electrochromic devices.

ORAL

HYDRATION PROPERTIES OF POLYMER HYDROGELS

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Polymer hydrogels have attracted much interest in recent years based on numerous applications mainly in biotechnology and medicine. Hydrogels based on natural polymers have become especially attractive in the field of tissue engineering because they have unique properties such as good biodegradability, biocompatibility, high water retention capacity and they provide a three dimensional environment for the proper differentiation of cells. In this work we investigate the hydration properties of a family of injectable hydrogels with a homogeneous distribution of gelatin (Gel) and hyaluronic acid (HA) chains by enzymatic gelation of aqueous solutions of different mixtures of both polymers [1]. With the term hydration properties we mean the particular organization of water in the hydrogel, which determines the properties of the water component, typically different than those of bulk water, and the impact of water on the properties of the polymer matrix itself. The results are discussed in comparison with hydration properties of synthetic polymer hydrogels [2].
The glass transition and the molecular dynamics of water in the hydrogels have been studied by employing differential scanning calorimetry (DSC), dielectric relaxation spectroscopy (DS) and water dynamical sorption - desorption measurements. Our results enable us to follow the evolution of the observed dynamics with hydration level. Regarding the dielectric relaxation processes, the emphasis has been given to those related to hydrogen bond network of non-crystallized water molecules (hydration water) organized in clusters. Additionally, we investigate miscibility issues in the hydrogels and search for differences and similarities of water dynamics in proteins, polysaccharides and synthetic polymer hydrogels.

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ORAL

POLYMERIZED IONIC LIQUIDS WITH POLYTHIOPHENE BACKBONES. SELF-ASSEMBLY, THERMAL PROPERTIES AND ION CONDUCTION

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Recently, there has been considerable interest in developing materials that combine electronic with ionic conduction[1]. Furthermore, earlier studies[2-3] concentrated on the decoupling of ion motion from segmental relaxation in Polymerized Ionic Liquids (PILs). Herein, single ion conductors, based on PILs with a polythiophene backbone bearing imidazolium salts are synthesized with six different counteranions ($[Br]^-$, $[BF_4]^-$, $[ClO_4]^-$, $[PF_6]^-$, picrate and $[B(Ph)_4]^-$) and four different alkyl (n) side group lengths (with n=4 (butyl), 6 (hexyl), 8 (octyl) and 10 (decyl)) and studied with respect to the thermal, structural and ion conduction properties[4]. Increasing side group length increases the room temperature conductivity by four orders of magnitude (internal plasticization). The anion size (anionic radii from 0.19 nm to 0.44 nm) affects both the structure (lamellar-smectic to amorphous by increasing anion radius as evidenced by WAXS) and the measured conductivity. The dc-conductivity increases by six orders of magnitude by increasing anion size at ambient temperature. As a result, conductivities as high as 2×10^{-3} S/cm could be measured at high temperatures. Differences in conductivity are discussed in terms of changes in glass temperature (T_g), anion size and value of dielectric permittivity. Overall ion transport in PILs based on polythiophene backbones is controlled by the low T_g, high dielectric permittivity, smectic layering and ion association lengths not exceeding a single smectic layer.

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ORAL

CONFORMATION OF GRAFTED-THROUGH HIGH GENERATION DENDRONIZED POLYMERS IN SOLUTIONS

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Dendronized polymer (denpol) are a subclass of hyperbranched polymers. They consist of dendrimer side chain, covalently linked to a linear polymer main chain. Their unique structure is expected to lead to "sausage"-like persistent nano-object. We investigate the conformation of a unique series of 4th, 5th and 6th generation ester dendrons.on poly(norborene) (PNB) and poly(*endo*-tricycle[4.2.2.0]deca-3,9-diene) (PTD) backbones. The grafting-through synthesis using ring-opening metathesis polymerization (ROMP) of macromonomers led to fully grafted and large degree of polymerization denpols with narrow polydispersity. The structure and conformation in dilute solutions were investigated in dilute solutions, by a combination of scattering techniques. The evolution of the gyration radius Rg with the degree of polymerization was measured with GPC coupled with Multiple Angle Laser Light Scattering (MALLS). Comparison with theoretical expression of Rg(N) for semi-flexible chain allowed the measure of persistence length lp of every denpol. Cross section radius Rcs, persistence length lp and contour length were obtained from Small Angle Neutron Scattering data analyzed by model form factor. lp ranged between 5 nm (G4) up to almost 20 nm (G6), much larger than lp of lower generation denpol [1]. Rcs was found to increase with generation up to and 2.8 nm. Measured diffusion coefficient compared well to semi-flexible cylinders models. As generation increases, denpol are expected to behave more like soft colloids, with limited overlap between denpols. Results of DLS and SANS in semi-dilute regime confirmed that tendency.

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ORAL

THE GLASS TRANSITION IN POLYURETHANES WITH HYBRID ORGANIC INORGANIC PARTICLES. EFFECTS OF CHAIN TOPOLOGY AND HARD SEGMENT FLEXIBILITY

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Polyurethanes (PUs) are segmented copolymers with a morphology of "hard microdomains" in a continuous "soft phase". The main glass transition of polyurethanes originates in the latter, and its thermal and dynamic characteristics depend strongly on the degree of microphase separation. On the other hand, Polyhedral Oligomeric Silsesquioxannes (POSS) reside in the grey zone between large molecules and nanoparticles: they consist of a sub-nanometric inorganic core surrounded by an organic shell. The organic shell allows for covalent bonding of POSS to polymer chains in several chain topologies, e.g. as side groups, as parts of the main chain, as crosslinks, as terminal groups etc.

In this work we study several PU-POSS systems with respect to their calorimetric and dynamic glass transition. The systems differ in chain topology, segment length as well as in flexibility of their hard segments. The study is conducted mainly by differential scanning calorimetry, dielectric spectroscopy and dynamic mechanical analysis, and is aided by morphological techniques, for a co-evaluation of the degree of microphase separation. The hybrid particles affect the calorimetric and dynamic glass transition by several mechanisms: directly immobilizing part of the polymer and creating a rigid amorphous fraction, acting as diluents, or altering the micromorphology, and hence, indirectly, the molecular dynamics. Which of the mechanisms is in each case prevalent, and to which extent, depends on all the parameters we varied. POSS as chemical crosslinks have the most intense decelerating effect, as a combined result of more dense crosslinking and disturbance of the microphase separation.

POSTER 2.1

CRYSTALLIZATION AND MOLECULAR DYNAMICS OF PRIMARY ALCOHOLS CONFINED WITHIN NANOPOROUS ALUMINA

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Hydrogen-bonded (HB) liquids play a significant role in numerous chemical and biological phenomena[1]. Two examples of HB liquids are water and alcohols, which have important differences. First, in alcohols, the three-dimensional HB network is disrupted, because the number of possible donated HBs per molecule is half the number of possible accepted HBs. Furthermore, alcohols are amphiphilic molecules, making them more complex to the HB dynamics as compared to water. Finally, alcohols are miscible with a range of both polar and nonpolar solvents. Herein, we investigate the phase state and molecular dynamics and conductivity mechanism in a range of primary monohydric ($C_nH_{2n+1}OH$ with *n* from 6 to 12) and dihydric alcohols in the bulk and under confinement. As a confining medium, we employ self-ordered nanoporous aluminum oxide (AAO) with pore diameters ranging from 400 nm down to 25 nm. AAO contains arrays of discrete-isolated, parallel cylindrical nanopores that are uniform in length and diameter providing a model 2D confining medium. The phase diagram (melting/crystallization temperatures vs inverse pore diameter) of 1.5-pentanediol revealed reduced crystallization and melting temperatures with respect to bulk with possible applications as anti-freezing agent. The effect was greater than in water confined within the same AAOs[2] and this was attributed to the disrupted three-dimensional HB network of alcohols under confinement.

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POSTER 2.2

INFLUENCE OF CHEMICAL ENVIRONMENT IN LIGHT INDUCED PATTERNING IN POLYDIENE SOLUTIONS

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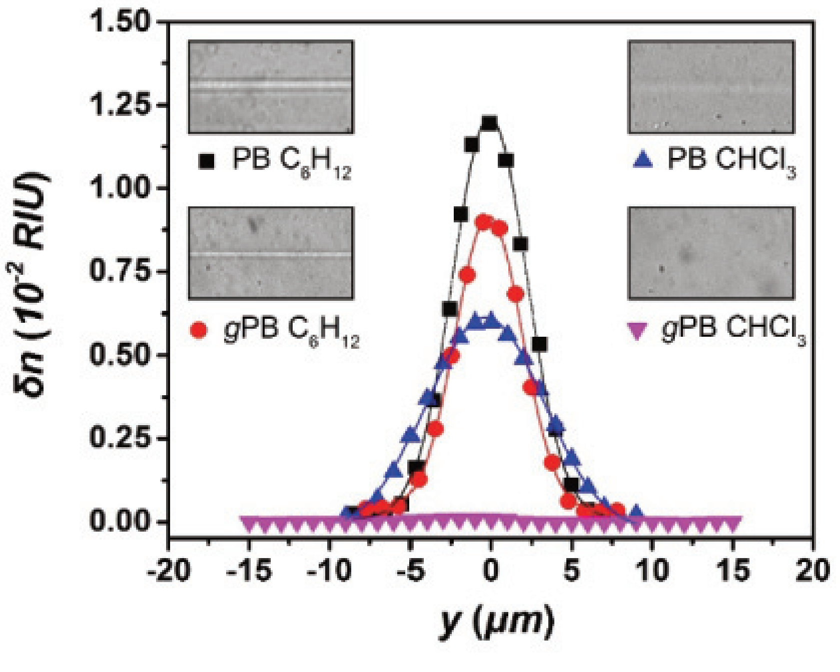
Mild red laser irradiation leads to a local change of the refractive index and the formation of patterns along the direction of beam propagation in polybutadiene and polyisoprene solutions. This unexpected formation of permanent structures upon mild laser illumination in fully transparent viscoelastic solutions was observed for a large variety of organic solvents. The light-induced structure formation was found to depend on the combined influence of the solvent as well the chemical nature and the relative concentration of the comonomer of the 1,4-butadiene. The qualitative differences of the formation mechanism (different pattern diameter, different kinetics type, complete pattern suppression) depend not only on the polymer repeating unit (homopolymer, copolymers) but also on the type of the solvent. Variations of solvents and comonomers affect both the pattern diameter and the refractive index contrast growth kinetics. In particular the fibrillar pattern observed in chloroform are twice as broad as the ones in alkanes. Moreover, a specific copolymer showed patterning in cyclohexane and none in chloroform. We tentatively attribute the laser-driven pattern formation seems to arise from a combination of a photon-triggered polymer-polymer attraction and an "assembly" process within the irradiated area most likely of photochemical origin.



POSTER 2.3

KINETICS OF LIGHT INDUCED PATTERNING IN POLYDIENE SOLUTIONS; INFLUENCE OF DISSOLVED O_2

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Polydienes solutions present an unexpected response to irradiation with red laser light: a local increase of the refractive index than can lead to self-focusing and self-propagation. The origin of the irreversible patterning has not been elucidated yet, many parameters like the type of solvent or comonomers were found to influence the kinetics. Here, we report an experimental study of the influence of dissolved molecular oxygen in the solutions on the kinetics of the patterning process. A dedicated experiment was designed that allow to control the O_2 content in the solutions. We use phase contrast microscopy to quantify the kinetics of refractive index increase. The study revealed a clear relation between the growth rate of the refractive index and the O_2 content, so that the growth rate increased linearly with the O_2 content. The strong influence of O_2 content points towards a photo-chemical effect, which is confirmed by the chemical modifications observed on the irradiated materials.

POSTER 2.4

EFFECT OF CONFINEMENT ON CHAIN CONFORMATIONS

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The behavior of polymers restricted in space or close to surfaces/interfaces can be very different from that in the bulk. In this work, the chain conformations in poly(ethylene oxide) / silica nanoparticles, PEO / SiO_2, nanohybrids has been investigated through a combined approach that involves Fourier Transform Infrared spectroscopy (ATR-FTIR) measurements and molecular dynamics (MD) simulations.[1] Systems with different polymer molecular weights, nanoparticle radii and concentrations have been employed to investigate the effect of the confinement on polymer conformations. Qualitatively similar behavior between experimental and simulation results is observed since in both cases an increase of *gauche* population for the OCCO angle is attained, in comparison to the respective of the bulk; this increase becomes larger as the degree of confinement becomes higher. On the contrary, the conformations of the C-O bond (COCC angle) seem to remain unaffected by the confinement, at least in the range of degrees of confinement covered computationally.

Rissanou, A. N.; Papananou, H.; Petrakis, V. S.; Doxastakis, M.; Andrikopoulos, K. S.; Voyiatzis, G. A.; Chrissopoulou, K.; Harmandaris, V.; Anastasiadis, S. H. *Macromolecules* **2017**, *50*, 6273-6284.

This work was supported by the project "National Research Infrastructure on nanotechnology, advanced materials and micro/nanoelectronics "(MIS 5002772) 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 the European Union (European Regional Development Fund).

POSTER 2.5

TAPERED BLOCK COPOLYMERS: EFFECT OF INTERFACIAL WIDTH

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Tapered block copolymers have scientific and industrial interest, owing to the enhanced miscibility[1] and the controlled mechanical properties. Herein, we report on the influence of interfacial width on the physical properties of tapered multiblock copolymers of polyisoprene and polystyrene (PI-PS) and of polyisoprene with poly(4-methylstyrene) (PI-P4MS) by (i) varying the number of blocks at a fixed molecular weight (M_w) and (ii) by varying the total M_w. PI-PS and PI-P4MS tapered n-block copolymers (n=2,4,6,8,10) were synthesized via statistical anionic copolymerization with a nearly symmetric composition[2] and studied with respect to the thermal, structural and mechanical properties by differential scanning calorimetry (DSC), small-angle x-ray scattering (SAXS) and rheology, respectively. DSC provided evidence of phase segregation as well an intermediate glass temperature. SAXS revealed lamellar morphologies with long-range order for the higher molecular weights. Rheological measurements were employed to determine the order-to-disorder transition temperature (T_{ODT}) as well as to compare the elastic moduli among the different chemical structures. An octablock copolymer of polyisoprene and polystyrene with a total M_w~240000 g/mol has the same T_{ODT} as a PI-b-PS diblock copolymer of only M_w~20000 g/mol due to the broader interface but shows superior mechanical properties. The results showed weaker segregation of PI-*b*-P4MS as compared to PI-*b*-PS. With rheology we further explored the influence of sequencing, *i.e.,* P(I-*b*-4MS) vs P(4MS-*b*-I) on the T_{ODT} , in diblock copolymers. We found a 5-10 K reduction in T_{ODT} in the normal copolymers meaning that there is a difference in reactivity ratio that has not been explored before.

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POSTER 2.6

JAMMING OF MULTI-ARM STAR POLYMERS VIEWED AS MODEL SOFT HAIRY COLLOIDS

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Recently, dense microgel suspensions were shown to exhibit a glass-to-jamming transition characterized by larger yield stress and strain and linear dependence of plateau modulus on concentration for the jammed state, as well as other fine differences in flow curves. On the other hand, it is well-known that linear polymer coils with homogeneous monomer density distribution, do not show comparable features, exhibiting a smooth evolution of their rheological properties from semi-dilute to entangled to melt regimes. To explore the role of density heterogeneities and associated microstructure on the rheology of dense systems, we report here our findings on highly concentrated suspensions of an 800-arm star polymer that encompasses properties of both colloids and polymers, and compare our results to moderately crosslinked polyelectrolyte microgel suspensions. Our study spans the entire range of concentrations from melt to dilute and we point out the qualitative similarities and differences between the two systems. We argue those differences come from the microscopic structure and especially the presence of dangling chains in the case of star polymers, that are virtually absent in the microgel systems. Based on the acquired experimental evidence, we can provide a map of rheological behavior as function of particle softness and internal microstructure.

POSTER 2.7

ULTRASONICALLY INDUCED BIREFRINGENCE IN POLYMER SOLUTIONS: THE CASE OF POLY-VINYL ALCOHOL – WATER SOLUTIONS

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Ultrasonically induced birefringence has been observed in various liquids and colloidal and polymer solutions [1]. For the small anisotropic molecules, the velocity gradient caused by ultrasound can directly induce the sinusoidal orientation. This causes the sinusoidal birefringence, which is proportional to the square root of the ultrasonic intensity $(W_U)^{1/2}$ [2, 3]. For large anisotropic particles, the orientational motion cannot follow the sinusoidal velocity gradient. However, the radiation pressure, which is one of the typical quadratic acoustic effects, produces the stationary torque on the particle that induces the uniform and stationary orientation of the particles in the solutions [2, 3]. In this case, the induced birefringence is proportional to the ultrasonic intensity W_U. The 'non-biased' detection technique was utilized for the ultrasonically induced birefringence measurements, which allows the detection of both the sinusoidal and stationary birefringence. If both the sinusoidal and stationary birefringence co-exists, the predominant birefringence will be observed. In this study, we performed concentration and temperature dependent measurements of ultrasonically induced birefringence. We obtained the intrinsic values of the stationary and transient birefringence for several polymer aqueous PVA solutions and related those to the segmental anisotropy in polarizability. The results indicated that the induced birefringence is proportional to the ultrasonic intensity. We also measured the frequency dependence of the stationary birefringence to progress on the comprehensive understanding of the mechanism of the ultrasonically induced birefringence phenomenology in polymer solutions.

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POSTER 2.8

MORPHOLOGY OF THERMORESPONSIVE MOLECULAR BRUSHES IN DILUTE AQUEOUS SOLUTION

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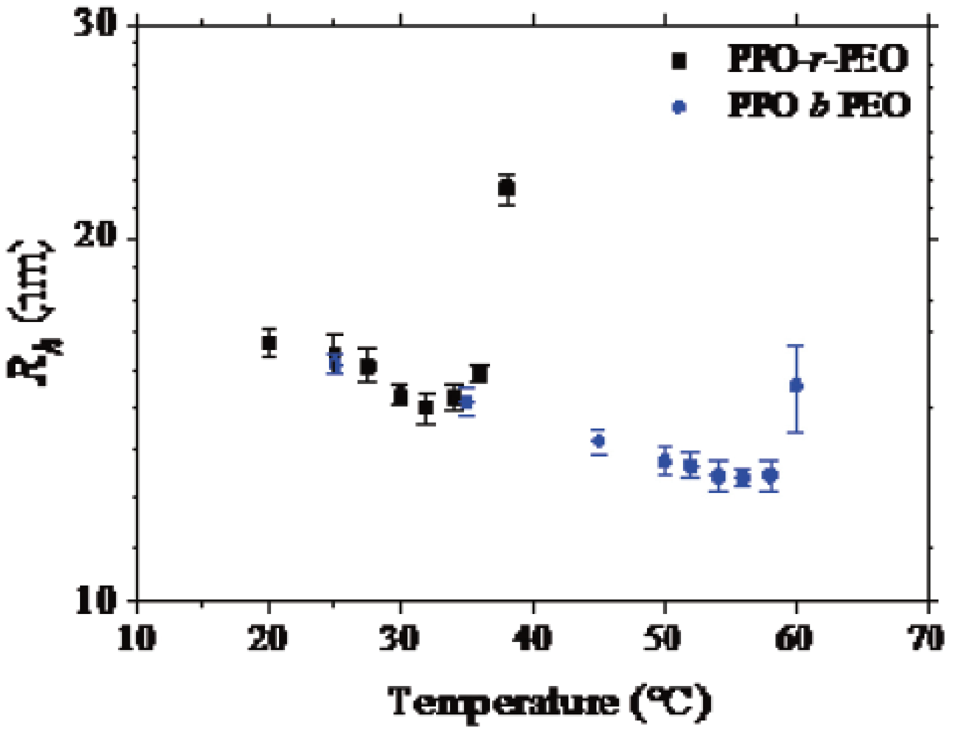
Introductions: Molecular brushes are densely grafted polymers composed of a polymeric backbone and side arms. Their complex architecture can easily be adjusted by changing the side arm architecture. In the present work, two amphiphilic molecular brushes differing in side arm architecture, diblock or random copolymer, are investigated, where the side arms contain poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO) segments. Since both monomers show lower critical solution behavior in aqueous solution, as the temperature is increased, a conformational transformation of the side arms is expected, and thus the molecular brushes.

Methods: The temperature-dependent conformation of the molecular brushes with PPO-*r*-PEO and PPO-*b*-PEO side arms in dilute solution (2 wt% in D_2O) is investigated by small-angle neutron scattering along with dynamic light scattering.

Results: As temperature increases from room temperature, both kinds of brushes show decreasing hydrodynamic radius. Thereafter, the size of random brush starts to increase and shows a steep jump at 38 °C, where the single brush expands; while for the block copolymer brush, the size is rather stable before the expansion sets in at 60 °C.

Conclusions: This model system provides insight into the effects caused by the thermoresponsive behavior of the PPO and PEO segments under the different steric constraints. With the same PPO/PEO weight ratio on the side arms, the temperature at which the molecule starts to expand is much lower for the random brush than that of the block copolymer brush.



POSTER 2.9

LOCAL AND GLOBAL (CHAIN) RELAXATION OF POLYISOPRENE IN MULTIBLOCK COPOLYMERS WITH A TAPERED INTERFACE

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Monomer pairs with strongly diverging reactivities are currently employed by industry to prepare multiblock copolymers (commercially relevant materials known as Styroflex® and Styrolux®). Herein we investigate the dynamics in a new class of tapered multiblock copolymers based on polyisoprene and polystyrene (PI-grad-PS) as well as to polyisoprene with poly(4-methylstyrene) (PI-grad-P4MS) with narrow molecular weight distribution. Unlike ordinary diblock copolymers, these multiblock copolymers have a broad interface but at the same time have superior mechanical properties due to the higher molecular weights[1]. We employ dielectric spectroscopy (DS) and temperature-modulated differential scanning calorimetry (TM-DSC) aiming at the local and global dynamics of PI. Block and multiblock copolymers of (PI-b-PS, PI-grad-P4MS) and (PI-b-P4MS, PI-grad-P4MS) are investigated with respect to: (i) the effect of chain stretching and junction point anchoring as a function of molecular weight, and (ii) the effect of mixing at the interface as a function of the effective interfacial width in the multiblock copolymers[2]. To this end we compare and contrast block and tapered copolymers to homopolymers, exploiting the distinctive dynamic behavior of polyisoprene. In the PI-b-P4MS case the main effect is the broadening and the retardation of both segmental and chain modes[3].

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POSTER 2.10

SYNTHESIS MOLECULAR AND MORPHOLOGICAL CHARACTERIZATION OF LINEAR AND NON-LINEAR BLOCK COPOLYMERS CONTAINING PS AND PDMS SEGMENTS

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Silicon containing BCPs such as PS-*b*-PDMS have been extensively studied because of their potential applications. The high etch contrast and the strong segregation strength are the intrinsic reasons to choose this system for BCP lithography. The synthesis of block copolymers containing polystyrene (PS) and poly(dimethylosiloxane) (PDMS) of (PS-*b*-PDMS)$_{n=1,\ 2,\ 3,\ 4}$ type was achieved via anionic polymerization, under high vacuum techniques in combination with chlorosilane linking chemistry. All samples were characterized through Size Exclusion Chromatography (SEC), from which the progress of all reactions was monitored and the average molecular weights and molecular weight distributions were verified. The characteristic groups and the final composition were verified through Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR). Differential Scanning Calorimetry (DSC) verified the values of glass transition temperatures of both blocks (PS and PDMS) which were very close to those of the corresponding homopolymers leading to initial conclusion concerning the successful microphase separation when the linear diblock and complex architecture copolymers self-assembly will be studied in bulk. In total three diblock copolymers, one triblock copolymer, one three arm star block copolymer and one four arm star block copolymer were synthesized. In each case, the final linear triblock copolymer and star-block copolymers were synthesized from the diblock copolymer precursors (PS-*b*-PDMS).

POSTER 2.11

APPLICATION OF SERS FOR THE CMC MONITORING OF CATIONIC BIOCIDAL SURFACTANTS AND THEIR RELEASE FROM ANTIMICROBIAL POLYMERS

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Introduction: The present study primarily focused on biocidal polymers and the release of electrostatically bound antimicrobial compounds probed by Surface Enhanced Raman Scattering, SERS. An attempt to understand the release profile revealed the importance of SERS as an alternative technique capable of determining the Critical Micelle Concentration-CMC of cationic surfactants without the use of specific Raman active markers. Comparison of the CMC values obtained with other widely applied methods, such as fluorescence and electrical conductivity, has been performed.

Methods: Nanocolloidal Ag suspensions were utilized as SERS substrates for both monitoring the release motive – in conjunction with UV-Vis absorption - and for the determination of the CMC of three cationic surfactants in sea water solutions: hexadecyltrimethylammonium bromide-CTAB, dodecyltrimethylammonium bromide-DTAB and benzalkonium chloride-BAC. CMCs have been experimentally determined and confirmed by two additional conventional methodologies: luminescence spectroscopy and conductivity measurements.

Results: Migration studies of biocidal cationic surfactants electrostatically bound to antimicrobial polymers and immersed in sea water solution were conducted by SERS. An immediate saturation of the SERS signal can be correlated to the CMC values. Although these surfactants present similar chemical structures, significant changes occur in the free surfactant concentration as the total surfactant release is located above the CMC, something that might be also noticed due to the formation of different shape and size micelles.

Conclusions: Raman-marker free SERS was utilized as an alternative technique to probe both the release of cationic surfactants electrostatically bound to biocidal polymers immersed in sea water solutions and the determination of the relevant CMCs.

POSTER 2.12

SYNTHESIS OF NEW TRIBLOCK TERPOLYMERS FOR APPLICATIONS IN NANOTECHNOLOGY

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We report the synthesis and molecular characterization of new ABC type triblocks, where A is the block of polystyrene (PS), B is 1,4 polybutadiene ($PB_{1,4}$) and C is polydimethylsiloxane (PDMS). This system was used primary for the well studied copolymer system of PS-*b*-PDMS, because of its high Flory-Huggins interaction parameter, that allows the existence of stable microstructures with dimensions below 10nm [1]. In this system, a new block was inserted, with very low average molecular weight, that of the $PB_{1,4}$. All samples were synthesized via anionic polymerization, with sequential addition of monomers and high vacuum technique. The synthesized terpolymers were characterized by Size Exclusion Chromatography (SEC), to elucidate the average molecular weight per number, the average molecular weight per weight and the polydispersity index. The successful synthesis, as well as the mass fraction of each block, was verified through ^{1}H-NMR.Furthermore, for the calculation of any thermal transition temperatures of the samples, differential scanning calorimetry (DSC) was employed. The total molecular weights, of the final polymers are very low (11,000g/mol and 13,100g/mol), while the mass fraction of the PB block is below 10 percent. The synthesis was successful and it seems that at least the two blocks, of PS and PDMS, are immiscible. Such systems could be used for applications in nanotechnology such as thin films for electric circuits, photonic crystals and for storage of information.

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POSTER 2.13

SELECTIVE SURFACE SEGREGATION OF MODIFIED NANOPARTICLES IN SYMMETRIC DI-BLOCK COPOLYMER AND TRIBLOCK TERPOLYMER

Dimitrios Moschovas[1], **George Zapsas**[2], **Konstantinos Ntetsikas**[2], **Apostolos Avgeropoulos**[1], **Nikolaos Zafeiropoulos**[1]
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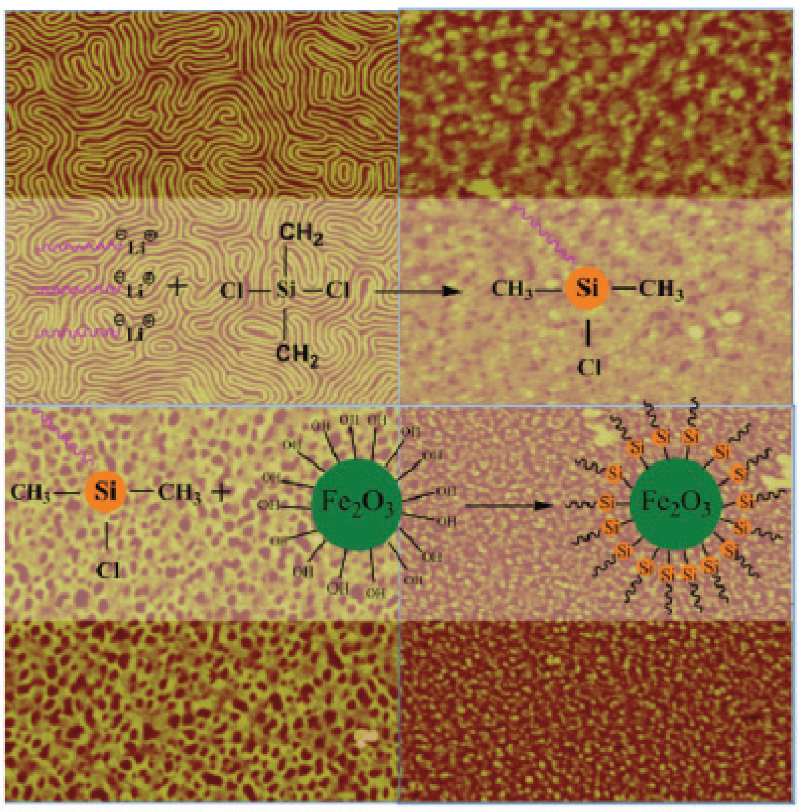
Block copolymers (BCPs) through their self-assembly provide an excellent guiding platform for precisely controlled localization of nanoparticles (NPs) with most applied being the utilization of diblock copolymers (di/BCP) due to their morphological simplicity. For the most of the cases, the success of this goal interprets as the selective decoration of NPs within several types of BCPs templates. Beyond the case of di/BCPs, the same incorporation attempts with in triblock terpolymers (tri/BCPs) remains limited and especially for high load of particles seems to be very difficult and rather problematic. To allow selective incorporation of NPs, several tasks need to be confronted in order to avoid particles from being embedded inside chemically dissimilar polymer domains.

In this work the structural evolution of diblock copolymer and triblock terpolymer hybrid patterned films through analysis of AFM. The recorded images prove that high amounts of loaded NPs (up to 10%) can be controllably localized within a desired block of an ABC terpolymer host. Towards this effort, the already known solvent vapor annealing (SVA) method was very helpful in order to selectively localize nanoparticles inside specific BCP domain without being the only prerequisite, since molar mass and block sequence of BCP scaffold are of major importance.



POSTER 2.14

SURFACE MODIFICATION ON SILICON SUBSTRATES AND MAGNETIC NANOPARTICLES OF PS/P2VP V-SHAPED POLYMER BRUSHES THROUGH THE "GRAFTING TO" METHOD

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The goal of the present study has been the fabrication of polymer brushes on planar and curved surfaces (nanoparticles). Using the "grafting to" method a V-shaped polymer brush of a amphiphilic diblock copolymer [polystyrene-Si(Cl)$_2$-poly (2-vynilpyridine) – PS-Si(Cl)$_2$-P2VP] which has been prefabricated via anionic synthesis polymerization was attached on the surface of Si wafers and of iron oxide nanoparticles.

Subsequently, the resulting polymer brushes were characterized with the use of XPS, FTIR, ellipsometry, contact angle measurements, AFM and DLS in order to verify the attachments of the polymer chains on the modified surfaces. The results of the characterization proved inadvertently that the formation of mixed polymer brushes upon the modified surfaces has been successful and that "smart" materials are able to adapt on different external stimuli such as pH and the presence of water, through switching hydrophilic and hydrophobic behavior.

POSTER 2.15

SYNTHESIS, MOLECULAR AND MORPHOLOGICAL CHARACTERIZATION OF LINEAR DIBLOCK COPOLYMERS OF THE PDMS-b-P2VP TYPE

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For the purpose of generating sub–10 nm nanopatterns, a high χ-low N block polymer is required. Consequently, research also focused on the synthesis of silicon-containing BCPs with extremely high χ value for sub–10 nm BCP lithography. Diblock copolymers of type PDMS-*b*-P2VP exhibit a significantly higher degree of tunability of pattern geometry and dimensions with an extremely large χ parameter. The synthesis of linear diblock copolymers containing poly(dimethylosiloxane) (PDMS) and poly(2-vinyl pyridine) (P2VP) was achieved via anionic polymerization, under high vacuum techniques in combination with chlorosilane chemistry. The molecular and thermal characterization of the final materials was achieved via size exclusion chromatography (SEC), ^{1}H-nuclear magnetic resonance spectroscopy (^{1}H-NMR) and differential scanning calorimetry (DSC) respectively. Finally, the morphological characterization was accomplished with transmission electron microscopy (TEM) and atomic force microscopy (AFM).All of the samples can be considered model polymers since they exhibited high molecular and compositional homogeneity, whereas the thermal transitions indicated the absence of mixing since the corresponding values were almost identical with those of the relative homopolymers.For the morphological characterization different solvents were used in order to study the microphase separation of the diblock copolymers of PDMS-*b*-P2VP type.

POSTER 2.16

SYNTHESIS AND CHARACTERIZATION OF POLYMER IONIC LIQUIDS PREPARED FROM DIBLOCK COPOLYMER PRECURSORS

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This study focuses in the synthesis and characterization of polymer ionic liquids which were produced by chemical modification of linear diblock copolymer precursors. The diblock copolymer of the $PB_{1,2}$-*b*-P4VP type, where $PB_{1,2}$: poly(butadiene) of very high 1,2-microstructure and P4VP: poly(4-vinylpyridine) were synthesized via anionic polymerization and exhibited narrow molecular weight distribution. In order to achieve an ionic liquid character all samples were chemically modified. Initially the nitrogen atoms of the block of P4VP were quaternized and kinetics were studied and followed separate reactions with two different salts consisting of a large organic group and a metal ion, succeeding the ionic liquid character to the polymer[1]. All samples were characterized via size exclusion chromatography (SEC) in order to calculate the average molecular weights and their polydispersity. IR spectroscopy was employed at first as a structural characterization in order to determine the successful synthesis of the samples through detection of characteristic absorptions attributed to the functional groups of the segments. In addition, ^{1}H-NMR spectroscopy also verified the successful synthesis since in all cases characteristic chemical shifts of protons from different groups appeared in the obtained spectra. Additionally, weight fractions of each block were calculated using the intensity of the characteristic chemical shifts. Finally, differential scanning calorimetry was performed in order to investigate the glass transition temperature of each block in both samples as well as to study the effect on these thermal transitions due to the various chemical modifications made in the initial copolymer precursors.

POSTER 2.17

WETTING OF SOFT SUPERHYDROPHOBIC MICROPILLAR ARRAYS

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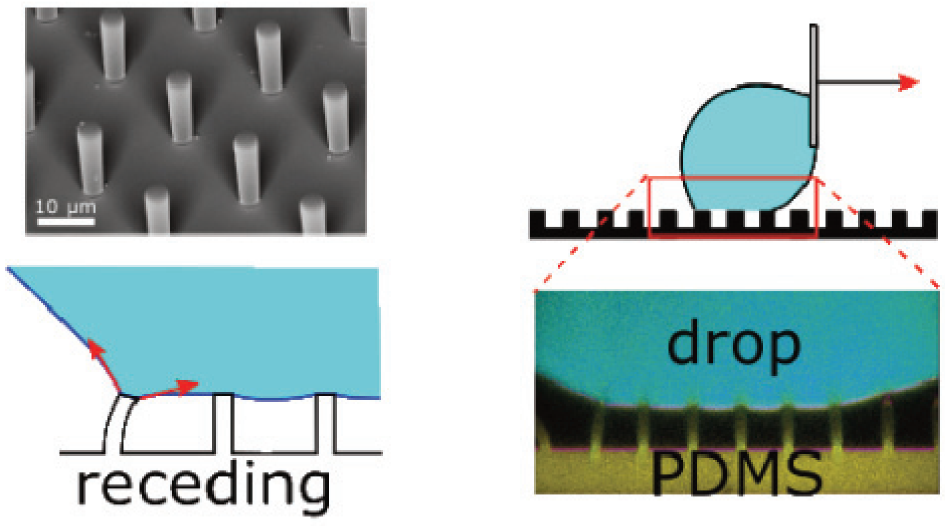
Superhydrophobic surfaces are usually assumed to be rigid so that liquids do not deform them. Here we analyze how the relation between microstructure and wetting changes when the surface is flexible.
Therefore we deposited liquid drops on arrays of flexible micropillars. We imaged the bending of micropillars and the drop's surface with confocal microscopy and analyzed the deflection of micropillars while the contact line advanced and receded.
The deflection is directly proportional to the horizontal component of the capillary force acting on that particular micropillar. In the Cassie or "fakir" state, drops advance by touching down on the next top faces of micropillars, much like on rigid arrays. In contrast, on the receding side the micropillars deform.
The main force hindering a drop to slide is pinning at the receding side, while the force on the advancing side is negligible. In the Wenzel state, micropillars were deflected on both receding and advancing states.



POSTER 2.18

SUSTAINABLE POLYMERS FROM RENEWABLE RESOURCES: SYNTHESIS AND SOLID-STATE CHARACTERIZATION OF THERMOPLASTIC POLYESTERS OF 2,5-FURANDICARBOXYLIC ACID

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Sustainable polymers from biomass recently have gained increasing interest. The thermoplastic polyesters of 2,5-furandicarboxylic acid (FDCA) are biobased alternatives to the fossil based terephthalate polyesters, like poly(ethylene terephthalate) (PET). In this work, a series of polyesters of 2,5-furandicarboxylic acid were synthesized and their solidification and solid state were studied. Blends of the polymers were also studied. Polyester samples were synthesized from the dimethylester of FDCA and corresponding diols including the aliphatic diols of type $HO(CH_2)_XOH$ with x=2, 3, 4 ,5 ,6, 8, 9, 10, 12 and also, Methyl-1,3,propylene diol, 2,2-dimethyl-propanediol, 1,4-cyclohexandimethanol, and isosorbide. Following molecular characterization, the polymers were studied with respect to their phase behavior and segmental dynamics using DSC, PLOM and Dielectric Spectroscopy (DS), respectively. Polymers from diols with x = 4-12 or CHDM crystallize faster than the rest and reach higher crystallinity values. Poly(isosorbide 2,4-furandicarboxylate) is a high T_g glassy material. The transition temperatures and crystallization kinetics of the polymers were evaluated. DS on neat polymers showed a reduction of the liquid-to-glass temperature, T_g, by about 100 K by increasing number of methylene units on the polymer backbone. A three-phase model was necessary to describe the segmental dynamics in PEF. DSC and DS provided evidence that a third of polymer segments are located within the restricted amorphous phase. Furthermore, the issues of thermodynamic miscibility and dynamic heterogeneity/homogeneity were investigated in blends composed of the polyesters. Reactive blending was found to increase miscibility. Overall, the thermodynamics and the molecular dynamics are dictated by the diol segment length.

POSTER 2.19

HIGH MOLECULAR WEIGHT CIS-1,4-POLYISOPRENE CONFINED IN NANOPOROUS ALUMINA: DYNAMICS OVER THE ENTANGLEMENT LIMIT

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The effect of confinement on polymer dynamics and the associated liquid-to-glass temperature, T_g, has been an issue of great interest in polymer physics. In this study, we investigate the effect of confinement in the nanometer scale on the dynamics of *cis*-1,4-polyisoprene with molecular weights in the vicinity and over the entanglement limit (M_w=8500-100000 g/mol), confined in self-ordered nanoporous alumina (AAO) with diameters, *d*, ranging from 400 nm to 25 nm. An earlier study [1] investigated the effect of confinement in PI with $M<M_e$ and found an unaffectedT_g under confinement with respect to the bulk. Another study [2] reported on the effect of interfacial energy on the segmental dynamics for different polymers confined in AAO. Broadband Dielectric Spectroscopy (BDS) and Temperature-Modulated Differential Scanning Calorimetry (TMDSC) measurements were employed to examine the effect of confinement on molecular dynamics and the thermodynamic T_g, respectively. For molecular weights higher than the entanglement limit (M_w>10000 g/mol), BDS measurements revealed consistently faster segmental dynamics under confinement with respect to the bulk, leading to a decrease in T_g with increasing degree confinement ($2R_g/d$). In addition, we provide evidence for an intermediate process with an Arrhenius temperature dependence whose dielectric strength increases with increasing degree of confinement. This is attributed to a "dead layer" consisting of partially immobilized chains next to the interface, discussed in recent imbibition studies of polymers in nanopores and confirmed by theory [3], [4]. We further report on the effects of annealing and quenching on the thermodynamics and dynamics [5].

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POSTER 2.20

POLY(ALKYLENE TEREPHTHALATE)S BINARY BLENDS

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Poly(ethylene terephthalate) (PET) dominates the thermoplastic polyester market. Poly(butylene terephthalate) (PBT) has also an important share in that market and it is used mainly for injection moulded parts. Poly(trimethylene terephthalate) (PTT) is a relatively new biobased polyester, used for the production of fibers. In fact, its industrial production was expanded during last two decades and after the industrialization of its diol monomer, 1,3-propanediol. Since 2009, biobased PET is industrially available. The Coca Cola Plantbottle 1.0 made of bio-PET was introduced in 2009. Sugar-based ethyleneglycol was used as one of the monomers for its synthesis. In 2011, the Plantbottle 2.0 was announced, being made of a bio-PET 100% from bioderived monomers, as technology was then available for production of both terephthalic acid and ethylene-glycol from biomass. Bio-PET as well as PTT and PBT are expected to play a key role in the future biobased economy. Three different series of polyester blends were prepared by combining PET, PTT and PBT. The thermal behavior and homogeneity of the blends were studied. It was found that PET-PTT, PTT-PBT and PET-PBT blends show single composition dependent glass transition temperature, over the whole composition range. The crystallization behavior of the blends was also studied by means of differential scanning calorimetry (DSC), wide angle X-ray diffractometry (WAXD) and polarized light optical microscopy (PLOM).

POSTER 2.21

TUNABLE RHEOLOGICAL SPECTRA OF ASSOCIATIVE HYDROGELS BASED ON THE BENZENE TRICARBOXAMIDE MOTIF

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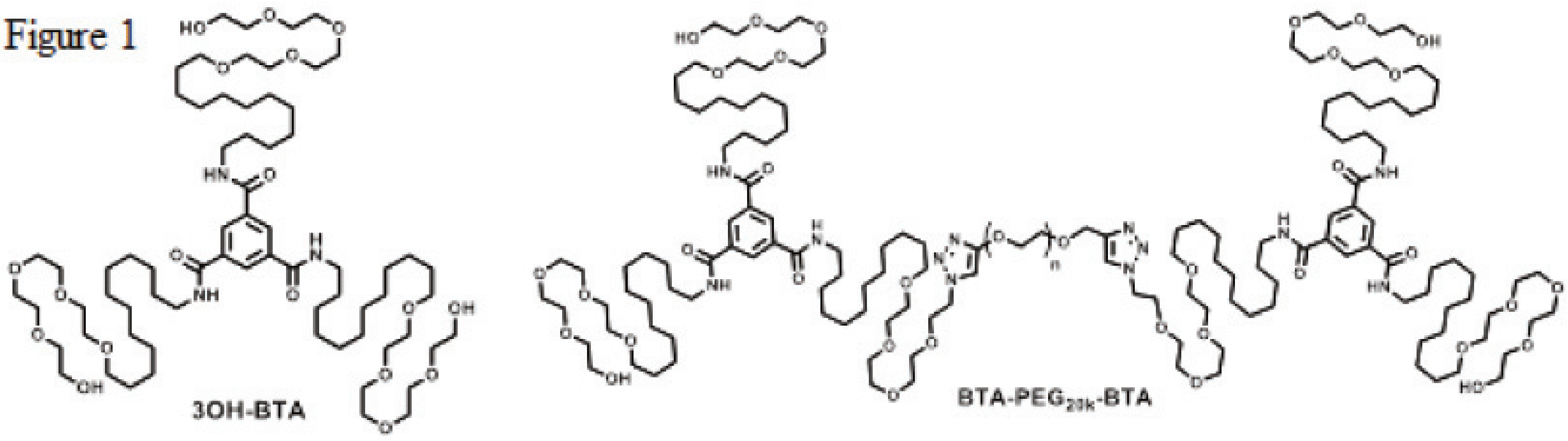
Networks formed from supramolecular polymers represent a relatively new class of soft systems with significant technological implications. The goal is to synthesize strong and resilient networks which can still uptake large amounts of water along with dynamic physical interactions that promote processability and self-healing. Here, we study the unusual rheological properties of a class of hydrogels made of fibrillar supramolecular polymers based on the 1,3,5-benzene-tricarboxamide motif decorated with aliphatic chains terminated by a tetra(ethylene oxide chain) (3OH-BTA), and in particular their tunable mechanical response, using oscillatory rheology. The 3OH-BTA unit is known to self-assemble into long, persistent fibrillar structures[1]which form physical networks akin to those of entangled polymers[2]. In addition, we used a second novel motif comprised from a telechelic poly(ethylene glycol) chain decorated with 3OH-BTA units on both ends (BTA-PEG-BTA). The BTA-PEG-BTA motif can also form gel-like materials in water albeit with different mechanical response compared to 3OH-BTA networks. By mixing the 3OH-BTA and BTA-PEG-BTA units in different compositions we observed a non-monotonic mechanical response, suggesting additional interactions between the two building units that enable fine tuning the mechanical properties. We discuss the origin of this behavior and its consequences on the tenability of hydrogel response.

Figure 1



Polymer Engineering

INVITED ORAL

THERMO-CHEMICAL RECYCLING OF POLYMERS FROM PLASTIC WASTES

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Introduction: The production and consumption of plastics globally has grown enormously during the last decades, in accordance with the increased standards of living and modern society demands. The short life-cycle of most plastics used in packaging or electronic equipment coming from the rapid technology developments and advanced features of the equipments, poses a significant issue as far as their disposal is concerned. Therefore, the necessity of developing a proper and efficient waste management method for plastic wastes is crucial for reducing the amount of waste, while at the same time recovering energy or secondary valuable materials.

Methods: Thermochemical methods will be presented for the recycling of several types of polymers and blends, including pyrolysis or microwave induced degradation.

Results: The existence of several polymers in plastic wastes results in synergistic effects which may decrease or increase the onset and final temperature of degradation during thermal degradation under inert atmosphere. Polymers may decompose in a great variety of compounds, depending on the polymer type, such as monomers, or other secondary value-added compounds(aromatic products, phenolic compounds, hydrocarbons, etc) that can be reclaimed afterwards.

Conclusions: The main conclusion from this investigation is that pyrolysis could be an effective method for the sustainable recycling of the plastic part of either packaging or WEEE resulting in a mixture of chemicals with varying composition but being excellent to be used as fuel retrieved from secondary recycling sources.

ORAL

A COMPARATIVE STUDY ON THE THERMOMECHANICAL PROPERTIES OF CARBIDES/ OR GRAPHITE/EPOXY COMPOSITES

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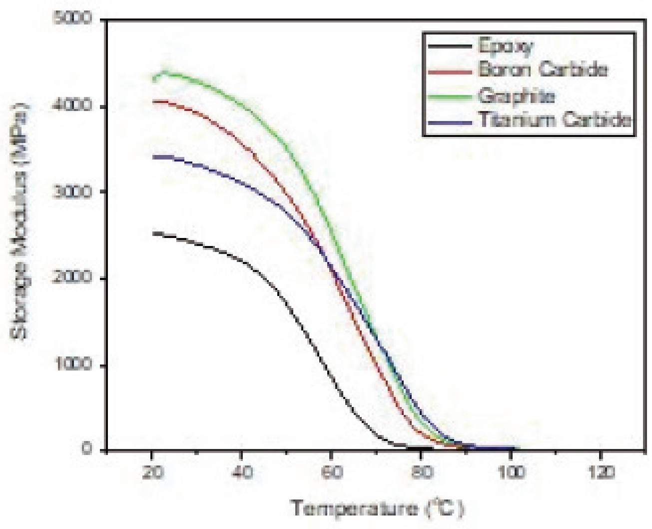
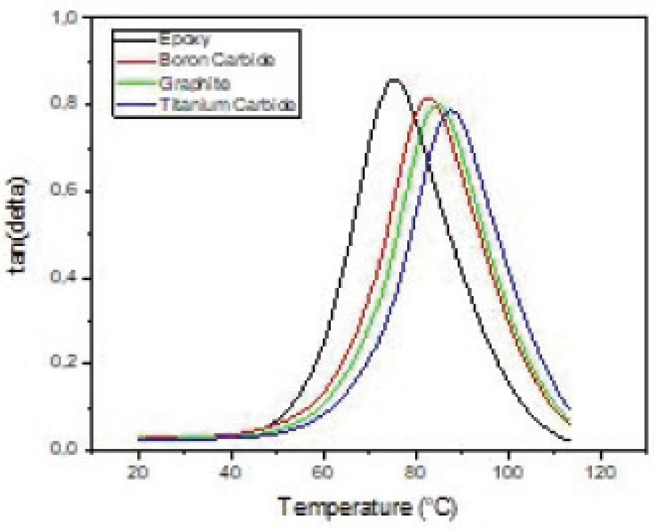
Polymer composites have been widely used as structural materials due to their extraordinary mechanical response, thermal stability, weight saving and anticorrosive properties. In the present study, three series of composites were manufactured varying the filler type and content. Epoxy resin was used as a matrix, while particles of Boron Carbide (B_4C), Titanium Carbide (TiC) and Graphite (C) were acting as filler. Their mechanical properties were investigated by means of Dynamic Thermomechanical Properties (DMA) in the temperature range from ambient to 120 ^oC. Storage modulus, in all cases, increases systematically with filler concentration. However, the optimal behavior depends on the filler's concentration. Specifically, composites with Boron Carbide, Graphite and Titanium Carbide show their optimal performance at higher, intermediate and lower filler concentration, respectively. Furthermore, the transition from glassy to rubbery state, determined via the tand spectra, shifts to higher temperatures, indicating strong interactions between the filler and the polymer matrix.





ORAL

EPOXY POLYMER ADDITIVES DERIVED FROM LIGNOCELLULOSIC BIOMASS: THE CASE OF ORGANOSOLV AND KRAFT LIGNIN

D. Giliopoulos, R. Kokoli, K. Karagiannidis, C. Pappa, A. Fotopoulos, P. Lazaridis,
A. Margellou, K.S. Triantafyllidis
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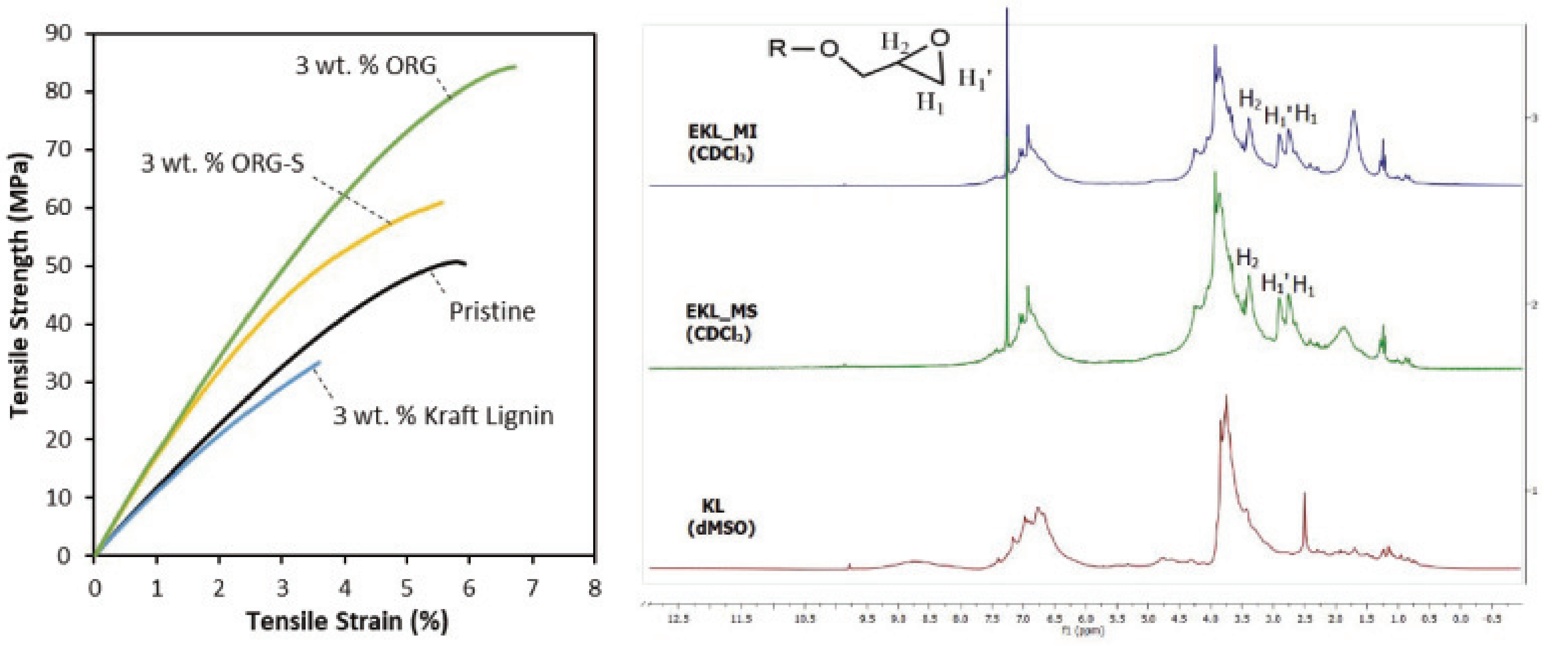
Over the last two decades, lignin has found increased valorization potential in various sectors, such as polymers/resins, binders, foams, etc. Nowadays, intensive research is being conducted on the development of efficient processes for the chemo- and bio-catalytic conversion of lignin towards high value chemicals/monomers that can be utilized in the polymer industry. In addition, pure isolated lignin or functionalized derivatives are also being studied as potential bio-additives polymers. In the present work, the epoxidation of lignin was achieved by reacting kraft lignin with epichlorhydrin in methanolic sodium hydroxide solution at 70-80^{o}C. A high purity organosolv lignin (ORG and ORG-S) was also obtained via hydrothermal treatment of hardwood in 50/50 ethanol/water medium. The various parent and epoxidized samples were tested as additives in epoxy polymers, diglycidyl ether of bisphenol A (DEGBA) epoxy resin with polyetheramine Jeffamine D-230 as curing agent. The respective composites were prepared by in situ polymerization. The lignin samples were characterized by ^{1}H-NMR, FTIR, TGA/DTG etc. The prepared epoxy polymer samples were tested for their mechanical properties via tensile strength measurements. The successful epoxidation of lignin is confirmed by the proton peaks related to the epoxy ring carbons (H_1, $H_1¢$, H_2) in the ^{1}H-NMR spectra (Fig 1(a)). The properties of the derived epoxy-lignin composites, (Fig. 1(b)) indicate that addition of the parent kraft lignin resulted in slight deterioration of the mechanical properties, while the epoxy-organosolv lignin composites exhibited improved behavior, both in terms of strength as well as elongation, compared to the pristine epoxy polymer. The epoxidized lignins afforded improved interactions and enhanced properties.

Figure 1. (a) ^{1}H-NMR spectra of parent and epoxidized kraft lignin, (b) Stress-Strain curves of pristine epoxy and composite polymers at 3 wt. % lignin loading



POSTER 3.1

LAYER BY LAYER POLYMER COATED MESOPOROUS SILICA MICROPARTICLES FOR DRUG DELIVERY POTENTIAL APPLICATIONS

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Mesoporous silica microparticles (MSMs) have recently gained much attention because of their promising biomedical applications. MSNs have become a novel drug vehicle due to their unique properties like high surface areas, tunable pore sizes, large pore volumes and rich morphology. This work focuses on the development of Layer-by-Layer (LbL) polymer-coated MSMs. Firstly, the negatively charged MSNs were coated with a pH-sensitive P2VP-PEO block copolymer through ionic bonding between opposite charges. The MSM@P2VP-PEO was further coated with the PS_nPEO_n star copolymer, using Tannic Acid as a connector between the layers, due to its ability to form hydrogen bonds with PEO *(Figure 1*). The PS_nPEO_n star forms unimolecular micelles, constituted of PS hydrophobic cores surrounded by the PEO soluble arms. Thus, the formed PS_nPEO_n layers bear hydrophobic pockets capable of carrying hydrophobic agents (e.g. Nile red), while the MSM can carry hydrophilic agents (e.g. calcein) (see fluorescence microscopy in Figure 1). The characterization of the prepared colloidal microparticles was performed with TGA,ζ-potential, SEM, TEM and Fluorescence Microscopy. Finally loading and release of model drugs from these complex MSM were studied in 37 ^{0}C and at various pH, in order to evaluate whether or not the above system exhibits pH-controlled drug release.

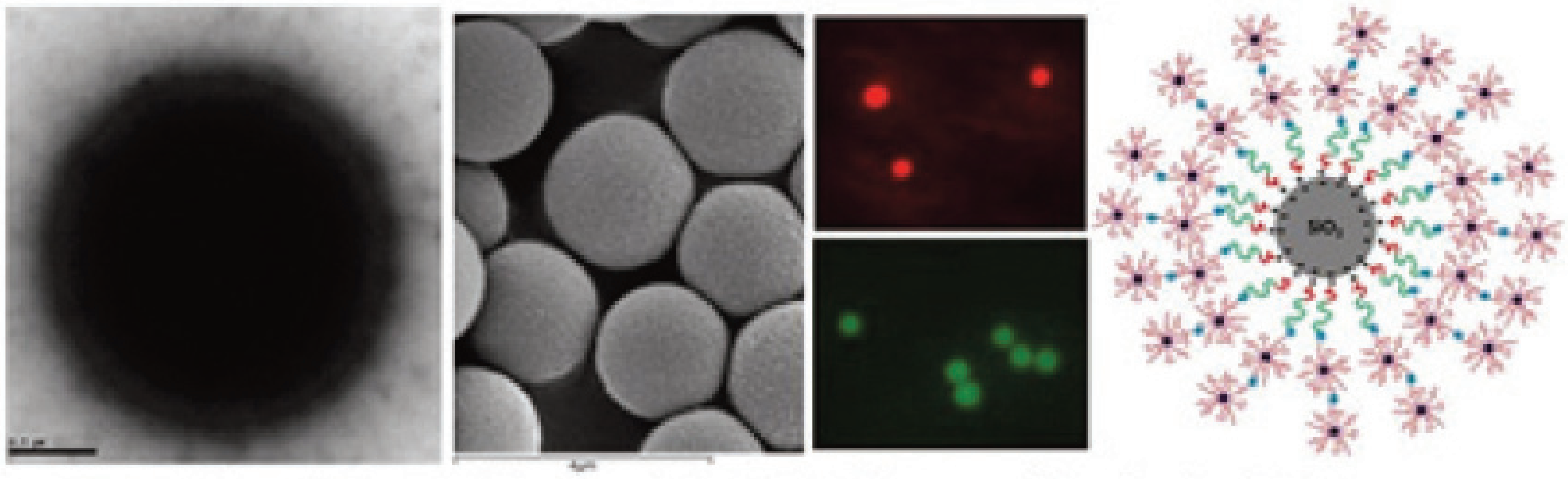

Figure 1: From the left to the right: TEM, SEM images of functionalized MSMs, fluorescence microscopy of functionalized MSMs loaded with Nile red (top) and calcein (bottom) and illustration of the LbL polymer-coated MSMs.

POSTER 3.2

DIRECT SOLID STATE POLYMERIZATION OF ALIPHATIC POLYAMIDE SALTS: STUDY OF CRITICAL PARAMETERS

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Introduction: The direct solid state polyamidation (DSSP) of aliphatic polyamide monomers exhibits significant practical interest as all problems associated with the high temperature of the solution melt technology are avoided. In this work hexamethylene diammonium adipate was polymerized, in a microscale reactor. Process parameters, such as temperature and particle size, and their impact mainly on the maintenance of solid state of the reacting material were investigated.

Methods: DSSP took place in a thermogravimetric analysis (TGA) chamber which simulates a polymerization reactor. Samples of dried PA66 salt of different particle size were left to react in the temperature range of 175-195°C under nitrogen flow. End products were characterized macroscopically as to the maintenance of the solid state, thermal properties and molecular structure.

Results: Polymerization rates were found lower in the case of large particles (>800 μm) which however allowed the maintenance of the solid state character of the reacting mass. The opposite was observed in the case of the smaller particle sizes (<125 μm).Reaction temperature was also found as the most critical parameter to the maintenance of the solid state: all samples, even the large ones, polymerized above 180°C were received in a quasi-melt state. Samples polymerized above 190°C were received in a fully melt state, thus demonstrating a direct link between reaction temperature and the solid melt transition phenomenon.

Conclusions: In this work the direct solid state polymerization of PA66 salt was examined and presented significant reactivity difference between samples of different sized grains.

Biopolymers & Applications

PLENARY ORAL

DISSOLVING THE INSOLUBLE

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The recalcitrance to dissolution hinders the processing of crystalline polymers. [Curr.Opin.GreenSustainableChem. 2018, 14, 40-52. DOI:10.1016/j.cogsc.2018.05.008] A phenomenological model is presented that captures the phenomena governing the dissolution of semicrystalline polymers, e.g., solvent diffusion, transformation from crystalline to amorphous domains, specimen swelling, and polymer chain untangling. The model is validated for the case of cellulose (cotton) fiber swelling and dissolution in various solvents. [Cellulose 2017, 24(2), 571-590. DOI:10.1007/s10570-016-1145-1] A parametric sensitivity analysis is carried out to assess the impact of various parameters on the dissolution of cellulose fibers. [AIChEJournal 2017, 63(4), 1368-1383. DOI:10.1002/aic.15615] [Biomacromolecules 2018, 19(2), 640-651. DOI:10.1021/acs.biomac.7b01745] To emulate large-scale processing of cellulosic biomass where the particles exhibit a distribution of size and degree of crystallinity, a model is developed in which the behavior of a population of particles is obtained from an ensemble of individual polymer particle dissolution models. [Chem.Eng.J. 2018, 350, 37-48. DOI:10.1016/j.cej.2018.05.167] Using this population ensemble model, various particle size distributions are analyzed for different dissolution parameters. The insights obtained from these studies would be useful for the rational design and optimization of solvent systems and processes for the dissolution of semicrystalline polymers such as cellulose, polyglycolic acid, and polyesters. [BioresourceTechnol. 2017, 228, 330-338. DOI:10.1016/j.biortech.2016.12.049]

PLENARY ORAL

POLYMERS AT SYNTHETIC AND BIOLOGICAL SURFACES

Harm-Anton Klok

Institute of Materials, EPFL, Switzerland

Polymer science provides a diverse toolbox to modify both synthetic and biological surfaces. The first part of this lecture will discuss the use of surface-initiated, controlled radical polymerization (SI-CRP) techniques for the preparation of thin, surface tethered polymer brushes. SI-CRP reactions possess a number of attractive features, such as the ability to prepare brushes (i) with precise control over chemical composition and film thickness; (ii) that present very high surface concentrations of functional groups; (iii) that conformally coat complex, 3D structured or porous substrates and which allows to (iv) tune the conformation of the surface grafted chains. This presentation will highlight the use of SI-CRP to generate polymer films with sensory or responsive properties as well as results from recent work, which shows that the conformation of surface grafted polymer chains also impacts their chemical reactivity, potentially opening avenues towards novel mechanically responsive surfaces.

The second part of this talk will concentrate on biological surfaces and more specifically the membrane of living cells. Living cells are attractive carriers to mediate transport of drug-loaded polymer particles. The successful use of cells as carriers for polymers and polymer particles requires chemical approaches that allow to immobilize (and release) the polymer or particle payload from the cell surface, without compromising cell viability and function. This presentation will discuss various polymer cell surface modification strategies and compare these different approaches in terms of the possibilities they offer to modify cell surfaces as well as their impact on cell viability and function.

INVITED ORAL

POLYMER NANOCOMPOSITES AS EFFECTIVE DRUG CARRIERS

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During the last decades, polymers are extensively used as biomaterials due to their encouraging properties such as good biocompatibility, simple design and preparation, diversity of structures and interesting bio-mimetic character. Polymers can be used in the form of films, gels, micro- and nanoparticles, etc., preparing formulations for immediate, controlled and targeted drug release. Another kind of materials that gained high interest for drug delivery applications are polymeric nanocomposites that combine the unique properties of neat polymers and nanoparticles. These materials offer new opportunities to modern medicine, in generating products for antibacterial treatment, tissues engineering, cancer therapy, medical imaging, dental applications, drug delivery, etc. Thus, the production of polymer nanocomposites containing nanoparticles such as mesoporous silica, layered silicates (clays), nanodiamonds, Ag, SiO_2, TiO_2, gold nanoparticles, multi walled carbon nanotubes, graphene, etc., are of great interest for the preparation of new and ideal pharmaceutical formulations. The added nanoparticles offer an additional advantage to the drug carrier, which is the huge surface area, ranging from 200-1500 m^2/g. However, the properties of polymer nanocomposites depend mainly on the characteristics of the used components (organic-inorganic) and on the interactions between polymer-nanofiller that can affect the release profile of the drug.

Many polymer nanocomposites based on natural polymers like chitosan (CS) and other polysaccharides or synthetic polymers such as poly(N-vinyl-2-pyrrolidone) (PVP), poly(vinyl alcohol) (PVA), polyacrylates, polyesters, etc., are studied as candidates for drug carriers. Such nanocomposites with different polymer matrices and nanoparticles have been extensively studied in our laboratory, with the aim of enhancing drug bioavailability or preparing controlled released formulations for oral or injectable applications. However, in order to be used as drug delivery systems, nanocomposites should possess the following requirements: drug vehicle should be bio-degradable, non-toxic, non-immunogenic, should be physically and chemically stable in vivo and in vitro conditions and readily eliminated from the body without any problems (low accumulation in organs). In this context, besides designing and synthesizing nanocomposites with optimal properties for as drug carriers for predefined drug release, emphasis was also given in the study of their toxicity. It was found that surface functionalization is the most promising approach in order to reduce the toxicity of nanoparticles.

Polymeric microparticles in the form of nanocomposites are also a new class of biomaterials of high importance in the pharmaceutical field due to their advantages; ability to encapsulate either hydrophilic or hydrophobic drugs, administration through different pathways to patients (oral, nasal, inhalation, parenteral), maintenance of the therapeutic concentration of drugs (shorter half-life) in plasma for longer period of time by controlling their release. These microparticles are used mainly as long term release carriers (long acting injectables), which are appropriate for increasing the therapeutic efficiency of several drugs.

INVITED ORAL

RESPONSIVE POLYMERIC NANOCONSTRUCTS FOR DRUG DELIVERY TO TREAT CANCER

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Maria Kasimati[1], Katerina Mathianaki[2], Diana Kazaryan[2],
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[2] *Industrial Chemistry Laboratrory, Department Of Chemistry, National & Kapodistrian University Of Athens Panepistimiopolis Zografou, Athens 157 71, Greece*

Introduction: Cancer treatment remains a major challenge in medicine. Pharmaceutical scientists are trying to shift from traditional to novel drug delivery systems (DDS) by applying nanotechnology to medicine. While traditional therapeutic agents have allowed for very little control in terms of their distribution in the body and clearing times, engineering at the nanoscale level has allowed for significant advances in optimizing the biocompatibility, biodistribution, and pharmacokinetics. Although research to identify more efficient drugs is rapidly advancing, the discovery of novel materials with the required functionality is not progressing at the same rate.

Methods: High vacuum techniques was used for the synthesis of the polymeric materials. Size exclusion chromatography, FTIR and NMR spectroscopy was used for the characterization of the polymeric materials. Static and Dynamic laser scattering was used for the characterization of the polymers and the nanoconstructs. Rheology was used for the properties of the hydrogels.

Results: The nanoconstructs that were synthesized encapsulated efficiently large amounts of well-known and certified drugs for cancer treatment, like gemcitabine and everolimus. The delivery was targeted and in a sustained release profile.

Conclusions: The collaboration of material as well as pharmaceutical scientists, biologists and clinical oncologists is imperative to produce efficient materials that possess advanced properties and required functionalities. Furthermore, advancements in drug design and the development of multifunctional nanocarriers from the combination of well-defined macromolecular architectures and smart materials are the future for the effective treatment of many lethal diseases such as cancer.

INVITED ORAL

BIOCHEMICAL PRODUCTION OF BIOPOLYMERS: CONTROL OF THE BACTERIAL METABOLIC PATHWAY AND THE MACROMOLECULAR POLYMER CHAINS

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Thermi, Thessaloniki, Greece, &
[2] *Department of Chemical Engineering, Aristotle University of Thessaloniki (AUTH), Greece*

Presently, the industrial-scale production of biopolymers (e.g., polyhydroxybutyrate-PHB) is impeded by several factors like the raw materials and downstream processing costs, low-productivities and the inability to control their molecular properties. Therefore, the optimal operation of microbial processes for large biopolymer productivities and tailor-made molecular properties is of significant commercial importance. In the present work, the bacterial strain *Azohydromonas lata* was selected to investigate the combined effect of nutritional and operational conditions on the intracellular synthesis of PHB in lab-scale batch and fed-batch experiments. The statistically analysed measurements were used to regulate the *A. lata* metabolic pathway towards the enhanced growth-associated accumulation of PHB. Moreover, a multi-scale mathematical model, consisting of metabolic, polymerization and macroscopic sub-models, was developed to intensify the bioprocess performance. The model was used to optimise the cultivation conditions, to efficiently upscale the optimal fermentation policies, to maximize the production rate of PHB and to control its molecular weight distribution. Two optimal policies were selected: (1) a nitrogen-limited single-step fed-batch policy, aiming at the maximization of the intracellular PHB content, and (2) a nitrogen-sufficient continuous fed-batch policy, aiming at the maximization of the PHB production rate. These two strategies resulted in a PHB content and productivity equal to 94% g/g and 4.2 g/(l·h), respectively. Furthermore, depending on the operating strategy, different PHB grades were produced: molecular weight values up to 1,513,000 g/mole. As a result, the present approach clearly presents a large potential as a generic tool for bioprocess optimization.

INVITED ORAL

SELF-ASSEMBLED POLYMERIC NANOPARTICLES FOR DRUG DELIVERY: DO THEY INTERACT WITH BLOOD PROTEINS?

Xiaohan Zhang[1], Petr Chytil[2], Sergey K. Filippov[2], Dmitri I. Svergun[3], Christine M. Papadakis[1]

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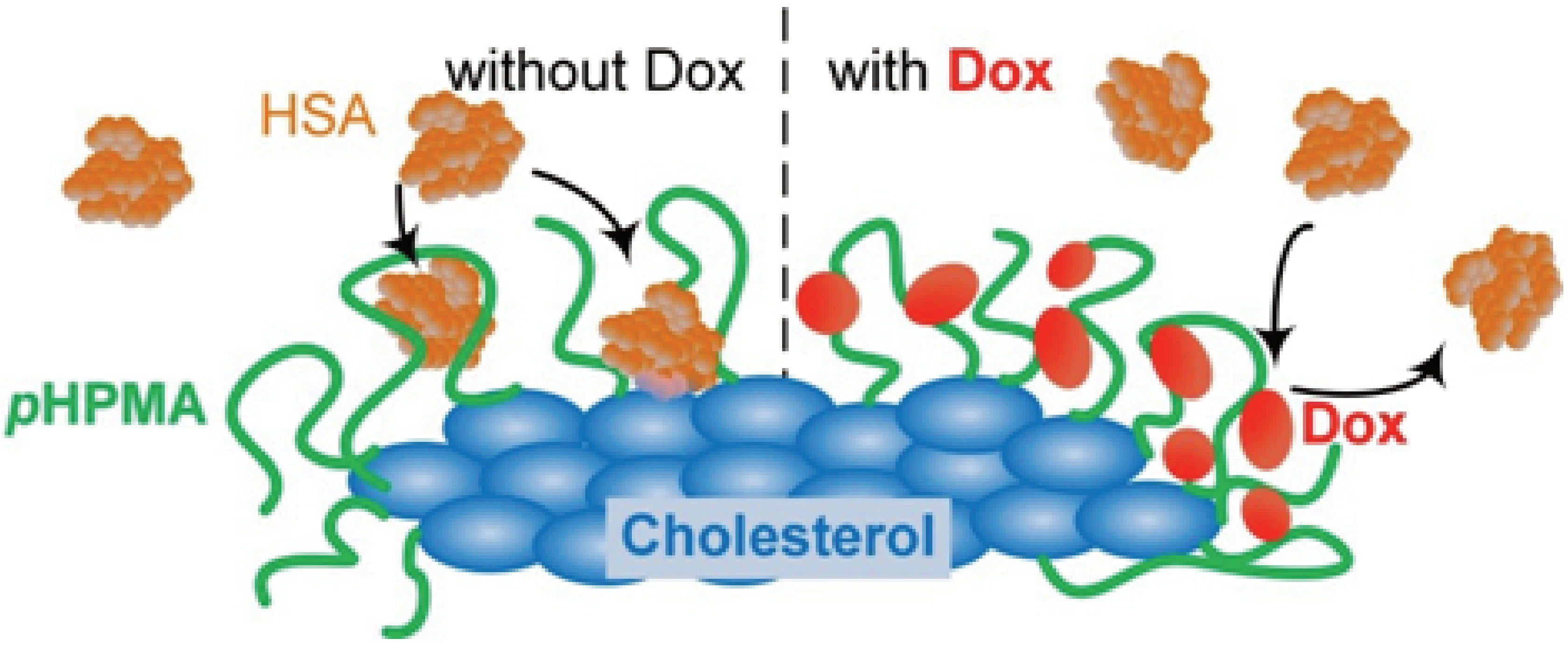
[2] Institute Of Macromolecular Chemistry, The Czech Academy Of Sciences, Prague, Czech Republic
[3] European Molecular Biology Laboratory, Hamburg Outstation, C/O Deutsches Elektronen-Synchrotron, Hamburg, Germany

For cancer treatment, polymeric drug carriers have proven to be very promising systems. The system based on poly(*N*-(2-hydroxypropyl)-methacrylamide) (*p*HPMA) copolymers bearing cholesterol moieties and the anti-cancer drug doxorubicin (Dox) bound to the backbone forms elongated nanoparticles (NPs) in phosphate buffered saline (PBS) with the cholesterol moieties forming the core of the NPs. In blood, however, proteins may interact with the NPs by forming complexes or by adsorbing onto the surface of the NP, hampering the drug delivery process.

Here, we investigate the behavior of the NPs in solutions of human serum albumin (HSA) in PBS. Mixed solutions of NPs and HSA are characterized by synchrotron small-angle X-ray scattering and isothermal titration calorimetry. The nature of the binding is characterized using fluorescence lifetime correlation spectroscopy on fluorescence-labeled copolymers as well as quenching of the intrinsic fluorescence of HSA.

We find that, for copolymers without Dox, few HSA molecules bind to the cholesterol groups. These interactions are strongly hindered by the presence of Dox, which is distributed in the *p*HPMA shell, i.e. the delivery of Dox by the NPs in the human body is not affected by the presence of HSA. The system is thus very promising for drug delivery.



INVITED ORAL

DESIGN OF A THERMO AND SHEAR-INDUCED INJECTABLE HYDROGEL

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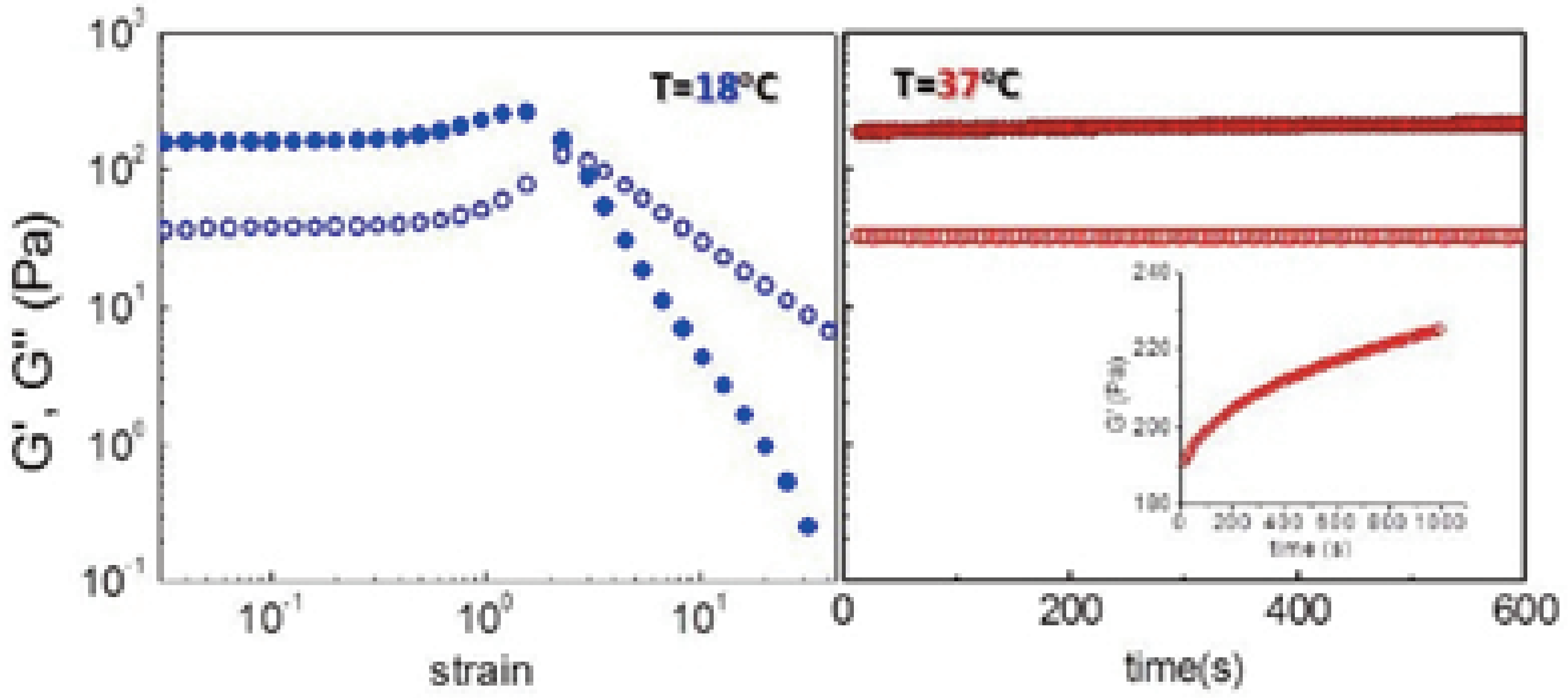
The motivation of this work was to design an injectable hydrogel behaving as a weak gel at room temperature and as a strong gel at physiological temperature. These kinds of hydrogels constitute good candidates for potential applications in cell transplantation through injection strategies. For this purpose a thermo-responsive gelator of (B-*co*-C)-*b*-A-*b*-(B-*co*-C) topology, comprising a poly(2-dimethylamino ethyl methacrylate) (PDMAEMA) weak polyelectrolyte as central block, end-capped by thermo-sensitive poly(tri-ethylene glycol methyl ether methacrylate/*n*-butyl methacrylate) [P(TEGMA-*co*-*n*BuMA)] random copolymers, was designed and explored in aqueous media. At low temperatures, the system behaves like a viscoelastic complex fluid (dynamic network) while, at higher temperatures, an elastic hydrogel is formed («frozen» network). The viscosity increases exponentially upon heating, about five orders of magnitude from 5 to 45 ^{o}C, which is attributed to the exponential increase of the life time of the self-assembled thermoresponsive stickers. The integration of thermo and shear responsive properties in the gelator endows the gel with the targeting injectability. Indeed, the gel flows under shear at room temperature and is rapidly recovered upon cessation of the applied stress at 37 ^{o}C, simulating conditions similar to those of injection through a 28-gauge syringe needle.



ORAL

PREDICTION OF TABLET STRENGTH OF HOT-MELT-EXTRUDED POWDERS

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Introduction

In the pharmaceutical industry hot-melt-extrusion (HME) is usually applied after milling the extrudate and compression into tablets. Since HME may alter the properties of the polymer the aim was to study the compaction of some pharmaceutical polymers before and after extrusion.

Methods

Materials: Eudragit RSPO, Eudragit L100-55 methacrylic polymers from Evonic, Kollidon, Soluplus polyvinyl based polymers and Lutrol 127 (plasticizer at 10% level) from BASF.

Extrusion: RCP-0250 Microtruder, Randcastle Extrusion Systems, NJ, USA [1].

Compaction: Powder extrudate (<425 µm, cutter mill, IKA A11, Germany) was compressed on instrumented press using 80 mg samples at: 6-mm flat-faced punches, 10 mm/min compression speed, 69-174 MPa and 200 Hz data acquisition. Work of compression (Wc) and Elastic recovery (ER%) were obtained from force-displacement profiles (Fig. 1) as the area under the compression curve and from $100*(Ho-H_1)/Ho$ respectively, were Ho the minimum recorded thickness and (H_1) that at ejection. Tablet strength was determined by diametrical loading.

Results

Successful formation of tablets with adequate strength depends on the ability of the material to form numerous strong interparticle bonds. This is directly proportional to the absorbed energy during compression, expressed by Wc. Opposing mechanism tending to separate the particles apart is elastic recovery. Therefore, the product Wc*ER% represents the effective interparticle bonding and should be correlated with the tablet strength. This was confirmed in Fig. 2.

Conclusions

Wc and ER% obtained from in-die compressions can be used to predict the ability of polymeric powders of different chemistry and thermal processing to predict their ability to form tablets.

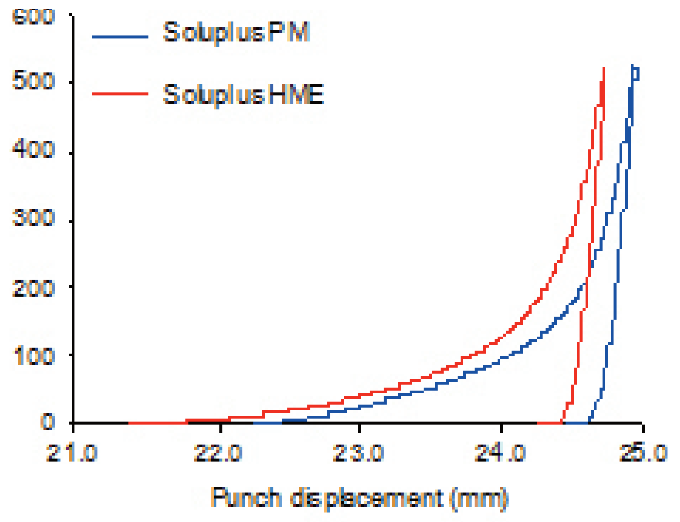

Fig. 1 Force-displacement profiles

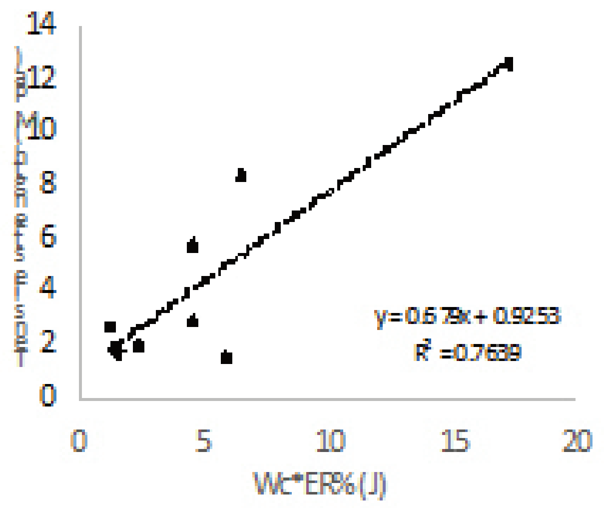

Fig.2 Plot of tensile strength vs (WC*ER%)

Reference

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ORAL

DEVELOPMENT OF NANOCARRIERS FOR NUTRACEUTICAL SUBSTANCES BY POLYSACCHARIDE/PROTEIN COMPLEXATION AND TEMPERATURE-INDUCED PROTEIN DENATURATION

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Introduction: We use polysaccharide/protein complexation[1] between chondroitin sulfate (CS) and bovine serum albumin (BSA) in acidic conditions in combination with temperature-induced denaturation of BSA[2] β-carotene.

Methods: Porcine CS in the sodium salt form (Na-CS) (Bioiberica), bovine serum albumin (BSA) (Sigma-Aldrich) and β-carotene (Sigma-Aldrich) were used as recieved. Light scattering on an ALV system, circular dichroism on a Jasco J-815 spectrophotometer and other methods were used.

Results: In Figure 1 it is proved that the molar mass of the nanoparticles can be tuned by the CS/BSA mass ratio. Upon thermal treatment their mass increases but more importantly when pH changes from acidic to neutral swelling occurs due to transition of BSA from positive net charge to negative. Additionally pH change is not able to disintegrate the nanoparticles after thermal treatment.

Conclusions: This study demonstrates the role of proteins as both building blocks and nanocarriers inside multifunctional nanoparticles and can be used as a guide for other systems of polysaccharide/protein pairs and bioactive substances.

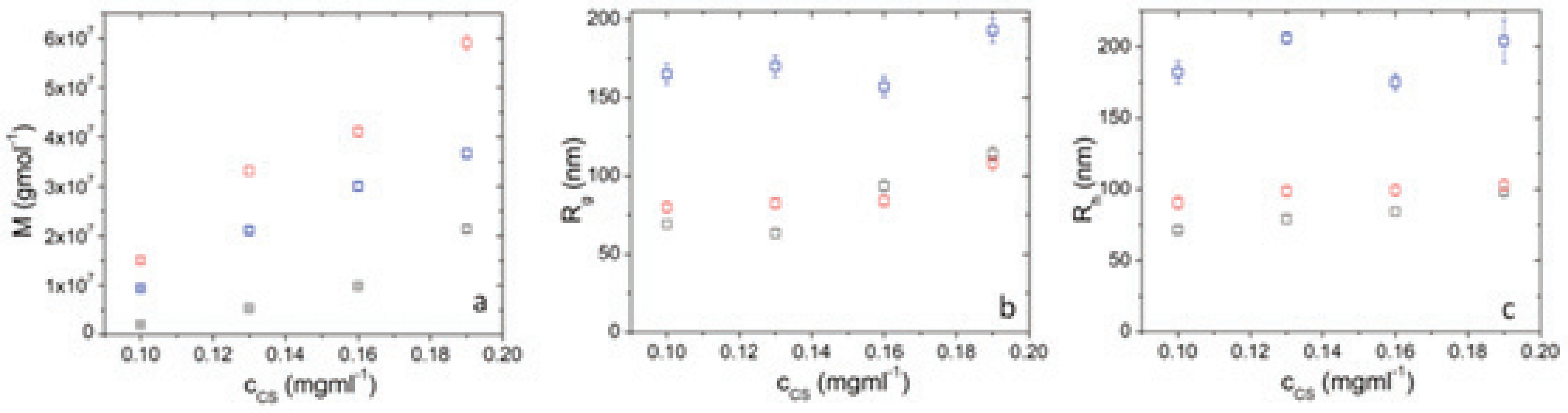

Figure 1: (a) Molar mass, (b) gyration and (c) hydrodynamic radius from CS/BSA nanoparticles (BSA 1 mgml^{-1}), pH 4.2 (black), after thermal treatment at pH 4.2 (red) and after thermal treatment setting pH to 7 (blue).

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ORAL

SIMULATION STUDIES OF BIO-INSPIRED POLYMERIC MATERIALS

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Recently, in the field of bio-inspired materials, the non-covalent self-assembly of relatively simple peptide based molecules has gained increasing attention for the formation of nanostructured, biologically functional materials, including nanofibers and hydrogels, all with nanoscale order. Moreover polypeptide self-assembly is often associated with human medical disorders. Understanding the physicochemical determinants that underlie peptide self-assembly is a fundamental step, in view of the rational design, or redesign of already existed nano building blocks for biotechnological and biomedical applications.

In the current study our computational approach proposes a novel multi-scale simulation method that combines atomistic and coarse grained (CG) simulations. Through a rigorous derivation of the effective interaction in the CG description, we are capable to quantitatively predict the structure and the dynamics of complex biological systems at realistic length and time scales. Up to now, our work concerns the modeling of small biological molecules (di-peptides)[1], where the self-assembly propensity as well as conformational properties, are studied through all-atom Molecular dynamics simulations. Furthermore more complex systems, such as the a-helical Rop protein (Fig.1) and its loopless mutation, RM6 have been simulated where, their structural, conformational properties, as well as their hydrogen bond network are characterized with atomic detail.

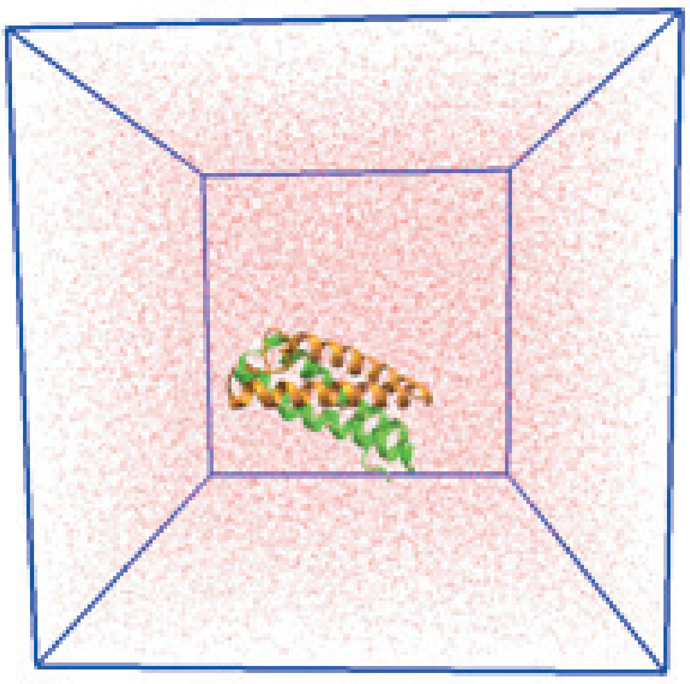

Fig.1 Rop protein in aqueous solution.

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ORAL

COMPOSITE THIN FILMS OF POLY(E-CAPROLACTONE) WITH BIPHOSPHONATE-LOADED NANOBIOGLASSES FOR TISSUE ENGINEERING APPLICATIONS

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Poly(ε-caprolactone) (PCL) is one of the most important polyesters in tissue engineering, due to its high biocompatibility and biodegradability. However, it is bioinert, and fillers are essential to promote hydroxyapatite formation and bone regeneration.is work, two types of nanosized bioglasses were incorporated into PCL matrix with spin coating, in concentration 10 %wt. The bioglasses used were ternary, with molar compositions 80SiO2-10CaO-10P2O5 (CaBG) and 80SiO2-10SrO-10P2O5 (SrBG). In order to further enhance the osteogenic effect of BGs, the bisphosphonate drug ibandronate was adsorbed in the BGs before their incorporation in PCL. The synthesized nanocomposite thin films were characterized in terms of morphology, dispersion, thermal properties, bioactivity, ion release, hydrophilicity, cell viability and osteogenic differentiation. The effect of the composition of the bioglasses and the presence of ibandronate on the properties of the films was evaluated.

The absorption of ibandronate was found to be 3.78 wt% for CaBG and 8.41 wt% for SrBG from TGA. WAXD patterns revealed that the drug was amorphous in the bioglasses. All films exhibited porous surfaces and good dispersion of the nanobioglasses. Concerning thermal properties, Tm values increased for all composites, while crystallinity reduced. All composites were more hydrophilic than neat PCL. Cell cultures of MG-63 cells showed that the cells were able to attach and proliferate on the surface of the nanocomposites, and metabolic activity was found increased. In conclusion, PCL/BG nanocomposites are suitable for bone tissue engineering applications, as they were found to be biocompatible, bioactive and able to induce biomineralization.

ORAL

POLY (LACTIC ACID) MATERIALS FOR DURABLE APPLICATIONS: FOCUS ON HYDROLYTIC STABILIZATION

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Introduction: A semicrystalline and an amorphous PLA grade were subjected to ageing at 70 °C and 80% RH in order to study the stabilization effect against hydrolysis of four additives. The aim was to improve the durability of PLA permitting its use in filament extrusion and injection moulding long-term applications.

Methods: The additives were an epoxy-based chain extender, an aromatic carbodiimide, an aromatic and an aliphatic polycarbodiimide (up to 1% w/w). Their incorporation was performed in a twin-screw extruder and hydrolysis runs were carried out on PLA films. Characterization involved viscosity-average molecular weight (MW), carboxyl group content, water uptake and thermal properties.

Results: Significant chain scission (88-97% MW decrease) was observed after 144 h of exposure of the unstabilized PLA grades, with the relevant data obeying autocatalytic hydrolysis kinetics. The epoxy-based chain extender failed to restrict PLA ageing, while stabilization was found significant for polycarbodiimide additives for both PLA grades (22-32% MW decrease after 240 h): the carbodiimide bond scavenges the free carboxylic end groups restricting the autocatalytic character of hydrolysis. On the other hand, the aromatic carbodiimide proved to be ineffective for the semicrystalline grade; this was correlated to its role as nucleating agent and its entrapment in the crystalline regions of the polymer.

Conclusions: The study focuses on the performance of four additives as anti-hydrolysis agents for semicrystalline and amorphous PLA. The stabilizing effect was detected for the carbodiimide-based additives; with the pertinent stabilizers, the use of biodegradable polyesters such as PLA can be supported for durable applications.

ORAL

POLYMERIC MATERIALS WITH SPECIAL FUNCTIONALITIES BASED ON WATER-SOLUBLE POLYMERS

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Research on polymeric materials based on water-soluble polymers with special functionalities such as functional water-soluble polymers, (self)-organized water-stabilized nanostructures, membranes/coatings or hydrogels, is always attractive and intense, since it may provide opportunities for several applications taking advantage of rather simple and versatile synthesis procedures.

An example of special functionality is the UV-triggered oxygen scavenging ability of polymers containing anthraquinone units. For instance, the copolymer P(DMAM-co-AQ) of N,N-dimethylacrylamide (DMAM) with a vinyl-modified anthraquinone (AQ) derivative has been proved an effective UV-triggered oxygen scavenger, leading to dissolved oxygen levels below 1 ppm [1].

A second example offer the antimicrobial coatings, interesting for under-water or aquaculture applications, based on reactive complementary copolymers bearing covalently and/or electrostatically attached quaternary nitrogen groups [2,3]. The temperature-controlled reaction between complementary units, like acrylic acid (AA) and glycidyl methacrylate (GMA) units, has been used to crosslink the complementary antimicrobial copolymers. The extent of crosslinking is a key factor controlling the biocidal properties of the final coatings. The rheology of aqueous solutions of simpler systems, i.e. mixtures of PAA and P(DMAM-co-GMA) copolymers, has been proved a useful tool to monitor the influence of temperature on this crosslinking reaction. Moreover, the release rate of releasable species from the coatings can be deduced from the conductivity variations of the surrounding medium.

Acknowledgements: This research has been co-financed by the European Union and Greek Ministry of Rural Development and Food in the frame of Operational Program ‘‘FISHERIES 2014-2020’’. Project title: ‘Development of Organic Biocidal Coatings for Aquaculture Nets’ (MIS: 5010930).

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POSTER 4.1

CONFORMATIONAL AND DYNAMIC PROPERTIES OF DNA MINICIRCLES IN AQUEOUS SOLUTION FROM ATOMISTIC MOLECULAR DYNAMICS SIMULATIONS

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Bio-polymers such as DNA or chromosomes present immense biological and technological interest, being involved in numerous applications, such as electrophoretic separation and enzymology, structural stabilization of proteins, as well as targeted drug delivery. In recent years, significant research interest is emerging towards the understanding of the role of the molecular architecture in the dynamic and rheological properties of DNA solutions. The objective of the work presented here is the determination of structural and dynamic properties of solvated linear and circular DNA molecules, and the understanding of the molecular mechanisms that govern these properties. To this end, detailed atomistic molecular dynamics (MD) simulations of aqueous solutions of DNA minicircles were performed.

Last generation force fields of the AMBER family were implemented, taking into account the most recent PARMBSC1 modifications specifically developed for DNA.[1] The resulting molecular dynamics trajectories were analyzed for the calculation of local conformational properties in terms of backbone torsion angles, and very good agreement was observed with respect to relevant experimental data. Furthermore, special emphasis was placed on the estimation of the mean radius of gyration, the center-of-mass self-diffusion coefficient and zero-shear rate viscosity, and the elucidation of the effects of molecular size, ionic strength and solution concentration. The computational results presented here constitute an essential stepping-stone towards the derivation of scaling laws for the conformational, dynamic and rheological properties of longer linear and circular DNA molecules.

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POSTER 4.2

SYNTHESIS AND CHARACTERIZATION OF NOVEL POLYPEPTIDES BASED ON ARGININE AND GLUTAMIC ACID FOR DRUG DELIVERY APPLICATIONS

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It is known that the use of chemotherapy as cancer treatment is limited by the toxic side effects of anticancer drugs. In recent years, studies have been carried out on polymers as anticancer drug carriers in order to suppress side-effects to normal cells and improve activity and selectivity towards the cancer cells. Although the use of polymers exhibits excellent effects, the problem of water solubility usually arises. The majority of drugs have a hydrophilic character. A very promising solution is the use of polymers in micellar structure, where a hydrophilic outer shell surrounds the hydrophobic inner core of the polymer, in which the drug is encapsulated. Various types of polymers, natural or synthetic, have been studied. In this work, the synthesis of the N-carboxyanhydride (NCA) of glutamic acid, the NCA of arginine and the NCA of histidine was initially achieved. Then, the homopolymers of poly-glutamic acid and poly-arginine were synthesized through the ring opening polymerization of the corresponding N-carboxyanhydrides, using dimethylamine as initiator and the copolymer PEO-*b*-P(Hist-*co*-Arg) was achieved, using m-PEO-NH_2 as macroinitiator.

High vacuum techniques were employed for the synthesis of the polymers. Gel Permeation Chromatography (GPC), Infrared Spectroscopy (IR), Proton Nuclear Magnetic Resonance Spectroscopy (^1H NMR), Static and Dynamic Light Scattering (SLS, DLS) were used for the characterization of the polymers.

The molecular characteristics were satisfactory as the polydispersity was good and the size of micelles desirable.

Finally the results showed that the polymers have potential biological applications and can be used as drug nanocarriers.

POSTER 4.3

SYNTHESIS, CHARACTERIZATION AND SELF-ASSEMBLY OF RESPONSIVE POLY(ETHYLENE OXIDE)-b-POLY(L-HISTIDINE) COPOLYMERS FOR DRUG ENCAPSULATION AND CONTROLLED DRUG RELEASE

Varvara Athanasiou, Hermis Iatrou, Panagiotis Christakopoulos, Dimitra Stavroulaki, Niki Roumelioti

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Introduction: Over recent decades, various systems, such as polymeric micelles, vesicles, liposomes, and nanogels have been developed as nanocarriers that can effectively achieve the controlled delivery of anticancer drugs and genetic agents. Nanocarriers have expressed many benefits for cancer chemotherapy due to the minimization of serious side effects, resulting in improved therapeutic efficacy. Of these systems, stimuli-responsive carriers that sharply respond to changes in microenvironments of some pathological sites, such as, pH, temperature, redox, enzyme, have received considerable attention as fascinated potential drug delivery vehicles.

Methods: The synthesis of polymers was achieved through a one-step ring-opening polymerization (ROP) process of the corresponding protected N-carboxy anhydrides, using an amine end-functionalized poly(ethylene oxide) macroinitiator. High-vacuum techniques were used for the synthesis of the well-defined copolymers. Extensive molecular characterization studies were conducted in order to confirm the successful synthesis of the polymers.

Results: These amphiphilic copolymers of theN_3-PEO-*b*-P(His) type possess the ability to self-assemble in aqueous media and form micelle-like nanostructures. The hydrophilic shell of the nanostructures was comprised of poly(ethylene oxide) chains, while the pH-responsive core was based on PHis.

Conclusions: This work opens avenues for the synthesis of multifunctional polymers containing this remarkable material that can allow for the fine tuning of the pH where the aggregates will be disrupted, leading to the control of the rate and choice of cellular compartment for the drug release. This is useful for the design of pH-stimuli responsive materials that can be effectively utilized for drug and gene delivery applications and theranostics.

POSTER 4.4

SYNTHESIS OF POLYPEPTIDE-BASED NANOCARRIERS FEATURING SURFACE MARKER FOR TARGETED DRUG DELIVERY TO CANCER CELLS

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

Cancer treatment remains a major challenge in medicine, with traditional cancer treatments including surgery complemented by radiotherapy and/or chemotherapy. In response, pharmaceutical scientists and clinicians are trying to apply nanotechnology to medicine, in order to deliver drugs, genes and proteins with enhanced therapeutic efficacy, reduced dose and low dosing frequency, resulting in fewer side effects.

In this work the synthesis of copolymers containing varius polypeptides such as poly(L-histidine) and a terminal moiety that overexpress selectively on the surface of cancer cells is reported. For that purpose, a bifunctional poly(ethyleneglycol) (PEG) was used, featuring a terminal amine group as well as a terminal azide group. The amine group was used as the initiating species for the ring opening polymerization of the N-Carboxyanhydrites (NCA) of the amino acids and the azide group for the conjugation of cancer cell surface markers, via click chemistry. Such markers are folic acid and β-glycyrrhetinic acid.

For the characterization of these polymers, a series of techniques took place like gel permiation chromatography (GPC), nuclear magnetic ressonance (NMR), infrarated and unltraviolet spectrospy (FT-IR, UV-vis) as well as dynamic and static light scattering (DLS, SLS). The results showed good molecular characterestics such as the polydispersity and the micelle size and it was also found that the cancer cell markers were attached at the copolymers.

POSTER 4.5

SOLID STATE POLYMERIZATION AS POST-ENCAPSULATION MODIFICATION TECHNIQUE

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Introduction: The encapsulation of active compounds in polymeric carriers is a widely used technology as it protects and improves the physical characteristics of the active compound and controls its delivery. The effectiveness of the polymeric microcapsules is strongly related to the molecular weight (MW) and the thermal properties of the polymeric shell. Therefore, the aim of this study was to increase the MW and/or improve the crystallinity of poly(lactic acid) (PLA) microcapsules *via* solid state polymerization (SSP).

Methods: PLA microparticles were prepared using double emulsion and their characterization mainly involved morphology, size, and process yield. SSP was performed in a fixed bed reactor for 16 h at 140^{o}C under nitrogen flow. Viscosity-average MW and thermal properties of the SSP products were measured.

Results: The double emulsion technique was efficiently applied to prepare PLA microparticles of three different molecular weights. The yield of the process was found at ca. 70 %, while microcapsules size was in the range of 2μm with similar melting characteristics. Then, the different PLA microcapsules were subjected to SSP in order to increase the molecular weight of the shell and/or improve its thermal properties having as efficiency criterion the maintenance of their spherical shape. Prior to microencapsulation, the same PLA grades in the form of powder were polymerized in the solid state for comparison reasons.

Conclusions: In the work, the perspective of modifying the properties of a low-molecular-weight PLA microcapsule via SSP was examined so as to improve encapsulation system performance.

POSTER 4.6

HYDROXYPROPYLCELLULOSE/GRAPHENE OXIDE NANOCOMPOSITE MACROPOROUS CRYOGELS: SYNTHESIS AND PROPERTIES

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Graphene is a material with unique properties combining exceptional thermal and electrical conductivity, mechanical properties, etc. In recent years, there is an increased interest in polymer composites containing graphene. Graphene oxide has all the advantages of graphene, but, unlike it, can be dispersed well in water. Composite materials from natural polymers are attractive because they are biodegradable, do not pollute the environment, possess very good bio-compatibility and are widely used in biomedicine.

In this study we report on the fabrication of novel super-macroporous nanocomposite cryogels based on hydroxpropylcellulose (HPC) and graphene oxide (GO) by UV-irradiation. Photocrosslinking of HPC was achieved using the water-soluble photoinitiator (4-benzoylbenzyl)trimethylammonium chloride and the crosslinking agent N,N′-methylenebis(acrylamide). The reaction was completed for 2 min irradiation with UV light at an irradiation dose rate of 5.7 J/cm^2 min. The nanocomposites obtained have a heterogeneous structure composed of large, interconnected pores filled with water and thin polymer walls, containing GO. The effect of graphene oxide concentrations on the crosslinking efficacy, swelling and mechanical properties of cryogels was studied in detail. It was found that the increase of GO content in the stock solution, decreased to some extents the gel fraction yield and elastic modulus of materials. On the other hand, the different content of graphene oxide did not affect the degree of swelling of the nanocomposite cryogels.

POSTER 4.7

HYBRID POLYLACTIC ACID (PLA)/MESOSTRUCTURED CELLULAR FOAM (MCF) SILICATE CARRIERS FOR THE ENCAPSULATION AND CONTROLLED RELEASE OF WATER INSOLUBLE DRUGS

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PLA is a promising polymer for biomedical applications, because it possesses numerous advantages compared to other polymers, such as biocompatibility, biodegradability, low cost, environmental friendliness, and easily modified mechanical properties. It is used in its neat form or as co-polymer. PLA is one of the most favorable materials used to produce a wide range of controlled drug delivery systems, such as nanoparticles, microspheres, hydrogels electrospun fibers and scaffolds.

The purpose of the present study is the production of hybrid PLA/mesostructured cellular foam silicate carriers, that would be able to absorb large quantities of the water insoluble, anticancer drug Paclitaxel (PTX), and to release the drug in a controlled way, as well. By using that type of carriers, the adsorption of the substance in crystalline form will be feasible, while the carriers could be further functionalized for targeted drug administration, resulting in the reduction of the unpleasant side effects for patients. The hybrid carriers are produced via the oil in water emulsification method, a technique that is widely applied in pharmaceutical industries.

MCF silicas were synthesized via the co-operative self-assembly method, with varying pore and window diameters, while their pores were decorated with organic moieties. The ability of the mesostructured silicas to be encapsulated in PLA microspheres. PVA was used as the emulsifier. The water/oil ratio, as well as the mixing type and speed were the parameters tested. The size of the initial emulsion micelles and the final hybrid microspheres were determined with electronic microscopy techniques.

POSTER 4.8

THERMORESPONSIVE PROPERTIES OF ALGINATE-BASED GRAFT COPOLYMERS

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Alginate is a natural polysaccharide with various applications in biomedical science and engineering due to its properties, such as biocompatibility and gelation. Hydrogels of grafted alginate have been particularly attractive in drug delivery, and tissue engineering, as these gels retain a structural similarity to the extracellular matrices in tissues. This work is focused on the synthesis and rheological studies of sodium alginate graft copolymers with a hydrophobic enrichment of amino-terminated PNIPAM (poly(N-isopropylacrylamide)) or P(NIPAM-co-NtBAM) (NtBAM: N-tertiary-butyl-acrylamide). The characterization of the polymers was studied by ^{1}H NMR and UV-VIS Spectroscopy while, the thermoresponsive properties of the hydrogels were investigated by rheological experiments. The Lower Critical Solution Temperature (LCST) of the side chains (LCST of PNIPAM ≈ 32 °C) should be close and below the physiological temperature to behave as sol at room temperature and as gel inside the human body. The results of this study present, the influence of hydrophobic enrichment of the grafting chains in the critical temperature of the sol to gel transition and the impact in the thermothickening behavior of the alginate graft copolymers. In conclusion, the prepared alginate-based graft copolymers meet the requirements for a biodegradable thermo-induced injectable hydrogel that could be used for biomedical potential application.

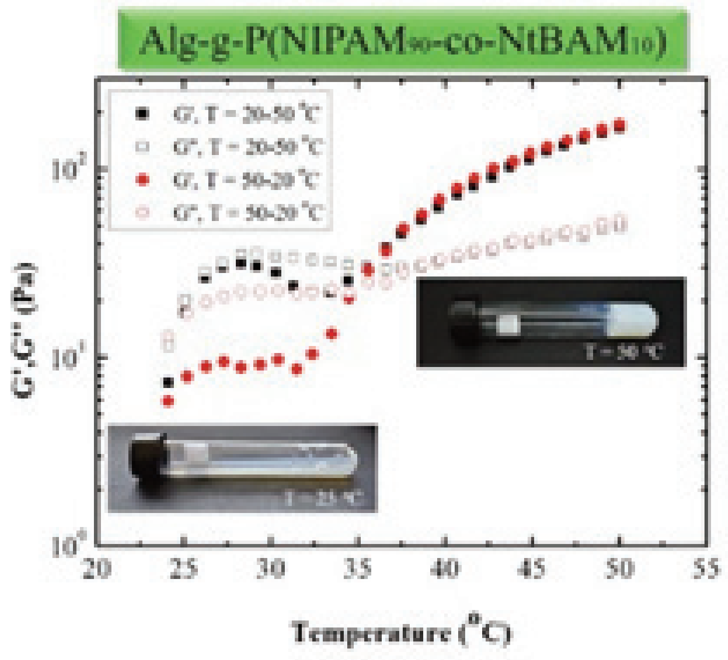

Figure 1. Temperature dependence of elastic moduli of Alg-g-P(NIPAM$_{90}$-co-NtBAM$_{10}$) copolymer (black data: heating; red data: cooling). Inset: photos of polymer solution at 25°C and gel formed at 50°C.

POSTER 4.9

EXTRACTION METHODS OF COLLAGEN FROM FISH (TROUT) WASTES AND CHARACTERIZATION: A COMPARATIVE STUDY

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Introduction: Collagen is a natural polymer and the main structural protein present in most animal tissues. Its main purpose is to I. The aim of this study was to extract collagen from fish wastes and its use to polymer scaffolds.

Methods: The fish wastes used, were head bones and backbones from trout fish. igation of the properties of the extracted collagen. The received collagen (from the three experimental courses) was characterized with various techniques (UV, FT-IR,SEM, DSC etc.) and qualitative and quantitative analyses were carried out.

Results: The produced high purity collagen, subsequently will be used in preparation of polymeric hydrogel scaffolds, aiming their use in biomedical applications and more specifically in skin tissue engineering (wound healing).

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POSTER 4.10

SYNTHESIS AND CHARACTERIZATION OF HYBRID COPOLYMERS CONTAINING TRYPTOPHAN AND STUDY OF THEIR APPLICATIONS FOR CANCER TREATMENT

Maria Kasimati, Katerina Mathianaki, Panagiotis Christakopoulos, Diana Kazaryan, Hermis Iatrou

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A series of polypeptides have been synthesized and used for drug delivery applications in cancer treatment, which still remains a major challenge in medicine. In this scientific research the synthesis of polypeptide homopolymer of poly(L-Tryptophan) poly(L-TRP), as well as, amphiphilic hybrid polypeptide copolymers, based on poly(ethylene oxide) (PEO) and poly(L-Tryptophan) were accomplished by ring opening polymerization (ROP) of the L-Tryptophan N-carboxyanhydride.

The different molar ratios of hydrophobic poly(L-TRP) to hydrophilic PEO, gave the possibility of thorough investigation of the responsiveness to pH changes, and the unique fluorescent emission of poly(L-TRP).

High vacuum techniques contributed to the high purity of the reagents and the controlled polymerization. For the characterization of the synthesized polypeptides, size exclusion chromatography (SEC), proton nuclear magnetic resonance (1H-NMR) and infrared spectroscopy (FT-IR) were employed. Circular dichroism (CD) was carried out to verify the correlation between the secondary structure of the polypeptides and the pH. Fluorescent spectroscopy was carried out in order to study the fluorescent properties of L-Tryptophan.

Considering the specific characteristics of L-TRP, the corresponding polypeptides could be very promising as anti-cancer drugs vesicles.

POSTER 4.11

SYNTHESIS AND CHARACTERIZATION OF GRAFTED POLYMERS BASED ON POLYPEPTIDES USING POLY(ETHYLE OXIDE) AS MACROINITIATOR

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Successful cancer treatment still remains one of the biggest challenges in the medical and pharmaceutical community due to the lack of effective drugs that do not present severe side effects on the patients. In order to overcome this issue an attempt of creating drug delivery agents that are capable of cancer cell targeting and controlled drug release is presented in this research. A series of novel hybrid block-graft copolymers containing polypeptides were synthesized in order to investigate their capability as drug nanocarriers as well as to determine their structure and properties in general. Due to the fact that amino acid are part of the polymeric structure these nanocarriers are naturally biocompatible, biodegradable and non-immunogenic. The experimental route was comprised of the synthesis of N-Carboxyanhydrites (NCA's) of Nim-Trityl-L-Histidine and Nε-Boc-L-Lysine followed by a ring opening polymerization (ROP) using modified poly(ethylene oxide) $PEO-NH_2$ as an initiator. High vacuum techniques were utilized in order to achieve controlled conditions and avoid by-products. The characterization of the polymeric materials was conducted via a series of techniques such as Gel Permeation Chromatography (GPC), FTIR and NMR spectroscopy as well as Static (SLS) and Dynamic (DLS) Light Scattering. The results showed that the synthesized polypeptides could self-assemble into micelles and could be very promising as drug nanocarriers.

POSTER 4.12

INJECTABLE HYALURONIC ACID BASED HYDROGELS FOR THE REPAIR OF CARTILAGE LESIONS

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In the present study, the synthesis and characterization of injectable hyaluronic acid (HA) based hydrogels is assessed. Methacrylated hyaluronic acid (MeHA) is initially synthesized and subsequently functionalized with a chondroitin sulfate (CS) binding peptide (CS-MeHA). MeHA based hydrogels were formed using a redox initiator system or a matrix metalloproteinase 7 (MMP7)-degradable peptide, as a crosslinker. The effect of various process parameters (e.g. degree of methacrylation (DM), HA molecular weight (MW), MeHA concentration, crosslinker concentration, degree of MeHA functionalization) on the final properties of the produced hydrogels (e.g. degree of swelling, storage modulus (G`) and degradation rate) was thoroughly assessed. MeHA macromers of various DM (15-50%) were successfully synthesized, and degrees of MeHA functionalization up to 5% were achieved. The G` of the hydrogels formed using the redox system was shown to increase with increased DM, HA MW and MeHA concentration resulting in the formation of more rigid hydrogels exhibiting lower degree of swelling and retarded degradation following first-order kinetics. Concerning the use of the MMP7-degradable peptide, an increase in the crosslinker concentration accelerated the onset of the crosslinking reaction and resulted in the formation of hydrogels with enhanced G' exhibiting slower degradation in the presence of MMP7 that followed zero-order kinetics. Finally, the use of CS-MeHA as a functional macromer resulted in a retardation of the gelation onset and the formation of softer hydrogels. By varying the process parameters, an appropriate gelation onset, corresponding to the time required for the in vivo injection, and suitable rheological properties could be achieved.

POSTER 4.13

DUAL-FUNCTION CONTACT-ACTIVE ANTIMICROBIAL POLYMER COATINGS

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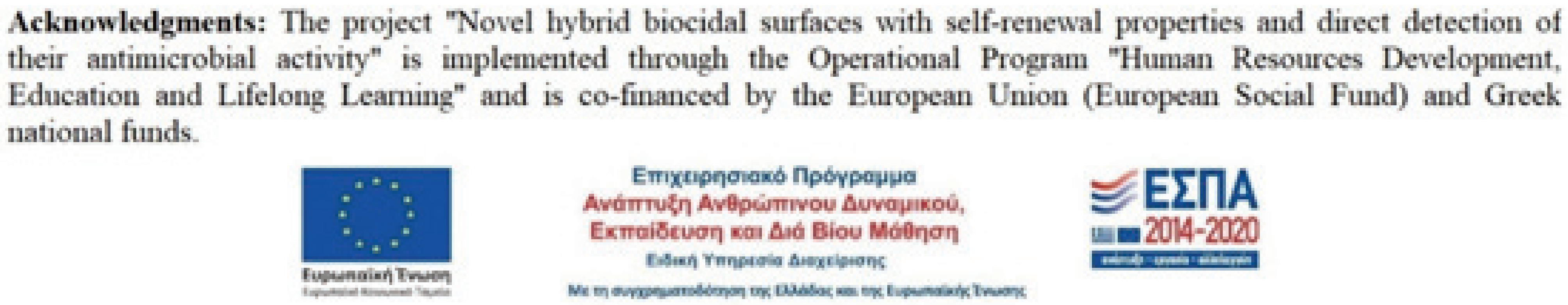
Antimicrobial surfaces that prevent biofouling are attractive in inhibiting the spread of microbial diseases. Two types of antimicrobial surfaces have been developed. Antifouling surfaces that repel microorganisms and bactericidal surfaces which kill microbes in the vicinity of the surface. Contact-active antimicrobial surfaces have been realized by tethering antimicrobial polymers onto a substrate and are continuously being developed for a plethora of applications.

The aim of the present work is the development of versatile, multi-functional polymer surfaces exhibiting controllable antimicrobial properties in the solid state. For this purpose, two types of polymeric materials were developed comprising (i) antifouling-bactericidal polymer brushes and (ii) self-polishing-bactericidal polymer films. Semi-fluorinated mixed amphiphilic polymer brushes were grown on silicon substrates by surface-initiated atom transfer radical polymerization (SI-ATRP). In addition, symmetric amphiphilic diblock copolymers comprising a hydrophobic and hydrolysable block and a hydrophilic polyamine block were synthesized by group transfer polymerization (GTP). Several alkyl halides were evaluated for the quaternization of the tertiary amine units of the hydrophilic polymer chains in order to introduce the optimum cationic biocidal groups along the polymer chains. The solvent responsive behavior of the polymer brushes and their bactericidal activity for both Gram-positive and Gram-negative bacteria strains were evaluated. On the other hand, the ability of the quaternized diblock copolymer thin films to form lamellae oriented parallel to the substrate, their bactericidal activity and the self-polishing properties of the ordered films were assessed. Overall, these polymer surfaces exhibit profound antifouling-biocidal and biocidal-self-renewal properties, respectively, which prolong their antimicrobial performance.



Acknowledgments: The project "Novel hybrid biocidal surfaces with self-renewal properties and direct detection of their antimicrobial activity" is implemented through the Operational Program "Human Resources Development, Education and Lifelong Learning" and is co-financed by the European Union (European Social Fund) and Greek national funds.

Ευρωπαϊκή Ένωση

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Ανάπτυξη Ανθρώπινου Δυναμικού,
Εκπαίδευση και Διά Βίου Μάθηση
Ειδική Υπηρεσία Διαχείρισης
Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

ΕΣΠΑ
2014-2020

POSTER 4.14

NOVEL NATURAL POLYMER COATINGS WITH SELF-RENEWABLE ANTIMICROBIAL PROPERTIES

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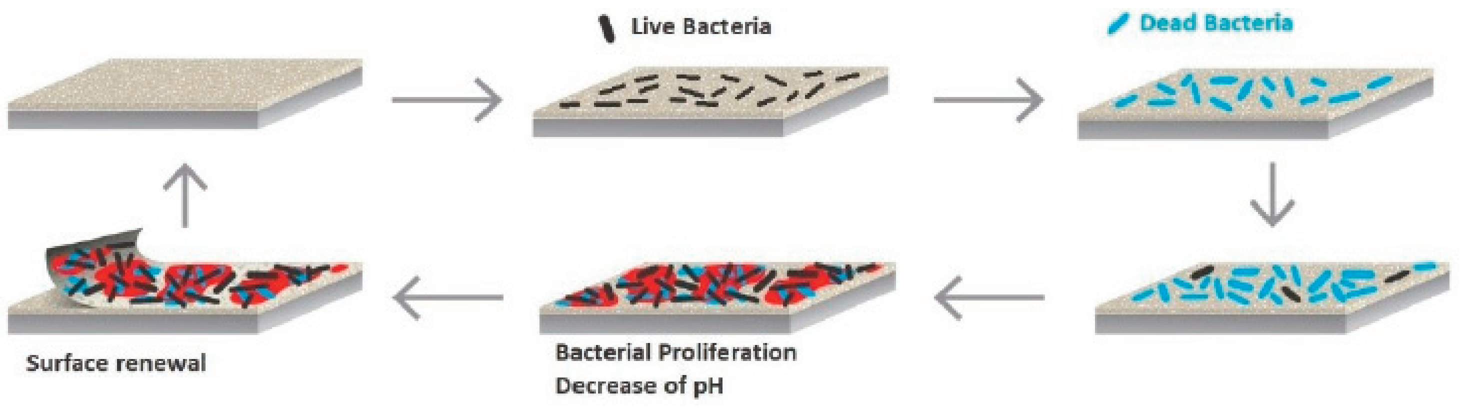
Microbial infectious diseases, occurring upon the contamination of surfaces by a plethora of pathogens, constitute a growing threat to human health, with major risks in food packaging, water filtration-purification, household sanitation and the biomedical field. Bacterial biofilm formation has been identified as the profound event leading to microbial contaminated surfaces. This emerging threat has triggered research towards the development of effective, long-lasting and environmentally friendly bacteria elimination methods.

The aim of this work is to develop novel, biodegradable polymeric coatings based on modified natural polymers bearing environmentally and toxicologically friendly biocidal groups, able to self-polish and regenerate their antimicrobial activity upon repetitive bacterial fouling. Antibacterial quaternized chitosan (QCS) was prepared by modification of the primary amine groups of the chitosan chains with a quaternary ammonium alkyl halide to enhance the water solubility and biocidal action of the natural polymer. Polymer films were deposited and cross-linked, using a water soluble and acid degradable cross-linker, in order to retain the film structure on silicon and glass substrates. The successful modification of chitosan was verified by proton nuclear magnetic resonance spectroscopy, whereas the thickness, wettability and morphology of the polymer films were assessed by ellipsometry, water contact angle measurements and scanning electron microscopy, respectively. The antimicrobial action of the polymer films was evaluated using two representative gram-positive and gram-negative bacteria strains. The controlled self-polishing and regeneration of the antimicrobial activity of the films were investigated upon the gradual degradation of the cross-links by local pH changes induced by the bacterial cell death.



Acknowledgments: The project "Novel hybrid biocidal surfaces with self-renewal properties and direct detection of their antimicrobial activity" is implemented through the Operational Program "Human Resources Development, Education and Lifelong Learning" and is co-financed by the European Union (European Social Fund) and Greek national funds.

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POSTER 4.15

DOUBLE RESPONSIVE CROSS-LINKED HYBRID COPOLYMERS BASED ON POLY(CYSTEINE) AND POLY(HISTIDINE)

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Drug delivery is one of the most emerging scientific area in the last decades. Lots of synthetic approaches have been designed in order to synthesize molecules with specific structure and properties which can transfer and release drugs in the desired target efficiently.

In this work, we synthesize a novel series of amphiphilic hybrid block copolymers based on poly(L-Cysteine) and poly(L-Histidine) taking advantage of each moiety's ability to respond to external stimuli. The synthesis of polymers was conducted via subsequent ring opening polymerization (ROP) of the corresponding protected N-carboxy-anhydrides using amine end-functionalized poly(ethylene glycol) monomethyl ether (mPEG-NH_2) as macroinitiator. High vacuum techniques were used both for the polymerization conditions and the purifications of reagents avoiding uncontrolled processes and impurities.

These amphiphilic copolymers have the significant property of self-assembling in aqueous media forming a hydrophilic mPEG-based outer corona, a PCys-based redox responsive shell and a PHis-based pH responsive hydrophobic core. Due to their biocompatibility, biodegradability, stimuli-responsive and self-assembling properties, these series of ABC triblock copolymers could be utilized as potential hydrophobic drug nanocarriers.

POSTER 4.16

CHITOSAN NANOPARTICLES CONTAINING SALMETEROL XINAFOATE FOR RESPIRATORY USE

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Chronic obstructive pulmonary disease (COPD) is a major public health problem affecting the lungs, characterized by long-term breathing problems and poor airflow. Inhaled bronchodilators are used extensively in COPD treatment as they are able to ameliorate symptoms and lungs' function. Salmeterol xinafoate a selective adrenergic beta-2 receptor agonist, is used in patients suffering from COPD. However its' sparingly solubility in aqueous solutions, as well as in body fluids, results in poor bioavailability. Chitosan, a natural polysaccharide can easily form hydrogen bonds due to its functional amino and hydroxyl groups with salmeterol, leading to its possible amorphization improving drug's bioavailability. Resulting in improving patient's life, since the proper formulation will be used in inhalation systems for better drug's administration. In this study, chitosan nanoparticles were synthesized by the ionic gelation technique using sodium tripolyphosphate as polyanion. Polyvinyl alcohol was also used as emulsifier. Nanoparticles' size was determined by DLS whilemorphological characterization was conducted by SEM. Interactions between drug and chitosan were evaluated by FT-IR while the physical state of the drug loaded nanoparticles was tested using X-ray spectroscopy. DSC and TGA measurements were performed to assess the thermal stability of the nanoparticles and their in vitro drug release was studied. Results revealed the successful nanoparticles' formulation while salmeterol was successfully incorporated in nanoparticles. Drug dissolution tests were also conducted.

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POSTER 4.17

PLA, PLGA75/25 AND PLGA 50/50 PATCHES WITH DISPERSED CHITOSAN NANOPARTICLES FOR TRANSDERMAL DELIVERY OF LEFLUNOMIDE

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Transdermal administration of drugs has advantages over conventional oral administration oradministration using injection equipment. The route of administration reduces the opportunity fordrug evacuation before systemic circulation, and enables long-lasting drug administration at amodest body concentration.In addition,the skin is an attractive route for vaccination, becausethere are many immune cells in the skin.Furthermore, nanocarriers made of lipids, metals, or polymers have beensuccessfully used to increase penetration of drugs or vaccines, control drug release, and target drugsto specific areas of skin in vivo.

Leflunomide is an inflammatory drug, poorly soluble in water used in rheumatoid arthritis. So far Leflunomide is used in oral administration formulations leading to the related problems, such as high concentrations in liver.In this study, it is proposed the transdermal delivery of the drug via chitosan nanoparticles. Chitosanis a natural polysaccharide which due to its amino and hydroxyl groups can easily form hydrogen bonds, leading to amorphization of the drug,improvingthis way itsbioavailability. Furthermore, chitosan nanoparticles can increase penetration of Leflunomide through skin.

In this study,chitosan nanoparticles were synthesized bya modified ionic gelation techniquefor nanoencapsulation of Leflunomide, using PVA as emulsifier. The nanoparticles formed were further dispersed in polymeric films (PLA, PLGA 50/50 and PLGA 75/25) via spin coating technique. All formulations were fully characterized by FT-IR, XRD, DSC and SEM. Dissolution study was also conducted. Results revealed the successful nanoparticles' formulation and incorporation of Leflunomide as well as nanoparticles dispersion in films.

POSTER 4.18

SYNTHESIS AND CHARACTERIZATION OF NANOCOMPOSITES BASED ON POLY(PROPYLENE 2,5- FURAN DICARBOXYLATE) AND ALUMINOSILICATE CLAYS

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Poly(propylene 2,5-furan dicarboxylate) (PPF) is a biobased alipharomatic polyester which is expected to replace its fossil-based terephthalate (PPT) and naphthalate (PPN) homologues. PPF possesses exceptional gas barrier properties but its slow crystallization rate might affect its success in specific applications in the future. Therefore, a series of PPF based nanocomposites with the nanoclays Cloisite®-Na, Cloisite®-20A and halloysite nanotubes (HNTs) were synthesized via the in situ transterification and polycondensation method. The effect of the nanoclays on the structure, thermal, thermomechanical and crystallization properties of PPF was studied with several methods including infrared spectroscopy (IR), Nuclear Resonance Spectroscopy (^{1}H-NMR), Wide-Angle X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA), Dynamic Mechanical Analysis (DMA), Differential Scanning Calorimetry (DSC) and Polarized Optical Microscopy (POM). IR and NMR spectroscopies confirmed the successful synthesis of the nanocomposites. DSC results showed an increased T_g for all materials compared with PPF neat and no T_m, suggesting that the as received materials were amorphous. The XRD patterns confirmed the above statement, and showed that after annealing, the materials' patterns are like PPF neat. Lastly, TGA results showed an improved thermal stability. In all, the incorporation of nanoclays in the polymer matrix, resulted in materials with improved thermal properties.

POSTER 4.19

A NOVEL VISIBLE-LIGHT PHOTO-ACTIVATED DRUG RELEASE SYSTEM

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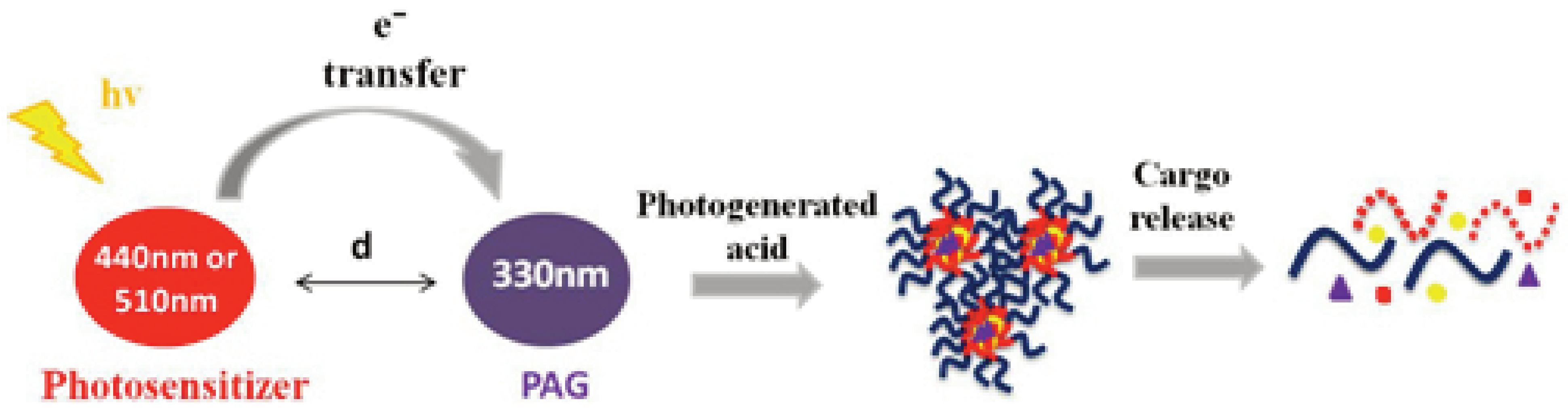
Near infrared (NIR) light has emerged as an appealing stimulus to trigger spatiotemporally controlled drug release because it can penetrate deep into the tissues without causing any damage. However, most reported NIR-sensitive systems require the incorporation of up-converting nanoparticles or the use of two-photon absorption processes which present major drawbacks for biomedical applications. Herein, we present a new photo-controlled drug release system which combines acid degradable nanoparticles based on PEG-*b*-polyacetal micelles, with a photo-acid generator (PAG) and photosensitizing molecules. The release is based on the acid catalyzed cleavage of the polyacetal block by acid molecules generated by the PAG via an "unusual" sensitization of the absorbing molecules (*Figure 1*) [1]. The polymers were synthesized via an acid catalyzed polycondensation reaction between a diol and a divinyl ether followed by end-capping of the precursor polymer with monohydroxy PEG to afford the final diblock copolymer [2]. Spherical micelles loaded with different PAG/photosensitizer mole ratios were prepared. The release of the cargo, following irradiation at 440 and 510 nm, was monitored by measuring the absorption of the released photosensitizer. An increase in the degradation rate of the micelles was observed when increasing the PAG/photosensitizer mole ratio within the micelles. The amplification mechanism was demonstrated for two different PAG/photosensitizer pairs exhibiting a maximum degradation rate of the nanocarriers at a 3/1 PAG/photosensitizer mole ratio. In conclusion, as a proof-of-principle, a very promising photo-activated drug delivery system, using harmless irradiation energy to activate the cargo release, has been demonstrated, rendering it promising for biological applications.



POSTER 4.20

SYNTHESIS OF N-VINYLPYRROLIDONE BASED COPOLYMERS VIA REVERSIBLE ADDITION-FRAGMENTATION CHAIN TRANSFER POLYMERIZATION

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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. PNVP can be perfectly polymerized with Reversible Addition- Fragmentation chain Transfer (RAFT) polymerization. RAFT polymerization is a well-established method for providing living characteristics to conventional radical polymerization.

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, the synthesis and characterization of N-vinylpyrrolidone statistical and block copolymers with various methacrylates such as benzyl methacrylate, 2-(dimethylamino)ethyl methacrylate, stearyl methacrylate and hexyl methacrylateis reported. Eventhought N-vinylpyrrolidone is a less active monomer compared to the methacrylates, both of them are successfully polymerized with the same Chain Transfer Agent (CTA). Actually, they have been used three different xanthates as CTAs: [(O-ethylxanthyl)methyl]benzene, [1-(O-ethylxanthyl)ethyl] benzene and O-ethyl S-(phthalimidylmethyl) xanthate. The reactivity ratios were estimated using the Fineman-Ross, inverted Fineman-Ross, Kelen-Tüdos, and extended Kelen-Tüdos graphical methods, along with the computer program COPOINT. All the methods indicate that the reactivity ratio of the methacrylate is much greater than that of N-vinylpyrrolidone, thus, the statistical copolymers are in fact pseudo-diblocks. The glass-transition temperature values of the copolymers were measured by Differential Scanning Calorimetry. Furthermore, the thermal degradation of the copolymers was investigated, compared with the respective homopolymers, by Thermogravimetric Analysis, within the framework of the Ozawa-Flynn-Wall and Kissinger methodologies. The block copolymers were synthesized by sequential addition of monomers. The synthesis was monitored by SEC and NMR.

POSTER 4.21

SYNTHESIS AND CHARACTERIZATION OF STIMULI-RESPONSIVE POLYPEPTIDES BASED ON PHENYLALANINE AND HISTIDINE FOR DRUG DELIVERY APPLICATIONS

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One of the most promising classes of polymeric materials for drug delivery applications is polypeptides, which combine the properties of the conventional polymers with the 3D structure of natural proteins such as α-helices and β-sheets. The synthetic pathways followed to develop well-defined stimuli-responsive polymer delivery systems based on polypeptides that have been prepared through ring-opening polymerization (ROP) of N-carboxyanhydrides.

The experimental route was comprised of the synthesis of N-Carboxyanhydrites (NCA's) of Phenylalanine. Herein we present the synthesis of homopolymer of poly(L-Phenylalanine), that synthesized through the ring opening polymerization of the corresponding N-carboxyanhydride. Furthermore, the copolymer PEO-Phe and PEO-b-P(Hist-co-Phe) was achieved, using an amine end-functionalized poly(ethylene oxide) m-PEO-NH_2 as macroinitiator.

High-vacuum techniques were used for the synthesis of N-carboxy anhydrides of a-amino acids, for the purification of solvents and for the isolation of well-defined polymers as well, ensuring the high purity of the system and the absence of impurities that would result in uncontrolled polymerization processes. All polymers were characterized with GPC, NMR and IR techniques to confirm the successful synthesis. Dynamic light scattering (DLS) and static light scattering (SLS) were used in order to investigate the ability of polypeptides to self-assemble into micelles.

The synthesized polymers present good molecular characteristics and possess the ability to self-assemble in aqueous media and form micelle-like nanostructures.

Due to their unique 3D structure polypeptides can mimic natural systems, facilitating the development of smart nanodevices, which are able to carry a pharmaceutical compound and, by modifying their macroscopic properties, offer controlled delivery of their cargo.

POSTER 4.22

DEVELOPMENT AND PHYSICOCHEMICAL CHARACTERIZATION OF IMPLANTS FOR CARDIAC REPAIR

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Introduction: Pulmonary hypertension constitutes an important health related problem worldwide. It is characterized by increased pulmonary vascular resistance, causing right ventricular pressure-overload that leads to right ventricular failure, an ominous disease-entity that portends a poor prognosis. The aim of this study is to present the development and characterization of polysaccharide-based membranes as efficient biomaterials in myocardial repair. More specific, in this work was studied the stability of membranes in a liquid environment.

Methods: Chitosan- based membranes were developed. The membranes specimens were immersed in water or PBS (pH=7.4) solution at 37±1 ^{o}C for 7 days. At fixed time intervals they were removed, weighed and returned to the liquid for the study of sorption characteristics. Then desorptioncharacteristics was studied by heating the membranes in a drying oven maintained at 37 ^{o}C. The sorbed or desorbed liquid at equilibrium, diffusion coefficient, solubility, and volume increase after sorption were calculated. The sorption/desorption cycle was repeated for a second time.

Results: It is observed similar behavior of chitosan membranes in water and PBS solution, as far as the sorption study is concerned. The amount of the sorbed liquid at equilibrium is greater than the amount of the desorbed liquid in the first and the second cycle, while the amount of the sorbed/desorbed liquid in the second cycle is less than this in first cycle. The sorption parameters of chitosan-based network depend on the internal structural characteristics such as the percentage of chitosan in the membrane, crosslink density of the network, the number of hydrophilic functional groups, etc.

POSTER 4.23

SYNTHESIS OF STIMULI-RESPONSIVE POLYPEPTIDES FOR DRUG DELIVERY APPLICATIONS

Dimitra Stavroulaki[1], Foteini Arfara[1], Panagiotis Christakopoulos[1], Panagiota Fragouli[2], Hermis Iatrou[1]

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In recent decades, synthetic polypeptides have shown promise for many bio-applications due to their biodegradability, biocompatibility, and their native secondary structures. Their ability to respond to external stimuli, such as pH, light, redox, temperature and enzymes renders them very popular as novel drug and gene delivery systems. Herein we present the synthesis of a series of hybrid polypeptide copolymers based on poly(L-Histidine), poly(L-Alanine) and poly(L-Cysteine). The synthesis of the polymers was achieved through a ring-opening polymerization (ROP) process of the corresponding N-carboxy anhydrides, using an amine end-functionalized poly(ethylene oxide) (m-PEO-NH_2) macroinitiator. High-vacuum techniques were used for the synthesis of N-carboxy anhydrides of a-amino acids and for the isolation of well-defined polymers, ensuring high purity of the system. The successful synthesis of the polymers was confirmed by SEC, ^{1}H-NMR and FT-IR. In addition, the relationship between the secondary structure of the polypeptides and pH and temperature was studied using circular dichroism (CD). Finally, dynamic light scattering (DLS) and static light scattering (SLS) were employed in order to investigate the ability of the polypeptides to self-assemble into micelles. The synthesized polymers could self-assemble in aqueous media and form micelle-like nanostructures. The outer hydrophilic corona of the nanostructures was comprised of poly(ethylene oxide) chains, while the hydrophobic core was based on either poly(L-Histidine) and poly(L-Alanine) or poly(L-Cysteine), polypeptides, which exhibit pH, thermo and redox- responsiveness, respectively.The ultimate goal was to create “stimuli-responsive” polypeptides, for targeted and controlled drug release applications to cancer cells.

POSTER 4.24

A NEW PHOSPHOROUS-CONTAINING STAR-SHAPED GLYCOPOLYMER FOR BIOMEDICAL APPLICATION

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Among the variety of nanostructures that are used in the biomedicine, the star-shaped polymers stand out because of their unique architecture and wide-ranging application. Star-shaped glycopolymers can mimic different biorecognition properties of biopolymers. The unique interaction and specificity of binding between different glycopolymers and proteins is a key tool in the communication and control of a large number of biological processes. In the present work a new star-shaped phosphorus-containing glycopolymer with glycopyranose residues was obtained for the first time via the Staudinger reaction.

A star-shaped polymer, consisting of oligomeric arms (oligo(oxyethylene H-phosphonate)) and a core (tris (2,3-epoxypropyl) isocyanurate) was synthesized. After that it was silylated using *N,O*-bis-trimethylsilyl acetamide and reacted *insitu* with a pre-synthesized aromatic sugar azide via the Staudinger reaction to produce a star-shaped glycopolymer. The multivalent interactions of the glycopolymer were studied with lectin (Concanavalin A). The product and its complexes with Con A were characterized using Nuclear Magnetic Resonance, Gel Permeation Chromatography, Dynamic Light Scattering, Atom Force Microscopy, Analytical Ultracentrifugation, Cytotoxicity tests.

The new phosphorus-containing star-shaped glycopolymer is water-soluble, low-toxic and biodegradable with a relatively narrow molecular mass distribution - $M_w/M_n = 1.67$, Mn = 8000 g/mol and a mean hydrodynamic diameter $D_h = \sim 10$ nm. The star-shaped glycopolymer forms different complexes with Concanavalin A with $M_n = 151 \div 838$ kDa and $D_h = 250\text{-}350$ nm.

The results proved the potential use of the newly obtained star-shaped glycopolymer in the biomedicine for the development of vaccines and drugs.

Polymers for Emerging Technologies

(Energy, Organic Electronics, Environment, Nanotechnology)

PLENARY ORAL

STRUCTURE - PROPERTY CORRELATIONS FOR THERMOELECTRIC POLYMERS: TOWARDS EFFICIENT MATERIAL DESIGN

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Conducting polymers (CPs) have recently gained the attention of the scientific community due to their prospective use in thermoelectric applications. Particularly, it has been proven that an important parameter for tuning the thermoelectric properties and the charge transport behavior of the CP is the shape of the DOS in the band edge, where a steeper band edge would be translated in a semi-metallic behavior for the system, with higher thermoelectric efficiencies. However this shape can also be affected by the oxidation levels of the systems. In the present study we managed to elucidate the correlation between material structure, electronic structure and electronic/ thermoelectric properties, through proper material design and keeping constant the carrier concentration of the CPs. Additionally, for these systems a metal-to-insulator transition was observed in low temperatures near 30K, which was diminished with increasing thin film crystallinity. Our results underline that CPs with higher crystallinity will result in a 2-D charge transport behavior and a steeper band edge, which are translated into higher carrier mobility (4.2 cm^2/Vs) and higher Seebeck coefficient (44μV/K). Finally, an experimental relationship between carrier mobility and Seebeck coefficient was extracted highlighting the importance of CPs with high carrier mobility for thermoelectric applications.

PLENARY ORAL

CONJUGATED POLYMERS IN BRAIN INTERFACING

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One of the most important scientific and technological frontiers of our time is the interfacing of electronics with the living systems. This endeavour promises to help engineer better healthcare. Recent advances in organic electronics have made available conjugated polymers with a unique combination of attractive properties, including mechanical flexibility, mixed ionic/electronic conduction, enhanced biocompatibility, and capability for drug delivery [1–3]. I will present examples of novel devices for recording and stimulation of neurons and show that conjugated polymers offer tremendous opportunities to study the brain and treat its pathologies.

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INVITED ORAL

MULTI-FUNCTIONAL GRAPHENE/POLYMER NANOCOMPOSITES

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Graphene has been termed the stiffest and strongest material known to date. Given its superior mechanical behaviour, combined with exceptional electrical and thermal properties, graphene is the ideal material for lightweight, high strength polymer composite materials with several multi-functionalities. So far, only graphene in a form of separated flakes, i.e. nanoplatelets (GNPs) or in general graphene-related materials (GRM), has been adopted for the production of composites for large scale applications. However, the actual mechanical performance of GRM composites are still below the expectations due to the small lateral size of the inclusions that result in poor transfer of stresses from the polymer matrix. Other –typical- limitations are due the difficulties of graphene dispersion and flake orientation in order to enhance the mechanical properties of commercial resins. However, in such cases other important properties such as the electrical and thermal conductivities and fire retardancy are greatly enhanced and that gives GRM composites an advantage vis-à-vis other competing inclusions in polymers.

The use of large-size graphene growth via Chemical Vapour Deposition (CVD) can lead to a new class of nanolaminates due to the (a) large lateral size of continuous graphene and thus efficient stress transfer, (b) uniform and controllable dispersion in the polymer matrix, and (c) controllable mechanical, electrical and thermal properties. The use of CVD graphene as reinforcement in polymer laminates has been recently proposed [1, 2]; however, due to difficulties in manipulating ultra-thin CVD graphene/polymer plies, the maximum graphene content that could be achieved was very small (less than 0.2%). We present here our recent attempts [3] to develop macro-scale CVD graphene/polymer nanolaminates based on the combination of ultra-thin polymer casting, wet transfer and floating deposition. By casting ultra-thin polymer films (<50 nm), higher graphene volume fractions can be achieved (up to 0.66%) and the resulting nanolaminates (at the macroscale) have the potential to outperform the current state-of-the-art graphene-based composite materials in both mechanical property and electrical conductivity enhancements (~ 60 S/cm).

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INVITED ORAL

DEVELOPMENT OF NEAR INFRARED (NIR) CONJUGATED POLYMERS AND ADVANCED CHARACTERIZATION SPECTROSCOPIC TOOLS FOR BIOIMAGING AND HEALTHCARE APPLICATIONS

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The exploration of conjugated polymers (CPs) for healthcare applications provides feasibility to build CP-based multimodal platform for both imaging and therapeutic applications in the clinic. It is believed that with the progress of in-depth research on CPs based basic research and clinical application, CP materials will achieve to detect molecular or physiological alterations that signal the presence of cancer when it is at a curable stage, and have the ability to evaluate cancer treatment protocols in real time, and to streamline the cancer drug development process, and therefore more CPs materials will be utilized to improve health care and clinical research.

To address the ever-changing and challenging needs of diagnosis, molecular imaging, and cancer therapy research, developing novel CPs with new features and capabilities including higher quantum yields, a narrowband emission/NIR emissions to fulfil drug screening, drug/gene delivery, and therapeutic applications are major issues in the ongoing works.

In this presentation, it will be shown the development of new NIR conjugated polymers based on BODIPY dyes and the establishment of the Comprehensive Cancer Center in Athens (ACCC-Athens Comprehensive Cancer Center) which involves a careful selection of laboratories, research centers and universities, public hospitals, and, potentially, a collaboration with companies from sectors such as pharmaceutical, biotechnology, diagnostics and bioinformatics.

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INVITED ORAL

SEMICONDUCTING MATERIALS AND HYBRIDS FOR ORGANIC ELECTRONICS

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Organic photovoltaics (OPVs) and polymer light emitting diodes (PLEDs) both employ polymer semiconductors and their blends as the "active layer" responsible for the devices' operation.
In typical OPVs, where polymer electron donors are combined with fullerene electron acceptors, the efficiency greatly depends on the active layer's morphology, among other factors. This can be modulated by incorporating a third component as compatiblizer and/or stabilizer. Specifically, hybrid polymer-fullerene additives comprising the electron donating polymer and the fullerenic acceptor part are presented herein in order to enhance the stability of the active blend. Alongside, organic non-fullerene electron acceptors are investigated based on perylene diimides (PDI), as more effective and efficient small molecular or polymeric electron acceptors.
In the case of PLEDs, semiconducting polymers, metallocomplexes or their combinations are used in order to obtain the desired colored emissions. Thus, we have developed various processable light emitting homo- and co-polymers with tunable light emission properties that will be presented herein.

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ORAL

DEVELOPMENT OF PHOTOSENSITIZERS FOR DSSCS OF IMPROVED LIGHT ABSORPTION AND STABLE BINDING ONTO INORGANIC NANOPARTICULATE PHOTOANODES

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In Dye-sensitized solar cell (DSSC) applications, the dye sensitizer is typically bonded onto the TiO_2 semiconductor's surface using carboxylic acid groups resulting in esteric bonds between the sensitizer and the semiconductor. However, these bonds are hydrolysable. To overcome this bottleneck, we have synthesized pentafluorophenyl substituted organic sensitizers that can be covalently attached onto the TiO_2 photoanode through stable non-hydrolysable Ti-O-C bonds. These have proven efficient for the sensitization of TiO_2 photoanodes, with impressive stability over extreme alkaline and temperature conditions. Further on and in an effort to increase the dyes' sensitization capacity we have made efforts to combine the purely organic molecules with terpyridine-Ru(II) complexes. These combined sensitizers show improved absorption properties in the UV-Vis region of the solar spectrum. Moreover, for DSSCs application in large area glass panels for greenhouse coverage, it is essential to permit the wavelengths that are necessary for the plants' chlorophyll to surpass the DSSC. Therefore, we have directed our synthetic efforts towards organic or mixed organic-Ru(II) dyes that fulfill this requirement.

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ORAL

FLUORINATED POLYMERS FOR HYDROPHILICITY SURFACE MODIFICATION VIA LITHOGRAPHY

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The design of surfaces having different hydrophilicity in specified areas is very important for guided biomolecule immobilization or cell adhesion. The predetermined immobilization of biomolecules on solid surfaces is critical for several biomedical and biotechnological applications such as biosensors, biological microelectromechanical systems (bio-MEMs) and microfluidic devices [1].

Lithography is a robust technique for the fabrication of well-defined structures with different shapes on surfaces. This technique is based on the solubility changes in a solvent (developer) of a polymer upon exposure. One common method is the deprotection of hydrophilic groups (e.g. carboxylic) with the help of a photoacid generator. Thus, the exposed areas are becoming more hydrophilic, than the unexposed ones, resulting in hydrophilicity changes on selected areas of the surface.

Taking advantage of the high hydrophobicity of fluoropolymers, as well as of the biomolecule-friendly solvents (hydrofluoroethers, HFEs) used for patterning on this polymer, we developed a process for biomolecule patterning on silicon surfaces by photolithography [2].

Different fluoropolymers (homo- and copolymers) were studied in function of patterning ability, hydrophilicity change upon exposure and biomolecule immobilization on the exposed and unexposed areas. The methods used for the biomolecule attachment to solid surfaces include physical adsorption and/or covalent coupling. We will discuss the solubility changes vs exposure dose, the effect of HFE and polar solvents on the exposed surfaces, as well as the ability of selective biomolecule immobilization.

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ORAL

UNVEILING THE UNIQUE PROPERTIES OF CONJUGATED POLYMERS. HORIZON MATERIALS FOR ORGANIC (BIO)ELECTRONIC APPLICATIONS

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Organic semiconductors (small molecules, oligomers and polymers) are materials where unique optical and electronic properties often originate from a tailored chemical structure. During the past few decades a vast number of organic semiconductors for organic light emitting diodes (OLEDs), organic field effect transistors (OFETs) and organic photovoltaics (OPVs) have been developed and various chemical modifications are used in order to engineer and optimize the chemical structure towards enhanced device performance. It is therefore evident that the enormous potential for practical applications from organic electronics increases the value of this research field. Polymeric semiconductors represent the most challenging category from the class of the organic semiconductors. The ability to control and optimize their chemical structure for different optoelectronic applications involves many parameters such as: (i) molecular weight, (ii) bond length alternation (BLA), (iii) planarity, (iv) aromatic resonance energy (E_{Res}), (v) substituents and (vi) intermolecular interactions. Nowadays, the proper design of polymeric semiconductors has been focused on the way with which the optoelectronic properties of the polymers and the resulting device performance can be affected. However, it is of outmost importance to gain an in depth understanding on the role of the chemical structure in (i) the establishment of the tendency for supramolecular self-assembly and corresponding morphological features and (ii) the optoelectronic properties of the polymeric semiconductors and the corresponding device performance. In this presentation we will present some of the unique properties of conjugated polymers that will lead to the design and synthesis of next generation polymeric semiconductors as attractive candidate materials of choice for high performance organic (bio)electronic applications.

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ORAL

DEVELOPMENT OF POLYMERIC IONIC LIQUID MEMBRANES FOR CO2 SEPARATION

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Membrane separation technology based on polymeric materials has become a promising alternative to conventional energy intensive gas separation methods and is used commercially for CO_2 recovery from natural gas, H_2 recovery and on site nitrogen production from air. Polymeric ionic liquids or poly(ionic liquid)s (PILs) as CO_2 separation membrane materials have become an emerging field with great potential in recent years, due to their high CO_2 sorption capacities and high absorption-desorption rates associated with their ionic liquid character [1]. Novel pyridinium based PILs have been synthesized through conversion of high molecular weight aromatic polyethers bearing main chain pyridine groups to their ionic analogues via N-methylation reaction, followed by anion exchange reaction [2]. The prepared PILs show high T_g nd have the ability to form very thin, free standing films with thickness ranging from 3 to 25 μm via a conventional solution casting method. PIL containing the TFSI anion showed higher CO_2 and CH_4 permeability compared to its analogue containing the BF_4 nion, denoting the important role of anion in gas transport properties. However, CO_2 and CH_4 permeabilities were low. To improve gas separation properties, PIL-IL composite membranes containing the $TFSI^-$ anion were prepared by blending PIL with different amounts of a pyridinium based IL. Both CO_2 and CH_4 permeabilities of the PIL-IL composite membranes were increased by increasing the IL content. The composite membrane with the highest IL weight percentage (45 wt%) showed the highest CO_2 permeability (11.8 Barrer) and a high CO_2/CH_4 selectivity of 35.

ORAL

EFFECT OF BIAXIAL STRETCHING ON THE STRUCTURE AND DYNAMICS OF ISOTACTIC POLYPROPYLENE FILMS

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For power applications, good mechanical performance of flexible components needs to be combined with excellent dielectric properties. Since production and processing is a very demanding process, tailored-made polymer design is required for matching the above requirements. In this work, we discuss the thermal, structural, and dielectric properties of isotactic polypropylene films at each stage of the biaxial orientation (BOPP) process. Films from three stages of the process were investigated, namely cast, machine-direction oriented and BOPP films. Additionally, film properties made of base resins with different molecular characteristics (polydispersity, M_W, isotacticity) are presented. Thermal properties of films and pellets were examined using differential scanning calorimetry. Polarizing optical microscopy (POM) measurements were conducted to observe the crystal phase of the iPP pellets, as well as macroscopic changes in these films. The dielectric properties of the corresponding pellets and films at each stage of the BOPP procedure were examined with broadband dielectric spectroscopy (DS). permittivity of the film also deviates from the bulk value: The decrease in ε´ is attributed to cavitation (i.e. the presence of air inside the films) as indicated by POM and further confirmed and analysed by films. The presence of a Maxwell-Wagner process in DS was also found to correlate with the complex dynamics in the resulting film morphology. The work shows how, through polymer design, film processing and end-use properties can be optimized.

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ORAL

SYNTHESIS AND CRYSTALLIZATION KINETICS OF GRAPHENE/POLY(BUTYLENE SUCCINATE) COMPOSITES

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Biodegradable polymer composites, filled by graphitic nanostructures, have attracted increased attention owing to their unique mechanical, electric, optical and thermal properties. Chemical functionalization of graphene surface by either oxidation procedure or physical adsorption/grafting protocols have been found to be a feasible and effective means for enhancing the interfacial interactions between the graphenes and the polymer matrix. The advantage of modifying the graphene surface by physical adsorption is that the structural integrity of the conjugated network remains unaltered. To the best of our knowledge, there is no related study on fabricating graphene/poly(butylene succinate) (PBS) composites by using noncovalently modified pristine graphene nanoplatelets. In addition, differential scanning calorimetry (DSC) data such as isothermal and non-isothermal crystallization kinetics have not been widely studied in such graphene/polymer composites. We discuss here a simple and environmentally friendly preparation of graphene/PBS nanocomposites by incorporating poly(butylene succinate-co-propylene succinate) (PBPS) random copolymer-modified graphenes into a PBS matrix by sonication-assisted solution mixing process. PBS is one of the most important biodegradable polymers. Its semicrystalline nature allows us to circumvent complexities of interpreting property changes associated with crystallization versus graphite addition. Here, we report a comparative study of PBS nanocomposites based on noncovalently modified graphene sheets. The effect of graphene content on the physical and thermal properties of PBS/graphene nanocomposites is investigated. The effect of filler's chemical functionalities as well as loading on various thermal transition parameters is studied in detail by Raman, XRD, FTIR, WAXD, polarized optical microscopy and DSC.

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POSTER 5.1

SEMICONDUCTING SMALL MOLECULES FOR OSCS

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Over the past decade, the performance of polymer solar cells (PSCs) has steadily increased owing to the development of more efficient electron-donors or electron-acceptors, the control and stabilization of their morphology and new device architectures. Furthermore, non-fullerenic, small-molecules or polymers have deen developed as electron acceptors in order to overcome some of fullerene's limitations. Among them, perylene diimide - based materials (PDI) stand out for their good electron accepting properties, charge carrier mobilities and their thermal, chemical and photochemical stability. Our efforts are focused on synthesis of new derivatives towards optimizing PDI's optoelectronic properties. A *weak acceptor -PDI - weak acceptor* **(A-A'-A)** and a *Donor - PDI- Donor* **(D-A-D)** strategy was developed for the synthesis of new PDI small molecular acceptors. Perylene Diimide was linked with Phenyl perfluorophenyl Quinoline moieties (Weak Acceptor) and with different carbazole derivatives (Donor). The optical and electronic properties of the new, soluble and processable perylene Diimide -based small molecules have been investigated.

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POSTER 5.2

METALLOCOMPLEXES COMBINATIONS WITH POLYMERIC CHROMOPHORES FOR POLYMERIC LIGHT EMITTING DIODES

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Organic or Polymeric Light Emitting Diodes, OLEDs or PLEDs, respectively, are the "green" lighting solutions for all future applications. Additionally, PLEDs show great promise since they can be applied in large-area photonic devices. For these LEDs, transition metal complexes with small organic ligands is one of the most widely studied family of luminescent materials, that have indeed provided great enhancement in OLEDs efficiencies as well as tuneable colour emissions. However, solution processability of the metallocomplexes and their compatibility with the polymeric or other monomeric chromophores of the device in terms of morphology and energy levels matching, are still open issues hindering the employment of such systems for large area, solution processable O(P)LEDs. Moreover, polymeric metallocomplexes have yet not met analogues attention probably due to difficulties arising from inadequate solubility of heavy metal loaded polymers.
Herein, we present our efforts on the development of Iridium based luminescent metallocomplexes using pyridine bearing ligands and their incorporation into various polymeric backbones aiming at solution processable, luminescent polymeric metallocomplexes. Furthermore, different combinations of the polymeric and their respective monomeric metallocomplexes with various polymeric hosts have been attempted and exhaustively evaluated for their optical properties, which are guided by the correct matching of the individual counterparts photonic and electrochemical properties.

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POSTER 5.3

TUNING THE MECHANICAL AND THERMAL PROPERTIES OF THERMALLY REVERSIBLE CROSS-LINKED POLYMERS

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Due to their sophisticated molecular architecture, polymers and polymeric materials constitute ideal candidates that can be "transformed" into self-healing materials by programming or designing their functionalities at the molecular level. These polymers constitute one of the most important categories of self-healing materials, that of the intrinsic or remendable healing polymers. In this case, repair is achieved through the inherent reversibility of bonding in the matrix phase, which acts as a healing agent.

Within the scope of this work is to investigate the effects of three different thermo-reversible cross-linking agents on the thermal and mechanical properties of the resulted self-healing epoxy systems. For this purpose, 3 different bismaleimide oligomers were introduced as cross-linking agents via a two-step process in a diglycidyl ether of bisphenol A (DGEBA) resin. Prior to the synthesis of the reversible polymers, size exclusion chromatography (SEC) was employed in order to study the average molecular weights and the polydispersities of the three oligomers. The thermal properties of the produced self-healing polymers were investigated using Differential Scanning Calorimetry while the healing efficiency was assessed using Raman spectroscopy after an on purpose damage.

POSTER 5.4

NOVEL $MnFe_2O_4$-LOADED POLYMERIC NANOCARRIERS FOR CONTROLLED AND TARGETED RELEASE OF THE ANTICANCER DRUG PACLITAXEL

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Magnetic nanoparticles (MNPs) encapsulated in polymeric systems are promising materials for cancer treatment providing controlled and targeted drug delivery. In a previous work, D,L-lactide was for the first time successfully co-polymerized with the renewable monomer ω-hydroxyacid (TEHA) resulting in a fully bio-based material. In this study, these TEHA-co-PDLLA copolymers (with different TEHA/lactide ratios) were used to prepare the nanocarriers, which were further loaded with the anticancer drug Paclitaxel (PTX) and $MnFe_2O_4$ NPs.

PTX-loaded MNPs were prepared using a solid-in-oil-in-water (s/o/w) modified single emulsion-solvent evaporation method. SEM micrographs verified the successful formation of mainly spherical nanoparticles and TEM images (*Fig. 1a*) revealed their core-shell structure: magnetic core-polymer shell. FT-IR spectroscopy confirmed the successful encapsulation of paclitaxel and X-ray diffraction indicated the complete amorphization of the drug. DLS analysis confirmed the narrow size distribution of the nanoparticles (110-150 nm) and *in vitro* cytotoxicity testing ensured their low toxicity toward healthy cells, but also their great anticancer activity. The drug loading efficiency was high (~15%) in all cases and all materials exhibited high release rates and improved drug dissolution. The size and T_g of the NPs have been found to play an important role on the drug release profile (*Fig. 1b*).

POSTER 5.5

EVALUATION OF CHITOSAN-CONTAINING ELECTROSPUN FIBERS IN U(VI) ADSORPTION

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Uranium is a (radio)toxic element and its concentration in the environment systems varies depending on the composition of the geological background. However, anthropogenic activities such as uranium mining and processing, as well as the use of depleted uranium weapons on battlefields have led to increased contamination of man's environment becoming a serious environmental issue [1]. Hence, the development of cost-effective, selective and efficient adsorbents that could be used for the removal of uranium ions from aqueous media even when this are present at low concentrations is of paramount importance.

Electrospun (nano)fibers, which exhibit high surface-to-volume ratios and high tailorability in terms of surface functionalization, have been successfully used in the removal of heavy metal ions and particularly U(VI) ions from aqueous solutions [2, 3]. The present study deals with the fabrication and characterization of electrospun fibers consisting of chitosan (a chitin-derived polyssacharide) and polyvinylpyrrolidone. In order to retain the fibrous morphology upon immersion in aqueous media, the as-prepared electrospun fibers were thermally-crosslinked prior to their evaluation as adsorbents for U(VI) ion in aqueous solutions. Among others, experiments on the effect of initial U(VI) concentration and pH on the separation efficiency were performed, demonstrating the high efficiency of these functional fibrous materials towards U(VI).

POSTER 5.6

ANTIMICROBIAL COATINGS BASED ON CROSSLINKED BLENDS OF QUATERNIZED AMMONIUM COPOLYMERS

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Antimicrobial coatings of copolymers bearing quaternized ammonium groups covalently and/or electrostatically attached on the polymeric backbones [1,2], were prepared via reactive blending. Based on previous results [3,4], the parameters affecting the synthesis of coatings were optimized and thus, their release behavior in water and saline was controlled in the studied systems.

The antimicrobial copolymers poly(4-vinylbenzyl dimethylhexadecylammonium chloride-co-acrylic acid) P(VBCHAM-co-AAx) and poly(cetyltrimethylammonium 4-styrenesulfonate-co-glycidyl methacrylate) P(SSAmC$_{16}$-co-GMAx) bearing covalently bound and electrostatically attached antimicrobial units respectively, were synthesized and further stabilized via reactive blending. The crosslinking reaction between the carboxylic group of AA and the epoxide group of GMA by curing at 120 °C was used in order to stabilize the coatings on the surface of glass slides. The quality of the coating obtained from different composition was evaluated and the best combinations were selected for further study. The release rate of the developed coatings was studied for a certain time period in water and saline. To further study the released species in water conductivity and Nile Red Fluorescence Probing measurements were used to investigate the release behaviour of the antimicrobial coatings.

In conclusion, control on the release rate of antimicrobial coatings was achieved in the various studied systems. The release rate as well as the release levels differed in each system due to complementary reactive groups' content and the type of antimicrobial species.

Acknowledgements
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POSTER 5.7

A Comparative Study of Full Factorial Design for PLA-HA and PLA-MMT Composites

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Polylactic acid (PLA) is a biodegradable, environmental friendly, biocompatible, easily processable and transparent polymer. Although PLA has these advantages, its applications are limited due to its high cost, thermal and structural properties. The physical, thermal or mechanical properties of PLA can be improved by several methods, such as modification, addition of additives or polymer blends. The one of the most effective methods is seen as composite materials. The composite films based on PLA could be improved for package and medical applications.

The goal of this study was to evaluate behavior of PLA/hydroxyapatite, PLA/montmorillonite and PLA/hydroxyapatite/montmorillonite composites. Films were prepared by using solvent-casting procedure and characterized by FTIR (Fourier Transform Infrared Spectroscopy), TGA (Thermogravimetric Analysis) and Water Absorption Capacity. Factorial design of experiments was employed to study the effect of montmorillonite amounts (5% and 20%), hydroxyapatite amounts (5% and 20%).

Main and interaction effects of three factors were analyzed using statistical techniques. A regression model suggested and it was found to fit the experimental data very well. The results were analyzed statistically using the Student's t-test, analysis of variance, F-test and lack of fit to define most important process variables affecting the percentage PLA amounts. After optimization studies, the most effective parameters were determined using the full factorial design method of experimental statistics.

POSTER 5.8

NANO-MODIFIED COMPOSITES: A DISPERSION MONITORING STUDY VIA IMPEDANCE SPECTROSCOPY

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Multifunctional composites offer numerus functionalities, including Structural Health Monitoring (SHM), self-sensing capabilities, energy harvesting, etc. One major obstacle to the multifunctionality of composites is the highly dielectric character of the epoxy resin. The addition of a conductive nano- or micro-scaled filler inside the dielectric epoxy matrix led to the improvement of the mechanical, electrical and thermal properties of the composites. According to various studies the most promising nano-fillers are Carbon Nano Tubes (CNT) due to their exceptional properties. As an alternative filler, Carbon Black (CB) is a widely used carbonaceous filler, capable of enhancing these properties. Hence, the homogenous dispersion of these fillers overcomes the obstacles of imparting functional properties to the epoxy resin.

Within the scope of this research was to monitor the dispersion of various protocols, as function of filler weight content and dispersion duration. Shear mixing was selected among other dispersion techniques to avoid degradation of the fillers and the matrix. A 45mm diameter toothed impeller disk was selected, offering medium shear forces to dispersion, to reduce agglomerates size. The conditions of all dispersion protocols were rotary speed at 3000 rounds per minute (rpm) and temperature at 25 C. Impedance measurements were performed using the Advanced Dielectric Thermal Analysis System (DETA-SCOPE) supplied by ADVISE, Greece. The specimens were placed between two parallel copper plates, where a sinusoidal voltage of 10V was applied. Scans were performed between two frequency values (0.01 Hz to 100 kHz) at 14 different frequencies.

POSTER 5.9

FUNCTIONAL NANOPOROUS POLYMERS FOR ENERGY AND ENVIRONMENTAL APPLICATIONS

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Nanoporous organic polymers have gained considerable scientific attention in gas separation and gas capture applications due to their facile synthesis, large surface area, high porosity, and the ability to introduce valuable chemical functionalities.[1] Recent studies have shown that the incorporation of aromatic groups and polar organic moieties, such as amine or carboxylic acid groups, into the polymer structure can induce favorable interactions between the porous matrix and CO_2 molecules, resulting to an enhanced CO_2 uptake.[2,3] In this work, we present the synthesis of a series of highly cross-linked porous polymers based on i) polystyrene nanoparticles with and without porphyrin moieties and ii) porphyrin networks of variable carboxylic acid contents. The polystyrene nanoparticles were prepared by emulsion copolymerization of styrene and divinylbenzene in water, whereas for the synthesis of the porphyrin-containing nanoparticles a tetra-functional porphyrin methacrylate cross-linker (Po) was employed as an additional cross-linker.[4,5] The porphyrin networks were obtained by the copolymerization of Po withvinylbenzoic acid (VBA) in DMF. Four different porphyrin-based networks were prepared by varying the Po/VBA molar ratio from 1/0 to 1/4. After synthesis, the porous polymer structures were attained by supercritical CO_2 drying of the materials. The morphology, size and porous structure of the dried nanoparticles were characterized by SEM and TEM, whereas the chemical structure of the porphyrin-based networks was determined by FTIR and UV/Vis spectroscopies. The influence of the polar moieties, porphyrin and carboxylic acid groups, on the porosity, CO_2 uptake and CO_2/CH_4 selectivity of the materials were investigated.

POSTER 5.10

SYNTHESIS AND CHARACTERIZATION OF NOVEL NANOCOMPOSITE MATERIALS BASED ON PMMA WITH Ag, TiO_2 AND ZnO NANOPARTICLES WITH ANTIMICROBIAL PROPERTIES

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Introduction: Nowadays, conventional polymeric materials such as poly(methyl methacrylate), PMMA, can improve their current properties or even obtain new characteristics as a result of their modification with inorganic nanoparticles (NPs). In recent years, Ag, TiO2 and ZnO NPs have been studied a lot due to their significant antimicrobial properties.

Methods: In this paper nanocomposites of PMMA with 0.2, 0.5 and 1% w/w silver, titanium oxide and zinc oxide nanoparticles were successfully prepared by an in situ radical polymerization technique. The reduction of Ag + took place during the reaction. A big variety of techniques such as thermogravimetric analysis (TGA), gel permeation chromatography (GPC), differential scanning calorimetry (DSC) were used in order to investigate the properties of pure PMMA and PMMA/nanoparticles composites.

Results: It was observed that the presence of the nanoparticles leads to the reduction of the reaction rate but it increases the number average molecular weight of polymer nanocomposites. The glass transition temperature was found to decrease with the amount of Ag and ZnO NPs but the converse happened in the case of PMMA/TiO2 NPs. The polydispersity of the MWD was lower in PMMA/ nanoparticles composites than those of pure PMMA. In order to confirm the presence of NPs in the final product we used X-Ray diffraction, horizontal Attenuated total reflection (HATRFTIR) and ultraviolet-visible spectroscopy (UV-Vis). Moreover, thermogravimetric analysis showed that the presence of NPs enhance the thermal stability of the nanocomposites. Finally, the antimicrobial properties of the nanocomposites were studied against bacterial strains of E.Coli and St.Aureus using pure PMMA as control agent.

Conclusions: Nanocomposites of PMMA with several NPs were successfully synthesized and they showed improved properties compared to neat PMMA.

POSTER 5.11

CARBON FIBER THERMOELECTRIC MODULE FABRICATION, INTEGRATION, EXPERIMENTAL AND SIMULATED POWER GENERATION IN 8-PLY LAMINATE EPOXY COMPOSITES

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Abstract

Polymer matrix composites containing a high proportion of continuous aligned carbon fibers as the reinforcement, are the dominant advanced lightweight materials for high performance structural applications. Although their structural performance is well established, the multifunctionality of these materials is a topic of active research. Multifunctionality means the ability to provide both structural and non-structural functions**.** In the present work, a carbon fiber based thermoelectric module was constructed and had been embedded to carbon fiber reinforced polymer for a self-powered advanced composite. Carbon fiber reinforced polymer multifunctional composites were manufactured by hand lay-up and vacuum bagging technique, consisted of a 7-ply alternating laminae with a 0/90 architecture of unidirectional carbon fabrics, while a carbon fiber based thermoelectric element generator has been integrated as the bottom lamina. The proposed structure depicted a total voltage output of 19.5 mV upon being exposed to ΔT=75°C. Simultaneously, numerical modeling using Finite Elements Methodology predicted and validated the thermoelectric efficiency of the multifunctional composite. This study addresses the materials science of the multifunctionality, particularly in relation to the thermoelectric power in the longitudinal direction of the prototype laminates, with encapsulation in epoxy matrix of a thermoelectric generator device by exploiting the carbon fiber yarns as thermoelements.

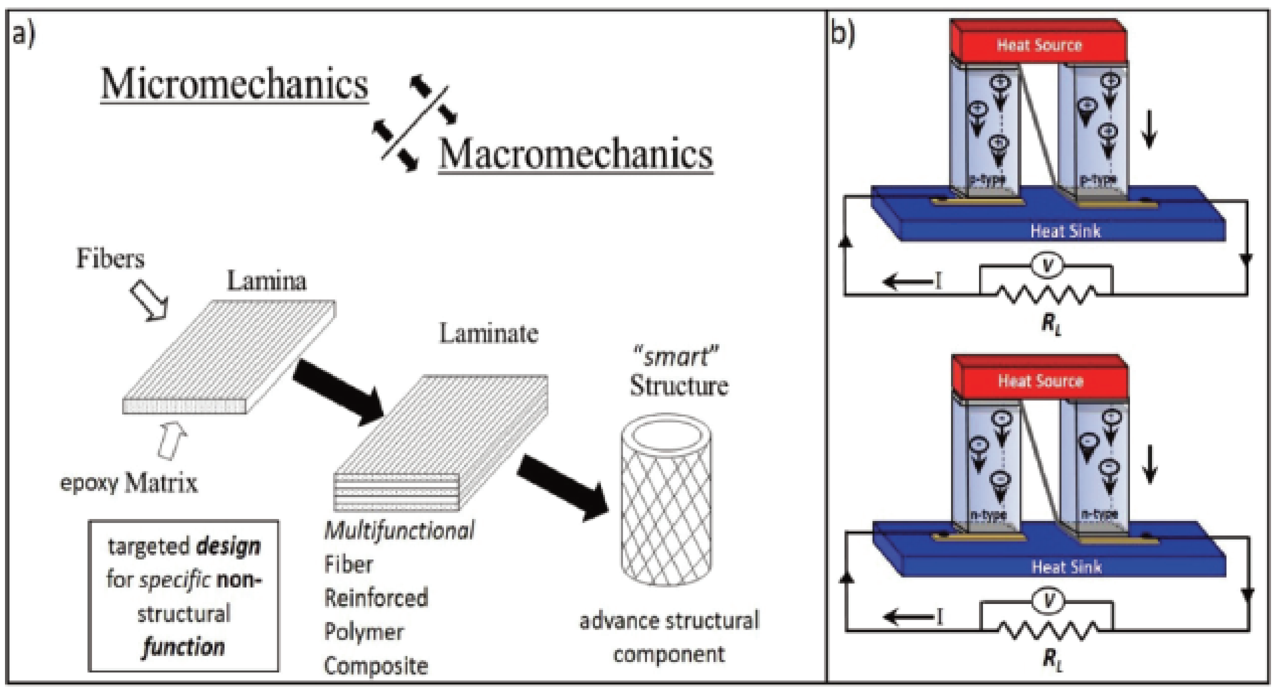

Fig. a) structural multifunctional composite approach, b) principles of Thermoelectric Element Generators.

POSTER 5.12

DESIGN AND SYNTHESIS OF NEW HIGH BANDGAP CONJUGATED POLYMERS FOR APPLICATIONS in ORGANIC PHOTOVOLTAIC DEVICES

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

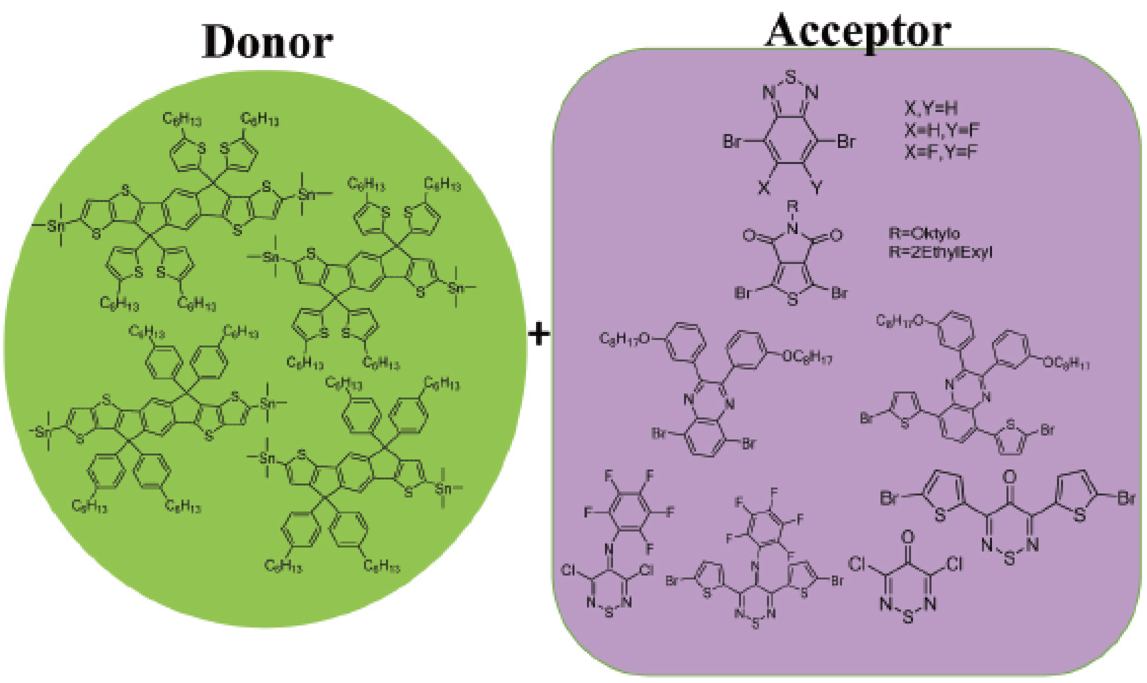

Figure 1: Chemical structures of the monomers used as donors and acceptors

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.

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POSTER 5.13

PREPARATION OF POROUS POLYMERIC MEMBRANES BASED ON A FUNCTIONAL POLYSULFONE-TYPE AROMATIC POLYETHER

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Water contamination is one of the most serious complications in modern society, including seawater and industrial wastewater treatment. Due to their compact modular construction and low chemical sludge effluent, membranes have become an important tool for water purification [1]. Between the two main categories, inorganic and organic polymeric membranes [2,3], the latter is widely used, because it possess several advantages. Thus, polymeric membranes based on a polysulfone-type aromatic polyether matrix were successfully developed via non-solvent induced phase separation (NIPS) method. The polysulfone-type polymer poly[2-(4-(diphenylsulfonyl)phenoxy)-6-(4-phenoxy)pyridine] (PDSPP) was used as the hydrophobic matrix and mixed in various concentrations with its hydrophilic sulfonated derivative (SPDSPP) and a polymeric porogen. The variables tested included PDSPP/SPDSPP/porogen w/w composition, type of solvent, type and temperature of non-solvent, type and concentration of porogen etc. Scanning Electron Microscopy (SEM), Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS), Water Uptake % (WU %), Porosity %, Pure Water Flux (PWF), Pure Water Permeability (PWP), Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Thermogravimetric Analysis (TGA) were the procedures and techniques used to evaluate the effect of the different parameters. The results shown that the use of different conditions led to membranes with controllable porosity and enhanced hydrophilicity. These properties can be proved very useful in water purification systems.

POSTER 5.14

TRANSFORMING POLYMER MICROCAPSULES TO ELECTRICALLY CONDUCTIVE MICRO-CONTAINERS FOR ENHANCED SELF-HEALING APPLICATIONS

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Inspired from nature, self-healing polymer composite materials are capable of restoring (healing) any possible damage. There are two main approaches, intrinsic and extrinsic. Intrinsic polymers have the ability to recover their properties through chemical or physical processes such as the thermo-reversible cross-linked Diels-Alder reaction. The extrinsic approach bases on the employment of external polymeric healing agents in the form of vascules or capsules. Vascule based composites mimicking the blood vessels of living organisms even with the use of hollow fibers or the incorporation of networks. In the capsule concept, micro or nano capsules, which contain a healing agent, are embedded at the polymer matrix.

In this study, conventional polymeric microcapsules transformed at electrically conductive micro-containers with the incorporation of multi-walled carbon nanotubes (MWCNTs) at the capsule poly(urea-formaldehyde) shell wall. Capsules shell wall and size distribution were examined through Scanning Electron Microscopy (SEM). Also, the incorporation of MWCNTs at the shell wall was confirmed with Raman spectroscopy. Thermogravimetric analysis exhibited high thermal stability of nanomodified capsules. The change of the electric profile of the polymer matrix was evaluated via Electrochemical Impedance Spectroscopy (EIS).

POSTER 5.15

IMPROVING THE HEMOSTATIC ACTION OF ACIDIFIED CHITOSAN WITH INORGANIC ADDITIVES

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Introduction: Chitosan (CS) is a biodegradable polysaccharide, biocompatible and non-toxic which considered to be a significant antimicrobial agent along with wound healing, hemostatic and analgesic characters.
The aim of the present study was to improve the hemostatic performance of chitosan by blending it with hemostatic inorganic additives.

Experimental: CS was dissolved in three different acidic solutions (citric, oxalic and acetic) in various proportions and then three inorganic additives ($Al_2(SO_4)_3xH_2O$, $Fe(SO_4)_3xH_2O$, $AlCl_3$) were added. All samples were dried at 60^{o}C overnight. The obtained thin films were grinded to powder. All samples were characterized by FT-IR, XRD and SEM (data not shown here).

Results: Thirty two acidified CS/inorganic additives composites were prepared.
FTIR measurements revealed that ionic interactions, namely hydrogen bonds are evolved between CS and the acids.
XRD measurements revealed the semi-crystalline form of chitosan. Upon the addition of the additives, the materials turn even more amorphous.
The morphology of samples was studied by SEM and EDX analysis and the successful addition of the inorganic additives was confirmed.
The water sorption capacity was improved upon the addition of a higher amount of inorganic additives.

Conclusions: All samples were successfully prepared. FT-IR, XRD and water absorption measurements confirmed the improvement of chitosan's properties with the use of inorganic additives.

POSTER 5.16

NOVEL NANOMATERIALS AS TEMPERATURE SENSORS IN FOOD PACKAGING INDUSTRY: Fe(II) COORDINATION COMPLEXES EXHIBITING SPIN CROSSOVER PHENOMENON (SCO) IN FOOD PACKAGING POLYMERS

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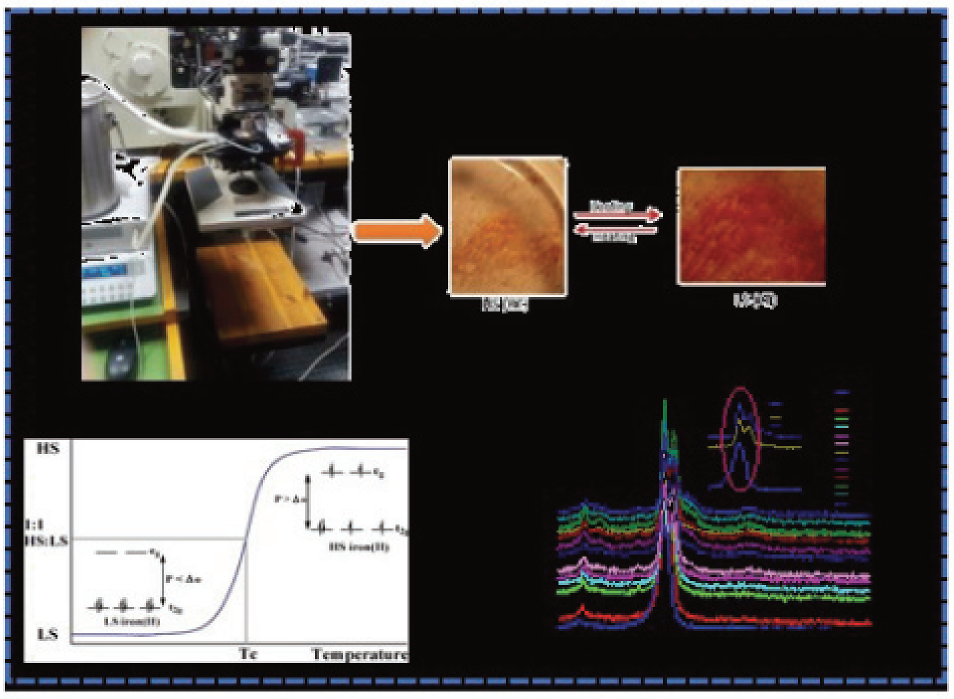
Introduction: A crucial issue for food packaging industry is to ensure the food quality and safety of the consumers. "Smart" food packaging materials exhibiting sensor-type properties, play a key-role in these purposes. Spin-Crossover Phenomenon is widely studied for numerous coordination complexes. One of the main characteristics of SCO complexes, is the temperature-dependent drastic colour changes accompanied by spin state conversion. Our study focuses on low nuclearity-Fe(II) SCO complexes that are subsequently incorporated into suitable polymers for their potential use as temperature sensors in refrigerated products.

Methods: The coordination complexes developed were characterized with various methods/techniques (Raman, ATR, p-XRD, UV/VIS, SEM). Temperature-dependent and low-frequency Raman experiments played a significant role for the meticulously examination of the SCO phenomenon. The second step of our efforts was the incorporation of the materials in conventional food packaging polymer matrices and in turn the eventual migration release study of the sensors in food simulants (based on EU regulations).

Results: The detailed study of the SCO materials gave promising outcomes concerning the characteristics of the final products. The investigation of the SCO properties *via* Raman spectroscopy was very informative. The starting materials of the SCO complexes were quantitative probed at very low concentration range by Surface Enhanced Raman Scattering measurements. The polymer matrices and the food simulants selected led to convincing results for further investigation towards potential commercial implementation.

Conclusions: The development of novel "intelligent" food packaging materials constitutes an important/challenging task. The results deriving from the present study might support further growth of this field.



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POSTER 5.17

MULTIWALL NANOTUBES DECORATED WITH GUANIDINYLATED HYPERBRANCHED POLYETHYLENIMINE AS EFFECTIVE DRUG DELIVERY SYSTEMS

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In the recent years, numerous nanodelivery systems have been proposed as drug carriers, including nanostructured carbon materials such as carbon nanotubes, fullerenes, graphene, etc.[1-2] On the other hand, during the last decades dendritic polymers[3] have been applied for various biological applications, e.g. as drug carriers,[4-6] mainly due to their unique structural characteristics. Specifically, their repeating groups, located in the interior of these polymers determine their microenvironment and consequently their solubilizing properties, while their external groups, which can be easily chemically modified, determine their solubility. The current study presents the development of innovative hybrid nanomaterials, i.e. CNTs@GPEI-5K and CNTs@GPEI-25K, obtained by the interaction of oxidized multiwall carbon nanotubes (CNTs) with guanidinylated hyperbranched polyethyleneimine derivatives (GPEI with MW of 5KDa and 25KDa) through electrostatic interactions or other intermolecular forces. Their aqueous dispersions exhibit extreme stability for more than one year without observing any precipitation. Furthermore, doxorubicin (DOX), a well-known anticancer drug, can be strongly bound at CNTs@GPEIs mainly via π–π stacking interactions. The inhibition of human prostate adenocarcinoma DU-145 and PC3 cell proliferation was assessed by the MTT assay. It was found that both nanomaterials were subtoxic, while the encapsulated DOX in both nanocarriers caused a significant viability decrease in both cell lines. The cellular uptake of CNTs@GPEI-5K/DOX and CNTs@GPEI-25K/DOX was determined by flow cytometry, while the intracellular localization of DOX was visualized by confocal scanning electron microscopy. Based on the above results, both hybrid nanomaterials can efficiently deliver DOX, leading to significantly increased efficiency of doxorubicin at low concentrations.

POSTER 5.18

ENERGY STORAGE AND HARVESTING IN BARIUM STRONIUM TITANATE/ EPOXY NANODIELECTRICS

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Introduction: The improvement of energy efficiency mainly in electronic devices is very important nowadays. Most electronic devices demand systems that are able to store a large amount of energy and deliver it back on demand when necessary. Therefore, there is a motivation in the direction of introducing new multifunctional materials which could act as energy storing devices. In this work nanocomposites constituted of an epoxy resin (ER) as matrix and barium strontium titanate (BST) nanoparticles as the reinforced phase, have been prepared and studied varying the filler content. The main target was the evaluation of the energy efficiency of each system.

Methods: Broadband dielectric spectroscopy (BDS) was employed for studying the dielectric response in every nanocomposite system. DC measurements were conducted in a wide range of applied DC fields and temperatures. The effect of the filler loading upon energy was also examined.

Results: Both energies E_charge and E_discharge increase as the applied DC field elevates and the coefficient of energy efficiency (n_eff) raises upon filler content.

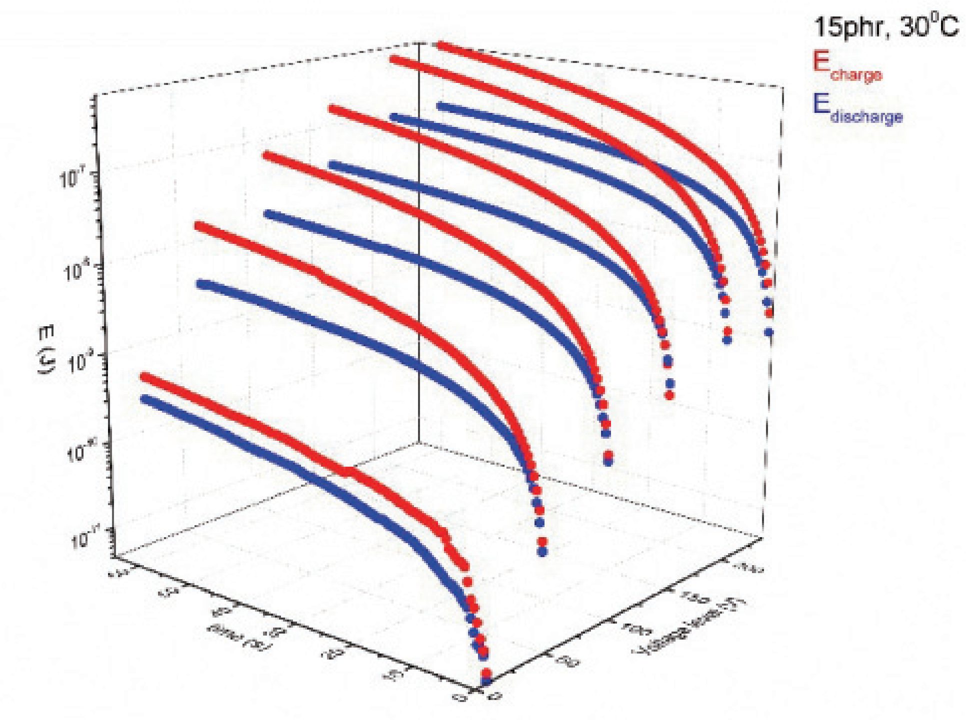

Figure 1. 3D spectra of stored and harvested energy as a function of time and DC voltage level for the 15phr BST nanocomposites at 300C.

Conclusions: The coefficient of energy efficiency (n_eff) increases significantly upon filler content acquiring the highest value of 65.9% for the 1phr BST nanocomposite at 50V.

POSTER 5.19

FUNCTIONAL BLOCK COPOLYMERS FOR TOP-DOWN AND BOTTOM-UP LITHOGRAPHY

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Patterning technologies are the key techniques for miniaturization of devices as well as the development of nanofabrication routes for novel devices fabrication. They are two different approaches: the top-down approach, mainly expressed by photolithography (exposure of aphotoresist film) and the bottom-up approach e.g. block copolymer lithography via microphase separation.

In the present work a diblock copolymer system allowing top-down and bottom-up lithography is presented. Amphiphilic poly(2-(dimethylamino)ethyl methacrylate)-*b*-poly(tetrahydropyranyl methacrylate) (PDMAEMA-*b*-PTHPMA) diblock copolymers of different volume fractions of the two blocks were synthesized by group transfer polymerization. Block copolymer films were prepared by spin-coating a copolymer solution in methanol on silicon substrates to obtain 30 nm thick films. Microphase separation of the block copolymer films on nanometer length scales, under controlled solvent annealing conditions, produced well-defined morphologies which were depended on the volume fraction of the blocks. The produced nanostructures are oriented either normal or parallel to the silicon substrate depending on the use or not of a random copolymer primer layer. The self-assembly of the films were verified by atomic force microscopy. The block copolymers were also evaluated as photoresists, in the presence of a photoacid generator, and allowed the development of 500 nm structures upon exposure to 254 nm contact printing. The chemically amplified lithographic ability of the copolymer is based on the acid catalyzed deprotection of the hydrophobic PTHPMA block. In conclusion, novel very promising amphiphilic block copolymers for device nanofabrication using top-down and bottom-up patterning technologies were synthesized.

POSTER 5.20

EFFECT OF THE NANOCLAY TYPE ON CURING KINETICS AND MECHANICAL PROPERTIES OF DENTAL NANOCOMPOSITE RESINS

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Introduction: The aim of this study was the synthesis and characterization of dental resin nanocomposites containing organomodified nanoclays with variant functional groups.

Methods: Nanocomposites were prepared by mixing BisGMA, TEGDMA, camphorquinone, DMAEMA, and incorporating different organomodified nanoclays.

Unpolymerized composites were exposed to visible light of a halogen lamp, and scanned by a FTIR spectrometer at different curing time intervals. The degree of conversion (DC %) at each time period was calculated. Bar- shaped specimens (25 x 2 x 2 mm) were prepared and polymerized. Flexural strength and modulus were measured by 3-point bending test.

Results: According to Figure 1, nanoclays with methacrylated groups can increase the DC (%) and flexural modulus of dental resins.

Conclusions: The different type of nanoclay organic modifier may significantly affect curing behavior and mechanical properties of dental nanocomposites.

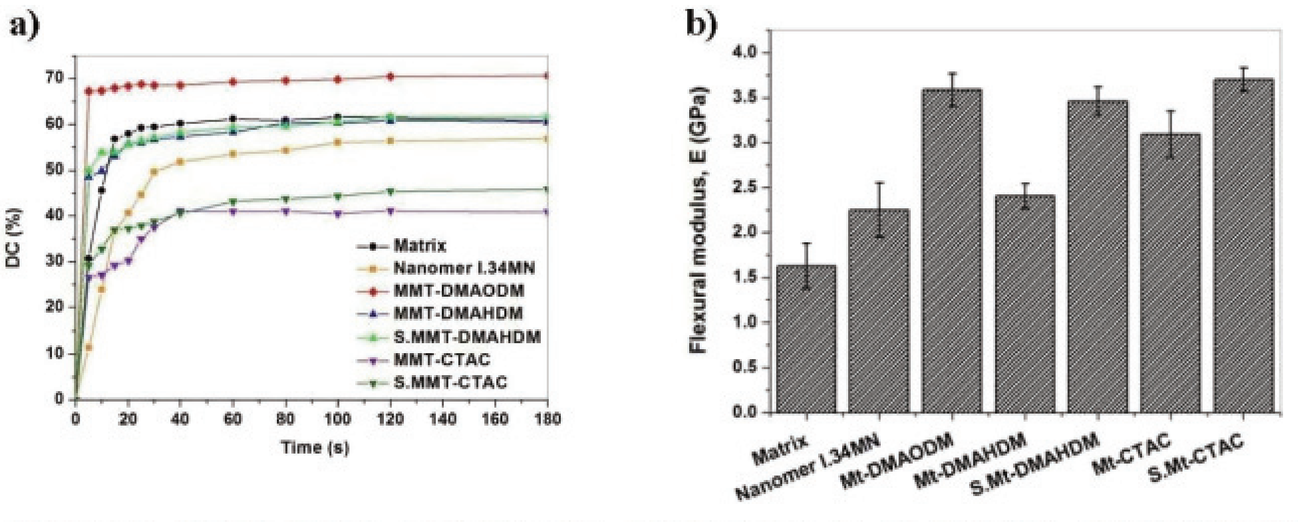

Figure 1. Effect of the different type of nanoclay on a) DC (%) and b) flexural modulus of dental resins.

POSTER 5.21

FUNCTIONALIZED DENDRITIC NANOCARRIERS AS EFFICIENT DRUG DELIVERY SYSTEMS TARGETING MITOCHONDRIA

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Emerging therapeutic approaches focus on the targeted delivery of therapeutic agents to subcellular organelles and, specifically, to mitochondria.[1] Strategies employing the use of drug delivery systems (DDSs) functionalized with mitochondriotropic moieties, such as the alkyl-triphenylphosphonium groups, are becoming increasingly popular as they can be proven to be generic platforms for loading a diversity of therapeutic agents.[2] In our previous works we reported the development of a novel hyperbranched mitochondriotropic nanocarrier and a mitochondrial-doxorubicin formulation with exceptional cytocidal properties, even in nanomolar concentrations.[3,4] In this study, two novel hyperbranched polymer-based nanocarriers were prepared, able to be used as mitochondria-targeting DDSs. Specifically, triphenylphosphonium groups (TPP) were introduced to a hyperbranched polyethyleneimine (PEI) of 5000 molecular weight through two different alkyl spacers, i.e. butyl or decyl. Controlling the hydrophobic assembly of these macromolecules resulted in ~200 nm diameter nanoparticles (PEI-C4-TPP and PEI-C10-TPP). These nanoparticles were loaded with doxorubicin (DOX) affording PEI-C4-TPP-DOX and PEI-C10-TPP-DOX and their cytotoxicity against human prostate adenocarcinoma DU-145 and PC3 cell lines was evaluated using the MTT assay. Their cellular uptake was determined by flow cytometry, while the intracellular localization of DOX was visualized by confocal laser scanning microscopy. It was found that both nanoparticles were subtoxic, while DOX encapsulated in both nanocarriers was internalized in mitochondria, causing a significant viability decrease in both cell lines compared to free DOX. Based on the above results, both TPP-functionalized hyperbranched PEI derivatives can efficiently target mitochondria and deliver DOX, leading to significantly increased efficiency of doxorubicin at extremely low concentrations.

POSTER 5.22

BARIUM TITANATE OR CARBON/POLYDIMETHYLSILOXANE NANO/MICRO-COMPOSITES: DIELECTRIC RESPONSE, FUNCTIONAL BEHAVIOR AND ENERGY STORAGE

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Introduction: The scientific and technological impact of nanostructured materials is well established and appreciated nowadays, because of the improvement in electrical, thermomechanical properties etc. and the resulting potential for numerous applications. One group of smart materials is nanodielectrics, which includes polycrystalline semiconducting or insulating materials, with grain diameter at the nanoscale level and polymer composites incorporating nanoinclusions. The dielectric behaviour of elastomer nanocomposites can be tailored by simply controlling the type, size and amount of the nanofiller. In this work polydimethylsiloxane composites reinforced with (1) microsize barium titanate ($BaTiO_3$), (2) nanosize barium titanate ($BaTiO_3$), (3) graphite nanoplatelets (GNP), (4) carbon black, (5) multiwalled carbon nanotubes (MWCNTs) were fabricated and studied, in terms of the type, size and amount of the filler content.

Methods: Dielectric measurements were performed via Broadband Dielectric Spectroscopy (BDS) in the frequency range from 10^{-1} Hz to 10^{6} Hz. Temperature was varied between 30^{o}C and 200^{o}C at steps of 5^{o}C.
Results: Both the real part of dielectric permittivity and energy storage increase with filler content and temperature and diminishing with frequency.

Conclusions: Dielectric spectra reveal the presence of two relaxation processes arising from the re-orientation of polar side groups of the polymer chains (β-mode) and the interfacial polarization, due to the accumulation of charges at the interfaces between crystalline, amorphous regions and filler.

Acknowledgments: «This research is implemented through IKY scholarships programme and co-financed by the European Union (European Social Fund - ESF) and Greek national funds through the action entitled ”Reinforcement of Postdoctoral Researchers”, in the framework of the Operational Programme ”Human Resources Development Program, Education and Lifelong Learning” of the National Strategic Reference Framework (NSRF) 2014 – 2020».

POSTER 5.23

ELECTROMAGNETIC RESPONSE AND THERMOMECHNICAL PROPERTIES OF MULTIFUNCTIONAL ZnFe2O4 / EPOXY NANODIELECTRICS

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Introduction: Polymer matrix-ceramic particles nanodielectrics especially those who demonstrate ferroelectric and ferromagnetic behavior are considered as novel engineering materials due to their electrical and electronic properties with many potential applications as capacitors, switches, electromagnetic shielding and energy storage devices[1–3]. Ferrites are one of the most important classes of magnetic ceramic materials and are used extensively in electronic devices[4]. $ZnFe_2O_4$ is of particular interest among ferrite spinels because of its transition from paramagnetic(bulk) to antiferromagneti(nanopowder) state[5].

Methods: In this study $ZnFe_2O_4$/epoxy composite nanodielectrics were fabricated and studied. The morphological investigation was conducted by SEM. The dielectric response was examined via BDS and the thermomechanical characterization was investigated via DMA and DSC. Magnetic characterization was conducted by means of a SQUID.

Results and Conclusion: The addition of the nanoparticles improves the dielectric and thermomechanical properties of the nanocomposites. Three relaxations were observed:Interfacial polarization, glass to rubber transition of the polymer matrix and re-orientation of polar side groups. The magnetic measurements confirmed the ferromagnetic nature of the nanocomposites. The magnetization loops shows a clear magnetic hysteresis behaviour with the saturation magnetization value increasing with filler content.

Acknowledgments: This research has been financially supported by the General Secretariat for Research and Technology(GSRT) and the Hellenic Foundation for Research and Innovation(HFRI)(Scholarship Code: 2383).

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POSTER 5.24

INVESTIGATING THE DIELECTRIC RESPONSE OF CARBON BLACK/ EPOXY NANOCOMPOSITES INCORPORATING MAGNETITE NANOPARTICLES

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Carbon-polymer nanocomposites have been widely considered as structural materials because of their remarkable mechanical properties. Their electrical properties can be tuned by controlling the type and amount of carbon nanofiller for applications like electrodes, electromagnetic shielding and conductive adhesives.[1–3] The incorporation of ceramic nanoinclusions in carbon nanocomposites can induce extra functionality like magnetic properties, piezoelectricity etc.[4]

In this study a series of nanocomposites were developed consisting of carbon black and magnetite nanoparticles incorporated into an epoxy resin varying the filler type and concentration. Their dielectric response was investigated by means of Broadband Dielectric Spectroscopy.

Depending on the filler type and concentration, nanocomposites exhibited either insulator to conductor transitions or dielectric relaxation phenomena arising from both the filler and the matrix. Three relaxation modes were recorded and were attributed to interfacial polarization, glass transition and motion of polar side groups. Both polarization and conductivity increase with carbon black content for all temperature and frequency range. The incorporation of low content of magnetite tends to enhance the conductivity and permittivity of the systems in most cases.

Acknowledgements: This research has been financially supported by the General Secretariat for Research and Technology(GSRT) and the Hellenic Foundation for Research and Innovation(HFRI) (Scholarship Code:2327).

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POSTER 5.25

THE USE OF FLY ASH FILLERS IN POLYMER COMPOSITES

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Fly ash is used as reinforcing filler in a variety of polymers (thermosets and thermoplastics: Epoxies, polypropylenes (PP), polyethylenes (PE), Nylons, Acrylo Nitrile Butadiene Styrene (ABS) and many others) to develop new composites with advanced properties [1,2]. In the present work, pristine fly ash and modified with organosilanes of the type $(RO)_3SiCH_2CH_2CH_2NH_2$ that are covalently attached to the surface of the particles are incorporated into the widely used epoxy (DGEBA) resin. The fly ash was produced at the power stations of Kozani region in northern Greece and it is rich in CaO due to the origin of the burned lignite. An epoxy was used as matrix along with a triethilentetramine (TETA) curing agent. Pristine and modified materials as well as the final nanocomposites were characterized by a combination of analytical techniques including SEM, DMA, FT-IR, DSC and XRD. The experimental data indicate that the surface modification of the fly ash particles improve the particle dispersion, change the interphase morphology, the particle-matrix bonding strength and affect the molecular mechanisms responsible for α- and β- relaxations. The results reveal that, fly ash with surface modification led to the substantial improvement to mechanical properties and thermal stability of the composites.

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POSTER 5.26

DEVELOPMENT, CHARACTERIZATION AND FUNCTIONALITY OF EPOXY RESIN- BARIUM ZIRCONATE NANOCOMPOSITES

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Nowadays, ceramic/polymer matrix nanocomposites present interesting mechanical, electrical, magnetic and thermal properties, which could be exploited in various applications. Furthermore, the incorporation of ferroelectric inclusions, in the polymer matrix, induces functional performance to the nanocomposite. In the present study, nanocomposites of epoxy resin and ceramic nanoparticles of $BaZrO_3$ were prepared by mixing process varying the reinforcing phase content. The electrical response of the fabricated composite systems was examined by means of broadband dielectric spectroscopy in a wide temperature and frequency range. The dielectric analysis of nanocomposites revealed the presence of two dielectric relaxations related to the polymeric matrix. The first relaxation is attributed to the transition from the glass to the elastomeric phase of the epoxy resin and is called α- relaxation, while the second one is related to the rearrangement of the lateral polar groups and is called β-relaxation. In addition, the phenomenon of interfacial polarization was observed, due to the presence of inclusions inside the matrix and to the electrical heterogeneity that impart to the composite material. Finally, the ferroelectric and/or anti-ferroelectric $BaZrO_3$ nanoparticles imparts functional performance to the composite system.

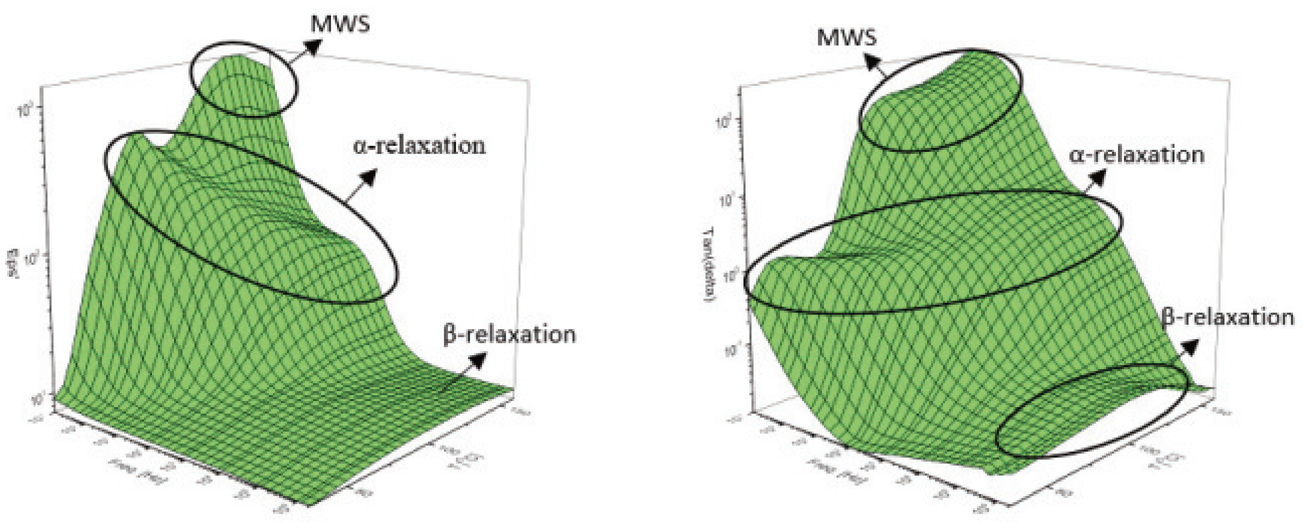

Figure 1. Real part of dielectric permittivity (left) and loss tangent (right) versus frequency and temperature for the nanocomposite with 10 phr $BaZrO_3$.

POSTER 5.27

DIELECTRIC AND MECHANICAL CHARACTERIZATION OF EPOXY RESIN/SILICON CARBIDE NANOCOMPOSITES

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Nanoparticles are widely used as reinfofcing phase in composites since they exhibit larger interfacial volume with the matrix, thus influencing a wide range of the composites' properties. In this study epoxy resin/ silicon carbide nanocomposites were manufactured varying the filler's content as well as the particle size of the silicon carbide nanoparticles.

The specimens were characterised using broadband dielectric spectroscopy, dynamic mechanical analysis as well as scanning electron microscopy. The BDS 1200 dielectric cell was used for the dielectric tests, the 3-point bending clamp configuration for the mechanical tests, and the carl zeiss evo ma 10 apparatus for the morphology characterisation.

SEM proved the fine dispersion of nanoparticles in the polymer matrix, while DMA was used to measure the storage modulus and calculate the Tg of the specimens. BDS revealed information about the nanocomposites' dielectric permittivity, ac conductivity and the relaxation processes occuring in the tested specimens. The activation energy of certain relaxations and the Tv was also calculated, along with the energy density of each specimen.

In conclusion, specimens were successfully manufactured using commercially available materials, tested with different characterisation techniques, and results about their properties were deducted.

POSTER 5.28

FUNCTIONALIZED ZINC PORPHYRINS WITH VARIOUS PERIPHERAL GROUPS FOR INTERFACIAL ELECTRON INJECTION BARRIER CONTROL IN ORGANIC LIGHT EMITTING DIODES

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Introduction: Although OLEDs represent a mature technology they continue to attract wide scientific attention due to their potential to find more applications especially as next generation flat panel lighting sources having the advantages of high brightness, solution processing, low cost and flexibility. The efficiency of OLEDs strongly depends on the balancedcharge injection, transport and recombination of both electrons and holes as well as on the efficient exciton decay and light extraction processes.

Results: Here, we use a simple and effective method to accomplish energy level alignment and thus electron injection barrier control in organic light emitting diodes (OLEDs) with a conventional architecture based on a green emissive co-polymer. In particular, a series of functionalized zinc porphyrinsbearingπ-delocalized triazine spacersfor efficient intramolecular electron transfer and different terminal groups such as glycine moieties in their peripheral substitutes are employed as thin interlayers at the emissive layer/Al (cathode) interface to realize efficient electron injection/transport. The effects of spatial (i.e. assembly) configuration, molecular dipole moment and type of peripheral group termination on the on the optical properties and energy level tuning are investigated by steady state and time-resolved spectroscopy and also by measuring the open-circuit voltages of complete OLED devices and surface work function of Al electrodes modified with the functionalized zinc porphyrins.

Conclusions: The performance of OLEDs is significantly improved upon using the functionalized porphyrin interlayers with the recorded luminance of the devices to reach values an order of magnitude higher than that of the reference diode.

POSTER 5.29

CATALYTIC PYROLYSIS AND DEGRADATION PRODUCTS OF POLYMERS USED IN PACKAGING MATERIALS

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Introduction: Research results on the thermal degradation under inert atmosphere of polymers originating in packaging is presented. Polymers may decompose to their monomers or other secondary value-added compounds that can be reclaimed afterwards.

Methods: A pyrolyzer combined with Gas Chromatographer/Mass Spectrometer (Py-GC/MS) was used in the experiments. A heating program in the GC oven using specific working temperature for pyrolyzer was applied. The chromatograph shows various peaks, corresponding to mass spectra and chemical structures eventually. The enriched MS NIST database helps us out to select the matching mother-molecule.

Results: The polyolefins PE and PP showed simple peak curves for the Evolved Gas Analysis, the decomposition takes place between 400-550 ^{o}C, while HDPE is more heat-endurable than LDPE. As for the halogenated polyolefins, PVC shows two decomposition steps between 300-500 ^{o}C while PTFE, known for its heat-resistance, is affected on higher temperatures. Simple molecules, monomers or oligomers are yiled during pyrolysis. The range of the olefins produced is C8-C38 molecules.

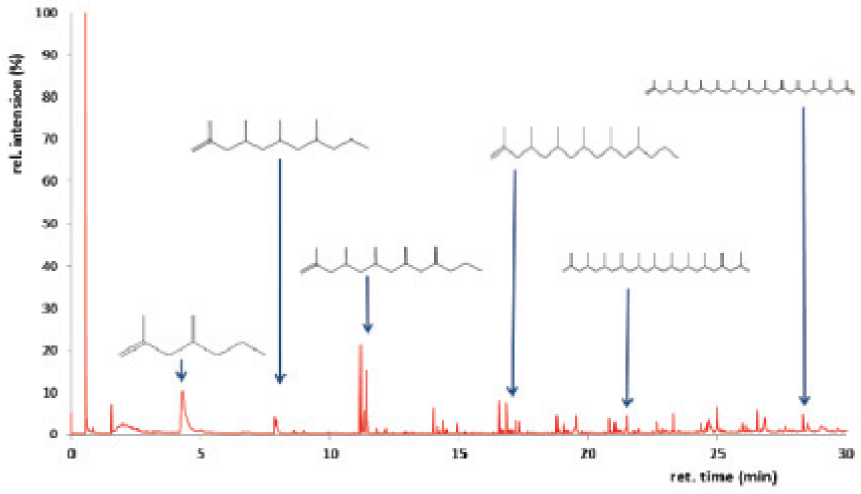

Fig. 1: Chromatogram of PP (isotactic) flash-pyrolyzed at 460 ^{o}C. Chain fragments for selected peaks.

Conclusion: Chromatographic results may be complicated due to the isomers produced during pyrolysis. The polyolefins decompose through a radical process, where depolymerization propagates until hydrogen abstraction occurs.

POSTER 5.30

PYROLYTIC DEGRADATION OF POLYMERS ORIGINATING IN ELECTRIC AND ELECTRONIC EQUIPMENT

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Introduction: Waste management of electronic and electrical equipment has changed over the last decades due to the possibility of converting organic waste into liquid hydrocarbons, gases and carbonaceous residues. Pyrolysis of materials such as ABS, HIPS and PC or their mixtures are the subject of this work.
Methods: The pyrolytic experiments of the samples were executed on a triple assembly of pyrolyzer-Gas Chromatographer/Mass Spectrometer. The database used is "F-Search All in one" Frontier Laboratory Ltd, Japan.
Results: Pyrolysis of ABS results in the production of the styrene monomer, aromatic compounds with phenyl rings and substituted nitriles. The pyrogram of HIPS involves mainly the monomer styrene, dimmer and trimmer, as well as several aromatic compounds with 1, 2 or 3 phenyl rings. As for PC, the monomer, bisphenol A was obtained in large amounts together with some CO and CO_2.

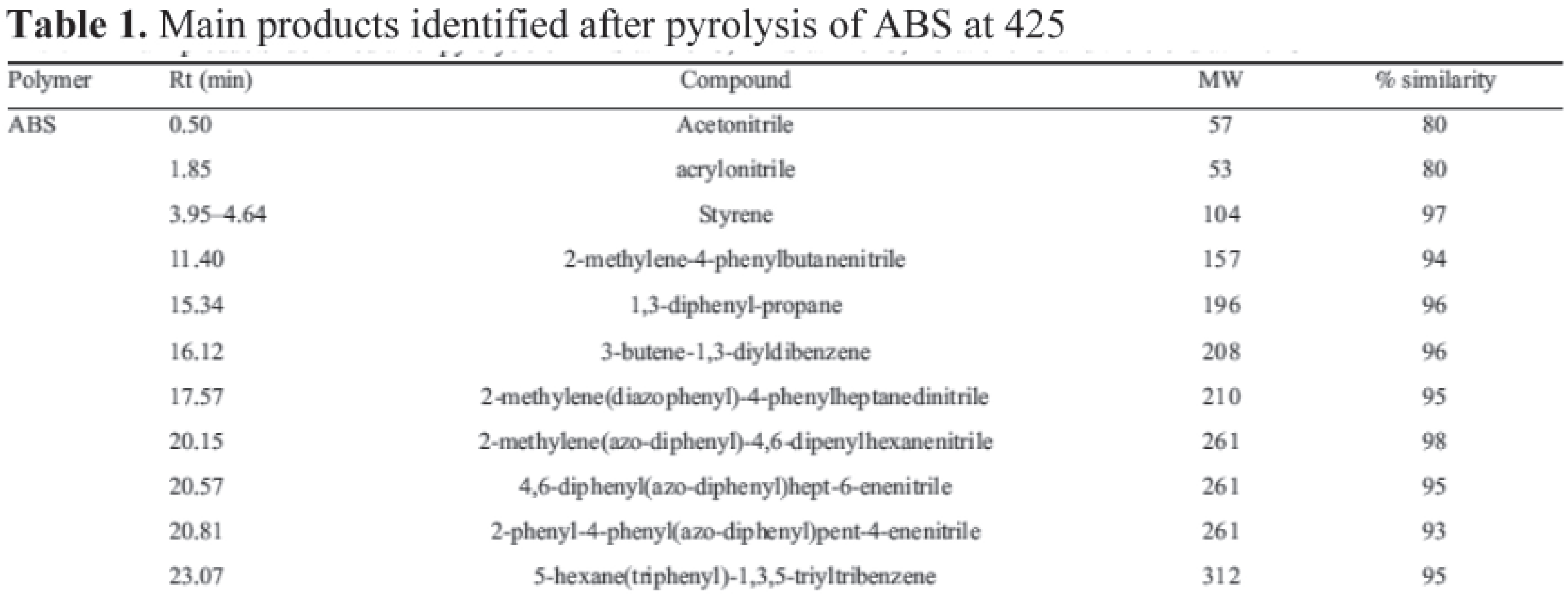

Table 1. Main products identified after pyrolysis of ABS at 425

Polymer	Rt (min)	Compound	MW	% similarity
ABS	0.50	Acetonitrile	57	80
	1.85	acrylonitrile	53	80
	3.95–4.64	Styrene	104	97
	11.40	2-methylene-4-phenylbutanenitrile	157	94
	15.34	1,3-diphenyl-propane	196	96
	16.12	3-butene-1,3-diyldibenzene	208	96
	17.57	2-methylene(diazophenyl)-4-phenylheptanedinitrile	210	95
	20.15	2-methylene(azo-diphenyl)-4,6-dipenylhexanenitrile	261	98
	20.57	4,6-diphenyl(azo-diphenyl)hept-6-enenitrile	261	95
	20.81	2-phenyl-4-phenyl(azo-diphenyl)pent-4-enenitrile	261	93
	23.07	5-hexane(triphenyl)-1,3,5-triyltribenzene	312	95

Table 1. Main products identified after pyrolysis of ABS at 425

Conclusion: Pyrolysis temperature affects the type and number of molecules produced, since higher temperatures cause a stronger fragmentation of the polymeric chain by releasing molecules of lower molecular weight.

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Vouvoudi E, Rousi A, Achilias D. Front. Environ. Sci. Eng. 2017, 11(5): 9

Advances in Polymer Theory and Simulations

PLENARY ORAL

POLYMER FLOW AND POLYMER TOPOLOGY: LINEAR CHAINS, RINGS AND KNOTS FLOW DIFFERENTLY

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Modifications of the topological state of polymers are extremely interesting and relevant operations for a vast domain of scientific inquiry ranging from knot theory and polymer science all the way to materials science and biophysics, where cyclic and knotted DNA plays a key role in biological processes. Recent work has demonstrated that joining the two ends of a linear chain to form a cyclic (ring) polymer has a number of significant consequences in the structural [1,2] and rheological [3] properties of concentrated or semidilute solutions of the same. Accordingly, a number of questions arise regarding the behavior of linear, cyclic and knotted ring polymers under flow: how does the topology of the dissolved polymer affect its orientational resistance, as well as its rotation-, tumbling- or tank-treading motion under Couette flow? What consequences does shear flow have for knot localization along a sheared polymer? Can one make use of the different flow properties of various polymer topologies to build microfluidic devices that act as filters/separators of topologically different polymers? By applying hybrid (MPCD/MD) simulation techniques that take into account the hydrodynamics, we address the questions above for polymers of varying topologies, knotedness and stiffness and we analyze quantitatively the influence of polymer topology on single-polymer properties under flow [4]. Polymer properties under Poiseuille flow will also be analyzed and on this basis concrete suggestions for the construction of topology-separating microfluidic devices will be presented [5].

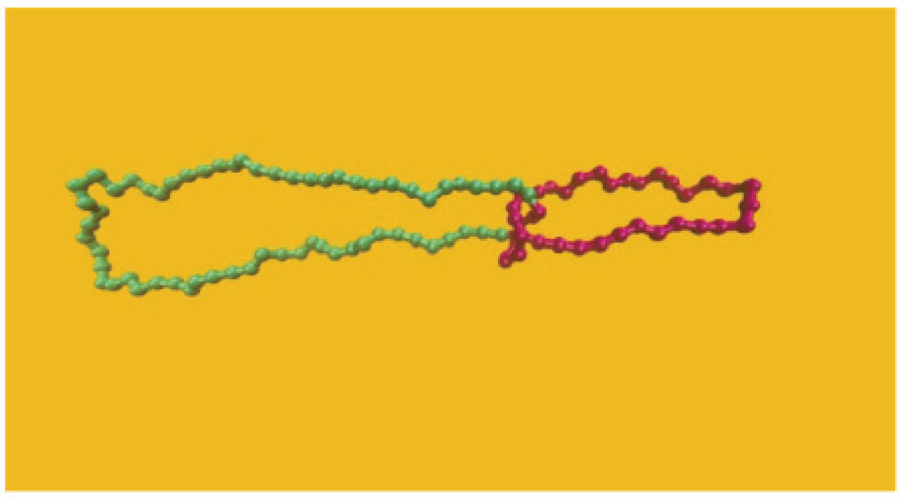

Fig. 1: A knotted ring polymer carrying a 3_1-knot under shear flow. The knotted part is rendered with magenta color.

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INVITED ORAL

MOLECULAR SIMULATIONS OF COMPLEX POLYMERIC NANOSTRUCTURED MATERIALS

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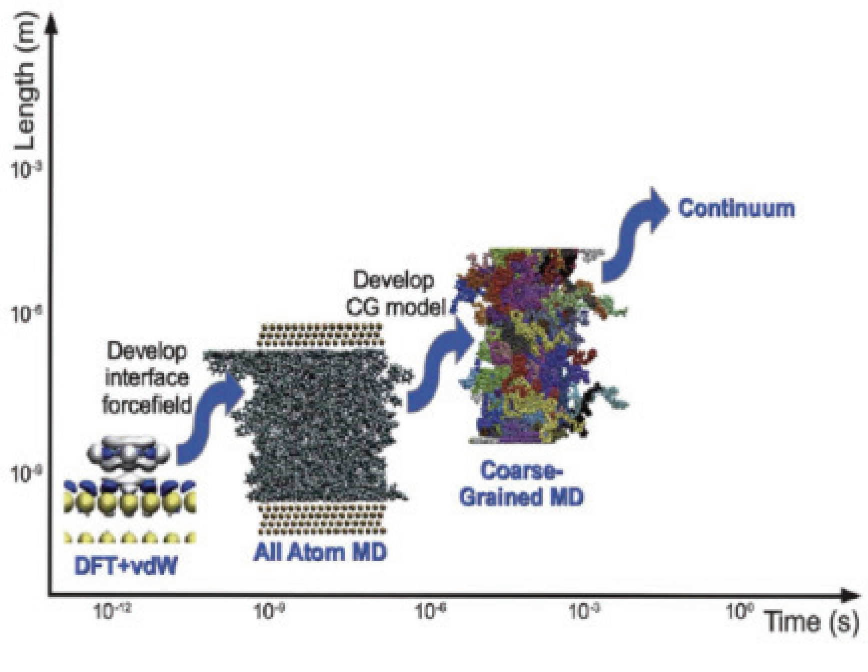
Multi-component polymeric nanostructured systems comprise a material class of growing technological and scientific importance. For example, polymer/particle nanocomposites or polymer/graphene heterosystems, promise diverse applications in surface and nanotechnology, including thin films, nanocomposites, organic photovoltaics or nanotribology. Here, we present a *hierarchical simulation approach* in order to study quantitatively heterogeneous macromolecular nanostructured systems, over a broad range of length and time scales. The proposed scheme involves several simulation methodologies: From *ab-initio* (density functional theory, DFT) calculations of small molecules, up to atomistic *molecular dynamics* (MD) simulations of low molecular weight polymers, and up to *coarse-grained* (CG) simulations of specific polymer/solid interfacial systems. Through the above methodology, results concerning structural, conformational and dynamical properties of various hybrid multi-component systems are presented:
(a) Thin polymer films supported by graphene, under equilibrium and non-equilibrium (crystallization and ultra-fast melting behavior) conditions [1,2].
(b) Polymer nanocomposites with graphene or silica nanoparticles (i.e. PS/Au and PB/Silica) [3], and
(c) Immiscible mikto-arm (PEO/PS) star polymeric nanoparticles [3].
In all cases, the spatial heterogeneities of the hybrid system are analyzed, resolving their effect on the structural and dynamical (Brownian motion) behavior of both polymer chains and the dispersed phase.



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INVITED ORAL

POLYELECTROLYTE/GRAPHENE-BASED NANOCOMPOSITE HYDROGELS: A DETAILED VIEW BY MOLECULAR DYNAMICS SIMULATIONS

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Fully atomistic molecular dynamics simulations are employed to study physical hydrogels formed by poly(acrylic acid) (PAA) and graphene oxide (GO) nanosheets. Effects of GO loading and of the PAA charging state on morphological and dynamic characteristics of the composite systems are examined in detail. Aspects such as the degree of the physical adsorption of the polymeric electrolytes on the GO surface, the motional mechanisms governing local and global polymer dynamics, the distribution of the counterions around the constituents and their mobility, are discussed as well. Such microscopic features are expected to affect drastically macroscopic properties of the hydrogels related to their mechanical and electrical response.

INVITED ORAL

A NOVEL SIMPLE METHOD FOR THE INTEGRAL THERMODYNAMIC CHARACTERIZATION OF POLYMERS AND COMPOSITE MATERIALS

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The thermodynamic behavior of polymers, in pure state or in mixtures, in bulk phases or at interfaces, is primarily dictated by their intermolecular interaction potentials. Advanced potentials are currently available, which often account even for rather peculiar subtleties of polymer behavior. Their use, however, requires skills and experience in molecular dynamics and molecular simulations in general. What seems to be much needed today are efficient sets of molecular descriptors for each polymer, which could substitute to a reasonable degree the interaction potentials and lead to thermodynamic frameworks significantly simpler to understand and use in ordinary desktop calculations. Partial Solvation Parameters (PSP) and the associated thermodynamic framework are recent attempts towards this end. This lecture will review the essential of PSPs, their quantum-chemical roots, the way they may be obtained from experiment, and their capacity to predict the thermodynamic behavior of polymer systems over a broad range of external conditions. The applications will include polymer foaming and tailoring polymer-(co)polymer miscibility windows.

INVITED ORAL

THE SCIENTIFIC ACHIVEMENTS OF PROFESSOR MARIOS KOSMAS

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Professor Kosmas belongs to the third generation of polymer scientists. This generation carried the complex but very accurate theories (Renormalization Group) from the study of the critical phenomena of Electrodynamics to polymers. Second-Generation Theories (two-parameter theory) were unable to describe polymers beyond Theta temperature and produce critical exponents of various conformational properties. Conversely, the continuous grouping of the polymer units from the Renormalization group theory leads to a compact sphere with a specific value of repulsive interaction (excluded volume) corresponding to the good solvent and accurately reproduces the critical exponents. While theoretical physicists rigorously applied the grouping of polymer blocks by working in the complex space, Kosmas followed a different approach. He used real-space perturbation theory as well as the theory of 2 parameters but applied it in the dimension $d = 4\text{-}\varepsilon$ instead of $d = 3$ of the 2-parameter theory and forced the solution to be an exponential function of the Molecular weight. The results are the same as those of the complex approach but the solution is obtained with fewer calculations and is understandable due to the real space by a chemist. Marios's methodology was named **Kosmas model** by Alessandrini and Pesci who used it to study the intrinsic viscosity of linear polymers. He developed the model during his post-doctoral studies at the Universities of Colorado (1978-80 Fixman) and Cambridge in England (1980-81 Edwards) He published using his model approximately 80 original papers in high-impact journals that include monographs or co-authored by his eight PhD students. His work covers a wide range of polymer science. He is the most well-known Greek applied analytical theory on polymers and won the respect and recognition of major field scientists such as De Gennes, Fixman, Edwards, Benoit, Binder, Stockmayer, des Cloizeaux and others.

ORAL

HIERARCHICAL MODELLING AND SIMULATION OF THE VISCOLEASTICITY OF POLYMER MELT NANOCOMPOSITES: NON-EQUILIBRIUM THERMODYNAMICS MODELING COUPLED WITH MOLECULAR SIMULATIONS

Pavlos S. Stephanou,(1),(2) **Dimitrios G. Tsalikis,**(2) **Emmanuel N. Skountzos,**(2) **Vlasis G. Mavrantzas** (2),(3)

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Introduction

Understanding the rheological properties of polymer melt nanocomposites (PNCs) is of paramount importance for the design of new, improved materials for targeted applications. In this work, we present a hierarchical approach to the problem through a methodology that couples nonequilibrium thermodynamics modeling for the formulation of the final transport equations with molecular simulations for the estimation of the parameters appearing in these equations.

Methods

For the derivation of the continuum transport equations we resort to the Hamiltonian formalism of dissipative processes through the use of a generalized bracket involving, in addition to the Lie-Poisson bracket, a dissipation bracket [1]. The final set of governing equations involves a set of differential equations for the mass density, the momentum density, the microstructure and the stress tensor of the polymer nanocomposite melt. For the determination of the parameters appearing in these equations, we resort to equilibrium and nonequilibrium molecular dynamics simulations of a model system with the same chemical structure and composition as the reference experimental sample under study.

Results

We have applied the new approach first to the case of an unentangled polyethylene glycol (PEG) melt filled with silica nanoparticles [2-4]. We will see that the parameterized continuum model provides a very satisfactory description of experimental data [5] for the viscometric functions in steady shear. It also provides a wealth of simulation predictions for the effect of shear on the conformational properties of the nanocomposite melt at several length scales (from the segmental to the level of entire chains).

Conclusions

Our approach seems to capture the key viscoelastic features of several short-molecular weight polymer melts filled with spherical nanoparticles and to provide a self-consistent picture of their conformational and rheological properties. It is currently extended to polymer melt nanocomposites consisting of highly entangled polymer melts [6].

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ORAL

FLOW BEHAVIOR OF PP-POLYMER NANOCOMPOSITES IN INJECTION MOLDING HYPERBOLICAL DIES

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NTUA Campus, Zografou, Greece

Nanocomposites based on layered silicates offer a remarkable potential in improving mechanical properties with filler loadings lower than 5%. For such polymer nanocomposites it is important to improve intercalation and exfoliation of the silicate layers by finding the right balance between these effects. Previous works showed that intercalation and exfoliation can be influenced by the use of an additional, extensional flow which can be generated by hyperbolical dies used in the injection molding process. Since such hyperbolical dies account for high shear rates, additional pressure drop and viscous dissipation, it is of high practical relevance to correctly predict the injection pressure needed. Besides conical geometries, hyperbolical die geometries are of importance due to their uniform elongational rate.

Using hyperbolical dies having different diameters, *D*, and length-to-diameter *L/D* ratios, a full rheological characterization has been carried out for a polypropylene-filled nanocomposite, and the experimental data have been fitted both with a viscous model (Cross) and a viscoelastic one (the Kaye - Bernstein, Kearsley, Zapas / Papanastasiou, Scriven, Macosko or K-BKZ/PSM model). Four injection molding dies have been also used to reach apparent shear rates up to 500,000 s^{-1}. Particular emphasis has been given on the pressure-dependence of viscosity. It was found that only the viscoelastic simulations were capable of reproducing the experimental data well, while any viscous modeling always underestimates the pressures, especially at the higher apparent shear rates and *L/D* ratios.

ORAL

STRUCTURE AND DYNAMICS OF HYBRID POLYMER/GOLD AND CORE-SHELL NANOPARTICLE SYSTEMS THROUGH MOLECULAR DYNAMICS SIMULATIONS

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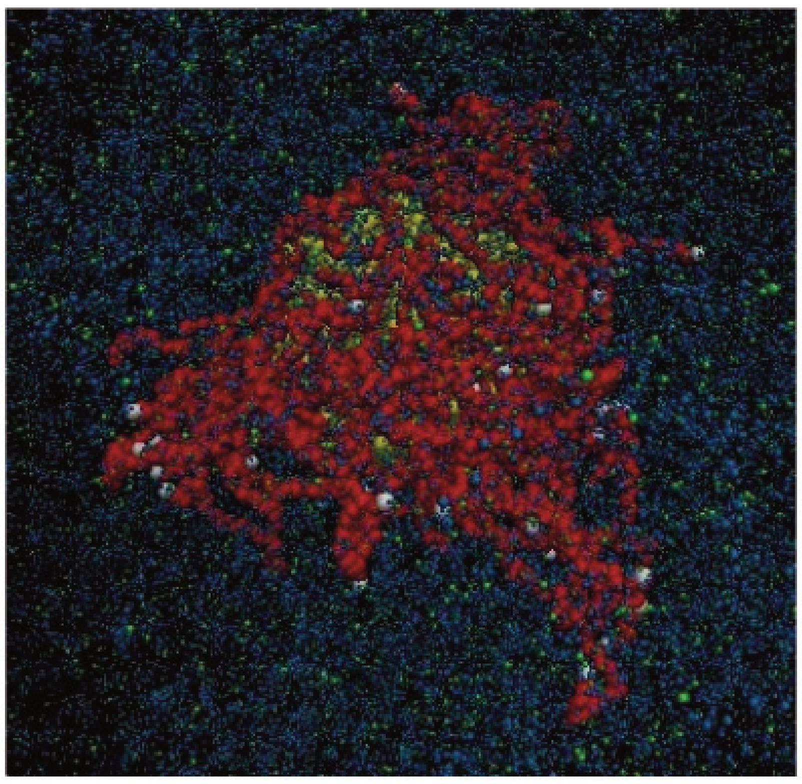
The study of Polymeric Complex Materials is an intense research area due to the broad spectrum of systems, applications, length and time scales. On Hybrid Polymer/Solid systems, nanocomposites are used to modify the properties of the entire system, like thermodynamics, mechanical properties, dynamical behavior and others.

The aim of the present work is to predict the properties of hybrid polymer/gold systems at the molecular level through molecular simulations and compared to the behavior of the bulk polymer system. Here, we study polyethylene (PE)/gold nanoparticle (Au NP) nanostructured systems. In more detail, the structural and dynamical properties of polyethylene chains around Au NPs and functionalized (core/shell) Au NPs are investigated using atomistic molecular dynamics (MD) simulations.

From our analysis we found that the polymeric anchors change the gold NP behavior/properties and especially the density profile. In addition, gold nanoparticle attracts polymers at distances close to it and all systems attain bulk value in all properties away from the gold NP. Moreover, the backbone vector of PE is oriented parallel to the gold surface. Furthermore, dynamics become slower close to the Au NP and terminal relaxation time decreases with the distance from the Au NP.



ORAL

ATOMISTIC SIMULATIONS OF PERFECT POLYETHYLENE NETWORKS: CHARACTERISTIC RELAXATION TIMES, CROSSLINK FLUCTUATIONS, UNIAXIAL, EQUIBIAXIAL AND MULTIAXIAL DEFORMATIONS, FINITE EXTENSIBILITY, AND STRAIN ENERGY DENSITY FUNCTION

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Three perfect polyethylene (PE) networks have been simulated by employing the united-atom TraPPE force field. The dynamical and mechanical properties of the networks have been characterized by estimating the characteristic relaxation times of chains and crosslinks, the density, the bulk and Young's moduli, the Poisson's ratio, the entanglement density, the tube diameter, etc., finding very good agreement with corresponding experimental estimates and previous simulations of PE melts. The networks have been subjected to uniaxial, equibiaxial, pure shear and sequential biaxial deformations. The generated stress-strain curves have been compared with the Neo-Hookean, Mooney-Rivlin and a variant of Gent's model which is suitable for the description of strain hardening and the estimation of finite chain extensibility (FCE). From the biaxial deformations we have been able to extract the strain energy density function.

The shortest and longest relaxation times of the networks were validated against individual strain-rate uniaxial deformations. The dynamics are typical of Rouse motion within a tube. We also identify two characteristic regimes of crosslink fluctuations. The second one is relevant to early tube dilation through diving modes of branch point motion along the tubes of each arm in star polymer melts. Regarding the stress-strain response we find that finite extensibility depends on the deformation mode. The reduced stress-strain curves of the networks overlap in considerable range of extensions when plotted against suitable reductions of the extensions by FCE parameters. The strain energy density function of PE shows similar characteristics with those obtained for NR, BR and SBR rubbers.

ORAL

CONFORMATION AND DYNAMICS OF RING POLYMERS IN DILUTE SOLUTIONS OF LINEAR MATRICES: RESULTS FROM A SYSTEMATIC MOLECULAR DYNAMICS SIMULATION STUDY AND COMPARISON WITH EXPERIMENTAL DATA

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Over the last decades ring polymers have received significant attention in the scientific community mostly because of the absence of free ends that bring them outside the conceptual framework of the reptation theory and because of the big interest in the properties of circular bio-macromolecules which play a prominent role in complex biological processes. Despite recent progress in the field, several outstanding issues remain still open such as that of the dynamics of ring polymers in linear matrices at small concentrations.

We address this issue here by means of molecular dynamics simulations. We have considered melt systems consisting of a small number of ring poly(ethylene oxide) (PEO) probes of a given size immersed in a host matrix of linear PEO chains, and we have calculated their relaxation and diffusive properties.

Consistent with recent experimental studies,[1] we find that unentangled rings in short unentangled linear chain matrices become significantly swollen and exhibit faster diffusive motion than in their pure melt. In striking contrast, in matrices of entangled chains, their dynamics is drastically altered with their diffusive motion being practically independent of the molecular weight of the host linear chains. Marginally entangled rings, on the other hand, display an intermediate behavior with a weak dependence on host size. An additional geometric analysis [2] revealed strong threading of all ring probes by the linear host chains.

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POSTER 6.1

A SYSTEMS APPROACH FOR NOSE-TO-BRAIN DELIVERY

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Hydrogels are highly water swollen, three-dimensional networks of cross-linked natural or synthetic polymer chains with applications in biomedical engineering, biotechnology, pharmaceutics, food packaging, etc. They can be easily formed under mild conditions, tuned with respect to their rheological/mechanical properties, degree of swelling, degradation, etc. Hyaluronic acid (HA) is a natural, biocompatible, biodegradable polysaccharide, enzymatically degraded by hyaluronidase and is completely resorbable through multiple metabolic pathways. HA based hydrogels can be formed by chemical modification of HA and subsequent crosslinking. Due to the fact that they are biocompatible and their properties can be effectively tuned, HA based hydrogels are considered very versatile materials for various clinical applications such as intra-articular viscosupplements, skin fillers, wound healing, drug delivery, etc. In the open literature there is a limited number of experimental/theoretical studies describing the crosslinking kinetics of formyl hyaluronate (HA-Ox) in the presence of a diamine crosslinker. A comprehensive series of experiments have been carried showing the effects of MW of formyl hyaluronate (HA-Ox), degree of substitution, temperature, pH and crosslinker concentration (O,O′-1,3-Propanediylbishydroxylamine dihydrochloride, POA) on the gelation kinetics/time and viscoelastic properties of the hydrogel matrix. The developed models can successfully predict the crosslinking kinetics, hydrogel swelling and rheological properties of HA based hydrogels. The effects of molecular weight of HA, cross-linker concentration, pH and degree of substitution on the gelation onset, degree of swelling, and storage modulus are assessed both experimentally and theoretically.

POSTER 6.2

FROM MOLECULAR TO PLANT SCALE COMPUTER AIDED DESIGN, MODELLING AND CONTROL OF MACROMOLECULAR ARCHITECTURE OF SYNTHETIC POLYMERS

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A major objective of polymerization process modeling is to quantify the effects of kinetic mechanism, physical transport phenomena (e.g., mass and heat transfer), thermodynamic phase-equilibrium, non-ideal mixing phenomena, residence time distribution, reactor configuration and operating conditions on 'polymer quality'. The last term includes all the polymer microstrucre properties (e.g., molecular weight distribution (MWD), copolymer composition distribution (CCD), sequence length distribution (SLD), long and short chain branching (LCB, SCB) distributions, etc.), as well as the morphological properties of the product. Moreover, it is of paramount importance the prediction of polymer end-use properties (i.e., thermal, mechanical, rheological, chemical, etc. properties) in terms of the polymer chain microstructure.

Thus, control of the polymer chain microstructure in a polymerization process is of profound interest. This presupposes a thorough knowledge of the polymerization kinetics, accurate quantitative descriptions of all thermodynamic, mixing and transport phenomena in a polymerization process and the availability of detailed mathematical models to quantify the effects of process operating conditions (i.e., temperature, monomer to comonomer molar ratio, initiator concentration, etc.) on the polymer molecular properties. Thus, to simulate the dynamic operation of complex polymerization plants, one needs to develop mathematical models, at different time and length scales, accounting for the physical and chemical phenomena taking place in a polymerization process. The present lecture presents a comprehensive, multi-scale approach for modeling the operation of lab-, pilot- and industrial-scale high- and low-pressure olefin polymerization processes for prediction of molecular and rheological polymer properties of produced polyolefins in multi-reactor configurations.

POSTER 6.3

CONFORMATIONAL, DYNAMIC, AND PERMEABILITY PROPERTIES OF ATACTIC POLY(METHYL METHACRYLATE) - CARBON NANOTUBE (PMMA-CNT) NANOCOMPOSITES FROM MOLECULAR SIMULATIONS

Panagiotis Mermigkis[1], Emmanuel Skountzos[2], Vlasis Mavrantzas[2]
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Understanding the packing properties of polymer chains around carbon nanotubes (CNTs) is prerequisite for the design of new polymer-based membranes with controlled permeability properties to small molecules.[1] In this work, Molecular Dynamics (MD) simulations are used to study model nanocomposites consisting of atactic poly(methyl methacrylate) (aPMMA) chains and randomly dispersed CNTs, at different concentrations and of different diameters. We are interested in the conformational and dynamic properties of the aPMMA chains in the vicinity of CNTs and in the permeability properties of the nanocomposite.

We find that local polymer density is significantly enhanced laterally nearby the CNTs due to strong attractive forces between the CNT carbons and aPMMA chains. Analyzing density profiles in the direction normal to the CNT mouths revealed significant aPMMA chain penetration inside CNTs even for small CNT diameters. For larger CNT diameters, aPMMA chains could fully penetrate CNTs. On the other hand, we observed no appreciable changes in the size of aPMMA chains due to the presence of CNTs. Additional calculations of the glass transition temperature (T_g) of the studied CNT-aPMMA nanocomposites showed only a minor increase in comparison to the pure aPMMA matrix.

We have also carried out a geometric analysis of free volume in the nanocomposite using Delaunay tessellation to calculate free volume distribution and cluster connectivity. In a next step, this will allow us to study the diffusive behavior of small molecules in the nanocomposite using transition state theory (TST).

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POSTER 6.4

POLYELECTROLYTE MICELLES IN SALT -FREE SOLUTIONS: MICELLE SIZE AND ELECTROSTATIC POTENTIAL

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The structural and electrical characteristics of polyelectrolyte micelles formed by diblock copolymers with one charged blockAand one solvophobic block B are studied by means of molecular dynamics simulations with Langevin thermostat. In particular, micelles formed by A_5B_{30}, $A_{10}B_{30}$ and $A_{20}B_{30}$ with varying ratio of charged A units α=1, 0.4, 0.2 at different Bjerrum lengthsl_B=1σ nd 0.1σ were studied using the Primitive model. We found that for partially charged short A blocks the micelle mass distribution function with respect to the aggregation number N agreement with theoretical and experimental findings[12-15]. The zeta potential is not a monotonic function of the length of the charged block N_A. More complex is the behaviors of zeta potential with respect to the ratio of the charged A unitsα. For micelles formed by A_5B_{30} and $A_{10}B_{30}$ copolymers zeta potential decreases as the ratio α decreases while for $A_{20}B_{30}$copolymers the variation is not monotonic. It is verified that if the ratio between the percentages of the confined counterions is less than 1.11, then the zeta potential increases as the length of charged block increases. For values of the ratio greater than 1.11 the trend is reversed and zeta potential decreases as N_A increases.

Polymers in Industry

ORAL

THE ROLE OF POLYMERS ON THE DEVELOPMENT OF ECO-FRIENDLY HOUSEHOLD PRODUCTS

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Laurent Heux[4], Jean-Francois Berret[1]
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Nowadays there is a growing environmental concern about the household and personal care products due to their high content of surfactants derived by palm oil. Fabric softeners are formulations that contain ~10 wt. % double tailed surfactants primarily synthesized by palm oil chemical treatment. Here we propose the replacement of 50 % surfactant with natural polymers in particular cationic and hydroxyl propyl guar, without detrimental effects on their performance.

The surfactants in these formulations were found to be assembled into large distributed (0.1 – 1 µm) vesicles (Fig.1 a). The effect of the polymers on the formulation properties was investigated by several physicochemical techniques. The reduction of surfactant is compensated by the guars as far as the rheological properties are concerned. In terms of performance, the role of the polymers and its chemical structure on the deposition of the vesicles, either on cellulose nanocrystals used as a model of cotton or on cotton fabrics was studied. Deposition studies such as scanning electron microscopy (Fig. 1b) and quartz crystal microbalance (QCM) indicate that guars enhance the surfactant deposition on cotton. This approach can thus be generalized to several formulations making polysaccharides a remarkable candidate for the development of eco-friendly household and personal care products.

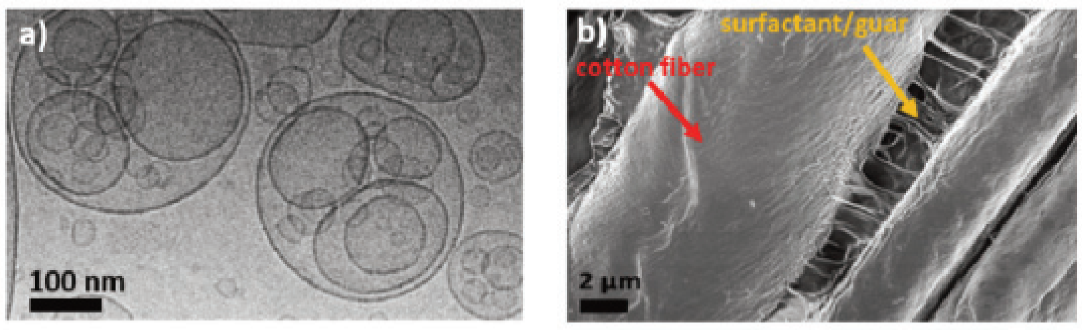

Figure 1: a) cryogenic transmission electron microscopy of double-tailed surfactant vesicles and b) scanning electron microscopy image of cotton fibers coated with surfactant/polysaccharide film

POSTER 7.1

POLYPROPYLENE/MAGNESIUM HYDROXIDE COMPOSITES: SYNTHESIS, CHARACTERIZATION AND THERMAL STABILITY PERFORMANCE

Maria Baikousi[1], Konstantinos C. Vasilopoulos[1], Georgios Georgiadis[2], Christos Karageorgiou[2], Stylianos Kakoulidis[2], Michael A. Karakassides[1]
[1] Department Of Materials Science And Engineering, University Of Ioannina, Ioannina, Greece
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Introduction: Polypropylene (PP) is widely used in diverse applications including packaging, plastic parts and reusable containers. Although PP shows high resistant to a wide range of solvents, PP-based products suffer from low resistance to flammability and tend to thermally decompose when exposed to ultraviolet radiation, at high temperatures or in oxygen-rich environment. During the last decade the introduction of nanoadditives into organic polymers resulted to competitive products with improved critical properties. In our study, $Mg(OH)_2$ particles have been developed and evaluated towards increasing PP resistance to thermal degradation.

Methods: $Mg(OH)_2$ particles with different sizes were synthesized by following a well-established method involving precipitation. Additional, organo-modified $Mg(OH)_2$ particles were synthesized, by adopting the same methodology in presence of coupling agents in order to improve compatibility with PP. $Mg(OH)_2$ nano-additives were incorporated within the PP matrix by a solution-precipitation approach.

Results: X-ray diffraction, infrared spectroscopy, thermal analysis and electronic microscopies were used to study the structure, morphology and thermal properties of $Mg(OH)_2$ particles. Various sizes (ranging from ~50 nm up to 2 μm) of pristine and surface functionalized $Mg(OH)_2$ ere obtained depending on the nature of metal salt. The presence of hydrophobic coupling agents leads to smaller particle sizes ~50% and the resulting PP/modified $Mg(OH)_2$ nanocomposites showed improved combustion resistance.

Conclusions: $Mg(OH)_2$ particles in different sizes, were synthesized by a simple scalable method. Compared with unmodified $Mg(OH)_2$particles, the introduction of organically modified $Mg(OH)_2$ ispersion within the polymer matrix.

POSTER 7.2

ANTIFOULING ENCAPSULATION SYSTEMS FOR MARINE COATING APPLICATIONS

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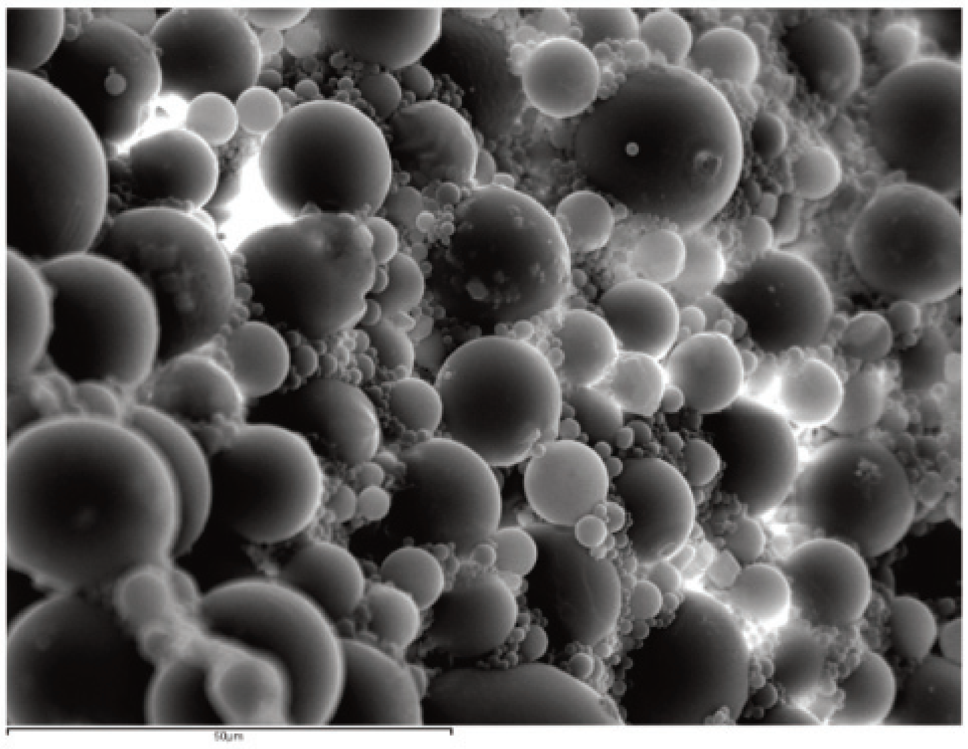
Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zographou Campus, Athens, 157 80, Greece

Introduction: Biofouling of water-immersed surfaces has severe environmental and economic impact especially to the shipping industry. Antifouling coatings are commonly utilized to prevent the growth of fouling organisms and usually contain inorganic components and organic booster biocides. However, poor control over the biocide release rate and paint degradation are important drawbacks. Biocide encapsulation could offer a promising solution to these problems.

Methods: Emulsification-solvent evaporation technique was used to achieve encapsulation of the biocide Zinc Pyrithione (ZPT) into Poly(methyl methacrylate) (PMMA) microcapsules, at a loading ratio of 10,9%. Characterization mainly involved size and homogeneity, thermal properties, and encapsulation efficiency.

Results: Loaded and blank PMMA microparticles (Figure 1) were prepared by emulsification-solvent evaporation technique indicating successful entrapment of ZPT with a process yield more than 70 %. Microparticles size ranged between 4 and 120 µm, while PMMA molecular weight and the ratio of the aqueous:organic phases were found to be of great importance for microparticles characteristics.dation profile of the physical mixtures (ZPT+PMMA) and the loaded microparticles proved to be a tool to monitor the efficiency of the encapsulation process. Preliminary release experiments indicated a controlled release profile.

Conclusions: Encapsulation of Zinc Pyrithione was achieved in PMMA microcapsules. Polymeric carrier properties and emulsification technique parameters had an important impact on particles characteristics.



POSTER 7.3

IGNITABILITY OF PPR PIPES FOR FIRE SPRINKLER SYSTEMS USING AN INSTRUMENTED UL-94 TEST

Georgios Maliaris[1], Ilias Sarafis[2]
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The scope of this work is to find the UL-94 ranking of different formulations with PPR as base polymer combined with four different fire–retardants. Also,the impact of the additives on the mechanical behavior was also determined through the conduction of tensile tests. The additives used were halogen 20%,halogen–free intumescent 20%, antimonium 20% and halogen–free intumescent 40%.

Six bar - shaped samples were harvested, for every formulation, from pipes extruded by Interplast SA,Greece. Three of them were used for the conduction of UL-94 test. With respect to the original UL-94 test,four thermocouples were used, with the lowest one positioned 5mm above the free end of the sample. The tensile tests (INSTRON 8801 UTM) were conducted with the rest three samples.

The sample with the 4th formulation had the best behavior during the conduction of UL-94 test. It did not ignite nor at the first nor at the second ignition, it melt-dripped as a non-flaming drop,leading to a UL-94 V0-ranking. The other specimens either are not classified due to complete burnout or get a V2-ranking. The results from the tensile tests revealed that the sample with the 4th formulation had the largest UTS (21MPa) and young modulus (~660MPa).

Considering the experimental results,the formulation with PPR+40% halogen–free intumescent is the best candidate for the production of pipes for fire sprinkler systems.

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POSTER 7.4

POLY(UREA-FORMALDEHYDE) MICROCAPSULES FOR SELF-HEALING COATINGS

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Introduction: Self-healing systems is a next-generation technology that offers autonomous crack repairs and increases the coating service lifetime. Microcapsules containing "healants" and in general microencapsulation technology can be used in that perspective and exhibit significant promise for advanced materials. In this study, the aim was the preparation of urea-formaldehyde microcapsules containing an epoxy resin as core material by in situ polymerization in order to use them in self-healing protective coatings.

Methods: Both single- and two-step processes were used for microcapsules preparation, utilizing either high speed homogenizing or mechanical agitation.1-Butyl glycidyl ether (BGE) was used as diluent for the epoxy resin. Microcapsules were characterized in terms of morphology, mean size, encapsulation efficiency, and thermal properties. Storage stability of microcapsules in different time periods was also evaluated.

Results: The main difference between single- and two-step process was the production of a prepolymer of urea-formaldehyde before the encapsulation of the epoxy resin in the second step. Single-step process was proved more efficient resulting in microcapsules with rough surface, mean size below 130 μm, mass yield above 50% and encapsulation efficiency in the range of 55-72%. Storage stability tests showed that encapsulation efficiency was decreased during the first two weeks due to epoxy release reaching the value of 30% after four weeks.

Conclusions: The study focuses on the synthesis of poly(urea-formaldehyde) microcapsules containing an epoxy resin. A one-step process using an epoxy diluent and high-speed homogenization was found as the most promising route for the preparation of the pertinent self-healing systems.

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