Polymers 2018: Design, Function and Application

Faculty of Biology
University of Barcelona
Spain
21 – 23 March 2018

Conference Chairs

Alexander Böker
Frank Wiesbrock

Organised by

Conference Secretariat

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Lynn Huang
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Sarai Rodríguez
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#Polymers2018

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Polymers 2018: Design, Function and Application
21 – 23 March 2018, Barcelona, Spain

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Wednesday 21 March 2018: 14:30 - 17:30 / Welcome Cocktail & Poster Session 17:30

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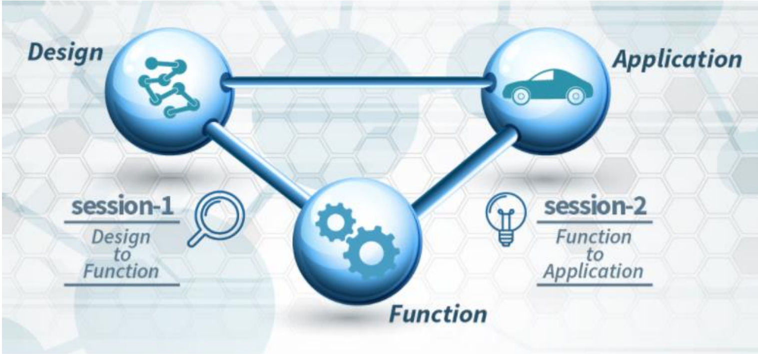
Polymers (ISSN 2073-4360; CODEN: POLYCK) is an international open access journal of polymer science published monthly online by MDPI. *Polymers* provides an interdisciplinary forum for publishing papers which advance the fields of (i) polymerization methods, (ii) theory, simulation, and modeling, (iii) understanding of new physical phenomena, (iv) advances in characterization techniques, and (v) harnessing of self-assembly and biological strategies for producing complex multifunctional structures.

Among other databases, *Polymers* is indexed by the Science Citation Index Expanded (Web of Science), Scopus, Ei Compendex, CAS, Polymer Library, EBSCOhost and Current Contents - Physical, Chemical & Earth Sciences.

Journal Webpage: http://www.mdpi.com/journal/polymers
Impact factor: 3.364 (2016); 5-Year Impact Factor: 4.330 (2016)

Conference Programme



Wednesday 21 March

14:30	Check-in
15:00 – 16:00	Meet the Editors Session
16:00 – 17:30	Young Investigator Award (YIA) Session
	Bernhard Schmidt "Novel Self-Assemblies via Double Hydrophilic Block Copolymers in Aqueous Solution"
	Haritz Sardon "New Trends in Organocatalyzed Poly and Depolymerizations: From Commodity Polymers to Plastic Recycling"
	Joseph Patterson "Liquid Phase Transmission Electron Microscopy of Block Copolymer Assemblies"
	Lei Fang "Integrating Molecular Rigidity and Soft Matter Characters in Ladder Polymers"
17:30 – 19:00	Welcome Cocktail and Poster Session (All Numbers)

Thursday 22 March

Session 1 – Design to Function
Chair: Frank Wiesbrock

08:30 – 08:45	Opening Ceremony
08:45 – 09:25	**Ulrich S. Schubert** "New Battery Systems Based on Polymers as Active Materials"
09:25 – 09:40	**Seema Agarwal** "Non-Ionic Polymers and Gels with UCST-Type Transitions and Thermophilicity in Water"
09:40 – 10:20	**Josef R. Wünsch** "High Performance Materials for Mobility"
10:20 – 10:35	**Dirk Kuckling** "Light-triggered Degradation in Aliphatic Poly(carbonate)s via Intramolecular Cyclization"
10:35 – 11:05	**Coffee Break and Poster Session (Even Numbers)**

Session 1 – Design to Function
Chair: Dirk Kuckling

11:05 – 11:20	**Cesar Petzhold** "Synthesis and Characterization of Hydrophobically Modified Polyacrylamide Having Oligo(Lactic Acid) as Hydrophobic Macromonomer"
11:20 – 12:00	**Klaus Müllen** "A Polymer Chemistry of Graphenes and Graphene Nanoribbons"
12:00 – 12:15	**Patxi Garra** "Unprecedented Photopolymerization of Very Thick Films and Access to Composites: Low Optical Densities vs. Latent Species Strategies"
12:15 – 12:30	**Svetlana Santer** "Light Responsive Objects: From Active Manipulation to Self-Propulsion of Small Particles at Solid Liquid Interfaces"
12:30 – 14:00	**Lunch**

Session 1 – Design to Function

Chair: Svetlana Santer

14:00 – 14:40	**Richard Hoogenboom** "From the Chemistry of Poly(2-oxazoline)s to their Use as Biomaterials"
14:40 – 14:55	**Philipp Marx** "Influence of Surface Interactions on the Dielectric Properties in Poly(2-Oxazoline)-Co-Polyester Nanocomposites"
14:55 – 15:35	**Yao Lin** "Revisiting the Helix-Coil Transition and Helical Chain Growth of Polypeptides"
15:35 – 16:05	**Coffee Break and Poster Session (Even Numbers)**

Session 1 – Design to Function

Chair: Richard Hoogenboom

16:05 – 16:20	**Niels ten Brummelhuis** "Controlling Monomer Sequence Using (Supramolecular) Cyclopolymerization"
16:20 – 17:00	**Helmut Schlaad** "Polymers from Amino Acids"
17:00 – 17:15	**Yeseren Saylan** "Molecularly Imprinted Bacterial Cellulose Nanofibers for Selective Recognition of Proteins"
17:15 – 17:30	**Stefan Reinicke** "New Immobilization Protocols for the Embedding of Enzymes in Ultrathin Polymeric Films"
17:30 – 17:45	**Ian Teasdale** "Design of Inorganic Polymers with Stimuli Responsive Cleavage and/or Degradation in Biological Environments"
17:45 – 18:00	**Sarah Glaß** "Poly(ethylene glycol) Diacrylate Hydrogels Used as Carriers for Photodynamic Therapy Photosensitizers"
18:00	**Conference Group Photograph**

Friday 23 March

Session 2 – Function to Application
Chair: Alexander Böker

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09:10 – 09:25	**Harald Brünig** "Advances and Challenges in Poly(Lactic Acid) Fiber Design for Biomedical Applications"
09:25 – 10:05	**Andreas Greiner** "New Biobased Polycarbonates as Functional Materials"
10:05 – 10:20	**Dániel Vadas** "Application of Melt-Blown Poly(Lactic Acid) Filaments in Self-Reinforced Composites"
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Session 2 – Function to Application
Chair: Greg Tew

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11:20 – 11:35	**Christophe Tribet** "Mixed Polymer Adlayers Allowing Remote Control of Cell Adhesion and Polarization via Click, Temperature, or Redox Triggers"
11:35 – 12:15	**Roy Shenhar** "Nano-Patterned Polyelectrolyte Multilayers: A Non-Lithographic Approach"
12:15 – 12:30	**Eleanor Dougherty** "Radial Dependence of Film Formation During the Spin-Coating of an Immiscible Polymer Blend"
12:30 – 14:00	**Lunch**

Session 2 – Function to Application

Chair: Roy Shanhar

14:00 – 14:40	**Katja Loos** "Enzymatic Polymerizations – Novel Ways to (New) Polymer Systems"
14:40 – 14:55	**Felix Plamper** "Electrochemically-Active Microgel Systems"
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15:10 – 15:25	**Tino Töpper** "Electrospraying of Nanometer-Sized Droplets for Sub-Micrometer-Thin Dielectric Elastomer Transducers"
15:25 – 15:40	**Teresa Poerio** "Sustainable Preparation of PVDF-based Membranes with Tailored Properties"
15:40 – 16:10	**Coffee Break and Poster Session (Odd Numbers)**

Session 2 – Function to Application

Chair: Katja Loos

16:10 – 16:50	**Greg Tew** "Building Simple Mimics of Natural Proteins Provides New Opportunities from T-Cell Delivery to Novel Amphiphilic Networks"
16:50 – 17:05	**Filippo Rossi** "Three-Dimensional Biomimetic Hydrogel to Deliver Factors Secreted by Human Mesenchymal Stem Cells in Spinal Cord Injury"
17:05 – 17:20	**Robert Luxenhofer** "Ultra-high Loaded Polymer Micelles for Drug Delivery"
17:20 – 17:35	**Pavel Semenyuk** "Thermoresponsive Polymers Exhibit Chaperone-like Activity and Recognize Unfolded State of the Protein"
17:35 – 17:50	**Ulrich Glebe** "Mimicking Natural Membranes Utilizing Transmembrane Protein-polymer Conjugates"
17:50	**Closing Remarks and Awards Ceremony**

Welcome Message by Alexander Böker and Frank Wiesbrock

Dear colleagues, friends, and researchers,

With great pleasure we welcome you to our first international conference 'Polymers: Design, Function and Application', organized by the MDPI open-access journal *Polymers*.
We are overwhelmed by the great response our call for papers received in the polymer community and are extremely happy to present an exciting mix of talks and posters from both, academia as well as industry. We would like to thank you, the researchers, for attending this conference and for sharing your knowledge and expertise.

The conference will highlight recent developments at the interface of 'design & function' and 'function & application' of polymers and polymer-based materials. With its focus on function- and application-driven polymer research, the conference aims to address the development and testing of the next generation of polymeric materials with previously unrivaled properties for advanced applications. In order to stimulate research activities in these fields, ample time for discussions and networking has been reserved in the agenda.

We believe that this conference will serve as an inspiring platform for scientific discussions and networking. Enjoy the conference!

Best regards,

Alexander Böker
Conference Chair

Fraunhofer Institute for
Applied Polymer Research
Potsdam-Golm, Germany

Frank Wiesbrock
Conference Chair

PCCL – Polymer Competence
Center Leoben
Leoben, Austria

General Information

MDPI, the Multidisciplinary Digital Publishing Institute, is an academic open access publisher, established in 1996. We publish over 180 peer-reviewed open access journals across ten different subject areas and offer publishing-related initiatives to scholars:

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If you would like more information about open access or any of our services listed above, be sure to talk to us at the conference. See you there!

Polymers: Design, Function and Application will be held at the Faculty of Biology, University of Barcelona, on March 21 – 23, 2018.

With its focus on function and application-driven polymer research, the conference aims to address the development and testing of the next generation of polymeric materials with previously unrivalled properties for advanced applications. This is an opportunity to discuss important breakthroughs in the field; broaden your knowledge, meet scientists from other areas and perhaps develop new mutually beneficial collaborations.

Conference Venue

Faculty of Biology, University of Barcelona
Avinguda Diagonal, 643, 08028 Barcelona, Spain

Registration Desk

The desk for registration, information and distribution of documents will open at 14:30 on 21 March 2018.

Certificate of Attendance

Upon request, the participants of the event will receive an electronic Certificate of Attendance by email once the event is concluded.

Barcelona and Catalonia

Catalonia has become one of the favourite tourist destinations of Spain, mainly because of Barcelona, a city that never sleeps and knows how to please the big majority. With a history among the oldest in Europe, Barcelona offers a mixture of inland and seaside charms that panders the interests of everybody. The variety of artistic treasures, Romanesque churches and the works of famous artists such as Dalí, Gaudí, Miró or Picasso will make of your visit to the city a remarkable experience.

Barcelona is the capital and largest city of Catalonia and Spain's second largest city, with a population of over one and half million people (over five million in the whole province).
This city, bathed by the Mediterranean Sea, has become one of most cosmopolitan cities of Europe which has transformed it into the very modern, yet incredibly old city.
This beautiful city is full of what European cities are known for (outdoor markets, restaurants, shops, museums and churches) and which makes it the perfect scenario to get lost in its picturesque streets and avenues. Moreover, Barcelona's extensive and reliable Metro system will take you to more far-flung destinations. The core centre of the town, focused around the *Ciutat Vella* ("Old City"), provides days of enjoyment for those looking to experience the life of Barcelona while the beaches the city was built upon provide sun and relaxation during the long periods of agreeably warm weather. [Source: www.wikitravel.org].

Parc Güell (Source: www.viajero-turismo.com)

The Faculty of Biology, University of Barcelona

The conference will be held at the Faculty of Biology of the University of Barcelona. Established in 1974, it became a pioneering institution in Spain and first appeared as a result of increasing knowledge in the field of life sciences at a time of relentless diversification.

The University of Barcelona (UB) is the most formidable public institution of higher education in Catalonia, catering to the needs of the greatest number of students and delivering the broadest and most comprehensive offering in higher educational courses. The UB is also the principal centre of university research in Spain and has become a European benchmark for research activity, both in terms of the number of research programmes it conducts and the excellence these have achieved.

Having been founded in 1450, the University's own history is closely tied to the history of Barcelona and Catalonia, it combines the values of tradition with its position as an institution dedicated to innovation and teaching excellence: a university that is as outward-looking and cosmopolitan as the city from which it takes its name. For these reasons, it plays a direct and active part in the urban fabric of Barcelona, becoming a hub of cultural activity for the city itself. [Source: www.ub.edu].

How to Reach the Venue

Address: Avinguda Diagonal, 643, 08028 Barcelona, Spain

Closest Metro Station
L3: Palau Reial

Venue

Venue Location (Source: www.google.es/maps/)

Contact persons during the event

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Emergency Information

All emergencies in Spain: 112 (no area code needed)

Ambulance (Ambulancia) and health emergencies: 061 or 112
Fire brigade (Cuerpo de bomberos): 080 or 112
Spanish National Police (Policía nacional): 091

Abstracts

Young Investigator Award Session

Novel Self-Assemblies via Double Hydrophilic Block Copolymers in Aqueous Solution

Bernhard V.K.J. Schmidt

Max Planck Institute of Colloids and Interfaces, Potsdam, Germany

Self-assembly of block copolymers has a long tradition in polymer science. Especially amphiphilic block copolymers have been utilized frequently in the formation of micellar or vesicular structures in aqueous solution.1 In the present contribution a novel approach is shown, utilizing completely water soluble double hydrophilic block copolymers for self-assembly.

The formation of nano- to micro-scale aggregates from completely water soluble block copolymers in aqueous solution is achievable, yet the choice of blocks is essential. Self-assembled structures are accessible even though completely water-soluble blocks are employed that do not show changes in water solubility in the observed temperature and pH range. The self-assemblies are formed due to significant differences in the hydrophilicity of the blocks and their distinct affinity to water, i.e. the hydrophilic effect.2 To facilitate future applications in drug-delivery, mostly block copolymers consisting of biocompatible blocks will be presented, e.g. poly(N-vinylpyrrolidone), poly(ethylene oxide), poly(2-ethyl-2-oxazoline) or poly(saccharides).3-7 As the formed structures entail a complete hydrophilic nature, significant enhanced membrane permeability compared to traditional amphiphilic systems is expected. Furthermore, increased and controllable stability of the formed assemblies can be obtained via crosslinking moieties that do not alter the hydrophilic nature of the self-assembled structures. Moreover, the utilization of DHBCs in the synthesis of metal-organic mesocrystals will be discussed.8 In such a way, crystal growth can be modulated to obtain unprecedented metal-organic polymer composites with remarkable morphologies.

In summary, a new concept of block copolymer self-assembly based on completely water-soluble and biocompatible polymers is presented as well as the effect of DHBCs on the formation of metal-organic mesocrystals.

References:

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3. Willersinn, J.; Drechsler, M.; Antonietti, M.; Schmidt, B.V.K.J. Organized Polymeric Submicron Particles via Self-Assembly and Cross-Linking of Double Hydrophilic Poly(ethylene oxide)-*b*-poly(*N*-vinylpyrrolidone) in Aqueous Solution. *Macromolecules* **2016**, *49*, 5331–5341.
4. Willersinn, J.; Schmidt, B.V.K.J. Pure hydrophilic block copolymer vesicles with redox- and pH-cleavable crosslinks. *Polym. Chem.* **2018**, doi:10.1039/c7py01214d.
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6. Willersinn, J.; Bogomolova, A.; Cabré, M.B.; Schmidt, B.V.K.J. Vesicles of double hydrophilic pullulan and poly(acrylamide) block copolymers: A combination of synthetic- and bio-derived blocks. *Polym. Chem.* **2017**, *8*, 1244.

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NOTES

New trends in organocatalyzed poly and depolymerizations: from commodity polymers to plastic recycling

Haritz Sardon

POLYMAT, University of the Basque Country, UPV/EHU, Donostia-San Sebastian, Spain

Organocatalysis has become a very powerful tool for polymer chemistry, as judged by the number of articles published in this field in the past decade. A variety of small organic molecules, including Brønsted/Lewis bases and acids, based on sulfonic acids, phosphoric acids, amines, phosphines or carbenes, but also on bi-component systems, have been employed as catalyst for the polymerization of miscellaneous monomers.1 One of the key reasons for transitioning to organocatalysis is their ability to be effectively removed from the final polymers in comparison to their metallic counterparts which are exceedingly difficult to remove. This fact is driving not only their utilization in some residual catalyst sensitive applications such as biomedical or microelectronics but also their investigation in commodity polymers to facilitate their recycling.2

In this lecture, some specific examples from our group about the use of organocatalysis in different applications will be described. First, the ability of organic acids to trigger the step-growth polymerization of polyurethanes will be described.3 Second, the unexpected discovery of 8-ring membered cyclic carbonates and their polymerization using organocatalysis will be explained.4 And finally, the use of thermally stable protic ionic compounds (resisting degradation up to > 400 ˚C) is investigated for polymer recycling.5 Our main goal is to push the limits of organic compounds in poly and depolymerizations extend their use in the polymer chemistry community.

References:

1. N. Ottou, H. Sardon, D. Mecerreyes, J. Vignolle and D. Taton, Prog. Polym. Sci., 2016, 56, 64–115.
2. Sardon, A. Pascual, D. Mecerreyes, D. Taton, H. Cramail and J. L. Hedrick, Macromolecules, 2015, 48, 3153–3165.
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NOTES

Liquid Phase Transmission Electron Microscopy of Block Copolymer Assemblies

Joseph Patterson

Eindhoven University of Technology, Eindhoven, The Netherlands

The evolution of soft matter in water is a key step in the formation of complex biological and synthetic materials. For block copolymer (BCP) assemblies, a delicate interplay exists between the kinetic and thermodynamic parameters, which govern their behavior in solution. There have been great efforts made to characterize the structural evolution of BCP assemblies, principally via in situ bulk scattering methods or ex situ microscopy. In situ scattering experiments are typically performed on simple systems, e.g., special micelles, providing a bulk overview of the sample dynamics, such as average micelle size or shape evolution. Ex situ microscopy is preferred for more complex structures, but is incapable of revealing the underlying dynamics and mechanisms of morphological transformations. Consequently, while highly complex structures can now be formed through BCP assembly, our ability to directly monitor these materials has not significantly improved in the last several decades.

In this paper, we will show how liquid phase electron microscopy can be used to obtain direct real-time nanoscale observations of block copolymer assembly processes. These direct observations offer a unique insight into both kinetic and thermodynamic processes during assembly. This provides a platform for the creation of new models to understand and control the structure and properties of block copolymer assemblies.

NOTES

Integrating Molecular Rigidity and Soft Matter Characters in Ladder Polymers

Lei Fang

Department of Chemistry, Texas A&M University, College Station, Texas, USA

My research group has been focusing on the chemistry and processing of conjugated ladder polymers, in which all the polymer backbone units are fused and π-conjugated. This type of structure mimics the constitution of graphene nanoribbons, endowing synthetic polymers with promising electronic, optical, and mechanical properties. These unique rigid structure features, however, also lead to difficulties in defect-free synthesis, solubility, and mechanical adaptability. Therefore, these materials are not yet widely applicable despite the theoretical promises. To resolve this dilemma, we aimed to integrate the seemingly incompatible features of rigid ladder polymers with the advantages of conventional non-ladder type soft polymers. First, we developed an efficient method to construct conjugated ladder polymer that is free of defect, using thermodynamically controlled ring-closing olefin metathesis1-3. This new methodology enabled the synthesis of a wide variety of novel fused-ring compounds that are not accessible before, such as extended benzo[k]tetraphene oligomers, and donor-acceptor ladder polymers. In addition, we synthesized a highly robust ladder-type poly(indenoquinacridone) polymer equipped with numerous intermolecular hydrogen bonds through a scalable kinetic annulation strategy.4 The processability challenge of this highly insoluble material was addressed by using cleavable protecting side-chains, allowing for its application as solution-processed yet solvent-resistant films and composites.5 These advancements directly addressed some of the most critical synthetic and processing issues associated with ladder polymers.6

Parallel to the synthesis and processing of covalent ladder polymers, we have also employed dynamic bonds to impart rigidity into conjugated molecules.7,8 These non-covalent intramolecular interactions, such as hydrogen bonds and Lewis acid-base coordination, provided unique opportunities to actively manipulate the conformations and therefore a wide range of properties of rigid molecular systems. These controllable dynamic bonds have been incorporated into backbones of conjugated polymers for global manipulation of their conformation and optical/electronic properties. This approach also provided an alternative strategy to address the aforementioned challenges of defect-free synthesis and solution processing associated with covalent ladder polymers.

References:

1. Lee, J.; Rajeeva, B. B.; Yuan, T. Y.; Guo, Z. H.; Lin, Y. H.; Al-Hashimi, M.; Zheng, Y. B.; Fang, L. Thermodynamic Synthesis Of Solution Processable Ladder Polymers, Chem. Sci., 2016, 7, 881-889.

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NOTES

Abstracts

Session 1: Design to Function

New Battery Systems Based on Polymers as Active Materials

Ulrich S. Schubert [1,2]

[1] Center for Energy and Environmental Chemistry Jena, Friedrich Schiller University Jena, Jena, Germany
[2] Max Planck Institute of Colloids and Interfaces, Potsdam, Germany

For renewable energy sources such as solar, wind, and hydroelectric to be effectively used in the grid of the future, flexible and scalable energy-storage solutions are necessary to mitigate output fluctuations. For systems that are intended for both domestic and large-scale use, safety and cost must be taken into account as well as energy density and capacity, particularly regarding long-term access to metal resources, which places limits on the lithium-ion-based and vanadium-based RFB development. Here, we describe an affordable, safe, and scalable battery system, which uses organic polymers as the charge-storage material in combination with inexpensive dialysis membranes, which separate the anode and the cathode by the retention of the non-metallic, active (macro-molecular) species, and an aqueous sodium chloride solution as the electrolyte. In parallel, printable solid-state polymer batteries were developed allowing a new generation of metal-free batteries (e.g., with application possibilities for smart labels, internet of things or smart clothes).

NOTES

Non-Ionic Polymers and Gels with UCST-Type Transitions and Thermophilicity in Water

Seema Agarwal

University of Bayreuth, Bayreuth, Germany

The talk will deal with the non-ionic synthetic polymers showing an upper critical solution temperature (UCST) in aqueous solution under practically relevant conditions. Examples of such polymers in comparison to the LCST-type polymers are very few. Therefore, our focus is on providing new examples that display UCST behaviour under mild and physiologic conditions undisturbed by electrolytes. The possible approaches to tune the phase transition temperature, sharpness of transition, hysteresis and effectiveness of phase separation are also studied.

Block-copolymers of UCST-type poylmers with poly(ethylene glycol) provide temperature-dependent self-assembled structures. They proved to be highly useful spatiotemporally controlled heat nanogenerators for combating drug-resistant cancer.

The thermophilic hydrogels are obtained by chemical/physical cross-linking of the corresponding thermoresponsive polymers and are used for actuation purposes with unique characteristics, such as ultrafast and directionally controlled actuation. Electrospinning was used as a tool for making porous thermoresponsive mono- and bi-layer gels for actuation.

NOTES

High Performance Materials for Mobility

Josef R. Wünsch

Advanced Materials & Systems Research, BASF SE, Ludwigshafen am Rhein, Germany

Whether walking, running, cycling or driving, mobility is enabled by materials that deliver safety, performance, design and comfort. These various functions of materials for mobility will be highlighted by several recent material innovations from BASF. Safety is provided by Polyacrylic acid-based superabsorbers; a unique running performance is achieved by high rebound foams made of Thermoplastic Polyurethanes; design opportunities for the car interior are given by a new translucent Polyamide; acoustic materials provide a comfortable and quiet driving experience.The key to the success of these materials, in their various applications, lies in the precise control over the properties at all length scales. Starting from the right chemistry, polymer composition and physico-chemical properties are at the nanoscale level or the level of the individual polymer chain to precisely control the material morphology; crystallinity and cell structure are at the micrometer level. These properties that are dominated by chemistry and processing, then need to be complemented by the right geometry to deliver the best performance for any application.The focus of the presentation will be the concise correlation between these properties at the different length scales to the final material properties and their link to the demands of modern mobility solutions.

NOTES

Light-Triggered Degradation in Aliphatic Poly(carbonate)s via Intramolecular Cyclization

Jingjiang Sun [1], Wolfgang Birnbaum [1], Marie-Theres Picker [1], Juliane Anderski[2], Dennis Mulac [2], Klaus Langer [2], Dirk Kuckling [1]

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Aliphatic poly(carbonate)s (PCs) with rapid and controlled degradation upon specific stimulation have great advantages for a variety of biomedical and pharmaceutical applications. To this end, we have synthesized a new poly(trimethylene carbonate)-based copolymer containing multiple photo cleavable groups along the backbone by ring opening polymerization (ROP).
The six-membered cyclic carbonate (LrM) has been prepared from 2-aminomethyl-2-methylpropane-1,3-diol and 4,5-dimethoxy-2-nitrobenzyl alcohol with a total yield of 62%. The copolymerization of LrM with trimethylene carbonate (TMC) catalyzed by 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) leads to the UV light-responsive copolymer (LrP). The light-triggered decomposition of LrM and LrP was studied by ^{1}H NMR, IR and UV/VIS spectroscopy, size exclusion chromatography (SEC), as well as ESI-ToF mass spectrometry (ESI-ToF-MS). Upon irradiation with UV light (320–480 nm, 607 mW/cm^2), the copolymer degraded rapidly via intramolecular cyclization into small molecules. After 15 min irradiation, more than 96% of *o*-nitrobenzyl protecting groups were cleaved, while the number averaged molar mass (M_n) decreased from 4000 g/mol ($Đ$ = 1.25) to 500 g/mol ($Đ$ = 6.28) as detected by SEC. Afterwards, the degradation products were separated and identified by coupling of advanced polymer chromatography (APC) and ESI-ToF-MS. The synthesized light-sensitive biodegradable copolymer was expected to be applied for precise controlled release.

NOTES

Synthesis and Characterization of Hydrophobically Modified Polyacrylamide Having Oligo(Lactic Acid) as Hydrophobic Macromonomer

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Hydrophobically modified polyacrylamides (HMPAAm) are water soluble polymers largely used for enhanced oil recovery (EOR) due to their associative properties in aqueous solution. In this work, HMPAAm were synthesized by aqueous copolymerization using an oligo(lactic acid) monomethacrylate, OLAMA, as hydrophobic macromonomer. Firstly, OLAMA, with around 4 and 9 monomer units, was prepared by bulk ring opening polymerization at 130 ^{o}C using *N*-hydroxyethyl acrylamide as the initiator and tin octanoate as the catalyst. Conversions higher than 85% and monomodal molar mass distributions (Đ < 1.3) were obtained. Copolymerization with acrylamide was performed with 0, 2, 5 and 10 mol % OLAMA using an ammonium persulfate/sodium bisulfite redox catalyst system at 40 ^{o}C for 24 h. A solvent mixture (1:1) water:THF or water:methanol was used due to the lower water solubility of OLAMA. The copolymers were characterized by ^{1}H-NMR, SEC, Brookfield viscosity and rheological properties. Nearly quantitative incorporation of OLAMA was achieved in all copolymerizations as well as an average number molar mass between 30–50 kDa (Đ > 2) in the water:THF mixture. A higher molar mass (200–300 kDa, Đ > 2) was obtained using methanol:water as solvent due to the better solubility of polyacrylamide. Consequently, the viscosity of the copolymers (30 ^{o}C, 2 g L^{-1} aqueous solution) synthesized in water:methanol is higher. In both copolymerization conditions, an increase of the viscosity was observed as the incorporation of OLAMA increases. The OLAMA block length (number of LA repetitive units) seems to be less pronounced in response to the increase in the viscosity.

NOTES

A Polymer Chemistry of Graphenes and Graphene Nanoribbons

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Carbon materials are of immense practical importance, but are known as structurally ill-defined “black stuff” such as soot. Graphenes and graphene nanoribbons (GNRs), their geometrical cutouts, are new additions to the carbon family which are praised as multifunctional wonder materials and playgrounds for physicists. Indeed, graphenes hold enormous promise as materials for energy technologies. Further, GNRs are regarded as a new generation of semiconductors superior to (i) silicon in view of the required miniaturization of printed circuits and superior to (ii) classical conjugated polymers due to better band structure control. Above all, graphene as a two-dimensional polymer and GNRs are true challenges for materials synthesis.

We approach graphene fabrication in two steps. “Top-down” protocols such as electrochemical exfoliation are applied for batteries, fuel cells and photodetectors. In the “bottom-up” synthesis of GNRs, repetitive cycloaddition in solution is shown to afford branched polyphenylene polymers which serve as precursors for perfectly “graphitized”, solution-processable GNRs as long as 600 nm. An alternative on-surface synthesis utilizes immobilization of suitable monomers and an in-situ STM-control of the polymerization to secure structural perfection.

It is a synthetic breakthrough which leads to new materials science and physics such as single-molecule field effect transistors from GNRs and even spintronics. The present study is far from robust technologies, but an attempt can be made at predicting some future trends.

NOTES

Unprecedented Photopolymerization of Very Thick Films and Access to Composites: Low Optical Densities vs. Latent Species Strategies

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Fascinating photopolymerization reactions are gaining more and more industrial applications: from the historical well known UV-cured coatings (<50 µm) [ISBN: 978-3-527-33210-6] to 3D printing, thick pigmented materials, biomaterials, composites, etc. For these latter applications, few answers to the huge light penetration issues have been found (particularly for filled samples). Many researchers are therefore currently proposing new strategies in order to overcome the light penetration challenges inherently present in thick films, shadow areas or composites photopolymerization [doi:10.1039/C7PY01778B]. Here, firstly, we will present an initial solution that uses the charge transfer complex (CTC) photoinitating strategy, keeping full spatial and temporal control of the photopolymerization. In detail, the CTCs involve *N*-aromatic amines and iodonium salt (Iod) complexation. Such systems present very **low optical densities** at 405 nm yet extremely fast photopolymerization kinetics in thin films. Therefore, we used them for **extremely thick photopolymerizations (9 cm and 31 cm)** under low irradiance light emitting diodes (LEDs) and, using the same highly versatile formulation, 50-µm resolved **3D printed photopolymers**.

Secondly, a different strategy will be proposed: this strategy involved the production of **latent species** generated in the irradiated areas (from Cu(I)/Iod/Tin(II) photoinitiating system). In detail, under air, *ROOH* latent species are classically a useless byproduct generated in situ in the irradiated areas. On the contrary, here, they were readily consumed by Cu(I) via a redox mechanism (Cu(I)/*ROOH*(in situ)/Tin(II) system, active without light) in order to form highly reactive $RO^\bullet$ species. **This strategy allowed our group to produce a 9-cm composite (45 wt% glass fillers), outranking the previous reference (3 cm) by less than 5 min under low irradiances (230 mW/cm² for a LED@405 nm).** Altogether, this communication will enable discussion of new perspectives and applications for light-induced polymerization processes.

NOTES

Light Responsive Objects: From Active Manipulation to Self-Propulsion of Small Particles at Solid–Liquid Interfaces

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I shall discuss a novel mechanism [1] to induce self-propulsion and to manipulate ensembles of micron-sized particles (artificial and biological) trapped at solid–liquid interfaces. The physical origin of our approach is related to the phenomenon of so-called light driven diffusioosmosis [1]. During inhomogeneous irradiation (e.g., with focused light) of a solution of azobenzene-containing surfactants, a corresponding flow pattern at the solid–liquid interface emerges. The resulting hydrodynamic forces are sufficient to swiftly clean the illuminated area from particles trapped at the interface. When the colloids are turned into Janus particles, homogeneous UV irradiation will also make them move, but this is due to self-propulsion initiated in the same kind of azobenzene-containing solution. I will discuss how to establish light-driven hydrodynamics as a useful and versatile tool for investigating collective motion of self-propelled particles and aggregation. In the second part of my talk, I will demonstrate how soft nano-objects such as polymer brushes, microgels and DNA molecules can be rendered photosensitive using azobenzene-containing surfactants. For example, light-sensitive microgel particles can reversibly be made to change their volume by up to a factor of 8 in response to illumination with the light of different wavelengths [2]. During irradiation, photosensitive polymer brushes can be structured reversibly or permanently at the nanometer scale [3]. DNA molecules can be compacted and decompacted by light in the presence of light-sensitive surfactants [4].

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NOTES

From the Chemistry of Poly(2-Oxazoline)s to Their Use as Biomaterials

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The living cationic ring-opening polymerization of 2-oxazolines has been studied in great detail since its discovery in 1966. The versatility of this polymerization method allows copolymerization of a variety of 2-oxazoline monomers to give a range of tunable polymer properties that enable, for example, hydrophilic, hydrophobic, fluorophilic, as well as hard and soft materials. Moreover, the chemical versatility allows orthogonal end-group and side-chain modification of the polymers. However, this class of polymers was almost forgotten in the 1980s and 1990s because of the long reaction times and limited application possibilities. In the new millennium, there has been a revival of poly(2-oxazoline)s because of their potential use as biomaterials and thermoresponsive materials, as well as the easy access to defined amphiphilic structures for (hierarchical) self-assembly.

Recent developments from our research group that illustrate the potential of poly(2-oxazoline)s will be discussed in this lecture, including the preparation of defined high-molar mass polymers as well as functional biomaterials. Specific examples that will be discussed include the use of poly(2-oxazoline)s as pharmaceutical excipients, evaluation of degradation and toxicity behavior, including pharmacokinetics, as well as the preparation of various side-chain functionalized polymers and their use for the preparation of hydrogel cell scaffolds.

In this lecture, the challenges that are posed for biomaterials will be addressed based on improved synthetic methodologies and screening of in vitro and in vivo toxicity of the materials. Altogether, we aim to develop poly(2-oxazoline)s as biomaterials by providing in-depth studies on the basic questions, such as biocompatibility and renal clearance as well as by providing proof of concept for the use of poly(2-oxazoline)s for various specific applications. Finally, we are working towards the commercialization of poly(2-oxazoline)s under the name Ultroxa®.

NOTES

Influence of Surface Interactions on the Dielectric Properties in Poly(2-oxazoline)-*co*-polyester Nanocomposites

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In high-voltage engineering, epoxy resins, polyesters, and polyamides are polymer classes commonly applied as insulating materials [1]. 2-Oxazoline monomers can be derived from renewable resources [2], and, correspondingly, crosslinked poly(2-oxazoline)s that show similar dielectric properties such as polyamides may be considered as 'green' alternatives for dielectrics. In this study, copoly(2-nonyl-2-oxazoline)-*stat*-poly(2-dec-9'-enyl-2-ox-az-oline) was crosslinked with bisfunctional glycol dimercaptoacetate by photoinitiated thiol-ene click reactions. The dielectric properties of the obtained poly(2-oxazoline)-*co*-polyester network were significantly improved by reinforcement with SiO_2, Al_2O_3 and hBN nanoparticles (10 wt.-%). While all nanocomposites were good insulators (loss factors of 0.06–0.08) at 20 °C and 50 Hz (industrial standard), the unfilled resin showed a high loss factor of 8.43. The high loss factor of the unfilled resin results from interfacial and dipolar polarization due to phase separation in the copolymer. By addition of nanofillers, the phase separation is disrupted due to surface interactions at the particle–polymer interface (Tanaka Model), and the polarizability decreases. This effect is most pronounced in the case of nanoparticles that bear OH-groups on their surfaces (SiO_2 and Al_2O_3) and can be correlated with the amount of hydroxyl functions. In DC breakdown tests, the SiO_2 and hBN composites have higher breakdown strengths (100 and 80 kV/mm) than the unfilled resin (60 kV/mm).

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NOTES

Revisiting the Helix–Coil Transition and Helical Chain Growth of Polypeptides

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In the 1950s, Doty and co-workers found that a polypeptide chain can reversibly convert between the helical and coiled form in solution. The theories of helix–coil transition were then proposed by Schellman, Zimm, Gibbs, Lifson and others, and developed into one of the most fruitful subjects in macromolecular science. Doty also discovered at that time, in the synthesis of polypeptides, that the addition of monomers to the helical form may occur a few times faster than that to the coiled form. A helical chain growth mechanism was proposed by Doty to explain the structure-based acceleration found in the kinetics of polymerization. However, the implication of this mechanism is not as extensively exploited as that of the helix–coil transition. Interestingly, the primary mechanism underlying the helical chain growth of polypeptides shares a remarkable similarity with that of helix–coil transition: both are a nucleation-controlled two-stage process, and a cooperativity factor can be defined to describe the sharp contrast between the two stages. Herein, we present some of our latest results that arose from revisiting the helix–coil transition and the helical chain growth behaviors in synthetic polypeptides. We have focused on the applicability of these models in describing the experimental model systems under the limiting cases, such as the polypeptides of very high molecular weights, or the polypeptides with local crowding owing to the macromolecular architectures (e.g., polypeptide-grafted comb-like or brush-like macromolecules). The aim is to integrate theoretical and experimental approaches to allow for model-driven engineering of complex, polypeptide-based systems in the future.

NOTES

Controlling Monomer Sequence Using (Supramolecular) Cyclopolymerization

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Controlling the monomer sequence in chain-growth polymerizations is highly challenging. If suitable methods are found to accomplish this feat however, it might be possible to create a whole range of new functional materials, as can be seen for biopolymers such as proteins.

One way of controlling the monomer sequence is to pre-organize comonomers, bringing the polymerizable moieties in close proximity to each other so that the chances of them being incorporated into the polymer chain together is greatly enhanced. Different methods of pre-organization can be used. Firstly, polymerizable moieties can be linked covalently, creating bi- or multifunctional monomers. Under suitable conditions, cross-linking can be circumvented, resulting in a cyclopolymerization, so called because of the cyclic structures in the resulting polymers. Alternatively, supramolecular interactions can also be used to pre-organize monomers.

Here, we show that pre-organized monomers can be incorporated into a polymer in their pre-organized sequence, thereby resulting in the formation of functional pairs of monomers in the chain. This concept can be used to increase the degree of alternation in a polymerization or to include functional pairs of monomers in a polymer chain.

NOTES

Polymers from Amino Acids

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Polymers made from renewable resources, i.e., amino acids, sugars, terpenes, etc., are gaining more and more attention and importance. Here, the synthesis of advanced functional/smart polymers made from amino acids (and sugars) will be discussed with a special focus on three topics:

(1) Statistical copolypeptides based on allylglycine and benzyl-L-glutamate were prepared by ring-opening copolymerization of corresponding amino acid *N*-carboxyanhydrides. The allylglycine units were functionalized with 2,3,4,6-tetra-*O*-acetyl-1-thio-beta-D-glucopyranose applying thiol-ene "click" photochemistry. Removal of the protecting groups yielded glycosylated poly(L-glutamate)s, which were capable of recognizing proteins (specific carbohydrate–lectin interactions) and changing solution properties (ionization and conformation) in dependence of solution pH.

(2) Poly(benzyl-L-glutamate-*co*-allylglycine) formed organogels at <2% *w*/*v* in toluene, tetrahydrofuran, or 1,4-dioxane, assisted by UV-crosslinking with dithiol. Subsequent debenzylation of the organogel yielded a pH-responsive poly(L-glutamate) hydrogel.

(3) Multi-heterofunctional poly(disulfide)s were prepared by olefin or disulfide metathesis polymerization of L-cystine-based macrocycles. Monomer conversion reached ~70–90% in equilibrium and the produced polymers exhibited high apparent molar masses (M_w^{app}) of up to 80 kDa and dispersities ($Đ$) of ~2. The polymers could be further functionalized with acid anhydrides and degraded by reductive cleavage of the main-chain disulfide.

NOTES

Molecularly Imprinted Bacterial Cellulose Nanofibers for Selective Recognition of Proteins

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The application of nanomaterials to biological systems and bioengineering has received increased interest in the past decades. In particular, bacterial cellulose nanofibers have been utilized in a wide range of applications, including the cosmetics, biomedicine, food, textile, and pharmaceutical industries. By employing biomedical methods such as molecular imprinting techniques, biomaterials have been produced in large-scale with high reproducibility. Recognition and adsorption modalities have received much attention in the field with biomaterials being integrated into precise biomedical methodologies.

In this study, by employing molecular imprinting tools, we design bacterial cellulose nanofibers as recognition elements for selective lysozyme detection. In this process, synthesized bacterial cellulose nanofibers were characterized to calculate the yield of polymerization. Various lysozyme concentrations ranging from 0.05 mg/mL to 1.5 mg/mL were evaluated, and the maximum adsorption capacity of the lysozyme-imprinted bacterial cellulose nanofibers was found to be 71 mg/g. The selectivity of the lysozyme-imprinted bacterial cellulose nanofibers was assessed with competitor proteins such as bovine serum albumin (5.33 mg/g) and cytochrome c (6.73 mg/g), and we observed the highly selective capture of lysozyme (12.3 mg/g) at the same concentration of protein. Kinetic calculations in the recognition process indicated a well-fit model to Langmuir adsorption instead of Freundlich and Langmuir–Freundlich adsorption models. After multiple adsorption–desorption experiments, the produced materials also provided high reusability capacity (>8 times). In conclusion, the presented work holds great potential for lysozyme recognition from biological matrices by integrating molecular imprinting techniques with bacterial cellulose nanofibers. Further, this study shows a versatile method that can be deployed to the recognition of other biomolecules, and potentially provides a new strategy to create new-generation biomaterial due to the formation of high recognition capacity, significant selectivity and excellent reusability in recognition systems.

NOTES

New Immobilization Protocols for the Embedding of Enzymes in Ultrathin Polymeric Films

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Enzymes are biocatalysts that enable highly efficient and selective chemical conversions, which would normally require harsh reaction conditions or the use of toxic and/or expensive co-components. However, a fundamental problem regarding the application of enzymes outside their natural environment is their lack of stability, which often prohibits a broad use for synthetical purposes. Fortunately, the stability and thus the usefulness of particular enzymes can be significantly improved by an immobilization of the respective biocatalyst.

2-deoxy-D-ribose-5-phosphate aldolase (DERA) is an enzyme that is used for the synthesis of enantiomerically pure dihydroxyaldehydes, which are important structural motifs for a number of pharmaceutically active compounds. In order to minimize the risk of the enzyme being deactivated at industrially relevant product concentrations, which is a common phenomenon for enzymes, the biocatalytic conversion must be coupled with a transport process. This, in turn, requires the immobilization of the enzyme in a thin film that can be penetrated by the reaction medium.

Taking DERA as an example, we present two mild but also adaptable immobilization strategies for enzymes that lead to biocatalytically active thin films which, in principle, can be used for the purpose described above. These strategies are either based on the adsorption of the enzyme within a pre-formed protein reactive polymeric film at the air/water interface or on the interfacial self-assembly of enzyme/poly(*N*-isopropylacrylamide) conjugates.

A special focus is put on the polymeric precursors in use, as they are designed in such a way that they remain structurally simple while being able to fulfil multiple tasks including the binding of the protein and the tuning of film properties.

NOTES

Design of Inorganic Polymers with Stimuli Responsive Cleavage and/or Degradation in Biological Environments

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Herein, we describe our work on degradable polymers, in particular polymers which are designed to be stable but spontaneously and quickly disintegrate upon exposure to certain triggers.

Firstly, a photolabile ruthenium-based complex is incorporated into polyurea hydrogels to give supramolecular photosensitive materials [1]. The gels were shown to undergo rapid photocleavage at wavelengths of 400–500 nm, as well as via a two-photon process in the NIR region (800 nm). The rapid de-gelation of the supramolecular gels also enabled spatiotemporal micropatterning by photomasking or pulsed NIR-laser irradiation. The long-wavelengths required for cleavage of the metallopolymers mean that they could have significant potential for biological applications, where materials which respond to mild, tissue penetrating irradiation are of particular importance. Furthermore, these supramolecular metallogels are also shown to be thermally reversible, thus opening opportunities in self-healing materials.

We also present a second set of materials based on the polyphosphazene backbone [2]. The backbone phosphorus atoms are quite prone to hydrolytic attack but can be “protected” by substitution with organic substituents. Hence, we designed hydrolyticially unstable polymers but with cleavable protecting groups along the phosphorus backbone. This allows us to create stable high molecular weight polymers, which can be rapidly degraded upon cleavage of the protecting group. Through the choice of protecting groups, macromolecules were also designed to respond to visible light, as well as to biologically relevant oxidative triggers [3].

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NOTES

Poly(ethylene glycol) Diacrylate Hydrogels Used as Carriers for Photodynamic Therapy Photosensitizers

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Hydrogels are water-swollen polymer networks that can be loaded with bioactive substances and drugs very easily. They can absorb a large amount of water and possess a high degree of flexibility [1,2].

In this study, we use poly(ethyleneglycol) diacrylate hydrogels. These are promising materials for biomedical applications such as drug delivery systems [3–5]. The produced hydrogels will be used as wound patches for infected or chronic infected wounds. Therefore, so-called photosensitizers will be incorporated into the hydrogels. These photosensitizers can act as antimicrobial substances due to singlet oxygen generation after irradiation with light [6,7].

To produce those antimicrobial wound patches, the hydrogels were synthesized by photopolymerization. Afterwards, they were loaded with various well-known photosensitizers, e.g., methylene blue, eosin y, and porphyrins. Their uptake and release kinetics were observed. In Figure 1, the high transmittance over a broad wavelength range of the gels is shown. This property is very important to ensure that the photosensitizers still absorb light after incorporation into the hydrogels.

Additionally, the hydrogels were investigated by different analyzing methods, e.g., scanning electron microscopy (SEM), infrared spectroscopy (IR), UV/VIS spectroscopy, and dynamic mechanical analysis. Furthermore, properties like swelling behavior, cytotoxicity and mesh size were determined.

The method presented here is a simple and effective preparation and loading technique for application as wound gels. They are great carriers for photosensitizers. Especially with respect to the growing number of antibiotic resistances, the gels are of great interest for future medical applications.

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NOTES

Abstracts

Session 2: Function to Application

Sponsored by BASF We create chemistry

Hybrid 3D Manufacturing of Smart Systems

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Hybrid 3D Manufacturing of Smart Systems (Hyb-Man) is an EU-sponsored consortium project with eleven industrial and academic partners from the Netherlands and Germany. The aim of the project is to develop hybrid additive manufacturing methods to enable flexible first-time-right production of smart systems for automotive and lighting applications. The new hybrid 3D manufacturing process establishes additive manufacturing as a core production technology, including the assembly and integration of electronic parts. The consortium covers the entire value chain from research to end users. In-line testing and quality monitoring will be an integral part of the complete production chain.

New 3D printable polymer-based formulations are needed as enablers of 3D hybrid manufacturing. Henkel Adhesive Technologies develops tailor-made polymer systems and formulations based on different polymer classes, including polyamides and polyolefins. These polymer systems exhibit excellent thermal conductivity to allow for the new design concepts. Further technical requirements need to be met to guarantee optimum functionality in the final printed part:

(i) Interlayer adhesion between the printed layers to produce parts with highly isotropic behavior. This target is addressed by special amorphous to semi-crystalline polyamides which are designed by means of an appropriate choice of starting monomers. (ii) Low water uptake of the filaments and powders is very important for a successful and smooth printing process. Due to their intrinsic hydrophobicity, special polyolefins are the best choice in this respect. By combining both polymer technologies into polymer alloys, it is possible to further tailor the required properties to obtain a best-of-both product.

Acknowledgments: The project is funded by the EUREKA Cluster PENTA—supporting innovation in micro- and nanoelectronics-based components and systems as key enabling technology for Europe.

NOTES

Advances and Challenges in Poly(lactic Acid) Fiber Design for Biomedical Applications

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Facing the extremely complex biological system that is the human organism, the requirements for scaffold materials in regenerative medicine are enormous and tremendously challenging. Therefore, the demands on scaffolds are well defined: biocompatibility, creation of a 3D-network with desired pore size and interconnectivity for directed cell growth and support of vascularization of the ingrown tissue, certain mechanical, physical and chemical properties and appropriate degradation characteristics with non-toxic residues. Textile implants exhibit the desired properties and are fascinating due to their high degree of design options and thus provide ideal living conditions for cells.

Poly(lactic acid) (PLA), the most common resorbable medically approved biomaterial, is often limited in its application due to the brittleness of specimens. However, fabricated into fibers, the remarkable potential of PLA is evident: silk-like fibers with 20–200% elongation of break and high tenacity up to 45 cN/tex can be fabricated and represent the fundamental unit of textile implants. Therefore, the careful processing followed by the thorough investigation of biopolymer-processing-structure-properties correlation in PLA fibers and the creation of various scaffold strategies is a major research task.

Herewith, we present an overview including different processing aspects within the area of biomedical PLA fiber creation by means of solvent-free melt spinning profiled, hollow and nano-scaled fibers in order to provide a large surface area-to-volume ratio and guidance structures, e.g., for peripheral nerve regeneration; the creation of biocomposite fibers mimicking the composite nature of real bone with inorganic fillers such as calcium carbonate to introduce mineral components promoting bone regeneration, fiber toughening by offline-drawing and annealing up to electron-induced reactive processing in order to create high-performance biopolymer fibers, e.g., for ligament repair. We finally address the critical issues in terminal sterilization of biopolymers.

NOTES

New Biobased Polycarbonates as Functional Materials

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Biobased polymers are promising alternatives to fossil-based polymers. Biobased polymers are of particular interest as they provide access to novel sets of physical and chemical properties. The organo-zinc catalysed copolymerization of trans-limonene epoxide and CO_2 yields high molecular weight polylimonene carbonate (PLimC) with a unique combination of physical and chemical properties [1]. PLimC forms highly transparent coatings, has a glass transition temperature of 135 °C, is scratch resistant, and shows good selectivity in gas permeation. Most interestingly, the lateral double bond in each repeating unit of PLimC makes it a perfect platform for functional polymers [2]. These double bonds allow a wide variety of chemical modifications of PLimC which result in polymers with a wide variety of novel properties.

PLimC shows unique permeation properties in combination with its excellent transparency which allowed the preparation of a completely new class of materials, which we have termed a “breathing glass” [3]. The high permeability of CO_2 allows an exchange with the surroundings through a closed PLimC window without any opening of windows.

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NOTES

Application of Melt-Blown Poly(Lactic Acid) Filaments in Self-Reinforced Composites

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As developing a sustainable, circular economy has become an important goal in society, biocomposites have gained much importance among other structural materials. Over the last few decades, a wide variety of biopolymers have been developed, among which poly(lactic acid) (PLA) has been considered as the most promising bio-based and biodegradable polymer. However, the poor impact strength and thermal stability of PLA have to be improved to make it suitable for durable applications. Self-reinforcement (SR) is a good way to increase the impact strength and heat deflection temperature (HDT) of a thermoplastic polymer; moreover, the SR composites are fully recyclable. Lately, researchers have found novel directions to achieve SR-PLA structures. Somord et al. [1] succesfully produced SR-PLA nanocomposites for the first time by hot-compaction of electrospun PLA fibres. This technique allowed a productivity of 0.32 g/h, which makes it hardly scalable. In this work, SR-PLA composites were produced using melt-blown PLA nonwoven mats as starting material. Three types of PLA differing at D-lactide content were processed by the solvent-free melt-blowing technology. As high as 120 g/h productivity and 2–16 µm filament diameter were achieved. The crystallinity of the PLA microfibres was enhanced by thermal annealing; 2–3 fold increase in the degree of crystallinity was obtained, as measured by differential scanning calorymerty (DSC). The obtained PLA mats were then processed via hot compaction technique and formed into SR-PLA composites. The preparation conditions were comprehensively studied focusing on the morphological, thermal and mechanical properties of the obtained unique, microstructural composites. The prepared SR-PLA sheets, composed of highly crystalline reinforcing fibres, can be characterised with enhanced thermo-mechanical properties. Furthermore, due to the high fibre–matrix interfacial area, substantial improvement in ductility and toughness was achieved when compared to isotropic PLA film.

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NOTES

Progress in Doped Polymer Optical Fibers for Photonic Applications

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Polymer optical fibers can be doped with a wide range of functional materials, thereby allowing for very interesting applications of these fibers in the fields of lasers, amplifiers, illuminators, switches, sensors, and luminescent solar concentrators [1–3]. On one hand, the fact that the material of the fibers is a polymer facilitates their manufacturing and reduces their cost, with the added advantage of having high safety and extremely high flexibility of the fibers. On the other hand, the waveguide geometry of the fibers provides optical confinement with long interaction distance, efficient heat dissipation and symmetric output beam profile. This work aims to review the latest progress in doped polymer optical fibers. Particularly, the features of manufacturing char, light propagation, generation and amplification in several doped polymer optical fibers are analyzed as relating to their potential photonic applications. The manufacturing processes of these fibers are also studied.

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NOTES

Mechanics, Topography, and Chemistry: How to Determine Multi-Parameter Influences on Cell Behavior

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Cell-surface interactions are influenced by various factors including surface chemistry, mechanics and nano-/micro-topography [1]. A lot of investigations show that these surface parameters can be used to direct cellular behavior. However, there is still little known about how combined surface parameters affect cellular behavior as there are so many different parameter combinations. Screening platforms of surface parameters in a gradient fashion [2,3] are being developed to elucidate which cellular behaviors are affected. The screening platform, based on silicone rubber (PDMS), combines four orthogonal double gradients of wettability, topography, and stiffness connected to automated cell imaging and analysis which allows substantial insights to be generated into multi-parameter influences on cell behavior. These screenings are expected to facilitate the translation of basic cellular behavior towards clinical applications related to implant materials and tissue engineering scaffolds.

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NOTES

Mixed Polymer Adllayers Allowing Remote Control of Cell Adhesion and Polarization via Click, Temperature, or Redox Triggers

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Polymer-coated surfaces are ubiquitous substrates for cell cultures in vitro. Passive, static substrates have, however, limited capacities to recapitulate the properties of a dynamic environment such as the natural extracellular matrix. A challenge in this field is accordingly to achieve spatial and temporal modulations of the presentation of guidance cues by artificial substrates to dynamically affect cell migration, proliferation or fate.

We design copolymers that enable coating of most usual surfaces, with adjustable layer compositions and an on-demand switchable display of peptides. This polymer “toolbox” is based on comb-like poly(lysine) derivatives (PLL). Spontaneous co-adsorption allows mixed layers to be deposited. Micropatterns are obtained by UV etching and sequential applications of polymer solutions. We will present (1) poly(lysine)-g-PEO chains that are activated in situ by either non-toxic copper-free click attachment of adhesion peptides or redox cleavages, (2) mixed PLL-g-PNIPAM with PLL-co-ligand layers that reversibly control the balance between cell repellency and specific adhesiveness upon temperature shift. The control of layer composition, thickness, and functionality was assessed by epifluorescence, QCM-D, and AFM. Tailoring the balance between repulsive, adhesive, and specific binding moieties, i.e., reaching optimal mixed layer functionality, was key to achieving a controlled interaction with living cells. A strategy based on co-deposition of grafted polycations is, in this context, straightforward, versatile, and easy to adopt by non-chemist biologists.

NOTES

Nano-Patterned Polyelectrolyte Multilayers: A Non-Lithographic Approach

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Nano-patterned materials exhibit unique properties, such as increased surface area and morphology-dependent response. However, obtaining nanoscale patterns usually requires the involvement of electron beam lithography, which is limiting when device-scale patterns (typically spanning square centimeter areas) are sought.

The presentation will describe a modular approach for the construction of *nano-patterned* polyelectrolyte multilayers. This approach utilizes the surface patterns that are formed spontaneously in thin films of block copolymers as templates, which guide the assembly of polyelectrolytes using electrostatic layer-by-layer deposition. The presentation will discuss the fundamentals of selective polyelectrolyte adsorption on confined nano-domains and will elaborate on recent developments.

NOTES

Radial Dependence of Film Formation during the Spin-Coating of an Immiscible Polymer Blend

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The mixing of polymer blends is thermodynamically unfavourable and phase separation can often be observed in the morphology of spin-coated polymer-blend films. Little work has been undertaken to determine the radial dependence of the spin coating process. In situ light scattering experiments have been extended to explore how the effect varies radially at 0, 4, 8, and 12 mm from the centre of the film for solutions of 2% and 4% polymer concentration by mass for spin-coating at 1000 and 2000 rpm. It is shown that there is a significant radial dependence on the film formation. Inertial forces initially govern spin-coating until solvent evaporation becomes dominant. The turbulent forces change with radius and thus the evaporation rate varies with the radius, resulting in radial variance. These results are discussed in terms of applicable models.

NOTES

Enzymatic Polymerizations—Novel Ways to (New) Polymer Systems

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The in vitro enzymatic synthesis of polymers via non-metabolic pathways is a relatively old area of precision polymer synthesis. The enzymatic polymerization of polysaccharides was, for instance, already reported more than 50 years ago. However, other polymerization methods using cheap petroleum-based monomers soon replaced research on biocatalytic polymerization techniques.

These days, the fast depletion of the petroleum stock and increase in the cost of petroleum-based monomers puts a limit on their future use and enzymatic polymerizations are currently facing a Renaissance.

Enzymes have excellent features (activity, selectivity, specificity) for designing synthetic processes to obtain a wide range of products under mild and environmentally friendly conditions. Typical characteristics of enzyme catalysis are high catalytic activity, a large acceleration rate of reactions under mild reaction conditions, high selectivity of substrates and reaction modes, and no formation of byproducts. In the field of organic synthetic chemistry, enzymes are already used extensively for the production of chemical and pharmaceutical intermediates and end products.

At present, petrol-based monomers are still predominately used in enzymatic polymerizations. By combining biobased monomers and enzymatic polymerizations in polymer synthesis, not only could the research field of enzymatic polymerization be greatly accelerated but the utilization of renewable resources will also be promoted. This will provide an essential contribution to achieving sustainability for the polymer and coatings industry, which will eventually play an important role in realizing and maintaining a sustainable society.

NOTES

Electrochemically-Active Microgel Systems

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Microgels are crosslinked polymeric particles consisting of a porous network swollen by a solvent. They often have the ability to undergo a volume phase transition with respect to environmental changes, allowing an adjustment of segmental proximity and network dynamics [1]. The introduction of charges into the microgel network leads to a possible interaction of the polyelectrolyte microgel with oppositely charged counterions based on electrostatic attraction (host–guest interplay). In the case of redox-active counterions, the charge of these guest molecules can be changed by electrochemical means [2]. Hence, we address thermoresponsive cationic microgels and their influence on the electrochemistry of hexacyanoferrates [3]. Further, we investigate the influence of the counterion guests on the swelling of the microgel hosts: the size of the cationic microgel can be reversibly modulated by electrochemical switching, leading to a redox-responsive microgel system [4]. Finally, other attempts to generate electroactive microgel colloids (e.g., with permanently linked redox-active units) and their applications are also discussed.

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NOTES

Tailoring Ioncell Fibers with Noble Metal Nanoparticles

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Due to their inertness, noble metals have served many applications throughout history ranging from jewellery to the food industry. In the form of nanoparticles, noble metal nanoparticles show unique optical properties, which are derived from their localized surface plasmon resonance. The collective oscillation of the conductive electrons results in strong light absorption and scattering. The light scattering by Au nanorods, for example, is several orders larger than the light emission from strongly fluorescent dyes. As a result, they display a broad range of colors, which could potentially replace conventional textile dyes, thus reducing the amount of chemicals employed in textile manufacturing. Under hydrothermal conditions, the reducing ends of cellulose enable the in situ reduction of noble metal ions to optically resonating nanoparticles, thus offering a “green” alternative to seed-mediated approaches. Herein, we report the preparation of nanoparticle-coated prehydrolysis kraft pulp, which is subsequently used as a substrate for dry-jet wet spinning in the Ioncell-F process. Through the dissolution of the cellulose component in [DBNH] OAc, the nanoparticles are targeted to be incorporated into the cellulose fiber matrix to yield Ioncell fibers with improved color fastness and enhanced antibacterial properties.

NOTES

Electrospraying of Nanometer-Sized Droplets for Sub-Micrometer-Thin Dielectric Elastomer Transducers

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Flexible and foldable hetero-nanostructures based on polymers provide access to nano-photonics, *tissue-like* soft electronics and dielectric nano-transducers. Nanometer-thin polymer and metal films can be fabricated by molecular beam deposition (MBD)—a technique that leads to the reliably of films with unique homogeneity [1,2]. The control of their surface morphology with sub-nanometer precision is enabled using in situ spectroscopic ellipsometry [2]. With growth rates increasing by orders of magnitude, electro-spray deposition (ESD) of polymers describes a cost-effective alternative to MBD and a potential up-scale process for soft polymer membranes [4]. Polydimethylsiloxane (PDMS) is widely used due to its biocompatibility for biomedical implants. Cross-linking of the single PDMS chains is realized via in situ ultraviolet light (UV) irradiation [3]. However, confluent polymer films fabricated by ESD exhibit micrometer-rough surface morphology [4,5]. In order to guarantee a homogenous formation of the sub-micrometer films, a comprehensive understanding and control of the polymer/solvent droplet size distribution is required and is presented within this communication. PDMS is solved in acetone/ethanol and deposited on bare Si(100) substrates. A controlled atmosphere allows for a stable tailor-cone spray. We will discuss the solvent's influence on the morphology of PDMS islands forming membranes with sub-micrometer thickness. The homogeneity of soft electro-sprayed polymer nano-membranes is key to allowing reliable low-voltage operation of dielectric elastomer nano-transducers to enter the application field of medically approved actuators or sensors, such as artificial muscles or skin [3].

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NOTES

Sustainable Preparation of PVDF-Based Membranes with Tailored Properties

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Polyvinylidenefluoride (PVDF) is one of the most used polymers as artificial membrane material [1]. However, many drawbacks are still involved in the production of PVDF membrane that usually imply the use of toxic and harmful solvents to dissolve the polymer [2].

In this work, a sustainable and scalable preparation method was developed to produce hydrophobic PVDF-based membranes using dimethyl sulfoxide (DMSO) as green solvent and a combination of vapor-induced phase separation (VIPS) and non-solvent-induced phase separation (NIPS). During the VIPS process, the adsorption of water vapors (water is a non-solvent for the polymer) permits the surface properties of roughness, porosity, pore size, surface wettability and transport properties to be modulated [3]. The NIPS step completes the membrane formation by immersion of the casted film in a water coagulation bath.

We found that the VIPS process is mandatory to obtain super-hydrophobic membranes. The VIPS process allows to obtain a porous and rough surface by a slow and controlled diffusion of the water vapor phase into the casted membrane.

The membrane properties were tailored acting on the polymer concentration and VIPS conditions (duration and air humidity content). The membranes produced were tested in the membrane distillation process showing high performance in terms of flux and rejection.

Acknowledgments: The authors would like to thank the European Union’s Horizon 2020, Future and Emerging Technologies programme FET-OPEN, for funding this work within the AMECRYS project (http://www.amecrys-project.eu/) under grant agreement no. 712965.

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NOTES

Building Simple Mimics of Natural Proteins Provides New Opportunities from T-Cell Delivery to Novel Amphiphilic Networks

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Our primary research aim is to create new materials using a combination of principles, many of which are inspired by biology. The combination of unique molecular scaffolds and guanidinium-rich side chains has produced an array of polymers with robust transduction (and delivery) activity. In this lecture, we will discuss our latest results in which we have successfully mimicked the biological activity of protein transduction domains (PTDs), such as HIV-TAT. Using ROMP, we have successfully developed an array of PTDs. We will discuss a detailed structure–activity relationship of a new PTD family of polymers and demonstrate their delivery of cargo into human primary T cells. Successfully delivered cargoes include siRNA, whole proteins, and full-size antibodies. Expanding the scope of biomimetic design, these principles were extended to new amphiphilic co-networks inspired by Resilin, a member of intrinsically disordered proteins. They demonstrate 100% resilience even at 300% strain and provide robust access to the co-continuous self-assembly morphology. As model networks, cavitation within soft matter is being studied.

NOTES

Three-Dimensional Biomimetic Hydrogel to Deliver Factors Secreted by Human Mesenchymal Stem Cells in Spinal Cord Injury

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Stem cell therapy with human mesenchymal stem cells (hMSCs) represents a promising strategy in spinal cord injury (SCI) [1,2]. However, both systemic and parenchymal hMSC administrations show significant drawbacks due to the limited number and viability of stem cells in situ. Moreover, cell therapy delivered systemically (intravenous injections) could lead to a limited efficacy due to the infeasibility of the cells to cross the blood–brain barrier [2]. In this study, we evaluate a new agarose/carbomer-based hydrogel that combines different strategies to optimize the hMSC viability, density and delivery of paracrine factors. The three-dimensional polymeric networks chosen correspond to a library of chemically nanostructured hydrogels, highly tunable in terms of molecular structure and biocompatibility [3]. In addition, we combined RGD tripeptide and 3D extracellular matrix deposition to increase the capacity to attach and maintain healthy hMSCs within the hydrogel over time. In order to optimize and evaluate the hMSC adhesion and viability, several hydrogel compositions and different loading protocols were developed and tested [4]. We first seeded hMSCs into HG RGD and we measured the ECM deposited over time. A progressive ECM deposition was observed from 1 up to 14 days, where ECM deposition reaches a "plateau". Thus, for a second hMSC seeding, we decided to deposit ECM up to 14 days and then we lyophilized the HG RGD + ECM to allow a new encapsulation of hMSCs by a sponge-like loading. This hydrogel with ECM is able to maintain hMSCs' viability for a longer period whilst also maintaining their stemness.

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NOTES

Ultra-High Loaded Polymer Micelles for Drug Delivery

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Polymer micelles have been discussed for drug delivery for many decades, but despite intensive research and development, very few polymer micelles have reached the clinic. One major limitation of polymer micelles for drug delivery has been limited drug loading, which rarely exceeds 20 wt.%. In contrast, we have developed a platform of polymer micelles based on poly(2-oxazoline)s and poly(2-oxazine)s, which enables not only extremely high drug loadings but also extraordinary high overall drug concentrations, and excellent formulation stabilities. Currently, we are investigating a large variety of structural variations with respect to the hydrophobic block and its impact on the drug loading and micelle properties. Thus, we have found that aromatic moieties may help with the drug loading of some drugs, but not others and that increasing the hydrophobicity of the polymer micelle often does not benefit the drug loading. In summary, intricate structure–property relationships are being revealed, which contradict many concepts for polymer micelles in drug delivery.

NOTES

Thermoresponsive Polymers Exhibit Chaperone-Like Activity and Recognize the Unfolded State of the Protein

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Synthetic polymers, including polyelectrolytes of different nature, are a promising tool to protect proteins against aggregation. Its efficiency at elevated temperature can be higher than that of natural chaperones—a family of proteins which protects enzymes against aggregation and/or inactivation and participates in the degradation of unfolded or misfolded proteins. However, most of these polymers efficiently interact with the native state of the enzyme and therefore can alter its structure and behavior. In the present work, the chaperone-like activity of thermoresponsive polymers based on poly(dimethylaminoethyl methacrylate) (PDMAEMA) was studied on two different client proteins: glyceraldehyde-3-phosphate dehydrogenase and chicken egg lysozyme. A PDMAEMA-PEO block of copolymers has been shown to protect the denatured protein against aggregation in contrast to PDMAEMA homopolymers. The polymers did not interact with the native protein at room temperature but formed a complex upon heating to either protein unfolding or polycation phase transition temperature. No effect of the polymers on the structure and enzymatic activity of the client protein was observed at room temperature. Hence, PDMAEMA-based polymers exhibit an ability to recognize the unfolded state of the protein that is the major property of natural chaperones. Secondly, synthetic polyelectrolytes share a different protective efficiency for different client proteins. Summarizing these results, we consider the charged polymers as a platform for the creation of artificial chaperones. The thermoresponsive polymers can also be used for reversible sedimentation of the folded enzyme.

NOTES

Mimicking Natural Membranes Utilizing Transmembrane Protein–Polymer Conjugates

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We aim to develop ultra-thin self-assembled membranes with tailored transmembrane proteins acting as the pores. Such membranes offer a promising alternative for conventional membrane fabrication, especially in the field of nano-filtration. The targeted protein is the well-studied ferric hydroxamate uptake protein component A (FhuA), a β-barrel transmembrane protein of *Escherichia coli*, and generated by our cooperation partners in the group of Prof. Schwaneberg. We formed protein–polymer conjugates from various engineered variants of FhuA. While the conjugate formation has been shown with many model proteins; this is the first example of targeting the class of membrane proteins. Crosslinkable polymer chains were grown from the lysine residues of FhuA via the grafting-from approach. FhuA–polymer conjugates self-assemble at the air–water interface due to their high interfacial activity. Crosslinking of the polymer chains leads to a stable ultrathin membrane which lies planar on top of a support after the evaporation of water. Consequently, the protein nanopores are embedded in a polymer matrix and act as the pores in the membrane. The responsiveness of the polymer chains is used to tailor the properties of the membranes. The presentation will give an overview of the fundamental characterization of the protein–polymer conjugates, as well as the crosslinking to stabilize Pickering emulsions on the one side and to form planar membranes for separation processes on the other side.

NOTES

Abstracts

Poster Exhibition – Session 1: Design to Function

1. “Microbial Cell Factories” to Produce Nanocapsules Coated by Custom Polypeptides

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The advances in metabolic engineering and synthetic biology over the last 20 years have markedly facilitated the use of microorganisms as “*microbial cell factories*”, capable of synthesizing non-natural molecules with high added value [1]. This strategy constitutes an eco-friendly alternative to chemical synthesis. ‘Microbial factories’ are emerging in material science, mostly in the field of biopoly(esters) [2], or production of temperature-responsive polypeptides (e.g., elastin-like polymers, ELP) [3]. Replacement of “in vitro” for “in vivo” formulation by rerouting the cell machineries could be of particular benefit to assemble complex systems and functionalize colloids in mild conditions. Here, we will illustrate the design of genetically-encoded polymer-coated microcapsules, similar to polymer-decorated liposomes [4]. The design of these biocapsules aims to achieve controlled display of functional moieties (e.g., fluorophores, temperature-responsive corona), via a solvent-free and mild handling processing approach.

We used the inner membrane proliferation induced by overexpression of a membrane protein (b subunit of ATP synthase) in C43 (DE3) *E. coli* cells [5], as the starting point to introduce artificial fusion polypetides in lipid bilayers. Enzymolysis, followed by mild mechanical shear, yields vesicles homogenous in size and composition, decorated with an outer corona of the polypeptide of interest. As a proof of feasibility of the customized surface modification of these lipidic capsules, we have explored the possible range of modulation of the surface functionality by genetically encoding fusions with fluorogenic and ELP polypeptide sequences. Future perspectives include encapsulation of liposomes loaded with biomolecules for cosmetic and biopharmaceutical applications.

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2. Graphene Oxide-Modified Shape Memory Polymer Composite

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Owing to bone fracture, osteoporosis and diseases, bone defect has become a common situation. Traditional synthesized materials applied for bone repair still have some issues such as unsatisfactory mechanical properties and biological performance. Shape memory polymer (SMP) is a kind of smart material that can memorize its shape and then recover under specific conditions, which has already been used in biomedicine. Nevertheless, single employment of the shape memory polymer may lead to different problems. In this study, we present a simple method to fabricate the graphene oxide (GO)-modified SMP composite with satisfied mechanical and shape memory properties for bone repairing. The nanofiller was added after the generation of SMP oligomer instead of the fabrication of final SMP production. Then, the structure, thermal and mechanical behaviors of SMP composites were all characterized. In addition, the shape memory effect of the composite was also investigated. The results suggest that the GO was successfully modified with SMP. In addition, Young's modulus of SMP/GO composite was demonstrated to be 2.5 times more than that of SMP at room temperature. Furthermore, the shape memory properties of SMP/GO are also noticeably improved. With the superior structure and properties, we believe that this composite will be an inspiration and consideration for the future application of smart composite in the biomedical field, especially in the area of bone repair.

3. Helical Alignment of Semiconducting Random Copolymer Films Enabled by Electrochemical Polymerization in Cholesteric Liquid Crystal

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Conjugated polymers have been attracting much attention for potential applications such as field-effect transistors, photovoltaic cells and electrochromic devices. So far, however, control over polymer orientation has still been difficult, resulting in failure to optimize the device performance. To overcome this issue, we have recently developed a novel orientation method for conjugated polymers called “electrochemical polymerization in liquid crystals”.

Electrochemical polymerization in liquid crystals uses liquid crystal as a solvent for polymer polymerization. The monomers in liquid crystal are spontaneously aligned along the director of liquid crystal molecules. Then, polymerization proceeds along the director when the appropriate potential is applied. As a result, the polymer film with liquid crystalline order was easily obtained. That is, polymer films transcribe the liquid crystal molecular order.

In this time, we employed two different monomers, 2,2’-bitiophene (BT) and 2,2’-bis(3,4-ethylnenedioxythiophene) (bisEDOT), to prepare random copolymer films with liquid crystal order. Cholesteric liquid crystal was used as solvent, which is prepared by the combination of 4-cyano-4’-pentylbiphenyl (nematic liquid crystal) and cholesterol pelargonate (chiral inducer) at an appropriate weight ratio. We successfully obtained BT-*ran*-bisEDOT copolymer films with one-handed herical order, which is characterized by in-situ absorption spectroscopy, and circular dichroism spectroscopy against different electrochemical potentials. Furthermore, a random copolymer under a high-intensity magnetic field (up to 12T) was also investigated to obtain the macroscopic unidirectional alignment of the film. As a result, we prepared the BT-*ran*-bisEDOT copolymer films whose helical axes were unidirectionally aligned.

We prepared the BT-*ran*-bisEDOT copolymer films with chiral order for the first time. This unique polymer alignment cannot be achieved with conventional methods. We believe that “electrochemical polymerization in liquid crystals” will be the new approach to prepare the interesting structures of the polymers for future electronic devices.

4. Isocyanate Microencapsulation: New Crosslinking Strategy for One Component, Self-Reactive and Eco-Innovative Adhesives

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Engineered polymer shell microcapsules that contain a variety of highly reactive isocyanate compounds in their core have been developed to respond to multiple external stimuli that take part in current industrial manufacturing processes (e.g., in the footwear, automotive and aerospace industry), such as a specified pressure, or temperature. To obtain microcapsules with unprecedented functionalities, we use designed oil-in-water emulsions that, combined with an interfacial polymerization method, lead to polyurea/polyurethane shell microcapsules with a high encapsulation efficiency of the desired isocyanate compound, either in the form of monomeric, or pre-polymer species, depending on the target application. We employ a new strategy for ensuring an efficient encapsulation of the desired isocyanates, which consists of putting together the isocyanate compound for encapsulation and a small amount of a more reactive isocyanate for rapid promotion, competinge in the formation of the polymeric shell. Also, varied active hydrogen sources were tested in this work, with different reactivity and functionalities, such as specific amines and designed silanes, in order to optimize the shell formation kinetics and achieve a higher encapsulation yield. The successful isocyanate encapsulation was confirmed by Fourier transformed infrared spectroscopy using an attenuated total reflectance accessory, thermogravimetric analysis, and differential scanning calorimetry, while the morphology and the microcapsules´ size distribution was assessed with scanning electron microscopy. Peeling strength tests were performed in order to evaluate the adhesive effect of the new adhesive formulations, containing the developed microcapsules, which enabled the study of the isocyanate release and type of failure of the adhesive joint. As a result, these new microcapsules were found to enable a strong adhesion and a structural type of failure of the adhesive joint. Proof-of-concept experiments are shown to illustrate the potential of these microcapsules as crosslinkers in one-component, self-reactive, safer and eco-innovative adhesives for highly demanding applications.

5. Transient Cross-Links in Lactose-Modified Chitosan: Implication for Mechanotransduction

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The conversion of mechanical information from the external microenvironment into intracellular biochemical signaling is termed “mechanotransduction” [1]. The present contribution deals with the effect of the addition of boric acid to chitlac solutions, a lactose--modified chitosan, which had previously shown intriguing features [2]. The binding of the borate ions was investigated in dilute solution by means of circular dichroism, viscometry, dynamic light scattering and NMR. Experimental results revealed a chain—chain association when limited amounts of borate ions are added. However, upon exceeding a borate limit dependent on the polysaccharide concentration, the soluble aggregates disentangle as single chains. Rheological measurements were carried out to study the borate—chitlac system. Experimental evidence highlighted a marked non—linear behavior depending on the amount of cross-linker. Strikingly, the presence of a limited amount of borate ions led to dilatant behavior under steady flow. In addition, strain hardening was detected upon exceeding a critical stress, indicating a transient nature in the formation of the cross-links [3]. The non--linear behavior of chitlac in the presence of borate compared surprisingly well with that shown by proteins composing the natural ECM [4,5], suggesting a possible role of mechanotransduction in the biological significance of chitlac.

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6. Graphene Oxide Modified Chitosan Film Production and Characterization

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Graphene is a two-dimensional carbon-based material, obtained from the low-cost material graphite. It has attracted attention because of its remarkable physicochemical and mechanical properties. Graphene oxide is a graphene derivative with great absorption capacity. Graphene oxide modified chitosan has been used in heavy metal adsorption and wastewater treatment, and it has potential application as biomaterial or packing material.

In this work, graphene oxide was synthesized from graphite by the modified Hummer's method. Chitosan/graphene oxide composite films have been prepared by stirring aqueous solution of chitosan and graphene oxide with different ratios in the presence of diluted acetic acid. It is critical that the polymer matrix has uniform filler dispersion and good interfacial adhesion between the filler and polymer matrix. Because of the interaction between polymer chains and graphene oxide sheets, a good dispersion of graphene oxide occurred in chitosan solution.

Characterization of graphene oxide and composite films has been made by the wide-angle X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetric analysis, differential scanning calorimetry and mechanical test.

7. Polyamide-6 Supported Chitosan Nanocomposite Membranes

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Chitosan (Ch) is a promising membrane material. However, the thermal stability, hardness, and gas barrier properties of Ch are not good enough to meet a wide range of applications. The chemical structure of chitosan, containing multiple functional groups, creates the possibility for new bonding between the chitosan chains and nano-filler particles such as clay (e.g., montmorillonite (MMT)), silica, and carbon nanotubes [1]. Polymer-layered silicate nanocomposites have received great interest over the last few years as a result of the superior properties of these materials compared to conventional composites. Several studies have shown that even a low percentage of layered silicates can lead to a significant enhancement of many properties, such as flame retardance or mechanical properties [2,3].

The aim of this work was to obtain composite and asymmetric membranes from polyamide 6/chitosan/montmorillonite clay nanocomposites. Asymmetric membranes were prepared by using a wet phase inversion process. The morphology of the membranes was investigated by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The separation properties of membranes in pervaporation of water/alcohol mixtures were examined. Binary water/ethanol and water/isopropanol solutions of different composition were used as feed. All pervaporation experiments were performed at 30 °C. The efficiency of separation was described in terms of permeation fluxes, separation factor and pervaporation separation index. The asymmetric membranes from polyamide 6/chitosan/montmorillonite clay nanocomposites exhibit better separation properties compared with Ch/MMT membranes in the dehydration process of both alcohols.

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8. Electrodes Modified with Poly(3,4-Ethylenedioxythiophene) Doped with Sulfonated Polyarylethersulfones: A Combined WAXS and Cyclic Voltammetric Study

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Among Polythiophene derivates, Poly(3,4-Ethylenedioxythiophene) (PEDOT) is one of the most successful conducting polymers due to its excellent environmental stability and high electrical conductivity.

Numerous researches have been conducted on PEDOT synthesis by electrochemical and chemical polymerization of 3,4-Ethylenedioxythiophene (EDOT). Chemical approaches performed by high-concentration water-based emulsion polymerization of EDOT with 2-Naphthalenesulfonic acid as doping agent, produce PEDOT precipitates as dark-blue powders, which are insoluble in water.

In the present work, we have synthesized PEDOTs characterized by high solubility in the chosen reaction solvents (*N*,*N*-dimethylformamide, dimethylacetamide, dimethyl sulfoxide and *N*-methyl-2-pyrrolidone), via a high-concentration solvent-based emulsion polymerization of EDOT.

To improve PEDOT conductive properties, the sulfonated dopants commonly used are 2-Naphthalenesulfonic acid and para-toluene sulfonic acid. Besides these species, also Sulfonated Polyarylethersulfone (SPAES), synthesized via homogeneous synthesis with different degrees of sulfonation (DS), can be used thanks to both the tight control over the DS and the charge separation present in the SPAES structure deriving from the pre-sulfonated comonomer.

The oxidative polymerization of EDOT with SPAES was successfully performed and the resulting polymers were casted onto glassy carbon electrodes; despite the low amount of SPAES used (1% *w*/*w* respect to EDOT), it was found that PEDOT_SPAES electrochemical properties, i.e., voltammetric peak heights, are in general better than those obtained for neat SPAES and for non-doped and commercial PEDOTs. Moreover, this effect is increased as SPAES's DS increases. The chemical structure of PEDOT_SPAESs was studied via wide-angle scattering (WAXS), comparing the crystalline structures of no-doped and commercial PEDOTs, with the amorphous structures of PEDOT_SPAESs. To the best of the authors' knowledge, this is the first time that SPAES was used as PEDOT dopant and that a study, albeit preliminary, of its effect on PEDOT_SPAES structural properties has been performed.

9. A Rational Design of Hydrogel with Electroactive Properties

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A biosynthetic poly-γ-glutamic acid (γ-PGA) has been used as a matrix to produce hydrogel composites with electroactive properties. Poly(3,4-ethylenedioxythiophene) (PEDOT) nanoparticles (NPs) were added to the hydrogel matrix as a nucleation point for the further electropolymerization of hydroxymethyl-3,4-ethylenedioxythiophene (HMeEDOT) monomers. γ-PGA was synthetized using cystamine as a cross-linker and 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide (EDC methiodide) as a condensing agent. PEDOT NPs were prepared by oxidative polymerization in dodecylbenzenesulfonic acid (DBSA) micellar solutions, which acts simultaneously as a surfactant and as a doping agent. The electroactive property was achieved after the treatment of PGA–PEDOT hybrid material with anodic electropolymerization of HMeEDOT in an aqueous solution, with LiClO4 as an electrolyte, and employing polyethylene terephthalate (PET) coated with a very thin layer of ITO as a flexible solid electrode. The new semiconducting hydrogel electrode is envisaged to be used as a sensor to discriminate between eukaryotic and prokaryotic cells determined by cyclic voltammetry experiments.

10. ABS-Based Flame Retardant Microcellular Foams for Automobile Applications

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Acrylonitrile–butadiene–styrene (ABS), owing to its high toughness and impact strength, chemical resistance and good processability, is an engineering thermoplastic vastly used in automobile parts, among others. Nevertheless, one of its drawbacks is its high flammability that limits its suitability in applications with fire retardant requirements. Thus, there is great interest in developing flame retardant formulations of ABS that maintain as much as possible its advantages of low cost, good processability, and high specific mechanical properties.

ABS is commonly used in the manufacture of automobile parts by means of the MuCell® microcellular injection molding process, with reported benefits of reduced cost and cycle time, improved dimensional stability, etc.

The present work deals with the study of flame retardant ABS formulation and the effect of its weight reduction on the ABS fire and mechanical performance. Phosphorus-based flame retardant additives (PFR), aluminium diethylphosphinate and ammonium polyphosphate, were used as a more environmentally friendly alternative compared with halogenated ones. A 25 wt% of such PFR system (1:1 proportion) was dispersed into the polymer melt by using a co-rotating twin-screw extruder. Subsequently, microcelullar foamed ABS and ABS-PFR specimens with 10, 15 and 20% of weight reduction, were prepared by means of MuCell® injection technology.

Overall, it was noticed that the presence of the PFR led to foams with smaller cell size and higher cell density, which was related to a heterogeneous cell nucleation effect promoted by such particles. Furthermore, despite the fact that the presence of PFR particles decreased the impact strength of ABS, they enhanced its specific stiffness determined by dynamic mechanical–thermal analysis. Moreover, the heat-release rate measured by means of a cone calorimeter was notably reduced with the presence of the mentioned PFR system, due to a prominent condensed-phase mode-of-action of such additives on ABS.

11. Acid-Degradable Polyesters Conjugated with Drugs or Corrosion Inhibitors

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The goal of this research was to prepare acid-responsive degradable polymers with active agents in their main chain. Dichlorophene (DC), as an effective anticestodal agent, and 4-(2-pyridylazo)resorcinol (PAR), as a corrosion inhibitor, were modified to form polymerizable bisacrylate derivatives. The derivatives were then copolymerized with aliphatic and aromatic dithiols. Due to the presence of acid-labile β-thiopropionate linkages in the backbone of the polymer chains, the polymers could be degraded gradually in mild acidic medium. The effect of catalysts, solvents, temperature and molar ratios of comonomers was studied to find the optimized reaction conditions. The products were characterized by ^{1}H-NMR spectroscopy and FTIR spectroscopy as well as gel permeation chromatography (GPC). Finally, the degradation and release of active agent from the polymer backbone were studied in acidic and basic conditions. The results showed that the degradation of poly(β-thioether ester) obtained from PAR was faster than the degradation of the polymers derived from DCP, due to the better leaving ability of PAR compared to DCP.

12. Advanced Biobased Polymers from Limonene Oxide

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The development of polymer materials derived from renewable resources for replacement of petroleum-based ones is gaining growing interest both in industry and in the scientific research community. Typically, 80% or more of the manufacturing costs arise from the monomers, which are derived from petroleum. The depletion of fossil resources prompts the search for an alternative carbon supply, such as CO_2, a waste by-product emitted by combustion of fossil fuels and coal-fired power stations, and non-food based biomass.

Terpenes represent a plentiful and inexpensive class of non-polar substrates with enormous potential for the synthesis of bio-based polymeric materials and limonene is the most common terpene. The (R)-enantiomer constitutes 90–96% of citrus peel oil lemons, oranges and grapefruits. Limonene oils are industrially obtained as a by-product of citric fruit juice processing and are then oxidized to form mono- as well as difunctional epoxides. (R)-limonene oxide (LOx) represents an excellent choice as a bio-renewable epoxide monomer for copolymerization with CO_2, thanks to several features such as low cost, abundance, and structural similarity to cyclohexene oxide (CHO).

Here, we present the synthesis of alternating polyesters through the reaction of succinic-, phthalic-, maleic- and norbornyl-anhydrides with LOx and CHO by using salen metal complexes (Metal = Cr, Al, Mn) with different cocatalysts, under various reaction conditions by Ring Opening COpolymerization (ROCOP) as well as the synthesis of polycarbonates based on LOx and CO_2. The resulting polyesters and polycarbonates have been fully characterized by thermal (DSC), molecular (SEC) and microstructural (1H and 13C NMR) analysis.

Acknowledgments: Project n. CARIPLO Foundation “Advanced POLymers from Limonene Oxide as sustainable feedstock-APOLLO” 2017–2019.

13. Aza-Michael Addition as a Selective Tool for the Design of Dumbbell and Dendronized Polyglycerols

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This work explores novel original synthetic routes for the design of dumbbell and dendronized polymers implementing selective aza-Michael additions of diacrylates prepolymers with core-amino-polyglycerols. Thus, Tert-butyl *N*-(2,3-dihydroxypropyl) carbamate is used as a novel precursor for the ROMBP of glycidol, leading to dendrons with molecular weights ranging from 200 to 1600 g/mol and displaying a focal amino functionality. In a second step, the primary amine of the focal group can react twice with two acrylates groups. By controlling the selectivity due to the reactivity difference and to the steric hindrance as well as the stoechiometry, it was possible to prepare in a controlled manner various macromolecular architectures from dumbbell-like structures to dendronized polymers with high molecular weights.

The implementation of such a chemistry allows to control the amphiphilic properties by selecting the constituting blocs and the way to introduce them into the macromolecular architecture. Such marcomolecular systems have been investigated in terms of viscosity behavior in diluted solution as well in bulk in order to establish the structure–properties relationships.

14. Bending under Light Illumination of Liquid Crystal Elastomer: Finsler Geomoetry Modeling

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It was reported that a piece of thin liquid crystal elasomer (LCE) starts to move on the water when it is illuminated by a laser light from up above [1]. The light illumination makes the thin LCE bend and swim on the water. This phenomenon has attracted a lot of attentions because LCE can directly transform the light energy to mechnanical energy. The mechanism of this is qualitatively well understood such that the temperature change makes the LC molecules isotropic or random on the position, on which the laser light is shedding, and this random LC direction is the origin of the bending. However, this phenomenon is unclear from the viewpoint of microscopic interaction, because the interaction of LC molecules and polymers is too complex. We proposed another approach to this problem using the Finsler geometry (FG) model defined on discrete lattices [2]. In this FG model, the complex interaction between LC molecules and polymers is simply replaced by the Finsler metric, and hence it has only a small number of parameters for this interaction [3]. This FG modeling technique was used to analyze several problems such as J-shaped stress–strain curves of biological materials and shape transformation of multi-component membranes [4,5]. In this talk, we show that the FG modeling technique can also be applied to understand the shape deformation of a thin piece of LCE under light illumination.

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15. Biocompatible, Thermoresponsive, and Printable Poly(2-Oxazoline)s Gels

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In recent years, many attempts have been made to develop improved biocompatible gels for different applications such as 3D bioprinting, in-gel printing or injectable drug depots. The placement of different cells within biomaterials into spatially defined structures, better known as 3D bioprinting, is finding increasing interest among engineers, scientists and clinicians [1]. Market research conducted by IDTechEx forecasts that the market for 3D bioprinting will reach $1.8 billion by 2027. With this predicted development and the ever-increasing visions on potential and actual applications, the need for suitable hydrogels can be seen as a potential bottleneck. Our aim is to develop and establish a highly adaptable and biocompatible hydrogel platform based on amphiphilic poly(2-oxazoline)s. In the last decades, they have been intensely investigated especially as thermoresponsive materials and for biomedical applications. Very recently, we introduced a shear thinning, biocompatible and thermoresponsive bioink candidate [2]. Bioinks have to fulfill various requirements such as consistent quality, sufficient quantity and customizable biological and physical properties. However, to broaden the field of potential applications, synthetic versatility is also paramount, as every application or cell type requires different mechanical as well as physico-chemical properties. Also, it is crucial to understand the correlation between nano-/microstructure and macroscopic properties. Here, we report the synthesis of novel thermogelling polymers, their cytocompatibility and structure–property relationships with respect to their rheological properties. Additionally, we present our results regarding cell survival during the printing process. Furthermore, small angle neutron scattering revealed an interesting nanoscopic structure, which will be discussed and compared with other thermogelling polymers-based hydrogels.

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16. Biosensor Platforms for Selective Neurotransmitter Detection

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Two different electroactive and biocompatible graft copolymers, consisting of the conductive polymer backbone [1] (polythiophene or polypyrrole) and randomly attached biocompatible thermoplastics (oligo-ε-caprolactone or polyethylene glycol), have been prepared by anodic electropolymerization using steel, ITO and glassy carbon as working electrodes. The macromonomers and polymeric films were characterized by spectroscopy and microscopy techniques. Additionally, electrochemical and biocompatibility properties were determined to evaluate the sensitivity of the hybrid films to detect dopamine or serotonin neurotransmitters. It was concluded that the optimal co-monomers feed ratio was 80:20 and, in order to obtain homogenous films, high electrochemical generation times were needed to allow the macromonomer migration to the electrode surface in a proper way. The present study shows the benefit of using electroactive graft copolymers for targeted application in bioengineering.

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17. Bringing New Functionalities to Polyesters and Polycarbonates with Isosorbide

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Isosorbide or 1,4-3,6 dianhydrohexitol, derivated from starch and more precisely from sorbitol, is one of the chemical intermediates of interest in the field of thermoplastic materials and for curable resin application. Hence, isosorbide found its place as a monomer suitable for polycondensates synthesis [1] such as polyesters, polycarbonates and thermoplastic polyurethanes. Concerning aliphatic [2] or semi-aromatic polyesters [3], the addition of isosorbide increases glass transition temperature, opening up several usual applications of amorphous polymers to this new polymer. The properties of other thermoplastics such as polycarbonates [4] or TPU can also be improved by the incorporation of isosorbide. The preparation of poly (ethylene-*co*-isosorbide) terephthalate with different ratios of isosorbide will be particularly detailed. The structure–properties relationship will permit a focus on the synthesis of polyesters with semi-crystalline or amorphous structures. The influence of isosorbide on the polymerization, on the processing of the resulting polyester as well as the modification of the final properties will be enlightened.

In polycarbonate, isosorbide is much more than just a solution for Bisphenol A replacement. Hence, Isosorbide-containing polycarbonates present significantly increased properties such as mechanical strength, heat resistance and optical properties with resulting properties between usual Polycarbonate and PMMA.

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18. Cellulose Nanocrystals Prepared in a Deep Eutectic Mixture of Choline Chloride and Urea

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Cellulose is the most abundant and renewable polymer which is widely used in different areas. However, because of its supramolecular structure and high crystallinity, cellulose is insoluble in water and common organic solvents. Ionic liquids (ILs) are intensively studied as a promising solvent for the preparation of different cellulose-based materials [1]. Deep eutectic solvents (DESs) as a green and cheap alternative for ILs have been recently proposed for pretreatment of cellulose during the production of nanofibers [2]. In this work, the possibility of application of DESs composed from choline chloride and urea for direct preparation of cellulose nanocrystals (CNs) from microcrystalline cellulose was studied. The influence of preparation conditions on the structure and morphology of CNs was investigated. Plasticized chitosan-based films reinforced with different content of CNs were prepared and their mechanical properties were investigated. It was found that the addition of 2% of CNs leads to the increasing of film strength from 13 to 28 MPa and Young's modulus from 19 to 76 MPa with no change in elongation at break.

Acknowledges: This work was conducted with financial support from Russian Ministry of Education within State Contract 14.W03.31.0014 (megagrant). The experimental work was facilitated by equipment from the Resource Centre of X-ray Diffraction Resource Centre, Centre for Optical and Laser Materials Research and Interdisciplinary Resource Centre for Nanotechnology of Saint-Petersburg State University.

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19. Conductive Polymer Brushes Based on Ethynyl-Pyridine Monomer

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Conjugated polymer chains grafted to the surface and forming polymer brushes have many advantages over classical polymer films, such as a highly ordered structure enabling directional transport of charges, and covalent attachment of macromolecules that stabilizes the system and facilitates charge injection to and from electrodes. These features are very desirable in electronic devices such as LEDs and photovoltaic cells.

In these studies, we used the self-templating polymerization approach as the formation method of the conjugated polymer chain. Bifunctional monomers containing methacrylate and ethynyl-pyridine groups were used in the synthesis of polymer brushes. In the first step, methacrylate groups were polymerized by surface-initiated photoiniferter polymerization (SI-PIMP) or by surface-initiated atom transfer radical polymerization (SI-ATRP). The formed polymer brushes containing pendant acetylene groups underwent polymerizations in two ways: via activation by quaternization of pyridine rings or using a rhodium-based catalyst. As a result, conjugated ladder-like polymer brushes were obtained exhibiting semiconducting properties. After doping with oxidative agents such as iodine or DDQ, a significant increase of their conductivity occurs. Relations between the molecular structure implied by the type of polymerization, type and level of doping of the formed polymer brushes and their optoelectronic properties were evaluated in this research using spectroscopic (FT-IR, UV-Vis) and microscopic (AFM, conductive-AFM) methods.

20. Custom-Made Surfaces: Tailoring the Isoelectric Point via Modification of Ester-Functionalized Poly(2-Oxazoline)s

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2-Oxazolines can be (co-)polymerized in a single step via the cationic ring-opening polymerization (CROP); poly(2-oxazoline)s are under current investigation for possible applications in medicinal and pharmaceutical areas. The alkaline hydrolysis of ester-functionalized poly(2-oxazoline)s (pEstOx) such as poly[methyl-3-(4,5-dihydrooxazol-2-yl)propanoate]s paves the way to carboxy-functionalized surfaces; extended reaction times (eventually including microwave-assisted reactions [1]) in acidic media also provide cleavage of the amide bonds yielding polyamines. Thiol-ene click-reactions involving side-chain double-bonds like in poly(2-dec-9′-enyl-2-oxazoline) (pDec$^=$Ox) enable the introduction of a manifold of functionalized groups into poly(2-oxazoline)s comprising alcohol functions.

For the preparation of functionalized surfaces, polyolefins may be blended with poly(2-oxazoline)s. In this study, polypropylene was blended with 5 wt.-% of the statistical copolymer pEstOx$_{20}$-*stat*-pDec$^=$Ox$_{80}$ as well as with its derivatives derived from hydrolysis in 1 M NaOH and/or thiol–ene click reactions with mercaptoethanol. To characterize the surfaces of the blends, zeta-potential measurements were used (among others), correlating the surfaces' isoelectric points with the hydrolysis degree (content of carboxylic acid groups) and/or the content of hydroxy groups (introduced by thiol–ene reactions): The surfaces' isoelectric points could be adjusted in the range between pH = 4–6 in a straightforward manner. For surface functionalization, the carboxylic acid groups as well as the hydroxy groups were used in reactions with acyl chlorides.

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21. Design and Characterization of New pH- and Thermo-Responsive Hydrogels Based on Dimethylacrylamide, *N*-Isopropylacrylamide and 2-Oxazoline Macromonomer

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In this research, we study the feasibility of synthesizing a new type of hydrogel which is sensitive to temperature and to the degree of acidity (pH) based on dimethylacrylamide (DMAA), *N*-isopropylacrylamide (NIPAAm) and 2-oxazoline macromonomer. For that purpose, we took as a model the study performed by Cipriano and colleagues at University of Maryland [1], in which the self-cross-linking ability of dimethylacrylamide was demonstrated.

The synthesized hydrogels were structurally characterized by Nuclear Magnetic Resonance (NMR) and infrared spectroscopy (FTIR). The response to temperature and pH was tested by weight measurements versus temperature and degree of acidity, respectively. The transition temperature (LCST) increased with a higher content of macromonomer and was more intense with the increase of NIPAAm. Likewise, the sensitivity to pH was a function of the content of the hydrolyzed macromonomer inside the hydrogel. The rheology behavior of the different hydrogels was determined by mechanical experiments.

At last, these new hydrogels would have potential applications in some fields such as drug controlled release, biotechnology and optics owing to their transparency, good mechanical behavior and sensitivity to pH and temperature.

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22. Design, Synthesis and Properties Investigation of Gradient-Like Block Copolymers

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Gradient copolymers are a class of copolymers whose composition varies along the length of an individual chain. They have shown appealing properties, such as broad glass transitions, which can be useful in shock- and noise-absorbing applications as well as in shape memory materials. Moreover, gradient copolymers have shown potential to act as novel interfacial stabilizers.

Nevertheless, the preparation of copolymers with a well-defined gradient monomer composition requires demanding synthetic procedures, such as complex processes with semi-continuous monomer feeding and constant feedback, to manipulate the copolymer composition at each stage of polymerization.

Gradient copolymers may be considered to be intermediate species between block and random copolymers. Our main interest lies in the ability of these intermediate structures to replicate or approximate the physical properties predicted for ideal gradient copolymers. We hypothesize that a simple block copolymer containing two or more random segments of differing compositions may replicate some of the properties found in gradient copolymers.

To this end, we have designed and synthesized a library of copolymers of identical composition but different structures to test this hypothesis. These tested structures are copolymers with a linear gradient of composition, and block copolymers containing a variable number of statistical segments of constant average composition. The structure–property relationships of the resulting copolymers in terms of their thermal properties and their self-assembly behavior in bulk and in solution were investigated.

23. Development and Characterization of Novel Acrylic-Based Foamable Inks for PolyJet Printing

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Foamable inks for PolyJet printing offer the opportunity to produce lightweight three-dimensional structures. PolyJet printing is an inkjet-based process, where a reactive photopolymer is jetted and cured by UV light, layer by layer, to form a 3D object. One approach to produce foamable inks involves the incorporation of thermally expandable core–shell particles (CSP) containing blowing agent (BA) into a photoreactive acrylate matrix. Foaming is induced through near-infrared lamps after jetting of each layer, followed by immediate UV-curing of the matrix to yield a stable foamed layer.

Another approach is the incorporation of BA into the acrylate matrix. The foaming procedure is in analogy to the previous CSP approach. However, the decomposition of the blowing agent should lead to an open cell foam with interconnected pores.

Besides the development of a jettable formulation, two other aspects are crucial: First, the optimum foaming parameters for producing parts with low density have to be found, while maintaining structural stability. Second, cure characterization of the acrylate matrix is important to allow short printing times. Characterization includes FTIR for curing kinetics and pore analysis by microscopy.

This work has received funding from the European Union’s Horizon 2020 program for research and innovation under Grant Agreement No. 685937.

24. Double Metal Cyanide (DMC) Catalyst mediated synthesis of Hydroxyl-Functional Polyether Copolymers

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Because of its extraordinary properties poly(propylene oxide) (PPO) is produced industrially on a megaton scale. In order to produce polyether polyols based on PPO, the double metal cyanide (DMC) catalyst is widely employed. PPO polyols play a key role in the synthesis of surfactants and flexible polyurethane foams due to their chain flexibility, i.e., low glass transition temperature of -70 °C and their amorphous nature. However, one drawback of PPO is the lack of functional groups at the polymer backbone. One may overcome this limitation by copolymerization of PO with functional epoxides. The highly reactive (DMC) catalyst is a promising system for this purpose. The underlying mechanism can be described as hetero-genous and coordinative. In order to combine linear polyglycerols with the PPO structure, PO was copolymerized with ethoxyethyl glycidyl ether (EEGE), utilizing the DMC catalyst. The copolymerizations were performed in bulk and led to molecular weights in the range of 2300 to 2900 g mol^{-1} and polydispersities (Đ) between 1.16 and 1.22. For the first time, the kinetics and resulting microstructure of the copolymerization were investigated by in situ ^{1}H NMR spectroscopy, revealing a tapered, block-like structure with reactivity ratios of r_{PO} = 14.8 and r_{EEGE} = 0.07. Acidic cleavage of the acetal protective groups of EEGE resulted in free hydroxyl groups at the polyether backbone. Thermal properties were investigated by differen-tial scanning calorimetry (DSC) and revealed amorphous polymers showing two glass transitions (T_g). The free hydroxyl groups were addressed with phenyl isocyanate in a model reaction. The hydrophilic, functional PPO copolymers offer promise for PPO-based structures for surface modification, biomedical purposes and soft segments in functional polyurethanes.

25. Electrically Conductive Polyetheretherketone-Based Filaments for Additive Manufacturing

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The preparation and properties of electrically conductive composites based on high-performance polymers has been the focus of intense research due to their possible applications in, for example, electrostatic dissipation, electrostatic painting, electromagnetic interference (EMI) shielding and lightning strike protection. For space applications, a combination of high electrical conductivity, good mechanical properties and high service temperature may be important. Polymers with aromatic rings along their backbone typically present excellent mechanical properties, high thermal resistance and favor the interactions with graphene-like surfaces such as carbon nanotubes (CNT) and graphite nanoplates (GnP) via π-π stacking. The present work reports the manufacture by melt mixing of an electrically conductive composite containing polyetheretherketone (PEEK), GnP and CNT, its processing into a continuous filament and its use in additive manufacturing. The compositions and processing conditions yielding the higher electrical conductivities were studied. Filaments were obtained by extrusion and the effect of post-extrusion conditions was assessed. Finally, parts printed by Fusion Deposition Modelling (FDM) were characterized by tensile testing, electrical conductivity, optical and electron microscopy.

26. Enhanced Anti-Cancerous Activity of Dual DrugLoaded Core–Shell Nanoparticles Composed of Metal-Free Fully Alternating Copolymer

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In recent years, polymeric nanoparticles have revolutionized the field of biomedical science with the development of novel nano-drug carriers for increasing the solubility and stability of hydrophobic drugs. These nanoparticles have increased the number of nano-drug formulations in clinical trials. The polymeric nanoparticles are generally composed of different types of copolymer, which are synthesized from different monomers using an organometallic catalyst during the ring-opening copolymerization reaction. The metal component of such catalysts is very toxic to healthy cells at its higher concentration. To overcome such toxic effect, we synthesized a metal-free fully alternating copolymer of approx. 9.3 kDa size, composed of *tert*-butyl glycidyl ether (*t*-BGE) and phthalic anhydride (PA). Further, this novel copolymer was used to prepare the single and dual drug-loaded core–shell nanoparticles using doxorubicin (DOX) and curcumin (CUR). The average diameter of these monodispersed nanoparticles ranged between approx. 200 and 300 nm. Moreover, these spherical nanoparticles showed sustained drug release behavior for both drugs in a defined physical environment. The anti-tumor efficacy of these nano-drug carriers was examined on several cancer cell lines of different origin and displayed higher toxicity on MIA PaCa-2 cells with very low IC_{50} value, suggesting the enhanced synergistic action of CUR with DOX drug in an in vitro platform. In addition, these drug-loaded nanoparticles also inhibited the proliferation of MIA PaCa-2 cells due to cell cycle arrest in the G2/M phase that induced apoptosis with increased ROS production and significant changes in mitochondrial membrane potential. Overall, this approach may open up novel avenues for a metal-free fully alternating copolymer in the field of biomedical science such as tissue engineering, biomaterial and drug delivery.

27. Entanglements in Model Polymers: A Hierarchical Simulation Study

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Topological constraints, in the form of entanglements between polymer chains, endow macromolecules with unique dynamical, mechanical and rheological properties [1,2]. We present results from a multi-scale, hierarchical modelling scheme [3] applied on random packings of athermal polymers in the bulk and under confinement. Macromolecules are represented as freely-jointed chains of tangent hard spheres of uniform length; confinement is realized through the presence of flat, parallel impenetrable walls in one or more dimensions [4]. First, we employ off-lattice Monte Carlo simulations [5], built around chain-connectivity-altering moves, to generate and successively equilibrate polymer packings at volume fractions from dilute up to the maximally random jammed (MRJ) state [6,7]. Then, we adopt the Z1 topological algorithm [8] to extract the primitive path (PP) network of entanglements from the corresponding atomistic chains. Present simulations allow to systematically gauge the effect of concentration, chain length, N, and level confinement/cell anisotropy on the salient characteristics of the primitive path network [9]. Finally, we test the general applicability of recently proposed estimators to calculate the entanglement length [10]. We conclude that such estimators provide accurate predictions on the true polymeric behavior from marginally entangled systems once a density threshold is met.

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28. Fluorescent S- and *N*-Containing Donor–Acceptor Polymers with Tuneable Band-Gap Architecture as Volatile Organic Compound Sensors

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Purely organic conjugated microporous polymers (CMPs) are gaining importance as materials for organic electronics, [1] energy storage [2] and photocatalysis [3]. Accordingly, we have previously developed band-gap-tuneable donor–acceptor (D–A) sulfur- and nitrogen-containing polymers (SNPs) as a subclass of CMPs via Sonogashira–Hagihara cross-coupling. Due to the open pore structure, these materials can be easily modified by post-synthetic p-doping with iodine and show good results in photocatalytic water splitting [4]. Here, we used Pd-catalysed Stille coupling to synthesise eight new materials to increase our knowledge about D–A polymers and expand the library of SNPs. As for electron-donor motifs, we used four thiophene-based linkers: thienothiophene (**TT**), dithiophene (**DT**), benzotrithiophene (**BTT**), and naphthodithiophene (**NDT**). On the other hand, triazine ring, a key building block of covalent triazine-based frameworks (CTFs), is known to be a good electron-acceptor. Commercially available cyanuric chloride (**1**) and easy-to-synthesise tris-bromophenyltriazine (**2**) were used as a source of triazine core. The combination of π-conjugated structure and D–A nature allows the control over the optical band-gap in the resulting materials (from 2.28 eV to 2.60 eV). The obtained materials have Brunauer−Emmet−Teller (BET) specific surface area and CO_2 uptake up to 656 m^2 g^{-1} and 2.04 mmol g^{-1} respectively. Moreover, prepared SNPs can be used as fluorescence-on and fluorescence-off sensors for organic volatile compound detection.

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29. Formation and Stabilization of Silver Nanoparticles in the Presence of Cationic Polymers and Copolymers in Aqueous Media

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The development and research of new charged/cationic polymers plays a pivotal role in the creation of a new functional system; on the one hand are nanomaterials and on the other hand is the further development of theories and models to describe the polymer behavior. To further optimize the efficiency and implementation of charged polymer systems, detailed information regarding their molecular and conformational characteristics is indispensable.

A comprehensive study of cationic homopolymer poly(2-aminoethyl-methacrylate)s and ternary copolymer poly(AEMA-*co*-MAEMA-*co*-DMAEMA)stat over a wide range of molecular masses by methods of molecular hydrodynamics and optics was recently accomplished [1,2]. The ability of these cationic homopolymers and copolymers to stabilize silver nanoparticles (NPs) in different media (H_2O, 0.2 m NaOH) using $NaBH_4$ as a reducing agent was demonstrated using a set of the following methods: UV spectroscopy, dynamic light scattering, SEM and AFM.

The kinetics of nanoparticle formation in different conditions was studied by varying NP medias, concentration and component (silver salt and polymer) ratios. By varying the mentioned parameters, the formation of stable NPs was accomplished. Consistent information on the size of NPs was obtained. Thus, conclusions about the influence of the chemical structure and charge of the polymer on the ability of cationic polymers to stabilize silver NPs were formulated. Also, data on the influence of molecular mass on the kinetics of formation of NPs, the stabilizing ability of the polymers and the size distribution of the final nanoparticle was obtained.

Acknowledgements: This research was supported by a grant from the Russian Science Foundation (project No 16-13-10148).

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30. Functionalized Phosphazenes with Immobilized Phenolic Antioxidants for Polyolefin Stabilization

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Background: Polyolefins such as polyethylene and polypropylene are the main components of some of the most widely used plastic materials worldwide. In order to improve and to maintain their mechanical and optical properties, the use of an additive is required. Small amounts of antioxidants are added as stabilizers to the polymers to prevent their degradation during their entire lifetime [1]. The low molecular mass of commercial antioxidants is a drawback, which results in the undesired leaching and migration out of the polymer [2].
Research: One approach to solve this leaching problem is to bind sterically hindered phenols as primary antioxidative stabilizers to cyclic phosphazene as well as to linear polyphosphazenes. Two different types of polyphosphazenes were produced. One polymer type was fully substituted with the stabilizer and the other polymer type contained an additional substituent to enhance the compatibility of the antioxidant (AO) with the polymer. All phosphazene-based antioxidants were characterized and their stabilizing effects were determined using DSC. Additionally, the hydrolysis resistances of the phosphazene-based antioxidants were determined in water at different temperatures. Recent results of this innovative approach using polyphosphazene carriers for AOs are presented.

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31. Hydrogel Formation via Photocrosslinking of Poly(Glycerol-*co*-Glycidyl Cinnamate) Copolymers

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Glycerol (G) can be considered as an ethylene oxide (EO) derivative with an additional hydroxyl group. Its multi-hydroxy functional polymers, the linear and hyperbranched polyglycerols, represent biocompatible and highly hydrophilic materials. Polyglycerols are structurally similar to poly(ethylene glycol) (PEG), albeit with functional groups at the polyether backbone. Linear polyglycerol structures can be generated when using suitable protective groups for glycidol, such as acetal groups in the case of ethoxyethyl glycidyl ether (EEGE) to prevent hyperbranching. Glycidyl cinnamate (GC) is the glycidyl ester of cinnamic acid and is characterized by its bifunctionality: it provides both a reactive epoxy and photosensitive cinnamoyl group.

GC and EEGE were copolymerized via the monomer-activated anionic ring-opening polymerization. Copolymers with molecular weights in the range of 2600 to 4400 g mol^{-1} and narrow polydispersities ($Đ$) around 1.20 were synthesized. Studies of the microstructure by in situ ^{1}H NMR kinetic measurements revealed a gradient-like distribution ($r_{EEGE} = 0.2$; $r_{GC} = 2.9$) of the (co-)monomers. The acetal protective groups of EEGE were cleaved without affecting the GC ester bonds (M_n = 1900–3700 g mol^{-1}). Thermal properties were investigated by differential scanning calorimetry and revealed a systematic increase in the glass transition temperature with increasing GC content. P(G-*co*-GC) copolymers were crosslinked by UV irradiation to generate hydrogels. The hydrogels were characterized according to their water uptake and via infrared spectroscopy.

P(G-*co*-GC) copolymers are promising materials for biomedical applications, for instance, for the delivery of pharmaceutically active agents.

32. Hydrogels Based on Poly(ethylene glycol) Obtained by Thiol–Epoxy Click Polymerization: Synthesis, Characterization and Functionalization

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Nowadays, multiple separation, absorption, contaminant removal and controlled drug release techniques are based on the use of macro porous polymer matrices. Given this situation, the idea of obtaining materials, especially hydrogels, that can adapt their removal, exchange or absorption capacities for specific substances, has become of great interest. This research attempts to confirm three main hypotheses: first, that the application of the click chemistry leads to the formation of hydrogels with secondary hydroxyl groups that may be functionalized. Second, that this functionalization could be done through simple esterification reactions. Finally, that the net structural characteristics and the functionalization will determine the absorption and liberation capacities of the material. With this hypothesis to be confirmed, the main objective of this research is to design poly(ethylene glycol) gels based on epoxy–thiol reactions, and their posterior functionalization; this will lead to the generation of materials for different specific applications.

Different methods were used during this investigation. The thiol–epoxy reaction was followed by FTIR spectroscopy. Once the gel was formed, the swelling rates were calculated by quantifying the change in weight suffered by the material when it was immersed in different solvents. The gel was functionalized by the immersion of the material in different solutions with stearic acid, and a range of solvents that were chosen according to the previous analysis of the swelling rates. The obtained material was studied by DSC and TGA, with the aim of analyzing the effect of the stearic acid and the different solvents on the material properties. Measures of the contact angle with the goniometer and analysis of ATR-FTIR were also performed to determine whether the functionalization was effective. Even though several tests were run, the confirmation of a successful functionalization has not been achieved yet.

33. Induced Ionization and Core–Shell Structure Formation in Star-Like Weak Polyelectrolytes

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The addition of COSAN (cobalt bis(1,2-dicarbollide)), anionic amphiphil, causes macroscopic precipitation of PS-PVP star-like micelles. Coarse-grained molecular simulations can explain this phenomenon on the molecular basis. Here, we employ the Hybrid Monte Carlo method, which combines Molecular dynamics and Monte Carlo to efficiently explore the phase space. We use the reaction ensemble, which enables us to sample weak polyelectrolyte ionization states. We set up the system of a weak polyelectrolyte star (20 arms, each arm 50 segments), interacting with hydrophobic counterions. Hydrophobic counterions accumulate in the star center, where they induce and stabilize the ionization of the star segments. The star collapses and forms a core–shell structure with ionized star segments and hydrophobic counterions in the core and non-ionized star segments in the outer shell. Therefore, we observe a steep decrease of the star size at the critical point of the addition of hydrophobic counterions. This corresponds to the observation of abrupt macroscopic precipitation of the PS-PVP micelle system upon addition of a critical amount of COSAN.

34. Investigation on Quantitative Nanomechanical Properties and Structure of Composite Based on the Polyheteroarylene Matrix and ZrO_2 Nanostars

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Aromatic heterocyclic polyimides and their composites are promising materials due to their superior chemical stability, good mechanical properties and excellent thermal stability. In this work, the polyheteroarylene nanocomposites modified with ZrO_2 nanostars were synthesized. The resulting films were investigated using a novel atomic force microscopy imaging mode, known as PeakForce quantitative nanomechanical mapping (PeakForce QNM). This method allows the quantitative mapping of the local mechanical properties, such as adhesion and elastic modulus, together with the topography of the polymer matrix near the polymer–inorganic boundary. The influence of ZrO_2 nanoparticles on the structure of the polyheteroarylene matrix was also studied with wide-angle X-ray scattering and scanning electron microscopy.

Acknowledgments: This work was supported by the Russian Science Foundation (RSF), grant 16-13-10164: Maria Sokolova, Michael Smirnov, and Alexander Toikka acknowledge the RSF for support in the synthesis of membranes, studies of their structural characteristics and analysis of results. Alexander Bugrov acknowledges St. Petersburg State University for the postdoctoral fellowship (grant 12.50.23.2014). Valentin Svetlichnyi acknowledges RFBR (No 18-03-00568 A). The experimental work was facilitated by the equipment of the Resource Center of X-ray Diffraction Studies and Nanotechnology Interdisciplinary Resource Center at St. Petersburg State University.

35. Investigations of the Magnetodielectric Effect in Magnetorheological Elastomers

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Recently, the interest in obtaining materials with a large magnetodielectric effect has greatly increased due to their potential applications in novel devices such as tunable filters, four-state memories, magnetic sensors, and spin-charge transducers. We have experimentally studied the magnetodielectric properties of magnetorheological elastomers in stepwise time-varying DC magnetic fields at room temperature. These composite materials contain micrometer-sized iron particles dispersed in compliant elastomer matrices. The ferromagnetic filler particles can rearrange in external DC magnetic fields. This leads to significant modulation of their physical properties. It is found that the imposition of a magnetic field significantly increases both the effective dielectric constant of these composite materials as well as their effective conductivity. These magnetodielectric effects are more pronounced for larger concentrations of soft-magnetic filler particles and softer elastomer matrices. The largest observed relative change of the effective dielectric constant in the maximum magnetic field of about 0.6 T is of the order of 1000%. In particular, we measured the largest, to the best of our knowledge, magnetodielectric effect in polymer-based composite materials at room temperature. The largest observed absolute change of the loss tangent is approximately 0.8. The transient response of the magnetodielectric effect to step magnetic-field excitations is studied in dependence on the step amplitude. A significant hysteresis of the magnetodielectric effect on the externally applied magnetic field is observed. The findings are attributed to the rearrangement of ferromagnetic filler particles in external magnetic fields.

36. Shear Modulus of Magnetorheological Elastomers in the Theoretical Framework of the Single-Particle Magnetostriction Mechanism

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Magnetorheological elastomers (MREs) are composite materials where micrometer-sized ferromagnetic particles are dispersed in a non-magnetic compliant elastomer matrix. A single-particle mechanism of magnetostriction in MREs is described, which involves the rotation of soft magnetic, mechanically rigid particles with uniaxial magnetic anisotropy in magnetic fields [1]. The notion of a single-particle mechanism means that the total magnetic anisotropy energy of the filling particles in the matrix is the sum over single particles. The effect of matrix deformation is clearly pronounced if the magnetic anisotropy coefficient K of particles is much larger than the shear modulus μ of the elastic matrix. An external magnetic field introduces torques on magnetic filler particles, creates mechanical stresses in the vicinity of inclusions, induces shear strain and increases the effective shear modulus of these composite materials [2]. Obtained theoretical results compare well with known experimental data. The concentration dependence of the effective shear modulus at higher filler concentrations has been estimated using the method of Padé approximants, which predicts that both the absolute and relative changes of the magnetic-field-dependent effective shear modulus will significantly increase with the growing concentration of filler particles [2]. The relation of the magnetorheological effect in MREs to the phase transition of the second order is discussed.

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37. Ionic Complexes of Polyacids with Low-Molecular Weight Organic Oligoamines as Cross-Agents

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All ionic polyelectrolyte complexes (polyelectrolyte-surfactant and interpolyelectrolyte complexes) should be insoluble in water; this is necessary to locate drugs inside the particles of these complexes and for their subsequent release. Polyelectrolyte complexes with low-molecular weight organic counterions have hardly been investigated, because polyelectrolytes do not form a water-insoluble product with the majority of simple organic counterions.

This work deals with the study of the interaction between carboxylic and sulfonic acid polyelectrolytes with specially designed oppositely charged low-molecular weight oligoamines, differing from each other in terms of hydrophobicity, number and pK_a of charged groups and other parameters. We used oligoethylene oligoamines as ionic cross-linkers and we have designed cationic counterions based on natural amino acids, and alcanoyl dicholines. Polyacrylic acid and poly-2-acrylamido-2-methylpropanesulfonic acid (PAMPS) were used as polyelectrolytes. Turbidimetry titration of aqueous solutions of polyelectrolytes with oligoamines was used as a main method to detect the formation of water-insoluble products.

Ethylene and hexamethylene diamines do not form insoluble products, whereas diethylenetriamine, triethylenetetramine and tetraethylenepetamine do form the products.

Besides, we have found that the most hydrophobic di- and tetramines based on amino acids (decamethylene diglycinate, decamethylene divalinate, and decamethylene dilysinate) are able to form water-insoluble products which precipitate on the bottom of a cuvette forming transparent gel-like films with all polyacids. It is interesting to note that sebacoyl dicholine does not form an insoluble complex with PAA-2000, but forms it with PAA-450000 and PAMPS.

The resulting products, if formed, were studied by NMR and IR spectroscopy, X-ray, SEM, and AFM.

The disassembly rate of the ionic complexes was investigated depending on pH and ionic strength.

38. Linear-Hyperbranched Hybrids and Dendronized Polymers Implementing RAFT Techniques and Specifically Designed Functional Hyperbranched Polyglycerols

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In the past few decades, due to the tremendous progress in controlled/living polymerization techniques, a large number of complex polymer architectures have been successfully synthesized including star polymers, graft polymers and/or dendrimers. Within these complex macromolecular architectures, block copolymers remain a topic of great interest, especially when combined with the hyperbranched polymer block.

In this work, several new block copolymer architectures including the hyperbranched polymer block were prepared thanks to the successful synthesis of a new multifunctional chain transfer agent (CTA). This new CTA, fully characterized thanks to ^{1}H NMR and ^{13}C NMR, was designed to integrate a polyol moiety while allowing the controlled polymerisation of various monomers. This specific structure allowed to prepare a wide library of copolymers through the reversible addition-fragmentation transfer (RAFT) polymerization of different types of acrylate and acrylamide monomers, including an acrylamide hyperbranched polyglycerol macromonomer, in a controlled fashion. Then, the polyol end-group was used in some cases to initiate the ring-opening polymerization (ROP) of glycidol to achieve a hybrid copolymer structure presenting a linear block copolymer and a hyperbranched polymer block. These polymers were characterized by means of ^{1}H NMR, size exclusion chromatography (SEC) and diffusion ordered spectroscopy (DOSY NMR).

One of the interesting aspects of such complex macromolecular architectures is their physico-chemical properties. Indeed, they are not only able to self-assemble in aqueous media to form different kinds of nano-objects (micelles, nanoparticles, vesicles) but also able to self-assemble on surfaces and thus present interesting nano-patterning properties.

39. Mechanism of Charge Storage in Electroactive Porous Hydrogels Based on Polyaniline Doped with Polyacid

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Supercapacitors have attracted much attention in recent years as promising devices for energy storage. Electroactive organic polymeric hydrogels are among the interesting candidates for application as electrode materials due to their unique physico-chemical properties and sustainability. In this work, we present an investigation of the mechanism of charge storage in hydrogels based on polyaniline doped with polyacid. The pseudocapacitance and double layer capacitance of materials prepared in different conditions were investigated with a number of electrochemical techniques. Trasatti's method of deconvolution of charge storage contributions based on the dependence of capacitance on scan rates at cyclic voltammetry measurements was used. The results were compared with data obtained by electrochemical impedance spectroscopy at different potentials and chronopotentiometry. Overall specific capacitance of electroactive hydrogels, as measured by the galvanostatic charge–discharge method, was found to be in the range 400–600 F/g, depending on the preparation conditions. The structure of prepared materials was investigated with scanning electron microscopy and wide-angle X-ray scattering.

Acknowledges: This work was supported by the RFBR (research project No. 18-03-01167-a). The experimental work was facilitated by equipment from the Resource Centre of X-ray Diffraction Resource Centre and Interdisciplinary Resource Centre for Nanotechnology of Saint-Petersburg State University.

40. Molecular Mechanisms of the Formation of the Composite Material Based on Chemical-Modified Cellulose and Calcium Phosphates. Molecular Dynamics Simulation

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Composite materials based on bacterial cellulose and calcium phosphates have perspective use as materials for bone implants; this is primarily due to their collagen mechanical properties which are similar to those of bacterial cellulose. To enhance the interaction between the mineral and organic phases, cellulose can be chemically modified by replacing the primary hydroxyl groups by groups that can undergo ionization in an aqueous solution. The most common modification for this purpose is phosphorylation.

In order to obtain properties of the composite material similar to those of bone tissue, the materials are often produced by mimicking the natural process of mineralization by soaking an organic matrix in solution-simulated body fluid. However, the material obtained by such an approach has heterogeneous distribution of the mineral phase on the cellulose surface. Typically, to achieve more homogenous distribution, the organic matrix can be preliminarily placed in calcium chloride solution. It is assumed that, in this case, the calcium ions adsorbed by the active groups on the surface of the matrix serve as centers for the crystallization of the minerals.

To give insight into the molecular mechanisms of the mineralization of phosphorylated cellulose, we performed molecular dynamics simulation of the phosphorylated cellulose models (with two different phosphorylated rates) in two types of solution ($CaCl_2$ solution and solution of the mixture of two salts $CaCl_2$ and NaH_2PO_4). The results of the simulation showed the difference in the mineralization methods in the different solutions. In the case of calcium chloride solution, adsorption of ions occurred ion by ion while in calcium phosphate solution ions are absorbed regularly as a part of clusters. This result showed the need of preliminary soaking in calcium chloride solution to obtain composite materials with better mineral coating.

41. Morphological and Tribological Properties of PMMA/Halloysite Nanocomposites

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From a cost perspective, research in recent years has focused on finding new additives, especially developed to improve the scratch resistance of plastics for the automotive industry, by blending directly into the polymer mass, eliminating the need for coating or painting. The tribological properties of polymers are generally improved with the addition of reinforcing and/or lubricating fillers. To achieve large improvements in stiffness and/or strength properties, important for scratch resistance (in terms of residual scratch depth), whilst keeping as many as possible of the other properties, nanoreinforcing additives are increasingly used. Holloysite nanotube (HNT), due to its unique structure, can be uniformly dispersed in a polymer matrix, resulting in a significant improvement in the polymer properties. Relatively very few studies have focused on nanoscratch damage in polymer nanocomposites.

In this paper, the relationship between morphological/structural (XRD, TEM, FTIR) and tribological (friction) properties of PMMA nanocomposites is discussed. In dynamical conditions by the melt processing method, nanocomposites with 2 wt.% HNT or HNT modified with *N*,*N*′-ethylenebis(stearamide) (EBS) were obtained. The dispersion of nanoparticles and their interaction with the PMMA matrix influence the behaviour of nanocomposites to nanoscratching (penetration depth and damage). Functionalization of HNT with EBS improves the dispersion of nanoparticles in the polymer matrix by increasing their interfacial compatibility through hydrogen bonding established by amide groups with silanolic and siloxane residues. The increased interfacial adhesion further improves the nanocomposite scratch resistance. The PMMA/HNT-EBS nanocomposite has a lower coefficient of friction and lower scratch penetration depth than PMMA/HNT nanocomposite.

Acknowledgement: Financial support by the EU Commission through Project H2020-686165-IZADI-NANO2INDUSTRY is gratefully acknowledged.

42. New Routes to Dendronized Polymers via Radical Polymerizations and Aza-Michael Addition Using Functionalized Hyperbranched Polyglycerols

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Dendritic polymers have attracted increasing interest since 1990 due to their nanometer-size and multifunctional macromolecular branch-on-branch architectures that lead to exceptional physical and chemical properties. Among them, hyperbranched polyglycerols display fascinating properties due to their peculiar and tunable macromolecular architecture [1,2]. These features make them valuable as polymeric nanotools in various technical areas such as drug delivery systems [3]. Recently, Frey et al. introduced new protocols to design new complex branched architectures such as dendrigrafts and hypergrafts [4,5]. In this paper, we explore several original routes to obtain dendrigrafts or dendronized polymers as well as linear-dendric hybrids implementing “grafting through”, “grafting to” and “grafting from” strategies as well as coupling methods for the design of such complex macromolecular architectures. Thus, dendronized polymers can be prepared via free radical polymerization or controlled radical polymerization (RAFT) of core-(meth)acrylated hyperbranched polyglycerols but also by selective aza-Michael poly-addition of core aminated polyglycerols and diacrylates.

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43. New Self-Assembling Copolymers via Polymer-Analogous Transformations in a Microwave Reactor for Skin Care Applications

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Currently, there is a strong need for novel functional products that realize skin thermal comfort, skin anti-ageing and skin natural antimicrobial control. These should have both an increased efficiency and cost benefits compared to the currently available products. A recently developed innovative nano-encapsulation technology (patented) makes use of specific materials' in situ self-assembly capabilities which opens pathways to fulfill these needs.

The high potential for using microwave irradiation as an alternative to heat source is unquestionable. The high velocity of chemical reactions, high yield of products, reduction of side reactions, very fast homogeneous heating, etc., are the most prominent advantages of this method.

In the present work, we have investigated classic and microwave routes of polymer-analogous transformations of nano-shell building copolymers containing maleic units (anhydrous, acidic and partial alkylester) in the main chain structure for nano-encapsulation of phase change materials (PCMs) for potential application in thermal comfort textiles and garments.

For improvement of the self-assembling ability of copolymers, Dodecanol-1, Octadecanol-1 and Dodecylamine-1 were used as modification reagents. Esterification or amidation reactions were carried out in ethanol medium in the presence of certain copolymers and appropriated alcohol or amine. Control of the reactions was carried out by IR-spectroscopy and titration (determination of the acid value).

The modified polymers self-assembled in NCs using the new in situ self-assembly nanotechnology. These NCs were characterized by the dynamic light scattering technique in terms of stability and particle size distribution, and compared to the reference polymer. The influence of the synthesis method on copolymers' properties is discussed.

Acknowledgement: SKHINCAPS project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 685909.

44. A Modular Approach to Double Hydrophilic Block Copolymers and their Self-Assembly

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Block copolymers have been in the focus of polymer science for a long time, e.g. amphiphilic block copolymers were utilized to form micellar or vesicular structures in aqueous solution.1 Nevertheless, self-assembly in aqueous solution beyond amphiphilic block copolymers is possible as highlighted in the present contribution. More specifically, the self-assembly of completely water soluble double hydrophilic block copolymers is shown.

A versatile route to double hydrophilic block copolymers is the modular synthesis via copper catalyzed azide alkyne cycloaddition (CuAAc). For the formation of nano- to micro-scale aggregates from completely water soluble block copolymers the choice of blocks and their respective volume ratios is essential. The self-assemblies are formed due to significant differences in the hydrophilicity of the blocks and their distinct affinity to water, i.e. the hydrophilic effect.2 Implementation of a modular approach allows easy assessment of ideal block combinations for self-assembly. Therefore, various building blocks were synthesized and combined, e.g. poly(N-vinylpyrrolidone), poly(ethylene oxide), poly(2-ethyl-2-oxazoline), poly(oligo ethylene glycol methacrylate) or poly(saccharides).3-7 Finally, the building blocks were coupled and self-assembly investigated via dynamic light scattering as well as cryo scanning electron microscopy.

In summary, we present a modular approach based on CuAAc for the synthesis of double hydrophilic block copolymers to study self-assembly behavior in water with respect to block type and molecular weight.

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45. Polymeric Systems Capable of Carbon Dioxide Sequestration

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Carbon dioxide is one of the main greenhouse gases. Atmospheric CO_2 concentration has increased by almost 150 ppm since its preindustrial level (280 ppm). This increase in gas content has affected the development of chemical and physical methods for more efficient CO_2 sequestration. In the literature, there have been reports concerning the application of polymers bearing free amino groups as absorbent materials, where the control of the gas absorption/desorption process is performed on the basis of changes in humidity environment. This is a promising alternative to industrial systems which allows the selective absorption of CO_2 [1,2].

The aim of this work was to investigate the CO_2 absorption/desorption ability of the polyglycerols containing amine groups. The absorption/desorption processes were performed on the basis of temperature changes.

The time required to saturate the material with carbon dioxide and time required for its desorption, as well as the condition under which these processes are undertaken, and the stability of the polymers were characterized.

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46. Polymerization of Innovative Materials Using Organocatalysis

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PET is one of the most popular polymers on the market, which has led to an increase in the production of this material, resulting in the accumulation of non-biodegradable waste in ecosystems, causing a high environmental impact. This problem demands the development of a PET with, to the greatest possible degree, a biodegradable chemical structure, without damaging the good properties offered by PET, and while maintaining economic viability. An innovative, sustainable and efficient strategy could be to incorporate biodegradable zones in the PET, maintaining the good properties of the material. In response to the above, one option is to copolymerize the PET with biodegradable polymers that give the PET a certain degree of biodegradability. Copolymers of PET with polylactide (PLA) can be formed, where PLA is a biobased and biodegradable polyester produced from biological or renewable sources [1–3]. Additionally, one way to reduce the environmental footprint of the synthesis of biodegrable polymers is the use of organocatalysis, because these catalysts are considered less toxic than metal-based catalysts.

In this work, innovative materials based on PET and PLA were synthesized using organocatalysis and subsequently characterized. Different PET/PLA compositions have been prepared and the properties of each one have been investigated.

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47. Polyolefin Thermoplastic Elastomers from Olefins Chain-Walking Polymerization: Synthesis, Structure and Properties

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This work reports the polymerization of 1-octene, 1-decene and 1-octadecene to yield semicrystalline, branched poly(ethylene)-like materials with high molecular weight and narrow molecular weight distribution. The polymerization of olefins was catalyzed by the diimine Ni(II) complex $[(ArN)C(CH_3)\text{-}(CH_3)C(NAr)]NiBr_2$ [Ar = 2,6-$(i\mathrm{Pr})_2C_6H_3$] in combination with Et_2AlCl. The effect of monomer length on the activity, selectivity of monomer insertion and polymer microstructure was investigated. The polymers were characterized by ^{13}C NMR for quantification of the total branching level and branch-type distribution. The numerous combinations of monomer insertions and chain-walking paths afford polymers with unique microstructure and properties, depending on the monomer length. The thermal properties and crystallinity of the polymers are strongly controlled by their microstructure: the presence of long branches interferes with the crystallization and melting behavior. The low melting temperature and broad melting range of 1-octene and 1-decene polymers are attributed to the fringed-micellar crystal structure with a broad size distribution. while *Â* the structural data and melting behaviour of 1-octadecene polymer evidence the presence of a lamellar structure. A comprehensive investigation of the mechanical behaviour of the polymers by means of uniaxial stretching until failure, step-cycle and creep tensile tests was carried out. Overall, the resulting polymers exhibit a broad spectrum of tensile properties, depending on their microstructure and crystallinity. 1-Octene and 1-decene polymers behave as elastomers with excellent mechanical properties, i.e., high elongation at break (up to 1500%) and good strain recovery, while the 1-octadecene polymer behaves as plastomers.

48. Porous Membranes based on Polypropylene–Ethylene Copolymers. Influence of Temperature on Extrusion, Annealing and Uniaxial Strain Stages

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Block and random copolymers of polypropylene–ethylene were selected to prepare porous membranes through the melt extrusion-annealing-uniaxial stretching technique (MEAUS), at a constant draw ratio. In some cases, these copolymers were blended with a homopolymer grade. The variation of temperature in the stages of extrusion, annealing and uniaxial strain was analysed. Several characterization techniques were employed to study this influence. The crystalline orientation was analysed by polarised infrared spectroscopy (FT-IR) and crystalline features were studied by Differential Scanning Calorimetry (DSC). The thermal stability of the membranes was checked through thermogravimetric analysis (TGA). Tensile tests were performed to ascertain the stiffness and ductility of the produced samples. The results were correlated with the porous morphology, global porosity and permeability to air. A close relationship was found between crystalline characteristics, porous morphology and the trends registered. An improved pore distribution along the membrane surface was found when copolymers were employed.

49. Properties of $CaCO_3$ Nanofiller in PEHD Polymer

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In this work, polyethylene/calcium carbonate (HDPE/$CaCO_3$) composites were prepared and characterized. Polyethylene nanocomposites containing 10–30 wt. % of $CaCO_3$ and HDPE with MFI (0.550 g/10 mn) were prepared with the co-extrusion process using extruders type Cincinati 90D**.** The different samples were characterized by FTIR and morphological observations. Thermal and mechanical studies were also made in order to determine the parameters for obtaining a material (corrugated pipe) with optimal properties. It was found that a much better dispersion of $CaCO_3$ was in the 20% samples. The addition of 30 wt. % $CaCO_3$ increased the thermal stability of PEHD at around 20 °C, decreasing the processing temperature of composites at 15 °C. Regarding the mechanical tests, the ring stiffness of the composites decreased with the addition of $CaCO_3$. According to the obtained results, we suggest that HDPE/$CaCO_3$ composites could be used in pipe production where tensile strengths higher than 25 MPa are not required and for service temperatures between 30 °C and 70 °C.

50. Replacement of Petroleum-Derived Diols by Bio Polyols in One-Component Polyurethane Foams

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This work reports on the development of eco-innovative rigid one-component polyurethane foam systems (OCF), by using bio polyols derived from waste biomass, obtained from liquefaction of cork powder residues and eucalyptus bark residues. This effort enables more sustainable materials and residue valorization, but also a reduction of the dependency on petroleum derivatives. Low-value industrial cork powder residues and eucalyptus bark shreds were successfully liquefied into high added value bio polyols, by a process based on acid-catalyzed liquefaction, at atmospheric pressure, with conversion ratios ranging from 58 to 79%. The obtained bio polyols exhibited low acid values (1 mg KOH/g) and relatively high hydroxyl numbers (272–280 mg KOH/g) and were introduced into OCF formulations, fully replacing the petroleum-derived polyether and polyester diols, present at the OCF formulation. The obtained rigid polyurethane foams exhibited a high output (16 g/s) and acceptable physical quality, assessed by optical and scanning electron microscopy. Their chemical structure, mechanical and thermal properties were assessed through Fourier Transformed Infrared Spectroscopy using an attenuated total reflection accessory, compression mechanical testing, and thermogravimetric analysis, respectively.

51. Structure Formation in Nanophase-Separated Polymers with Lamellar Morphology

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Comb-like polymers with rigid backbones and flexible alkyl side chains form an interesting class of functional materials which find potential applications in organic semiconductor light emitting diodes, electrolyte fuel cells and light-weight composites. Similarly, precision polymers incorporating functional groups placed regularly along a linear chain composed of methylene units synthesized by the ADMET polymerization method have received a lot of attention recently. Both these classes of polymers often exhibit lamellar morphology due to the nanophase separation of longer methylene sequences and ring-like sub-units on length scales of 1–3 nm. Here, we present a comparative study focusing on structural features and the packing state of alkyl nanodomains in different comb-like polymers like alkoxylated polyesters (PPAOTs) and alkoxylated polyphenylene vinylenes (AOPPVs) with varying side chain lengths (C = 6–12) as well as precision polymers incorporating a 2,6-diaminopyridine group (PDAPS) with different spacer lengths (16–20 CH_2 units) by X-ray diffractometry. The packing states of alkyl nanodomains are classified by quantifying the volume occupied per CH_2 unit (V_{CH2}) based on the crystallographic unit cell analysis. This approach works without additional assumptions regarding the inter-digitation or tilting of ideally stretched chains commonly used in other structural models. While AOPPVs show clear indications of a densely packed, crystal-like packing of the methylene sequences in alkyl nanodomains, PPAOTs show two polymorphs (A and B) with either crystalline or amorphous alkyl nano-domains depending on the thermal history and side chain lengths [1]. Interestingly, the investigated PDAPS polymers show indications of disordered alkyl nanodomains [2].

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52. Supported Cu^0 Nanoparticles Catalyst for Controlled Radical Polymerization Reaction and Block-Copolymer Synthesis

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The synthesis of Cu^0 nanoparticles on different supports and their activity in controlled living radical polymerization processes is presented. The type of support influences the final size of the copper nanoparticles as well as their adhesion to the support. These aspects have a direct influence on the characteristics of the polymers obtained. The best results were obtained for SiO_2 particles, which afforded a good molecular weight distribution (Mw/Mn = 1.25). The activity, recovery and recycling of the catalyst was explored for the ultrafast polymerization reaction of butyl acrylate. Further, the terminal bromine reactivity was used for the synthesis of a block poly(n butyl acrylate-block-styrene). The influence of ligand type on the control of the reaction was studied. Also, a straightforward polymerization procedure without any ligand afforded a polydispersity value of 1.38.

53. Surface Plasmon Resonance-Based Sensors for Detection of Aflatoxin

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Aflatoxins, among the most important mycotoxins, are highly toxic and carcinogenic secondary metabolites produced by fungal species such as *Aspergillus flavus* and *Aspergillus parasiticus*. These organisms contaminate agricultural products and produce aflatoxins B_1, B_2, G_1, and G_2. Animals that ingest food contaminated with AFB_1 and AFB_2 can hydroxylate these aflatoxins and yield dairy products contaminated with Aflatoxins M_1 (AFM_1) and M_2 (AFM_2). They have been listed as group I carcinogens by the International Agency for Research on Cancer (IARC), primarily affecting the liver. The molecular imprinting technique has been extensively applied in the preparation of polymer materials able to recognize small molecules in recent years. The methodology mainly depends on molecular recognition. It is a type of polymerization which occurs around the interesting molecules, known as a template, and creates specific cavities in the highly cross-linked polymeric matrices.

In this study, the AFM_1-imprinted SPR sensor was developed. The molecularly imprinted nanofilms on the SPR gold surfaces are prepared via UV polymerization reactions, which consist of *N*-methacryloyl-l-phenylalanine as a functional monomer. An SPR sensor was characterized by using FTIR, AFM, ellipsometry and contact angle measurements. The aflatoxin-imprinted SPR sensor was successfully applied to a milk sample for the determination of aflatoxin with high sensitivity and selectivity.

The real-time measurements on the SPR sensor provide a detection range from 0.003 to 2.0 ppb. Kinetic, isotherm, and selectivity studies with SPR sensors have been carried out for both an imprinted and non-imprinted sensor. The AFM1-imprinted sensors are easy to perform and show high sensitivity and cost effectiveness due to their reusability. Real-time and fast measurement, high sensitivity and specificity, and no need for labeled reagents are the unique properties of SPR sensors.

54. Synthesis and Characterization of New Conjugated Polymers for Solar Cell Applications

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Organic photovoltaics technology has attracted a great deal of research interest as a cost-effective alternative to current solar cell technologies. A new series of conjugated polymers for solar cell applications have been made and will be presented in this work. Benzothiadiazole (BT) moiety was used as an acceptor unit for the preparation of a range of polymers with naphthalene, anthracene and pyrene units with a varying number of thienyl groups as donor units. To increase the solubility of the targeted polymers, branched alkyl chains were attached to the donor moieties. The UV-visible studies showed that the band gap of the prepared polymers varies between 1.71 eV and 2.10 eV. The introduction of fluorine substituents on the BT moieties was investigated and resulted in both the HOMO and LUMO levels of the polymers being lowered according to the cyclic voltammetry (CV) studies. The optical and electronic properties of these novel materials are presented and discussed in this work.

55. Synthesis and Characterization of the Cross-linked PLA-PEG-PLA Triblock Copolymer

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The polylactide-polyethylene glycol-polylactide PLA-PEG-PLA block copolymers are biodegradable amphiphilic copolymers, widely used in the biomedical field (suture threads, matrix for the controlled release of the active ingredients, medical implants, probes, catheters, etc.) [1] and in food packaging. The conventional methods for synthesizing this type of copolymer consist in the use of metal alkoxide type catalysts (e.g., tin octanoate) which are toxic and require costly purification operations for the total elimination of the reaction product. In this work, we use a green catalyst based on natural clay (Maghnite), carillonnement type, to catalyze the synthesis reaction of PL-PEG-PLA copolymers. Maghnite has been used as a nonpolluting green catalyst in several vinyl monomer and heterocyclic polymerization reaction [2]. This simple and effective method provides completely purified trace catalyst materials by simple filtration.The products of the reaction were characterized by several spectroscopic methods such as, IR, 1H NMR and DSC. A kinetic study was carried out on the effects of the reaction parameters (catalyst quantity, temperature, time) on the reaction yield and on the average molar mass of the resulting copolymer.

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56. Synthesis and Evaluation of Novel Block Copolymers as siRNA Delivery Agents

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One of the biggest challenges in developing siRNA-based therapies is the delivery of these therapeutic nucleic acids to their targets. Since siRNAs are negatively charged, hydrophilic and relatively big molecules, their intracellular uptake is substantially limited. Additionally, these molecules are not stable in physiological fluids. In order to overcome these major obstacles, various delivery systems including polymeric carriers have been designed. Among polymer-based carriers, diaminoethane motif-bearing polymers stand out because of their superior features such as high buffering capacity and endosomal escaping ability.

In this work, novel diaminoethane motif-bearing block copolymers were synthesized and their potential in siRNA delivery was determined. For this aim, a spermine-like monomer (2-((tert-butoxycarbonyl) (2-((tert-butoxy carbonyl)amino)ethyl)amino)ethyl methacrylate (BocAEAEMA)) was first synthesized by following a previously reported procedure (Kurtulus et al., 2014). Poly(oligoethylene glycol) methyl ether methacrylate (POEGMA) homopolymers at varying molecular weights were then prepared by RAFT polymerization and used as macro-RAFT agents to obtain block copolymers, POEGMA-*b*-P(BocAEAEMA). Block copolymers were characterized by NMR and GPC. The ability of the deprotected polymers (POEGMA-*b*-P(AEAEMA)) to form electrostatic complexes with siRNA was investigated by gel retardation assays. Hydrodynamic diameter of the polymer-siRNA complexes (polyplexes) was determined via DLS. The cytotoxicity of the polymers was investigated on the Skov-3 (human ovarian cancer) cell line by MTT assay. Polymers were found to form efficient complexes with siRNA independent of POEGMA block length and showed insignificant toxicity on the Skov-3 cell line at high POEGMA block lengths. DLS results showed that the formed complexes displayed monodisperse size distribution at low polymer/siRNA amount. In conclusion, the preliminary studies yielded promising results on the potential of POEGMA-*b*-P(BocAEAEMA) polymers as siRNA carriers.

Acknowledgments: The authors acknowledge The Scientific and Technological Research Council of Turkey (TUBITAK) for grant 115R301.

57. Synthesis of 2-Deoxy-d-ribose-5-phosphate aldolase (DERA)/PNIPAm Conjugates and Their Self-Assembly into Biocatalytically Active Thin Films

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2-Deoxy-d-ribose-5-phosphate aldolase (DERA), as a particular representative of the class of aldolases, can efficiently catalyze an aldol-reaction in which acetaldehyde and a second aldehyde are linked to yield enantiomerically pure mono- and diyhydroxyaldehydes. These compounds are valuable building blocks for a number of pharmaceutical blockbusters, like atorvastatin. However, the enzyme used in such a process is sensitive to industrially relevant substrate and product concentrations. In this contribution, we show how the conjugation of the enzyme with poly(*N*-isopropylacrylamide) (PNIPAm) can significantly improve its stability. Polymeric precursors for the conjugation, exhibiting a cysteine reactive pyridyldisulfide end group, were obtained via RAFT using a respective functional chain transfer agent. Next to the increased stability, the conjugation provides the enzyme with an enhanced interfacial activity compared to the pure enzyme, which gave us the opportunity to assemble the conjugates into thin enzyme-containing films at the air/water interface. In this contribution, we discuss the conjugation conditions, the interfacial properties of the conjugates, the film properties and finally assess the enzymatic activity before and after the film formation step.

58. Synthesis of a CarboraneContaining Triblock Terpolymer Designed for Dual Drug Delivery

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Block copolymers have numerous applications, including the capacity to form multicompartment nanoparticles with different functionalities, which is a key tool for simultaneous multi-drug delivery. These nanoparticles are obtainable through triblock terpolymers. Here, we designed a triblock terpolymer consisting of poly(acrylic acid)-block-poly(4-hydroxystyrene)-block-poly(carboranyl-styrene), PAA-PSO-PSC. The polymer was prepared by RAFT polymerization and post-polymerization modification, yielding nanoparticles with carborane-rich inner compartments inside a hydrophobic matrix and a stabilizing corona of poly (acrylic acid). These nanoparticles may simultaneously carry boron cluster-based drugs and hydrophobic drugs in separate compartments. Alongside the triblock, an identical diblock copolymer, PAA-PSO, was synthesized without the short PSC block to compare their self-assembly behavior and the presence of inner compartments. Micelles were obtained from the diblock copolymer and triblock terpolymers by dialyzing the polymers into water from various THF:water mixtures. This technique yielded various nanostructures, ranging from worm-like micelles at high-THF and high-water contents, to large spherical micelles at a 1:1 THF:water ratio. Nanostructures were studied using scattering techniques (LS, SAXS and *Electrophoretic LS*) and visualized by Cryo-TEM. Fluorescence spectroscopy was used to monitor the simultaneous solubilization of two chemically different model drugs (naphthalene and 7-methoxycoumarin carborane) within the micellar cores of multicompartment micelles consisting of lipophilic poly(hydroxy styren) and *borophilic* poly(styrene carborane).

Acknowledgments: We acknowledge the support from the Czech Science Foundation—Czech Republic, grant no. 17-00289Y.

59. Synthesis of Functional Polyglycerols Containing Amine Groups

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Functional polyglycerols have recently gained considerable interest due to their potential in biomedical applications. Particularly interesting are branched polymers containing amine groups. Such architectures containing amine groups demonstrated an ability to complex DNA and showed a lower cytotoxicity compared to the typically used poly(ethyleneimine)s (PEI)s. They can be used for gene therapy due to their potential for treating chronic diseases and genetic disorders, as well as an alternative method to traditional chemotherapy for cancer management. Hyperbranched polymers appear to be optimal candidates for the intracellular delivery of therapeutically important oligonucleotides [1].

Hyperbranched polyglycerols containing primary amine groups (A-HBPGs) were synthesized in a two-step procedure including co-polymerization of the phthalimide-epoxy monomer with glycidol in an anionic ring-opening polymerization followed by hydrazinolysis of phthalimide groups. Polymeric products of both synthetic steps were characterized using NMR, FT-IR and MALDI-TOF.

Acknowledgments: This work was supported by National Science Centre (Agreement No. 2015/17/B/ST5/00350).

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60. Synthesis of Novel Poly(dimethyl siloxane) (PDMS) Based ABC Triblock Copolymer and Achieving Sub-10 nm Morphologies

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Block copolymers consist of two or more chemically different polymers covalently connected. Owing to their thermodynamic incompatibility and chain connectivity, the phase separation between two (or more) blocks, happens only in the tens of nanoscale length. Block copolymer (BCP) self-assembly offers an immense hope to achieve low-cost scalable well-ordered nano-pattern devices, such as magnetic storage media, membranes, and semiconductors. Due to the difference between the surface energy of the silicon-containing block and the other organic blocks, there is a challenge to obtain a well-ordered morphology using the thermal annealing process. Herein, different poly(dimethyl siloxane) (PDMS) based block copolymers (AB, AC, and ABC) were synthesized and then the self-assembled nanostructure morphology was investigated. Poly(dimethyl siloxane)-b-polystyrene (PDMS-*b*-PS), poly(dimethyl siloxane)-*b*-poly(methyl methacrylate) (PDMS-*b*-PMMA), and a new structurally well-defined ABC triblock copolymer, i.e., poly(dimethyl siloxane)-*b*-poly(methyl methacrylate)-b-polystyrene (PDMS-*b*-PMMA-b-PS), were synthesised by atom transfer radical polymerization (ATRP). Chemical structures are proved by NMR and the morphology of block copolymers is studied by TEM. It is concluded that adding PS to PDMS-b-PMMA leads to smaller nanostructure feature sizes.

61. Synthesis of Poly(phenylene methylene) with Unexpected Photoluminescence Caused by Homoconjugation

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Poly(phenylene methylene) (PPM) was synthesized by catalytic polymerization of benzyl chloride with $SnCl_4$ or $FeCl_3$, leading to polymers with a broad range of molar masses from 1200 to 61,000 g mol^{-1}. The latter is an order of magnitude above previously reported values. The increase in molar mass as a function of the conversion closely corresponds to the Schulz–Flory distribution, which implies a step-growth mechanism. DSC and TGA analyses revealed a glass transition temperature of 65 °C and an exceptionally high decomposition temperature of above 470 °C [1].

Remarkably, PPM exhibits photoluminescence between 400–600 nm in the solid as well as in the dissolved states. This phenomenon cannot be caused by a π-electron delocalization of alternating double and single bonds. Instead, the results of extended investigations are in line with homoconjugation as the origin of the photoluminescence [2]. Homoconjugation only arises in special chemical structures for which conjugation across individual π-electron systems can occur by overlap of p-orbitals although those systems are separated by an electronically insulating group, e.g., a methylene group [3,4]. Notably, π-stacking, aggregation/crystallization and impurities were excluded as the origins of fluorescence [2].

The HOMO–LUMO gap of PPM of 3.2–3.3 eV corresponds to an onset of optical absorption at approximately 375–390 nm, which is in agreement with homoconjugation. PPM also shows a remarkably long photoluminescence lifetime of 8.55 ns (thin film) and a quantum efficiency of 69% (solution) [2]. We believe that poly(phenylene methylene) will serve as an example of a new class of fluorescent polymers characterized by homoconjugation along the main chain.

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62. The Effect of Reactive Ionic Liquid or Plasticizer Incorporation on Physicochemical, Equilibrium, and Transport Properties of Cellulose Acetate Propionate-Based Membranes

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Pervaporation is a membrane separation technique which uses the polymeric and/or ceramic membranes. In the case of pervaporation processes applied to dehydration, the membrane should preferentially transport water molecules. The reactive ionic liquid (RIL) (3-(1,3-diethoxy-1,3-dioxopropan-2-yl)-1-methyl-1*H*-imidazol-3-ium) was used to modify cellulose acetate propionate (CAP) membranes applying the phase inversion technique based on solvent evaporation. RIL reacted with CAP forming the ester bonds during polymer modification by the transesterification reaction.

The various physicochemical, mechanical, equilibrium, and transport properties of CAP-RIL membranes were determined and compared with the properties of CAP membranes modified with plasticizers, i.e., tributyl citrate (TBC) and acetyl tributyl citrate (ATBC).

Thermogravimetric analysis (TGA) testified that CAP-RIL membranes as well as CAP membranes modified with TBC and ATBC are thermally stable up to at least 120 °C. The tensile tests of membranes revealed the improved mechanical properties reflected by the reduced brittleness and increased elongation at break achieved for CAP-RIL membranes in contrast to pristine CAP membrane. RIL plasticizes the CAP matrix and CAP-RIL membranes possess preferable mechanical properties in comparison to membranes with investigated plasticizers.

The incorporation of RIL to CAP membranes tuned the surface properties of CAP membranes enhancing their hydrophilic character. Moreover, the addition of RIL into CAP significantly improved the separation factor in comparison to pristine CAP membrane in pervaporation dehydration of propan-2-ol. The separation factor β increased from ca. 10 for pristine CAP membrane to ca. 380 for CAP-16.7-RIL membranes contacting an azeotropic composition of water–propan-2-ol mixture.

63. Use of Nanoindentation Experiment to Investigate the Optical and Mechanical Properties of Polyurethane Coating Containing Polyhedral Oligomeric Silsesquioxane Nano Structure

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An octahydroxyl functional polyhedral oligomericsilsesquioxane (POSS) was used as a reinforcing nanostructured building block to improve the mechanical properties of hybrid polyurethane (PU) clearcoat. The effect of POSS content on the optical and mechanical properties of hybrid coatings was studied. Prepared clear coatings were characterized using Fourier transform infrared (FTIR) spectroscopy and nanoindentation experiments. Visible spectroscopy confirmed that the addition POSS into the polymeric matrix did not have any negative effect on clearcoats transparency; it revealed good compatibility between the two phases in the hybrid coating. By incorporation of 4 and 8 weight percent of POSS into the polyurethane matrix, nanohardness and elastic modulus, criteria of mechanical properties, dramatically increased. By increasing POSS content (exceeding 2 wt%) due to the hard nature of POSS, surface hardness increased up to 0.132 GPa and the surface elastic modulus increased up to 4.76 GPa. Dynamic mechanical thermal analysis (DMTA) showed that POSS addition in high loading did not affect the glass transition temperature. Strength relaxation in DMTA showed that POSS incorporation reduced viscous behavior and increased the storage contribution.

64. Viscoelastic Analysis of Polymers Used for Magnetic Tapes

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Polymers used for advanced digital magnetic tapes were characterized to determine their role in dimensional stability. Polyester-based poly(ethylene terephthalate) and poly(ethylene naphthalate) substrates were studied in addition to aromatic polyamide-based substrates. Viscoelastic analysis of these substrates, including creep studies and dynamic mechanical analysis (DMA), showed the presence and influence of relaxations in the polyester-based substrates that were not present in the aromatic polyamide-based substrates. The location and magnitude of these relaxations shift with temperature and test frequency, and can be present in the operating range of the tape. As a result, dimensional changes can occur in the polyester-based tapes, which can limit their ability to adequately store information for extended time periods. Post-processing of DMA results led to informative viscosity information such as the in-phase dynamic-viscosity, η′, or "loss" component, which is related to energy dissipated due to viscous behavior. This is in addition to standard information about storage modulus, E′, loss modulus, E″, and tan(δ). A custom-built test apparatus was also used to measure dynamic mechanical response at frequencies below that used by commercial DMA test equipment. Comparisons were made to study how the relaxations shift as frequency decreases or temperature increases, and these relaxations can occur at longer time periods during archival storage.

65. Modelling polyelectrolytes: coupling of conformational and ionization equilibria in solution

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The conformational and protonation properties of linear polyelectrolytes are studied by means of accurate Statistical Mechanics models and Monte Carlo Simulations. Statistical Mechanics is a very useful tool in polymer science, since it allows to connect the polymer chemical structure with physical properties such as gyration radius, persistence length, end-to-end distance, optical and elastic properties, etc. A classical technique, the Rotational Isomeric State (RIS) model proposed by Flory [1], has been used to study a wide range of such physical properties of neutral polymers.

However, many polyelectrolytes of interest are able to regulate their charge depending on the conformational state. Here it is shown that the RIS model can be coupled with the Site Binding (SB) model. SB model represents a generalization of Ising-type models, for which the ionisable sites, interacting at the short-range level, can adopt two states: protonated or deprotonated. The resulting combined scheme, the SBRIS model, allows analysing conformational and ionization properties of polyelectrolytes on the same time [2]. It is also shown that this formalism can be extended to include long-range interactions by introducing a modified free energy involving only effective short-range interaction parameters [3]. By using these techniques, we also analyse the response of polymer to stretching, which can be experimentally measured by means of single-molecule manipulation techniques (e.g. AFM) [4]. Theory and Monte Carlo simulations are compared and the role of charge regulation and long-range interactions discussed.

Acknowledgements: We acknowledge the financial support from Generalitat de Catalunya (Grants 2014SGR1017, 2014SGR1132 and XrQTC). J. L. Garcés also acknowledges the Spanish Ministry of Science and Innovation (project CTM2016-78798-C2-1-P). Sergio Madurga and Francesc Mas acknowledge the funding of the EU project 8SEWP-HORIZON 2020 (692146). Pablo M. Blanco also acknowledges the financial support from grant (FI-2017) of Generalitat de Catalunya.

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66. Bottlebrush Polymers: From Dilute Solutions to Super-Soft Rubbers

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Polymer bottlebrushes provide intriguing features being relevant both in nature and in synthetic systems. While their presence in the articular cartilage optimizes synovial joint lubrication, bottlebrushes offer pathways for fascinating applications, such as within super-soft elastomers or for drug delivery. However, the current theoretical understanding lacks completeness, primarily due to the complicated interplay of many length scales. During the talk, an analytical model will be presented which demonstrates how structural properties of bottlebrushes depend on the concentration, ranging from dilute solutions to highly concentrated melts. The validity of our model is supported by data from extensive molecular dynamics simulations. We demonstrate that the hierarchical structure of bottlebrushes dictates a sequence of conformational changes as the solution concentration increases. The effect is mediated by screening of excluded volume interactions at subsequent structural parts of the bottlebrushes. Our findings provide important insights that should enable improved customization of novel materials based on the architectural design of polymer bottlebrushes.

67. Synthesis of Functionalizable Periodic Copolymers

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Nature provides innumerable examples of highly complex and functional structures based on biopolymers such as proteins, nucleic acids and/or carbohydrates. The defined monomer sequences of these macromolecules are strongly related to their properties. Though a similar degree of control over the primary structure is currently not possible in chain-growth polymerization, material properties of synthetic polymers are equally dependent on their microstructure.

By controlling the sequence in chain-growth polymerization, it might be possible to create polymers with novel properties which, for example, prove beneficial for application in the fields of catalysis or materials chemistry.

In this contribution, we present the periodic free-radical copolymerization of functionalizable, electron-rich limonene derivatives with electron-deficient *N*-phenyl maleimide or derivatives thereof. The influence of different Lewis acidic solvents, such as 1,2-dichloroethane or 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol, is investigated. Different types of monomer sequences, such as AB-r-A (where A is the maleimide and B the limonene derivative) or ABA-periodic copolymers could be attained. Reactive moieties in the side-chains of the monomers could be used in post-polymerization functionalization reactions to give rise to a variety of functional polymers with defined monomer sequences in a modular fashion.

68. Configuring Surface Morphing with Planer Structural Confinement

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Elastic instabilities, i.e., wrinkling, creasing and folding, could enable a convenient and cost-effective strategy to generate surface patterns. Here, we report the experimental and theoretical studies on the formation and evolution of elastic instability morphologies on designed compliant surface. By pre-placing the structural confinements on the soft layer, the surface can be guided to form/grow instability patterns in response to the imposed constraints when being compressed, thus yielding a reliable hierarchical surface. We successfully obtain the 2D periodic wrinkle network under uniaxial compression, by using the Bravais lattice micro-patterns to regulate the strain energy distributions. At higher compression, the observed harmonic wrinkle pattern further develops into period-doubling bifurcation, then a symmetry breaking to initialise the wrinkle-creasing transition which is guided by the local curvature. By testing the theory against experiments on the designed surfaces with centred rectangular array, we show a quantitative agreement between the analytical simulation and experimental results. We also reveal a targeted formation of wrinkle-to-crease transition to yield a hierarchical surface as a result of the reorganization of surface strain field. By verifying the geometrical inputs, we demonstrate control over the stepwise evolution of surface morphologies. These results have relevance to many emerging applications of morphing surfaces in wearable/flexible electronics, bio-medical systems, optical devices, etc.

69. Modeling the Thermomechanical Behavior of ESTANE

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In contrast to Shape-Memory Alloys, which can only be deformed in certain strains, Shape-Memory Polymers (SMPs) can be stretched to large deformations and recover such induced strains when exposed to an appropriate stimulus such as heat. These emerging classes of functional polymers have attracted much interest and found applications in areas spanning pharmacy, medicine and engineering. They can be utilized, for instance, as smart self-deployable structures, hernia meshes or heat shrinkable tubes. However, prior to any application, their physical and mechanical properties must be thoroughly studied and understood in order to make predictions or to design structures thereof. In this contribution, the viscoelastic behavior of a polyether-based polyurethane (ESTANE) and its rate- and temperature-dependence have been experimentally studied by Dynamic Mechanical Thermal Analysis and through large deformation relaxation tests at different constant temperatures. Based on our previous work, a finite viscoelastic material model was used to simulate its complex thermo-mechanical behavior in inhomogeneous deformations and loading conditions. The model-inherent material parameters are identified with the assumption of the thermo-rheological complexity of ESTANE. The ability of our model to simulate the thermo-mechanical properties of ESTANE was evaluated by data-rich experimental observations on two different deformation types: (I) tension and (II) torsion in various temperature ranges. The experiments include inhomogeneous tests containing a large variety of information about the functional properties of ESTANE.

70. The Influence of the Ammonium Pendant Groups on the Photophysical Properties of Polythiophene-Based Polyelectrolytes with Phosphonium Ionic Groups

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Water/alcohol soluble π-conjugated polyelectrolytes (CPEs), representing dual conductivity (ionic and electronic) and providing harmless processing conditions, have found various applications in different photoelectronic devices such as light-emitting diodes, organic field-effect transistors, and photovoltaic cells [1,2]. Their luminescence and ability to interact with oppositely charged systems allowed them to be used for the development of luminescence chemo-sensors [3].

This contribution reports the synthesis and properties of the novel conjugated cationic polyelectrolytes prepared by simple modification of highly regioregular polymer precursor poly[3-(6-bromohexyl)thiophene] (PHT-Br) using quaternization reaction with tributylamine or tributylphosphine, respectively. Incomplete ionization of the bromide end-groups of the (PHT-Br) polymer precursor with tributylamine (about 50%) allowed the addition of the tributylphosphine, providing quantitative transformation of all remaining bromide groups. This approach allows the preparation of luminescent conjugated polyelectrolyte bearing both phosphonium and ammonium pendant groups simultaneously in the same polymer main-chains.

The photophysical properties of the prepared materials were investigated in water and water-miscible solvents by UV/vis, luminescence, NMR spectroscopies, light scattering and thermogravimetric analysis. The main efforts were subjected on luminescence sensor testing of the synthesized polyelectrolytes using model pollutants potassium ferrocyanide and potassium ferricyanide, applying Stern–Volmer methodology. The performed experiments showed that prepared materials interact well with the mentioned model pollutants, resulting in luminescence quenching. The observed behavior paves the way for potential luminescence-based chemo-sensors.

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71. Synthesis, Characterization and Foaming of Thermoplastic Polyurethane Synthesized with Different Soft/Fard Segment Ratios and Graphene Nanoplatelet Contents

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Foaming polymers possess value-added properties such as low density, low thermal conductivity and adaptable mechanical properties as a function of relative density. Due to these interesting properties, foamed polymers are widely used in almost all industrial sectors. In recent years, the study of foams based on thermoplastic polyurethane (TPU) has been gaining importance mainly because it is one of the most elastic thermoplastically processable materials and also because it can be reprocessed or recycled.

A promising technique used to produce thermoplastic foams is the gas dissolution foaming process. To date, many studies have been published on the foaming of different polymers by using this technique. However, the number of reports dealing with thermoplastic polyurethane (TPU) foams is still scarce. TPU foams, due to inherent properties of TPU and the widening of properties provided by foaming, could be very interesting materials for several industrial sectors. For these reasons, we have focused our research on obtaining synthesized TPUs with different characteristics to produce optimum TPU foams.

In particular, thermoplastic polyurethanes (TPUs) with different soft/hard segment (SS/HS) ratios have been synthesized using the prepolymer method, as well as TPU nanocomposites with different contents of graphene nanoplatelets (GNPs). In addition, synthesized TPUs have been characterized by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and Wide Angle X-ray diffraction (WAXS). Furthermore, the influence of the SS/HS ratio and also GNP content on TPU foaming is studied herein.

72. Triazine Dendrimers: From Synthetic Methods Development to Treating Prostate Cancer in Mice

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For almost 20 years, our efforts have focused on the development of methods to synthesize triazine dendrimers. At the heart of these strategies is the employment of diamines to connect triazines derived from cyanuric chloride. The ability to execute stepwise substitution of the latter combined with a wealth of commercially available or readily prepared building blocks of the former has led to structural diversity that can be married with excellent compositional control.

Over time, studies have moved through comparisons of convergent and divergent strategies for synthesis, the exploration of amine reactivity, the influences that composition has on physical properties, to the creation of targets—a generation 13 dendrimer—that match the size of viruses.

Along the way, these molecules have been probed for biological application including exploring the design criteria of LPS mimics for septic shock, delivery vehicles for DNA and RNA, and platforms for multivalent display of bioactives including chelators and chemotherapeutics. The use of triazine dendrimers for diagnostic imaging has also been explored.

The current state-of-the-art of these platforms rests in an ability to “cure” human prostate cancer in mice models at dosings equivalent to the standard of care, a noteworthy feat given the nature of the drug conjugation and pharmacokinetics of the constructs. Current and future endeavors focusing on the realization of targeted theranostics is the current goal and the status of efforts to these ends will be reported.

73. Microstructure Evolution of Immiscible PP/PVA Blends Tuned by Polymer Ratio and Silica Nanoparticles

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Polymer blending is a classical strategy for new material design; related research is still focused on this area and shows potential [1]. Polymer blends are normally immiscible due to the low mixing entropy of polymers. Thus, they represent a possible way to prepare the porous material: the removal of one of the phases, i.e., a sacrificial polymer. The morphology of the blends directly determines the final microstructure of the scaffold. The expected morphology can be induced by the introduction of a block copolymer, and now with the development of nanotechnology, more industrialized and easily available nanoparticles are utilized to tailor the microstructure. If the nanoparticles can be localized at the interface, after the etching of the sacrificial phase, a surface-modified scaffold with nanoparticles can be obtained. It provides a possibility to prepare functional surface material.

Nanoparticles with different wettability will localize unevenly in different positions, thus influencing the rheological behaviors and final morphology of the polymer blends. In this study, various ratios of polypropylene (PP) and poly(vinyl alcohol) (PVA) have been melt extruded in a twin screw extruder. Fumed silicas with different wettability, including hydrophilic Aldrich silica, partially hydrophobic R816 silica and hydrophobic R972 silica, were incorporated during the melting process. Co-continuity degrees of the polymers were measured, and localization of silicas was also investigated. The rheological behaviors of the blends were emphatically discussed, and the storage modulus and the slope of the storage modulus were illustrated. The corresponding phenomena were tightly related to the microstructure evolution of the PP/PVA blends.

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74. Fabrication of Silica Nanocontainers with a Thermoresponsive Gating System

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The ultimate goal of this study is to create a silica-polymer system that may serve as a nanoreactor. Silica pores may be filled with appropriate reagents and undergo reactions in a confined environment. Their products may be released by opening the thermoresponsive polymer brushes' valves.

Silica particles with a solid core and mesoporous shell were synthesized and characterized. The presence of a solid core in this system was proposed for ease of isolation from a solution and improves the mechanical properties of such a system. The samples were prepared as a function of temperature, resulting in various core and shell thicknesses which can be fitted by an exponential curve.

Thermoresponsive (P-NIPAM) brushes were then successfully grafted from particle surfaces using surface-initiated Atom Transfer Radical Polymerization (ATRP). Such brushes on the surface are able to dramatically change their conformations upon small changes of temperature, ensuring flow control of substances in and out of the pores. The same silica/polymer system without pores was synthesized and characterized to verify whether the gating system works well and fluorescent probe molecules diffuse inside pores or stick to the brushes. Both ATRP porous and non-porous systems were characterized using cryo-TEM, thermogravimetry and elemental analysis. The above methods helped to determine the structure of the nanoparticles and the lengths of the polymer brushes. ATRP on presented materials is a very rapid reaction.

The loading and unloading process of the porous and unporous system was examined using model fluorescent dye: rhodamine 6G. The nanoparticles with different brush lengths were filled with rhodamine via its stable adsorption from aqueous solution. The effective outflow of the fluorescent probe is caused by the small addition of methanol to water.

75. Poly(dodecyl methacrylate-*co*-2-(diethylamino)ethyl methacrylate) Gels: Swelling Kinetics, Network Structure and Characterization

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Polymer gels, cross-linked networks, have the ability to absorb large quantities of solvents depending on their chemical structure. The presence of hydrophobic functionality is advantageous for the sorption of aromatic compounds from water [1]. In this study, poly(dodecyl methacrylate-co-2-(diethylamino)ethyl methacrylate) P(DDMA-co-DEAEMA) gels were prepared in ethanol by the free radical cross-linking polymerization method and their toluene and benzene absorptive properties were evaluated. Poly(dodecyl methacrylate) (PDDMA) was also prepared and used for comparison. In the preparation of homopolymer and copolymer gels, poly(ethylene glycol)(M = 600 g/mol) (10 wt %) was used as pore former to investigate its effect on the swelling behavior, density of gels, and network characteristics. The swelling kinetics was investigated in toluene and benzene and the diffusion mechanism type was determined. P(DDMA-*co*-DEAEMA) gel showed Fickian swelling behavior; it was also confirmed that the swelling process followed second order kinetics. Both swelling rate and swelling capacity are very high, showing the efficient toluene and benzene-absorptive property of the gels for environmental applications**.** The polymer−solvent interaction parameters (χ), mesh size (ζ), and experimental average molecular mass between the cross-links (M_cD) of gels prepared using PEG600 is higher than the conterpart gels without PEG600. In addition, characterizations of the gels were performed by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), Thermal Gravimetric Analysis (TGA) and X-Ray Diffraction (XRD) techniques.

Acknowledgments: This work was supported by Scientific Research Project Coordination Unit of Istanbul University. Project number: 49467.

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76. Visible Light-Regulated Polymerization of a Photo-Responsive Monomer: Formation of Light-Cleavable Nanoparticles

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Although several methods to synthesize polymers bearing *o*-nitrobenzyl moieties have been established in the literature, there have only been a few reports on their fabrication via controlled/living radical polymerization (CLRP) yielding well-defined and low dispersity polymers. In particular, the controlled polymerization of o-nitrobenzyl methacrylate (NBMA) monomer has been shown to present challenges, when using techniques such as atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization. In this study, we developed a novel approach for the polymerization of this photocleavable monomer using photoredox catalysts to activate the polymerization under visible red ($\lambda = 610–655$ nm, 0.7 mW/cm^2) or yellow ($\lambda = 560$ nm, 9.7 mW/cm^2) light according to a Photoinduced Electron Transfer Reversible Addition Fragmentation Transfer (PET-RAFT) mechanism. We demonstrated for the first time the potential of two photoredox catalysts for controlling the polymerization with rational evidence of a controlled/living radical polymerization process at room temperature. Well-defined poly(*o*-nitrobenzyl methacrylate) (PNBMA) homopolymers with good control over the molecular weight and polymer dispersity were successfully synthesized by varying the irradiation time and/or targeted degree of polymerization. Chain extension of a poly (oligo (ethylene glycol) methyl ether methacrylate) (POEGMA) macro-chain transfer agent with NBMA was carried out to fabricate photocleavable amphiphilic block copolymers which were consequently self-assembled into micellar nanoparticles. Alternatively, a process known as polymerization-induced self-assembly (PISA) has been implemented to yield self-assembled light-responsive polymeric nanoparticles in situ. Finally, photocleavage of these self-assembled nanoparticles under UV light was demonstrated, suggesting that the photoresponsive character of NBMA is not altered during the polymerization under yellow or red light. Such photoresponsive polymeric nanoparticles can be potentially used for the remote-controlled drug delivery systems.

77. Polymer Capsules with Magnetic Properties

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Remote navigation, magnetic drug targeting as well as remote magnetically controlled release of biologically active compounds are the current challenges in the development of intelligent, multifunctional drug delivery systems. Nano and microcarriers can be loaded not only with chemotherapeutic drugs but also with magnetic nanoparticles what ensure the possibility of manipulation by an external magnetic field so the carriers can be guided to the desired tissue; local heating by a radio-frequency field for hyperthermal cancer therapy; labeling of organs to enhance the contrast in Magnetic Resonance Imaging; triggered release by the thermal and vibrational behavior of magnetic nanoparticles in an alternating magnetic field [1,2].

Herein, we propose nano-microcapsules with magnetic properties. Such capsules consist of amphiphilic graft polymer as the shell and magnetic emulsion as the core. At the water–oil interfaces, amphiphilic graft polymers anchor hydrophobic arms into the oil droplets ensuring their stabilization without the need to add surfactants. Such polymers provide a unique core–shell architecture wherein the hydrophobic core serves as a natural carrier environment for hydrophobically modified magnetic nanoparticles with hydrophobic drugs and the hydrophilic shell allows particle stabilization in aqueous solution [3,4].

Physicochemical parameters as well as stability of the obtained magnetic capsules were examined using dynamic light scattering and Zeta Potential measurements. Moreover, Atomic Force Microscopy indicated the spherical shape of capsules. Magnetic Force Microscopy confirmed the magnetic response of the obtained structures.

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Abstracts

Poster Exhibition – Session 2: Function to Application

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78. In-Silico Design, Synthesis and Evaluation of a Nanostructured Hydrogel as a Dimethoate Removal Agent

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This study describes the in-silico design, synthesis, and evaluation of a cross-linked PVA hydrogel (CLPH) for the absorption of organophosphorus pesticide dimethoate from aqueous solutions. The crosslinking effectiveness of 14 dicarboxilic acids was evaluated through in-silico studies using semiempirical quantum mechanical calculations. According to the theoretical studies, the nanopore of PVA cross-linked with malic acid (CLPH-MA) showed the best interaction energy with dimethoate. Later, using all-atom molecular dynamics simulations, three hydrogels with different proportions of PVA:MA (10:2, 10:4, and 10:6) were used to evaluate their interactions with dimethoate. These results showed that the suitable crosslinking degree for improving the affinity for the pesticide was with 20% (*W*%) of the cross-linker. In the experimental absorption study, the synthesized CLPH-MA20 recovered 100% of dimethoate from aqueous solutions. Therefore, the theoretical data were correlated with the experimental studies. Surface morphology of CLPH-MA20 by Scanning Electron Microscopy (SEM) was analyzed. In conclusion, the ability of CLPH-MA20 to remove dimethoate could be used as a technological alternative for the treatment of contaminated water.

79. Design and Characterization of Mucoadhesive Formulations of Acyclovir Based on Iota-Carrageenan, Pectin and HPMC

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Genital herpes is one of the most common sexually transmitted infections around the world, with a global estimate of 536 million people infected and an annual incidence of 23.6 million cases [1,2]. Acyclovir (ACV) is a safe and effective drug for vaginal administration, and numerous benefits have been observed in the treatment of primary or recurrent lesions due to genital herpes [3]. With these precedents, the objective of this work is to develop mucoadhesive formulations of ACV with natural polymers in order to determine the most suitable formulations of controlled release.

ACV tablets based on *iota*-carrageenan (I), pectin (P) and hydroxypropylmethylcellulose (H) have been prepared: ACV-I, ACV-P, ACV-H, and from a mixture of I or P with H: ACV-IH1, ACV-IH2, ACV-PH1, ACV-PH2. All batches contain 100 mg of ACV. Swelling, release and mucoadhesion tests were performed in simulated vaginal fluid [4].

Results show that the mixture of HPMC with I increases the capacity of medium uptake. Thus, increasing the volume and consistency of the formed gel controls the release of ACV. However, the incorporation of HPMC to pectin compacts does not significantly modify the swelling process or the drug release.

Consequently, it is possible to conclude that the formulations of HPMC/I produce more sustained ACV release profiles, which will be useful in the prevention of genital herpes.

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80. Agarose-Based Systems Tailored for the Controlled Release of Highly Soluble Drugs within a pH-Progressive Medium

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Agarose has demonstrated to be an excellent platform to develop controlled drug release formulations of poorly soluble drugs such as tolbutamide [1,2]. In this work, the purpose was to expand the use of agarose-based systems for the controlled release of highly soluble drugs. Three additives (Eudragit® S-100, RL-PO and Labrafac®) were included within these systems together with Theophylline. The release of this drug from the freeze-dried systems was evaluated in deionized water and in a pH-progressive medium that simulates the conditions under an oral administration. Considering the results obtained in the preliminary release test in water, only the Eudragit®-containing compositions were further characterized. The theophylline release in a pH-progressive medium shows two different patterns that primarily depend on the additive nature: those systems containing Eudragi®t S-100 show a similar behaviour to that observed in the absence of additives, while the presence of Eudragit® RL-PO yields a progressive and pH-independent release. This effect can be mainly attributed to the presence of quaternary ammonium groups that causes a sieving effect during the agarose network rehydration but also to the generated pore architecture and the interactions of the drug nanocrystals with the other components. Agarose-based systems are capable of accommodating additives; this allows a tailored, controlled and pH-independent release of theophylline within a pH-progressive medium.

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81. Bilayer Mucoadhesive Films for Vaginal Tenofovir Controlled Release for the Prevention of Sexual Transmission of HIV

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Vaginal microbicides are promising tools to empower women in the fight against sexual HIV transmission [1]. In this area, mucoadhesive films may be an interesting option, due to their high comfort compared to other systems and their easy manufacture [2]. With this background, the aim of this study was the development and evaluation of mucoadhesive bilayer films for Tenofovir controlled release.

Films containing two layers were prepared; the first layer comprised Ethylcellulose (a hydrophobic polymer which may modulate the drug release [3]) while the opposite layer contained a natural hydrophilic mucoadhesive polymer namely Karaya Gum, Tragacanth Gum or Xanthan Gum. They were prepared in proportions 1:1, 2:1 and 4:1 of Ethylcellulose and the natural polymer respectively. Finally, the same formulations were prepared adding 30 mg of Tenofovir. Plasticizers were added in previously optimized concentrations to all of the films.

The physico-chemical properties—dimensions, burst strength and flexibility—of the films were assessed using a Texture Analyzer. Swelling behaviour and Tenofovir release were characterized in simulant vaginal fluid and mucoadhesion time was determined in the same medium using bovine-excised vaginal mucosa.

All films showed to be flexible and resistant enough for their purpose. Their swelling was moderate and the release of the drug lasted up to two weeks. Besides, some of the formulations remained attached for more than two weeks, thus releasing all of the drug. Taking this into account, bilayer films must be considered as a proposal for the future in the prevention of sexual transmission of HIV in women.

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82. Freeze-Dried Polymer Bigels Containing Tenofovir as New Vaginal Microbicides in the Prophylaxis of HIV Sexual Transmission

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According to AIDS data, published by UNAIDS, women represented around 48.5% of all people living with HIV in 2016. Furthermore, sub-Saharan Africa was the most affected area in the world, with about 64% of daily new HIV infections [1]. Therefore, the development of new tools to prevent the sexual transmission of the virus to these women is necessary. As gels are the best accepted form of vaginal dosage by their potential users [2] and bigels have emerged as innovative formulations [3], we propose vaginal bigels as a new option for the mentioned purpose. With this background, eight batches of biphasic systems—composed by an aqueous gel and an organic one—were formulated. They contained Tenofovir (TFV) as the antiretroviral drug and a mucoadhesive polymer (pectin, chitosan, carboxymethylcellulose or hydroxypropylmethylcellulose) at two different concentrations as the excipient able to form the hydrogel and to control the release of the drug. The organic phase was based on a sorbitan monostearate-sesame oil gel. The resulting systems were freeze-dried and subjected to different tests in order to determine their suitability for the proposed objective. In this way, the developed formulations showed TFV release profiles for 72 h, mucoadhesion times up to 96 h (so, enough time to allow the release of the total dose) and moderate swelling behaviour (lower than 250% in all the cases). Thus, they would be an interesting choice as vaginal microbicide systems for the prevention of HIV sexual transmission.

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83. Optimization of Natural PolymerBased Vaginal Film Composition for AcyclovirControlled Release in the Treatment and Prevention of Sexual Transmission of HSV

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Vaginal formulations for the prevention of sexually transmitted infections are currently gaining importance in drug development. Natural polymers, such as Guar Gum, Locust Bean Gum and Pectin have the capacity of binding to mucosa, thus representing promising excipients for this purpose [1].

Films containing either Pectin, Chitosan or Locust Bean were prepared with and without Acyclovir and containing increasing proportions of glycerol as a hydrophilic plasticizer.

All the films obtained were characterized using a Texture analyzer in order to determine their physicochemical properties (burst strength and flexibility). Furthermore, their gel-forming gel capability was characterized in simulant vaginal fluid using a brand new method. Drug release studies were carried out in the same medium and the permanence time of the bioadhesion was determined ex vivo using bovine vaginal mucosa as a substrate. Eventually, the biocompatibility of the components was assessed through in vitro cellular toxicity assays [2].

The materials had no cytotoxicity at the maximum concentration tested and all the polymers assessed were shown to form a gel once in contact with the medium. Moreover, it was demonstrated that glycerol is not only necessary to improve the physicochemical properties of the films, but also to modify the release process, thus representing a determining component in this system.

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84. Prevention of Sexual Transmission of HIV through Tenofovir-Controlled Release from Vaginal Films of HPMC/Zein

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Given the urgent need to obtain a vaginal microbicide that protects women from HIV transmission, different pharmaceutical forms have been investigated. One of the most recently studied options is vaginal films. Numerous polymers of different nature were studied for the elaboration of these films. In our case, we have used Hydroxypropylmethylcellulose (HPMC), a hydrophilic polymer that gels in the vaginal environment, and Zein, a highly bioadhesive hydrophobic material. Tenofovir (TFV), an antiretroviral drug, was added to develop formulations that prevent the sexual transmission of HIV. The incorporation of different plasticizing agents (Glycerol, Polyethyleneglycol 400 (PEG), Tributylcitrate and Oleic Acid (OA)) into the films has been studied in order to evaluate their physicochemical characteristics and their ability to control the release of TFV. It has been observed that the addition of the appropriate amount of PEG to the HPMC films remarkably improves its properties, as occurs with the incorporation of OA into the Zein films. The combination HPMC/Zein/PEG in a 5/25/12 ratio allows the development of a vaginal film that releases the TFV in a sustained manner during 144 h, remaining adhered to the vaginal mucosa during all that time, which would allow the prevention of the sexual transmission of HIV.

85. Application of the Combination of Polymers of Different Nature for the Development of Mucoadhesive Vaginal Tablets to Prevent the Transmission of HIV

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The search for a vaginal microbicide to protect women against the sexual transmission of HIV has been especially intense in recent decades. The greatest success achieved was the development of a 1% Tenofovir vaginal gel, which proved to be capable of decreasing HIV transmission. However, its main drawback was that it was a formulation that required daily application, and the effectiveness decreased significantly when adherence to treatment fell. To avoid this, the objective of this work is to develop sustained-release mucoadhesive vaginal tablets, to achieve protection lasting several days, thus reducing the number of applications and consequently increasing the adherence of women to prophylactic treatment. For the development of these formulations, three different polymers have been used; one of natural origin (chitosan), one semi-synthetic (hydroxypropylmethylcellulose), and a synthetic one (Eudragit® RS). Vaginal tablets of these polymers have been prepared alone and in combination. The parameters evaluated were the time of the bioadhesion—determined ex vivo using vaginal bovine mucosa as a substrate—the drug release profiles from the formulation to the medium (simulated vaginal fluid), and swelling profiles in the same medium. The combination of hydroxypropylmethylcellulose and chitosan forms a gel in the presence of vaginal fluid that showed an excellent control of the release of the drug. Finally, tablets were manufactured combining two control systems: Tenofovir-loaded granules of Eudragit® incorporated in a hydrophilic matrix of hydroxypropylmethylcellulose and chitosan. This formulation allows the sustained release of TFV for 144 h, remaining always adhered to vaginal mucosa.

86. Effect of the Organic Ligand Isoform on the Optical and Biological Properties of Cationic Chitosan Salts

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The optical activity of chitosan salts with ascorbic acid diastereoisomers was studied by the circular dichroism and optical rotation dispersion methods. The molar ellipticity and specific optical rotation dispersions of aqueous solutions of the chiral polysalts were obtained; the rotational and dispersion constants were calculated. It has been established that the solutions of chitosan L- and D-ascorbates are characterized by such values of specific optical rotation [α] which are close in magnitude but opposite in sign. At the same time, the differences in the [α] values are determined by the amino group/acid ratio used to prepare the polysalt. The effect of the organic ligand isoform on the dispersion characteristics of the polysalts was also revealed.

In vitro experiments revealed a difference in the effect of the chiral chitosan polysalts on eukaryotic and prokaryotic cells, which depends on the sign of their specific optical rotation. Chitosan D-ascorbate was shown to exhibit higher antimicrobial activity against both Gram-positive and Gram-negative bacteria.

The wound healing activity of hydrogels based on chiral chitosan polysalts was evaluated in vivo on biological animal models by the treatment of third-degree burns. The application of our chitosan D-ascorbate hydrogel significantly increases the wound healing rate and the shrinkage rate of the wound surface area in comparison with traditional therapy and chitosan L-ascorbate hydrogel. The reduction of inflammatory processes in damaged tissues is suggested to occur due to some steric features of chitosan D-ascorbate.

87. A Novel Azobenzene-Containing Diblock Copolymer as Highly Sensitive Chemosensors for Thermal, Light and Transition Metals Sensing

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This paper reports on studies regarding the multiple stimuli-responsive sensings and self-assembly behaviors of a novel amphiphilic diblock copolymer, (poly(NIPAM-*b*-Azo)), through two-step reverse addition-fragmentation transfer (RAFT) polymerization. NIPAM macro-CTA and poly(NIPAM-*b*-Azo) exhibited moderate thermal decomposition temperatures of approximately 351.8 and 370.8 ^{o}C, respectively, indicating that the enhancement of the thermal stability was due to the incorporation of azobenzene segments into the block copolymer. The diblock copolymer exhibited the lower critical solution temperature (LCST) at approximately 33.0 ^{o}C. Poly(NIPAM-*b*-Azo) showed a larger photoisomerization rate constant (k_t = 0.1295 s^{-1}) compared with azo monomer (k_t = 0.088 s^{-1}). After UV irradiation, the fluorescence intensity gradually increased, suggesting that self-assembled cis-isomers of azobenzenes experience fluorescence enhancement upon UV irradiation. Photoluminescence titrations demonstrated that the diblock copolymer showed high sensitivity toward Ru^{3+} and Ba^{2+} due to the crown ether acting as a recognition moiety between azobenzene units. Micellar aggregates with a mean diameter of approximately 205.8 and 364.6 nm were formed by dissolving in 25.0 and 40.0 ^{o}C, respectively. The results of this study contribute to the literature regarding the development of photoresponsive and chemosensory polymer materials.

88. Bacteriophages Adsorption onto Microfibers Prepared from Mixtures of PLA and PEUR Based in Arginine

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The development of new materials for biomedicine is continuously being researched. One of the major problems associated with materials and devices used in reparative and regenerative medicine is bacterial infections. However, the abuse of antibiotics has generated a growing problem of bacterial resistance to these drugs. Therefore, bacteriophages (bacteria-specific viruses) have attracted particular attention as a system for the control of various pathogenic bacteria (named bacteriophage therapy).

In the present work, the adsorption of bacteriophages on scaffolds, constituted by microfibers of mixtures of polylactide (PLA) and cationic poly(ester urethane) (PEUR) composed of amino acid arginine, was studied. The constituent fibers of the scaffolds were prepared by electrospinning from the solution of PLA/PEUR in DCM/DMF 1:1 mixture (*v*:*v*).

PLA/PEUR microfibers were made after optimization of electrospinning control parameters (solvent, dissolution time, polymer concentration, flux, etc.). The obtained fibers were analyzed by scanning electron microscopy (SEM) to determine their morphology and diameters. In general, the PLA/PEUR fibers showed diameters around 600 nm, and these were lower than those obtained for the PLA fibers (961 ± 23 nm). A relevant characteristic for the PLA/PEUR matrices was their high hydrophobicity determined by the measurement of the contact angle of the surface of the matrices. Finally, these scaffolds were loaded with specific bacteriophages against the bacterium *Pseudomonas aeruginosa* by simple sinking in the liquid phage, demonstrating that these bacteriophages can be attached to the surface of the fibers via electrostatic forces, and they thus maintain their biological activity (10^8 PFU/g of matrix). The developed new antibacterial materials could be considered as a promising advance in the design of materials for controlling bacterial infections.

Acknowledgments: The authors acknowledge support from MINECO and FEDER (MAT2015-69547-R), and the Generalitat de Catalunya (2014SGR188).

89. Combining Acrylate Endcapped Urethane-Based Poly(Ethylene Glycol) Precursors with Modified Polysaccharides for Wound Dressings

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Wound healing is a complex, fragile and dynamic process of replacing devitalized tissues. Despite their commercial availability and their biocompatible properties, part of the current generation of wound dressings suffer from some major drawbacks including inferior mechanical characteristics (e.g., Young's modulus below 0.2 MPa for Duoderm, Granufoam). In the current research, photo-initiator-free acrylate end-capped, urethane-based poly(ethylene glycol) (AUP) precursors with UV cross-linking potential were developed. By varying the PEG molecular weight (2000–20,000 g/mol), which resulted in gel fractions exceeding 95%, the physico-chemical properties could be varied thereby creating swelling potentials ranging from 4 to 46 $g/g_{polymer}$ of their own weight, moisture uptake capacities up to 90% of their dry mass at a relative humidity of 95% and Young's moduli up to 0.6 MPa (tensile test after swelling in PBS buffer for 24 h). Additionally, stress relaxation tests indicated that the ratio of the equilibrium elastic modulus over the initial elastic modulus ranges between 92 and 96%, rendering them useful for wounds at elbows, heels or knees, areas with an increased possibility of detaching from the injury. In a subsequent step, these AUPs are combined with methacrylated polysaccharides to create up to three times higher swelling capacities. Through electrospinning or co-extrusion electrospinning, these materials are further processed to create a porous electrospun bed which allows a strong gas exchange for the wound.

90. Controlled Surface Modification of Polyamide 6.6 Fabric with $CaCl_2/H_2O/EtOH$

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In this study, polyamide 6.6 fabrics modified with solutions of $CaCl_2/EtOH/H_2O$ were analysed. Influences of the modification on the sorption behavior and physical properties such as roughness and diameter of polyamide 6.6 fibres were detected and reported in a previous work. It was found that a solution with 10 mol% $CaCl_2$, and with a mole ratio of $H_2O/EtOH$ greater than 2.5, is optimal for forming a swollen layer on polyamide 6.6 fibres. Because of these observations, the modification of the polyamide fibers was adapted to polyamide fabrics. The treatment was applied to different fabric types consisting of polyamide 6.6 fibres. The applicability of polyamide 6.6 fabric is extended by the surface modification with the eco-friendly solution of $CaCl_2/EtOH/H_2O$. The high water retention value of treated fabric makes it suitable for the application in medical textiles such as wound dressings. Various new fields of application are opened for polyamide 6.6 by the surface modification and subsequent new properties of the fabrics. The advantage of this method is the environmentally friendly solution which is used for the treatment and furthermore the mechanism of the modification. Through complexation and de-complexation, the surface can be modified without causing any hydrolysis of the polymer, which was proven by DSC measurements. Analyses such as UV-permeability, stiffness and air permeability were carried out and interesting results were obtained.

91. Development and Characterization of Antibacterial Wound Dressing for Biomedical Applications

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Wound dressings play an effective role in the management of the warm moist wound environment and these dressings also protect the wound from the environmental microorganisms, thus facilitating the wound healing process. Different types of fibers such as cotton, polyester, rayon, nylon, polyolefin, acrylic elastomeric, chitosan and alginate, etc., are used to produce the dressings for the wound care. The aim of this study was to develop an antibacterial and high fluid absorption wound dressing by electrospinning nanofibers on cotton gauze treated with chitosan. Four samples of gauze were coated with different concentrations of chitosan (1, 2, 3 and 4%) by using the dip coating method. Then nanofibers of alginate/polyvinyl alcohol (PVA) with 60/40 ratio were electrospun on chitosan-coated dressing. The antimicrobial study was done according to the AATCC147-1998 standard method against Gram-negative bacterium Escherichia Coli (AATCC 4157) and Gram-positive bacterium Staphylococcus Aureus (AATCC 6538). The streaming potential was determined for all treated samples and an untreated sample. The potential of −8.1967 to 0.8671 mV of untreated and chitosan-treated samples confirmed the varying concentrations of chitosan. Finally, the fluid absorption was tested for the developed wound dressing in solution A and saline solution which are more identical to body fluid. The maximum fluid absorption values were 8.88 and 6.62 (g/g) for the absorption saline solution and solution A, respectively.

92. Effect of Chitosan Coating on the Surface Properties of Native and Phosphorylated Thermoplastic Starch Films Obtained by Reactive Extrusion

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An agricultural mulch film is a thin plastic film that is placed directly on the ground in the early stages of plant growth. The insulating effect of the film helps to maintain the temperature, humidity and structure of the soil, preventing erosion and improving water management, an important issue in areas with limited water resources. For the most part, these films are made of polyethylene and do not biodegrade. In this work, the possibility of developing a film for its replacement based on biopolymers such as starch and chitosan was studied. The first is a natural polymer from renewable, abundant and low-cost resources, capable of forming continuous thermoplastic films by the processing methods currently used for petroleum-derived polymers. For its part, chitosan is a linear chain cationic polymer derived from chitin. Its main properties are as a bactericide, fungicide, antiviral, and biostimulant or growth stimulant and as an inducer of defense mechanisms in plants. Such properties confer high potential for its application in agriculture. The objective of this work was to obtain films of native and phosphatized thermoplastic starch by reactive extrusion and to study the effect of a chitosan coating on the interaction of these materials with water. For this purpose, Fourier Transform infrared spectroscopy, thermogravimetric analysis, water contact angle, moisture absorption and scanning electron microscopy of the surface assays were carried out.

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93. Effect of Storage Time and Moisture on Properties of Starch/Bentonite Nanocomposites

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The use of starch as a raw material for the manufacturing of biodegradable products has been studied intensively in recent times, with clear indications of the advantages and limitations imposed by the use of this raw material. Due the hydrophilic nature of starch, products are sensitive to changes of ambient humidity and have poor mechanical properties. If stored under controlled conditions, the mechanical properties have been observed to change, and were found to be correlated with changes in crystallinity. Researchers investigated strategies to improve thermoplastic starch properties, including chemical modifications and introduced nano-reinforcements. Chemical modification by esterification produces a side growth of starch chains and improves the thermoplastic property of the material. The introduction of ester groups plays an internal plasticizing role and reduces the degree of starch crystallinity. Additionally, the ester group can improve the hydrophobicity of the starch-based materials. Biopolymer–clay nanocomposites are new materials with potentially improved mechanical and thermal properties. These composites are prepared by the addition of low amounts of clay to the biopolymer matrix. The main challenge for preparing nanocomposites with enhanced properties is the nanoscale dispersion of clay in the polymer matrix. To improve clay dispersion, organic cations can be used to exchange with the sodium ions residing in the interlayer of clay. The objective of this work was to prepare biodegradable TPS/organobentonite nanocomposites by melt intercalation using the reactive extrusion technique. For this purpose, pristine bentonite was firstly exchanged with benzalkonium chloride. The resulting organobentonite was used as nano-reinforcement of the thermoplastic starch matrix. The derivatization of starch was performed with maleic anhydride and once modified it was processed in the presence of a plasticizer in a twin screw extruder. The effect of clay modification on the morphology, thermal properties, water absorption, mechanical response and biodegradability of nanocomposites was studied as a function of store moisture and storage time.

94. Effect of Hard Segment Contents on the Properties of Self-Curable Waterborne Polyurethane Dispersions for Leather Finishing

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Room temperature self-curable waterborne polyurethane dispersions (PUDs) were synthesized via the acetone process using 5 wt% of (3-aminopropyl) triethoxysilane (APTES) as curing agent. The insertion of alkoxysilane through a sol–gel process was confirmed by ATR-FTIR. The effects of hard segment contents were investigated with different 1,4-butanediol (BDO) amounts (5.7 and 7.2 wt% based on total solid). Higher BDO concentration induced an increase in mean particle size from 28 to 55 nm. Moreover, the values of particle size distribution are 0.18 and 0.2, indicating a fairly homogenous particle size distribution. Increasing the level of chain extender also had a significant influence on mechanical properties: tensile strength improved from 16.3 to 22.9 MPa, and elongation at break decreased from 355 to 284%. Finally, water vapor permeability (WVP) of PUDs showed a reduction from 37.8 to 26.7 g/(m^2 24 h) by rising BDO content. The decline in WVP might be attributed to the decrease in flexibility which was confirmed by tensile results. However, the permeability results were still in the suitable range. The overall promising performance of coatings revealed that silanized PUDs can be successfully used as top coats in leather finishing.

95. Embedded, Fully Spray-Coated Sensor for Pressure Measurement Using a Capacitive Transducing Mechanism

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Measuring the pressure inside an enclosed system is an important aspect of condition monitoring for systems and components. This can be achieved by embedding a functional sensor layer into coatings of one or more components. In this work, a fully spray-coated embedded pressure sensor is presented which is suitable for high pressures and high-temperature surroundings.

The sensor is manufactured on a steel substrate, which is spray-coated first with a layer of polyurethane-based coating, followed by three layers of a custom-made polyamide-imide-based coating. This coating consists of 40 wt% n-methyl-2-pyrrolidone, 27 wt% p-xylene, 32.9 wt% polyamide-imide (Rhodeftal210 ES by Huntsman Advanced Materials) and 0.1 wt% surfactant (BYK310 by BYK Additives&Instruments). Each coating is applied by airbrush and dried separately. Subsequently, an electrode of silver composite coating (KA801 by Dupont) is airbrushed onto the polyamide-imide. The electrode is patterned by an adhesive mask. After contacting the silver layer, the sensor is encapsulated. The thickness of the sensor setup does not exceed 15 µm.

The sensing principle utilizes the change in mutual capacitance of the substrate and conductive silver layer when pressure is applied to the electrode. This change in capacitance is measured by a capacitance evaluation module (FDC2214 by TI).

The sensor has been tested by applying mechanical pressure to the top electrode. The measurements result in a 10% change in capacitance for a pressure of 3.7×10^5 Pa when measuring at room temperature. Therefore, even changes in the order of several kPa can be detected. The sensitivity increases with increasing temperature, yielding a 27.5% increased change in capacitance at 90 °C (when compared to room temperature) and a 42.5% increased change at 130 °C for the same pressure load. The sensor output is stable over several hundred cycles after a set in phase of 20 cycles.

96. Encapsulation of Hydroxyapatite Nanoparticles Loaded with Chloramphenicol into Polylactide Nanofibers

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Hybrid composites consisting of hydroxyapatite (HAp) as an inorganic material and biodegradable polymers have a high and increasing potential for biomedical applications. In fact, hydroxyapatite is one of the most important implantable materials due to its biocompatibility, bioactivity and osteoconductivity. Multiphase materials can be designed to combine the advantages exhibited by each component and provide structures with properties and composition similar to those found in nature. The importance of these materials for medical applications also lies in the chemical characteristics of HAp that allow the encapsulation of various substances. HAp particles can be used as target cell nanovehicles or to control the release of a selected drug in order to achieve greater efficiency.

In this work, the incorporation of chloramphenicol (Chlo) to both amorphous (ACP) and crystalline hydroxyapatite (HAp) has been considered. This antibiotic is highly interesting since it is capable of inhibiting mitochondrial biogenesis and can be used, for example, to erradicate cancer cells. In this sense, the possibility of accumulating HAp in the cytoplasm is vital in order to slow the release of the drug in the digestion process and to avoid an immediate excretion that would not give rise to a therapeutic effect.

Drug release was evaluated in a typical phosphate buffered saline (PBS) medium as well as in its mixture with 70 *v*-% of ethanol. Electrospinning allowed the successful encapsulation of loaded and unloaded nanoparticles into PLA fibers while the activity of Chlo was preserved as demonstrated through the inhibition of bacterial growth. The encapsulation of nanoparticles into the PLA nanofibers led to a delay of the release of Chlo in PBS, which was an essential feature since the viability and proliferation of cells (e.g., Cos-1, Saos-2 and Vero) were not hindered.

97. Enhancing the Applicability of Polymers Combined with Dyes for Laser Protection

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Lasers are becoming increasingly common and can seriously damage eyes and sensors. So, one needs a way to protect them. One possibility is the use of filters with optical limiting properties. The transmittance of these filters is attenuated, when an incident laser beam has a higher energy than a specific threshold. Then, a nonlinear optical mechanism, such as nonlinear absorption, leads to decreased transmittance and the laser beam is blocked, so the dangerous energy cannot reach the eye or sensor. We have already demonstrated the use of dyes as initiators for the ring-opening polymerization of a poly(DL-lactide)-transparent filter with good nonlinear properties [1]. This approach was also used for the polymerization of ε-caprolactone with Eosin Y as an initiator for poly(caprolactone) [2]. However, there are still some problems that remain to be resolved. The homogeneity and the transparency of the filters have to be improved. One possibility is the use of enhanced purification. An additional way is to vary the initiator content. This has an impact on the linear transmittance and the yield of the reaction. Decreasing the initiator content increases the linear transmittance and often also the yield of the reaction. The influence of varying the initiator content on the optical limiting properties is currently being analyzed [1]. Hege, Cordula S.; Muller, Olivier; Merlat, Lionel (2016). Laser Protection with Optical Limiting by Combination of Polymers with Dye, manuscript submitted for publication [2] Chen, Hung-Hsia; Anbarasan, R.; Kuo, Long-Sheng; Chen, Ping-Hei (2011): Synthesis and Characterizations of Novel Acid Functionalized and Fluorescent Poly(e-caprolactone). In: J Mater Sci (46), S. 1796–1805. DOI: 10.1007/s10853-010-5003-5.

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98. Film Formation of Electro-Sprayed Polydimethylsiloxane/Acetone Droplets for Soft Nanometer-Thin Membranes

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As a cost-effective and fast fabrication method, electro-spray deposition (ESD) of polydimethylsiloxane (PDMS) has shown great potential to realize sub-micrometer thin elastomer membranes [1,2]. Due to its biocompatibility, PDMS is widely used for biomedical implants. Cross-linking of the PDMS chains is realized via ultraviolet light (UV) irradiation [2]. The film formation as well as the final surface morphology can be resolved using in situ spectroscopic ellipsometry with sub-nanometer precision [1]. Recently, sub-micrometer thin confluent PDMS films have been realized; however, they exhibit micrometer-rough surface morphology [3]. AFM nanoindentations revealed the elastic moduli, which can be tailored between 10 down to 0.1 MPa based on the UV-irradiation dose. Such homogenously polymerized soft PDMS nano-membranes can qualify to mimic human tissue mechanics [3]. For comprehensive understanding and control of the homogenous formation of the sub-micrometer films, we will resolve the film formation of electro-sprayed polydimethylsiloxane (PDMS) solved in acetone/ethanol deposited on bare Si(100) substrates. The membranes consist of entangled PDMS networks based on end-linking of thiol-functionalized PDMS chains by UV irradiation of a mercury lamp. Atomic force microscopy (AFM) serves to resolve the surface morphology for varied spraying times from single islands towards confluent films and beyond. We found an oscillating dependency of the membrane`s surface roughness with time and thus, with increasing film thickness. We found a stepwise growth of PDMS droplets with step heights of (32 ± 2) nm after UV curing. Finally, the film`s homogeneity is the key for reliable low-voltage operation of dielectric elastomer nano-transducers to enter the application field of medically approved actuators or sensors, such as artificial muscles or skin [4].

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99. Flash Nanoprecipation as a Simple Route to Produce Smart Polymeric Drug Delivery Devices

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Flash nanoprecipitation (FNP) was proven to be a promising technology for the industrial production of drug-loaded nanoparticles; however, to date, only applications with hydrophobic compounds have been studied in depth [1]. The presents research aims at demonstrating the possibility of encapsulating a strongly hydrophilic compound (caffeine) by FNP while maintaining the control over product quality. Caffeine-loaded poly-ε-caprolactone nanoparticles were produced in a confined impinging jet mixer using acetone as solvent and water as antisolvent. Caffeine was dissolved alternately in acetone or in water to investigate the effect of the two different process configurations. The nanoparticle quality was assessed in terms of Loading Capacity (LC%), Encapsulation Efficiency (EE%) and in vitro release kinetics in order to investigate the incorporation and release of the active substance. The nanoparticle structure and dimension were analysed for the two process configurations by means of dynamic light scattering, scanning electron microscopy and X-ray photo electron spectroscopy. A preliminary study of the product shelf life was conducted both on the colloidal suspension and on the dried product by differential scanning calorimetry, infrared spectroscopy and thermogravimetric analysis. The produced nanoparticles were effective in terms of incorporating and slowly releasing caffeine. A good control over the size of particles was obtained by finely tuning the process parameters. The particle structure changed according to the selected configuration, i.e., the active substance was more concentrated in the inner core of the particle when dissolved in water and more adsorbed on the surface when dissolved in acetone; therefore, the two structures displayed different release kinetics.

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100. Fully Bottom-Up Printed PEDOT:PSS-Based Electrochromic Display for Embedding in Organic Coatings on Sheet Steel

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In this work, we present our research towards the realization of a Poly3,4-ethylenedioxythiophene-polystyrenesulfonate (PEDOT:PSS)-based electrochromic display suitable for integration into the organic coatings on rough metallic substrates. In contrast to previously reported electrochromic displays, the display presented in this work is built in a bottom-up process and features a vertical electrode arrangement.

The manufacturing process starts with the screen printing of the bottom electrochromic layer onto the substrate. Afterwards, this electrochromic layer is coated with the solid polymer electrolyte, and finally the top electrochromic layer is screen printed on top of the electrolyte.

For the use of the display, we investigated the electrochemical stability (using voltammetry) and the conductivity (using impedance spectroscopy) of the utilized PMMA/PVC-based solid polymer electrolyte. The identified operational voltage range of the device turned out to be +/− 3 V and the conductivity was $(7.8 \pm 0.2) \cdot 10^{-5}$ S/cm between 1 and 10 Hz.

Furthermore, the influence of the electrochromic layer height on the color contrast and the influence of the electrolyte height on the display switching time have been examined. It was found that through optimization of the paint composition and the mesh size of the screen, the color contrast ΔE^* (in the LAB color space) can be increased from $\Delta E^* \approx 14$ up to $\Delta E^* \approx 25$. Additionally, the time for coloring the display can be reduced down to 1.3 s and the bleaching time down to 0.4 s by varying the electrolyte height.

101. Gold Nanoparticle-Doped PPX Nanotube Nonwovens for Highly Efficient Catalysis

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Gold nanoparticles (AuNPs) are highly attractive for heterogeneous catalysis due to their large surface area. However, free NPs have several disadvantages including catalyst removal, reusability, and agglomeration. For this reason, AuNPs need to be immobilized on a heterogeneous support without the loss of catalytic activity [1,2].

Previously, nonwovens consisting of poly(p-xylylene) (PPX) nanotubes doped inside by AuNPs were prepared by the “tubes by fiber template” process [3]. These nanotubes were prepared by coating of electrospun polylactide (PLA)/AuNP composite nanofibers with PPX, followed by selective removal of PLA by thermal degradation. The resulting nonwovens showed an increased catalytic activity in the alcoholysis of silanes, resulting in shorter reaction times even at room temperature and multifold reusability following a tea-bag concept. Nevertheless, the template removal process by pyrolysis generates agglomerated nanoparticles inside the nanotubes and hence diminishes the catalytically active surface.

Changing the template removal method for PLA to extraction results in nanotube nonwovens with well-separated nanoparticles showing five times faster silane conversion with a gold amount 350 times lower than before [4]. Furthermore, the PPX nanotube nonwovens exhibit fast reactant permeation, high reusability, stability against solvents, and no catalyst leaching. The high activity and easy handling as a tea-bag-like system provides an extremely wide application perspective for high-efficiency catalysis, for example, in hydrogen transfer reactions.

Acknowledgment: The authors are indebted to SFB 840 (DFG) for financial support.

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102. Highly Dispersed LaserActivated Metal Oxide Particles via Surface Modification for 3D-MID Application

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A composite of laser-activated particles (LAPs) and super engineering plastic (SEP) of polyphenylene sulfide (PPS) was fabricated via melt-mixing. The LAP surfaces were modified using sodium hydroxide and three different silane coupling agents. The LAPs dramatically deteriorate the mechanical properties of PPS because of its low compatibility with the polymer. However, surface modification, especially via amino silane treatment, effectively prevented the degradation of thermal and mechanical properties upon adding LAP, while modification with phenyl silane had the reverse effect. In order to confirm the different effects, solubility parameters obtained by theoretical calculation via the group contribution method were compared. Thermally and mechanically enhanced LAP/PPS composites were fabricated for laser direct structuring and electroless plating applications.

103. In Situ Cationic *o*- *m*- and *p*- Polyionene as n-Dopant Agent of Poly(3,4-ethylenedioxythiophene)

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An electrochemical synthesis of n-doped PEDOT film electrodes was done by the reduction of (PEDOT) films with a cationic *o-, m-, p-* 1,4-diazabicyclo[2.2.2]octane-based polyionene bearing *N*,*N*′-(meta-phenylene)dibenzamide linkages, as an alternative option to small dopants such as tetramethylammonium (TMA). The n-doping electrodes were achieved by a three-step process: PEDOT film synthesis (1.40 V with $LiClO_4$ Acetonitrile (ACN) as electrolyte), dedoped (−1.30 V in ACN) and redoped (–1.10 V in water with -PI). In all the different cationic isomers, the film obtained showed nanosegregates that coincide with previous Molecular Dynamics simulations using PEDOT: Poly(styrenesulfonate)(PSS) as a dopant. The SEM and AFM analyses revealed some segregation between the PEDOT matrix, retaining the typical globular and porous morphology and the polyionene that were arranged into nanospheres and ultrathin sheets. The doping level obtained was not so far to the TMA doping level (0.069): 0.035 for *o*-PI, and 0.050 for *m*- and *p*-PI. The capacitances obtained were 4.75 F/g, 3.76 F/g and 3.65 F/g for *m*-PI, *o*-PI and *p*-PI respectively, this perhaps being the difference between PEDOT:TMA and the PEDOT:ionene material properties. Parallel to these, the loss of electro stability is lower for the *o*-PI (20%), and increases for *p*-PI (27%) and *m*-PI (51%). Additionally, the *o*- and *p*-PI ability of gelation in acidic medium (HCl 0.1M), the thermostability and hydrophilicity, around 26 ± 5° in all cases, are advantageous properties to the electrode material as a potential emblematic conducting polymer. The studies demonstrated that the isomers of polyionenes can be successfully used as n-dopant agents, offering an important additional property in the case of the gelation with respect to conventional TMA dopant, with *o*-PI being the best option in terms of initial capacitance and the cyclability stability, adding to the gelation property.

104. Influence of Hot Chlorinated Water and Stabilizer Package on the Fatigue Crack Growth Resistance of Glass Fiber Reinforced Polyamide Grades

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In the last two decades, great effort has been made to improve solar-thermal systems in terms of costs, weight, and overall performance by providing better alternative materials. In order to replace conventional materials by polymeric materials, the envisaged materials must withstand the environmental and the mechanical loading conditions. Solar-thermal systems are constantly exposed to different media (e.g., air, heat carrier fluid) and operate at elevated temperatures.

The objective of this research work is to investigate the effects of water and chlorinated water, with varying chlorine contents at an elevated temperature, on the properties of glass fiber-reinforced polyamide (PA-GF30). Three grades of glass fiber-reinforced polyamides, differing in the stabilizer types, were investigated.

In order to characterize the fatigue crack growth (FCG) resistance at different media at 80 ^{o}C, a superimposed mechanical–environmental loading test setup with compact type (CT) specimens was used. The various PA-GF30 grades revealed a different behavior, as the FCG resistance of amino-based (PA-GF30-A) and the phenol-based (PA-GF30-P) polyamide was reduced at higher chlorine contents. While the FCG rate of basic stabilized PA-GF30-C was enhanced by a factor of 4.8 at 10 ppm compared to 1 ppm, it was improved only by a factor of 1.8 for PA-GF30-P. This can be attributed to the addition of the phenolic stabilizer package. The FCG resistance of PA-GF30-A remained stable at various chlorine contents and only a slight decrease in the slope was observed at higher chlorine contents.

105. Influence of Mesoporous Silica Content on the Chemical, Thermal and Tribological Properties of Polyimide Nanocomposites

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Inorganic–organic hybrid nanocomposites have attracted much interest due to their superior properties. Therefore, they have been used in many industrial applications. In this experimental study, high performance polyimide nanocomposites containing 5, 10 and 15 wt.% mesoporous silica (MS-Pi) were synthesized via the in-situ polymerization method. Chemical, thermal, texture and tribological properties were investigated by using Fourier Transform Infrared Spectroscopy (FT-IR), thermo-gravimetric analysis (TGA), Barrett–Joyner–Halenda (BJH) and friction and wear tests at room conditions, respectively. It was observed that MS-Pi nanocomposites were synthesized successfully. New vibrations and minor shifts regarding MS-Pi were observed in the FT-IR spectra. Pore size of the MS-Pi decreased with the increment of MS content. Silica enabled lower thermal stability in the obtained MS-Pi nanocomposites. The coefficient of friction values increased but specific wear rate values decreased with the increment of mesoporous silica.

106. Influence of Macromolecular Architecture on the Optical and Humidity Sensing Properties of Poly(n,n-dimethylacrylamide)-Based Block Copolymers

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Complex macromolecular structures, formed by covalently bonded blocks or material segments of different thermodynamic features, are subject of immense research interest due to their unique properties in solution as well as at surface. In this aspect, the macromolecular architecture can be used as an advanced tool in attempts to tailor the copolymer properties for specific applications.

In this paper, the influence of the macromolecular architecture of block copolymers containing poly(*N*,*N*-dimethyl acrylamide) (PDMAA) on the optical characteristics and sensing properties of the corresponding thin films is discussed. Series of hydrophilic PDMAA-based copolymers of different chemical composition and chain architecture such as di- and triblock, star-shaped as well as cross-linked, were synthesized. The copolymers were characterized by using conventional spectroscopic techniques as well as methods for the characterization of copolymer macromolecular characteristics in solution, namely size-exclusion chromatography and light scattering, both static and dynamic. Thin films of the copolymers of nanometer scale thickness were deposited on silicon substrates by the spin-coating method. The refractive index and extinction coefficient of the copolymer films were calculated from the reflectance spectra by using the non-linear curve fitting method, and the *composition–structure–optical properties* relationships were evaluated. The humidity-sensing properties of the films were studied by measuring the reflectance spectra of the films at relative humidity range from 5 to 98 RH%. The color change of the film was quantified through calculation of the color coordinates, and the implementation of the copolymer films as a color indicator of humidity was justified and discussed.

Acknowledgments: The financial support of Bulgarian National Science Fund under the project DN08-15/14.12.2016 is highly appreciated.

107. Marine Biopolymers to Culture In-Vitro Meat

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In recent years, in-vitro meat has emerged as a new concept in the field of food biotechnology. In-vitro meat uses tissue engineering tools to produce an edible muscle without slaughtering animals. The methods to produce in-vitro meat employ the growth of muscle-cells on a polymeric material (called scaffold) suspended in a culture medium within a bioreactor. The design of edible materials where muscle-cells can live and proliferate is a critical manufacturing stage. The main problem emerges because the current knowledge about the design of scaffolds uses mammalian polymers (bovine gelatin, collagen, fibrin, hyaluronic acid and others). If not slaughtering mammals is the paradigm, then scaffolds made from them must also be replaced. In this work, edible materials were designed using marine biopolymers such as fish-gelatin, alginate, agar and agarose; to be used as scaffolds. The freeze drying process was used to produce the polymeric materials. The physical, mechanical and biological properties of the scaffolds were evaluated. The polymeric materials showed an adequate microstructure and biocompatibility with muscle cells. Additionally, the biological properties of the edible polymeric scaffold allowed an adequate myogenic behavior and cell distribution. The system composed by the edible scaffold and muscle-cells can be used in the production of in-vitro meat.

108. Microcapsule-Type Self-Healing Protective Coating Having Capability Low-Temperature Self-Healing

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Protective coatings can be damaged by microcracks in the coatings themselves or in their substrate materials such as concrete and metals. Most self-healing protective coatings have the ability of autonomic healing of the damaged region. Conventional self-healing systems have been evaluated mostly at room temperature and reports on low-temperature self-healing are rare. We have developed a low-temperature (−20~0 °C) self-healing protective coating using a silanol-terminated polydimethylsiloxane (STP) and dibutyltin dilaulate (DD). STP undergoes condensation reaction in the presence of DD to give a viscoelastic substance at low-temperature (−20 °C). It was demonstrated by an advanced rheometric expansion system that the reaction product showed viscoelasticity in a temperature range of −20~30 °C STP- and DD-containing microcapsules were prepared by in-situ polymerization and interfacial polymerization methods, respectively. The size and morphology of the microcapsules were characterized by optical microscopy and scanning electron microscopy (SEM). The microcapsules were blended into commercial enamel paint formulations, which were applied on steel panels and mortar to make dual-capsule self-healing protective coatings. The self-healing coatings were stored and scratched in a low-temperature (−20 °C) chamber. It was demonstrated by optical microscopy that, when the self-healing coating was scratched, STP and DD were released from ruptured microcapsules and filled the scratched region. The self-healing of the damaged region was demonstrated by release test, anticorrosion test, saline solution permeability test and electrochemical test.

109. Modification of Poly(dimethylsiloxane) by a Laser Treatment as a Preparation for Electroless Metallization

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Due to its physical and chemical properties, poly(dimethylsiloxane) (PDMS) is appropriate for microelectromechanical systems or long-term medical implants. The possibility to metallize it selectively further expands its application area through designing electric circuit geometry, using the advanced method of laser pretreatment for activation. The presentation first describes the negative ablation (swelling) of the material caused by low-frequency excimer pulse irradiation. The observations obtained by optical microscopy, μ-Raman spectrometry and X-ray micro-tomography are demonstrated. Then, the morphology modifications and surface chemistry of PDMS during the laser treatment preceding the electroless metallization are investigated by SEM, μ-Raman spectroscopy and XPS analyses. Because of the ablation process, tracks with very coarse relief are formed. Raman spectra illustrate the well-defined dependence of the chemical composition on the laser fluence, pulse duration, number of pulses and wavelength. An extra peak at about 520 cm^{-1} is observed after the laser processing of the surface. It is assigned to crystalline silicon. The curve fitting of Si 2p and O 1s peaks, obtained by XPS after the laser treatment, shows Si oxidation degree due to the irradiation. Therefore, the very first stable effect of laser beam absorption is to produce local separation of the organic part of the molecular structure of PDMS from its inorganic counterpart. Thus, PDMS decomposition takes place as a function of laser fluence and number of pulses. In addition, the irradiated parts become hydrophilic in contrast with the rest of the material, which remains hydrophobic. This is the condition that enables successful selective electroless metallization in the tracks, without application of masks or external templates. The formation and morphology of electroless deposited nickel and platinum are considered specifically in another poster presentation.

110. Selective Metallization of Poly(Dimethylsiloxane) by Electroless Deposition

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Owing to its biocompatibility, oxidative stability, strength, durability, flexibility, gas permeability, moldability and transparency, poly(dimethylsiloxane) (PDMS) has a wide range of uses. Another advantage of PDMS for its applications in electronic industries is its low-cost process compatibility. Due to its properties, PDMS is an important material for the development of microelectromechanical systems or long-term, medical implants. For building electrical microcircuits on PDMS, a selective electroless metallization is applied to areas activated by laser irradiation. This presentation describes first the principles of electroless deposition. Particularly, applying hydrazine as a reductor, the plating of pure nickel or platinum is enabled inside the laser-formed tracks. An important benefit of the laser irradiation is the elimination of the sensibilization and chemical activation inevitably preceding the selective electroless deposition on supports that are inert to this process. In this way, selective metallization without the application of masks or external templates is performed. The evolution of morphology during the growth of deposits, both inside the tracks and on flat metal substrates, is compared. The formation of nanoflowers or spikes of the deposited material is illustrated. The significance of this morphology for the electric properties of the circuits is explained. This metallization is successfully accomplished after visible radiation laser treatment. It is found that, when nanosecond or visible femtosecond lasers are applied, the time interval between laser treatment and metallization is not a critical process parameter. It is concluded that the electroless metallization in PDMS tracks becomes possible after reaching a suitable balance between the photochemical and photothermal effects of the irradiation.

111. *N*-Sulfopropyl Chitosan as a Reducing and Stabilizer Agent in AgNPs Synthesis with Antimicrobial Properties

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Silver nanoparticles (AgNPs) have antimicrobial properties that depend on their size and shape. AgNPs can be produced by silver ion reduction using chemical agents. Due to the tendency of the AgNPs to aggregate, it is necessary to use capping agents to stabilise the AgNPs. Green synthesis of metallic nanoparticles, avoiding the use of toxic chemicals, is of great interest in fields where high purity and the absence of toxicity is needed. Several natural polymers have been used both as reducing agents and AgNps stabilisers.

Chitosan is a polymer with relevant biological and technological properties, but it is not soluble in physiological environments which has hindered its application in biomedicine and pharmacy. Sulphated chitosan derivatives are soluble in physiological environments and have interesting properties such as antimicrobial and antioxidant among others. It has been reported that sulfated polymers such as heparin or chondroitin sulphate are useful to produce AgNPs. In this work, chitosans with different Mw and DD were chemically modified to produce *N*-sulfopropyl chitosan samples. The ability of these derivatives to reduce Ag^+ in a thermal reduction and to stabilise AgNPs was evaluated for the first time with these chitosan derivatives. The production of AgNPs was followed by UV-spectroscopy and TEM. Different temperatures and reaction times were tested. Antimicrobial and antifungal activities of the polymers and the AgNPs stabilised in polymer solutions were evaluated.

Data reveal that the modified polymers exhibited moderate antimicrobial activity against *S. aureus* and *P. aeruginosa* larger than the parent chitosan. AgNPs produced, assisted by the sulphated polymers, showed antimicrobial activity against *S. aureus* and *P. aeruginosa*. This activity was higher in terms of CMI and CMB when particles were synthesised at 90 °C. Nevertheless, no antifungal activity against *Candida albicans* and *Saccharomyces cerevisiae* was observed at the concentrations assayed.

112. Peptide Enhancement of Gold Nanoparticles Exploited for an Exceptional Anticancer Effect on Colon Carcinoma Cells

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In recent years, metal nanoparticles have often been embedded and used as polymeric materials for the delivery and targeting of pharmaceutical, therapeutic and diagnostic agents in cancer therapy alongside food packaging and other applications. The further steps in nanoparticle-related research are deviating towards combining and strategically engineering multiplexed systems which may enhance the effects of nanoparticles as therapeutics. These multifunctional nanoparticles are supposed to show superior effects on cancer cells. This study was conducted to observe the difference between the effect of a biologically important peptide, gold nanoparticles, and their conjugates. Gold nanoparticles were biosynthesized using fungal extracts of *Aspergillus* species in our respected laboratory and a biologically active peptide (Boc-L-^{D}P-L-OMe) was acquired from a known source, which was subjected to conjugation under standard conditions. These conjugates were tested against the colon cancer (HT 29) cell lines. The results clearly depicted the improved activity of the conjugates compared to the peptide and gold nanoparticles only. At a very low concentration of only 1 µg/mL, the conjugate showed inhibition of 63.83%, whereas peptides or gold nanoparticles independently demonstrated less than 50% inhibition on cancer cells. Further experiments such as fluorescent imaging and DNA fragmentation assay were carried out to confirm the capability of these conjugates. The results were duly compared with the effect of these nanoparticles, peptides, and conjugates on normal cell lines as well.

113. Photochemical Modification of a Medical Grade Polyamide Using a Plasma-Based Pre-Treatment

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Introduction: The surface modification of hydrophobic polymers (polyamide 12, PA12) offers a method to increase the hydrophilicity of the surfaces of polymeric medical devices. Plasma is a suitable technology but unfortunately, the modification is reversible, and the hydrophilicity decreases in short time. Otherwise, surface modification with photo-reactive chromophores, namely phenyl azide (PhAz), offers an alternative and irreversible method for the surface hydrophilization.

Methods: The aim of the present work was to combine plasma technology and the azide's photo-reaction to increase the PA12 hydrophilicity. In the first process step, the polymer surface was activated using plasma reaction. Afterwards, a solution of PhAz was sprayed on the activated polymer surface. Finally, the samples were treated with ultraviolet light to trigger the chemical reaction between the polymer chemical groups and PhAz.

Results: Untreated, plasma-treated, and photo-modified polymers were compared in terms of wettability by means of the contact angle (CA) measurements (immediately, 1 week and a month from the reaction). The hydrophilicity increase of treated surfaces was estimated through "deltaCA", the decreasing of CA compared to the untreated polymer. Plasma-treated samples were initially very hydrophilic, but hydrophilicity was significantly reduced after 1 week and almost completely lost after 1 month. PhAz-treated samples were significantly more hydrophilic if compared with untreated polymer and after 1 month deltaCA was unchanged. The samples produced by plasma activation followed by treatment with PhAz were very hydrophilic. Some hydrophilicity reduction occurred over time, but after 1 month "deltaCA" was stabilized and still considerably high.

Conclusions: The plasma-based pre-activation process was able to improve the PhAz surface process modification of PA12. Conceivably, new chemical groups generated by the plasma reaction can react with PhAz chromophores and increase the yield of the photochemical reaction, making the polymer surface more hydrophilic if compared with the other processes.

114. Plasma Functionalized Surface of Commodity Thermoplastics and Conducting Polymers for Dopamine Detection

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We have fabricated potentially generalizable sensors based on polymeric-modified electrodes for the electrochemical detection of dopamine, an important neurotransmitter molecule. Sensitive and selective sensors have been obtained by applying cold-plasma treatment to electrochemically inert plastics, such as polyethylene, polypropylene, polyvinylpyrrolidone, polycaprolactone and polystyrene; and semiconducting polymers, such as poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(*N*-cyanoethylpyrrole) (PNCPy). This simple physical treatment offers several advantages with respect to the sophisticated chemical methods usually reported (e.g., functionalization, incorporation of catalytic nanoparticles, etc.). The effects of the plasma in the electrode surface activation, which is an essential requirement for the dopamine detection when inert polymers are used, have been investigated using X-ray photoelectron spectroscopy. Results indicated that the exposure of polymer-modified electrodes to cold plasma produces the formation of a large variety of reactive species adsorbed on the electrode surface, which catalyse the dopamine oxidation. Thus, we have defined a paradigm for the fabrication of electrochemical sensors by using cheap and recyclable plastics. The invention has been recently patented by UPC [1] and the results have been reported elsewhere [2].

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115. Polyimide/Graphebe Oxide Nanocomposite-Based Nonvolatile Resistive Memory Device

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Polyimides (PIs) have been widely used in microelectronics and organic electronics due to their excellent mechanical, dielectric, thermal, and chemical properties. Also, PIs exhibit promising application in various optoelectronic devices as they offer the opportunity to adjust the optoelectronic properties. Recently, resistive random access memory (RRAM) has been studied as a next generation nonvolatile memory, because of its simple metal–insulator–metal (MIM) structure and excellent operating characteristics such as fast operating speed, low power consumption, and low unit cost. In this work, GO was used as a composite material with polyimide, because it has been demonstrated to be a promising candidate for dielectric materials or charge-trapping layers. The graphene oxide-based polyimide (PI-GO) nanocomposite was prepared and later used as a memory layer in the fabrication of a RRAM device. The PI-GO was prepared by an in situ polymerization method. The device showed write-once-read-many-times (WORM) characteristic with a high ON/OFF current ratio of 3.41×10^8, which is superior compared to the reported current ratios of a polymer-based RRAM device. This outstanding current ratio was attributed to the high charge-trapping ability of GO. In addition, the device had good endurance until the 100th cycle and retention time of 1500 s. These results suggested that PI-GO as an active layer in RRAM is an attractive candidate for applications in next generation nonvolatile memory.

116. Preserving Nanodroplets' Integrity by Their Entrapment in Nanofibers

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Nanodroplets of different hydrophobic liquids such as essential oils or monomers are interesting in medicine, food science, and self-healing applications. Unfortunately, their applications are limited because nanodroplets have short-time stability. Moreover, nanodroplets are usually kept in the form of liquid emulsion. Therefore, they require large volume and weight for their storage because of the continuous phase surrounding the droplets. Herein, we report a method for preserving the structural integrity of nanodroplets and reducing the volume and weight of storage of nanodroplets. The method consists in first synthesizing nanodroplets such as peppermint oil with 150 nm and subsequently embedding nanodroplets in polymer nanofibers by the colloid-electrospinning technique. The obtained nanofibers display a smooth surface with a diameter around 220 nm. After dissolution of the nanofibers, the embedded nanodroplets were still stable and could be kept at room temperature for several weeks. The nanofibers were applied for the storage of a monomer and a catalyst used as healing agents in self-healing materials.

117. Semiconducting Polymers and Hybrids for Organic Electronics

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Over the past two decades, significant progress has been achieved in the preparation of semiconducting polymers and successful commercial devices based on them are now gradually beginning to appear. More specifically, for organic photovoltaic (OPV) cells, the power conversion efficiency has increased from just a few per cent to around 13%, and the stability has increased from hours to years. The performance of polymer solar cells (PSCs) has steadily increased owing to the development of more efficient electron-donors or electron-acceptors and the control and stabilization of their blend’s morphology. Our efforts are focused on the scale-up synthesis of the different efficient polymeric electron donors as well as developing a synthetic methodology for creating more complex hybrid materials based on semiconducting polymers/fullerene nanostructures acting as potential compatibilizers in electron donor–electron acceptor blends. The semiconducting units are directly attached to different carbon nanostructures resulting in hybrid structures that combine properties of the polymers for the electron donor and the fullerene acceptor. Such complex structures have been used as compatibilizers for the donor/acceptor active layer (1–3). Also, semiconducting species combined with pyridine units that could non-covalently interact with the fullerene part have also been developed.

In the case of PLEDs, both semiconducting polymers and polymeric metallocomplexes are used in order to obtain the desired colored emission. We focused on developing an efficient route towards new materials with controllable light emission. Variable light emissions have been achieved, developing soluble light emitting polymers from rigid flexible alternating polymers containing conjugated segments (4) and such materials have been used for the device construction and testing of PLEDS (5).

118. Study of Flexible Electrodes for Supercapacitors Based on the Supramolecular Assembly of Biohydrogel and Conducting Polymer

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A flexible p-type doping based on conductive organic polythiophene:hydrogel electrodes was developed by two-step processes: first, the synthesis of poly(3,4-ethylenedioxythiophene) (PEDOT) microparticles dispersed into a poly-γ-glutamic acid (γ-PGA) hydrogel matrix with alumina filler addition followed by the electropolimerization of poly(hydroxymethyl-3,4-ethylenedioxythiophene) (PHMeDOT) using these PEDOT particles as polymerization nuclei. Flexible p-doping electrodes were obtained using a polymerization time of 7 h and a dopant of $LiClO_4$; the final electrode possesses a specific capacitance of 45.4 ± 0.7 mF/cm^2 from cyclic voltammetry and charge–discharge long-term stability. The applicability of these electrodes in lightweight and flexible energy-harvesting systems—useful for energy-autonomous, low-power, disposable electronic devices—has been proved by powering an LED bulb. Finally, a highly flexible and lightweight free-standing electrode was obtained by functionalizing g-PGA hydrogels with PEDOT particles and PHMeDOT. The g-PGA hydrogel provided a support with consistency, robustness and an open internal structure, a matrix that allows the ion diffusion process and the conduction of the dopant. PEDOT particles played a key role in the electropolymerization of HMeDOT monomers, enhancing the homogeneous distribution of PHMeDOT chains across the hydrogel, thus improving the capacitance of the material. The film shows a specific capacitance achieving 45–47 mF/cm^2; additionally, the film possesses an excellent cycle durability as determined by GCD. The [PEDOT/g-PGA]PHMeDOT(q = 7 h) composite is a potential good electrode material for different applications such as textiles (e.g., wearable electronics) biomedic (sensors) and energy storage applications (supercapacitors) where robustness and flexibility is required.

119. Study on Color Retention of ASA Resin under Accelerated Weathering Test

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Not only do the physical properties of plastic automobile parts deteriorate when exposed to a harsh external environment such as UV radiation, high temperature, and humidity, but the exterior also discolors due to the oxidation of polymer material. For this reason, many plastic parts are generally coated with paint. However, due to the high percentage of defects in the painting process and environmentally hazardous substances generated during the process, the demand for unpainted resin is also high. Therefore, there is an increasing demand for research related to materials that do not suffer discoloration problems in long-term use even without painting. This study investigated the discoloration tendency of acrylonitrile–styrene–acrylate (ASA) resin used as a material for the exterior parts of automobiles under SAE J 1960 condition and analyzed the trend of Delta E change indicating the degree of discoloration. In this study, the discoloration trends of different color samples and the discoloration tendency by dye and pigment were studied by the application of dyes and pigments capable of expressing color constituting Delta E value.

120. Surface Appearance and Mechanical Properties of Polyamide-Based Paintless Metallic Nanocomposites

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Polyamide (PA)/aluminum flake (Al) composites show high-gloss pre-colored plastic with metallic appearance in automotive parts. However, flow mark occurs in PA/glass fiber (GF)/Al composites to improve the mechanical properties. Nanocomposites are a new class of composites, which are particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometer range. Several advances in the field of polymer nanocomposites for applications such as the automotive, packaging, aerospace, and agricultural sectors have been established in recent years. This is because the properties of polymers can be tuned precisely by the incorporation of nanofillers. PA/montmorillonite (MMT) nanocomposites have attracted great industrial interest due to potential applications; PA/MMT nanocomposites exhibit significant improvements in mechanical and thermal properties over conventional composites. In this study, we prepared PA/MMT/Al nanocomposites with different organo-MMT content (1.0~5.0 wt%) by melt intercalation and then conducted a characteristic study on these PA/MMT/Al nanocomposites. As a result, PA/MMT/Al nanocomposites are a high-gloss material that features metallic brilliance and high stiffness. The paintless metallic nanocomposites are characterized using a glossy meter, color meter, universal testing machine (UTM) and IZOD impact tester.

121. Thermodynamic Model for a Reversible Desalination Cycle Using Weak Polyelectrolytehydrogels.

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The recently proposed use of hydrogels for water desalination is based on the decrease of salt concentration in the gel upon compression. To make this approach competitive with membrane-based desalination methods, it should work close to maximum thermodynamic efficiency. Desalination cycles used in first desalination experiments with hydrogels involved an irreversible mixing step, which inevitably reduced the thermodynamic efficiency. In this work, we develop a thermodynamic model for compression of weak polyelectrolyte hydrogels in open and closed systems. We use this model to design a reversible desalination cycle which can, in principle, achieve the maximum thermodynamic efficiency. We also show that if weak polyelectrolyte hydrogels are used at low salinity of the desalinated solution, then the variable ionization of the hydrogel leads to a non-monotonic dependence of salt concentration on the compression of the gel. Therefore, the use of weak polyelectrolytes at low salinities requires a modified design of the desalination cycle.

122. Synthesis and Characterization of $BaTiO_3$/Polypyrrole Composites with Exceptional Dielectric Behaviors

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There is a challenging demand for high dielectric constant materials in different fields, especially the electronic industry. $BaTiO_3$/polypyrrole composites with exceptional dielectric and thermal properties have been synthesized by in-situ polymerization of pyrrole in a very slightly acidic medium. $BaTiO_3$ was dispersed to synthesize composites (1 to 5%). These composites were characterized for their structure and thermal stability by an X-ray diffractometer (XRD), Fourier transform infrared (FT-IR) spectroscopy and thermo gravimetric (TGA) analysis respectively. The structural morphology of the prepared samples was probed using the images obtained from scanning electron microscopy (SEM). An impedance analyzer (LCR meter) was utilized to investigate the dielectric parameters. FT-IR data confirmed the presence of the two phases and their interaction, inferred from the shifting of normal Ppy peaks towards shorter wave number. The data obtained from XRD confirmed the presence of both amorphous phase and crystallites. TGA analysis (25 ^{o}C to 600 ^{o}C) confirmed the thermal stability of the prepared composites in a wide temperature range. It was found that the composite with 5 wt% $BaTiO_3$ was most stable. The SEM analysis reveals that the introduction of $BaTiO_3$ particles changed the hemispherical shaped grains of the matrix to rod shaped grains engaged in clusters with clear grain boundaries. The size of the grains was estimated to be 0.2–0.5 µm with very small porosity in the composite's structural morphology. The dielectric constant of the composites was enhanced with filler contents from 418 to 522 at 1 MHz for 1 wt% and 5 wt% $BaTiO_3$ respectively. It is concluded that the introduction of $BaTiO_3$ into the polymer matrix created such interfaces which had an effect on the final dielectric behavior of the composites.

123. Obtaining Composite Paper from Cellulose and Plastic Waste

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The reuse of waste natural fibres as polymer reinforcement is a sustainable option of benefit for the environment. The present work aims to find new original forms by making use of sub-products of the agriculture and plastic industry; these wastes are abundant and a source of pollution, so we offer some solutions to replace plastic materials of petrochemical origin. Biodegradable composite material is obtained by the association of natural cellulose and plastic wastes, using simple mixing in a common solvent by blending polystyrene and polyacrylamide with cellulose. To characterize these composites, some tests were conducted on, for example, the crystallinity rate IR, morphological structure and absorbent properties. The proposed new composites are in agreement with the research in the field on recycling lignocellulosic waste to obtain new ecological, environmentally friendly materials.

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