**Macromolecular Chemistry and Physics**

**Flower-Like Multicompartment Micelles with Janus-Core Self-Assembled from Fluorocarbon-Terminated Pluronics**

Multicompartment micelles (MCMs), whose cores have at least two compartments, show potential applications in various areas, but the synthesis of polymers for preparing MCMs is usually tedious and time-consuming. In this work, two well-defined telechelic fluorocarbon-terminated triblock copolymers, F8-PEO100-PPO65-PEO100-F8 (F8-F127-F8) and F8-PEO132-PPO50-PEO132-F8 (F8-F108-F8), are synthesized via a single-step coupling reaction of Pluronics F127 or F108 with perfluoro-1-octanesulfonyl fluoride and characterized by Fourier-transform infrared and NMR spectroscopies, as well as gel permeation chromatography and surface tensiometry. Both of these fluorocarbon-terminated Pluronics can self-assemble into spherical MCMs with Janus-core in aqueous solution, as evidenced by transmission electron microscopy imaging. Since the lipophilic block (PPO) and fluorophilic segments (F8) are separated by the hydrophilic blocks (PEO), these fluorocarbon-terminated Pluronics will loop to give rise to flower-like MCMs, and the calculations based on thermodynamics and dynamics support the formation of such unique aggregates. A “pre-self-assembly” mechanism is proposed to explain the formation process of flower-like MCMs with Janus-core prepared by these telechelic fluorocarbon-terminated triblock copolymers. Multicompartment micelles (MCMs) with Janus-core can be obtained by self-assembly from fluorocarbon-terminated Pluronics. The fluorocarbon-terminated Pluronics will loop to form flower-like MCMs due to lipophilic block, and fluorophilic segments are separated by hydrophilic blocks. The calculated results from thermodynamics and dynamics support the loop formation. A “pre-self-assembly” mechanism is proposed to explain the formation process of such flower-like MCMs with Janus-core.

**Phase Transitions of Polyaniline Induced by Electrochemical Treatment**

It is known that semiconducting polymers undergo structural changes only during overoxidation, which is simultaneously connected with the degradation of these polymers. However, if their electrochemical performance is studied within a potential window in which the polymer is stable, no morphological and/or structural changes are observed. It is demonstrated for the first time that polyaniline is able to undergo phase transitions (morphological/structural changes) between the potential cut-off limits of 0 and 0.7 V, within which no degradation is observed. Scanning electron microscopy measurement provides evidence that the polymer surface changes from porous to smooth film, and differential scanning calorimetry and X-ray diffraction data are used to investigate and confirm structural changes during the electrochemical treatment. Electrochemical performance is studied for polyaniline before and after phase transitions and is higher for polymer, in which morphological/structural changes occur. These results demonstrate that morphological/structural changes predetermine physical–chemical performance. In particular, the rearrangement of the polyaniline chains during electrochemical treatment has a crucial impact on the ability of the polymer to store energy. Polyaniline is able to undergo phase transitions (morphological/structural changes) during electrochemical treatment, which has a crucial impact on the ability of the polymer to store energy.

**Tuned Surface and Mechanical Properties of Polymeric Film Prepared by Random Copolymers Consisting of Methacrylate-POSS and 2-(Methacryloyloxy)ethyl Phosphorylcholine**

Poly(2-(methacryloyloxy)ethyl phosphorylcholine) (PMPC) is known as a biocompatible polymers. Copolymerization of 2-(methacryloyloxy)ethyl phosphorylcholine (MPC) and hydrophobic monomers is a general approach that gives bioinert functions to solid materials via the surface coating. However, due to the amorphous nature and super hydrophilicity of the MPC-based copolymers, both the surface and the mechanical properties are not controlled for biomedical applications. Here, the modulated mechanical property and the surface wettability of the MPC-based copolymers are shown by using a
polyhedral oligomeric silsesquioxane (POSS) methacrylate. MPC is copolymerized with POSS methacrylates bearing different vertex groups of ethyl (C2H5), hexyl (C6H13), and octyl (C8H17) via radical polymerization. It is found that only the C2H5-POSS induces the increased mechanical strength, low surface wettability, and cellular attachment, suggesting that the C2H5-POSS moiety restricts the motion of PMPC chain. The finding is anticipated to be tuned for both surface and bulk functions of PMPC for biomedical applications. A random copolymer of polyhedral oligomeric silsesquioxane (POSS) methacrylate and 2-(methacryloyloxy)ethyl phosphorylcholine (MPC) improves both surface and bulk properties. It is found that only the POSS bearing ethyl group induces the increased mechanical strength, low surface wettability, and cellular attachment. The finding is anticipated to be tuned for both surface and bulk functions of poly-MPC for biomedical applications.

**Synthesis and Characterization of Isoindigo-Based Polymers with Thermocleavable Side Chains**

Stability of bulk heterojunction films for organic solar cells is a critical factor for commercial viability. One method to stabilize these films is to include cleavable side chains, which reduce the solubility of the polymers when removed. In order to study the stabilizing effect of cleavable side chains, a series of random copolymers using isoindigo with 0, 10, 20, 50, and 100% thermally cleavable side chains based on the tert-butyloxycarbonyl (t-BOC) group are synthesized. The polymers show a distinct one-step thermal cleavage of the side chains, with no separable dealkylation and decarboxylation steps. The thermal stability in film is studied with transmission electron microscopy and atomic force microscopy. The polymer with all t-BOC side chains on isoindigo significantly improves thermal stability with regard to crystal growth and phase separation in film. These results suggest BOC-substitution can be used for large scale processing to produce insoluble polymer films with a high degree of thermal stability. A series of donor–acceptor random copolymers bearing thermocleavable side chains is synthesized and characterized. The isoindigo-based polymers undergo a one-step thermal degradation corresponding to cleavage of the side chains below 200 °C. The effect on thermal stability in blend films with PC61BM is investigated using transmission electron microscopy and significant stabilization of the morphology is found.

**Fluorescence Recovery after Photobleaching in Ultrathin Polymer Films**

Fluorescence recovery after photobleaching (FRAP) is a widely used technique to study the transport of molecules in biological systems. Recently, FRAP has been used to study molecular transport in polyelectrolyte multilayers (PEMs). Through numerical simulations verified by experiments, it is shown that the FRAP behavior of PEM films in an aqueous medium differs significantly from that in previously explored systems such as single cells. This is because fluorescence recovery can take place through the aqueous medium surrounding the PEM film. The simulations show the critical role of the time scale of the different processes, namely, diffusion through PEM, diffusion through surrounding medium, and the unbinding rate of fluorophore-labeled species in the interpretation of FRAP data. An important conclusion from the numerical and experimental study is that, for ultrathin PEM films with ≈100 nm thicknesses, recovery is dominated through the solution medium and hence, classical FRAP analysis is not sufficient to probe diffusion in PEM. The numerical study reveals several aspects of the FRAP phenomena in thin polymer films that are critical for the proper interpretation of experimental data. The fluorescence recovery after photobleaching in a multispecies system such as polyelectrolyte multilayer (PEM) is initiated after it is introduced to an aqueous medium. Often, researchers neglect the recovery through aqueous medium, citing low diffusion coefficient. Surprisingly, the routinely used analysis can have significant error in the case of ultrathin (=100 nm) PEM.

**Smectic-B Liquid Single Crystal Elastomers as Efficient Optical Mechanotransducers**

Carbazole-based liquid single-crystal elastomers (LSCEs) are valuable materials to convert mechanical
forces into optical signals, i.e., optical mechanotransduction. The identification and rationalization of the different structural factors governing the mechanotransduction process are essential to guide the future design of these smart sensing materials. Herein, how the type of mesophase displayed by the elastomer impacts its transducing capabilities is explored. Remarkably, smectic-B LSCEs are significantly more efficient mechanotransducers than their nematic analogs, independent of the length of the flexible spacer that connects the fluorogenic monomers to the main polymeric backbone. In this instance, the fluorogenic moieties are located within the smectic lamellae formed by the mesogenic units, thereby forcing a stronger interaction between both the platforms and resulting in a much more effective fluorescence quenching upon deformation. Smectic-B liquid single crystal elastomer (LSCE)-containing carbazole-based fluorophores within their polymeric networks are valuable systems for optical mechanotransduction under ambient conditions. Remarkably, smectic-B LSCEs are more effective transducing materials than their nematic counterparts, independent of the length of the flexible spacer connecting the carbazole fluorophores to the main polysiloxane chain.

A New Environmentally Friendly Approach to Lignin-Based Cyclic Carbonates
Herein, a novel synthesis of a fully renewable lignin-based building block equipped with cyclic carbonate functionalities is presented. In an efficient two-step procedure, organosolv lignin from ethanol–water pulping of beech wood is oxyalkylated with glycerol carbonate to insert adjacent hydroxyl groups. The oxyalkylated lignin is then reacted via transesterification with dimethyl carbonate or ethylene carbonate in dimethyl sulphoxide under alkaline conditions producing cyclic carbonate functionalized lignin. This transesterification is studied as a function of time, catalyst type, and catalyst amount using NMR spectroscopy as well as size exclusion chromatography. Transesterification reactions with K2CO3 as catalyst (0.4 eq.) afford lignin-based cyclic carbonate with almost complete conversion (96%) within 6 h, as analyzed by 31P and 13C NMR spectroscopy. This green building block represents a reactive prepolymer for the synthesis of nonisocyanate polyurethanes. Cyclic-carbonate-functionalized lignin is obtained via a straightforward, environmentally friendly approach. This two-step procedure using organosolv lignin from ethanol–water pulping of beech wood allows the synthesis of a renewable prepolymer for the synthesis of nonisocyanate polyurethanes.

Unique Transitions in Morphology and Characteristics of Porous Poly(Lactic Acid) Enantiomers
This study examines unique changes in the morphology and physical properties of monolithic poly(lactic acid) (PLA) enantiomers. It is revealed for the first time that PLA monoliths containing stereocomplex (sc) crystals are successfully produced using enantiomeric poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) using a simple phase separation process with ternary solvent (1,4-dioxane/2-butanol/water). The basic structure of the monoliths is changed drastically from needle-like to spherical morphology until reaching a PLLA/PDLA ratio to equivalence. The PLA monolith prepared from a stoichiometric amount of PLLA/PDLA has high sc crystallinity without any homochiral crystals, and it shows higher melting temperature (226 °C), surface area (131 m2 g−1), and water contact angle (144.5°) compared with those of neat PLLA (180 °C, 86 m2 g−1, and 137.5°, respectively). Moreover, this sc-PLA monolith exhibits excellent resistance to several good solvents of PLLA, whereas the pristine PLLA monolith is dissolved instantly in these solvents. Poly(lactic acid) (PLA) monoliths with stereocomplex formation exhibiting both excellent heat and chemical resistance are designed by newly developed phase separation. A basic structure of the monoliths is changed drastically by the ratio of poly(L-lactic acid)/poly(D-lactic acid) (PLLA/PDLA): The PLA monolith prepared from neat PLLA or PDLA shows interconnected needle-like morphology whereas that prepared from PLLA/PDLA exhibits spherical structure.
Temperature and pH Controlled Self-Assembly of a Protein–Polymer Biohybrid
A novel pH and temperature dual-responsive bioconjugate is prepared by grafting thermoresponsive polymer chains from a pH-responsive protein amelogenin via atom transfer radical polymerization. To the best of our knowledge, this is the first time that amelogenin is exploited to prepare a hybrid biomaterial with new stimuli-responsive property. In both basic and acidic solutions the protein–polymer bioconjugate is able to self-assemble into uniform and stable nanoparticles when heated to above the lower critical solution temperature of the polymer. The amelogenin-based stimuli-responsive bioconjugate may be of great use in the fields of bioseparation and drug/gene delivery, and the synthetic approach reported here should provide a convenient means to preparing amelogenin-based functional biohybrid materials. A novel pH and temperature dual-responsive protein–polymer conjugate is prepared by grafting poly(N-isopropylacrylamide) chains from the pH-responsive protein amelogenin via atom transfer radical polymerization technique. This hybrid biopolymer is able to self-assemble into highly uniform nanoparticles by adjusting environmental conditions and is promising for applications in bioseparation and drug delivery fields.

Polyolefins Made with Dual Metallocene Catalysts: How Microstructure Affects Polymer Properties
Slow crack growth resistance correlates with the lifetime of polyethylene pipes. Since this measurement may take considerable time, alternative ways to estimate it help expedite the development of new polyethylene resins. The primary structural parameter (PSP2), calculated from the distribution of molecular weight and short chain branching of polyethylenes, can predict the stress crack growth resistance of polyethylene resins without needing to measure it over long periods of time. In this investigation, a model is developed to calculate PSP2 of ethylene homopolymers and ethylene/1-hexene copolymers made with two metallocene catalysts. For each metallocene, the effect of the following parameters on PSP2 is investigated: (1) polymer mass fraction, (2) polymer average molecular weight, and (3) average comonomer fraction. The simulation trends agree with previously published experimental results. The generated 3D surface response plots are useful guides for the design of polyethylenes having optimized slow crack growth resistance. A model is developed to show how the primary structural parameter (PSP2) is affected by the microstructure of polyethylenes made with two single-site catalysts. Since PSP2 is related to slow crack growth resistance, the 3D plots serve as guides for product design.

Double Hydrophilic Block Copolymer Self-Assembly in Aqueous Solution
Self-assembly of double hydrophilic block copolymers (DHBCs) in water is an emerging area of research. The self-assembly process can be derived from aqueous two-phase systems that are composed of hydrophilic homopolymers at elevated concentration. Consecutively, DHBCs form self-assembled structures like micelles, vesicles, or particles at high concentrations in water and without the use of external triggers that would change solubility of individual blocks. Careful choice of the two hydrophilic blocks and design of the polymer structure allows formation of self-assembled structures with high efficiency. The present contribution highlights recent research in the area of DHBC self-assembly, including the polymer types employed and strategies for crosslinking of the self-assembled structures. Moreover, an overview of aqueous multiphase systems and theoretical considerations of DHBC self-assembly are presented, as well as an outlook regarding potential future applications in areas such as the biomedical field. Double hydrophilic block copolymers form self-assembled structures in aqueous solution; for example, particles, micelles, or vesicles. The self-assembly relies significantly on polymer concentration and utilized polymer blocks. Moreover, self-assembled structures can be stabilized via crosslinking chemistry. Here, a variety of examples is reviewed with respect to formed structures and concentration range as well as theoretical background and aqueous multiphase systems.
Conjugated Microporous Polytetra(2-Thienyl)ethylene as High Performance Anode Material for Lithium- and Sodium-Ion Batteries

A novel, thiophene-rich conjugated microporous polymer of polytetra(2-thienyl)ethylene (PTTE) is synthesized via FeCl₃-catalyzed oxidative polymerization and applied as an anode material for lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs). Owing to the high surface area, high redox-active thiophene content, and the plentiful nanoporous structures in PTTE, the assembled LIBs exhibit a high specific capacitance of 973 mA h g⁻¹ at 100 mA g⁻¹ with excellent rate performance, and the SIBs show a capacitance as high as 370 mA h g⁻¹ at a current density of 50 mA g⁻¹, excellent rate capability, and outstanding cycling stability with a capacity retention of 230 mA h g⁻¹ at 200 mA g⁻¹ after 100 cycles. These results demonstrate this thiophene-rich conjugated microporous polymer as a promising electrode material for next-generation energy storage devices. Conjugated microporous polymers of polytetra(2-thienyl)ethylene as an anode exhibit excellent electrochemical performance for Li and Na storage.

Simple Photochemical Route to Block Copolymers via Two-Step Sequential Type II Photoinitiation

A simple method for the preparation of block copolymers by a two-step sequential Type II photoinitiation is described. In the first step, amine functionalized poly(methyl methacrylate) (PMMA-N(Et)₂) is prepared by photopolymerization of methyl methacrylate at λ = 350 nm using benzophenone and triethyl amine as photosensitizer and hydrogen donor, respectively. Subsequent benzophenone-sensitized photopolymerization of tert-butyl acrylate using PMMA-N(Et)₂ as hydrogen donor yielded poly(methyl methacrylate)-block-poly(tert-butyl acrylate). The obtained hydrophobic block copolymer is readily converted to amphiphilic polymer by hydrolysis of the tert-butyl ester moieties of the block copolymer as demonstrated by contact angle measurements. All polymers are characterized by NMR, Fourier transform infrared and UV–vis spectroscopies, and differential scanning calorimetry (DSC) thermal analyses. A simple method for the preparation of block copolymers by a two-step sequential Type II photoinitiation is described. The method pertains to the use of triethylamine as hydrogen donor in benzophenone-sensitized photopolymerization of methyl methacrylate resulting in the formation of amine functional polymers. Similar photopolymerization of tert-butyl acrylate using thus-formed polymers yields poly(methyl methacrylate)-block-poly(tert-butyl acrylate).

Protein/Polysaccharide-Based Hydrogels Prepared by Vapor-Induced Phase Separation

The preparation of hydrogels via vapor-induced phase separation (VIPS) has received limited attention. VIPS consists of exposing a solution containing a gelling agent to a vapor that induces gelation via mass transfer at the gas/liquid interface. Using mixtures of gelatin B and xanthan gum exposed to acetic acid vapor, it is demonstrated that VIPS is efficient for the preparation of protein/polysaccharide mixed gels. This method prevents the typical precipitation of protein/polysaccharide complexes observed in the strong electrostatic attraction regime. It significantly extends the pH window associated with gel formation, and yields mechanically stronger gels as compared to other preparation techniques such as using glucono delta-lactone or the conventional dropwise pH adjustment technique. Finally, VIPS yields gels at very low gelling agent content, and for a variety of other mixed systems, including globular proteins such as bovine serum albumin. Hydrogels prepared by vapor-induced phase separation (VIPS) consist in exposing a solution containing a gelling agent to a vapor that induces gelation via mass transfer at the gas/liquid interface. Using mixtures of gelatin B and xanthan gum exposed to acetic acid vapor, it is demonstrated that VIPS is efficient for the preparation of robust protein/polysaccharide mixed gels at very low concentrations.

A Novel Approach to Increase the Stability of Liposomal Containers via In Prep Coating by Poly[N-(2-Hydroxypropyl)Methacrylamide] with Covalently Attached Cholesterol Groups
Highly stable liposomes are developed by coating phosphatidylcholine liposomes with amphiphilic N-(2-hydroxypropyl)methacrylamide copolymer. Two approaches in the preparation of coated liposomes are employed: the copolymer is added during (“in prep”) or after (“ex post”) the liposome formation. The influence of polymer concentration and coating method is evaluated using the cryogenic transmission electron microscopy, dynamic light scattering, and small-angle X-ray scattering techniques. The in prep modification significantly increases, up to four weeks, the stability of liposomes against aggregation and makes the liposomal membrane nonpermeable toward an inorganic salt. Such enhanced longevity is attributed to the different structure of in prep coated liposomal membranes. “In prep” and “ex post” coated liposomes shows higher stability compared with uncoated liposomes in both longevity and preservation of the loaded compound. In prep coated liposomes manifest the highest stability over one month, which is also fair for the physiological media. The highest stability of in prep coated liposomes is attributed to the unique structure of their membrane, which is proved by small-angle X-ray scattering experiments.

Liquid-Phase Exfoliation of Hexagonal Boron Nitride into Boron Nitride Nanosheets in Common Organic Solvents with Hyperbranched Polyethylene as Stabilizer

Large-scale production of boron nitride nanosheets (BNNSs) is of significant importance for their various applications. Herein, a facile strategy is well demonstrated for BNNS fabrication via liquid-phase exfoliation of bulk hexagonal boron nitride (h-BN) in common organic solvents with hyperbranched polyethylene (HBPE) as stabilizer. Synthesized from commercially abundant ethylene stock via a simple process, the HBPE is found to effectively promote h-BN exfoliation both in tetrahydrofuran and chloroform under sonication, to render stable dispersions of high-quality monolayer or few-layer BNNSs with adjustable concentrations. This has been confirmed to originate from the noncovalent CH–π interactions between the HBPE and BNNS surface, which results in irreversible HBPE adsorption on the latter to effectively prevent their reaggregation. The resultant HBPE-functionalized BNNSs are highly dispersible in chloroform or N,N-dimethylformamide at a concentration as high as 10.0 mg mL−1, and can be successfully used as nanofiller for a fluorinated copolymer. Large-scale, liquid-phase exfoliation of high-quality boron nitride nanosheets (BNNSs) from bulk hexagonal boron nitride is well demonstrated in common organic solvents (tetrahydrofuran or chloroform) with a hyperbranched polyethylene (HBPE) as stabilizer. The resultant HBPE-functionalized BNNSs can significantly improve dielectric performance of a fluorinated copolymer, with dielectric constant increasing by 2.6 times by adding only 0.5 wt% of the BNNSs.

Gain Properties and Distributed Feedback Laser Performance of 7F6/Poly(Styrene) Blend Films: Potential Core Material for Plastic Optical Fiber Expanding the Bandwidth to Visible Region

Optical gain properties of blue emission oligomer 7-unit 9,9-dihexylfluorene (7F6) and its blends with polystyrene (PS) are reported. 7F6 demonstrates high photoluminescence quantum yield (65%), low amplified spontaneous emission threshold (EthASE = 0.6 kW cm−2), high gain coefficient (g = 90.9 cm−1), and extremely low distributed feedback laser threshold (Ethlaser = 86 W cm−2). Unlike polymer gain materials, the phase separation between 7F6 and PS is small even in a high blending ratio. The 70 and 50 wt% 7F6/PS blends display excellent gain properties with g = 70.7 and 64.3 cm−1, EthASE = 1.1 and 2.1 kW cm−2, and Ethlaser = 0.3 and 0.41 kW cm−2, respectively. The photostability and thermal stability are improved significantly by blending 7F6 into PS. These results promise 7F6/PS blends as a potential core material for expanding the bandwidth of plastic optical fiber. 7-unit 9,9-dihexylfluorene (7F6), exhibits excellent optical gain properties. Very weak phase separation is observed from 50–70 wt% 7F6 doped polystyrene (PS). High gain and low laser threshold of the 7F6/PS, together with improved photo and thermal stabilities, demonstrate 7F6 as a promising core material for plastic optical fibers, to expand the bandwidth to the visible region.
Research on the Preparation of Polycaprolactone Porous Films with Decoration of Protein Arrays via the Emulsion-Based Breath Figure Method

A facile method to fabricate honeycomb-patterned biocompatible polycaprolactone (PCL) films with cavities that are selectively decorated with protein by one-step method is developed in this study. To carry out this method, proteins carried in water are dispersed into chloroform solution of PCL to form inverse emulsion with the assistance of the chitosan particles serving as emulsifier. The evaporation of the organic solvent in the inverse emulsion on substrate under a high-humidity atmosphere leads to the formation of ordered porous arrays incorporated with proteins on the inner surface of the cavities. The method, based on the combination of breath figures and inverse emulsion template, provides a reliable route for the directed assembly of water-soluble materials into patterned polymer matrix. It has the potential to be further established as a novel procedure to fabricate a multifunctional hybrid porous structure containing hydrophilic component based on the breath figure method. Chitosan particle-stabilized inverse emulsion containing the protein in the emulsion droplet is prepared as casting solution for breath figures procedure. The obtained honeycomb-structured pore arrays are proven to be successfully decorated with oriented assembled proteins as well as chitosan particles. Protein arrays with ring-like morphology are conveniently fabricated using this one-step technique, which combines the breath figures with inverse emulsion.

Mesoporous Poly(divinylbenzene) Fibers Based On Crosslinked Nanoparticles

Poly(divinylbenzene) (PDVB) nanofibers are synthesized by electrospinning dispersions of PDVB nanoparticles (diameter 40–90 nm) derived by miniemulsion polymerization. Interparticle crosslinking is achieved by addition of a radical starter after electrospinning endowing the fibers with high solvent-stability. The fibers exhibit a Brunauer–Emmett–Teller (BET) surface area in the range of ≈30–70 m² g⁻¹ due to internal mesoporosity, which originates from the interparticle space. Spinning parameters like the concentrations of spin polymer and nanoparticles, as well as the nanoparticle diameter, are systematically varied to investigate the influence of these parameters on the mesopore structure. The fiber morphology is studied by scanning electron microscopy and the mesopore size, volume, and BET surface area are determined by nitrogen physisorption measurements. The findings indicate that the pore size mainly depends on the PDVB nanoparticle diameter. As a main finding, the fiber diameter can be adjusted by the concentration of spin polymer or nanoparticles without changing the mesopore diameter. Chlorine-functionalized fibers are synthesized by electrospinning of poly(divinylbenzene-co-4-vinylbenzyl chloride) nanoparticle dispersions. Chlorine groups are further used for the covalent immobilization of an organocatalyst (2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)). Crosslinked poly(divinylbenzene) nanoparticle fibers are prepared by suspension electrospinning. The pore structure of the fibers is investigated in dependence of different spinning parameters.

Copolymerization of Epoxides and CO₂ by Cobalt(II) Oxaporphyrins with Mechanistic Explorations on Poly(Propylene Carbonate) Formation

Two cobalt(II) oxaporphyrins (OTPPCoCl and OTPPCoSbF6) are synthesized in this work and are characterized, including by X-ray crystallography. Both complexes are tested as catalysts in the copolymerization of propylene oxide (PO)/cyclohexene oxide (CHO) and CO₂. Polycarbonate is obtained in CHO/CO₂ copolymerization with OTPPCoCl as a catalyst, whereas in the case of PO, cyclic carbonate (CC) is majorly formed. An anion exchange from Cl⁻ to SbF₆⁻ of the cobalt(II) oxaporphyrin leads to a drastic change in the product selectivity: sole polyether is afforded for both epoxides. The polyether formation by OTPPCoSbF6 is postulated to proceed via a cationic mechanism. Further, an equivalent admixture of OTPPCoCl and OTPPCoSbF6 allows the formation of poly(propylene carbonate). In this
copolymerization, the latter catalyst acts as a PO activator, while OTPPCoCl functions as the initiator. In addition, density functional theory (DFT) calculations reveal a lower ring-opening energy of PO by OTPPCoSbF6, compared with the usual propagating species, OTPPCo-alkoxides and OTPPCo-carbonates. Cobalt(II) oxaporphyrins with different anions (Cl- and SbF6 -) catalyze PO/CO2 copolymerization to form distinct products. A mechanistic study on this phenomenon is carried out, in particular upon the polycarbonate formation with the admixture of both catalysts. In addition, cobalt(II) oxaporphyrin chloride is proven to be an efficient catalyst for poly(cyclohexene carbonate) formation.