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Block Copolymers for Nanotechnology Applications

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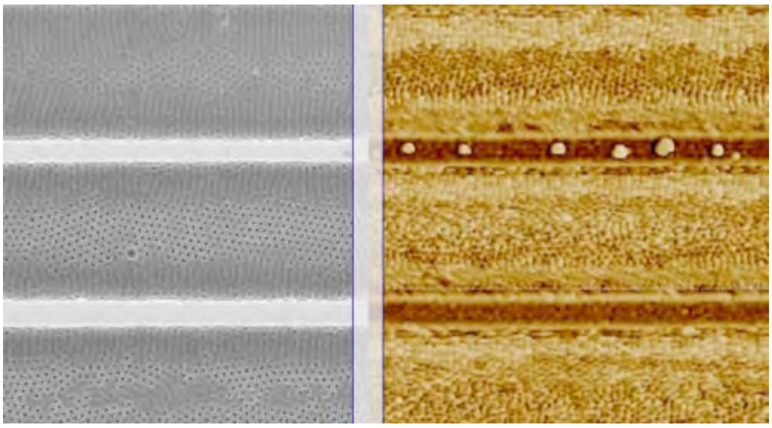

Organization

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- Technische Universität München
- Associazione Italiana di Scienza e Tecnologia delle Macromolecole
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- University of Milan, Milan

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INVITED LECTURES

IL 1

DIRECTED SELF-ASSEMBLY (DSA) OF PERFORMANCE MATERIALS

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Abstract

DSA of block copolymer films on chemically nanopatterned surfaces is an emerging technology that is well-positioned for commercialization in nanolithography and nanomanufacturing.

DSA of (PS-*b*-PMMA) films on lithographically defined chemically nanopatterned surfaces is one focus of our activities in which the main research objectives revolve around understanding the fundamental thermodynamics and kinetics that governs assembly, and therefore patterning properties such as 3D structure, perfection, and processing latitude. A second focus is to use the physical and chemical principles that we have elucidated for DSA of PS-*b*-PMMA towards the development of block copolymer systems capable of self-assembling into the sub 10 nm regime and continuing to meet the stringent constraints of manufacturing.

The research is enabled by the recent development of techniques to combine metrology tools (TEM tomography, GISAXS, RSoXS), theoretically informed course grained models, and evolutionary algorithms to quantitatively determine and predict the independent process and material parameters that result in different 3D structures of assembled domains. Finally, DSA of block copolymer films may be applied to applications in nanomanufacturing beyond lithography.

Here we will discuss some of our very recent work in DSA related to energy related materials and membranes.

IL 2

DIRECTED SELF ASSEMBLY OF BLOCK COPOLYMERS: FROM MATERIALS TO INTEGRATION

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Abstract

Density multiplication of patterned templates by directed self-assembly (DSA) of block copolymers (BCP) stands out as a promising alternative to overcome the limitation of conventional lithography.

Using the 300mm pilot line available in LETI[1] and Arkema's materials[2], the main objective is to integrate DSA directly into the conventional CMOS lithography process in order to achieve high resolution and pattern density multiplication, at a low cost. Thus we investigate the potential of DSA to address contact and via level patterning by performing either CD shrink or contact multiplication.

Our approach is based on the graphoepitaxy of PS-*b*-PMMA block copolymers. Lithographic performances of block copolymers are evaluated both for contact shrink and contact doubling (see fig. 1). Furthermore, in order to prevent design restrictions, this approach may be extended to more complex structures with multiple contacts and non-hexagonal symmetries. These results show that DSA has a high potential to be integrated directly into the conventional CMOS lithography process in order to achieve high resolution contact holes.

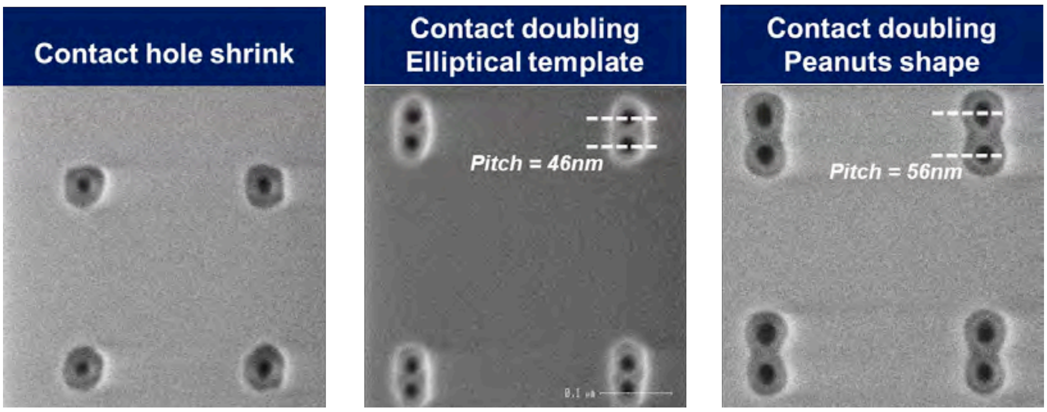

Fig 1. Examples of contact hole shrink and contact multiplication using a PS-b-PMMA block copolymer

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[2] X. Chevalier et al., Proc. of SPIE 9425, 94251N, 2015

IL 3

ORIENTATION AND LATERAL ORDERING IN ASYMMETRIC PS-*b*-PMMA THIN FILMS

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Abstract

The effective exploitation of self-assembled block copolymer (BCP) thin films as templates for nanolithography requires the capability to control the orientation (relative to the plane of the substrate) and lateral ordering of the nanodomains in the polymeric film. The most robust strategy to promote the perpendicular orientation in BCP thin films relies on the surface modification, using end functional poly(A-*r*-B) random copolymers (RCP) chemically grafted to the substrate in order to form a neutral brush layer.[1] In particular, the use of functional hydroxyl-terminated poly(styrene-*r*-methyl methacrylate) (P(S-*r*-MMA)) RCP is a viable solution to induce perpendicular orientation of nanodomains in polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) BCP thin films.

In this work we critically revised the most recent results on the capability to control orientation and lateral ordering in asymmetric PS-*b*-PMMA thin films by proper selection of the brush layer thickness and processing conditions. To this aim, hydroxyl-terminated P(S-*r*-MMA) RCPs with molecular weights (M_n) ranging from 1.7 to 69 kg/mol and styrene unit fraction of approximately 61% were synthesized and subsequently grafted onto a silicon oxide surface by means of a rapid thermal processing (RTP) treatment at high temperature ($T > 200$ °C) that allows achieving the formation of a brush layer in a limited amount of time ($t << 900$ s).[2] The brush layers were subsequently used to investigate the orientation of nanodomains with respect to the substrate, in cylinder-forming PS-*b*-PMMA BCP thin films with M_n ranging from 54 to 132 kg/mol. By decreasing M_n of the macromolecules it is possible to reduce the thickness of the RCP layer that is necessary to promote the perpendicular orientation of the nanodomains in the PS-*b*-PMMA films. In particular, for $M_n = 1700$ g/mol, a 2.0 nm thick brush layer is sufficient to induce the perpendicular orientation of the PMMA cylinders in the PS-*b*-PMMA BCP film.[3]

The effect of the different brush layers on the lateral order evolution in the BCP films upon RTP treatment at high temperatures was investigated as well. We observed that thicker the brush layer, higher the lateral order in the PS-*b*-PMMA films. We demonstrated that the initial solvent, that is naturally trapped in the RCP + BCP system after the deposition process, significantly affects the lateral order of the self-assembled BCP films. The solvent content embedded in the total RCP + BCP system is directly related to the thickness of the neutral brush layer. The effect of the initial solvent content on the grain coarsening kinetics was investigated as a function of the thickness and molecular weight of the PS-*b*-PMMA. The appropriate supply of solvent supports a grain coarsening kinetics following a power law with a growth exponent that is directly dependent on the M_n of the PS-*b*-PMMA BCP. A 1/3 growth exponent was obtained for hexagonally ordered cylinders in the case of 30 nm thick PS-*b*-PMMA thin films with $M_n = 54$ kg/mol.[4]

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IL 4

EFFECT OF SOLVENT IN NANOSTRUCTURED BLOCK COPOLYMER FILMS

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Abstract

In addition to the thermal annealing of block copolymer films and enforced domain orientation by electric field, vapors of various solvents are used as efficient tool for improvement of nanodomain structure in the films. In this paper, we describe a number of effects caused by absorbed solvent in swollen diblock copolymer films. It has been demonstrated that initial swelling of parallel (with respect to the substrate) lamellae is affine and later on the structure reveals undulations resulted in lamella breaking. The final structure exhibits higher number of lamellae, each of them is thinner than the lamella in the dry state.[1] The swelling in a non-selective solvent is accompanied by inhomogeneous distribution of the absorbed molecules: higher solvent concentration corresponds to AB interfaces.[1] As a result, a faster swelling of the film is achieved at perpendicular domain orientation. Due to the predominant localization of the solvent at the interfaces, the "pathway" for the solvent flow in the swelling process is shorter in the case of the perpendicular lamellae and the parallel lamellae act as a potential barrier for the swelling. Swelling kinetics of micellar vs lamellar films, (see Figure) demonstrates essential difference.[2] Mechanical deformation of the swollen lamellar sample can result in additional redistribution of the solvent between the lamellae and interfaces which is controlled by the solvent quality, incompatibility of the blocks and the average concentration of the solvent.[3] Thus, the predicted effect can be promising for pumping of the solvent at nanoscales.

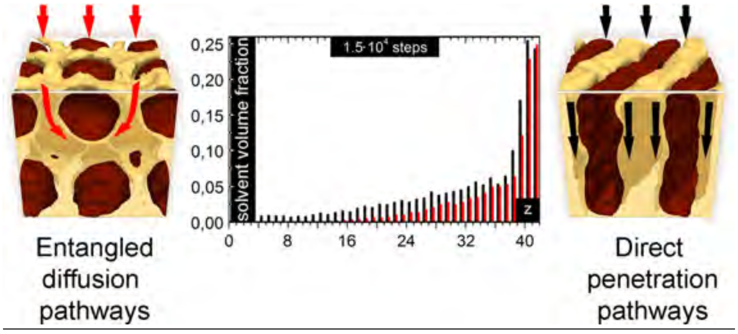

***Figure.** Schematic presentation of diffusion pathways in micellar and lamellar films. (middle) Solvent volume* fraction as a function of normal coordinate in the beginning stage of the solvent uptake.

Acknowledgement. Financial support from the Russian Science Foundation, project # 15-13-00124 is gratefully acknowledged.

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IL 5

PROCESSING OF BLOCK COPOLYMERS FOR LONG RANGE ORDER USING SOLVENT VAPOUR AND LASER SPIKE ANNEALING

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Abstract

Directed self-assembly (DSA) of block copolymers is a practical alternative to DUV lithography for next generation nanopatterning. It is being implemented for via production and situations where small features, unattainable by 193 nm immersion lithography, are part of a more complex process flow. In particular, high χ block copolymers are becoming a focus of recent efforts in DSA because more conventional block copolymers such as polystyrene-block-poly(methyl methacrylate), PS-block-PMMA, are limited in their final resolution due to their relatively weak phase separation. In this presentation, the processing of several high χ block copolymer pairs will be discussed. Solvent vapor annealing is a powerful technique to accelerate the ordering process of block copolymers through increasing chain mobility. The annealing of single and mixed solvent vapors will be discussed. If a solvent selectively swells one block, the solvent vapor annealing process will change the volume ratio between blocks thus altering the anticipated morphology. Both poly(α-methyl styrene)-block-poly(hydroxy styrene), PαMS-block-PHOST and poly(hydroxyethyl methacrylate), PHEMA-block-PMMA have been successfully annealed using selective solvent vapor annealing and the latter polymer when annealed with a mixture of THF and methanol is capable of forming non-equilibrium, but kinetically trapped phases ranging from spheres to cylinders to a gyroid phase depending on the solvent mixture. In contrast, polystyrene-block-poly(dimethyl siloxane), PS-block-PDMS, was studied using extremely rapid thermal annealing methods to form sub-10nm half pitch if processed through a controlled order-disorder transition. Previous studies using PS-block-PMMA materials indicate that as a function of thermal annealing temperature, the rates of microstructure perfection follow Arrehenius behavior. This implies that going to higher temperature should permit much faster organization of microstructure. In our studies, we used a diode laser to heat block copolymer films of PS-block-PDMS to high temperatures and simultaneously decrease the thermal annealing time to less than 10ms which is 10^{-4} to 10^{-6} orders of magnitude smaller than conventional oven or hot plate annealing. The long range order of the cylindrical morphology increased with increasing temperature and annealing time. The effects of neutral layer chemistry on the correlation length were also studied. With the help of graphoepitaxy and surface modification, PS-block-PDMS polymers can assemble with long range order in milliseconds. In summary, we are able to rapidly achieve ordered sub-20nm structures using graphoepitaxy directed self-assembly and do this in less than 20 ms using PS-block-PDMS and laser spike annealing.

IL 6

MOLECULAR TECHNOLOGY FOR BLOCK COPOLYMER LITHOGRAPHIC MATERIALS FORMING PERPENDICULARLY ORIENTED LAMELLAR STRUCTURES

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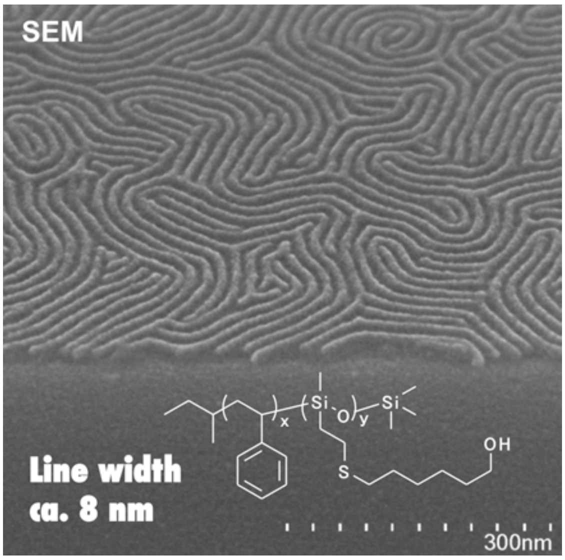
Abstract

The directed self-assembly (DSA) of block co-polymers (BCPs) can realize next-generation lithography for semiconductors and a variety of soft materials. It is imperative to simultaneously achieve many requirements such as a high resolution, orientation control of micro-domains, etch selectivity, rapid and mild annealing, a low cost, and compatibility with manufacturing for developing suitable BCPs. Here, we describe a new design of two different kinds of silicon-containing BCPs targeted for sub-10-nm-wide lines, which are able to form perpendicularly oriented lamellar structures in thin films[1].



First example is a new series of silicon- and fluorine-containing polymethacrylate BCPs, PMAPOSS-*b*-PTFEMA, which are designed in focusing on a good balance of surface free energy between the blocks. PMAPOSS-*b*-PTFEMAs are able to form the perpendicularly oriented lamellar structures with ca. 8 nm features in the thin films by thermal annealing at 130 °C for one minute without any neutral layers. The second one is that the hydroxyl groups in the side chains introduced in the polysiloxane block provide a good balance with the polystyrene surface free energy, thereby leading to the perpendicular orientation. Moreover, this orientation can be also completed in only one minute at 130 °C in an air atmosphere. Oxygen plasma etching for the thin films results in the achievement of a line width of ca. 8 nm.

Achknowledgements: This work was supported in part by New Energy and Industrial Technology Development Organization (NEDO) under the EIDEC Project (PMAPOSS-*b*-PTFEMA) and the Japan Science and Technology Agency (JST), Precursory Research for Embryonic Science and Technology (PRESTO) on the Molecular Technology and Creation of New Functions (Polysiloxane-based BCPs).

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IL 7

CRYSTALLINE BLOCK COPOLYMERS: CONTROLLING MORPHOLOGY THROUGH CONTROLLED CRYSTALLIZATION

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Abstract

A study on the structure and morphology of crystalline di-block copolymers (BCP) is presented. Polyolefin BCPs containing one crystallizable block linked to an amorphous block or two linked crystallizable blocks have been analyzed. In crystalline BCPs containing one or more crystallizable blocks, microphase separation can result from incompatibility of the blocks and/or crystallization of the blocks. Crystallization and microphase separation in the melt may be competing processes resulting in a wide range of morphologies[1,2,3] that depend on the interplay between the two competing phase transitions. Different microdomain structures can be obtained if the crystallization occurs from a homogeneous melt or from an already microphase separated heterogeneous melt. In the latter case microphase separation precedes crystallization and provides a microstructure within which crystallization must take place, resulting in a crystallization confined within preformed microdomains or breaking out of the microphase separated structure. However, the presence of a crystallizable component can be exploited for controlling the final morphology[4] and improving physical properties.

We report a structural characterization of BCPs formed by crystalline polyethylene (PE) or syndiotactic polypropylene (sPP) blocks linked to amorphous ethylene-propylene random copolymer block and of BCPs formed by crystalline PE block linked to crystalline sPP or isotactic polypropylene (iPP) blocks of different block lengths. The dependence of the thin film BCP morphology on the sequential crystallization from the melt of the crystallizable blocks has been investigated. The BCPs have been epitaxially crystallized onto crystals of a substrate to achieve a better control over the crystallization. Ordered nanostructures where the two blocks are organized in separated alternating lamellar domains guided by the orientation of the crystalline lamellae are obtained. We demonstrate that, tuning the block length and using a specific substrate, it is possible to control the crystallization process and obtain large-sized, well-oriented lamellar microstructures with long range order achieved over the area in contact with the crystalline substrate. Possible applications of these nanostructures are discussed.

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IL 8

STRUCTURE FORMATION IN DONOR-ACCEPTOR BLOCK COPOLYMERS FOR PHOTOVOLTAIC APPLICATIONS

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Abstract

To achieve efficient separation and transport of charges polymer solar cells require a nanoscopic percolating donor-acceptor two-phase structure, which is typically prepared via a quenched demixing process often coupled to the crystallization of the components. In this context block copolymers offer the potential of forming a stable microphase-separated donor-acceptor morphology controlled by the chemical structure of the polymer and self-assembly.

We will present investigations about structure formation in several model systems consisting of P3HT donor blocks and acceptor blocks carrying pendant perylene bisimides[1] or fullerene derivatives[2]. Structure formation in these systems typically results from a competition between liquid-liquid microphase separation and crystallization of the component materials. We show that in bulk samples for high enough molecular weight microphase separation in the melt state combined with confined crystallization can result in a well-defined donor-acceptor nanostructure[3]. The formation of the resulting hierarchical structure can be well analysed by X-ray scattering experiments and follows the common rules of block copolymer self-assembly. In thin films structure formation is more complex. The fast drying process occurring during spin coating patially supresses the formation of well-defined ordered structures, and during annealing or crystallization interfacial interactions additionally affect the orientation of microdomains and crystallites[4]. The resulting materials can sustain ambipolar transport, and the mobilities of the nanostructured systems are controlled by the transport properties of the individual components as well as the connectivity of the microstructure.

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IL 9

ELABORATION OF NOVEL ORGANIC ELECTRODE MATERIALS BASED ON BLOCK COPOLYMER ARCHITECTURES AND HYBRID TECHNOLOGIES FOR ADVANCED ENERGY STORAGE SYSTEMS

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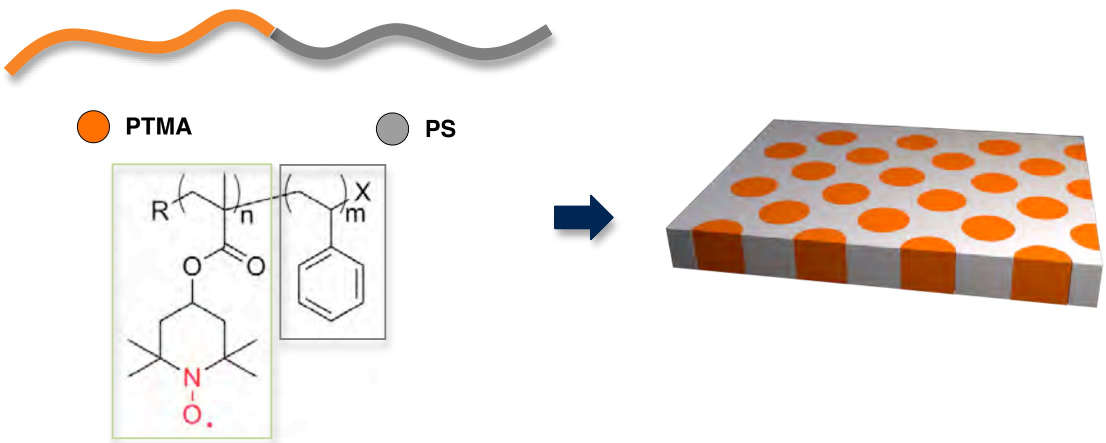
A rational management of the energy resources and consumption is at the center of the preoccupations of a world in constant development. In this context, a sustainable development and exploitation of the energetic resources is asked, necessitating practical and quick solutions to direct the economy towards an energetic autonomy. This paper is centered on the development of novel energy storage systems with enhanced performances through original organic electroactive material chemistry and engineering approaches. Deciphering the fundamental flaws and building better organic batteries will be my primary target, the long-term goal of this research being the development of sustainable all-carbon-based batteries. Based on this, we will focus on three complementary yet, distinct directions with specific goals: improve and develop new organic radical materials for pseudo-capacitive energy storage by engineering high energy density nitroxide radical containing block copolymer architectures; develop novel block copolymer architectures for high performance solid polymer electrolytes and develop either hybrid organic-inorganic electrochemical energy storage materials or hybrid supercapacitor redox polymer gels that combine best-of-both worlds characteristics. Accordingly, this research aims the design and development of novel electroactive organic materials and architectures and, by doing so, develop faster, safer & longer-lasting organic batteries, capacitors and their hybrids.



A nanostructured cathode incorporating a PTMA redox active polymer block.

IL 10

STRUCTURAL CHANGES IN BLOCK COPOLYMER THIN FILMS DURING SOLVENT VAPOR TREATMENT – IN-SITU, REAL-TIME GISAXS INVESTIGATIONS

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Abstract

Block copolymer thin films are of interest for a number of applications, such as nanolithography and as dielectric reflectors. Mostly, well-defined and defect-free nanostructures are required. Solvent vapor treatment (SVT) allows control of the structures in block copolymer thin films. For instance, defects present after spin-coating can be healed, and the orientation of the microdomains and even the morphology itself can be altered. Time-resolved, in-situ studies with grazing-incidence small-angle X-ray scattering (GISAXS) together with white-light interferometry give insight into the structural changes during swelling with solvent vapor and during drying.

We have been studying lamellar thin films spin-coated from polystyrene-*block*-polybutadiene (PS-*b*-PB) diblock copolymers. Three examples will be discussed, namely from thin films featuring initially the parallel orientation[1], the random orientation[2] and the perpendicular orientation.[3] The films are swollen in solvent vapor using a bubbler and were dried by continuously reducing the vapor flow and increasing the flow of dry nitrogen gas. It is expected that the lamellae deswell during swelling with solvent vapor, because the molecular conformations of the blocks tend to be more Gaussian than in the dry state. Complex processes have been observed during SVT: In the case of initially parallel lamellae, additional lamellae form during swelling with cyclohexane vapor.[2]

In the case of initially randomly oriented lamellae, the swelling behaviour of the lamellae in ethylacetate depends on their orientation.[2] In the later stages of swelling, only parallel lamellae persist. In both cases, the lamellae deswell during drying. In the case of initially perpendicular lamellae, the lamellae tilt during swelling with cyclohexane vapor, which enables them to deswell without large-scale mass transport.[3] During drying, the lamellae stay perpendicular. At the surface, a thin wetting layer from PB forms. During drying, it retracts, and PS domains protrude (Figure 1). To conclude, time-resolved GISAXS allows to elucidate manifold processes during SVT and to optimize the SVT conditions.

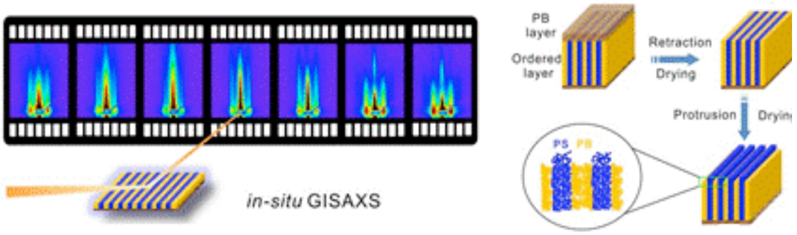

Figure 1. Representative 2D GISAXS maps from a block copolymer thin film featuring perpendicular lamellae during drying. From Ref. 3

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IL 11

FORMATION OF ISOPOROUS MEMBRANES FROM BLOCK COPOLYMERS IN FLAT SHEET AND HOLLOW FIBRE GEOMETRIES

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Abstract

Amphiphilic block copolymers can spontaneously from integral asymmetric isoporous membranes by evaporation-induced self-assembly in flat sheet and hollow fibre geometry. The parameters influencing the structure formation will be discussed. The critical structural evolution steps occur within the first hundred seconds after solvent casting. By using synchrotron small angle X-ray scattering employing a specially designed solvent casting apparatus, the kinetics of the structural evolution was monitored *in situ*. Sometime after solution casting first structural features on length scales of 30-70 nm are observed. During the subsequent period of solvent evaporation the length scales increase continuously towards a plateau value of 80-120 nm, depending on the molecular weight of the block copolymer. The time evolution of the characteristic length scales follow a simple exponential saturation curve for all block copolymers, irrespective of molecular weight, composition, and addition of salts. Furthermore immersion in water during solvent evaporation leads to a nearly instantaneous increase of the characteristic length scale to its plateau value. The addition of salts leads to structures with smaller characteristic length scales, but still following the same kinetic evolution.

Pore size control can be performed by blending similar block copolymers of the same monomers, which only vary in molecular weight or composition. Morphological results of membranes and dense bulk materials indicate a different dependence of the periodic length scale from the molecular weight, as shown by comparison of investigations by scanning, transmission electron microscopy and small angle X-ray scattering.

IL 12

BLOCK COPOLYMER DIRECTED NANOSTRUCTURED HYBRIDS

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Abstract

Solutions to global problems including energy conversion and storage, clean water and human health require increasingly complex, multi-component hybrid materials with unprecedented control over hierarchical length scales and local order. This talk will give examples for the rational design of novel functional polymer hybrid nanomaterials with hierarchical order from the near-molecular to the meso-scale. These materials are based on the self-assembly of block copolymer structure directing molecules into polymer-inorganic hybrid materials. Discussion will include formation of porous materials with amorphous, polycrystalline, and epitaxially grown single-crystal structures. Experiments will be compared to theoretical predictions to provide physical insights into formation principles. The aim of the described work is to (i) understand the underlying fundamental chemical, thermodynamic and kinetic formation principles enabling generalization of results over a wide class of materials systems and to (ii) open a wide range of applications for these hybrids enabled by the simplicity of the processing steps. The talk will cover the formation of hierarchical structures at equilibrium as well as via processes far away from equilibrium. Examples for applications of these nanomaterials will include all laser-induced microfluidic devices with mesoporous floors, mesoporous electrodes for energy conversion and storage devices ,as well as separation and catalysis.

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IL 13

PROBING NANOSTRUCTURES GENERATED BY BLOCK COPOLYMER SELF-ASSEMBLY USING ADVANCED SCATTERING TECHNIQUES

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Abstract

Block copolymer self-assembly is a fascinating approach to fabricate functional nanostructured materials. Highly ordered nanostructures are achieved by micro-phase separation of the block copolymer. Incorporation of these nanostructures in devices typically requires a thin film geometry, which gives rise to morphological changes induced by the interface interactions. As a consequence, complex inner film morphologies can result, which may significantly deviate from equilibrium bulk morphologies. To fully characterize these nanostructures is an inherent challenge. With advanced scattering techniques the nanostructures of block copolymer films are probed in a non-destructive manner and with high statistical relevance[1,2]. In addition to surface structures commonly probed with imaging techniques, inner film structures are accessible in such scattering experiments, which is of high relevance for many applications such as in energy conversion and storage. Moreover, surface-near structures can be accessed[3,4,5]. In-situ measurements give further insights into the morphology development during film preparation as well as in morphology transformations induced by changes of external control parameters[6].

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KEY NOTE LECTURES

KN1

HIGHLY ASYMMETRIC LAMELLAR NANOPATTERNS BASED ON BLOCK COPOLYMER SELF-ASSEMBLY

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Abstract

Lithography based on block copolymer self-assembly has received significant attention due to the ability to achieve morphologies with dimensions in the range of 10 to 20 nm or even below. Block copolymer lithography is a cost-effective, parallel, and scalable nanolithography for densely packed periodic arrays of nanoscale features, whose typical dimension scale is beyond the resolution limit of conventional photolithography

Typically, the block copolymer microdomains used for this purpose are periodic lamellar microdomains. Such lamellar microdomains usually arise only in a narrow range of block compositions in which the volume fractions of the two components are approximately the same.

However, for the next-generation nanoscopic patterns required in lithography, the above strategies need to be extended to achieve highly asymmetric line patterns in nanoscale (i.e. the microdomain width of one of the nanopatterns is significantly different from the other), similar to those which could be obtained by top-down method such as e-beam lithography, which is a slow and extremely expensive process. Unfortunately, however, when the volume fraction of one block is quite different from the other block, lamellar (or line) patterning is impossible due to the formation of more stable nanostructures of cylindrical or spherical shapes.

In this talk, I will present a conceptually new and versatile approach to produce highly asymmetric lamellar morphologies by the use of binary blends of block copolymers whose components are capable of the hydrogen bonding. To illustrate the impact upon potential lithographic applications, the strategy was transferred to thin film morphologies. For this purpose, we used solvent vapor annealing to prepare thin films with vertically oriented asymmetric lamellar patterns.[1-2]

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KN2

CARBOHYDRATE-BASED BLOCK COPOLYMER SELF-ASSEMBLY: SUB_10nm RESOLUTION THIN FILMS

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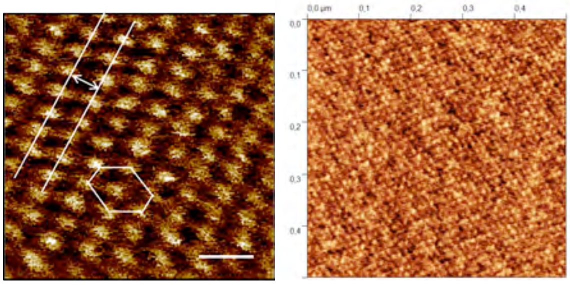
Abstract

Current knowledge in macromolecular engineering allows for the preparation of a myriad of tailored block copolymer morphologies, which play distinguished, multifaceted roles in nanoscience and technology (nanolithography, photonics, pharmaceutical, biomedical…). Such systems exhibit a remarkable ability to self-assemble into a great variety of supra-macromolecular structures both in solution (nanoparticles) and in solid state (thick and thin films), whose domain spacing span from few to hundred nanometers. Their final nano-organization results from the interaction between molecular "elementary bricks" and architectures, the block composition or volume fraction and, in the case of solvent annealing, the affinity of the solvent with the different blocks. Most of those systems are, however, derived from petroleum: A resource that is being rapidly depleted!

While the self-assembly of synthetic block copolymer systems is limited today to 20 nm features (domain and size spacing) and in some cases to sub_10nm with "heavy" chemical modification, we have recently developed novel glycopolymer (carbohydrate-based) leading by self-assembly process to thin films shooting down to few nm-high-resolution nanoscale pattern which found a number of key applications, spanning from nanolithography, pharmaceutical, and biomedical engineering flexible electronic devices. Recent results will be presented on the self-assemblies of poly/oligosaccharide-based block copolymer leading to controlled shape and size glyco-nanoparticles and ultra-thin films (sub_10nm resolution) for next generation of flexible opto- and bio-electronic devices.[1]



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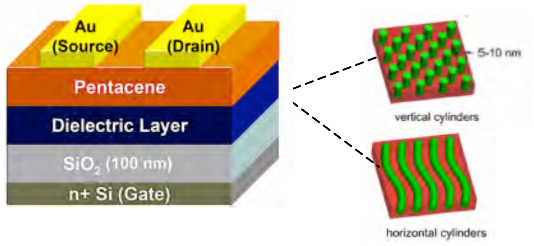

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ORAL CONTRIBUTIONS

OC1

DIRECTED SELF-ASSEMBLY OF ABA TRIBLOCK COPOLYMERS ON CHEMICAL PATTERNS

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Abstract

Directed self-assembly (DSA) of block copolymers (BCPs) on chemical patterns shows promise for meeting a sufficiently inclusive set of manufacturing constraints for applications in semiconductors[1]. Previous studies on DSA of BCPs mainly use AB diblock copolymers, especially polystyrene-*b*-poly(methyl methacrylate)(PS-*b*-PMMA)[2]. AB diblock copolymer can only equilibrate on chemical patterns with the pattern period (L_s) deviating 10% from the BCP period (L_o) and fabrication of different structures needs to use different BCPs. We are working on the fabrication of mixed structures with a range of feature dimensions and pattern geometries by directing the assembly of the ABA triblock copolymer in one assembly process. ABA triblock copolymers are different from AB diblock copolymers in that the central B blocks of ABA triblock copolymers can form bridges between two different A domains. The bridge/loop conformations in ABA triblock copolymers influence their assembly behaviors in thin films. We show that symmetric PMMA-*b*-PS-*b*-PMMA triblock copolymer domains could equilibrate on stripe patterns with dimensions up to ~55% larger than L_o[3]. This range over which an ABA triblock copolymer can tolerate incommensurable L_s is significantly larger than that (~10%) of the corresponding AB diblock copolymer[4]. Such a unique assembly behavior may provide an opportunity to fabricate a set of structures of different geometries by one triblock copolymer. We further demonstrate that asymmetric PMMA-*b*-PS-*b*-PMMA triblock copolymers can be directed to assemble on chemical patterns of arrays of square and hexagonal spots and stripes with L_S up to 34%, 30%, and 46% larger than L_o through surface reconstruction. Defect-free assembly of asymmetric PMMA-*b*-PS-*b*-PMMA triblock copolymers into square and rectangular arrays cylinders and perpendicular lamellae is achieved on chemical patterns in one assembly process.

This work was financially supported by the National Natural Science Foundation of China (Nos. 51173181, 51373166), "The Hundred Talents Program" from the Chinese Academy of Sciences and the International S&T Cooperation Program from Department of Science and Technology of Jilin Province (No. 20160414032GH).

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OC2

DENSITY DOUBLING AND TRIPLING OF BLOCK COPOLYMER NANOPATTERNS

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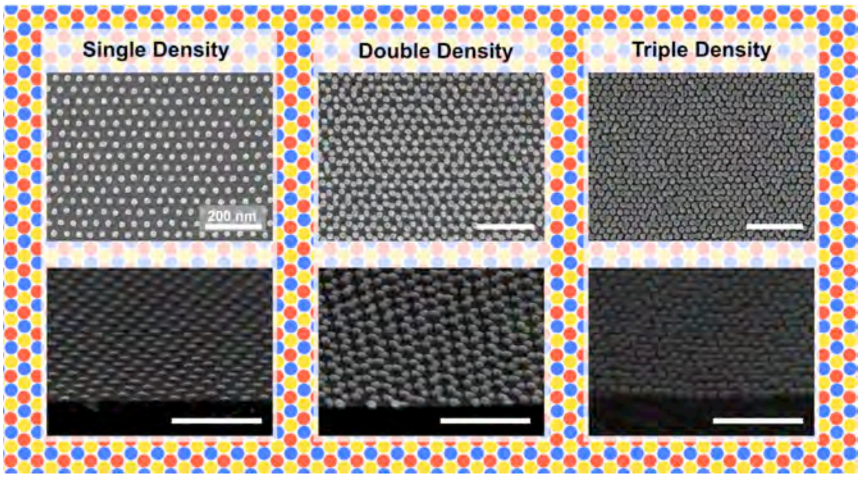
Abstract

As a versatile and cost-effective patterning method, block copolymer self-assembly has attracted attention from the semiconductor industry as a candidate for next-generation lithography.[1,2] With the aim of increasing pattern density, in past two decades, block copolymer research has focused on the synthesis of block copolymers with small molecular weights with a high chi parameter, as the native pitch of a block copolymer is mainly dependent upon its molecular weight.[3,4] The challenge of such an approach is that pattern quality, including defect density and line edge roughness, may be sacrificed due to a lower segregation strength. As an alternative approach, we are presenting a multi-step protocol that surpasses the native pitch of block copolymers, increasing the density by 2 or 3 fold.[5,6] This approach enables the use of well-established, higher molecular-weight block copolymers that routinely form high quality single layer patterns as the foundation upon the pattern is assembled; with subsequent deposition and annealing of one or two more block copolymer thin films, a doubling or tripling of pattern density is observed. In this presentation, we will discuss the generalities of this approach, the algorithm developed to analyse the defect density of the resulting pattern, and mapping of defects and grain size.



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OC3

SELF-ASSEMBLY OF TRIBLOCK COPOLYMERS CONFINED VIA MULTILAYER COEXTRUSION

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Abstract

Block copolymers have proven to be of great interest especially for their ability to spontaneously self-assemble in a diversity of ordered nanostructures, depending on molecular weight, volume fraction of blocks and Flory interaction parameter but also on physical effects such as confinement[1]. Nevertheless, the control of these morphologies over long distances remains an experimental challenge.

In this work, triblock copolymers will be nanoconfined using an industrially scalable technique, namely multilayer coextrusion, which allows the fabrication of films made of thousands of alternating layers with thickness tuned down to a few tens of nanometers [2,3]. The goal of the study is to examine whether the nanostructure of the triblock can be influenced by the process and controlled over long distances and to probe the effects on the mechanical properties (such as impact resistance) of the resulting materials.

Acrylate triblock copolymers were supplied by Arkema from their Nanostrength® technology. These copolymers are usually blended with brittle polymers such as poly(methyl methacrylate) (PMMA) to improve their impact resistance. Forced assembly coextrusion (see schematic Figure 1a) was then used to produce multilayer films of triblock copolymer confined by PMMA at 10-90 and 30-70 wt%, respectively. Films having 513 or 2049 layers were obtained by setting the number of mixing elements (see figure 1A). Different draw ratios (Dr) using a chill roll have been studied to tune the thicknesses of the confined layers from 50 to 500 nm.

The morphology of the confined triblock has been studied via TEM. SAXS experiments were also performed to investigate the orientation and morphology of the nanoconfined self-assembled copolymers. Films consisting of alternating layers of PMMA and confined layers of self-assembled copolymers were directly obtained without additional annealing due to an order-disorder transition temperature (T_{ODT}) of the triblock well above the processing temperature. Furthermore, the flow in the extrusion direction and the confinement induced by both the number of mixing elements and the draw ratio influence the orientation of nanostructure (see Figure 1b). Finally, the influence of nano-confined structuration of the copolymer on the mechanical response of films will be discussed.

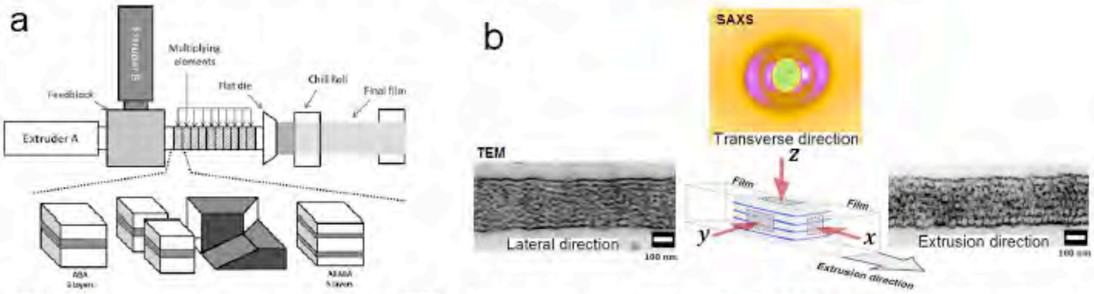

Fig. 1 *a) Coextrusion scheme. b) TEM cross-section image of a PMMA / triblock copolymer coextruded film in $\bar{x}$ and $\bar{y}$ directions, and SAXS image in $\bar{z}$ direction.*

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OC 4

THE ROLE OF THE SOLVENT IN THE FORMATION OF THE CONFORMATIONAL STRUCTURE OF THE COPOLYMER ELEMENTARY UNITS AND THE CONTROL OF THE COPOLYMER FILMS SURFACE PROPERTIES

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Abstract

Polymer functional materials are widely used in various fields of science and technology. The development of synthetic polymer chemistry made possible the creation a new functional (co)polymers by adjusting of the chemical composition, polymer chain architecture and morphology of the polymers in the products and materials. At the same time the improvement of the approaches to the controlled synthesis of a wide variety of (co)polymers with different structure there is ahead of understanding of the mechanism of the influence of the chemical composition and the microstructure of the polymer chain (block, random, gradient distribution of monomeric units in the chain) on the properties of polymer films: the surface energy, adhesion, permeability and selectivity.

The simplest method of polymer films and coatings formation is the irrigating of the polymer solution on a solid substrate. In this method of preparation the solvent functional group can form noncovalent bonds with the functional groups of the polymer. In the result, their orientation along the main chain, i.e. its original position in the macromolecule, is changing.

In this work the effect of the nature of the solvent on the conformational structure and surface properties of the films of styrene and n-butyl acrylate copolymers with various microstructure (10, 30, 60 % styrene; random, block, gradient distribution of monomeric units in the chain) was studied. The ATR spectroscopy, quantum-chemical modeling and contact angle measurements were used for these investigations.

Both methods showed the difference in the values for films of the same copolymer, but formed of different solvents (toluene, acetone).

The conformational differences in the copolymers elementary unit due to the noncovalent interactions of its functional groups with a solvent were established. These interactions led to the different values of the surface energy of polymer films. It is found that the sensitivity of energy characteristics of polymer films formed from the different solvents to the solvent chemical nature is determined by microstructure of polymer chain established by way of synthesis. Namely this fact may promote to the gentle regulation of physical-chemical properties of polymer films by means of varying of conformational composition of macromolecules and, consequently, packing of the polymer chains.

The results showed that modern high-precision scientific equipment and combinations of methods of research help to study the influence the delicate low energy interactions on the structural and physical-chemical parameters of polymeric objects.

We have shown that a correlation of microscopic parameters of the elementary level, such as conformational composition (ordering) the functional groups of units and the macro parameters of polymer films and coatings take places. The solvent is capable to form the noncovalent bonds with the functional groups of the polymer and thereby change the conformational set of macromolecules. This approach can be used for "delicate" control of the conformational structure of the copolymer elementary unit, and as a "probe" of the peculiarities of the polymer chain microstructure.

ACKNOWLEDGEMENT

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OC5

PARAMETER STUDY OF THE OHTA-KAWASAKI MODEL IN PS-*b*-PMMA THIN FILMS

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Abstract

Directed self-assembly (DSA) of block copolymers (BCP) has recently gained popularity as an enhancement in nanolithography. The poly(styrene)-*b*-poly(methylmethacrylate) (PS-*b*-PMMA) block copolymer (BCP) has demonstrated the strong potential of the directed self-assembly technology to produce periodic mesostructures of resolution around 20 nm, which can be subsequently transferred into various substrates. Predictive and efficient modeling capabilities are required to meet this challenge. To this end we have implemented two variants of the Ohta-Kawasaki (OK) model based on the density functional theory (DFT). They offer low computation times in comparison to more detailed approaches like self-consistent theory or single chain in mean field. The OK models are defined by several phenomenological parameters which impact the morphology of a BCP, including volume fraction and BCP asymmetry.

An OK parameter study has been performed for DSA of PS-*b*-PMMA BCP for hexagonal packing in thin films (PMMA cylinders inside PS matrix). The aim of the investigation was determining the relation between OK parameters and BCP physical properties. Also, it was important to determine which of two variants of the OK model better applies for prediction of DSA results by comparing both of them with experiments. The morphology in such systems is defined by the ratio of the mean diameter of cylinders to the mean distance between cylinders without defects (i.e. having exactly 6 neighbors). For several OK parameter values, simulations have been performed resulting in morphologies differing in terms of the above mentioned ratio. Simultaneously, thin film DSA process of PS-*b*-PMMA BCP has been carried out experimentally on a neutral layer (PS-*r*-PMMA thin layer) towards PS-*b*-PMMA BCP. After the DSA process the PMMA phase has been removed by wet development. Cylinder diameters and distances between defectless cylinders have been extracted from simulation results and CD-SEM images by defining a threshold value and using Delaunay triangulation (see Fig. 1). Then, the ratio values of the mean cylinder diameter to the mean cylinder distance have been calculated for both simulation and experimental results. The applicability of both variants of the OK model has been investigated by comparing resulting ratio values. Results will be shown in the presentation.

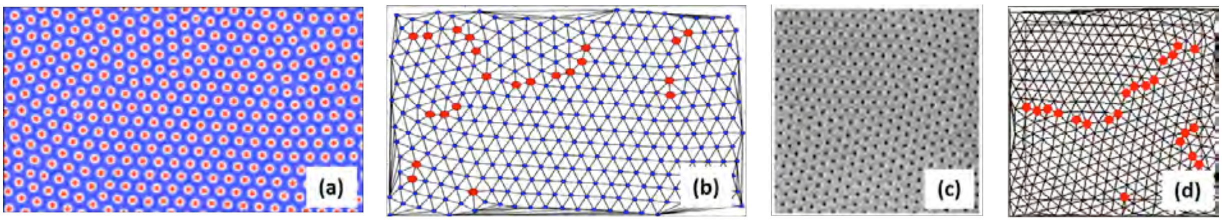

Figure 1. Simulation result and CD-SEM images of the DSA process, (a) & (c). Both images have been used to extract cylinder diameter values. Delaunay triangulation has been performed on both images to extract distances between nearest-neighboring cylinders, (b) & (d). Only defectless cylinders (i.e. having exactly 6 neighbors) have been taken into account. Red spots mark defects in the hexagonal packing of PS-*b*-PMMA.

OC6

MOLECULAR WEIGHT DEPENDENCE OF LATERAL ORDERING GROWTH RATE IN ASYMMETRIC PS-B-PMMA THIN FILMS

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Abstract

The self-assembly of block copolymers (BCPs) into a nanometric ordered structure and the chemical similarity with the photoresist materials employed in standard photolithography have triggered the application of BCPs as template masks. Asymmetric polystyrene-b-polymethylmethacrylate (PS-b-PMMA) can form perpendicularly oriented nanodomains since the surface interactions are easily balanced by grafting the appropriate P(S-r-MMA) random copolymer (RCP) to the surface. The development of long-range lateral order is a key requirement for BCP integration in nanolithographic processes.

In this work the self-assembly of asymmetric PS-b-PMMA BCPs with molecular weight of 54-67-82-102 kg/mol over a 2 nm and 19 nm thick P(S-r-MMA) grafted layer was accomplished through a fine tuning of the annealing temperature (T_{ANN} = 140-290 °C) and time (t_{ANN} = 1-900 s) in a rapid thermal processing (RTP) machine. [1, 2] Cylindrical PMMA structures perpendicularly oriented with respect to the substrate with different level of lateral order were obtained. The grafted RCP brush layer acts as an extensively distributed reservoir of solvent: the thicker the brush layer, the higher the amount of solvent available for the self-assembly of the BCPs. Scanning electron microscopy (SEM) inspection of the samples at different stages of the grain coarsening process allows investigating the grain-growth as a function of the RCP brush layer thickness (2 or 19 nm) and determining the growth rates for each BCP molecular weight (54-67-82-102 kg/mol). For the thick RCP brush layer, the collected data indicate that the cooperative effect of solvent and temperature is sufficient to sustain the grain coarsening process over the range of t_{ANN} we explored. [3] In particular, the growth exponent results constant for each BCP molecular weight at all the explored t_{ANN}. However, the growth rates change as a function of the BCP molecular weight ranging from 0.08 for 102 kg/mol to 0.34 for 54 kg/mol [Figure 1].

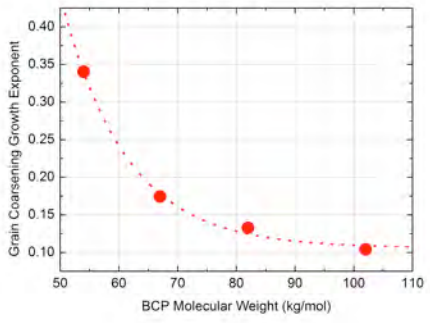

Figure 2 Grain coarsening growth exponent as a function of the molecular weight of the PS-b-PMMA BCP.

[1] F. Ferrarese Lupi, T. J. Giammaria, G. Seguini, F. Vita, O. Francescangeli, K. Sparnacci, D. Antonioli, V. Gianotti, M. Laus, M. Perego, "Fine Tuning of Lithographic Masks through Thin Films of PS-b-PMMA with Different Molar Mass by Rapid Thermal Processing", ACS Appl. Mater. Interfaces 10, 7180–7188 (2014).

[2] K. Sparnacci, D. Antonioli, V. Gianotti, M. Laus, F. Ferrarese Lupi, T. J. Giammaria, G. Seguini, M. Perego, "Ultrathin Random Copolymer-Grafted Layers for Block Copolymer Self-Assembly" ACS Appl. Mater. Interfaces 7, 10944–10951 (2015).

[3] G. Seguini, F. Zanenga, T. J. Giammaria, M. Ceresoli, K. Sparnacci, D. Antonioli, V. Gianotti, M. Laus, M. Perego, "Enhanced Lateral Ordering in Cylinder Forming PS‑b‑PMMA Block Copolymers Exploiting the Entrapped Solvent", ACS Applied Materials & Interfaces (2016).

OC7

ROLE OF INTERFACE ENERGIES IN THE DIRECTED SELF-ASSEMBLY OF BLOCK COPOLYMERS IN WIDE CHEMICAL PATTERNS

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Abstract

Directed Self-Assembly (DSA) of Block Copolymers (BCP) is becoming a well-established method with a high potential of gaining industrial relevance since it allows patterning surfaces with high resolution and throughput and, on the other hand, it also offers a process simplification compared with alternate approaches[1,2]. One of the methods to guide the BCP is chemical epitaxy, which consists in creating chemical patterns on a surface with areas that present larger affinity to one of the blocks of the BCP[3]. Therefore, by properly tuning the chemical affinity between the surfaces, highly oriented and ordered structures can be achieved. In this communication we present a method to experimentally determine the surface free energies and a quantitative correlation between the surface affinity strength and the guidance capability of the chemical patterns. By adequately adjusting the strength of these interactions, chemical guiding patterns formed by wide backgrounds and guiding stripes can properly direct the alignment of BCP, relaxing the requirements on the lithography process in terms of resolution.

The difference of surface free energy of each segment of the BCP and the confining boundary (γ_{SA} - γ_{SB}) is the main driving force in chemical epitaxy DSA. It is experimentally defined by determining the contact angle between PS and PMMA in a homopolymer blend, which has previously been processed in the same way as the block copolymers (Figure 3). In this way, the surface free energy difference between the species can be estimated by using the Young's equation $\gamma_{SA} - \gamma_{SB} = \gamma_{AB} \cdot \cos(\phi_{AB})$, where γ_{SA} and γ_{SB} are the interface tensions between the homopolymers and the substrate.

The optimal experimental conditions to align three different BCP based on PS-b-PMMA have been determined and the behavior has been rationalized by the balance between surface free energy and grain boundary free energy according to the results of self-consistent field theory and simulations.

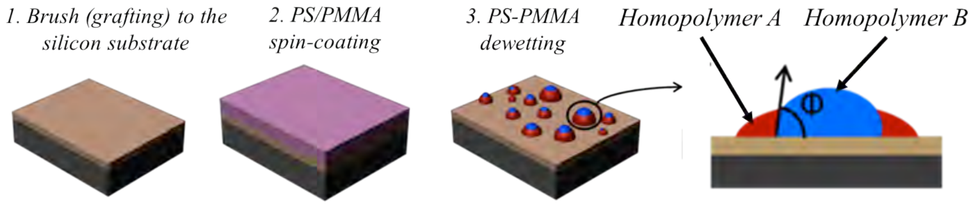

Figure 3. Overall process to determine the interface energies with homopolymer blends.

The research leading to these results received funding from the European Union's Seventh Framework Programme FP7/2007-2013, under project CoLiSA. L. Evangelio acknowledges MECD for the PhD contract FPU13/03746.

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3. Ferrier, N. J., Pablo, J. J. De & Nealey, P. F. Epitaxial self-assembly of block copolymers on lithographically defined nanopatterned substrates. *Nature* **424,** 411–414 (2003).

OC8

RATIONAL DESIGN OF BLOCK COPOLYMER NANOSTRUCTURES WITH CONTROLLED MORPHOLOGY AND DYNAMICS OF ASSEMBLY

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Abstract

Applications of block copolymer nanostructures in soft nanotechnology and in medicine impose, as general requirements, precise control over dimensions and morphology of the nanostructures in combination with pronounced stimuli-responsive properties. We aim to highlight theoretical guidelines and experimental approaches to achieve both objectives by the solution self-assembly of block copolymers with rationally designed macromolecular architecture.

The statistical thermodynamic theory enables us to predict how the morphologies of the self-assembled structures can be on purpose tuned by varying not only the intra-molecular solvophilic/solvophobic balance, but also by changing macromolecular architecture, i.e., replacing conventional linear block copolymers by miktoarm starlike, linear-cyclic and linear-dendritic block copolymers. In particular, the theory predicts that copolymers with cyclic or dendronized associating blocks demonstrate stronger tendency to form wormlike micelles or polymersomes as compared to homologous linear diblock copolymers.

Polymeric nanoparticles with non-conventional multicompartment structure, including asymmetric Janus or patchy particles, can be obtained upon assembly of triblock terpolymers comprising three chemically different blocks in selective solvent. These particles may serve as building blocks for hierarchically assembled materials. Our theoretical model enables us to predict morphology of the particles (number and shape of different nanodomains) as a function of the terpolymer composition and interaction parameters and to analyze relationships of microphase separation into distinct domains within the copolymer assemblies. The theoretical predictions are compared to existing experimental data.

Amphiphilic ionic block copolymers are promising as building blocks for stimuli-responsive nanostructures performing in aqueous environment as e.g. non-viral gene vectors, smart nanocontainers, etc. However, in experimentally relevant situations conventional ionic/hydrophobic block copolymers often form "frozen" nanostructures which can not be re-arranged by changing the interaction strength for soluble blocks. As a perspective strategy to create "dynamic" nano-structures we explored combination of hydrophobic and hydrophilic pH-sensitive monomer units in a gradient sequence within the associating hydrophobic block. Such copolymers were synthesized by robust "one pot" technique using Nitroxide Mediated Polymerization. The reversible and stimuli-responsive character of assembly of the resulting copolymers was unambiguously proven by combination of DLS and SANS experiments and by rheological studies on solutions of homologous triblock copolymers. The latter demonstrate ability of reversible sol-to-gel transition in aqueous solutions triggered by variation of pH or ionic strength of the solution.

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OC9

BLOCK COPOLYMER SOLVENT VAPOUR ANNEALING OPTIMISATION AND BRUSH LAYER MODIFICATION USING OXYGEN PLASMA

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Abstract

Molecular self-assembling block copolymers (BCPs) are ideal tools to tackle the challenges with conventional lithography methods such as 1) output power associated with short wavelengths, 2) fabrication of defect-free masks, and 3) the considerable cost. The ability of BCPs to phase separate at the molecular scale, teamed with the capabilities of conventional lithographic methods, means that sub-10nm features can be achieved[1]. Despite these advantages, the limitations associated with annealing techniques and the numerous processing steps involved with achieving these BCPs patterns need to be addressed before this method can be integrated into semiconductor fabrication processes. In this work, we tackle the limitations associated with current oven-based solvent-annealing processes by using a custom-built solvothermal-annealing chamber (Figure 1). We also show how brush layers can be modified using oxygen plasma in order to generated BCPs films with controlled orientation.

Large-scale dewetting of BCP films can be eliminated using a custom-built state-of-the-art solvothermal annealing chamber. This novel method of solvent-annealing BCP films provides a complete controlled process whereby BCP films can be prepared without dewetting occurring and with shorter processing times than with conventional oven-annealed samples. The chamber is capable of processing up to 4-inch wafers and allows for in-situ monitoring of a solvent annealing cycle by monitoring film swelling via optical reflectometry.

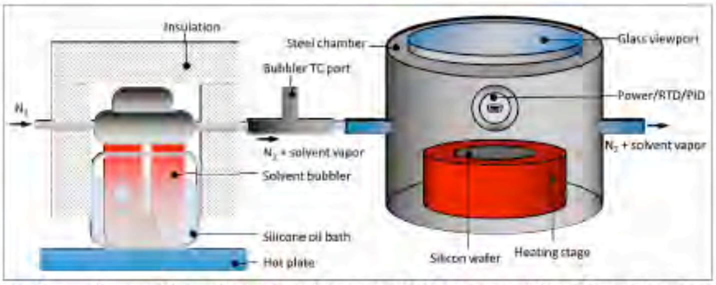

Figure 1. Diagram of solvothermal annealing chamber with control of nitrogen inlet flow. Chamber is capable of processing up to 4-inch wafers and allows for in-situ monitoring of film thickness via spectral reflectometry with light transmission through a borosilicate glass viewport.

In order to guide phase separation of BCPs to the correct orientation, surface chemical modification is used in the form of brush layers. These brush layers, normally consisting of a homopolymer or a random copolymer, provide a surface wettability, which is either preferential to one block or neutral to both blocks. With this interaction, along with chain-length, orientation of the BCP film can be controlled. Previous work has shown that orientation of the BCP films can be controlled by modifying the wettability properties of the surface using an oxygen plasma[2]. In this work we demonstrate how modification of new brush layers with an oxygen plasma effects the wettability and surface energy.

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OC10

VERSATILE BRUSHLESS LITHOGRAPHY TECHNIQUE USING PS-PDMS AND ITS APPLICATIONS IN NANOTECHNOLOGY

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Abstract

In tact with the demand for diminished length-scale of nano-devices, self-assembly is gaining momentum relative to the more traditional and increasingly costly top-down fabrication methods. In particular block copolymer (BCP) nanolithography has been recognized as a key alternative to top-down nanolithography techniques for the future nanofabrication between 5 to 50 nm length scales.

We demonstrate a straightforward method using BCP lithography to produce various nanostructures with well-defined morphologies, which at the same time offers new conceptual design of nanofabrication. By judicious choice of annealing conditions we create highly ordered BCP structures over the entire 4-inch silicon wafers without any surface treatment which is routinely applied in this field. We believe it greatly advances the use of solvent vapor annealing for efficient, reproducible, cost-effective and high-quality large area patterning by BCP nanolithography.

We are not only showing high quality pattern over large area, but also demonstrate a versatile pattern transfer process to create a rich library of silicon nanostructures including nanohole, nanopillar, and nanotube arrays. We believe that the presented findings are highly relevant for many applications outside nanolithography. In fact, this presented method has lead to several collaborations at DTU (Technical University of Denmark) Nanotech and Photonic departments, comprising of selective area growth of quantum dots and nano-wires, nano-imprint mold for plastics fabrication, nano-structured graphene and in particular, plasmonic substrate for sensing. As an example, we demonstrate that the fabricated nanopillar arrays can be utilized as high-performance surface-enhanced Raman scattering (SERS) substrates. This scalable and facile fabrication approach offers numerous pathways in designing nanoplasmonic materials with desired optical properties, which will facilitate both fundamental studies and commercial applications.

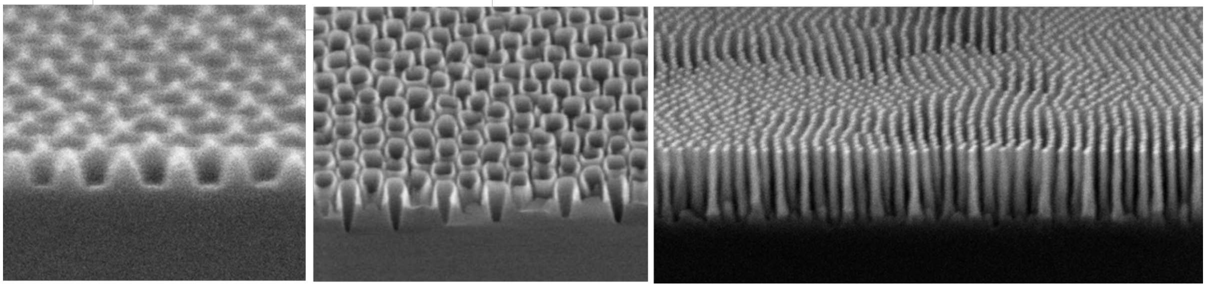

Figure.1. various silicon nanostructures derived from this study.

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[1] Tao Li, Zhongli Wang, Lars Schulte, and Sokol Ndoni, Substrate Tolerant Direct Block Copolymer Nanolithography. Nanoscale, 2016, 136-140.

2 Tao Li, Kaiyu Wu, Tomas Rindzevicius, Zhongli Wang, Lars Schulte, Michael Schmidt, Anja Boisen, Sokol Ndoni, High Performance Surface-enhanced Raman scattering (SERS) Substrate via Block Copolymer Lithography. ACS Appl. Mater. Interface, under review.

OC11

SELF-ASSEMBLY OF AMPHIPHILIC BLOCK COPOLYMERS IN SELECTIVE SOLVENT AND ITS CONTROL

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Abstract

Amphiphilic triblock copolymer can self-assemble into a vast variety of micelles in selective solvents, which provides many possibilities for the future applications of amphiphilic block copolymers. We investigated, both experimentally and theoretically, the self-assembly behavior of amphiphilic block copolymers in selective solvent. It was found that the pathway of the self-assembly depended on the cooling rate, initial condition and external field. This phenomenon can be attributed to the existence of many metastable states in the system. Moreover, it was found that in uniform shear flow, the size distribution of the vesicles was much narrower than that in nonuniform shear flow and the uniformity of the vesicles increased with increasing shear rate. The results show that the metastable states in the system can be modulated and the self-assembled morphology can be controlled by shear flow.

Acknowledgements

This work is supported by the National Natural Science Foundation of China for Major and General Program (Project Nos. 51433009 and 21374118).

OC12

UV-induced self-assembly of amphiphilic di- and triblock polyoxazoline-based polymers: two convergent routes

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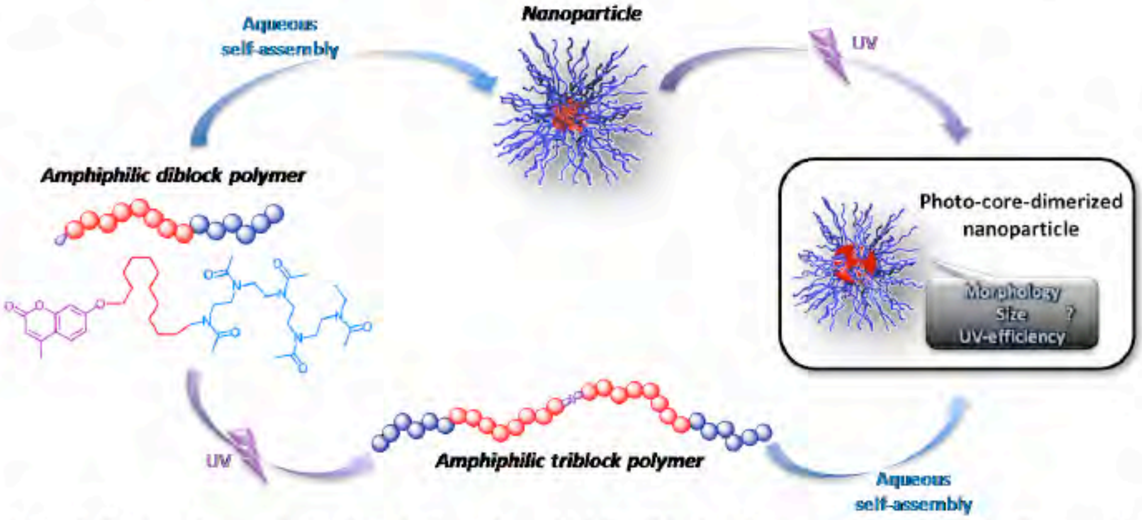
Abstract

The increasing interest of amphiphilic copolymers is mainly due to their ability to self-assemble in solution into a wide variety of morphologies giving nano-objects such as micelles, vesicles, polymersomes. As a result, they are prominent actors in numerous applications including surfactants, emulsifiers or drug delivery systems.

To stabilize the morphology and the size of those nano-objects, their core or their shell can be cross-linked by covalent bonds or interactions using selective reactions or external stimuli (pH, temperature, etc). Among these different methods, Zhao has demonstrated the efficiency of the photo-cross-linking in the presence of UV-sensitive groups.[1]

In our work, knowing the manifold possibilities of "decoration" of the polyoxazolines,[2] we have chosen to synthesize an amphiphilic diblock polyoxazoline-based polymer bearing an UV-sensitive coumarin end-group. After the self-organization in aqueous solution of such polymers into nanoparticles, the dimerization of the photochromic coumarin moiety was undertaken in order to stabilize the nanoparticles core.[3]

Alternatively, a second route based on the prior dimerization of the initiator to yield amphiphilic A-B-A triblock copolymers was proposed (scheme 1). The key question is now: how does this last strategy impact on the nanoparticles morphology and on the efficiency of the coumarin dimerization under UV irradiation?



Scheme 1: Routes of core-photo-dimerization of amphiphilic diblock polymer naoparticles and self-assembly of photo-induced amphiphilic triblock polymer

[1]: Zhao Y. *Macromolecules* 2012, 45, 3647-3657.
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OC13

SELF-ASSEMBLY OF BIOCOMPATIBLE BLOCK COPOLYMERS FROM A VARIETY OF GOOD SOLVENTS

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Abstract

Polymeric nanoparticles (NPs) are very promising carriers for intravenous drug delivery thanks to the tunability and stability of particle morphology and size. The poly(ethylene oxide)-*block*-poly(lactic acid) (PEO-*b*-PLA) amphiphilic system has already reached the clinical test stage and offers significant advantages, notably PLA degradation by hydrolysis within a few days preventing accumulation and PEO opsonisation resistance[1] that ensures sufficient circulation time.

Since fabrication of homogeneous micelles[2] for biomedical application has been the main driving force underlying the study of this system, little attention has been devoted to broad-spectrum investigation of self-assembly in different conditions. Nonetheless, the ability to modulate the size and shape of the NPs is of considerable interest to increase the transport capacity of drugs and to improve their interaction with biological systems.

In this contribution, a systematic study of self-assembly by nanoprecipitation in water of PEO-*b*-PLA copolymers, starting from different non-selective organic solvents, is reported. A series of mPEO_{113}-*b*-PLA_x diblock copolymers (BCP) with hydrophilic volume fraction (f_{PEO}) ranging from 0.50 to 0.13 was synthesized by ring-opening polymerization (ROP) of *rac*-lactide initiated from a fixed mPEO chain of 5000 g/mol. In contrast to the commonly used tin (II) octoate, 1,8-diazobicycloundec-7-ene (DBU) was used as a metal-free catalyst[3].

Four organic solvents with different polarity and H-bonding ability (DMF, acetone, THF, 1,4-dioxane) were chosen as non-selective medium in which each polymer was dissolved, and filtered deionized water was added to induce nanoparticle formation. Thanks to Dynamic Light Scattering (DLS) analyses and TEM imaging, the effect of starting solvent on final particle shape and inner organization was investigated, and a more extensive morphology map was traced. Moreover, both hydrophilic and hydrophobic drug loading ability was assessed by incorporation of either Rhodamine B or Coumarin 6 as model molecules.

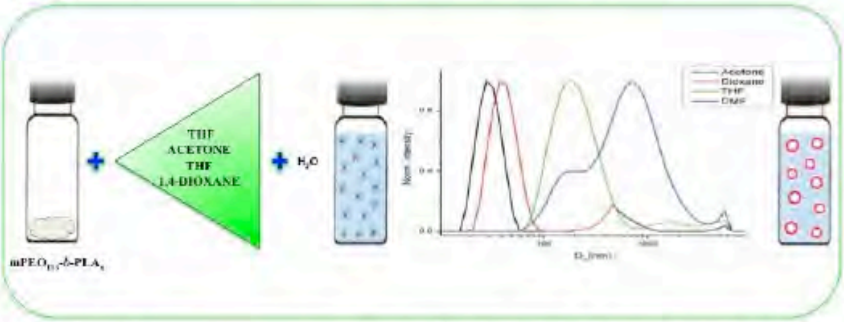

Fig. 1 – Concept scheme of nanoprecipitation of a single mPEO-*b*-PLA copolymer from different solvents. Dramatic change in particle size and morphology is demonstrated by the four DLS distributions.

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[1] O. Diou, S. Greco, T. Beltran, D. Lairez, J.-R. Authelin, D. Bazile, *Pharm. Res.* (**2015**) 32,3188–3200.

[2] T. Riley, S. Stolnik, C. R. Heald, C. D. Xiong, M.C. Garnett, L. Illum, S. S. Davis, *Langmuir* (**2001**), 17, 3168-3174.

[3] H. Quian, A. R. Wohl, J. T. Crow, C. W. Macosko, T. R. Hoye, *Macromolecules* (**2011**), 44, 7132–7140.

OC14

HIGHLY-ORDERED CYLINDRICAL, LAMELLAR AND GYROID DOMAINS PRODUCED FROM CRYSTALLIZABLE SILICON-CONTAINING BLOCK COPOLYMER THIN FILMS

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Abstract

The self-assembly of solvent-annealed block copolymer thin films susceptible to microphase separate into cylindrical, lamellar and gyroid phases is investigated. Here, we report on untemplated and templated semicrystalline poly(1,1-dimethyl silacyclobutane)-*block*-polystyrene (PDMSB-*b*-PS) thin films enabling the production of highly-ordered patterns with sub-10 nm features. These periodic structures, consisting of easily etchable PDMSB cylinders or lamellae with an out out-of-plane orientation separated by PS domains, are suitable for next generation lithography. We also explore the directed self-assembly of sub-100 nm thick PDMSB-*b*-PS layers into a double gyroid structure with long-range 211 plane ordering achieved by using topographical substrates (see **Fig. 1**). Such a morphology consisting of two continuous interpenetrating networks in 3D space makes them a good candidate to fabricate efficient device active layers.

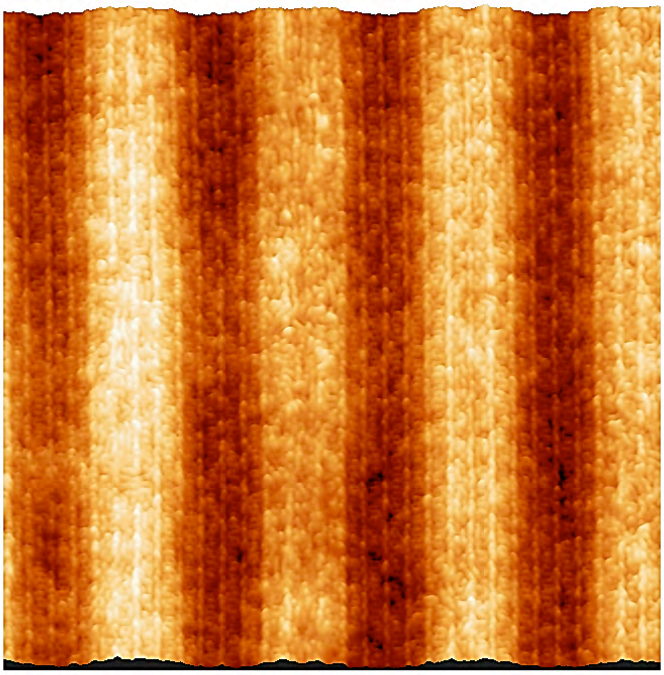

Figure 1: (2 x 2 μm^2) AFM topographical view of a solvent-annealed PDMSB-*b*-PS thin film deposited on a topographical substrate. (211) planes of the double gyroid phase are oriented along the groove direction.

OC15

[6.6.6] Archimedean Tiling and Hierarchical Lamellar Morphology Formed by Semicrystalline 3-Miktoarm Star Terpolymer thin films

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The directed self-assembly of solvent-annealed 3-miktoarm terpolymer thin films into an asymmetric hierarchical lamellar morphology and a hexagonal [6.6.6] Archimedean tiling pattern is investigated. Here, we report on templated semicrystalline (poly(1,1-dimethyl silacyclobutane)-*arm*-polystyrene-*arm*-poly(D,L lactide acid)) (PDMSB-*arm*-PS-*arm*-PLA, 3 μ-DSL) thin films enabling the production of a long-range-ordered lamellar microstructure with a period of ~ 38 nm (see **Fig. 1(left)**). This hierarchical phase with a *p2mm* symmetry can be described as cylinders-within-lamellae where the most incompatible domains (PDMSB and PLA) are efficiently separated by a shell of PS domain. The use of this asymmetric lamellae could provide a great convenience in lithography application since many asymmetric lithographic line and space patterns are required and, cannot be straightforwardly achieved by conventional block copolymer self-assembly. By increasing the size of the PLA block attached to a mid-functionalized PDMSB-*b*-PS, a thin film [6.6.6] Archimedean tiling with a *p6mm* symmetry was produced (see **Fig. 1(right)**). This three-colored hexagonal pattern with a period of ~ 32 nm consists of coaxial prisms which are not of equal size as revealed by AFM images after removing selectively PDMSB or PLA phases with fluorine- or oxygen-rich plasma, respectively. This "three-colored" pattern, which cannot be obtained from a linear terpolymer, provides a new toolset to generate dense array of nano-objects such as dots, pillars or holes with utility in microelectronic patterning.

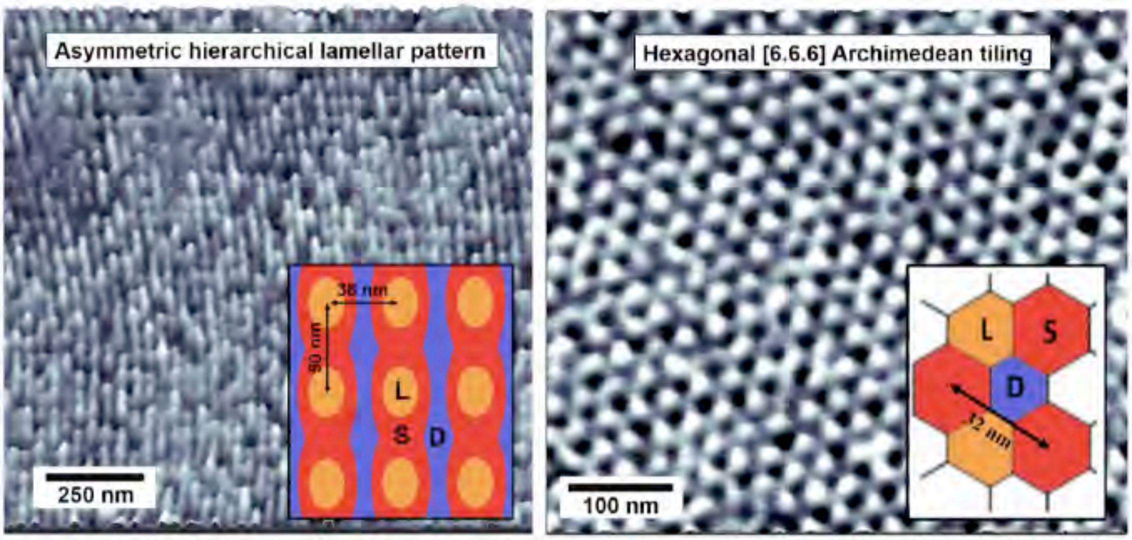

Figure 1: SEM images of solvent-annealed 3 μ-DSL terpolymer thin films with different compositions: (left) D:S:L = 27:56:17 and (right) D:S:L = 22:46:32.

OC16

SURFACE NANOPATTERNING VIA ETCHLESS TECHNIQUES USING SELF ASSEMBLED BLOCK POLYMERS THIN FILMS

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Abstract

Microphase segregation observed in block polymers can be used to form nanopatterns similar to the elements defined in conventional lithographic processes, allowing to go beyond the characteristic length limits imposed by the fabrication techniques. As etching becomes ever more challenging as the targeted features sizes are reduced, advanced "etchless" approaches that lead directly to nanostructures without the requirement of developments in mask and lithography technologies are highly desirable. In this approach, selective inclusion of inorganic additives is performed upon exposure of a self-assembled film to inorganic precursors in a dilute solution or in vapor phase. Subsequent UV/ozone or thermal degradation of the film removes the organic polymer scaffold and generates a metal oxide in situ, thereby readily replicating the structure of the initial template.[1]

In this talk we will present various templating methods using liquid and vapor deposition of the inorganic precursors to prepare ordered metal oxide features starting from different block polymer systems including poly(styrene)-b-poly(4-vinylpyridine) (PS-b-PVP), poly(styrene)-b-poly(lactide) (PS-PLA) and poly(cyclohexylethylene)-block-poly(ethylene oxide) (PCHE-PEO). [2] For this latter one the formation of exceptionally small feature sizes (6 ± 1 nm see Figure 1), due to a relatively large interaction parameter (estimated from mean-field analysis of the order-disorder transition temperatures of compositionally symmetric samples), is reported in the case of the low molar mass versions of the polymer. This confirms that "high χ" polymers (where χ is the Flory-Huggins interaction parameter) represent a very important class of materials, useful for nanopatterning at extreme dimensions.[3] For this latter system, we will detail the synthesis of the polymer, the preparation of the film, the control of the morphology by adapted post-treatment of the film as well as the optimized templating method.

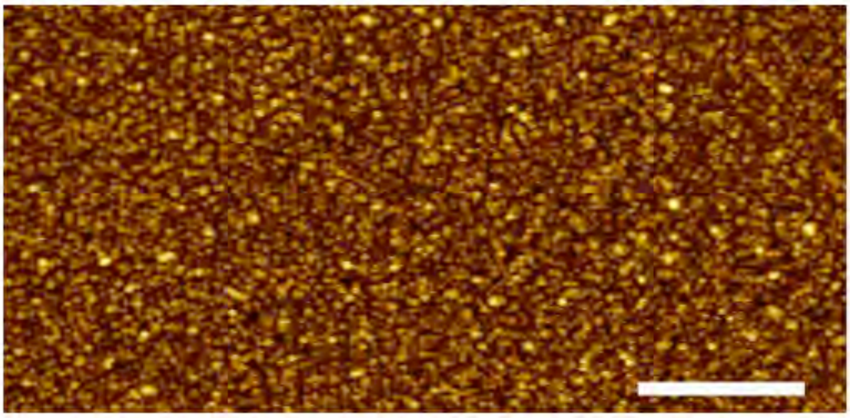

Figure 1. Iron oxide nanoparticles templated from PCHE-PEO (4.1 kg.mol^{-1}, f_{PEO}=0.24) following a selective solvent annealing. The resulting features are 6 ± 1 nm. Scale bars represent 200 nm.

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OC17

TRIPLE CRYSTALLINE BIODEGRADABLE PEO-*b*-PCL-*b*-PLLA TRIBLOCK TERPOLYMERS: SEQUENTIAL CRYSTALLIZATION AND MORPHOLOGY

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Abstract

The sequential crystallization of poly(ethylene oxide)-*b*-poly(ε-caprolactone)-*b*-poly(L-lactide) (PEO-*b*-PCL-*b*-PLLA) triblock terpolymers, in which the three blocks are able to crystallize separately and sequentially from the melt, is presented[1]. The study of these novel triple crystalline triblock terpolymers provides new fundamental insights on the formation of mixed triple crystalline spherulites and sequential crystallization of triblock terpolymers[1-4]. Two terpolymers[5] with identical PEO and PCL block lengths and two different PLLA block lengths are compared ($PEO_{29}PCL_{42}PLLA_{29}^{16.1}$ and $PEO_{23}PCL_{34}PLLA_{43}^{19.9}$). Thus, the effect of increasing PLLA content on the crystallization behavior and morphology was evaluated.

Both terpolymers exhibit a homogeneous melt morphology (as confirmed by SAXS) which is evidence of the miscibility of the three blocks in the melt. WAXS and DSC experiments performed on cooling from the melt confirmed the triple crystalline nature of the terpolymers and revealed that they crystallize in sequence: first the PLLA block, then the PCL block, and finally the PEO block. Because PLLA crystallizes first, it affects the subsequent crystallization of PCL and later, both PLLA and PCL crystals restrict the crystallization of PEO. The crystallization of the PLLA block forms a superstructural template for the morphology of the other two blocks. PLOM observations revealed that the triblock terpolymer with a lower PLLA content had an axialitic-like morphology formed by the PLLA block. But at higher PLLA content, the crystalline superstructure is more similar to spherulites. Upon further cooling from the melt, the subsequent crystallization of the PCL and PEO blocks do not alter the already formed superstructure. These two blocks crystallize inside the interlamellar regions of the PLLA template. Mixed spherulitic superstructures are formed and clear changes in the birefringence reflect the sequential crystallization of each block. This unique triple crystalline morphology where three different types of lamellae coexist has been observed for the first time.

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OC18

CONTROL OVER MICROPHASE SEPARATION, CRYSTALLIZATION AND MOLECULAR ORIENTATION OF ALL-CONJUGATED DIBLOCK COPOLYMERS

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Abstract

All-conjugated block copolymers containing two different conjugated blocks can self-organize into well-defined structures at the nanometre scale both in solution and the solid state, driven by factors such as immiscibility or crystallizability difference between the blocks of all-conjugated diblock copolymers poly(p-phenylene)-block-(3-hexylthiophene) (PPP-b-P3HT, denoted as BnTm). In this paper, we investigate the influences of relative strength of crystallization on morphology, competition between microphase separation, break out crystallization and confined crystallization of the two conjugated blocks, the transformation between face-on and edge-on molecular orientation, and the self-epitaxial crystallization between the two blocks will be discussed in detail[1-4]. We investigated the molecular orientation and tuned self-epitaxial crystallization of B39T18 by controlling the heating process. Three different self-epitaxial crystallization circles were conducted in order to see the orientation change of the two blocks. First, when the pristine film was heated to 120 ℃, above the melting temperature of PPP blocks, P3HT started crystallizing with edge-on orientation in the heating process when PPP blocks were molten since the edge-on orientation was a more stable state for P3HT blocks. During cooling, PPP blocks also crystallized with an orientation of edge-on induced by the formed edge-on P3HT crystals previously via self-epitaxial crystallization. Second, when the pristine film was heated in the melting temperature region (78 ~97 ℃) of PPP blocks and underwent isothermal crystallization for 30 minutes, the partly melting of PPP blocks promoted the extension of P3HT blocks to result in P3HT blocks crystallizing in a face-on orientation due to the steric limitation effect exerted by the face-on PPP blocks. The face-on orientation of P3HT was stable even when PPP blocks were melted totally in the heating process. During cooling, PPP blocks crystallized with face-on orientation under the self-epitaxy of P3HT blocks. Thus, the PPP and P3HT blocks crystals were both adopted face-on orientation after this heating-cooling circle. Furthermore, by heating above the melting points of the two face-on blocks (230 ℃), the crystal nucleus of self-epitaxy for the PPP and P3HT blocks were absent. However, P3HT blocks with the higher melting point crystallized with a more stable edge-on orientation again during cooling, which acted as self-epitaxy template to induce an edge-on orientation of PPP blocks. We also observed that the self-epitaxy crystallization induced by limitation effect only in B39T18, while no such phenomenon was found in B39T9, B41T44 and homopolymers blends of PPP and P3HT. This result was attributed to the satisfaction of the two necessary requirements for self-epitaxial crystallization, one was the covalent bonding between blocks, and the other was P3HT transition from amorphous to crystalline through annealing.

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OC19

HETEROGENEOUS COPOLYMERIZATION: INSIGHT FROM COMPUTER SIMULATIONS.

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Abstract

We develop a computer model to study heterogeneous copolymerization, including living processes. We use computer simulations by Dissipative Particle Dynamics and predict in details the polymerization process and resulting system structure while some segregation can occur during the chain growth. During copolymerization of initially miscible bicomponent blend of monomers the microphase separation can occurs under certain conditions. That process change dramatically the system morphology and average blockiness of the chain. The model verification with experimental data and other available literature data on styrene-acrylic acid copolymerization was performed. Finally we propose a promising system to prepare one-step synthesis of system with Polymerization Induced Microphase Separation by gradient copolymers.

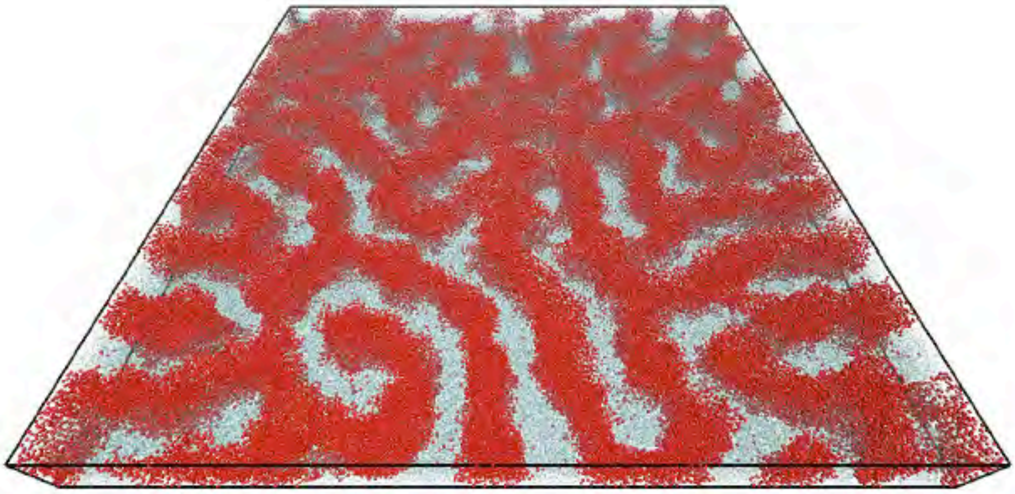

Figure 1. A slice of microphase-separated random-block copolymer at high conversion.

Acknowledgments: RSCF project 14-13-00683.

OC20

SYNTHESIS OF HIGHLY REGULATED CRYSTALLINE-FLEXIBLE BLOCK COPOLYMERS VIA STEREOSELECTIVE COORDINATION POLYMERIZATION OF CONJUGATED DIENES WITH STYRENE AND OTHER MONOMERS

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Abstract

Block copolymers are usually synthesized by anionic mechanism, which are weak of stereo-control. Meanwhile, the coordination polymerization is specific selective to afford polymers with stereo-regular microstructures that are crucial to endow the polymers high performances, such as isotactic polypropylene and syndiotactic polystyrene *etc* plastics possessing high melting temperatures as compared to their amorphous atactic analogues, and the highly *cis*-1,4 polyisoprene and polybutadiene being high performance rubbers while 3,4-polyisoprene and 1,2-polybutadiene being plastics. However, the coordination polymerization usually encounters the problems of chain-transfer and β-proton elimination and chain-walking *etc* side reactions, therefore living coordination polymerization has been challenging project of polymer science.

Herein we report a series of novel diblock or pseudo diblock copolymers with different regularities have been synthesized by coordination polymerizations using the novel rare-earth metal complexes in combination with co-activators. The aminophenyl cyclopentadinyl rare-earth metal cationic catalyst catalyzed the copolymerization of butadiene and styrene to afford the flexible highly *cis*-1,4 regulated polybutadiene and crystalline syndiotactic polystyrene diblock copolymers with variable sequence lengths, surprisingly no matter by sequentially adding or mixing together of the two monomers. The bis(phosphino)carbazoide rare-earth metal catalyst initiated the living highly cis-1,4 selective polymerization of isoprene followed ring opening polymerization of ε–caprolactone to give the polar and none polar diblock copolymer. The NSN-tridentate rare-earth metal complex was an efficient catalyst for the highly *cis*-1,4 selective block copolymerization 2,3-dimethyl-1,3-butadiene (DMB) and butadiene to give a crystalline-rubber product. All these block copolymers are difficult to access with anionic polymerization manner, which have unique morphologies and mechanical properties.

OC21

STEREO-CONTROLLED SYNTHESIS OF DIBLOCK COPOLYMER OF CONJUGATED DIENES BY USING RARE-EARTH METAL PRECURSOR

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Abstract

2,3-Dimethyl-1,3-butadiene (DMB) is one kind of conjugated diene monomer with a simple and symmetrical structure, which can be polymerized in *cis*-1,4, *trans*-1,4 and 1,2 fashion. *cis*-1,4-Poly(2,3-dimethyl-1,3-butadiene) (*cis*-1,4-PDMB), possessing high crystallinity and a high melting temperature, is a promising thermoplastic. *cis*-1,4-PDMB was first synthesized by Yen using $TiCl_4/Al^iBu_3$ initiator more than 70 years ago[1]. Recently, Porri et al. found that iron catalysts can also exhibit high *cis*-1,4 selectivity for the DMB polymerization at room temperature[2]. Although rare-earth metal-based catalysts demonstrated excellent regio- and stereoselectivity for the polymerization of many conjugated diene monomers,[3] however, few rare-earth metal catalysts were reported to show high active and selectivity for the DMB polymerization[4]. Meanwhile, *cis*-1,4-polybutadiene (*cis*-1,4-PBD) (> 97%), as one type of important synthetic rubber, possesses many advantages such as superior tensile strength, excellent abrasion resistance, and dynamic performance. In consideration of thermoplastic *cis*-1,4-PDMB and elastic *cis*-1,4-PBD, incorporating these two type of dissimilar substructures into one single polymer to form diblock copolymer is an interesting work. *cis*-1,4-PDMB is highly crystalline and hard to process and then the incorporation of “soft” *cis*-1,4-PBD segment can improve toughness of “hard” *cis*-1,4-PDMB. On the contrary, *cis*-1,4-PDMB can reinforce the elastic *cis*-1,4-PBD. To date, no catalyst systems display dual catalysis for the copolymerization of DMB and BD with high *cis*-1,4 selectivity and high activity. In this presentation, we report a heteroleptic gadolinium dibenzyl precursor, which can efficiently initiate DMB and BD copolymerization to give diblock copolymer with well-defined stereochemistry while controlling molecular weight, and molecular weight distribution. More remarkably, diblock copolymers containing “hard” *cis*-1,4 PDMB block and “soft” *cis*-1,4 PBD block could be invariably obtained regardless of sequential addition or concurrent addition of both monomers.

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OC22

TAILOR-MADE POLYOLEFIN-BASED BLOCK COPOLYMERS AS COMPATIBILIZERS FOR POLYMER BLENDS

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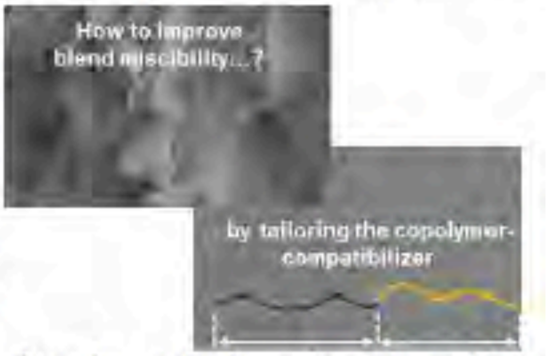
Abstract

Polyolefins are of paramount importance in the world of polymers due to their technological and economic potential.[1] However, their apolar character significantly restricts the compatibility and adhesion properties, which consequently limits their versatility. Producing blends, consisting of polyolefins and more polar polymers, provides an entry to new materials revealing desirable or improved properties that cannot be achieved with the individual homopolymers. Nevertheless, most polymer pairs are thermodynamically immiscible. For this reason the materials have poor morphologies and mechanical properties.[1-3] Employing appropriate block copolymers as compatibilizers can be a solution to the problems related to incompatibility of polymer blends. Copolymers, consisting of blocks that are identical to or miscible with the matrix or dispersed phase of the blend, tend to segregate to the interface of the matrix and dispersed phase where they lower the interfacial tension and promote the formation of an improved morphology of the compositions.

A new class of block copolymers with the potential to address these challenges for polyolefin-based blends are amphiphilic copolymers consisting of polyolefin and polyester blocks.



The current contribution deals with a fundamental study on the use of polypropylene-polyester block copolymers as compatibilizers for polypropylene/polycarbonate blends. The tailor-made PP-*block*-polyester copolymers were obtained by either metal-catalyzed ring-opening polymerization of lactones or by transesterification of a pre-synthesized polyester initiated by hydroxyl-functionalized iPP. The hydroxyl-functionalized iPP was produced by both reactive extrusion and catalysis.

To unravel the composition, mobility and crystal structure of the copolymers the combination of liquid-state and solid-state NMR together with XRD techniques were employed. The polymer blends were characterized in terms of their mechanical properties and morphology.

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OC23

Optical Manipulation of Block Copolymer Nanostructures

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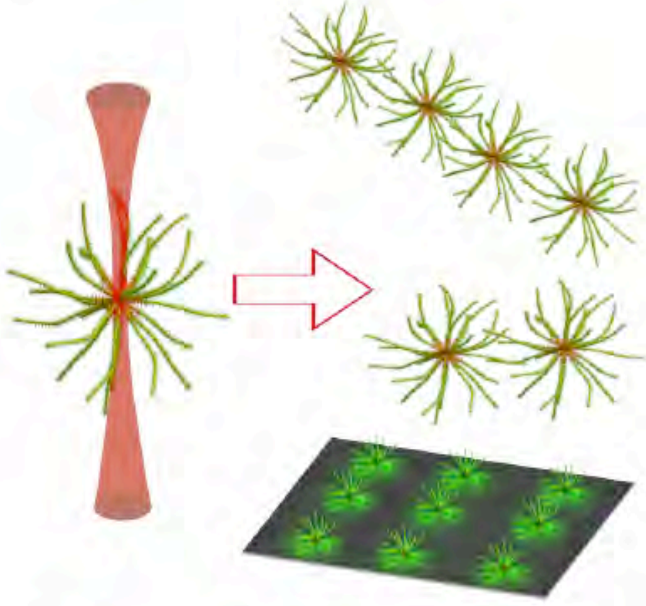
Abstract

Block copolymers (BCP's) offer many opportunities for the creation of complex structures with technological applications. The use of a short crystalline core-forming block (e.g. poly(ferrocenyldimethylsilane), PFS) has allowed for new levels of control in the construction of robust assemblies with applications including photonic crystals and dispersants[1]. When crystalline-coil diblock copolymers are placed in a selective solvent for the coil block, crystallization of the metal-containing core drives the self-assembly of these BCPs to form low-curvature structures such as cylinders and platelets with a high refractive-index [1]. Further, by tailoring the amphiphilicity or coronal chemistry of the BCP micelle, complex supermicellar structures can be created [2].

Here we combine the self-assembly of PFS block copolymers and dynamic holographic assembly (optical tweezers) enabling the creation of novel, complex and kinetically stable superstructures far from equilibrium [3]. For example individual micellar structures or building blocks can be held in desirable conformations, where in-situ cross-linking is used to attach them. Furthermore, optical tweezers allow for the directed deposition and immobilisation of large block copolymer assemblies, creating arrays of soft-matter objects with potential applications in optoelectronics [4] and catalysis. The crystalline nature of these materials allows for the epitaxial growth of further unimer from the deposited structures, enabling controlled nucleation.



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OC24

NEW APPROACHES IN BLOCK COPOLYMER SYNTHESIS: ONE-POT PREPARATION AND CONTINUOUS MICROREACTOR-BASED GENERATION OF BLOCK COPOLYMERS WITH CONTROLLED POLYDISPERSITY

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Rapid and facile synthetic routes for well-defined block copolymers are highly desirable, given the vast application potential and promise of this class of materials, particularly to generate ordered, phase-segregated nanostructures. Here we present a one-pot strategy for AB diblock copolymers that is applicable for a broad molecular weight range up to ultra-high molecular weight block copolymers. The approach relies on the *in-situ* monitoring of the simultaneous carbanionic copolymerization, which permits direct observation of the monomer consumption.1) This method is applicable for copolymerizations carried out in apolar solvents, such as cyclohexane or toluene due to the rather slow reaction kinetics in such media. From the decrease of the monomer concentrations the incorporation probability for each monomer at every position of the polymer chain can be determined with unprecedented precision. In-situ kinetic studies of a variety of carbanionic copolymerizations have been carried out in our group.2) Both copolymerization of structurally similar, protected hydroxy-styrene derivatives, i.e., *p*(1-ethoxy ethoxy)styrene (*p*EES) and 4-*tert*-butoxystyrene (*t*BuOS) and the copolymerization of chemically different monomers have been studied.

Copolymerization of isoprene and styrene (I/S) in cyclohexane leads to a strong gradient, since isoprene reacts considerably faster than styrene. In the context of a reinvestigation of this system, the in-situ NMR technique enabled precise assessment of the comonomer gradient, resulting in copolymerization parameters of r_1=15.5 (isoprene) and r_2=0.05 (styrene). The subtle change from styrene to *p*-methylstyrene (I/*p*-MS) as a comonomer led to a surprising result. Extremely divergent copolymerization parameters are obtained (i.e., r_1=140 for I and r_2=0.02 for *p*-MS), which enable a one-step synthesis of gradient structures with a very narrow gradient between both blocks (Figure 1). The respective structures behave like block copolymers and form highly ordered phase-segregated nanostructures that offer great promise for block copolymer nanotechnology. 3) In addition, the preparation and study of block copolymers with controlled polydispersity, prepared in a continuous process in a microreactor setup, will be presented.

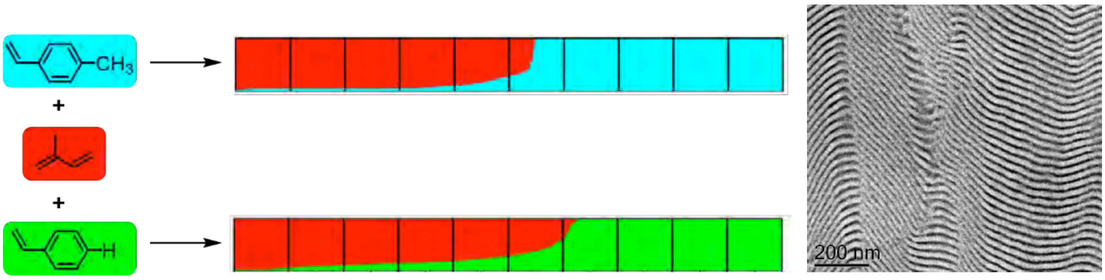

*Figure 4, left: Schematic image of comonomer distribution in copolymers of isoprene/p-methyl styrene (top) and isoprene/styrene; right: highly ordered lamellar morphology (TEM) of poly(isoprene/*p*-methylstyrene) block like copolymers obtained in one step by simultaneous copolymerization; ratio I/p-MS 50/50; M_n = 60,000 g/mol*

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OC25

DESIGN AND SYNTHESIS OF FUNCTIONAL NANOPOROUS CATALYTIC SUPPORTS FROM DIBLOCK COPOLYMERS BEARING CLEAVABLE JUNCTIONS

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Abstract

Because of the variety of applications and properties of organic porous materials, nanoporous polymer-based materials have attracted significant attention within the research community.[i] The applications for these materials are diverse, *i.e.* filtration and separation techniques, heterogeneous supported catalysis, as well as biosensors or biomedical devices.[ii] Organic porous materials present unique properties compared to their inorganic nanostructured analogues, such as simplicity of functionalisation, tunable mechanical properties, and above all low-cost production.[iii] The preparation of porous materials has been reported with pore sizes ranging from some nanometers to some micrometers. More interestingly, block copolymers develop well-defined equilibrium domain morphologies, and thus constitute arguably ideal nanostructured precursors for the formation of ordered mesoporous polymers.[vi] In this particular case, the copolymer is composed of at least one sacrificial block that should allow, after etching process, for well-defined and -ordered porosity. The removal of the sacrificial block can be achieved by using two main pathways. In particular, the selective hydrolysis of the PLA block associated with polystyrene-*block*-poly(D,L-lactide) (PS-*b*-PLA) diblock copolymers allowed for controlling the porosity and the functionality of resulting polymers in previous contributions.[v] Nevertheless, a somehow "smarter" strategy carried out under milder conditions allowed for the removal of the sacrificial component by selective degradation of the chemical junction present between both the sacrificial and the remaining blocks.[vi]

In this context, we herein describe the preparation of PS-*b*-PLA diblock copolymers possessing different cleavable functions (*e.g.*, disulfide, acetal) at the junction point between both blocks *via* straightforward methodologies from heterodifunctional initiators. Their macroscopic orientation, followed by the cleavage of the functional bridges joining both blocks leads to the formation of nanoporous polymeric materials with specific functions on the pore surface. First, heterobifunctional initiators containing either a disulfide bridge or an acetal function within their structure and terminated by both a tertiary alkyl bromide (C–Br) and an alcohol group have been prepared. Such asymmetric initiators have enabled successive initiation of styrene and D,L-lactide polymerization *via* Atom Transfer Radical Polymerization and Ring Opening Polymerization, respectively, thus allowing for the generation of well-defined PS-*b*-PLA diblock copolymers with low polydispersity indexes ($Đ < 1.3$)and a PLA volume fraction close to 0.35. Then, these copolymers have been oriented *via* solvent annealing or channel die processing. A specific chemically-mediated cleavage of the junctions has permitted to remove the sacrificial block, *i.e.* PLA, thus generating nanoporous frameworks with pore walls lined with either thiol or aldehyde groups. Such functional nanopores could be further decorated by adsorption of *in-situ* generated gold nanoparticles. The resulting hybrid materials have successfully been used as heterogeneous catalytic supports in model reactions, such as nitro compounds reduction[vii] or C-C coupling.

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OC26

SYNTHESIS AND CHARACTERIZATION OF DOPED POLYVINYLALCOHOL USING METALLIC IONS

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Abstract

The incorporation of inorganic nanoparticles (NPs) into polymers is an attractive approach to obtain new polymeric materials with large-scale properties and remains a significant challenge [1]. Several techniques and methodologies have been regularly proposed in order to improve their properties. Among them, in situ synthesis is considered as a versatile approach. In this study, it is aimed to synthesize polyvinylalcohol (PVA); and then mixed with a variety a small amount of metallic ions such as Cu^{2+}, Mg^{2+} and Ni^{2+}. The phase behavior and thermal stablity of the obtained mixtures are explored using FTIR and TGA analysis.

It is well known that the thermal stability and the flam retradency are the most important properties of polymer materials. In this context, we have focused our efforts on the metallic ion amount effect allowing their best incorporation into the polymeric matrix and giving the best thermal stability. As an example, the figure 1 shows the FTIR spectra resulting to the kinetic conversion of polyvinylacetate (PVAc) to polyvinylalcohol (PVA). As can be seen, PVAc shows only one carcterstic band localized at 1740 cm^{-1} assigned to free carbonyl groups, while the PVA is not abosorbed in this region.

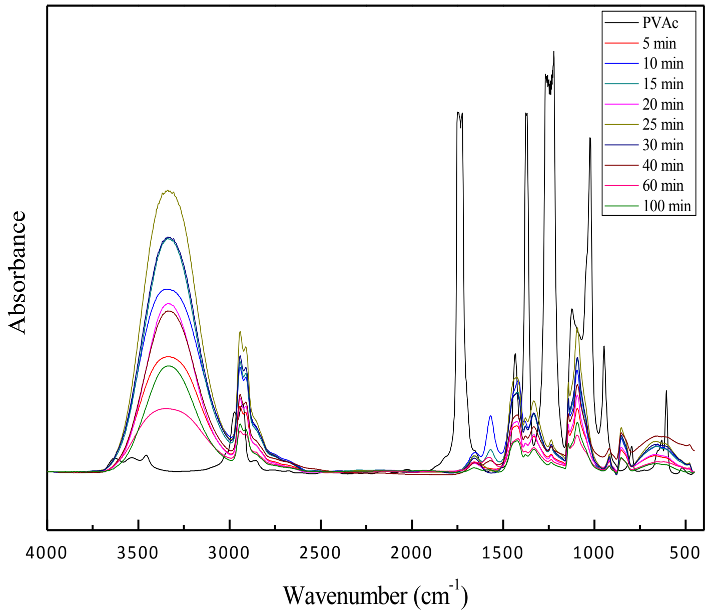

Figure 1: *FTIR specta resulting to the alcolization of PVAc.*

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OC27

"CLICK"OSYLATION OF POLYMERS: THE SYMBIOTIC ASSOCIATION BETWEEN PLANT- AND PETRO-SOURCED MATERIALS

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Abstract

Today, polymer synthesis has attained a control of the architectures at the molecular level allowing a fine-tuning of final properties. At the opposite, even if significant progress have been achieved over the last decades, carbohydrate chemistry still suffers in the control of polyfunctionality and stereochemistry(chirality) of carbohydrate building blocks. From the association of polymer & glyco-science was born the term glycopolymers which are defined as pendant sugar moieties along the polymer backbone or at the end of the chain. Glycopolymers are able to strongly interact with proteins, carbohydrates or others species through multivalent interactions, mimicking natural polysaccharides.

Since 10 years, in the "Physico-Chemistry and Self-assembly of Glycopolymer" group of CERMAV, a new research area has emerged with the preparation and studies of self-assembly of block or graft amphiphilic copolymers. These sugar-based BCPs self-assemble in solution to give nanoparticles made of outer corona of sugars and in thin film giving rise to controlled nanostructured materials. The applications areas are diverse and includes cosmetic, nanomedecine and nanoelectronic. A significant breakthrough was realized with the obtaining of nano-organized thin films made from hybrid glycopolymers with size and domain spacing approaching 10 nm while the state-of-the-art is 20 nm when using petroleum molecules.[1] For both applications, the introduction of biosourced poly-/oligo-saccharides block is highly desirable in regards to their high hydrophilicity, chemical functionalities, biocompatibility, biodegradability and their relevant biological activities.

To achieve a high degree of homogeneous and ordering nanostructures, narrow molecular weight distribution of blocks are mandatory. Well-defined maltoheptaose and cyclodextrin as well as oligosaccharides from xyloglucan, chitosan and chondroitin sulfate were coupled to various synthetic and functional polymers.

Usually, the synthesis of carbohydrate-based copolymers followed a three-step strategy consisting of:

- 1) preparation of scalable and size-homogeneous oligosaccharides from biosourced polysaccharides obtained by enzymatic or chemical processes;
- 2) conjugation with "clickable" functions at anomeric position. The regioselective introduction of clickable functions into specific positions of unprotected oligosaccharides is one of the key steps. The traditional reductive amination, modified Kotchekov reaction and Shoda's activation using 2-chloroimidazolinium salt in aqueous solution were used.[2]
- 3) « Click » coupling of pre-formed blocks referred as « grafting onto » method. Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) was first performed with high yield. Residual metal catalyst in BCPs could limit their future development. Currently, we investigate the metal-free and/or cleavable click reaction such as thiol-maleimide addition.[3]

All those systems are generally characterized with the state-of-the-art techniques including: NMR, MALDI, GPC,…, and light scattering.

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OC28

FUNCTIONAL BLOCK COPOLYMERS AS PLATFORMS FOR PATTERNED IMMOBILIZATION

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Abstract

Chemical patterning in the sub-50 nm range is a challenge which has so far only been achieved by a few methods, e.g., dip-pen nanolithography, scanning near-field photolithography. Despite being sophisticated, these techniques can present some disadvantages in terms of costs of the apparatus and time in case of large-area patterning.

Our aim is to develop a new bottom-up approach to organize molecules on synthetic solid surfaces by making use of a well-known technique relying on block copolymer (BCP) self-assembly[1]. BCPs phase separate and self-assemble into various nanosized morphologies, such as lamellae and cylinders in the solid state, e.g., in the form of thin films. The type of resulting nanosized motif depends on the overall molecular weight of the copolymer, the relative volumic fractions of the distinct blocks, and the relative incompatibility of these blocks.

Our methodology relies on the introduction of a low percentage of reactive groups into well-known self-assembling block copolymers (see Figure 1). We select from the toolbox of modular ligation methods[2] for anchorage of single molecules in close proximity. Recent examples validate our approach[3]. We will present our results on the synthesis and the self-assembly behavior of these reactive block copolymers, namely polystyrene-*block*-polyisoprene (PS-*b*-PI) and poly(methyl methacrylate)-*block*-polystyrene (PMMA-*b*-PS) derivatives and introduce our first attempts at utilizing them as nanostructured immobilization supports.

Figure 1: *AFM Phase image*. Typical thin film structure obtained by spin-coating and thermal annealing from a solution of reactive PMMA-*b*-PS onto a neutralized Si wafer.

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OC29

REMOVABLE RESIST TEMPLATES FOR DIRECTED SELF-ASSEMBLY OF NANOPHOTONIC STRUCTURES

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Abstract

Directed self-assembly (DSA) of block copolymers (BCP) has garnered an increasing amount of interest in both academia and industry as a nanofabrication method that could overcome some of the fundamental limitations of conventional lithography. New high-χ BCPs have the capability to produce features down to the sub-5 nm range [1]. Chemical or graphoepitaxial templating offers an inexpensive way to manufacture well-organized, high-density pattern arrays from block copolymers, but it also enables the formation of complex geometries such as junctions, bends [2,3] or bilayer nanomeshes [4].

We demonstrate a fast way to create well-ordered BCP nanostructures using guiding motifs consisting solely of negative-tone, very high resolution (non-chemically amplified) resist patterned by electron-beam lithography (EBL). With no need for surface functionalization or pattern transfer onto the underlying substrate, the method has less processing steps than conventional graphoepitaxy. We have used asymmetrical poly(styrene-*b*-2-vinylpyridine) (PS-P2VP), which was spin-coated onto the developed template and rapidly annealed in THF vapor. Guiding motifs with different curvatures directed the cylinder-forming PS-P2VP to conform into atypical lattice structures as seen in Fig.1. Previous works in negative EBL resist templating have utilized silica-like hydrogen silsesquioxane (HSQ) [5], which is difficult to remove, whereas ours is removable by a brief oxygen plasma treatment. With removable resists, several templates can be constructed onto the same wafer consecutively. This opens up the possibility to integrate multiple layers and various block copolymer morphologies into the same design. These templates allow us to direct the organization of plasmonic nanostructures or epitaxial and colloidal quantum dots using BCPs. Controlled array geometries let us investigate near field energy- and charge transfer, electromagnetic field enhancement and optical metamaterials.

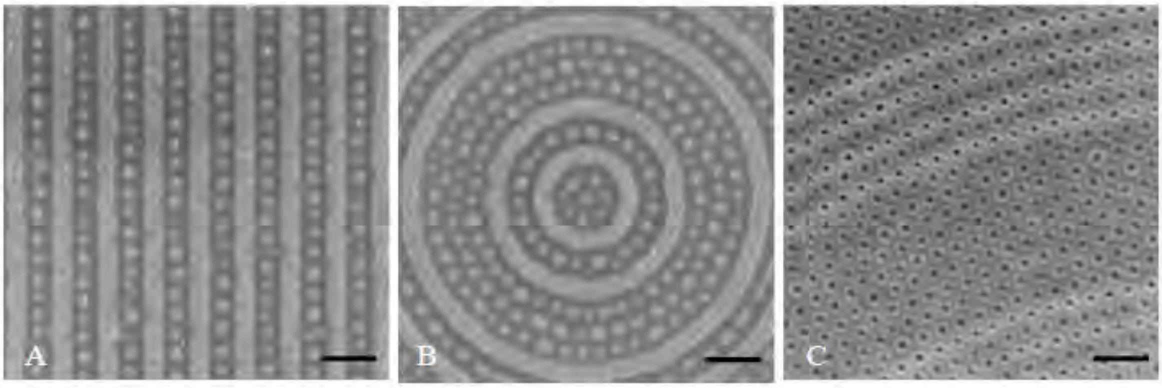

Figure 1. (a) Topographic line patterns and (b) circular patterns made from high contrast negative resist and (c) normal, etched circular trenches were used to investigate the flexibility of the hexagonal assembly of PS-P2VP. The P2VP domains can be either converted into metal nanoparticles (a,b) or reconstructed into holes (c). Scale bars 200 nm.

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OC30

Self-assembled lamellar metallo-polymer nano-composites with strong optical anisotropy

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Abstract

Novel optical properties in the visible range are foreseen when organizing nanoresonators, which can be performed by the self-assembly of plasmonic nanoparticles prepared by wet chemistry. In this project, we prepare and study thin films of nanocomposites of polymers and gold nanoparticles. Our goal is to relate the structure of the composites, and in particular the nature, density and spatial organization of the nanoparticles, with their optical index. The anisotropic nanocomposites are produced by the assembly of gold nanoparticles (NPs) templated by ordered matrices of diblock copolymers. In particular, lamellar nanocomposite films are obtained by self-assembly of poly(styrene)-b-poly(2-vinyl pyridine) (PS-P2VP) copolymers, followed by gold NPs selective incorporation, and studied by X-ray scattering and scanning electron microscopy (SEM). They consist in periodic lamellar stacks of alternating layers of pure polymer (dielectric) and of composite of polymer loaded with a high density of 9 nm-diameter gold nanoparticles, with a total thickness between 200 and 600 nm and the subwavelength characteristic size d_o chosen between 20 and 70 nm. The amount of gold in the composite layers can be varied up to typically 40 volume%.

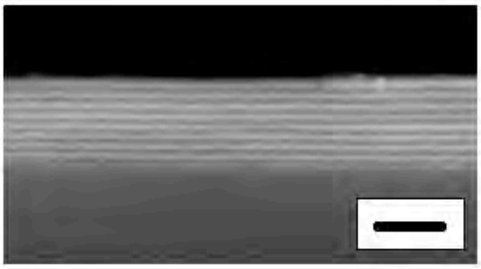

Figure 1.*Backscattering SEM micrograph of the side view of a thin film of a layered gold-polymer nanocomposite, deposited on a silicon substrate. Gold nanoparticle-rich regions appear in white and polymer regions in dark grey. Bar=200nm*

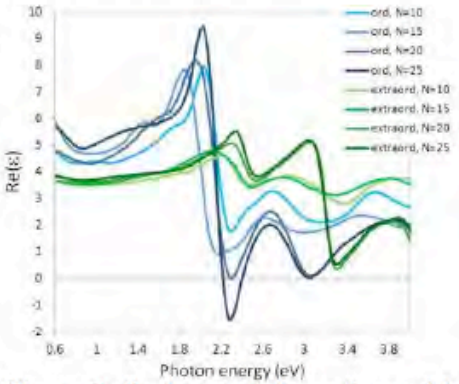

Figure 2*. Real part of the ordinary (blue) and extraordinary (green) components of the dielectric permittivity, with increasing gold volume fraction (given by the value of N).*

The optical properties of the nanocomposite films are determined by variable angle spectroscopic ellipsometry and analyzed by appropriately developed effective medium models. As can be seen on an example shown in Figure 1, the films are structurally uniaxial and homogeneous, and we can define their dielectric permittivity tensor with the ordinary (parallel to the substrate) and extraordinary (normal to the substrate) components. The analysis of the lamellar structures allows the extraction of the components ε_o and ε_e, both presenting a resonance close to 2.3 eV, with a significantly stronger amplitude for ε_o. When the gold load is high enough and the couplings between particles are strong enough, the values of ε_o become negative close to the resonance, and the material reaches the so-called hyperbolic regime, which constitutes a step towards applications in hyper-resolution imaging.

OC31

AMPHIPHILYC LOW BAND-GAP ROD-COIL BLOCK COPOLYMERS: ISSUES IN THE SYNTHESIS AND PHOTOVOLTAIC APPLICATIONS

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Abstract

Low band gap (LGB) polymers are characterized by a band gap below 2 eV, thus absorbing light with wavelengths longer than 620 nm.[1] Their polymeric chains are constituted by the alternating electron-rich and electron-poor units. LGB were widely studied in last decades to improve the efficiency of organic photovoltaics (OPVs) due to a better overlap with the solar spectrum, leading to a maximum photon harvesting in the devices.[2]

Combining this intrinsic feature with the appealing capability of the block copolymers (BCPs) to nanosegregate, we obtained new rod-coil BCPs with a rigid segment constituted by a LBG polymer and a flexible one made up of poly-4vinylpyridine (P4VP) or a segmented poly(styrene-*random*-4-vynilpyridine). P4VP allows the interaction with commonly used acceptor materials for organic or hybrid PVs.[3] Two strategies were applied to the preparation of the target polymers, combining a nitroxide-mediated radical polymerization and a Suzuki polycondensation. A *step-growth like* approach, consisting in the synthesis, purification, and characterization of the two blocks separately, that were then coupled through a further Suzuki reaction, and a *chain-growth like* method, constituted by the early synthesis of a properly activated rigid macroiniziator for the subsequent polymerization of the flexible block. The two pathways led to two series of materials differing particularly in controlling the coil block length. Due to the strong differences in chemical-physical properties of the two blocks, the purification and characterization procedures of the obtained materials have to be *ad hoc* tailored for a correct determination of their molecular structure, crossing the data from different techniques.[4]

These materials showed, together with their self-assembling capability, interesting features exploitable for photovoltaic applications. Some of the obtained materials were successfully employed as nanostructuring additive in hybrid solar cells, with inorganic semiconductor nanoparticles of CdSe, as acceptor.[5] New trials are in progress for the realization of composites nanostructures with PCBM in aqueous medium, to be used as active layers in bulk heterojunctions solar cells. Preliminary results of these studies will be presented.

Acknowledgments: research supported by Project AQUA-SOL - *Aqueous processable polymer solar cells: from materials to photovoltaic modules* (PRIN 2012A4Z2RY)

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OC32

Photocatalytic nanostructuring of graphene guided by block copolymer self-assembly

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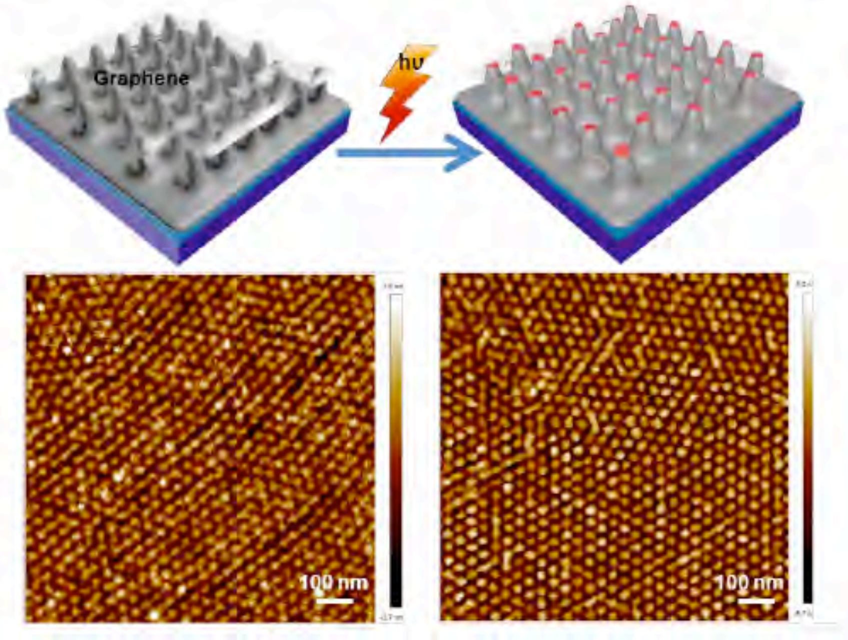
Abstract

Nanostructured graphene exhibits many intriguing properties. For example, precisely controlled graphene nanomeshes can be applied in electronic, photonic or sensing devices. However, the fabrication process of nanopatterned graphene with periodic supperlattice remains a challenge. In this work periodic graphene nanomesh (GNM) was fabricated by photocatalysis of single-layer graphene suspended on top of TiO_2-covered nanopillars. Vertically aligned TiO_2-covered nanopillars were grown on SiO_2/Si substrate by combining block copolymer nanolithography with atomic layer deposition (ALD). Graphene was transferred on top of the TiO_2-covered nanopillars and UV-assisted catalysis of the graphene sheet at the contact spots with the nanopillars resulted in formation of graphene nanomesh. Graphene nanoribbons were also prepared by the same method applied to a line-forming block copolymer template. This mask-free and non- chemical/non-plasma route offers an exciting platform for nanopatterning of graphene and other UV-transparent materials for device engineering.



OC33

BLOCK COPOLYMER-TEMPLATED CARBON NANOSTRUCTURES FOR MOLECULAR SENSING

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Abstract

Self-assembly of block copolymer micelles offers access to ordered nanodomains with tunable dimension and structure through control of such molecular parameters as volume fraction and molecular mass. We fabricated three-dimensional hierarchical porous carbon (3D-HPC) with an interconnected network structure and with nitrogen-rich functional groups through a pyrolysis procedure of multiple layers of closely-packed diblock copolymers micelles.

The resultant 3D-HPC with a considerable specific surface area serves as an excellent substrate for surface-enhanced Raman spectroscopy (SERS), coupled with fluorescence quenching, for sensing of adsorbed dye molecules. The abundant nitrogen atoms terminated on the surface of 3D-HPC nanostructures play a critical role in promoting large chemical enhancement generated via charge transfer and dipole-dipole interactions. Most importantly, the observed enhancement factors show clear dependence on the mesoscaled porosity within 3D-HPC, indicating that the chemical enhancement can be steadily tuned by controls over interfacial areas as a function of nanosphere size and packing density. The unique architecture of 3D-HPC based on the construction of a well-defined core-shell nanosphere network building block provides a new design strategy for fabricating SERS substrates.

OC34

BLOCK COPOLYMERS FOR NANOSCALE METROLOGY

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Abstract

Block copolymers (DBCs) are extensively investigated as key materials for nanofabrication technology. The integration of conventional top-down approaches with the bottom-up self assembly of BCs allows BCs films to be employed as precisely registered organic templates. Among the manifold applications, the preparation of standards for calibration at the nanoscale, featuring length scales ranging from 10 to 70 nm, represents a stimulating challenge. Single grains extending over the entire length of a prepatterned multitrench structure can be obtained with a very low defect density.

In this contribution, the geometric relations among the morphological features of a cylinder forming PS-*b*-PMMA (54 kg·mol^{-1}, styrene fraction 70%) were studied once confined within periodic SiO_2 trenches of different width (W, ranging from 75 to 600 nm) but fixed length (L, 5.7 μm).

In particular, the characteristic dimensions (L_0) of the nanometric PMMA cylinders were studied by finely tuning the trench width W and compared to those obtained on the flat surface ($L_0 = 27.8 \pm 0.5$ nm) of the same samples. The center-to-center distance (L_{0l}, Figure 1a), in the direction parallel to the long side of the trenches results substantially equal to the L_0 measured on the flat surface, whereas along the perpendicular (L_{0w}) direction, appreciable variations are observed (ΔL_{0w} = 6 nm) as a function of W.

These results suggest that this structure can be employed to calibrate metrological instrumentations with a double confirmation thus opening the possibility to produce a BC-based lateral length standard at the nanoscale.

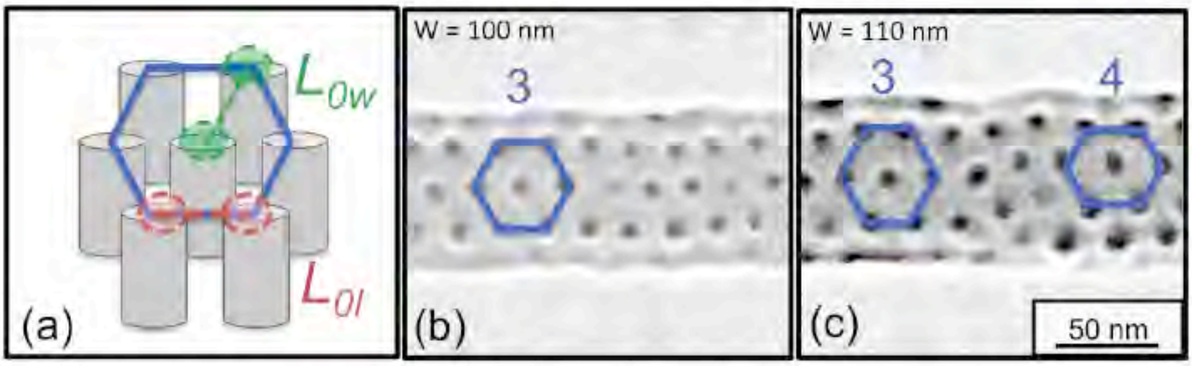

Figure 1. Scheme of HCP DBC structure, with L_0 in evidence, (a); regular HCP BCP structure in a commensurate trench, (b); stretched and compressed HCP DBC structure in a non-commensurate trench

OC35

ANALYSIS OF BLOCK COPOLYMER AND OLIGIOMER DEFECTS, CORRELATION LENGTHS, AND LINE EDGE ROUGHNESS WITH IMAGEJ

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Abstract

While block copolymer (BCP) thin films are widely considered as a means to expand lithographic capabilities for semiconductor patterning, there remain challenges to overcome. In particular, the nanoscale, self-assembled, phase-segregated polymer domains, which form the BCP etch mask typically present topological defects, as well as feature roughness, which are undesirable for semiconductor patterning and integrated circuit fabrication. Mass manufacture requires extremely low levels of defectivity and line-edge roughness, in addition to uniformity and feature registration. Suitable patterns are typically achieved through ordering techniques: graphoepitaxy, chemoepitaxy, and annealing. Quantification of defects (line edge roughness, orientation, and defectivity) is essential for screening newly developed BCP architectures, annealing methods, and substrate designs. To facilitate this, we have developed a tool set for use with ImageJ (a cross-platform image analysis program) for the automated analysis of line patterns templated from BCP thin films.[1] We have applied such analysis to metallic nanopatterns templated from polysturene-*block*-poly(2-vinylpyridine) in combination with various annealing methods, including thermal with microwave[2-4] and conventional heat sources, solvent annealing[5], and solvothermal annealing[3,4], in addition to studies of polymer composition *via* blending[4]. Together, the data provides insight about how these processes affect the pattern development in terms of the kinetics of defect elimination and the variety of topological defect types observed. Such tools can enable those designing new BCP systems to evaluate their potential for nanolithography, without the need for extensive image analysis skills. Moreover, moving beyond typical block copolymers, these analyses are currently being extended to study the self-assembly of oligiomeric, siloxane-based liquid crystalline materials which form similar morphologies while possessing smaller, sub-10-nm features.

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OC36

ORDERING PROCESS OF CYLINDER FORMING PS-*b*-PMMA BLOCK COPOLYMERS INSIDE PERIODIC TRENCHES

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Abstract

In this work, we systematically investigated the ordering process of cylinder-forming PS-*b*-PMMA block copolymers (BCPs) when disposed on periodic gratings and compared with the results obtained on the flat surface. The periodic gratings, consisting in groups of 10 parallel trenches, were defined by conventional Electron Beam Lithography and propagated into the SiO_2 substrate by means of Reactive Ion Etching. Subsequently, the topographically patterned substrate is neutralized using a functional P(S-*r*-MMA) random copolymer. The BCP solution is then spun over the neutralized surface and annealed at temperatures ranging from 180 to 230 °C. When the self-assembly process takes place on topographically patterned substrates, many phenomena have to be considered. First of all, the concomitant presence of the backwash effect around the gratings and the BCP flux from the zone located between adjacent trenches into the inner part of the trenches produces a significant thickness variation of the confined BCP film. Consequently, within each group of trenches the BCP thickness progressively decreases from the external to the central trenches composing the periodic grating. As the ordering process is strongly affected by the thickness of the BCP film within the trenches, different orientations of the microdomains within the trenches occur, as shown in Figure 1.

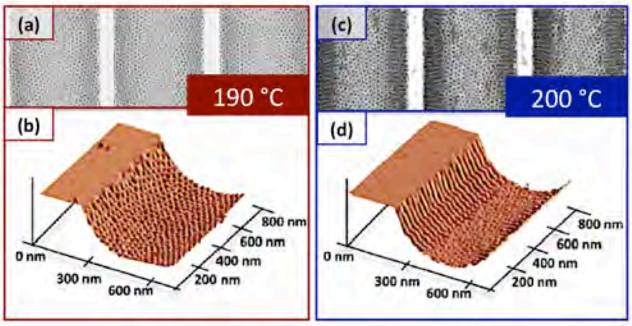

Figure 1: SEM and AFM micrographs representing the morphology of the BCP film confined inside periodic trenches with W = 600 nm, treated at 190 °C (a)-(b) and 200 °C (c)-(d).

In particular, when the samples are annealed at 190 °C (Figures 1a,b) a precise confinement of the BCP film within the trenches is observed. At higher temperatures, parallel or mixed orientations (Figures 1c,d) of the microdomains are obtained as a function of the trench width.

OC37

IN SITU GISAXS AS AN EFFECTIVE MEANS OF ACHIEVING LATERAL ORDER IN SOLVENT ANNEALED BLOCK COPOLYMER FILMS

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Abstract

The self-assembly of block copolymers (BCPs) is a powerful tool for the fabrication of nanostructured morphologies in two (2D) and three dimensions (3D). In the 2D confinement of a thin film, BCPs are useful, for example, for the generation of masks for nanolithography applications.[1] In 3D, on the other hand, BCPs can self-assemble into more complex morphologies, e.g. a bicontinuous gyroid structure. Such bicontinuous 3D networks are very promising candidates for the fabrication of photonic crystals or optical metamaterials.[2] Regardless of the final morphology, an annealing process is required to produce nanostructured assemblies with the desired degree of lateral ordering and orientation of the polymer microdomains. While solvent vapour annealing has recently emerged over thermal annealing as a more effective means for controlling and manipulating the self-assembly of BCPs, a comprehensive understanding of the self-assembly process has yet to be achieved. In this talk I will present examples of obtaining detailed structural information of BCP films in the swollen state, or as solvent is removed, by means of *in situ* grazing-incidence small-angle X-ray scattering (GISAXS). These *in situ* GISAXS studies of solvent annealed BCP films of different morphologies resulted in larger grain sizes of cylindrical microdomains,[3] deswelling-induced symmetry breaking of in-plane sphere order,[4] and enhanced lateral ordering of gyroid-forming BCPs of different molecular weights.[5]

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OC38

PS-*b*-PNIPAM BLOCK COPOLYMERS FOR THERMORESPONSIVE MEMBRANE APPLICATIONS

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Abstract

Responsive pores are receiving a great deal of attention in membrane systems for their advantages against fouling and easy cleaning properties[1,2]. Block copolymer self-assembly is of interest, because well-defined nanosized pores can be obtained[3,4] and stimuli-responsive functions can be incorporated[4,5]. In our study, we synthesized well-defined high molecular weight polystyrene-*b*-poly(*N*-isopropylacrylamide) (PS-*b*-PNIPAM) block copolymers by RAFT polymerization. The PNIPAM block in the copolymer acts as the temperature responsive part due to its lower critical solution temperature (LCST) of 32°C. In principle, the pore sizes of the membrane should increase at temperatures above the LCST of PNIPAM, due to collapsing of the PNIPAM chains. Membranes were prepared by (a) spin-coating on a porous substrate and solvent annealing to the desired morphology or by (b) using a phase inversion procedure, in which a viscous polymer solution was cast on a glass substrate and transferred to a water bath after a certain evaporation time. Morphological properties of the block copolymer membranes were investigated by a variety of techniques including Atomic Force Microscopy (AFM), Grazing Incidence Small Angle X-Ray Scattering (GISAXS) and Scanning Electron Microscopy (SEM).

Membrane preparation using the phase inversion procedure resulted in nanoporous membranes and temperature dependent permeability experiments showed that our membranes have a thermoresponsive character. Reversibility tests proved that the membranes can be used repeatedly at temperatures between 20 and 50°C.

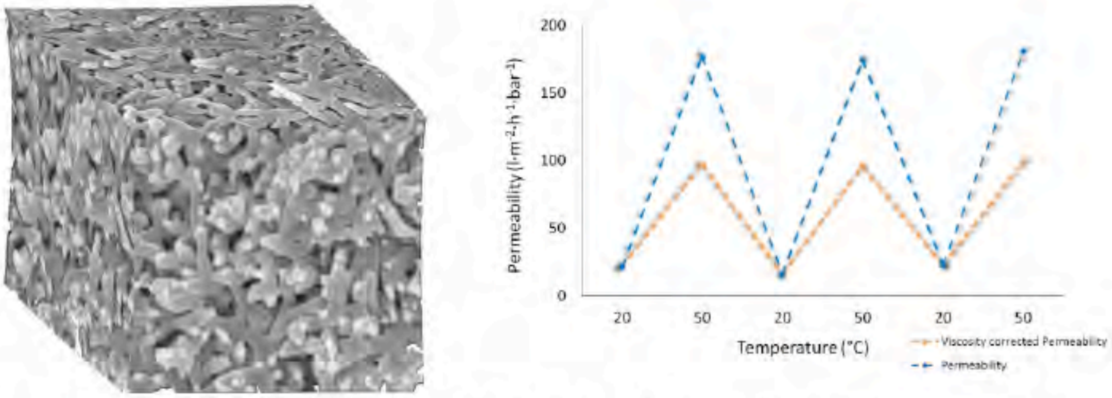

Figure. Membrane structure by SEM (*left*) Reversibility of the permeabilities versus temperature (*right*).

Acknowledgements
This project is financially supported by Dutch Polymer Institute (DPI) under project #766.

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OC39

DOUBLE-LAYER ISOPOROUS HOLLOW FIBER MEMBRANE FABRICATION BY IN-SITU HYDROGEN BOND FORMATION BETWEEN LAYERS IN THE SPINNING LINE

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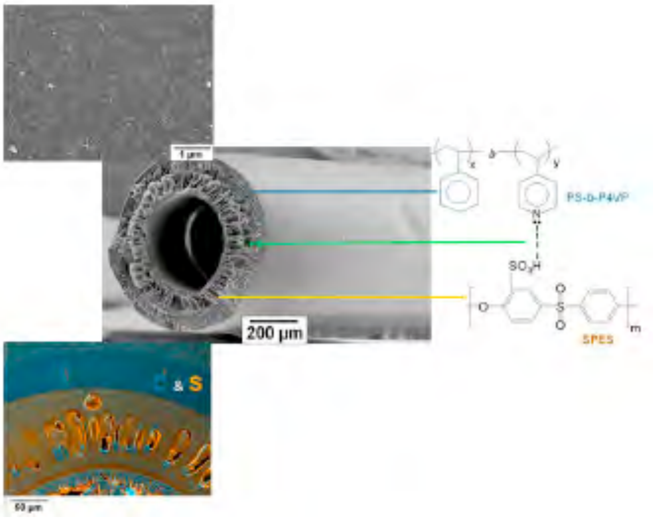
Abstract

Block copolymer self-assembly is a key tool for fabricating membranes with high pore density and pore uniformity. The process of membrane fabrication where the self-assembly of the block copolymers combines with the non-solvent induced phase separation (SNIPS)[1], offers an easy and intribuing way to prepare isoporous structures on the selective surface of the membranes. In this study, we have fabricated a double layer hollow fiber where an isoporous surface of polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) is fixed on a support layer of a nomopolymer/random copolymer blend by co-extrusion. The random copolymer is composed of a partially chemically modified (sulfonate) commercially available polymer. Due to the sulfonation, delamination of the two layers is suppressed without the necessity to increase the number of subsequent processing steps for isoporous composite membrane formation. Good interfacial integrity between block copolymer and the blends is confirmed by scanning electron microscopy (SEM). Elemental analysis by scanning electron microscope-energy-dispersive X-ray spectroscopy (SEM-EDS) unveils the existence of a high sulphur concentration in the interfacial region by which in-process bond formation between layers is evidenced. For the very first time, our study reports a facile method to fabricate sturdy isoporous double layer hollow fiber.[2]



Acknowledgement: Brigitte Lademann, Thomas Emmler, Silvio Neumann, Anke-Lisa Metze, Sofia Dami, Maren Brinkmann are acknowledge for their support in synthesis and characterization of polymers and fibers.

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OC40

THE REVERSIBLE PORE OPENING AND CLOSING OF BLOCK COPOLYMERS INDUCED BY SELECTIVE SWELLING

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Abstract

Switchable nanoporous membranes which can repeatedly alternate their porosities are of great interest in a diversity of fields. However, most of these intelligent materials can only change their porosities in relatively narrow ranges, typically under wet conditions, severely limiting their applications. Our work develop a new system based on an amphiphilic block copolymer membrane, polystyrene-*block*-poly (2-vinyl pyridine)(PS-*b*-P2VP), which is capable of reversibly switching between a highly porous and a nonporous state for dozens of times regulated simply by exposure to selective solvents of the corresponding blocks, as shown in Figure 1. Trhough systematical microscopic and ellipsometric characterizations, the porous structures obtained by immersion in P2VP-selective solvents following the selective swelling-induced pore generation mechanism[1] are confirmed to recover to the original dense conditions and the thickness also falls down to the initial value after soaking in PS-selective solvents. We also find that higher temperature, longer immersing time as well as solvents with higher affinities towards PS blocks lead to a more complete closing status. Moreover, the cycling between pore-opening and –closing canrepeat for at least 20 times, with a slight increase in membrane thickness as affirmed by ellipsometry. To demonstrate the potential applications of this reversible process, the antireflective (AR) and controlled release properties of the membranes at different opening or closing extents are tested. The AR property fluctuates with the switching between pore-opening and –closing in both visible light and near-infrared regions. The release rate of the loaded bovine serum albumin (BSA) can be controlled through closing the membrane for different periods of time and the release of the BSA filled in the membrane which is closed in cyclohexane for 30 s can last at least 20 days without an initial burst.

Figure 1. The reversible switching of the polystyrene-block-poly (2-vinyl pyridine) membranes by exposure to selective solvents of the corresponding blocks

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OC41

MONOLITHIC MEMBRANES WITH DESIGNABLE GEOMETRIES AND SIZES VIA RETARD EVAPORATION OF BLOCK COPOLYMER SUPRAMOLECULES

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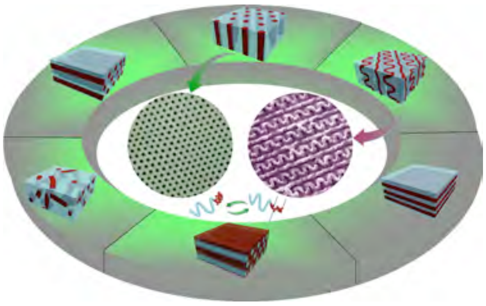
Abstract

We develop a retarded evaporation approach for the alignment of cylinder-forming block copolymer supramolecular monoliths, 3-*n*-pentadecylphenol (PDP)-hydrogen-bonded polystyrene-*b*-poly (4-vinylpyridine) (PS-*b*-P4VP). A variety of highly ordered, aligned morphologies are produced by varying the dosages of PDP in the supramolecules. Treatment of the aligned supramolecular monoliths in hot ethanol leads to the dissolution of PDP and the selective swelling of P4VP, yielding enlargeable ordered mesopores along the original P4VP/PDP domains. Particularly, from supramolecular monoliths aligned in the morphology of perpendicular cylinders and gyroids, we obtain highly ordered monolithic membranes containing enlarged straight pores and bicontinuous pores, respectively. The straight and gyroidal pores were filled with phenol-formaldehyde resol and further carbonized to produce well-defined carbon nanostructures including nanofibers and reversed gyroids, demonstrating the pore accessibility and the promising templating functionality of the resulted monolithic membranes.



Scheme 1. Various aligned morphologies of supramolecular monolithic membranes obtained at different $f_{\mathrm{P4VP(PDP)}}$.

OC42

BLOCK COPOLYMER VESICLE ASSEMBLY AND BURSTING INTO WELL-ORDERED NANOPOROUS THIN FILMS

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Abstract

In the last decade the self-assembly of amphiphilic copolymers have attracted significant interest mainly because of their ability to form fascinating nanostructures[1]. This ability allows the fabrication of a variety of bottom up nanostructured materials[2]. Recently, we have used block copolymer assembly to enable the fabrication of ordered porous polymer films with applications in membrane filtration[3]. Here we report the preparation of polymersome clusters that assemble and burst in a collective and controlled way upon solvent drying giving birth to isoporous films with a honeycomb-like morphology (**Figure 1**). A series of ABA triblock copolymers of polystyrene-b-poly(sodium 4-styrenesulfonate)-b-polystyrene was prepared by RAFT polymerization and self-assembled into various solvent mixtures. The structure of polymer aggregates was correlated with the solvent composition and polymer concentration resulting in a certain degree of adjustability. When targeting vesicular aggregates, honeycomb-like films were produced with a well-defined pore size which could open a new route towards the preparation of isoporous filtration membranes.

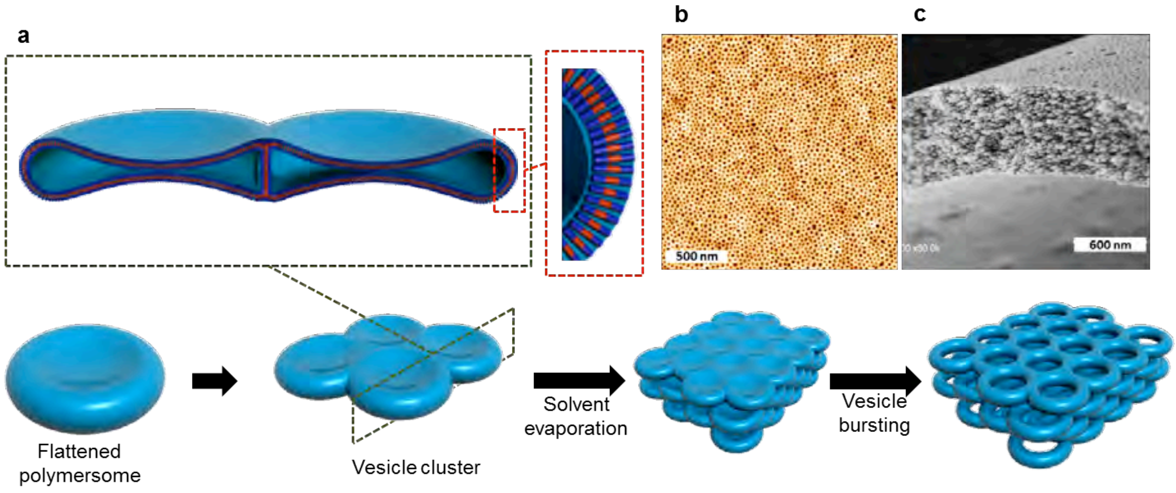

Figure 1: Nanoporous polymer film from ABA triblock copolymer vesicular assembly. **a**, schematic representation of the film formation. **b**, AFM top view. **c**, SEM top and cross-section views.

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OC43

STRUCTURE AND DYNAMICS OF NANOCOMPOSITE HYDROGELS BASED ON HEUR POLYMERS AND MAGNETITE NANOPARTICLES

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Abstract

We present the structural and the dynamic investigation of a novel type of nanocomposite hydrogels based on hydrophobically modified ethoxylated urethanes (HEUR) and hydrophobically coated magnetite nanoparticles (MNP). The structural characterization is performed through Small Angle Neutron Scattering (SANS). The structure of the HEUR polymer matrix in water is described in terms of a 3-dimensional network having as non-covalent cross-links the hydrophobic domains formed by the hydrophobic ends of the HEUR polymer molecules[1]. The embedding of the hydrophobic MNPs, which interact mainly with the hydrophobic domains of the HEUR network, leads to an increase of their size and of the distance between them. We observe that at MNP concentration below 1 wt%, the dispersion is quite homogeneous, while at higher MNP concentration, large MNPs clusters coexist with single MNPs. We find an influence of the MNPs also on the dynamics of the HEUR network. The dynamics of the nanocomposite hydrogels is investigated mainly with Dielectric Relaxation Spectroscopy (DRS) and Neutron Spin Echo (NSE) spectroscopy[2]. As observed in the structural characterization[1], the incorporation of the MNPs within the hydrophobic domains of the HEUR network leads to an increase of the size of these domains and to an increase of the domain size of the network. The size increase leads to a dilution of the polymers nearby the hydrophobic domain, allowing higher mobility of the smallest polymer blobs close to the "center". This is reflected in the decrease of the activation energy of the β-process detected in the DRS data. The increase in distance leads to an increase of the size of the largest hydrophilic polymer blobs. Therefore, the segmental dynamics of the largest blobs is slowed down. At short time scales, i.e. 10^{-9} s $<\tau<$ 10^{-3} s, the suppression of the segmental dynamics is reflected in the α-relaxation processes detected in the DRS data and in the decrease of the relaxation rate Γ of the segmental motion in the NSE data with increasing the concentration of magnetic nanoparticles. On the other hand, the glass transition temperature (T_g) decreases with increasing the MNP loading, indicating an acceleration of the segmental dynamics at long time scales ($\tau \sim 100$ s). Therefore it would be possible to tune the T_g of the hydrogels by varying the MNP concentration.

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OC44

EFFECT OF SOLVENT VAPOR ANNEALING ONTO THE STRUCTURE OF BLOCK COPOLYMER THIN FILMS

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Abstract

Block copolymer films (BCFs) are usually prepared via the non-equilibrium spin-coating process, often resulting in a poorly ordered nanostructure. Annealing of the film by exposure to the vapor of organic solvent, i.e. by solvent vapor annealing (SVA), is a simple and cheap technique to relax defects of the nanostructure, to implement long-range order and to control nanodomain orientation. SVA can strongly facilitate the usage of block copolymers in nanolithography, photovoltaics, photonics ets., but comprehensive understanding of this method has not been established yet.

Using dissipative particle dynamics (DPD), the effect of the solvent quality and selectivity onto the long-range order and orientation of cylindrical domains in BCFs during SVA was extensively investigated.[1] We simulated asymmetric diblock copolymers with the block lengths $N_A = 5$ and $N_B = 15$ in the regimes of intermediate and strong segregation, i.e. at $\chi(N_A + N_B)$ values ranging from 33 to 83. Effects of the film thickness and surface tension were also considered.

While simulated thermal annealing of the considered BCFs mostly resulted in horizontal hexagonally packed cylinders, simulations of SVA in the same systems produced different final structures depending on the conditions. In these simulations, a BCF is left to dry from a spatially disordered, highly swollen state with the initial solvent volume fraction $\phi_S = 0.5$. Upon drying, the segregation increases, and microphase-separation takes place. Firstly, disordered micelles appear all over the film. Later they merge into disordered worm-like nanodomains. We found that the solvent selectivity plays a key role for the final alignment and orientation of these domains. A vertical orientation of the cylindrical nanodomains, shown in the Figure, appears when the solvent is selective for the longer blocks. If the solvent is selective for the shorter blocks, a horizontal orientation of the nanodomains is stabilized. SVA with a non-selective solvent results in mostly disordered worm-like nanodomains.

We suppose that reorientation of domains upon SVA from equilibrium horizontal to the less thermodynamically probable vertical orientation is governed by the a non-equilibrium effects: diffusion-driven solvent flow through the system of nanodomains having different viscosities and permeability (compared to the matrix), as well as by the interfacial flows of components along interdomain interfaces, triggered by the gradient of surface tension (so-called Gibbs-Marangoni effect). We also demonstrated the importance of the proper relationship between transport and relaxation processes during SVA, which are captured by DPD. Our observations may be helpful in the design of more efficient experimental protocols of SVA.

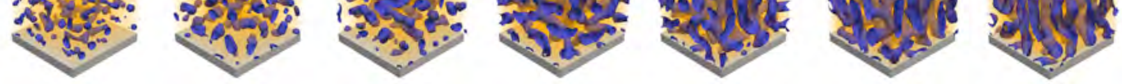

Figure. Vertical orientation of nanodomains upon film drying. Shorter and longer copolymer blocks are shown in blue and yellow, respectively.

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OC45

TOWARDS THE CONTROL OF NANODOMAIN FORMATION IN LARGE HYBRID POLYMER/LIPID UNILAMELLAR VESICLES (LHV)

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Abstract

Polymersomes, based on the self-assembly of amphiphilic block copolymers, have been viewed as potential formulation for multiple applications in nanomedicine field. Over the last few years, Hybrid Polymer/lipid Vesicles became even more attractive structures since they can associate the benefits of polymersomes (stability, chemical versatility) with the benefits of liposomes (biofunctionality, biocompatibility)[1]. However, the control of their properties which is obviously linked to their structuration (domain formation via phase separation) is still far from being understood up to now, particularly at nanoscale.[2] Here, we have analysed Large Unilammellar Hybrid Vesicles (LHV) through different techniques. LHVs were obtained by association of DPPC, a lipd gel state at room temperature with various block copolymers based on poly(dimethylsiloxane) and poly(ethylene glycol) with different molar masses allowing to tune membrane thickness. Small Angle Neutron Scattering (SANS) and contrast variation technique, which offer the unique possibility to study the structure of these complex mixtures at nanometric scales, Time-Resolved Förster resonance energy transfer (TR-FRET) and cryo-transmission electron microscopy (Cryo-TEM) were used. We first show that hybrid lipid/polymer shell form factor and more generally that one of the important parameters governing the membrane structuration and the obtention of hybrid vesicle is the hydrophobic mismatch at the polymer/lipid boundaries.

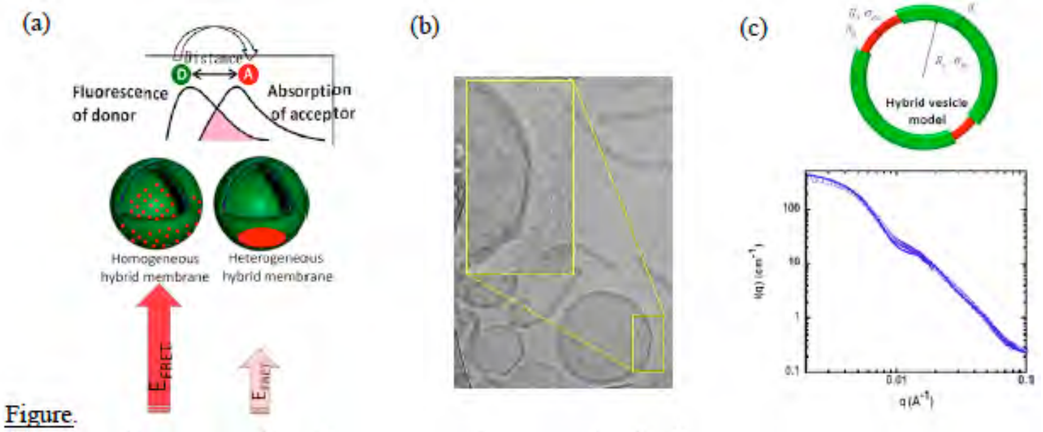

Figure.
(a) Schematic representation of TR-FRET to detect nanodomains in LHVs
(b) Illustration of visualisation of lipid domain in thick polymersome membranes
(c) A SANS curve fitted by holey shell form factor to evaluate nanodomains formation in LHVs.

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OC46

TAILOR-MADE SELF-ASSEMBLING BLOCK COPOLYMERS TO BUILD MULTIFUNCTIONAL NANOPARTICLES

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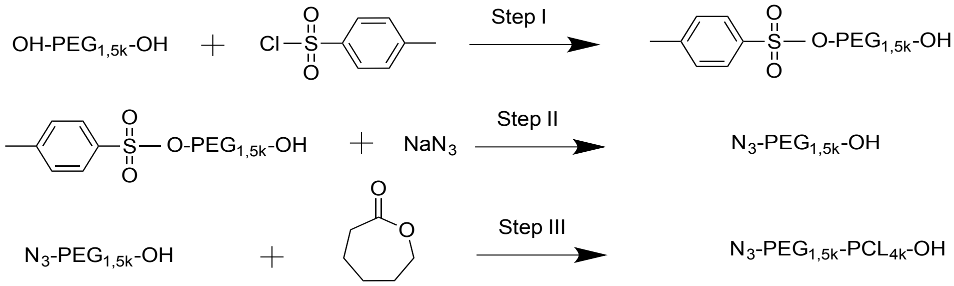
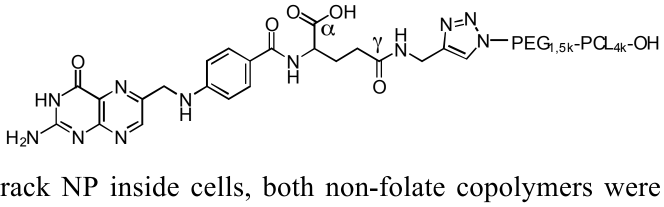
Abstract

This work is based on the development of a simple and elegant route of synthesis for poly(ethylene glycol)-poly(ε−caprolactone) (PEG-PCL) diblock copolymers tailed with an azido group, useful for conjugation with opportunely modified molecules of biological interest. The purpose is to improve the targeting ability of nanoparticles (NPs) prepared by self-assembling of these copolymers. Initial tailoring of PEG is performed through a method that allows selective introduction of functional groups at only one end[1]. In step 1, the use of a proper catalyst fully avoids formation of bifunctional PEG, as confirmed through ^{1}H-NMR:



N$_3$PEG-PCL is synthesized through ring opening polymerization (ROP) of CL initiated by the –OH of N$_3$PEG. The azido group has then been used in Copper-catalyzed Azide-Alkyne Cycloaddition “click” reaction. This reaction is highly selective, do not produce by-products, require mild conditions and was successfully performed with copper wires as catalyst. An example of molecule “clicked” through this route is folic acid, one of the most extensively employed targeting moieties to enhance nanocarrier accumulation in cancer cells. Folic acid was previously modified with propargylamine through carbodiimide chemistry to introduce an alkyne group. A systematic study of the reaction through HPLC and mass spectroscopy allowed to select the optimal reaction conditions in order to minimize formation of α-conjugate and by-products.[2]



Fol-PEG$_{1500}$-PCL$_{4000}$ was used in various percentages with PEG$_{1000}$-PCL$_{4000}$ or PEG$_{2000}$-PCL$_{4000}$ to prepare NPs by nanoprecipitation technique. The use of PEG blocks with different lengths is expected to vary the exposition of folate on NP surface. In order to track NP inside cells, both non-folate copolymers were conjugated with Rhodamine B as a fluorescent probe through the terminal hydroxyl of PCL block. Preliminary *in vitro* uptake studies in cells overexpressing folate receptor demonstrate a higher extent of uptake for NPs exposing folate on short PEG blocks due to receptor-mediated endocytosis.

Acknowledgments The financial support of AIRC IG 2014 #15764 is gratefully acknowledged.

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OC47

REAL TIME OBSERVATION OF METAL NANOPARTICLES GROWTH ON BLOCK COPOLYMER THIN FILMS

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Abstract

Metal nano-patterns with a particular structural symmetry, characteristic length scale and periodicity are of growing interest, e.g. for photonic applications and high-density memory devices[1-5]. The characteristic metal affinity towards the minority block of the self-assembled block copolymer (BC) templates plays an essential role to fabricate highly-order and well-defined metal nanopatterns. Though, ions of metal are highly selective towards the ionic polymer block, the metal atoms show an opposite behavior, an extreme selectivity towards the neutral block A simple explanation based on like-dissolves-like is ruled out. Experiments are performed by depositing gold in its atomic state on several block copolymer films with DC magnetron sputtering. At time resolution of 15 milliseconds, the nucleation/growth kinetics of gold nanoparticles on the polymer films is monitored using in-situ GISAXS. An extreme selectivity of the metal atoms is observed on the neutral block with an exponential growth of metal particle size. The coalescence behavior of the inert metal is mainly dominated by the improved atom mobility within the neutral polymer block.

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OC48

FUNCTIONAL NANOOBJECTS FROM SELF-ASSEMBLED BLOCK COPOLYMER STRUCTURES

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Abstract

Self-assembled block copolymers (BCP) provide perfect platform for the fabrication of hybrid polymer/inorganic materials. These hybrids initially prepared as bulk, could be disintegrated into isolated core-shell nanoobjects, such as nanospheres, nanofibers or nanosheets, using very simple selective solvent approach. Furthermore, these nanoobjects can be functionalized either in the core[1] or in the shell.[2] BCP may also be exploited as dual templates to produce multifunctional nanohybrids bearing diverse functionalities in the core and in the shell.[3] Confinement effects provided by BCP structures may induce formation of hierarchical superstructures with very interesting densely packed nanoparticle assemblies inside. Additionally, coated with an appropriate inorganic shell, core-shell nanoobjects can be further converted into hollow structures, such as nanotubes or nanospheres,[4] or yolk-shell type particles. In overall, such hybrid nanoobjects are very interesting for both fundamental and application oriented research. In this work we will demonstrate the feasibility of method for the fabrication of various nanohybrids and give some examples of their application, e.g. as catalytic nanoreactors.

Acknowledgements: This research was supported by a grant from Department of Science and Technology, India (Project No. SB/S1/PC-016/2013) and by Deutsche Forschungsgemeinschaft (project STA 324/51-1).

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OC49

H-BONDED VS IONICALLY SELF-ASSEMBLED AND HIERARCHIZED BLOCK COPOLYMER COMPLEXES: ENCODING COMPLEXITY AT DIFFERENT LENGTH SCALES AND OPENING DOORS TO FUNCTIONS[1]

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Taking inspiration from *mother Nature* for a successful encoding of functions (*e.g.* efficient and/or selective ion or dimensionality-controlled electron/hole transfers) into self-assembled and hierarchized soft-matter require understanding and mastering the appropriate (but yet very) delicate balances existing in between micro/nano-phase segregation processes and non-covalent interactions at work across many length scales in between chemically incompatible but linked sub-blocks within multi-block architectures. Based on examples selected from the recent literature and from our past five years efforts, we will discuss in particular how the combination of synthetic (PS-*b*-P4VP)[2] or biosourced (PBLG-*b*-PLL)[3] diblock copolymers, surfactants (phosphonic acid diesters) or pro-mesogenic steroïds (cholesterol hemisuccinate) allows for block copolymer complexes self-assembled and hierarchized simultaneously at two different length scales (Figure). We will exemplify pathways to control their hierarchical liquid-crystalline assemblies by competing interactions and molecular packing frustrations to finally present and discuss advanced solutions towards next generation of ionically or electronically conducting soft materials for energy and information technology-related applications[4].

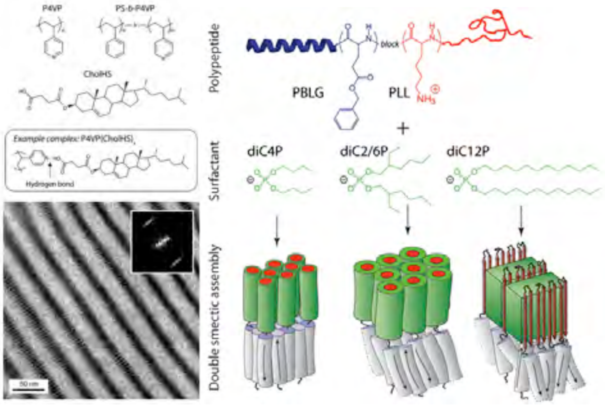

Figure: Left. Chemical structures of P4VP, PS-*b*-P4VP, pro-mesogenic steroid CholHS and TEM image of the *smectic*-within-*lamellar* hierarchical structure developed within PS_{40k}-*b*-$P4VP_{5.6k}(CholHS)_{0.75}$. Right. Chemical structures of PBLG-*b*-PLL, dialkyl phosphate surfactants and schematic representations of their resulting *double-smectic* diblock copolypeptide complexes.

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OC50

THERMORESPONSIVE RANDOM AND BLOCK COPOLYMER MICROGELS (COMPUTER SIMULATION STUDY)

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Abstract

Microgels are colloidal stable, soft, cross-linked macromolecular objects that show unique behaviour in a bulk,[1,2] at liquid[3] or solid interfaces. They are characterized by the high sensitivity and fast response to the external stimuli, for instance, T, pH, hv, E etc. Microgels have attracted notable attention due to their possible applications in both polymer chemistry and the (bio) material sector including such areas as drug delivery[4], semiconducting materials, sensor technology, and many others.

There is steadily growing interest in the synthesis of complex copolymer microgels with a specific affinity to nanoparticles, biopolymers or drugs. Ones of the key challenges during polymerisation process are how to control spatial distribution of different comonomers in the microgels and how does the spatial distribution of comonomers influence on microgel swelling behaviour, internal structure, interaction with guest molecules and etc. In the present study we have investigated the properties of microgels with random and block copolymer morphologies using a coarse-grained model with a molecular simulation techniques (DPD and MD). In particular we consider the correlation between the internal multicomponent structures of thermo-responsive copolymer microgels and their swelling-to-collapse transition in dilute solution in response to pH and temperature stimuli. We take into account different chemical structure of comonomers, their distribution inside the gel and also crosslinking density of the particles. Moreover we have investigated the peculiarities of copolymer microgels spreading at the liquid/liquid interface.

Acknowledgments: (DFG) within Collabolative Research Center SFB 985 "Functional Microgels and Microgel Systems" and the (RFBR) projects 15-33-21151 and 16-03-00266 is gratefully acknowledged. Simulations were performed on multi-petaflops "Lomonosov" supercomputer at Moscow State University.

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OC51

EVEN A CINDERELLA POLYMER CAN PROVIDE A SANDBOX OF MORPHOLOGIES

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Abstract

Block copolymer (BCP) amphiphiles' ability to spontaneously segregate in distinct phases due to opposed interactions with a selective solvent is a powerful tool for the fabrication of polymeric nanoparticles in solution. The final particle morphology can be predicted to some extent from structural (hydrophilic volume fraction *f*, overall molecular weight, interaction parameter χ) or solution parameters by thermodynamic considerations, but the picture is further enriched by kinetic effects rising from the macromolecular nature of the amphiphiles. A wide literature exists on nanostructure formation from PEO-*b*-PS, PAA-*b*-PS, PEO-*b*-PB[1] and Pluronic® systems, which allowed to map the accessible morphologies in varying assembling conditions.

In this contribution, we report on the self-assembly of poly(N,N'-dimethylacrylamide)-*b*-poly(styrene) (PDMA-*b*-PS) copolymers by nanoprecipitation from DMF[2]. In spite of its simplicity and non-responsiveness to stimuli often used to trigger chain rearrangement – i.e. temperature or pH –, this system can yield particles of a wide variety of morphologies and different hierarchical levels of organization.

By exploring a total molecular weight range spanning an order of magnitude (11.3 – 99.5 kg/mol) and hydrophilic volume fractions (f_{PDMA}) ranging from 0.75 ("star-like" regime) to 0.06 ("crew-cut" regime), it's possible to observe all the basic micellar structures, from monodisperse "hairy" micelles[3] (Fig. 1, left) to rods and hollow vesicles. Additionally, complex structures arise from second-order assembly: single micelles coalesce in "pomegranate" particles[4] and small lamellae intertwine to form large bicontinuous sponges (Fig. 1, right).

A combination of techniques needs to be implemented in order to have an all-round characterization of such a wide array of morphologies: particle imaging was performed by AFM, FIB-sectioning/SEM, conventional and cryo-EM and cryo electron tomography (CET). Mechanical properties and inner particle structure were studied using atomic force spectroscopy.

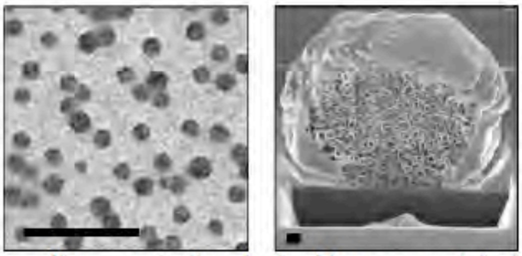

Fig. 1 – (Left) TEM image of monodisperse micelles obtained by nanoprecipitation of PDMA$_{817}$-*b*-PS$_{105}$. (Right) SEM image of a bicontinuous sponge obtained by nanoprecipitation of PDMA$_{20}$-*b*-PS$_{97}$. Scale bar = 200 nm.

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OC52

FABRICATION OF PATCHY PARTICLES VIA SELF-ASSEMBLY OF BLOCK COPOLYMER

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Abstract

Patchy particle is an important building block for hierarchical structures because of its discrete patches on their surface. However, the well-defined fabrication of patchy particles with controllable numbers and sizes of patches is still under development. In this work, we proposed a simple route, by using computer simulation method, to fabricate patchy particles with controllable patch symmetry via self-assembly of a polymer chain[1]. In our simulation, various kinds of patchy particles were obtained, simply by the self-assembly of a single model block copolymer chain in a poor solvent for both components. We obtained one-patch, two-patch, three-patch, four-patch, and cross-ribbon patchy particles. Then we studied the self-assembly of patchy particles with different softness and deformability by varying the cross-linking densities in different parts of the particles[2,3]. We found different nanostructures, such as hydrophobic matrix structure and inter-connected membrane structure, by changing the cross-linking density of the particles. As a comparison to our simulation work, we used two polystyrene-b-poly(4-vinylpyridine) (PS-b-P4VP) diblock copolymers with different composition to study the fabrication of patchy particles. We first dissolved the copolymer in a good solvent. Then we used water as the poor solvent for both components. We can obtain patchy particles with different patch numbers by changing the quality of solvent slowly. Our work demonstrates that a rational bottom-up design of patchy particles with controllable symmetry is possible by manipulating the block copolymer chain length and solvent quality.

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POSTER CONTRIBUTIONS

P1

POLYETHYLENE TEREPHTHALATE / CLAY NANOCOMPOSITES: RHEOLOGICAL, THERMAL, PERMEABILITY AND MECHANICAL PROPERTIES OF PET NANOCOMPOSITES

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Abstract

Polyethylene Terephthalate nanocomposites (PETNC) were prepared by melt mixing using a twin-screw extruder. The rheological behaviour of PET with various nanoclays (Somasif MAE, Somasif MTE and Cloisite 25A) at different concentrations (1, 3, 5 and 20%) was studied in the molten and film state thermal, rheological, permeability and mechanical properties. In the thermal properties, it has been observed that the clays enhanced the crystallisation temperature and accelerate the crystallisation rate of PET nanocomposites with increasing nanoclay content. In the Oscillatory tests, at low shear rates, an increase in the shear viscosity, storage modulus and loss modulus was observed in the PETNC with increasing nanoclay content while the viscosity decreased with increasing nanoclay content at high shear rates. Cox-Merz rule has been studied. Films of each PETNC were tested using uniaxial and biaxial stretching. It was observed that the nanoclay significantly enhanced the barrier properties of the PET film by up to 50%. The viscosity was observed to deviate from Newtonian behaviour and exhibited shear thinning at certain wt. %. It is possible that the formation of aggregates of clay is responsible for an increase in shear viscosity. It was observed that all three nanoclays used in this project act as nucleation agents for crystallisation by increasing the crystallisation temperature from the melt and decreasing the crystallisation temperature from the solid and increasing the crystallisation rate, while retaining the melt temperature and glass transition temperatures without significant change. The PETNC nanocomposites exhibit an increase in the tensile modulus of PET nanocomposite films by up to 125% which can be attributed to many reasons including the good dispersion of these clays within the PET matrix. The tensile test results for the PETNC nanocomposites micro-moulded samples shows that the injection speed is crucial factor affecting the mechanical properties of polymer injection moulded products.

P2

BLOCK COPOLYMER BASED NANOPLASMONIC SURFACES

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Abstract

Metal-dielectric nanocomposites are attracting a lot of attention for optical applications, due to their capacity to support designed surface plasmon waves. These nanocomposites are prominent in optical metamaterials, which are artificially structured materials engineered to gain optical properties not only from their composition, but from their design. Their geometry, size and arrangement can affect the propagation of light in an unconventional manner, giving rise to properties which are not available in bulk materials. Metamaterials and nanophotonic devices are classically fabricated by lithography techniques, but alternative simpler techniques are needed to reach characteristic sizes of a few tens of nanometers.

Scheme 1: General diagram of the fabrication process starting from a nanopatterned copolymer thin film, A)Spin coating of the gold precursor, B) Remove the excess of precursor, C) Oxygen plasma treatment

In this work we present a straightforward method to obtain patterned metal-dielectric nanocomposites, from quasi-continuous gold lines to discrete gold nanoparticles arrays, using the self-assembly of block copolymers as a nanostructured templates. Perpendicular lamellar structures of poly(styrene)-b-poly(2-vinyl pyridine) (PS-P2VP) copolymers were obtained using chemically modified substrates, followed by the metallic precursor deposition, which is selectively incorporated to the P2VP domains. Tuning the subsequent oxygen plasma treatment used to reduce the gold precursor allows obtaining different structures as shown in Figure 1. Grazing-Incidence Small Angle X-ray Scattering, Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectrometry, and Kelvin Probe Force Microscopy have been used to follow each step of the process. Besides, the plasmon resonances of the nanostructures are studied by variable-angle spectroscopic ellipsometric.

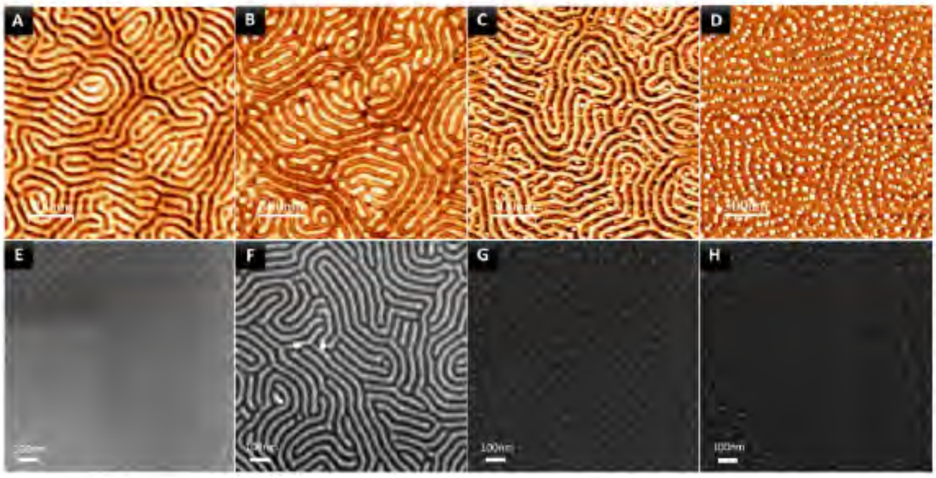

Figure 1: AFM (up) and SEM (down) top-view micrographs of PS-b-P2VP lamellar films (A,E) after spin coating of the gold precursor (B,F) and after 10s (C,G) and 60s (D,H) of oxygen plasma.

P3

ULTRA-THIN RANDOM COPOLYMER GRAFTED LAYERS FOR BLOCK COPOLYMER SELF-ASSEMBLY

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Abstract

Tailoring surface energies is the key factor to control the orientation of nanoscopic structures in block copolymer (BCP) thin films. Perpendicular orientation of the BCP features can be achieved with non preferential interactions at both the bottom and top interfaces. A common approach to the formation of a neutral surface consists in using end-functional poly(A-*r*-B) random copolymers to induce the perpendicular orientation of polyA-*b*-polyB diblock copolymers. As the random copolymer chemical composition can be precisely controlled, a fine-tuning of the surface characteristics is possible.
In this work, a series of hydroxyl terminated poly(styrene-*r*-methyl methacrylate) random copolymers was prepared, with equal composition but different molar masses, ranging from 1700 to 69000 g/mol.

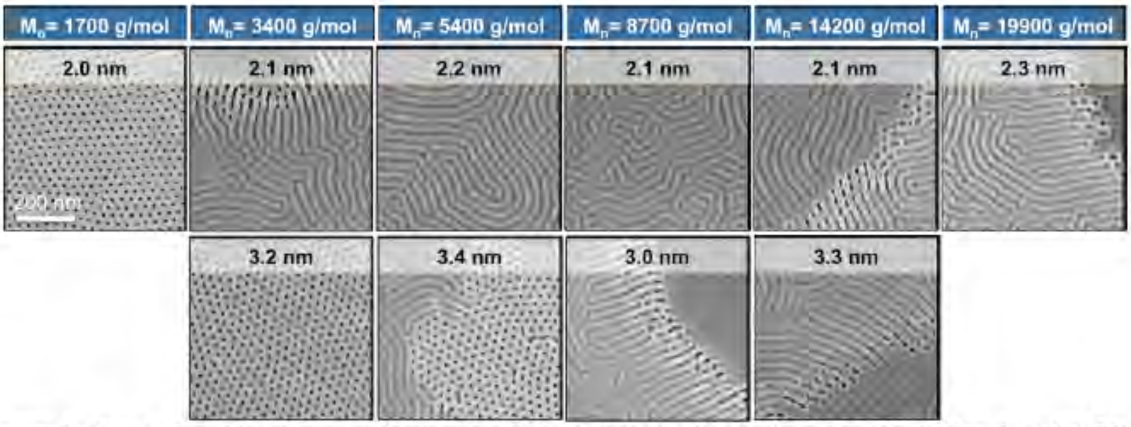

Figure 1: SEM plan view images illustrating the evolution of nanodomain orientation in BCP films deposited on top of a ~ 2 nm (top) and ~ 3 nm (bottom) thick RCP layer with different molecular weight.

The Rapid Thermal Processing (RTP) technology was employed to perform flash grafting reactions of the random copolymers to the activated silicon wafer surface at different temperatures for time periods ranging from few seconds to several minutes. The characteristics of the grafted layer were delineated as a function of the molar mass of the random copolymers. The subsequent ordering propensity of a symmetric polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA) diblock copolymer was found to be dependent on both the grafting temperature and the molecular weight of the random copolymer employed. Efficient neutral wetting brush layers with thickness lower than 2 nm were obtained. These results shed new light on the nature of the surface neutralization and indicate that several concepts and preconceptions of the molecular design of the self assembling materials should be reconsidered.

P4

SYNTHESIS AND CHARACTERIZATION OF POLY-LACTIC ACID / ε-CAPROLACTONE BLOCK AND RANDOM COPPOLYMERS FOR TISSUE ENGINEERING APPLICATIONS

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Abstract

Tissue engineering *scaffolds* are polymeric artefact whose aim is to help the adhesion and the proliferation of human cells, to promote the reconstruction or the implementation of damaged human tissues. For this purpose scaffolds must obviously be highly biodegradable and biocompatible, with a 3D porous structure, mechanical properties and degradation times similar to those of the tissue we want to repair [1].

In recent years *bionanocomposites*, multiphase materials where both the polymeric matrix and the *nano-filler* are biodegradable and biocompatible) took the place of conventional polymeric composites for the realization of tissue engineering scaffolds, because of their high biodegradability and biocompatibility, their low cost and the modulability of their mechanical properties.

In this work different types of bionanocomposites were synthesized using Cellulose Nanowhiskers (CNWs) as nanofiller. CNWs in fact proved to enhance significantly the resistance to degradation of the nanocomposites without a loss of mechanical properties [2-3].

This filler was modified with biodegradable copolymers, to enhance their hydrophobicity, by a non-conventional approach named *grafting to*, modifying the terminal groups of the copolymers with isocianate functionalities and then linking them to the groups on the surface of CNWs. For the modification were used two different types of of lactic acid/ ε-caprolactone copolymers, a di-block copolymer and a random one, both obtained by a living *Ring Opening Polymerization*.

A comparison of the properties of the two types of nanocomposite was performed , studying the structure of the obtained bionanocomposites by ^{1}H-NMR spectroscopy, GPC and scanning electronic microscopy, while their thermal properties were investigated by TGA and DSC.

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P5

ALL-POLYMER OPTICAL SENSORS FOR ALCOHOLS DETECTION

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Abstract

Thanks to their low cost, ease of fabrication, and the possibility to be integrated in portable devices,[1] all-polymer distributed Bragg reflectors (DBRs) are rapidly emerging devices for sensing applications.[2,3] Notwithstanding these advantages, low sensitivity and selectivity to vapors analytes without chemical labelling represent a drawback.

We demonstrate chemical labelling free DBR sensors which exhibit a relatively fast response to low concentrations and broad selectivity to short-chain alcohols. Our proof of concept device consists in a stack of alternated polystyrene and cellulose acetate thin films fabricated by spin-coating to form a dielectric lattice (Figure 1a). Such DBRs show photonic band gaps of the first and second order across the visible and near infrared spectral range, which give rise to a bright and uniform color (Figure 1b). The permeation of alcohols within the DBR induces a variation of the polymers thickness and refractive index, which leads to a shift of the diffraction peaks (Figure 1c). The spectral shift was interpreted as a non-equilibrium diffusion of molecules in a slab and was used to calculate an effective diffusion coefficient for every analyte. This approach gives us the capability to discriminate among short chain alcohols and their mixtures for concentration down to about 200 ppm.

These results open new perspectives in the use of polymer photonic crystals for the fabrication of lab-on-a chip devices with high sensitivity and broad-band selectivity to vapors.

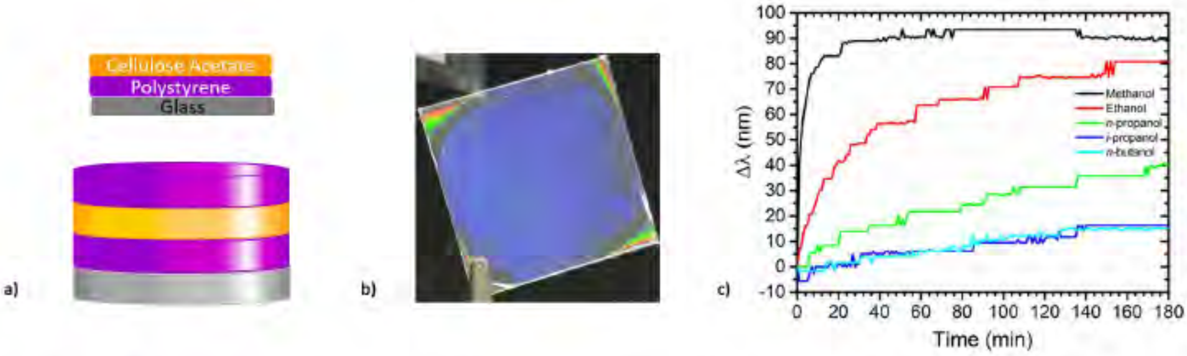

Fig. 1: a) scheme of the DBR structure; b) structural colour of the DBR; c) dynamic profile of the variation of the optical response of the DBR to pure alcohol vapors.

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P6

SYNTHESIS AND CHARACTERIZATION OF DIBLOCK COPOLYMERS CONTAINING MONOTHIO-ORTHOESTER FUNCTIONS USING RAFT POLYMERIZATION TECHNIQUE

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Abstract

Over the last two decades, the living radical polymerization has been the subject of much academic and industrial research. It is well known that the dithioesters are widely used in RAFT technique due to their large chain transfer constant compared to trithiocarbonates[1]. In this contribution, we will describe, firstly, the synthesis of a new chain transfer agent such as the benzyl-4-methyldithiobenzoate (BMDTB), the monomer, methyl-4-vinyldithiobenzoate (MVDTB) and modification of MVDTB in acyclicmonothio-orthoesters (MMMS) and cyclicmonothio-orthoesters (MVPOCO). Our second aim in this work is to prepare some homopolymers and the diblock copolymers by the RAFT method using the synthesized monomers such as styrene standard (S), 2-vinylpyridine (2VP), and 4-vinylpyridine (4VP).

As can be seen in Figure 1, the ^{1}HNMR spectra revels the presence of several peaks localized, respectively, at 3.2 and 3.1 ppm which can be attributed to methoxy groups of MMMS and homopolymer PMMMS. While, the peak localized around 1.66 ppm may be assigned to methylthio (SCH_3) groups. The peak observed at 2.3 ppm in block polymer PMMMS is assigned to CH_3Ph of RAFT agent. The polymerization was confirmed by the absence of peak in the chemical shift between 5.2 and 6.7 ppm, regularly attributed of protons of the monomer.

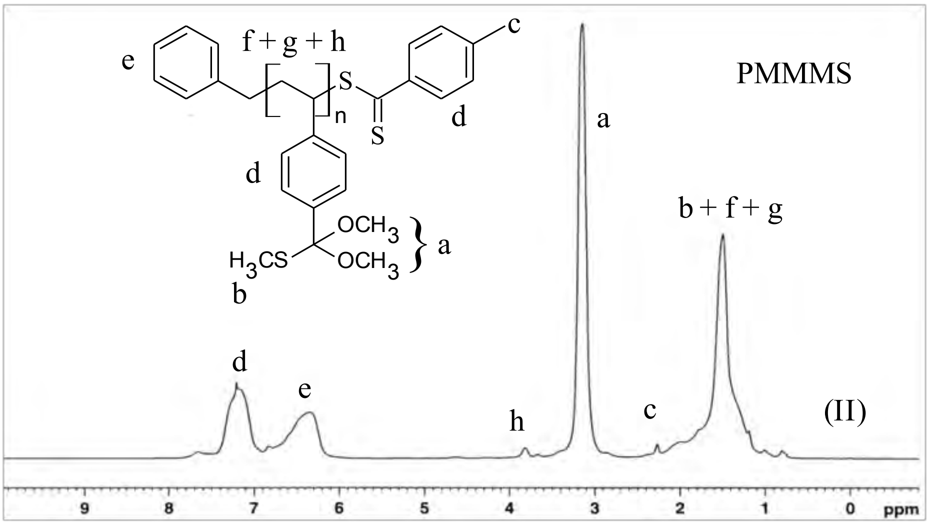

***Figure 1**: ^{1}H NMR spectra of PMMMS polymer recorded in $CDCl_3$. The letters indicate the attributed protons*

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P7

POLYMERIZATION-INDUCED SELF-ASSEMBLY AS A TOOL FOR THE FABRICATION OF AMPHIPHILIC BLOCK COPOLYMER SOFT-CORE NANOPARTICLES

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Abstract

Amphiphilic block copolymers (BCP) are among the most versatile building blocks used for the fabrication of phase-separated nanoparticles (NP) with different morphologies and structures by self-assembly[1]. A precise control over copolymer chain composition and molecular weight, as well as over the self-assembly process, is needed in order to effectively predict and reproducibly obtain particles with the desired size and shape.

A well-established approach to NP fabrication consists in nanoprecipitation of a pre-formed amphiphilic BCP into a selective solvent for one of the blocks. An alternative route is offered by Polymerization-Induced Self-Assembly (PISA): a pre-synthesized hydrophilic block is extended, via controlled/living free radical polymerization (CRP) in water, with a second hydrophobic block[2]. Self-assembly is induced during the polymerization since it's carried out in a poor solvent for the growing hydrophobic block. In these conditions it's possible to fabricate functional NP in a one pot synthesis using a green solvent and avoiding several purification steps.

In this contribution, we present the optimization of the one-pot synthesis and nanoparticles assembly of a set of poly(acrylic acid)-*block*-poly(n-butyl acrylate) (PAA-*b*-PBA) copolymers by PISA. A RAFT-synthesized PAA block is used as macroCTA for chain extension with butyl acrylate[3]. The reaction was carried out in aqueous dispersion, where the PAA-CTA acts as a stabilizer of BA droplets and controls the polymerization. Different total chain lengths and hydrophilic volume fractions were imaging and DLS analysis were employed to study the polymeric dispersions.

Due ot its low Tg, PBA is rubbery at room temperature, and is therefore a suitable host for hydrophobic up-converting (UC) molecules for bioimaging applications[4], whose efficiency dramatically drops in rigid environments. One-pot loading of the NP in the polymerization stage with UC molecules is reported.

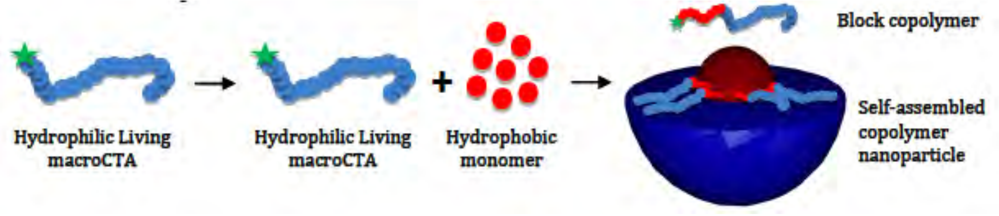

Figure 1. General principle of the polymerization-induced self-assembly method

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P8

A NOVEL NANO BIOCOPOLYMER SYSTEM FOR CONVERSION OF CARBONDIOXIDE

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Abstract

Enzyme and protein blocks corporation in nano structure brought a new view into protein based block copolymers in the aspect of unique functionality and physical property when compared to conventional block copolymers.

In this study, this approach lead the synthesis of formate dehydrogenase (FateDH) and cytochrome C (Cyt-C) in the same bionano-interface as a formation of formate dehydrogenase-co-cytochrome C using **A**miNoAcid (monomer) **D**ecorated and **L**ight **U**nderpinning **C**onjugation **A**pproach (ANADOLUCA)[1] method for conversion of CO_2 into formic acid. According to this method, FateDH-co-Cyt-c has polymerized in the same nano structure using poly vinyl alcohol (PVA) microemulsion polymerization technique. This technique also provides the cross-linking of the relevant proteins or enzymes with ruthenium based aminoacid monomers. In this study, cross-linking of FateDH and Cyt-c with ruthenium based aminoacid monomers during polymerization process brought stability in different reaction conditions, reusability and functionality the protein based block polymer system when compared the traditional methods. The synthesized protein-polymer based nano block copolymer system has characterized using Transmission Electron Microscopy (TEM) images, zeta size analysis and Circular Dichroism (CD). At the second stage of the study, synthesized nano block copolymer system has been embedded into 2-hydroxy ethyl methacrylate (HEMA) based cryogel[2] columns to develop a supporting polymeric material in CO_2 convesion cycle. During the experiments, CO_2 saturated water has passed through the cryogel column and the conversion of CO_2 into formic acid has been investigated by High Performance Liquid Chromatograpy (HPLC). The optimum parameters for the conversion such as pH, CO_2 flow rate and CO_2 concentration have been determined.

Experimental studies showed that the CO_2 conversion into formic acid has been effectively realized and the synthesized system is reusable many times without any deformation in its structure.

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P9

THE EFFECT OF THERMORESPONSIVE MICELLAR STRUCTURE ON THERMAL HYSTERESIS

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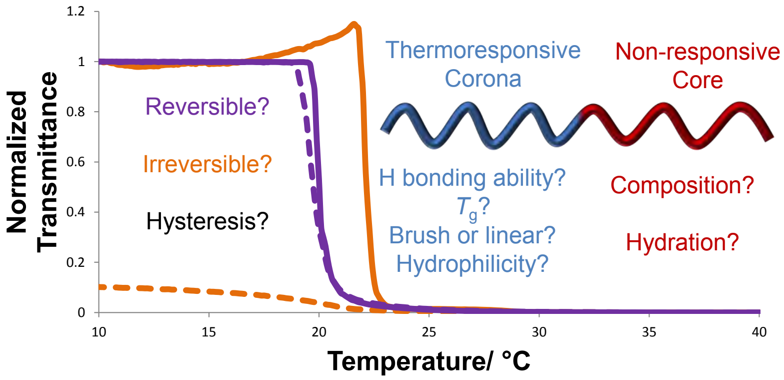
Abstract

Thermoresponsive polymers are of great interest as switchable smart materials.[1,2] Poly(*N*-isopropylacrylamide) (pNIPAM), an important thermoresponsive polymer, has been widely studied but the question of its slow reversibility, or thermal hysteresis, may limit its potential.[3] Herein well defined amphiphilic block copolymers, composed of a thermoresponsive corona-forming block (pNIPAM) and a non-responsive core-forming block (poly(*n*-butyl acrylate-*co*-*N,N*-dimethylacrylamide)) were synthesized using RAFT polymerization. Their subsequent self-assembly in aqueous solution was studied and it was determined by light scattering experiments that micelles had formed whose aggregation numbers (N_{agg}) could be tuned by varying the core block composition. Behavior at the molecular and macroscopic level was probed using complimentary variable temperature multi-angle dynamic and static light scattering, turbidimetry and microcalorimetry analyses. Our results showed that the degree of thermal hysteresis increased as a function of core hydrophobicity, which was attributed to differences in core hydration.[4] Similar micellar series were then used to probe different thermoresponsive coronas, such as those with low glass transition temperatures (T_g), non-linear brush-like coronas and those with no hydrogen bond donors, in order to better understand the origins of thermal hysteresis in these systems. These results highlight the need for consideration of the effect that self-assembly plays on the responsive behaviour of particles when compared with free unimers in solution. Both the polymer's molecular and supramolecular (self-assembled) structure played an important role in determining the overall phase behavior.



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P10

PM-RRAS AND AFM ANALYSIS OF PE-b-PEG DIBLOCK COPOLYMERS CRYSTALLIZATION ON CHEMICALLY GRAFTED SUBSTRATES

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Abstract

Amphiphilic copolymers are surfactants able to adsorb selectively on a substrate with different macromolecular orientation and conformation of both blocks, hydrophobic or hydrophilic. This organization will be governed by the substrate surface chemistry and will depend on the interactions between polymer chains. In the literature, many studies focus on the structuring effects during their adsorption of block copolymers containing one semi-crystalline block. Nevertheless few studies concern the effects of adsorption of amphiphilic block copolymers containing two semi-crystalline blocks.

The interest of this work is to understand how crystallinity of amphiphilic copolymers containing two semi-crystalline blocks is modified in thin films. Four diblock copolymers of various molar masses and PE / PEG ratio are studied in order to highlight the influence block lengths and composition. PE and PEG homopolymers whose molecular weights are the most representative of the blocks present in the copolymers PE-b-PEG are also studied. Their properties are compared with those of diblock in order to better highlight the changes in properties due to the presence of an immiscible block and changes due to interfacial phenomena.

These PE-b-PEG copolymers were adsorbed on metallic substrates by spin-coating. The surface chemistry of the substrates was controlled by chemical grafting using thiols. The influence of the hydrophilic or hydrophobic nature of the substrate on the organization and structuration of copolymers of different compositions was then studied.

Characterization of thin films of copolymers requires the use of specific characterization techniques. Polarization-Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS) spectroscopy is and innovative and original spectroscopy that was used for "in situ" reflectivity experiments to characterize thin films of PE-b-PEG copolymers deposited on reflective substrates. Due to the polarization modulation of the incident IR wave, its reflection at the interface according to surface selection rules increase the sensitivity of the spectral response, allowing determination of molecular orientation and structuring effects. The orientations and conformations of adsorbed PE and PEG copolymers blocks on a substrate were determined by comparison of the spectral bands of the isotropic state (bulk) with those of the anisotropic state (thin film).

Atomic Force Microscopy (AFM) analyses were also performed on the same copolymers in thin films, in order to access the surface morphology and to distinguish the amorphous and crystalline phases of PE and PEG blocks.

Chains orientations and conformations as well as surface morphologies were thus characterized in order to understand the competition between chains/chains and chains/substrate interactions, which will have a direct effect on the crystallization of the blocks. Results show that adsorbed on a chemically inert substrate, semi-crystalline copolymers became disorganized. This was explained by changes in the balance of chains/chains vs chains/substrates interactions. Surface chemistry alters the balance between these interactions significantly, allowing for an hydrophilic substrate to favor the crystallization of PEG block, and for an hydrophobic substrate to favor the PE block crystallization. The modification of the crystalline phase content, morphology and molecular orientation of the crystalline structures of the adsorbed films indicate that a strong competition between interfacial forces and intra and intermolecular forces intervenes.

P11

DIRECTED ASSEMBLY OF DENDRON-JACKETED BLOCK COPOLYMERS FOR USE AS TEMPLATES TO SYNTHESIZE NANOARCHITECTURED MESOPOROUS TIO_2 FILMS

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Abstract

In this work, we proposed a smart method to synthesize mesoporous TiO_2 films with directional channels using cylinder-forming dendron-jacketed block copolymer (DJBCP) templates processed by doctor-blade casting or spin casting. The DJBCP is formed with amphiphilic dendrons (**3D*n***), selectively incorporated into the P4VP block of poly(styrene)-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP). To solve the problem in terms of the collapse of the cylinder nanostructures after etching walls of pores, a critical procedure of transplantation was designed in the DJBCP-templated synthesis for keeping the walls within films. The supramolecular dendrons act as an important role for stabilizing the cylindrical morphology of DJBCP films and guiding the titanium precursors into P4VP domains. Epitaxial-like growth via order-order phase transition was adopted for obtaing the perpendicular cylinders in the DJBCP films. This way is highly parallel in nature and able to form large-scale ordering rapidly by facile procedures with very low costs for industrial production. The mechanism of order-order phase transitions was systematically investigated using GISAXS, TEM, SEM, and AFM. Beyond being practical applications for the directional mesoporous TiO_2 films converted by the DJBCP films, this work also revealed fundamental aspects on kinetic routes of DJBCP self-assembly.

P12

MONTE CARLO SIMULATION OF ASYMMETRIC VESICLE MEMBRANE STRUCTURE AND ITS FORMATION

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Abstract

Vesicle is attracting more and more researchers' interests due to its unique hollow structure. Most vesicles reported have symmetric layer structure, i.e., the inside and outside surfaces are formed by the same block species. In some practical application area, vesicles with asymmetric layers, in which the inside and outside hydrophilic layers of vesicles are formed mainly by different species of blocks, have more advantages. Using Monte Carlo simulation, we studied the formation and micro-phase behavior of asymmetric vesicles formed by ABC triblock copolymers in solvent selective for blocks A and C. Simulation results show that the hydrophilicity of blocks A and C determines not only the vesicle formation but also micro-phase behavior. If blocks A and C are of equal length, block A (with lower hydrophilicity) is likely to aggregate on the inner surface, whereas block C (with higher hydrophilicity) tends to move to the outer surface, forming the ABC (from inside to outside) three-layer vesicle. Simulation results also reveal that if the hydrophilicity difference between the two blocks is sufficiently low, the ABC three layers are formed after the membrane closes. Otherwise, the ABC three layers are formed before the membrane closes.

Acknowledgements

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P13

MODULATION OF MICRODOMAIN FORMATION IN HYBRID POLYMER/LIPID VESICLES

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Abstract

Over the last few years, amphiphilic copolymer combined with phospholipid into a single membrane, namely hybrid polymer/lipid vesicles, has attracted interest of many different scientific communities[1,2]. This new vesicular formulation can be exploited indeed at either nanoscale (drug delivery system) or microscale (cell membrane model) with a stunning association of benefits of polymersomes (stability, chemical versatility) with the benefits of liposomes (biofunctionality, biocompatibility).

However, the control of their properties which is obviously linked to the membrane structuration (domain formation via phase separation) is still far from being understood up to now. In this work, our purpose is to map a global picture of phase separation within 10 – 50 μm Giant Hybrid polymer/lipid Vesicles (GHVs) by using various copolymers based on poly(dimethylsiloxane) and poly(ethylene oxide) with different architectures (grafted, triblock) and molar masses allowing to tune membrane thickness, combined with lipid in a fluid (POPC) or gel state (DPPC) at room temperature. From confocal imaging and advanced fluorescence microscopy techniques (FLIM, FRAP), we demonstrate that in addition to the lipid/polymer fraction or lipid physical state, the line tension at the lipid polymer/lipid boundaries (modulated by the molar mass of the copolymer) and membrane tension (modulated either by osmotic shock or micropipettes suction) are the most important factors involved in formation of stable lipid domains of different size and morphologies in GHVs.

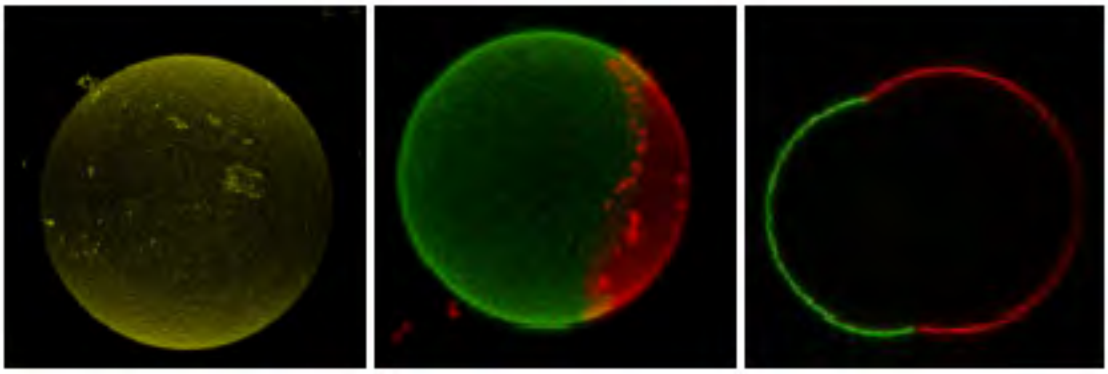

Figure. Different stable morphologies of GHVs obtained by playing on line tension or membrane tension

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P14

MOLECULARLY IMPRINTED PARTICLES CONTAINING ELECTROSPUN BLOCK COPOLYMER MEMBRANES

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Abstract

Molecularly imprinted nanoparticles were encapsulated into polymer nanofibers with a simple electrospinning method[1]. When the template was removed, imprinted binding sites were left in the nanofiber materials that are capable of selectively rebinding the target molecule. In this study, block copolymer nanofibers from melamine imprinted nanoparticles, polyvinylpyrrolidone (PVP)/poly(acrylic acid) (PAA) were prepared by electrospinning. The composite nanofibers can be used as affinity membrane to greatly simplify solid phase extraction of melamine from sample. The diversity in physical and mechanical properties of the nanofiber were characterized by scanning electron microscopy, FTIR spectroscopy and mechanical testing. The adsorption of melamine was studied under equilibrium (batch) conditions. To describe the adsorption capability of the synthesized block copolymer nanofibers, Langmuir and Freundlich models were used. To evaluate the adsorption capacity in the presence of interferents experiments on samples were also performed[2,3].

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P15

ENZYME-POLYMER NANO BLOCK COPOLYMER SYSTEM FOR HYDROLYSIS OF PECTINES

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Abstract

Protein-polymer block copolymer systems are attractive and efficient copolymers in different applications. Block copolymerisation system provides the strategie for proteins preserving high levels of protein activity.

In this study, a novel nano block copolymer consisting pectinase enzyme and poly vinyl alcohol (PVA) has synthesized via **A**miNoAcid (monomer) **D**ecorated and **L**ight **U**nderpinning **C**onjugation **A**pproach (ANADOLUCA)[1] method. Pectinase enzyme is used in food industry widely in hydrolysis process of pectines[2] especially for the production of clear fruit juice[3].

At the first step of the study, nano block copolymer of pectinase particles have been synthesized according ANADOLUCA method and characterized by transmission electron microscopy (TEM) and zeta sizer. In the second step, the hydrolysis of pectin has been investigated using newly synthesized nano block copolymer of pectinase particles and free pectinase enzyme separately and compared to each other. The different conditions that affect the hydrolysis of pectin such as pH, thermal stability, storage stability and reusability have been investigated. In addition to these studies, the reusability data of nano block copolymer of pectinase particles has been investigated comparatively free enzyme.

So, the data showed that newly synthesized nano block copolymer of pectinase particles are very attractive for hydrolysis of pectin substances and they will have a great usage area in industrial process.

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P16

STEPWISE DESIGN OF DONOR-ACCEPTOR BLOCK COPOLYMERS: A STRUCTURAL INVESTIGATION

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Abstract

Organic photovoltaics require a donor-acceptor nanostructure for efficient charge separation and collection. Block copolymers with their intrinsic behavior to form an equilibrium structure on the nanometer scale are an elegant approach to produce such a desired nanostructure avoiding problems of limited structural long-term stability. Here we report about the morphological investigation of different design steps towards two donor-acceptor block copolymer systems. While poly(3-hexylthiophene) (P3HT) was chosen as a donor material, the morphological evolution of two acceptor materials was followed from small molecule compounds to the final acceptor blocks.

Starting from low molecular weight phenyl-C61-butyric methyl ester (PCBM) and perylene bisimides (PBI) with an oligoethylene-glycol swallow-tail side-chain polymers were created by attaching them onto a polystyrene like backbone. Finally, the side-chain polymers were combined with P3HT to a diblock copolymer. The morphological changes from the low molecular weight materials to the final block copolymers were studied by a combination of small and wide angle X-ray scattering in transmission, reflection and grazing incidence geometry as well as with optical, electron and scanning force microscopy.

The step from low molecular weight compound to side-chain polymer leads to a significant reduction of the crystalline order. In both cases crystallization is completely suppressed. This property allows high PCBM loading with grafting densities of up to 60 wt% without formation of unfavorable PCBM nanocrystals. The structure of the acceptor polymer is preserved in the final block copolymer. The combination with P3HT leads to a crystalline-amorphous donor-acceptor block copolymer. In addition to the structure of the individual homopolymers the block copolymers show a nanostructure with a periodicity in the range of 30- 40 nm. While microphase separation of cylindrical morphology was observed for the PBI containing block copolymer, only an incomplete microphase separation was found in the PCBM containing block copolymer. The reason is most likely the high glass transition temperature of the PCBM-block restricting the dynamics during structure formation.

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P17

EFFECT OF THE SOLVENT CASTING BOILING POINT ON THE SELF-ASSEMBLY KINETICS OF POLYDIMETHYLSILOXANE-CONTAINING BLOCK COPOLYMER

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Abstract

Diblock copolymers (DBCs) thin films have become the subject of an intense research activity because they self-assembly (SA) into periodic ordered nanostructures with different morphology (spherical, gyroid, cylindrical, lamellar). In particular, DBCs containing polydimethylsiloxane (PDMS) have recently attracted more and more attention because they form high-resolution nanostructures with dimensions below 10 nm. Moreover, the PDMS block can be oxidized to form SiO_x nanostructures that can be exploited as nanolithographic masks perfectly suitable for microelectronics application. [1] The SA of the PDMS-containing DBCs can be achieved by means of different approaches but thermal annealing processes would be highly desirable. [2] Interesting, the solvent employed to deposit the DBC thin films plays an important role in the definition of the final morphology of the self-assembled nanostructures because the solvent could preferentially swell one of the blocks thus driving a specific morphology. The dependence of the final morphology on the solvent affinity and boiling point (Bp) in thermal annealed samples has been previously reported. Qualitatively the solvent Bp for fixed affinity does not influence the morphology and the order of the nanostructures. [3] Nevertheless, in a different DBC system was demonstrated a solvent-induced morphological diversification related to the solvent Bp. [4]

In this work, we report a systematic study on the SA kinetic of cylinder-forming polystyrene-block-poly(dimethylsiloxane-random-vinylmethylsiloxane) PS-b-P(DMS-r-VMS) thin film, with molar mass of 22 Kg/mol (d = 9 nm, L_0 = 20 nm), by means of a Rapid Thermal Processing (RTP) machine on flat surfaces using solvents casting with fixed selectivity but different Bp. The SA kinetic was valuated considering the evolution of the lateral order (ξ) as a function of the annealing time (t) that follow a power law dependence of $\xi \sim t^{\Phi}$, where Φ provides information about the kinetic grain coarsening.

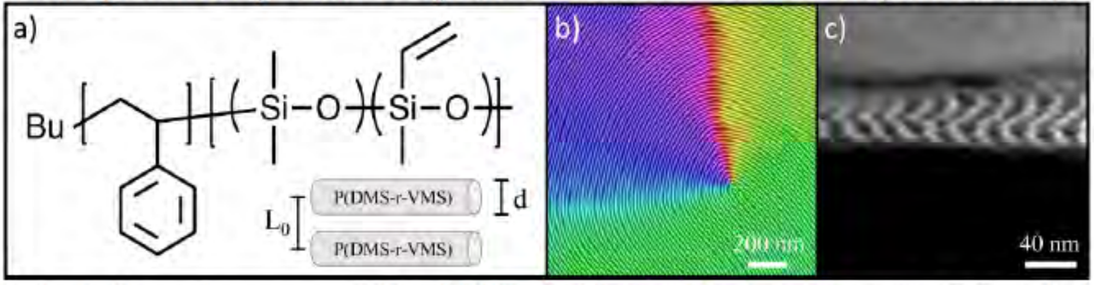

Figure 1: a) Chemical structures of PS-b-P(DMS-r-VMS) b) SEM plan view image of the cylindrical nanostructures merged with the orientational color scale c) SEM cross section image of the cylinders.

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P18

COMPOSITION DETERMINATION IN GRAFTED MULTICOMPONENT POLYMERIC THIN FILMS BY HYPHENATED TGA-GC-MS

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Abstract

Grafted multicomponent polymeric systems represent the starting point for the creation of scaled high-resolution polymer nanostructures including nanometer scale membranes, templates for fabrication of nanoobjects such as metal, ceramic nanodots and wires, and nanopattern masks for subsequent additive or subtractive processing of the underlying substrate. In addition, the exploitation of more sophisticated surface interactions, such as various directed self-assembly (DSA) approaches, can lead to structures featuring improved lateral ordering and reduced structural defects.

From the analytical point of view, these systems can be conceived as ultrathin films ($h < 10$ nm) of polymer chains grafted to a solid substrate. Consequently, their evaluation represents a rather demanding analytical task due to the very small amount of material to be detected. Moreover, these materials should be analyzed still grafted to the substrate because their detachment from the surface implies major structural modifications. These two distinct requirements limit the number of analytical techniques suitable to obtain information about their structure and composition.

The use of hyphenated thermal and mass spectrometric techniques is well established and widely applied to the investigation of the polymer structures under distinct thermal conditions. Recently in our laboratory a highly versatile TGA-GC-MS apparatus was developed[1] and successfully applied[2,3] to the analysis of a number of samples featuring substantial scale difference, i.e. bulk materials, thick films (few μm), thin (dozens of nm), and ultrathin films (few nm) without any sample pretreatments.

In the present contribution, the TGA-GC-MS technique was addressed to the quantitative determination of the composition of ultrathin films obtained from the "grafting to" of functional PS-b-PMMA and P(S-r-MMA) copolymers. The calibration of the system was performed by model systems of functional P(S-r-MMA) with different composition. Once the system calibration was properly set up, the grafting process of binary mixtures of functional polymethylmethacrylate (PMMA) and polystyrene (PS) homopolymers to an activated and preferential silicon surface was elucidated.

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P19

SYNTHESIS OF ALTERNATING DONOR-ACCEPTOR (BLOCK) COPOLYMERS VIA GRIM POLYMERIZATION

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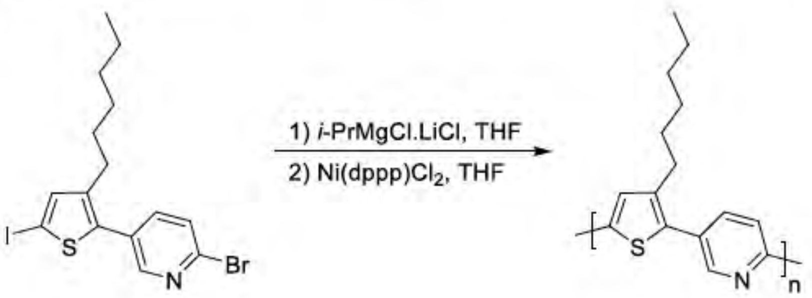
Abstract

Low bandgap donor-acceptor type alternating copolymers, nowadays very popular in the field of polymer solar cells, are generally synthesized by transition metal catalyzed polycondensation reactions. The most well-known examples are the Stille and Suzuki polymerizations, whereby the polymer is formed in a step-growth fashion. As a result, rather poor control over the polymer molar mass, dispersity and end groups is achieved, often affording ill-defined materials. On the other hand, controlled chain-growth transition metal catalyzed polycondensations allow precise control over the above-mentioned polymer characteristics. On top of that, they enable the synthesis of fully conjugated block copolymers and other advanced macromolecular structures via one-pot polymerizations. Such materials can give rise to interesting morphological structures and enhanced light absorption, beneficial for their use in (for example) organic photovoltaics.[1] From literature, an example is known wherein an alternating copolymer is synthesized by performing a controlled Grignard metathesis (GRIM) polymerization (Kumada catalyst transfer polymerization or KCTP) of a monomer that consists of two donor-type components.[2] It would be very interesting to extend this approach to the synthesis of low bandgap donor-acceptor copolymers. Since both polythiophenes and polypyridines have already been synthesized in a controlled way via GRIM, we chose to create a push-pull monomer consisting of a thiophene and a pyridine unit. This monomer was then polymerized via GRIM. In this presentation, the polymer synthesis and characterization will be discussed, as well as the tests performed to analyze the controlled character of the polymerization and the extension of the synthetic procedure to block copolymers.



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P20

AMPHIPHILIC TETRAETHYLENE GLYCOL METHACRYLATE-PERFLUOROALKYL ACRYLATE BLOCK AND RANDOM COPOLYMERS: SYNTHESIS AND SELF-ASSEMBLING IN WATER SOLUTION

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Abstract

Amphiphilic block and random copolymers with perfluoroalkyl segments can efficiently provide self-assembled polymeric nanostructures[1], including micelles, vesicles, and nanogels, in water and organic solvents, via the intermolecular association or intramolecular self-folding of the copolymer chains[2]. These nanomaterials may display anti-biofouling properties against proteins, cells and organisms[3]. Moreover, perfluoroalkyl polymers have several attractive features: the polymers are immiscible with both water and common organic solvents, yet have selective interactions with fluorinated compounds resulting in unique association and molecular recognition.

Focusing on these features we have synthesized block and random copolymers of tetraethylene glycol methyl ether methacrylate (PEGMA) and 2-(perfluorohexyl)ethyl acrylate (FA). Owing to the controlled ATRP reaction, the molecular weight, composition and sequence of the amphiphilic block and random copolymers could be tuned in a predictable way.

In this contribution copolymers with PEGMA:FA ratios 70:30 and 90:10 are reported. The philic/phobic balance directly affected the self-assembling behaviour in bulk and in solution. Above a critical concentration in water (0.5 g/L), the copolymer chains are characterized by a bimodal size distribution (Fig.1, left), comprised of nanometer and submicrometer structures. While the larger structures were due to self-assembled, intermolecular aggregates, the smaller ones were attributed to single, intramolecular folded chains. Moreover, we found a sharp thermal transition depending on the copolymer composition (Fig.1, right). Above the transition temperature, one almost monodisperse stable phase existed, with size increasing from ~500 nm to ~1500 nm with copolymer concentration from 0.5 g/L to 5 g/L. Heating and cooling cycles showed the complete reversibility of these copolymer systems. The narrow size distributions accomplished for both copolymers above the thermal transition are ascribed to the formation of intriguing thermoresponsive polymersomes with homogeneous size.

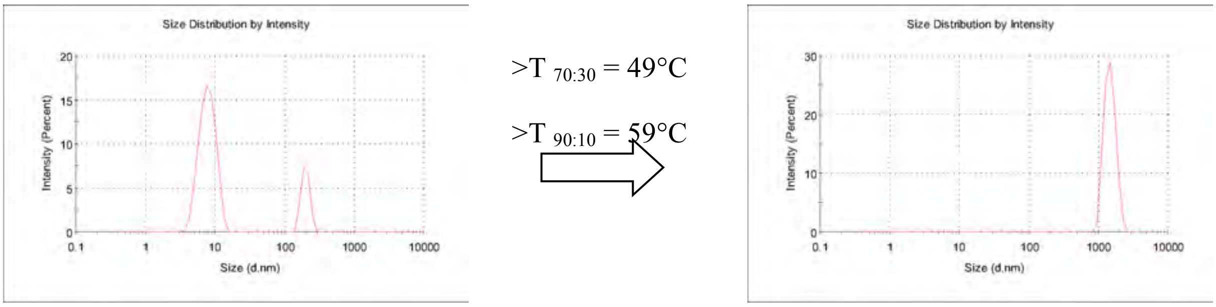

Fig. 1. Size distribution representatives of 70:30 and 90:10 copolymers, 5 g/L, as measured by photocorrelation spectroscopy below (left) and above (right) the respective transition temperatures.

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P21

ARBORESCENT COPOLYMER MOLECULES AS TEMPLATES FOR NANOTECHNOLOGICAL APPLICATIONS: A COMPUTER SIMULATION STUDY

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Abstract

Arborescent (dendrigraft) polymers are known to be the class of dendritic molecules of high molecular weight. In contrast to hyperbranched molecules and similarly to dendrimers, the arborescent polymers can be obtained with a well-defined molecular structure - their inital “buiding blocks” are monodisperse linear chains, which are succusessively “grafted onto” the polymeric substrate by generation-based scheme. The number of grafts and their chemical compostition in each generation can be varied and thus the highly branched copolymers can be achieved. Such multi-component molecules can be used in number of contemporary applications such as templates for nanoparticles[1] with defined shape and form, efficient microemulsion stabilizers[2] or even building blocks of complex molecular aggregates in polymer melts and solutions. In the present research we have performed a series of computer experiments using the dissipative particle dynamics simulation technique (DPD) to study the arborescent copolymers of particular architecture shown in Figure 1 in following cases: (a) single molecules in a selective solvent; (b) molecular self-assembly in solution; (c) the mixture of arborescent molecules and linear diblock-copolymers with identical chemical composition. In particular, the results of our simulations revealed the existence of network-like aggregates formed by the considered molecules in solutions under certain conditions and stability of gyroid-like structures in the melt. We believe that our findings could be useful in obtaining of stimuli-responsive solutions and block copolymer films with stable 3D percolated morphologies.

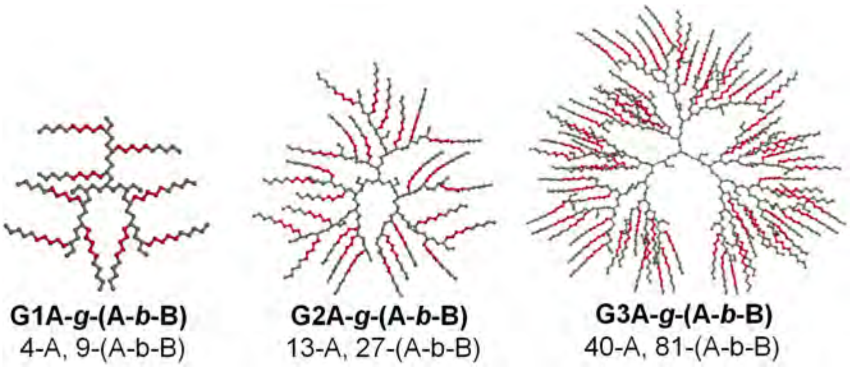

Figure 1. The models of arborescent copolymers considered in simulations. The numbers below images depict the generation of each molecule (G#) and the number of chains of homopolymer and block copolymer graft chains (A and A-b-B respectively)

Acknowledgements
The financial support of the Russian Foundation for Basic Research (project 16-33-00256) and the Russian Science Foundation (project 15-13-00124) is gratefully acknowledged. The simulations were performed on multiteraflop supercomputer Lomonosov at Moscow State University.

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P22

MONTE CARLO SIMULATION OF THE ADSORPTION BEHAVIOR OF MULTIPLE PROTEINS ON END-GRAFTED POLYMERS

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Abstract

Protein adsorption behavior on surface is affected by various specific interactions, including hydrogen bonding interaction, hydrophilic and hydrophobic interactions, and electrostatic interaction. Understanding the effects of these interactions on protein adsorption behavior and micro process during adsorption is crucial to the preparation of biomedical polymer material with excellent hemocompatibility. Monte Carlo simulation is employed to study the protein adsorption behavior on the surfaces grafting with polymer chains with different length, density and hydrophilicity. The simulation results indicate that the protein adsorption amount firstly decreases and then increases with an increase in the hydrophilicity of polymer brush. For the polymer brush with moderate hydrophilicity, a dense layer of polymer molecules is formed which can prevent the adsorption of proteins. On the other hand, when the hydrogen bonding between protein and polymer brush is introduced, the simulation results indicate that the protein adsorption amount on the polymer brush with longer chains but lower graft density is relatively small. The simulation results are quite consistent with corresponding experimental results, which can provide necessary theoretical evidence for the preparation of biomedical polymer material with high performance.

Acknowledgements

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P23

MULTI-BLOCK COPOLYMERS OF GLUCAN DERIVATIVES

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Abstract

Aqueous solutions of methyl cellulose demonstrate thermo-responsive gelation behavior. Hydrophobic-hydrophobic interactions play a key role in gelation mechanism; accordingly, preparation of block copolymers of glucans having defined and highly substituted blocks of fully methylated glycosyl units is of interest to study the structural requirements of this phenomenon. Cationic ring opening polymerization (CROP) of cyclodextrin derivatives, as well as transglycosidation of cellulose derivatives have been utilized to generate multi-block copolymers of glucans (Fig. 1).[1-3]

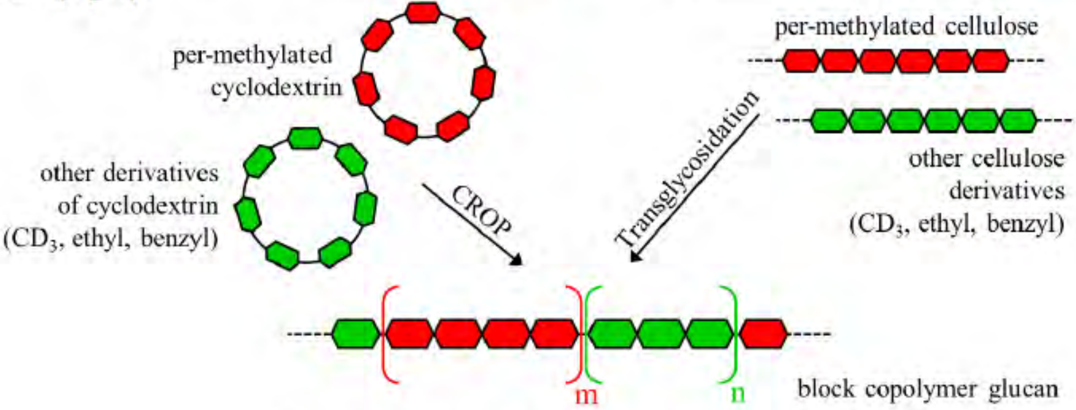

Figure 1. Synthesis of block copolymer glucans

Current project includes transglycosidation of per-methylated cellulose and a supplementary benzylated methyl cellulose derivative. The desired block copolymer can be obtained by deprotection of the protecting benzyl groups.

Supplementary substitution of un-substituted hydroxyl groups of glycosyl units by deuterated methyl groups, tagging the analytes with m-amino benzoic acid, and subsequent electrospray ionization mass spectrometry (ESI-MS) enable us to determine the average block length and block length distribution over the synthesized copolymers.

A brief overview of performed model studies on transglycosidation of cellulose ether derivatives[3], as well as principles of ongoing research project will be presented.

Acknowledgment

Scientific research work of our former colleagues, Marko Rother and Andreas Bösch, is cordially appreciated. We gratefully acknowledge support by the Braunschweig International Graduate School of Metrology B-IGSM, the DFG Research Training Group GrK1952/1 "Metrology for Complex Nanosystems" and the Deutsche Forschungsgemeinschaft (DFG, Mi398/10-1).

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P24

HIGHLY TUNABLE COMPLEMENTARY MICRO/SUBMICRO-NANO PATTERNED ARRAY

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Abstract

Fabrication of micro-nano patterned structures while maintaining ordering at microscale and nanoscale with low cost and high resolution is highly desired in microelectronics and biological areas.[1-4] In this work, the large-area ordered and highly tunable micro/submicro-nano patterned array in a complementary manner were successfully generated by combining block copolymer self-assembly and colloidal lithography (Fig.1). Ordered monolayer of polystyrene (PS) colloidal spheres assembled at the water-air interface was lifted off onto the pre-treated hydrophilic PS-*b*-P2VP and PS-*b*-P4VP block copolymer micelle films, afterwards the micelle films were patterned using different sizes of PS colloidal spheres as etching mask through oxygen plasma treatment. In this approach, microstructures are provided by the colloidal monolayer, which enabling to control the ordering, patch size and periodicity at micro/submicroscale, meanwhile the ordering, density and morphology at nanoscale can be significantly altered by the different block copolymer parameters and micelle preparation conditions. Moreover, by modifying the surface of micro-nano patterned gold arrays, it can be used as flexible template to pattern BSA molecules. We believed that the proposed fabrication strategy can be very powerful alternative, which may provide a new platform for fabrication of micropatterned nanoarrays with high tunability and controllability.

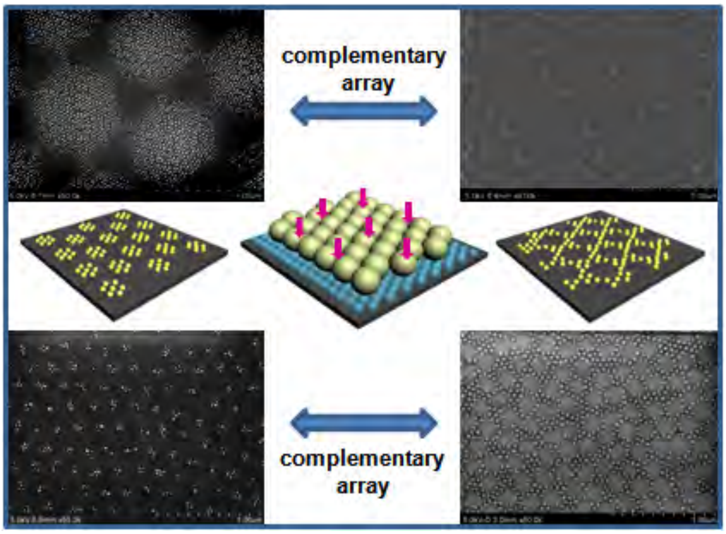

Fig.1 The ordered micro/submicro-nano patterned metal arrays with different patch sizes and the corresponding honeycomb-like metal array in a complementary manner.

Acknowledgments: This work was supported by National Natural Science Foundation of China (Grant 21474108, 21274148, 21574133).

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P25

BOVINE SERUM ALBUMINE NANO CARGOES

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Abstract

Protein based block copolymers have drawn more attention for the usage of many area such as industrial area, drug delivery, diagnosis, imaging systems etc. The appropriate selection, positioning and designing of proteins in block copolymerization system provides the high levels of protein activities and utilities.

In this study, bovine serum albumin (BSA) based nanocargoes have been synthesized according to **A**miNoAcid (monomer) **D**ecorated and **L**ight **U**nderpinning **C**onjugation **A**pproach (ANADOLUCA)[1] method. In this method, BSA particles have cross-linked horse radish peroxidase (HRP) enzyme to obtain photosensitive materials via poly vinyl alcohol (PVA) polymerization media. At the end of the synthesis, star-shaped block copolymer has been obtained. The enzyme horseradish peroxidase (HRP) reacts with its substrate, hydrogen peroxide, in the presence of an electron donor (i.e. diamino-benzidine) to yield a brownish reaction product. This reaction product can be visualized by light microscopy. 3,3′-diaminobenzidine (DAB) has been used as the substrate in HRP catalysis reaction[2]. The synthesized BSA nano cargo has been characterized by Transmission Electron Microscopy (TEM) images and zeta size analysis. Beside this, the fluorescent emmission has been visualized by fluorescence spectrophotometer by exciting nanocargoes at 310 nm. Lastly, the interaction between DAB and HRP conjugated BSA nanocargo has been investigated.

By synthesis of nano cargoes, a photosensitive, reusable without any deformation in its structureand effective nano block copolymer, nanocargo, has obtained. This nanocargo is highly effective in peroxide presence and could be used as a labelling agent in nano biotechnology area effectively.

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P26

FAST ANNEALING OF BLOCK COPOLYMERS VIA MICROWAVE HEATING

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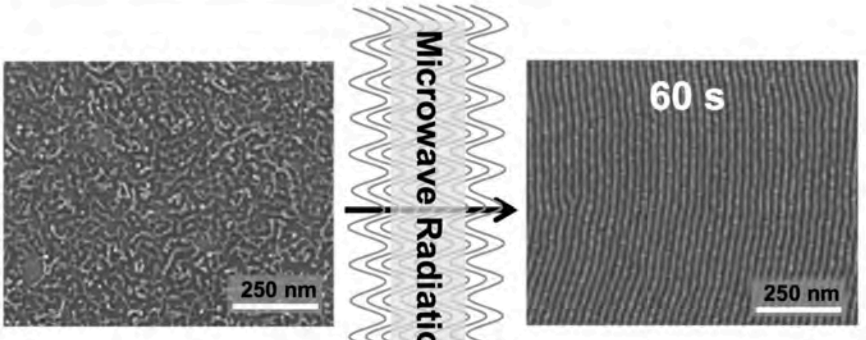
Abstract

As potential candidate for next-generation lithography, block copolymer self-assembly has been demonstrated to form sub-20 nm simple periodic arrays (i.e lines, hexagonal packed dots, circles), as well as complex patterns, including bends, terminations, and junctions, as a potential innovative technology for integrated circuit and hard disk drive production.[1,2] In terms of throughput, the process by which phase separation of the block copolymer generally takes hours to days by conventional thermal or solvent annealing method, which too slow for commercial photolithography (~200 wafers/hour). Recently, microwave heating and intense laser illumination have been shown to be alternative methods to simple direct heating to dramatically reduce the time required for annealing.[3] [4]While the microwave annealing work has been mentioned by the ITRS as a potential route to fast annealing,[5] there have been some differences of opinion with respect to the mechanism by which the microwave-induced heating takes place. In this presentation, we will talk about our latest results concerning microwave annealing, which suggests that the substrate heating is, in fact, the source of generated thermal energy, which drives the fast annealing.[6] We then show this microwave annealing method can be extended to non-microwave absorbing substrates, including flexible plastic (Kapton), glass, and indium tin oxide, which suggests that microwave annealing could be amenable to other electronic applications beyond silicon, such as flexible electronics and related areas.



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P27

AMPHIPHILIC TETRAZOLE-CONTAINING PAIRED POLYMERS

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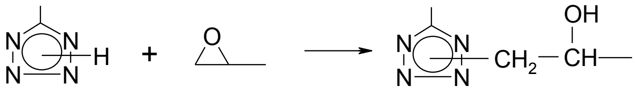
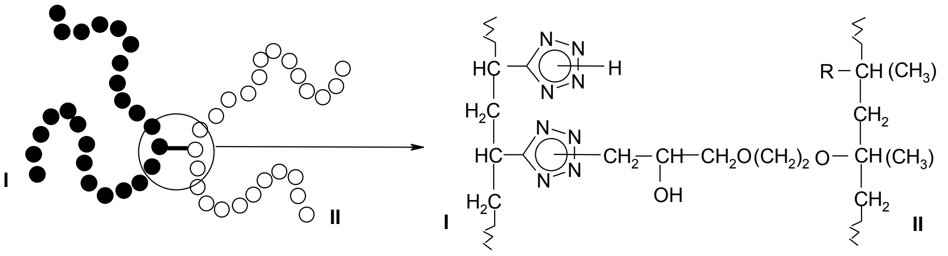
Abstract

Chemical reactions between functional groups of macromolecules of various types make it possible to perform the forced blending of even a completely incompatible pair of polymers. These reactions are characterized by low conversions of functional groups due to weak interpenetration of reacting macromolecular coils. Moreover, the above mentioned version of the combination of polymers can be of interest for the formation of multicomponent polymer systems in which the properties of individual components must be retained. For example, as in block or graft copolymers, in one macromolecule, chain fragments of hydrophilic and hydrophobic natures may be combined. The problem of forced blending of polymers of various types may be solved through the choice of "anchor" functional groups, which provide the synthesis of paired polymers (interpolymers) under relatively mild conditions. For the example of the synthesis of tetrazole-containing polymers, it was demonstrated that the unsubstituted N–H tetrazole cycles of the first polymer and the oxirane cycles of the second polymer provide for the covalent bonding of macromolecules. The alkylation of a tetrazole cycle with an epoxy reagent



proceeds at moderate temperatures (below 100°C) without additional initiation. As a result of the reaction macromolecular coils bond via spacer groups into a single formation called an interpolymer.



The degree of crosslinking determines whether the interpolymer is soluble or inclined toward limited swelling. The network structuring and amphiphilic nature of the reaction products determines their inclination toward limited swelling in organic and aqueous media. With allowance for the high complexing capacity of tetrazole-containing polymers, gels based on the interpolymers can be doped with a variety of metal ions.

Hydrogel samples saturated with differ metal ions were treated with $NaBH_4$ in an aqueous solution. The process was accompanied by the formation of molecular hydrogen and darkening of hydrogels due to reduction of Me^{n+} to Me^0. When stored in an atmosphere of argon, the hydrogel containing copper nanoparticles remained unchanged for a sufficiently long time. During contact with atmospheric oxygen, the reverse oxidation of Me^0 to Me^{n+} occurs rapidly in hydrogels (within one day).

$$Me^{2+} \underset{O_2}{\overset{NaBH_4}{\rightleftarrows}} Me^0$$

Note that the reduction and oxidation of metals in the hydrogel composites is reversible and can be conducted repeatedly. With allowance for the ability of tetrazole-containing polymers to form complexes with a wide set of metal ions, hydrogels based on this polymer show promise as matrices for the design of nanocomposites for various applications.

P28

CONCENTRATED DISPERSIONS AND MELTS FROM MICELLAR SOLUTION: COMPUTER SIMULATIONS

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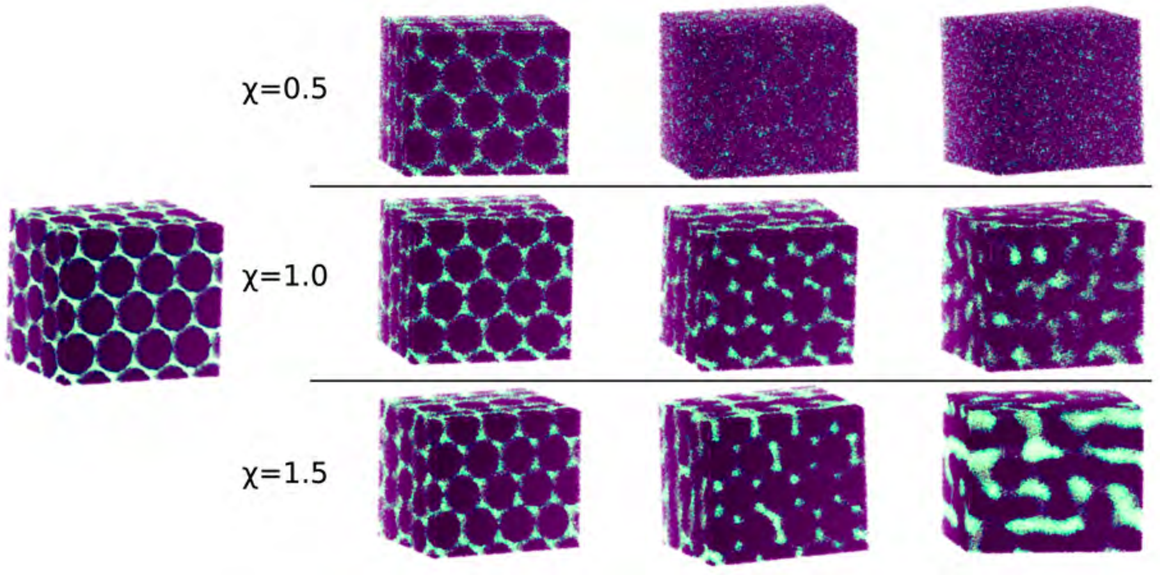
Abstract

It is well-known that the process of microphase segregation, that occurs in the melts of thermodynamically incompatible block-copolymers, leads to the formation of ordered structures with different morphologies (spherical and cylindrical domains of one phase into another, lamellar structures, gyroid structures, etc). However, the formation of a segregated film with well-defined order is a complicated problem from the viewpoint of technical implementation owing to a number of labor-intensive procedures, such as selection of common solvent, regime of solvent evaporation and film annealing. To investigate the easier production of nano- and micro-structured films, the approach, based on film formation from preliminary self-assembled objects in dilute solution followed by solvent evaporation may be proposed. In this research we study the films formed by block-copolymer micelles (core-shell particles) by means of DPD simulation technique. We test the melt stability and compare system morphology with equilibrium phase diagram for regular diblock-copolymers.



Acknowledgement

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P29

PVC POLYMER MATRIX PLATISIZED WITH IONOPHORE IONIC LIQUIDS : TETRADECYLPHOSPHONIUM SALTS FOR CONSTRUCTION OF ION-SELECTIVE ELECTRODE MEMBRANES FOR CLOSO-BORANE ANION DETERMINATION

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Abstract

Ion-selective sensors containing only two components: polymer (PVC) and the ionic liquid, which served as twin function agent (ionophore and PVC plasticizer) were recently proposed for the determination of lipophilic anions. The ionic liquids were firstly shown to be well combined with PVC in various weight ratios at room temperature by E. Pungor and co-workers[1,2]. Here we present new supramolecular system containing polyvinylchloride and liquid ion exchanger based on ionic liquids with closo-borane anions for ion-selective membrane of potentiometric sensors.

Ionophores representing the salts of tetradecylphosphonium with closo-borane anions were produced as ionic liquids $(C_{10}H_{21})_4P)_2[B_{10}H_{10}]$ and $(C_{10}H_{21})_4P)_2[B_{12}H_{12}]$ with the melting point < 15° C by the extraction method (ion exchange extraction). The membrane composition were examined for PVC contents (40 - 60)% - (60 - 40)% $(C_{10}H_{21})_4P)_2A$ where $A = [B_{10}H_{10}]^{2-}$ or $[B_{12}\ H_{12}]^{2-}$. Before the measurements, the electrodes were conditioned in 10^{-3}M solutions of the corresponding closo-borane salts of cesium during one day. The direct method of the selectivity coefficient determination in mixed solutions[3] at a constant concentration of interfering ions was applied for ion concentrations varying in the range of 10^{-2} M - 10^{-7} M.

The electrodes with the best characteristics contained 40% PVC - 60% $(C_{10}H_{21})_4P)_2A$. These electrodes provided with the detection limits pX=6,8 for anion $[B_{10}H_{10}]^{2-}$ and pX =7,3 for $[B_{12}H_{12}]^{2-}$. The lower limit detection is improved with the increasing number of boron atoms in the boron cluster anions $[B_nH_n]^{2-}$. This is due to the increase in the anion lipophility. The change of pH in the range of 2 to 10 has no influence onto the potentials of the studied electrodes.

The values of selectivity coefficients in the serie follow as: $[B_{12}H_{12}]^{2-} > [B_{10}H_{10}]^{2-} > ClO_4^- > NO_3^-$. The selectivity to the closo-dodecaborane anion is by factor 10^2 higher than to the closo-decaborane anion. Selectivity to boron cluster anions is explained by the change of hydration energy of these ions water solutions.

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P30

POLYMERIZATION-INDUCED SELF-ORGANIZATION OF RAFT-BASED AMPHIPHILIC BLOCK-COPOLYMERS

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Abstract

The ability of amphiphilic block-copolymers to undergo microphase separation in melts and selective solvents allows forming of nano- and micro-structured films. In some cases due to co-existence in polymer film of dense hydrophobic areas and thin hydrophilic channels, the latter formed from the blocks bearing charged functional groups, allow producing the systems possessing simultaneously the high mechanical strength and conductivity. Combination of these properties is of particular urgency for production of different membranes.

In the present research we formed structured polymer films using special approach based on formation of "core–shell" block-copolymer particles via heterophase controlled radical polymerization of low soluble in aqueous phase monomer mediated by hydrophilic oligomer bearing trithiocarbonate group either in the middle or on the end of the oligomeic chain.

Hydrophilic oligomer was prepared via RAFT polymerization using symmetrical (R–SC(=S)S–R) and non-symmetrical (R–SC(=S)S–R′) RAFT agents based on trithiocarbonates. The polymerization kinetics, molecular weight characteristics of the block-copolymers and particle size distribution depend crucially from the length of hydrophilic chain and the location of trithiocarbonate group in it. The location of trithiocarbonate group in the middle of the chain of hydrophilic oligomer provides formation of stable monodisperse colloid solution of core-shell structured particles. The synthesized dispersions were applied as "building blocks" for formation of polymer films with percolating branched structure (Figure 1) confirming the above conclusion of better properties of hydrophilic oligomer with the middle location of trithiocarbonate group.

Results of computer simulations are in a good agreement with experimental data.

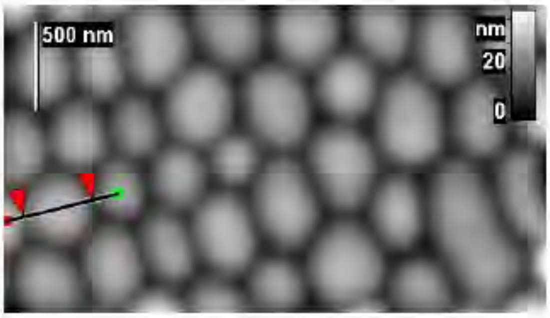

Figure 1. Structure of thin film formed by the "core–shell" block-copolymer particles

Acknowledgements

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P31

ANTIMICROBIAL NANOCOMPOSITIONS MADE OF AMINO ACID BASED BIODEGRADABLE POLYMERS

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Abstract

Bacteria easily colonize the surfaces of tissues, surgical devices (implants, orthopedics, catheters, etc.), and instruments causing surgical device related infections. Therefore, the battle against bacteria and the prevention of surgical devices from biofilm formation is one of the main challenges of biomedicine today. Our strategy to the solution of this problem consists in using antimicrobial polymeric coatings as effective “shields” to protect surfaces from bacteria’s colonization and biofilm formation. As one of the most promising approaches look the use of antimicrobial bioerodible polymeric nanocomposites containing silver nanoparticles(AgNPs). We assume that the combination of an erodible polymer with a strong bactericide should put obstacles to bacteria to occupy the surface and to form biofilm. It has to be noted that this kind of nanocomposites are also promising as wound dressing materials to treat infected superficial wounds.

Various synthetic and natural polymers were used for creating biocomposites containing AgNPs as both particles' stabilizers and matrices forming elastic films at surfaces. One of the most effective systems to fabricate AgNPs is an ethanol solution of polyvinylpyrrolidone(PVP) with dissolved $AgNO_3$–ethanol serves as a $AgNO_3$ reductant and PVP as AgNPs stabilizer (through interaction of nanoparticles with nitrogen atom of the amide group). Though PVP is biocompatible and film-forming polymer, it is not a good candidate to design either "biofilm shield" or wound dressing material because of a high solubility in water – though the solubility of PVP provides the desirable release of AgNPs from the matrix, but the coating is easily washable away from the surfaces. More promising as matrices look water insoluble but bioerodible polymers which can provide the release of AgNPs and form long-lasting coatings at the surfaces.

For creating bioerodible water insoluble antimicrobial coatings containing AgNPs, we selected amino acid based biodegradable polymers(AABBPs)–poly(ester amide)s, poly(ester urea)s, their copolymers containing amide and related groups capable to stabilize AgNPs. Among a huge variety of AABBPs reported [1] we selected the polymers soluble in ethanol. For preparing AgNPs containing nanocompositions AABBPs and $AgNO_3$ were dissolved in ethanol and subjected to photochemical reduction using daylight-irradiation. The formation of AgNPs was observed visually by coloring the solutions in brownish-red.

The obtained AgNPs were characterized by UV-spectroscopy, transmission electron microscopy(TEM), and dynamic light scattering(DLS). According to the UV and TEM data the photochemical reduction resulted presumably in spherical AgNPs with rather high contribution of the particles below 10 nm that are known as responsible for antimicrobial activity. DLS study showed that average size of nanoparticles formed after photo-reduction in ethanol solution ranged within 50 nm.

The *in vitro* antimicrobial activity study of the new nanocomposite material is in progress now.

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P32

DEVELOPMENT OF PHENYLBORONIC ACID-FUNCTIONALIZED NANOPARTICLES FOR EMODIN DELIVERY

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Abstract

Stable and monodisperse phenylboronic acid-functionalized nanoparticles (PBA-NPs) were fabricated using the 3-((acrylamido)methyl)phenylboronic acid homopolymer (PBAH) via the solvent displacement technique.The diameters of the PBA-NPs could be easily tuned by adjusting the initial polymer concentration and the proportion of methanol. Based on the PBA-diol interaction, the resulting PBA-NPs could successfully encapsulate emodin, a polyphenolic drug, and the drug release profile from nanoparticles follows a pH-dependent manner. The PBA groups located on both the outermost and interior of PBA-NPs, which was benefited to encapsulate polyphenolic drugs and interact with sugar compounds on the cell surface at the same time. We believe our study will pave the way for new application of PBA polymers in targeting polyphenolic drug delivery to the cancer cells.

Acknowledgements
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P33

LABEL FREE SELECTIVITY IN POLYMER PHOTONIC CRYSTALS SENSORS

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Abstract

Photonic Crystal (PhC) sensing relies on the penetration of an analyte within a dielectric lattice and the consequent variation of its optical response.[1] In the recent years, self-assembled block copolymers PhC sensors for liquid become highly researched in this field,[2] but detection of vapors with these materials, has not been deeply investigated yet.

We propose a vapour sensors capable of fast and selective detection of vapor analytes without chemical labelling. The sensor, which is made by alternated layer of spun-cast poly(*para*-phenilenoxide) (PPO) and cellulose acetate, promises to place the foundation for new concept block-copolymer sensors suitable for the selective detection of vapour analytes without chemical targeting.

The devices exploit the capability of amorphous PPO to form co-crystalline phases with different optical properties upon intercalation of organic molecules.[3] Figure 1 schematizes the working principle of the multi-layered sensor where, alternated thin films of amorphous PPO and cellulose acetate form a mono-dimensional dielectric lattice. The PhC is characterized by a photonic bandgap centred in the visible spectrum (green line). In the same figure, the intercalation of benzene or carbon tetrachloride induces the formation of two different co-crystalline phases. Ellipsometric measurements show that in the case of benzene, the intercalation strongly reduces the polymer refractive index and swells the thin films. This phenomenon causes a red-shift of the multilayer photonic band gap (red line). The intercalation of carbon tetrachloride, results instead in a different PPO crystalline phase which induces in a blue-shift of the peak (blue line). Similar results were achieved for other aromatic homologues demonstrating the discrimination capability of the system.

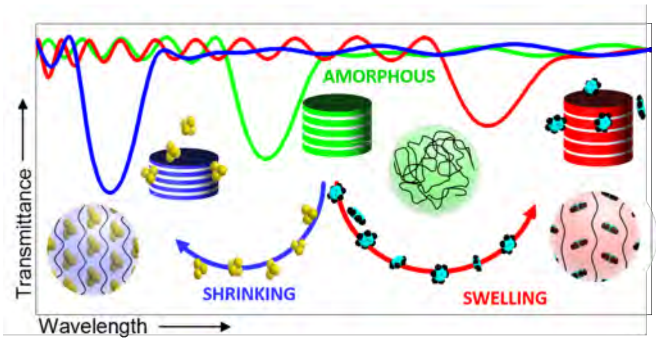

Figure 1: Scheme of the optical response of poly (para-phenilenoxide) - cellulose multilayers to carbon tetrachloride and benzene.

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P34

A DIFFERENT POINT OF VIEW ON PHASE SEPARATION: MOBILITY RESOLUTION USING TIME DOMAIN NMR

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Abstract

Time domain (TD)-NMR is a branch of nuclear magnetic resonance where the evolution of the magnetization vector in the domain of time is directly analysed. By eschewing Fourier Transform and its requirement of high homogeneity of the magnetic field, low-field benchtop instruments can provide information about polymer mobility rapidly and accurately. Specific NMR sequences allow the measurement of crosslink density in rubbers[1] or the kinetics of gelation and crystallization.[2] The technique is particularly suited for the study of phase-separated systems such as many block copolymers. In fact, several relevant systems such as thermoplastic elastomers or self-assembled drug carriers are composed by blocks of starkly different mobility, with one rigid block providing structural stability and a softer block providing functionality. Here, different phases can be resolved, probing their glass transition at the microscopic level or measuring the domain size.[3]

By exploiting mobility contrast in poly(*n*-butylacrilate)/poly(styrene) (PBA/PS) nanospheres depicted in Fig. 1, we proved that the inner PBA core and the external PS shell evolve independently as two homopolymers: significant changes in the rigid fraction take place at PBA and PS characteristic T_g. Moreover, by performing a precise quantification of relative amount of PS and PBA within the system at intermediate temperature we found out correspondence between the PS composition and the rigid fraction, demonstrating strong phase separation and the absence of significant interfaces[4].

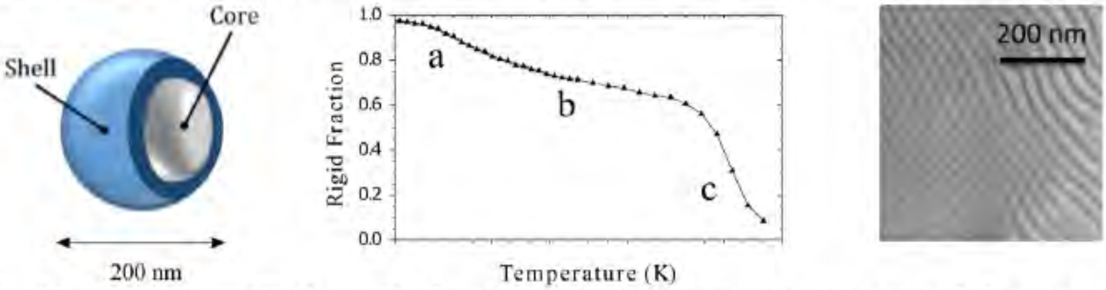

Fig. 1 – The plot in the middle depicts the dependence of rigid fraction on temperature in 2-phase systems, exemplified by the nanostructured particle on the left and by the TEM picture of a block copolymer film on the right. Region (a) in the graph is the glass transition of the low T_g block, while (c) is the glass transition of the more rigid block. In region (b) the thickness and behaviour of interphases can be assessed.

Furthermore, we investigated a bulk poly(styrene)-b-poly(ethylene-co-butene)-b-poly(styrene) (SEBS) copolymer, where the EB phase is nanoconfined by glassy PS regions in a lamellar morphology. WAXS and DSC on samples with 7% ethyl side chains indicated crystallization, not detected in similar EB polymers. Multiple Quantum TD-NMR instead indicated dynamic inhomogeneity with highly dipolar coupled regions over the EB melting temperature, suggesting a rotator phase. Mobility contrast is not limited to temperature activation: we also present the case of PS-b-poly(dimethylacrylamide) (PS-PDMA) polymer films where both phases are below T_g in anhydrous conditions, but PDMA can be selectively plasticized by adsorption of water vapor.

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P35

CHALLENGES WITH NANOIMPRINT OF BLOCK COPOLYMERS

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Abstract

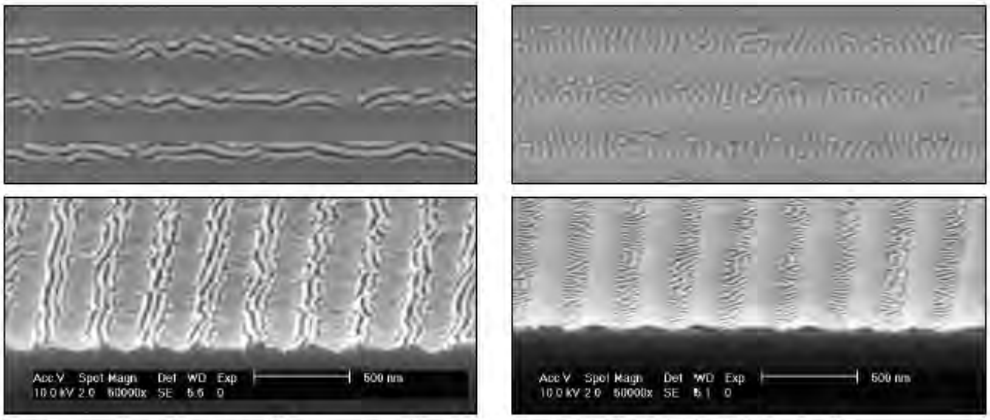
Directed self-assembly (DSA) with block copolymers (BCP) typically is performed by grapho- and/or chemo-epitaxy[1]. Such methods rely on a pre-treatment of each single substrate, so that a specific surface energy can be achieved.

On account of this, the investigation of alternative methods is advised. Here, we explore the suitability of nanoimprint for DSA. Two different imprint techniques are investigated, thermal nanoimprint[2] (T-NIL) and capillary force lithography[3] (CFL). T-NIL works with hard stamp and a high external pressure. In contrast, flexible stamps are used for CFL and no external pressure is applied[4].

The examples shown in the figure on the left, were realized with a stamp replica made from OrmoStamp (T-NIL). The CFL experiments, figure on the right, were performed with a PDMS stamp. The substrates are provided with a 40 nm BCP layer (PS-b-PMMA) on Si wafers without any pre-treatment.

The results from T-NIL show a perpendicular phase separation in the stamp cavities, only. A trend of orientation parallel to the stamp lines can be observed. Results from CFL also exhibit a perpendicular phase separation, however, not in the stamp cavities, but in the areas of stamp contact. Furthermore, the predominant orientation of the perpendicular phase separation is perpendicular to the stamp lines.

We will discuss the impact of the process parameters for nanoimprint, which comprise the imprint pressure, the imprint temperature and the imprint time. A further issue is the effect of the surface energy of the stamp. The stamps have to be provided with an anti-sticking layer. If it is possible to induce the DSA from the top (by means of the stamp), the stamp offers the advantage of a multiple use which can replace the laborious pre-treatment of each substrate.



Imprint results with sinusoidal stamp profile obtained with PS-b-PMMA (104 kg/mol).
Left: T-NIL (150°C/100 bar/1h/ OrmoStamp). Right: CFL (180°C/0.1 bar /1h/ PDMS).

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P36

THERMAL STABILITY AND NON-ISOTHERMAL DECOMPOSITION KINETIC OF A POLY (STYRENE-CO-ACRYLIC ACID)/MAGHNIA BENTONITE NANOCOMPOSITE

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Abstract

Thermal stability and degradation kinetic of synthetized pure copolymer poly(styrene-co-acrylic acid) SAA-7 and its nanocomposite based on poly (styrene-co-acrylic acid)/Maghnia bentonite SAA-8/OBT2 (where 7, 8 and 2 are respectively 7 and 8 % mol of acrylic acid and 2 weight % of organically modified OBT) were carried out by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under an inert atmosphere. The results show an improvement of the thermal stability of nanocomposite.

The kinetic methods of KAS (Kissinger–Akahira–Sunose), FWO (Flynn–Wall–Ozawa) and Tang were applied to study the kinetics and mechanisms degradation of materials. The apparent activation energies (E_a) of thermal decomposition of the elaborated materials, calculated by Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO) methods, were higher than those of the virgin copolymer, reflecting the OBT stabilizing effect upon the matrix's decomposition.

The TGA kinetic study revealed that the thermal degradation mechanisms of virgin copolymer (SAA-7) and its nanocomposite (SAA-8/OBT2) are different under the effect of the clay and obeys in case of SAA-7 to kinetic model R2 called Phase boundary reaction, $n = 2$ ($g(\alpha) = 1 - (1 - \alpha)^{1/2}$), whereas for SAA-8/OBT2, the kinetic model is A1,5 called Avrami-Erofeev, $m = 1.5$ ($g(\alpha) = [-\ln(1 - \alpha)]^{2/3}$.

Keywords: Poly (n-butyl methacrylate-co-acrylic Acid), Structure, Morphologie, Clay, Nanocomposites, non-isothermal decomposition kinetic, MET and TGA.

P37

TAILORING ULTRAFILTRATION MEMBRANE STRUCTURE AND PERFORMANCE WITH PEO-*b*-PMMA DIBLOCK COPOLYMERS

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Abstract

In this work, poly(ethylene oxide)-*block*-poly(methyl methacrylate) (PEO-*b*-PMMA) diblock copolymers were established as functional additive for polyvinylidene fluoride (PVDF) ultrafiltration membranes and as novel self-assembling membrane material.

The copolymers were synthesized via an Atom Transfer Radical Polymerization (ATRP) with commercially available poly(ethylene oxide) methyl ether as first block. PEO methyl ether is available with molar masses between 350 and 20,000 $g \cdot mol^{-1}$, permitting a wide range of block ratios and molar masses of the copolymer.

When the copolymer is used as an additive, the hydrophilicity of the PVDF-based membrane is increased, which decreases fouling. Additionally it was found that copolymer micelles can be induced by complexing the PEO block with several metal salts. These micelles lead to a higher surface porosity and a more regular barrier pore structure, presumably through microphase separation during the nonsolvent induced phase separation process (NIPS) used for membrane preparation. It was possible to tailor the molecular weight cut-off (MWCO) between 30 kDa and 110 kDa by varying the type and amount of salt in the otherwise identical casting solution. The permeability of the developed membranes was significantly higher than for comparable commercial reference membranes from PVDF.

When the copolymer is used as novel membrane material, its self-assembling properties can be used to obtain membranes with a narrow barrier pore size distribution as well as a very high number density of pores, which should lead to a sharp sieving curve and a high permeability. These membranes have been prepared as thin-film composites by spin-coating on PET track-etched support membranes (see Fig. 1) and via NIPS with and without nonwoven support. Until now, the membranes from PEO-*b*-PMMA show some promising results, but have not reached the expected performance yet.

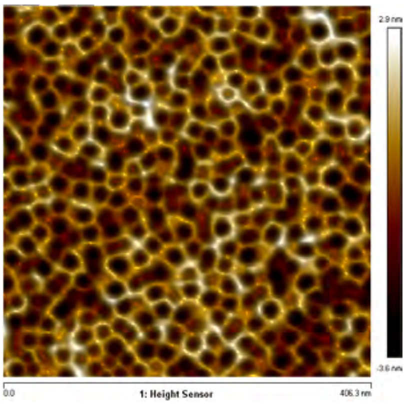

Fig. 1: AFM image of the top surface of a PEO-*b*-PMMA membrane prepared by spin-coating. Average pore diameter: 11 ± 2 nm (calculated with Bruker NanoScope Analysis 1.5).

P38

HETEROCYCLIC AMINE-MODIFIED POLYETHYLENIMINE AS GENE CARRIERS FOR TRANSFECTING CANCEROUS AND STEM CELL LINES

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Abstract

WITHDRAWN

P39

POLYISOBUTYLENE BASED POLYURETHANE NANOCOMPOSITES: EFFECT OF SULFUR ATOM IN SOFT PHASE

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Abstract

A sulfur containing polyisobutylene based polyurethane nanopcomposite (PIBs-NPU) was synthesized by using a new polyisobutylene diol, HO-CH_2CH_2-S-PIB-S-CH_2CH_2-OH, as soft segment and conventional hard segments in the presence of minor amount of organically modified montmorillonite (OmMMT) . Soft segment was the prepared via thiol-ene chemistry based terminal functionalization of ally-telechelic PIB . The OmMMT was the ion exchange product of sodium montmorillonite (Na^+MMT^-) and quaternary ammonium salts of a tertiary amine carrying a -NH_2 functionality which is expected to lead to defoliation of the nanolayers and to act as an additional chain extender due to the reaction between free -NH_2 group and diisocyanates . Properties of nanocomposite , containing both 72.5% PIB and 0.5 % OmMMT were investigated specifically and compared to unmodified PIB_S-PUs. It has been found that the addition of 0.5% MMT modified with $N^+Me_3CH_2CH_2CH_2NH_2$ to PIBs-PU produces clear films with enhanced tensile strength, elongation, oxidative-hydrolytic stability, and creep resistancy relative to that of unmodified one. FTIR spectroscopy indicates H bonded S atoms (N-H…S) between soft and hard segments as well as nanolayers, which noticeably affect ultimate properties. DSC and XRD studies suggested randomly dispersed low-periodicity crystals as well as urea formation between the galleries making the nanolayers integral part of polyurethane.

P40

SYNTHESIS of 3-in-1 TYPE CORESHELL REINFORCER-TOUGHENER-COMPATIBILIZER for RIGID MATRICES via GRAFTING APPROACH

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Abstract

Poly(ethyleneoxide) blocks (PEO) were synthetically grafted onto polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene (SEBS) by the reaction of the maleated SEBS and hydroxyl terminated poly(ethylene oxide). The comb-branch copolymers consist of a hydrophobic SEBS triblock backbone (approximate 45 000 MW with 30 wt % of styrene content) and crystalline poly(ethyleneoxide) (PEO) pendants of 1000 molecular weight in structure . An idealized morphology was created and verified by Scanning Electron Microscopy and AFM techniques. The grafting efficiency was followed by NMR, FTIR spectroscopic as well as gravimetric techniques. In the observation of their phase behaviors and thermal stabilities, DSC and TGA were intensively used. The graft copolymer having suitable polar sites were then reinforced with minor amount of silica nanotubes, Halloysite by using high shear mixing technique in solution. Special attention was paid to emphasize the differentiative effect of expanded halloysite against original one on morphology, mechanical and impact strength as well as melt viscosities of the resultant structures. It is believed that nanosilica based zones will be surrounded by polyethyleneoxide chains attached to continuous nonpolar SEBS matrix by creating a reinforcer/toughener/compatilizer activity for the classic nonpolar rigid engineering polymers.

P41

BLOCK COPOLYMER BY THE SIMPLE BOTTOM-UP "BREATH FIGURE" (BF) METHOD: DESIGN FUNCTIONAL "HONEYCOMB"-PATTERNED POROUS POLYMER FILMS AS MICRO-OPTICAL COMPONENTS

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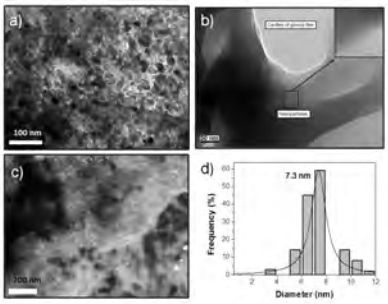
Abstract

Structuring polymer surfaces by the simple bottom-up "breath figure" (BF) method has proved to be a pertinent process to design "honeycomb" (HC)-patterned porous polymer films exhibiting a hexagonal array of pores in the range of 0.5-4 µm.[1-4] These materials are considered as important for the preparation of semiconductor quantum dots and their applications include electronics, optoelectronics, magnetic and non-linear optic materials. In this context, the present work is focused on the preparation of luminescent honeycomb (HC)-patterned microporous films by self-assembly of inorganic nanoparticles synthesized *in situ*, which has potential applications in many fields such as templates, devices, nanocontainers, photonic band gap materials. The amphiphilic block copolymer will be governed by the honeycomb film formation with micron-sized pores and the walls will be filled with the precursors of NPs. ZnO and ZnS (QD) semiconducting metal sulfide nanocrystals will be synthesized into the HC-patterned microporous films.

In this work, the preparation of functional ZnO NPs into porous-structured block copolymer films via breath figure (BF) fabrication result in ZnO nanostructures with an average diameter estimated in less than 10 nm. The NPs were dispersed homogeneously in the hydrophilic interface into honeycomb patterned porous films. From the UV-Vis absorption spectra, the average size of ZnO NPs was calculated be about 65 Å for **HHC$_{20\%}$** (326 nm), and 45 Å for **HPHC$_{20\%}$** porous structured films (300 nm), a result that was in accordance with those obtained by TEM images; 74 Å and 37 Å, respectively. The functional porous structured films were able to absorb UV radiation below 350 nm, indicating that these ZnO nanostructures exhibited good UV screening effects. The enlargement of band gap energies for **HHC$_{20\%}$** and **HPHC$_{20\%}$** porous polymer films can be determined from absorption spectrum that reveals a blue shift in absorption edge from 3.37 eV (ZnO bulk), to 3.41 eV and to 3.44 eV, the severity of the blue-shift is then determined by the physical dimensions of the nanostructures, where smaller dots cause larger blue-shift.



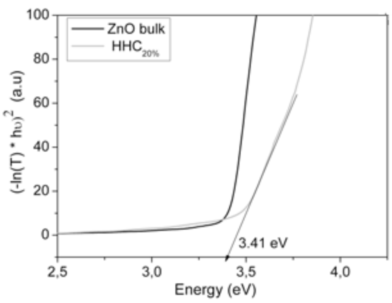


Figure 1 (a) Bright–field / dark–field TEM images and histograms of the ZnO nanoparticles into **HHC$_{20\%}$** porous block copolymer films (b) **HPHC$_{20\%}$** block copolymer films for the characterization of crystalline inorganic nanoparticles. **Figure 2** Optical band gap for the **HPHC$_{20\%}$** block copolymer films was determined from the diffuse reflectance with UV/Vis measurements.

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P42

SYNTHESIS AND ANTIMICROBIAL ACTIVITIES OF PEI-G-CHITOSAN POLYCATIONS

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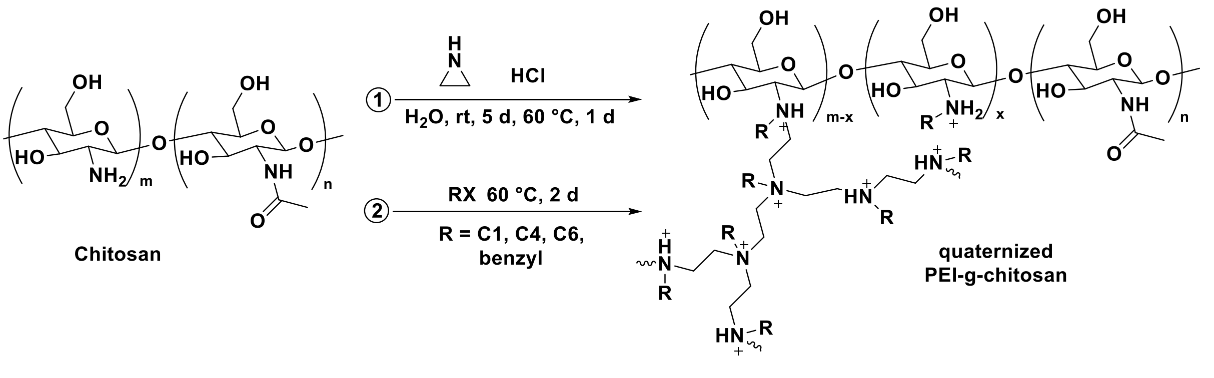
Abstract

The widespread and prolonged usage of antimicrobials can lead to emergence of antimicrobial-resistant microorganisms, which is a terrible threat to human health and environment. In order to overcome these threats, in this study, a series of biomass-based antimicrobial polymers (quaternized PEI-*g*-chitosan) were synthesized (Scheme 1). The obtained PEI-*g*-chitosan and Q-PEI-*g*-chitosan polymers were characterized by ^{1}H NMR, ^{13}C NMR and GPC. It is the first time to report the synthesis Q-PEI-*g*-chitosan. The MIC results show that the Q-PEI-g-chitosan exhibits good antimicrobial activity against both Gram-negative and Gram-positive bacteria. The Q-PEI-*g*-chitosan has a potential application to be used as biomass-based antimicrobial agents, for example, to replace the common used chemical biocides in liquid detergent to reduce environmental pollution, and this research study is currently undergoing in our group.



Scheme 1. Synthetic route for quaternized PEI-*g*-chitosan

P43

NOVEL SILICONE THERMOPLASTIC ELASTOMERS WITH TAILORED PERMEATION PROPERTIES

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Abstract

Our research deals with the synthesis and properties of polymers containing soft segments of dimethylsiloxane and hard urea segments. In order to determine structure-property relations, regarding to permeation properties, the chemical structure was varied.

In this study thermoplastic silicone elastomers, based on polydimethylsiloxane oligomers with amino groups and different diisocyanates, were synthesized according to the literature[1]: The main-chain urea-siloxane copolymers were characterized by nuclear magnetic resonance (NMR) and infrared (FTIR) spectroscopy. The formation of hydrogen bonding of the hard segments was investigated by temperature dependent FTIR-spectroscopy, which displayed the thermal stability of the elastomer.

Membranes of the polymers were prepared and investigated with respect to the permeation properties of organic solvents. Vials sealed with the polymer films were filled with a mixture of an aromatic (toluene) and an aliphatic hydrocarbon (iso-octane). The weight of the vials was periodically measured to investigate the permeation of the polymers. The weight loss of solvent over a period of 7 days was determined. Additionally the composition of the residual solvent mixture was investigated by the GC-MS-technique (figure 1).

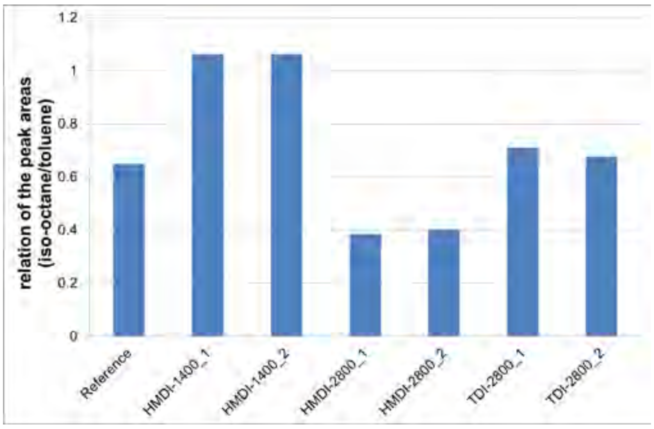

Figure 1: GC-MS data of the residual solvent mixture in the vials

The concentration of residual solvent mixture was measured by the relation of the peak area of the two solvents. Figure 1 depicts that a separation of the solvent mixture occurred. The synthesized novel main-chain urea-siloxane copolymers have selective barrier properties. These polymers are highly permeable for organic solvents depending on the chemical structure. The permeation properties are important with respect to the application as membrane material in oil field applications.

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P44

DISSIPATIVE PARTICLE DYNAMICS STUDY OF ELECTROSTATIC CO-ASSEMBLY IN AQUEOUS MIXTURES OF OPPOSITELY CHARGED DIBLOCK COPOLYMERS

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Abstract

Text: Contributions of various effects on electrostatic co-assembly of copolymer polyelectrolytes is still not fully understood, even though it can play important role in many fields (such as targeted drug delivery or environmental applications) due to stimuli responsive properties (change in pH, temperature, etc.) of co-assembled nanostructures.

The electrostatic association (EA) in mixtures of diblock copolymers composed of one neutral block and one either positively or negatively charged polyelectrolyte (PE) block in aqueous solutions has been studied by means of the dissipative particle dynamics with explicit electrostatic interactions of all charged species. Apart from systems containing the same total charge on oppositely charged PE blocks, three different systems with a surplus of positive charge on the copolymer chains were used: system with added positively charged chains, with prolonged positively charged PE blocks and with the positive beads' charge to higher values. In all cases, the volume fraction and properties of negatively charged copolymer chains remained the same and small counterions (CI) are added to ensure overall system neutrality. The neutral block is easily soluble, while the solubility of the PE block and the compatibility of the two copolymer blocks as well as the compatibility PE block with CI have been varied.

In the case of PE with solvophilic backbone, only dimers are formed which are overall neutral. Well defined roughly spherical core-shell associates are formed only in systems with significantly unfavorable interactions of PE segments with water and with segments of the water-soluble block. In systems containing the same copolymer charge of both signs, the associates are preferably neutral, while in systems with an excess of positive copolymer charge the associates carry a macroscopic positive charge and a fraction of excess chains remains free in the non-associated state. Higher electrostatic energy of charged associates leads to destabilization of larger associates and increasing surplus of positive charge therefore leads to smaller association numbers. The macroscopic charge of the associates tends to concentrate on the core-shell interface, while the inner part of the associate core is neutral, or even slightly negatively charged. This effect is most pronounced in systems containing copolymer beads with increased positive charge, where the charge density is higher.

Although the opposite charges on different polymer molecules are a prerequisite for EA, our study shows that the solvent quality for the PE backbone and incompatibility of the PE block with the neutral one and CI together with the ratio of positive to negative charge on polymer beads also play an important role.

P45

THIOL-BASED DUAL FUNCTIONALIZATION OF DISTINCT BLOCK COPOLYMER SEGMENTS BY CONTROL OF CHEMICAL ORTHOGONALITY

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Abstract

Block copolymers (BCPs) have gained attraction due to their ability to microphase separate and self-assemble into nanostructures in bulk or in solution[1]. Besides looking for improvements in synthetic efficiency and structural control, enrichment of the chemical diversity of BCPs is also challenged to create multifunctional polymers and to utilize them in potential applications. The versatility of BCPs can be enhanced by introducing small amounts of functional moieties by postpolymerization protocols, while inheriting the properties of the main backbone.[2] When one aims at the functionalization of distinct segments of BCPs, the ability to precisely direct molecules to one block without contamination of the other block(s) is essential.

Since many thiol derivatives are commercially available or easily synthesized and at the same time there is a great interest for related chemistries (e.g., radical thiol-ene/yne, Michael addition),[3] we sought to find conditions of orthogonality for two thiol-based chemistries.[4] We focused on photo-triggered radical thiol-ene and the so-called *para*-fluoro thiol reaction. To this aim, diblock copolymers carrying allyl and pentafluorophenyl-ethylalkyl groups, respectively, were synthesized. We showed that by appropriate choice of parameters such as the reaction sequence order or the concentration of thiols and catalysts, it is possible to carry out specific reactions with similar grafted molecules on distinct parts of the macromolecules (Figure 1). Optimizated reaction sequences with quantitative double function-alization in less than 20 min were developed.

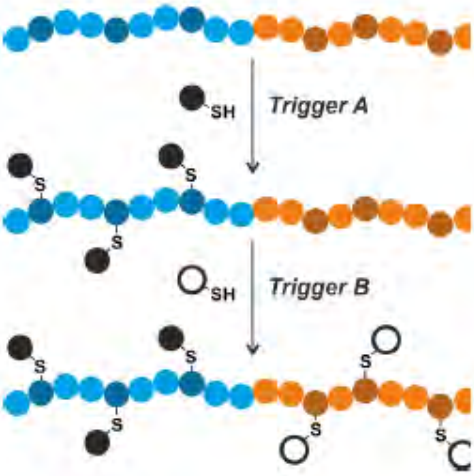

Figure 1. General concept for the thiol-based orthogonal dual function-alization of block copolymers.

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P46

SELF-ASSEMBLY OF BLOCK COPOLYMER AND CARBON DOTS INTO NANOCLUSTERS FOR BIOIMAGING APPLICATIONS

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Abstract

Block copolymers are well known to self-assemble into micelles with a core-shell structure, which are commonly biocompatible and potentially suitable for biological applications. Carbon dots as fluorescent contrast agent possess high brightness and low cytotoxicity; however their sub 10 nm sizes often hamper long term in vivo applications due to rapid clearance of small particles in renal system. In this presentation, we introduce simple engineering strategies to prepare nanoclusters based on the self-assembly of block copolymer and carbon dots. The sizes of the final nanoclusters are tunable from 15 nm to 170 nm, through varying the feeding ratio of the block copolymer to carbon dots. Cellular imaging application was successfully demonstrated in MCF-7 cell line. Together with their low cytotoxicity, these types of nanoclusters are potentially useful for future in vivo bioimaging applications.

P47

NANOPOROUS SEPARATION MEMBRANES FROM MICROPHASE-SEPARATED MULTIBLOCK COPOLYMERS

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Conventional polymeric membranes based on standard polymers such as cross-linked aromatic polyamide for nanofiltration (brackish water or water softening) have reached their performance limits, and they have also insufficient chemical resistance against important disinfectants which makes the process more complicated. Significant improvements could be achieved if the random packing of segments like in classical amorphous polymers [1] would be replaced by controlled microphase-separated structures in "tailor-made" membrane polymers [2]. This work makes a contribution to the development of novel microphase-separated block copolymers to obtain "nanoporous" membranes with barrier pore diameters in the range between < 1 and ~2 nm. Functionalized copolymers with glass transition temperature over 200 °C are synthesized as membrane material. This is realized by routes combining corresponding telechelic macromonomers (fluoride-terminated and hydroxyl-terminated, with different chain lengths) obtained by a molecular-weight controlled polycondensation according to Carothers´ equation and a subsequent second polycondensation step. The obtained poly(arylene ether sulfone) multiblock copolymers are then functionalized to create in a block-selective fashion cation- and anion-exchange polymers [3] (Figure 1).

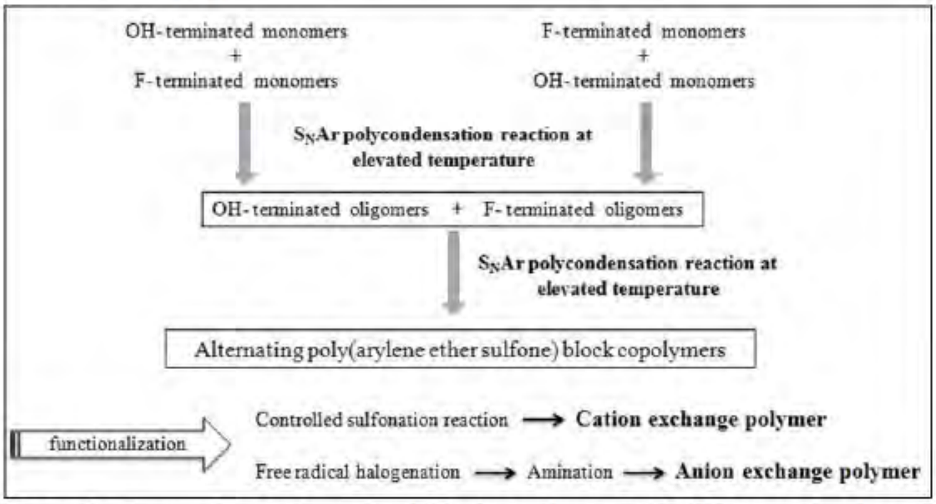

Figure 1: Schematic synthesis route for a variety of multiblock copolymers with different molecular weights and different degrees of block-selective functionalization with cation- and anion- exchange groups.

The focus is on anchoring anion-exchange groups on the main chain of these polymers because the knowledge about the potential of such materials for nanofiltration is much less explored than that about cation-exchange polymers. On the basis of the characterization of polymer films (SEM, AFM, TEM, DSC, SAXS, ion exchange capacity and swelling) and thin-film composite membranes obtained via evaporation-induced phase separation (flux and salt rejection), relationships between polymer synthesis and processing on the one hand, and obtained membrane structure and properties on the other hand will help to improve separation performance of nanoporous membranes by macromolecular design.

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P48

TWO STEP SYNTHESIS OF PCL-*b*-PAA AND ITS APPLICATION FOR EMULSION ELECTROSPINNING

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Abstract

Polycaprolactone-*b*-poly(acrylic acid) (PCL-*b*-PAA) is used for a variety of biomaterials applications and is commonly synthesised via a four step process: ring opening polymerization (ROP), functionalization of chain ends, atom transfer radical polymerization and deprotection of the carboxylate.[1] Additionally, this approach often uses transition metal catalysts, making it poorly suited for biomaterials applications.

Using a ‘double headed’ alkoxyamine initiator[2] capable of initiating both ROP and nitroxide mediated polymerization (NMP) an efficient, metal-free, two-step synthesis of PCL-*b*-PAA has been developed. The block character of the copolymer was confirmed by the formation of micelles under aqueous conditions, and the response of these micelles to varying pH.

The PCL-*b*-PAA was used as a surfactant to combine two immiscible polymer solutions: PCL and poly(vinylphosphonic acid-*co*-acrylic acid) (PVPA-*co*-AA). The resulting emulsion was then spun into nanoscale fibres using electrospinning.

This work details the synthesis of the dual initiator, the two step synthesis of PCL-*b*-PAA, characterisation of the block copolymer and its use for emulsion electrospinning.

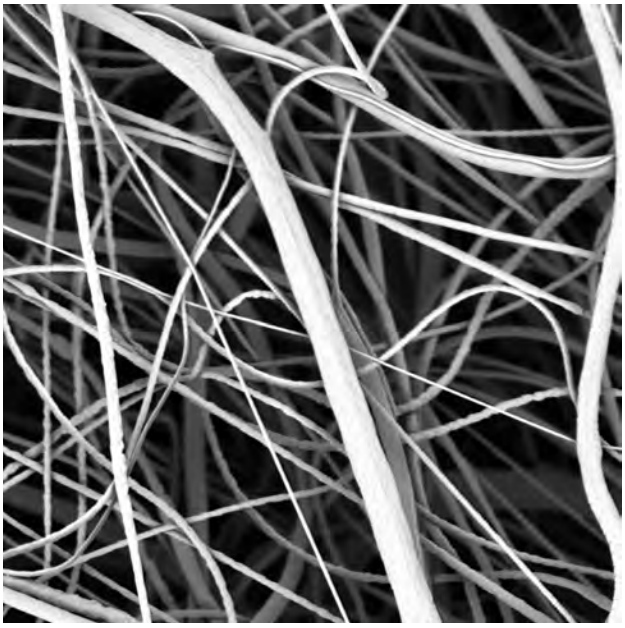

Fig 1: Composite fibres of PCL, PVPA-*co*-AA and PCL-*b*-PAA produced via emulsion electrospinning

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[1] C. Yuan, H. C. Lu, Q. Z. Li, S. Yang, Q. L. Zhao, J. Huang, L. H. Wei and Z. Ma, *J. Polym. Sci., Part A-1: Polym. Chem.*, 2012, **50**, 2398-2405.

[2] N. Chagneux, T. Trimaille, M. Rollet, E. Beaudoin, P. Gérard, D. Bertin and D. Gigmes, *Macromolecules*, 2009, **42**, 9435-9442.

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TRANSFER OF VERTICAL LAMELLAR PATTERNS OF PS-*b*-PMMA DIBLOCK COPOLYMER INTO FUSED SILICA BY REACTIVEION BEAM ETCHING

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The patterning of surfaces and thin films made from application-related functional materials with structure dimensions of less than 50 nm is challenging, especially when the fabrication costs are to be kept low. However, self-assembly mechanisms provide an alternative approach of pattern generation with these dimensions and enable a wider application due to the less demanding fabrication process and the cost saving of self-assembly. Potential applications of diblock copolymer (DiBCP) patterns transferred to functional materials can span the range from optical subwavelength structures to high-density storage technologies.

The current work focuses on the transfer of lamellar patterns of DiBCPs into silicon dioxide by reactive ion beam etching with fluorine gas mixtures.

Thin films of diblock copolymers were prepared from Poly(styrene-block-methyl methacrylate) (PS-b-PMMA, average M_n 104 kg/mol, block ratio 1:1, Sigma Aldrich). By annealing of spin-coated DiBCP films with a thickness of 55 nm on non-preferential substrate surfaces well-ordered DiBCP films with perpendicular oriented lamellar structures were achieved. These films were imaged by AFM and SEM after developing the ordered DiBCP lamellas (see Fig. 1). Therefore, the annealed DiBCP films were exposed to the UV light of an excimer lamp for 8 s and developed with e-beam developer AR 600-56 from Allresist GmbH for 90 s to remove the PMMA domains of the DiBCP patterns. The feature size measured by AFM and SEM is approximately 24 nm and corresponds with the length scale l_0 of the utilized DiBCP ($d_0 = 48$ nm). The lamellar pattern height was measured at cross sections of annealed and developed DiBCPs to be 50 nm. Despite the wet chemical development free-standing lamellas with vertical orientation were achieved.

These lamellar DiBCP patterns were employed as etching mask for reactive ion beam etching (RIBE). A semi-industrial ion beam etcher equipped with a 150 mm diameter Kaufman-type ion beam source enables the program-controlled etching of wafers up to four inches. The DiBCP-masked samples were clamped to the water-cooled substrate holder that was rotated with 10 rpm. The pattern transfer was performed with CF_3H gas at an ion beam voltage of 500 V for 4 min. The SEM top view image of Fig. 2 shows the pattern etched into silicon dioxide. The shape of the lamellas and the lateral lamella pattern size do not significantly change during the RIBE process. A pattern depth of 82 nm was achieved with 50 nm high DiBCP lamellas at an etching time of 4 min. However, the remaining DiBCP masking patterns probably enable deeper etched patterns [1].

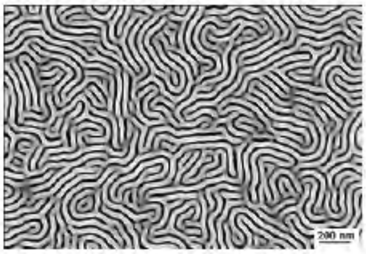

Fig. 1: PS lamellas after cracking of the PMMA block via UV exposure with an excimer lamp, followed by development in acetic acid (80%) for 4 min.

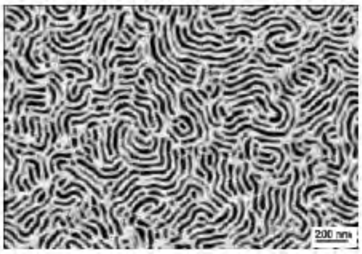

Fig. 2: Vertical lamellas after RIBE transfer into SiO_2 (CHF_3 / 500 V beam voltage / 4 min). The obtained etch depth is 82 nm.

[1]: J. Zajadacz, P. Lorenz, F. Frost, R. Fechner, C. Steinberg, H.-C. Scheer, K. Zimmer, Reactive ion beam etching of fused silica using vertical lamellar patterns of PS-b-PMMA diblock copolymer masks, Microelectron. Eng. 141 (2015) 289-293.

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