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Nanostructures and Functionalities in Polymer Thin Films

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Summary: Several examples of self-organization in thin polymer films are considered for the fabrication of nanopatterned surfaces and nanoscopic objects. Mixed polymer brushes of statistical distribution at the surface, composed of two immiscible polymers covalently bonded to the substrate phase, segregate in the sub-micrometer scale. Interplay between lateral and perpendicular (sandwich-like) segregation effects switching behavior of the thin films upon exposure to different environments. The switching between brush morphologies is used for the fabrication of adaptive/responsive surfaces. Fabrication of nano-domains based on microphase segregation in block-copolymer systems is used for structures with lateral dimensions as small as 5-50 nm. The ordered copolymer structures are applied as templates for the fabrication of membranes, nanofibers and nanoparticles.

Keywords: block-copolymer; morphology; nanolayers; nanotechnology; phase-separation

Introduction

Patterned thin films and surfaces at nanometer scale are of interest for several possible applications, where also specific functionalities are desired. There are several different approaches by which to fabricate thin polymer films with nanostructures. We discuss here three different methods that can be used to produce nanopatterns and nanoparticles utilizing self-assembly in polymer systems.

Firstly, a quite versatile technique based on self-organization of polymers is the use of phase segregation phenomena. One example comprises using mixed polymer brushes of statistical distribution at the surface, which are covalently bonded to the substrate and consist of different chains with different functionality.[1] Grafting restricts the possibilities of lateral segregation, and phase separation structures are in the sub-micrometer scale. Interesting switching functionalities

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can be achieved with these mixed brushes. This is a result of a combination of lateral and perpendicular phase segregation of components.[2] Wetting experiments reveal that these surfaces can adopt a hydrophobic or hydrophilic behavior, where one or the other functionality is achieved after dipping in different selective solvents for the components.[3] Utilizing structures of different length scales in addition to hydrophilic and hydrophobic switching behavior, a so-called ultra-hydrophobic surface can also be generated.[4]

Secondly, fabrication of nano-domains based on microphase segregation in block-copolymer systems is useful for structures with lateral dimensions as small as 5-20 nm. Typical structural size depends on the dimension of microphase-separated structures. The structures in diblock copolymers are, for instance, of lamella, cylindrical or spherical type, depending on the composition of components.[5] One can use the ordered copolymer structure as a template for further processing. In this case it is necessary to remove one of the components, which leaves, for instance, cylindrical holes in the polymer film. Another possibility comprises the use of an additional third, low molecular weight component, which is selectively incorporated in one of the phases, and which can be removed by washing.[6] By appropriate selection of the third component it is possible to obtain an orientation of the cylindrical domains in a thin film, perpendicular to the surface, and to fabricate regularly patterned, chemically heterogeneous surfaces.[7] The hole diameter can be of nanometer size and the morphology is ordered laterally on a relatively large scale. Holes can be filled with metals and, by complete dissolution of the polymer matrix, thin metallic nanorods on the surface can be obtained.

Thirdly, self-assembly of diblock copolymers can lead to microphase separation. This can be extended to macroscopic scale upon large external fields to achieve anisotropic properties. To produce anisotropic block-copolymer structures they have to be macroscopically aligned. Alignment of block copolymer structures under large stress fields can lead to considerable orientation of the morphology over a large scale in the range of several μm or even up to millimeters. Other external fields, such as oscillatory flow and electrical field, have been used to induce alignment[8-11]. Application of shear field provides an efficient and versatile tool to achieve macroscopic alignment, as demonstrated by materials subjected to extrusion,[12] oscillatory and steady shear,[13,14] extensional flow[15] and roll casting.[16] The aligned block-copolymer complex with the third low molecular weight component can be used for the fabrication of relatively long polymer nanofibers when the third component is incorporated into the matrix-forming phase and then the third component is selectively dissolved.

Experimental

Fabrication of mixed brushes. Clean Si-wafers were treated with (3-glycidoxypropyl)-trimethoxysilane (GPS, from ABCR) from a 1% solution in anhydrous toluene for 14 h in a dry atmosphere. They were then washed twice with anhydrous toluene in a dry atmosphere and thrice times for 5 min in an ultrasonic bath with methanol. In the next step diethylamine was deposited on the surface of the Si-wafers from a 1.5% solution in ethanol for 2 h. The resulting samples were rinsed five times with ethanol. The acid chloride derivative of 4,4'-azobis(4-cyanopentanoic acid) (ABCPA, from Fluka) was prepared by adding a slurry of phosphorus pentachloride to a suspension of ABCPA in dry dichloromethane at 0 ^{o}C and mixing overnight at ambient temperature in dry atmosphere. The product (Cl-ABCPA), after crystallization from dry hexane at 0 ^{o}C, was washed and dried *in vacuo*. In the next step Cl-ABCPA was deposited on the surface of the Si-wafers from a 1% solution in dichloromethane, with ca atalytic amount of triethylamine at room temperature for 12 h. The resulting samples of Si-wafers with chemically attached initiating groups were rinsed with ethanol in an ultrasonic bath. Oxygen was removed from the solution of the monomer styrene or 2-vinylpyridine (5-6 mol/l) and 4,4′-azobis(isobutyronitrile) (AIBN, from Fluka) ($5\text{-}9\times10^{-4}$ mol/l) in THF using five freeze-pump-thaw-cycles. The samples of the Si-wafers with the chemically attached initiator were placed in a monomer solution under argon atmosphere in a glass flask. The flasks were immersed in a water bath (60 ± 0.1^{0}C) for 12 h. In the next step the same procedure was used to graft the second polymer using the Si-wafers with the first grafted polymer. The ungrafted polymers were removed by a cold Soxhlet extraction after each polymerization step for 1 and 8 hours, respectively, using THF. Every step of the modification of the Si-wafers was controlled by ellipsometric measurement of the layer thickness.

Fabrication of nanomembranes. Polystyrene(M_w=35500)-*block*-poly(4-vinylpyridine)(M_w=3680) (PS-*b*-P4VP, M_w/M_n=1.06, Polymer Source, Inc.) and 2-(4'-hydroxybenzeneazo)benzoic acid (HABA, ≥99.5% pure, Fluka) were used in an equimolar ratio between P4VP-block and HABA and dissolved in 1,4-dioxane (Acros Organics). The solution was kept overnight to complete hydrogen bonding and filtered directly before use. Films of the PS-b-P4VP + HABA assembly were deposited by dip-coating on cleaned silicon wafers. Solution concentrations of 1–3 % w/v resulted in film thickness of 20-90 nm. Finally, HABA was washed out by rinsing in methanol (Acros Organics), yielding nanoporous films. The films were characterized by ellipsometry (the Multiscope Optrel, Germany), Atomic Force Microscopy (AFM, the Dimension 3100, Digital Instruments, Inc.) in tapping mode, and UV-vis spectroscopy (the Cary 100 Scan UV-Vis spectrophotometer, Varian, Inc.).

Fabrication of nanofibers. Poly(styrene-b-4-vinyl pyridine) PS-b-P4VP had a (Polymer Source, Inc,), polydispersity index of M_w/M_n=1.07. The molecular weights of PS and P4VP were Mw=21400 g/mol and 20700 g/mol, respectively. 3-n-pentadecyl phenol (PDP) was purchased from Aldrich (purity 90-95%). It was distilled under reduced pressure (10^{-3} bar at 185 °C) and then recrystallised twice with cyclohexane to obtain a higher degree of purity. PS-b-P4VP was dissolved in analytical grade chloroform. A stoichiometric amount of PDP was added to the solution (one alkyl phenol for each pyridine group in the P4VP block). The solvent was allowed to evaporate slowly. The PS-b-P4VP (PDP) film was then dried at 60°C under vacuum for 24 h. The experiment then was carried out with a self-constructed piston-type spinning device. The upper part of the device consisted of a drive train, a heated cylinder with piston, and a single-hole die. The diameter of the capillary hole was 0.3 mm and its length was 0.6 mm. A low-speed winder was fixed below the die to try to wind up the extruded fiber. For melting, the material was heated up to 120°C within the cylinder, and a volume flow rate of 0.156 cm^3/min was adjusted by the drive train. The extruded fiber was quenched by air at room temperature and collected or wound up at 2-4 m/min.

Mixed Brushes

The "grafting from" approach via a two-step, surface-initiated radical polymerization[1] was used for the synthesis of mixed polymer brushes (MPB) of a high grafting density (0.05-0.15 nm^{-2}) and a relatively large grafted amount (10-120 mg/m^2). The lateral distribution of the grafting points of the two polymers is assumed to be random. The covalent bonding to a substrate restricts segregation of the polymer species to the scale of a mean chain end-to-end distance.[2] Segregation of two polymer species in a MPB occurs in lateral and perpendicular (sandwich-like) directions and can be controlled by external factors (solvent, temperature). Heating above the glass transition temperatures of the brush polymers causes segregation of the polymer with lower surface energy to the brush surface. A selective solvent swells a favourite polymer and pulls it to the brush top, while the non-favourite polymer collapses and occupies the bottom brush layer. A good non-selective solvent swells both polymers, hence both of them are present on the brush top. The perpendicular segregation in MPBs was studied with water contact angle measurements on polystyrene/poly(2-vinylpyridine) brushes (Figure 1). Toluene and ethanol are selective solvents for PS and P2VP, respectively, while chloroform is a good non-selective solvent. PS as the less polar polymer than P2VP (thus providing the lower surface energy) segregated to the brush surface upon annealing.

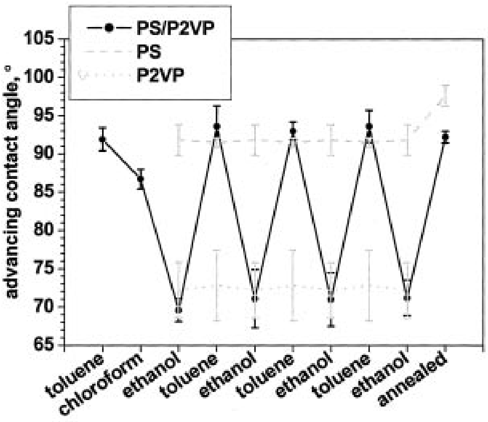

Figure 1. Reversible switching of a surface energetic state of a mixed PS/P2VP brush upon exposure to organic solvents of different selectivity and annealing for 24 h at 135°C. The behavior of monocomponent PS and P2VP brushes after the same treatment is shown as reference. The water advancing contact angle was determined with a sessile drop technique. The time of exposure of the brush to a solvent was 5 min; immediately after the exposure the brush was rapidly dried in nitrogen flux

Segregation in the lateral direction was studied with tapping mode AFM in the repulsive regime. A self-consistent field theory (SCF)[2] predicted for MPBs in solvents: (1) a ripple morphology composed of alternating lamellae of two brush polymers in a non-selective solvent, (2) a dimple morphology of round clusters of non-favorite polymer surrounded by a matrix of the favorite polymer in a selective solvent. Round clusters were found on PS/P2VP brushes after exposure to toluene and ethanol (Figure 2 a, c) and a worm-like structure (distorted lamellae) after exposure of these brushes to chloroform (Figure 2 b). The best phase contrast, originating from different viscoelastic properties of the polymers[17], was found for the brush exposed to chloroform. The sharp phase contrast after the non-selective solvent supports the theoretical assumption about the presence of both polymers on the brush top and is in good agreement with the contact angle values (Figure 1).

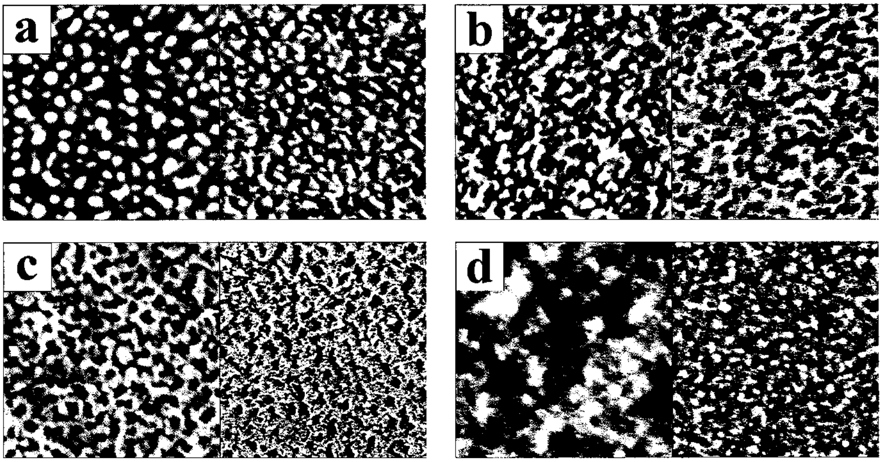

Figure 2. Repulsive tapping mode AFM of a PS/P2VP brush after exposure to the organic solvents (a,b,c) and annealing (d). Thickness 10 nm, 68 wt. % PS, Mw(PS)= 137000, Mw(P2VP)= 234000, Mw/Mn= 2,1 for both species. Left - topography, right – phase contrast. Scale 1x1 μm. The images obtained after treatment of the brush with toluene (a), z scale 15 nm and 15°; chloroform (b), z scale 3 nm and 5°; ethanol (c), z scale 10 nm and 7°

Nanomembranes

Films of PS-b-P4VP + HABA assembly (Figure 3), prepared by dip-coating, are optically homogeneous and smooth, both macro- and microscopically. We found no contamination of the films by HABA crystals. Washing the films in methanol, which is a selective solvent for HABA, leads to disappearance of the characteristic absorption peak in the UV-vis spectra (382 nm), indicating the effective elimination of HABA from the films. The film thickness before and after washing in methanol was measured by AFM (a scratch test). No appreciable difference was found that gave an evidence of porous nature of the washed films.

AFM provides us with information on the surface topology of films of PS-*b*-P4VP. As prepared, the films are featureless, with rms roughness of 0.15 nm. Rinsing the films in methanol results in a drastic change of the surface topology. Independently, based on film thickness, AFM images (Figure 4, a) show close-packed, round pores, in quasi-hexagonal order, with a mean periodicity of about 21 nm. From the composition of the assembly, where P4VP + HABA is a minor block with a volume fraction of 25.5%, we can assume that this block forms cylinders in a PS matrix.[5]

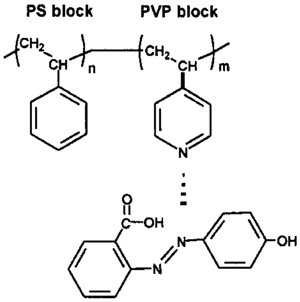

Figure 3. PS-b-P4VP + HABA assembly

Elimination of HABA from microdomains of the minor block results then in the formation of cylindrical pores with P4VP brushes on the walls.[6] In AFM images the cylindrical pores appear oriented perpendicular to a film surface. They are arranged in a hexagonal lattice with a relatively narrow distribution of the distances between centers of neighbouring pores (the standard deviation is about 4 nm). There exists, however, no long-range lateral order as follows from an uniform ring of 2D FFT. We suppose that aggregation of HABA molecules attached to a P4VP block by hydrogen bonds plays a key role in the formation of the well developed, perpendicular aligned microdomain structure immediately after the deposition of the assembly.

Fast evaporation of solvent from the film surface during dip-coating results in "quenching" of film morphology in a partially ordered state. To impel further ordering we swelled films of the assembly in saturated vapors of 1,4-dioxane. A solvent in a swelled film serves as a plasticizer, inducing segment mobility.[18] Indeed, after vapor treatment we observed considerable improvement of the hexagonal order within relatively large domains (a few micrometers in size, see Figure 4, b). At swelling ratios of 2.5-3 (as monitored with *in-situ* ellipsometry) the best ordering was achieved. The mean distance between pore centers was 25±1 nm with a standard deviation of 2.2-2.5 nm.

We performed successful electrochemical growth of nickel dots into pores of the above described films (data are not presented here). This may be considered as a strong argument for cylindrical morphology of the films, where P4VP + HABA cylinders are aligned normal to the film surface.

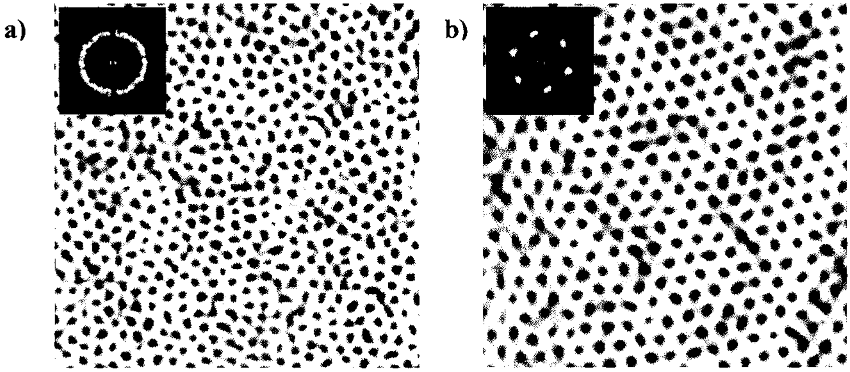

Figure 4. AFM images 0(.5×0.5 μm^2) and corresponding 2D FFT (as insets) of films of PS-b-P4VP + HABA assembly dip-coated from 1,4-dioxane: 40-nm thick, washed in methanol (a), 53-nm thick, swelled in vapors of 1,4-dioxane to a swelling ratio of 2.5, washed in methanol (b)

Nanofibers

The influence of the melt extrusion process of PS-b-P4VP diblock copolymer with addition of surfactant PDP on the morphology was investigated. Cylindrical nanostructures are formed by microphase separation in the melt. Large-scale orientation of PS cylinders within the P4VP/PDP matrix is studied by AFM, when only low flow rates are applied. After removal of PDP by ethanol, polymeric nanofibers are observed. The nanofibers are formed from a PS core with P4VP shell. These nanostructures can be produced in large quantities, because extrusion is a continuous process, and they can serve as templates for further modifications such as metallization. They may also be applied in nanocomposites to achieve enhanced mechanical properties. Self-assembly of block copolymers has been used to prepare individual polymeric nano-objects and nanostructures. Mäki-Ontto et al.[6] have demonstrated interesting ways of preparation of hairy tubes upon supramolecular organization in PS-PVP/PDP block copolymer complexes. The polymeric complex consisting of PS-b-P4VP, hydrogen bonded with PDP, shows a hexagonal morphology under equilibrium conditions, consisting of PS cylinders in the P4VP/PDP matrix. Melt extrusion and melt spinning of the material should increase the orientation of the PS-cylinders. A closer inspection of the filaments by AFM confirmed our assumption of oriented PS cylinders. PS cylinders had a thickness of about 90 nm in the P4VP/PDP matrix.

The final step in the production of nanofibers is the selective dissolution of the P4VP/PDP matrix. This process was already used by De Mole et al [19] to prepare PS nanofibers by using ethanol as solvent. However, with isotropic samples one usually may achieve nanofibers with a length of only about a few hundred nanometers.

Figure 5 shows PS nanofibers prepared by selective dissolution of the matrix and precipitation of the filaments on a substrate. The nanofibers exhibit lengths on the µm-scale, much larger than observed by previous authors, demonstrating the possibility to produce anisotropic nanofibers with considerable lengths. The cross section image in Figure 5 is used to determine the size of the nanofibers. PS nanofibers are smooth and macroscopically oriented, with considerable lengths. The width of the PS nanofibers is about 100 nm, slightly larger than observed in the P4VP/PDP matrix. This increase in diameter is due to the presence of a P4VP layer around the PS nanofibers.

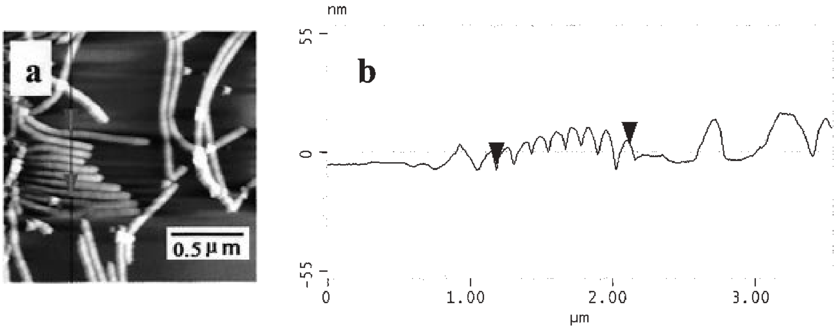

Figure 5. AFM images of PS nanofibers coated with a P4VP layer prepared on a Si-substrate (a) and cross section (b)

Conclusion

We have shown that self-organization in polymer films can be tuned and adjusted to the fabrication of nanostructured materials for diverse applications. Mixed polymer brushes demonstrate an example of responsive materials with switched morphologies. Phase segregation in block copolymers is used for the fabrication of either regular arrays of nanochannels or for the preparation of polymeric nanofibers. Both of the materials can serve as templates for the fabrication of metallic nanorods and nanowires.

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