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Block Copolymers As Nanoscopic Templates

Thomas P. Russell*[a], Thomas Thurn-Albrecht[a], Mark Tuominen[b], Elbert Huang[a], Craig J. Hawker[c]

[a] Department of Polymer Science and Engineering and [b] Department of Physics and Astronomy, University of Massachusetts, Amherst, MA 01003, U S A
[c] IBM Almaden Research Center, 650 Harry Road, San Jose,
CA 95720; US A

SUMMARY: Block copolymers self-assemble into well-ordered, microphase separated morphologies having dimensions on the molecular scale. The key to the use of these nanoscopic structures lies in controlling the spatial orientation of the morphology, particularly in thin films. The preferential interactions of the segments of the blocks with interfaces forces an alignment of the morphology parallel to the interface. Here we describe the use of controlled interfacial interactions and electric fields to manipulate the orientation of the morphology and subsequent steps towards the generation of nanoporous templates as scaffolds for nanoscopic structures.

Introduction

Polymeric materials offer a wealth of morphologies that span length scales ranging from the submolecular to the macroscopic. In thin films of multicomponent polymer systems, for example, block copolymers or polymer mixtures, making full use of these morphologies requires precise control over the spatial orientation of the morphology. This, in the absence of an external field, reduces to controlling the interfacial energy between the phases, γ_{AB}, which is proportional to the segmental interaction parameter, χ_{AB}; the interfacial energy between the components and the substrates, γ_{AS} and γ_{BS}; the surface energies of the components, σ_A and σ_B; and the commensurability between the film thickness, t, and the natural length scale of the polymeric system[1-4)]. For example, with an A-B diblock copolymer, the relative magnitudes of σ_A and σ_B, will dictate which components segregate to the air surface. The relative magnitudes of γ_{AS} and γ_{BS} will dictate which component resides preferentially at the substrate interface. γ_{AB} or χ_{AB} will determine the energy required

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to sustain an interface between components A and B. Finally, the natural repeat period of the copolymer, i.e. the lattice constant, in comparison to the total film thickness will define whether the copolymer chains must stretch or compress or form a surface topography to accommodate an imposed frustration or whether the morphology will change its orientation with respect to the surface to minimize the free energy. If we examine each of these parameters for a specific A-B diblock copolymer, σ_A, σ_B, and χ_{AB} are dictated by the chemical composition of the copolymer and they are invariant. While the fundamental period of the copolymer is fixed, the film thickness of a specimen can readily be changed in the preparation. This leaves γ_{AS} and γ_{BS} as the only variables in the problem. By gaining a control over the interfacial interactions with the substrate, a means to manipulate the orientation of morphologies in thin films can be achieved.

Recently, a simple, robust route to control interfacial interactions was reported[5, 6)]. Here, a random copolymer is anchored to a substrate by a terminal functional group. The synthesis of the random copolymer allows the composition of the copolymer to be varied from pure A to pure B or any fraction of A and B in the chain. The chemical variations along the chain are on the monomer or several monomers scale and, hence, the interaction experienced by an entire chain will reflect the average composition of the random copolymers, in particular, random copolymers of styrene and methylmethacrylate prepared by a "living" free radical polymerization with a terminal hydroxy group. These were anchored to a silicon oxide substrate. Contact angle measurements of thin polystyrene (PS) and poly(methylmethacrylate) (PMMA) films cast on the substrates modified with the random copolymer showed that there was one composition of the anchored random copolymer where the interactions of PS and PMMA were balanced. Block copolymers of PS and PMMA, denoted P(S-b-MMA), prepared on such "neutral" surfaces showed that the microdomain morphology of the copolymer oriented normal to the substrate or film plane. Thus, using this very simple surface modification, precise control over the orientation of the microdomains can be achieved.

In cases where such surface modification is not possible or where thicker films are required and the influence of the surface is lost due to defects, alternative methods must be used. In particular, an external field must be used to achieve the desired microdomain orientation. In the bulk, mechanical shearing has been shown to be the most effective means of orienting the microdomains of copolymers7,8,9). This, however, is not possible or practical in thin films. Any particulate impurities in a film preclude the possibility of maintaining two surfaces parallel over any reasonable lateral length scales. Electric fields, on the other hand, have been shown to be a viable means of orienting the microdomain structure in block copolymers10,11). However, in the bulk, it has been shown to be inefficient, with large voltages required to produce the desired orientation. More recently, other researchers12,13) have shown that by placing the electrodes in close proximity, small applied voltages produce substantial fields and are quite effective in orienting the copolymer morphology. This work has recently been extended to thin films where the electrodes are placed on both surfaces of the film14). An additional contribution from the difference in the interfacial energies between the components enters into this problem and a threshold field strength is observed, above which, full alignment of the copolymer microdomain structure normal to the film surface is found.

Here, we report some recent results on the use of these controlled morphologies to produce novel, nanoporous media using block copolymers as templates. While there has been a tremendous effort expended in understanding the thermodynamics of the microdomain structure and there has been much research on copolymers justified by the potential applications of these structures for nanoscopic device application, little has been done to realize the potential. Here, it is shown that by coupling the control of the microdomain structure in thin films with standard methods to degrade one of the components, exceptional nanoscopic structures can be produced in a straightforward manner. Two examples will be discussed for P(S-b-MMA) using both controlled interfacial interactions and electric fields to achieve controlled microdomain orientation. The generation of nanoporous films will be shown and a brief discussion of possible uses of these structures will be presented.

Synthesis

P(S-r-MMA), with a styrene fraction of 0.60 (as determined by NMR), was synthesized in bulk via a TEMPO "living" free radical polymerization using a unimolecular initiator. This provided random copolymers with one hydroxy and one TEMPO terminus. The weight average molecular weight, M_W, and polydispersity, M_W/Mn, was determined to be 9,600 and 1.80, respectively, by size exclusion chromatography. The preparation of the unimolecular initiator and the polymerization of the random copolymer have been described previously15-19).

Several asymmetric, diblock copolymers of polystyrene (PS) and poly(methylmethacrylate) P(S-b-MMA), having narrow molecular weight distributions with molecular weights ranging from $4\text{-}7\text{x}10^4$ and with PMMA volume fraction of 0.29 were synthesized anionically. X-ray scattering was performed with Ni-filtered Cu-$K\alpha$ radiation from a Rigaku rotating anode, operated at 8KW. A gas-filled area detector (Siemens Hi-Star) was used.

A layer of P(S-r-MMA) was anchored to a silicon substrate as described previously5). Excess random copolymer was washed away with toluene. The composition of the random copolymer was ~60% by volume of styrene, which, for PS and PMMA, represents a neutral surface. Onto this heated surface, a solution of

P(S-b-MMA) in toluene was spin coated. The total thickness of the film was ~40 nm. Without further surface treatment, the sample was heated to 170°C for 72 hrs under vacuum. Upon cooling to room temperature, atomic force microscopy studies clearly showed a hexagonally close-packed array of PMMA cylindrical microdomains at the surface.

Subsequent electron microscopy studies on fractured surfaces showed that the cylindrical microdomains extended from the air-surface to the substrate6). Consequently, the balancing of the interfacial interactions at the substrate interface, coupled with the film thickness, which places constraints on the microphase separated morphology1-4), was sufficient to force the cylindrical microdomains to orient normal to the surface of the film.

This film was then exposed to UV light, which served two very important functions. First, PMMA is a well-known UV resist. Consequently, the PMMA will degrade upon exposure to UV light. Secondly, UV light crosslinks the PS matrix. This immobilizes the matrix, thereby, retaining the initial structure of the copolymer. The sample was washed with acetic acid and water to remove the degradation products of the PMMA. Two different field emission scanning electron micrographs are shown in Figure 1a and 1b. Figure 1a shows a view from the top of the sample, whereas Figure 1b shows a side view of the sample. There are several features of these images that are noteworthy. First, the morphology has been preserved. In fact, small angle x-ray scattering experiments have shown that there is absolutely no change in the separation distance between the cylindrical domains before and after removal of the PMMA. Secondly, the PMMA appears to have been completely removed from the sample with the cylindrical pores running from the surface to the substrate.

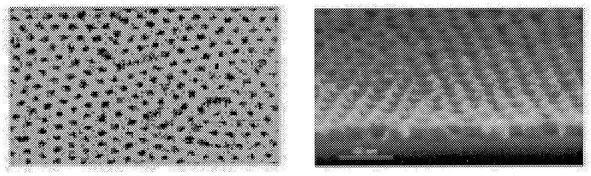

Fig. 1: (a) Field emission scanning electron micrograph (top view) of a nanoporous film made from an asymmetric P(S-b-MMA) diblock copolymer on a "neutral," random copolymer surface. (b) Field emission scanning electron micrograph (side view) of a nanoporous film made from an asymmetric P(S-b-MMA) diblock copolymer on a "neutral," random copolymer surface.

The films shown in Figures 1a and 1b offer numerous potentials for applications, either as scaffolds in which to build nanoscopic elements; as well-defined nanoporous media for separation purposes; or as templates to transfer the structure in the polymer film to the underlying substrate. It is this final application that will be demonstrated here.

The nanoporous film in Figure 1b was placed in a reactive ion etcher (RIE) using CF_4 as an etchant. The CF_4 will etch both the polymer template and the underlying silicon substrate. However, the presence of the polymer template on the surface will, of course, prevent the etching of the silicon underneath the polymer template initially. With time, the RIE etching will remove the polymer and begin etching the silicon. The exposed silicon substrate will already have been etched, however, thereby transferring the template into the substrate. A side-view FESEM image of the substrate is shown in Figure 2. The light region in the image is the silicon. What is evident from this image is that the pattern transfer into the silicon has clearly occurred. At the surface, one sees a very well-defined surface roughness with lateral feature sizes that are identical to the initial polymer film.

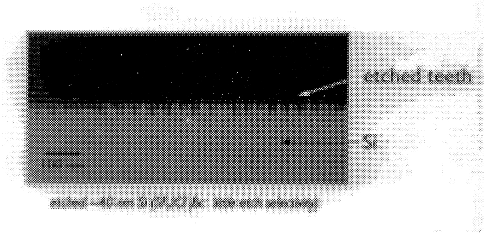

Fig. 2: FESEM image of a silicon substrate RIE etched with CF_4 where there was a copolymer template on the surface.

The image shown in Figure 2 is quite promising in terms of applications. It is, of course, clear that the aspect ratios must be increased to be of any commercial interest. Nonetheless, the effectiveness of the transfer is evident. What is more remarkable is the simplicity of the process. Within very few steps, a nano-textured surface in silicon can be generated in a very efficient and effective manner, relying only on the modification and neutralization of interfacial interactions.

The major limitation of this process is the ability to synthesize a random copolymer of the right composition to balance interfacial interactions. In some cases this may not be possible and, as such, an external field is required to achieve the desired orientation of the copolymer microdomains. Recently, we have shown that electric fields are a very effective means to this end. In these experiments, the diblock copolymer is sandwiched between two electrodes and the sample is annealed in the presence of a field. The anisotropic shape of the domains, coupled with the difference in the dielectric constants of the components comprising the domains should orient the mirodomains in the direction of the field lines.

Shown in Figure 3 are three transmission electron micrographs of a P(S-b-MMA) copolymer having PMMA cylindrical microdomains annealed between two electrodes. The substrate (one electrode) was a gold layer that was evaporated onto an Ultem poly(etheretherimide) plaque. This substrate facilitates subsequent microtoming of the sample. The second electrode was an aluminized Kapton sheet that was simply placed on the surface of the copolymer.

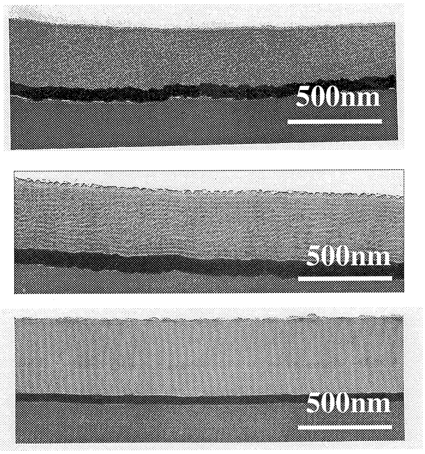

Fig. 3: (a) TEM micrograph of an asymmetric P(S-b-MMA) diblock copolymer having cylindrical microdomains. The film was cast on a gold substrate (dark band in film) and annealed with no electric field. (b) Same as in 3a, however, a field strength of several V/µm was applied during annealing. (c) Same as in 3a, however, a field strength of several 10V/µm was applied during annealing.

The uppermost image in Figure 3a is that of a microtomed P(S-b-MMA) film after annealing without any applied external field. The microphase separated structure of the copolymer is evident though the alignment of the microdomains parallel to the substrate is poor, due to the sample thickness and the slight preference of PS to segregate to the substrate. Upon the application of a low field, Figure 3b, a rather startling result was observed. Rather than aligning parallel to the surface, the cylindrical microdomains aligned normal to the field lines, i.e. parallel to the substrate surface. This result was precisely opposite to the expected result and suggests that a partial polarization of the microdomains occurs and the interaction between the microdomains enhances the ordering. At higher field strengths, Figure 3c, the cylindrical microdomains are seen to align parallel to the field lines, i.e.

normal to the surface. The cylindrical microdomains are seen to extend from the substrate through the sample to the air interface. More detailed studies have shown that orientation of the microdomains does not occur until a threshold field strength is exceeded$^{14)}$. This threshold field strength is greater than the field strength required to orient the diblock copolymer in the bulk. The difference between the field strengths required to align the bulk and thin film field strength is directly related to the difference in the interfacial energies of the two components with the substrate.

A very convenient means of probing the orientation of the cylindrical microdomains in the polymer films in a nondestructive manner is by use of x-ray scattering. To make sure of x-ray scattering, the substrate must be transparent or semi-transparent to the x-rays. To this end P(S-b-MMA) films were cast onto a 75μm thick Kapton film coated with a thin layer of aluminum (0.1μm in thickness). A similar Kapton film served as the upper electrode. After annealing the film at 180°C under a field of 24V/mm, the x-ray beam was passed through the sample at an incidence angle of 45°. Weak reflections characteristic of the oriented copolymer morphology were observed. At small values of the scattering vector $q(=(4\pi/\lambda)\sin(\theta)$ where λ is the wavelength and 2θ is the scattering angle), the scattering in the equatorial direction decreased monotonically with a small maximum characteristic of the oriented PMMA cylinders. Since the film is only 1.3μm in thickness, the total scattering volume is small. In addition, the electron density difference between PS and PMMA, is not very large. Both factors contribute to the weak yet clearly observable scattering maximum. Exposing the copolymer film to UV radiation, washing with acetic acid and drying produced a dramatic change in the scattering. The two dimensional scattering pattern shown in the l.h.s. of Figure 4 shows two intense reflections along the equator. The dramatic increase in the scattering is clearly seen in the azimuthal scans of the intensity at a fixed-q corresponding to the maximum. Shown in the r.h.s. of Figure 4 is a comparison of the azimuthal scans before and after irradiation. The ratio in the peak intensity before and after the UV treatment shows an increase in the scattering by a factor of 55. If the UV treatment has generated a porous structure then the scattering would increase by a factor of $(\rho_{PMMA}-\rho_{PS}-\rho_{PMMA})^2$ where ρ_i is the electron density of component i. This calculated factor is 53, in quantitative agreement with the observed increase in the scattering. These results show that the PMMA cylinders have been quantitatively removed from the film while maintaining the structure characteristic of the initial block copolymer film. If we consider the film thickness of 1.3μm then the pores have an aspect ratio of over 100! AFM measurements along with other electrochemical experiments clearly show that these cylinders extend from the substrate interface all the way to the air surface.

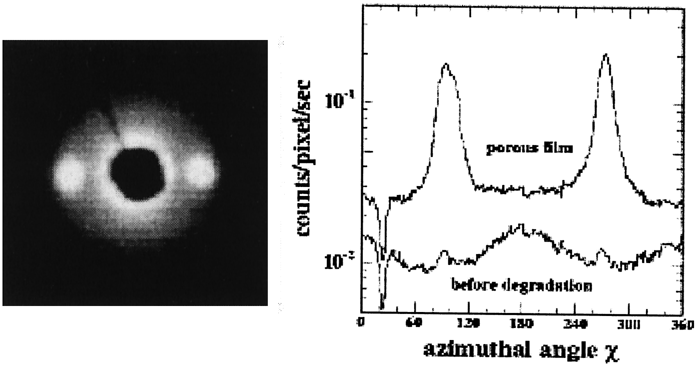

Fig. 4: (l.h.s). Two-dimensional SAXS pattern of a porous film made from an oriented P(S-b-MMA) copolymer having cylindrical PMMA microdomains. (r.h.s.) Comparison of azimuthal scans intensity for a P(S-b-MMA) diblock copolymer before and after degradation of the PMMA microdomains.

Thus, the two examples shown demonstrate easy, robust methods for generating nanoporous structures in thin films with well-defined orientations of the cylinders with respect to the surface. While one can easily imagine that such structures are ideal candidates for separations media, it is worthwhile to consider some of the other possible areas that such structures may impact. With the nanoporous films on a conducting surface, the film can be placed in an electrochemical bath and metal can easily be deposited within the scaffold defined by the porous film. This indeed has been done with cobalt, a magnetic material, forming an ordered array of magnetic nanowires in the film. Alternatively, catalysts can be anchored to the exposed substrate and polymerization can be conducted within this confined geometry. Functional polymer chains can, also, be anchored to the exposed substrate which forms the basis of a sensing array.

It is evident that the possible uses of such structures are numerous. However, the key elements to enabling such applications and potential commercialization are that one can manipulate the self-assembling structures of polymers in thin films in an easy, robust and reproducible manner. It is precisely this which has been described here.

Acknowledgments

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