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The influence of molecular weight on nanoporous polymer films

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Abstract

Asymmetric diblock copolymers of polystyrene (PS) and poly(methylmethacrylate) (PMMA), PS(S-*b*-MMA), having cylindrical microdomains of PMMA, are model systems to generate nanoporous thin films. With controlled interfacial interactions or applied external electric fields, the cylindrical microdomains can be oriented normal to the surface. Exposure to deep UV radiation degrades the PMMA and crosslinks the PS matrix. After rinsing with a selective solvent, a nanoporous film is obtained. By changing the molecular weight, smooth porous films with hexagonal arrays of pores having diameters ranging from 14 to 50 nm were obtained. The results show that molecular weight is a convenient, simple means of controlling pore diameter. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Diblock copolymers; Nanopores; Microdomains

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1. Introduction

Diblock copolymers, comprised two homopolymers joined together at one end, microphase separate into ordered, periodic arrays of spheres, cylinders or lamellae, with an equilibrium period, L_0, depending on the volume fraction of the components. Due to the connectivity of the blocks, the domains are of molecular dimension and, as such, nanoscopic [1]. In thin films, the self-assembly of the block copolymers makes them attractive candidates as templates for assemblies of nanoscopic magnetic and electronic media [2–5].

Critical to these applications is the alignment and ordering of the microdomains into densely packed arrays oriented normal to the surface of the film. In the bulk, shearing provides a very efficient route in aligning the copolymer microdomains [6,7]. For ultra thin films, L_0 or less, shearing is not possible and balancing interfacial interactions has been shown to be effective [8–11]. Also, hydrogen passivation has been shown recently to yield similar results [12]. With thicker films, external electric fields can be used to overcome interfacial interactions and affect the alignment [3,4,13–15].

Diblock copolymers, having a minor component volume fraction of 0.3, self-assemble into cylindrical microdomains of the minor component in a matrix of the major component. After aligning the cylindrical domains normal to the surface and removing the minor component, an ordered array of nanopores is produced. The characteristics of the porous array are dictated by the initial copolymer morphology. Thus, by changing the molecular weight of the copolymer, the size of the microdomains can be changed. However, there are inherent limitations to the accessible size scales. The smallest size attainable is limited by the product χN, where χ is the segmental interaction parameter and N is the number of monomers in the copolymer. For $\chi N < 10.49$, the copolymer is phase mixed [16]. The large size scale limit is set by the kinetics of ordering, which is excessively slow for the higher molecular weight copolymers. Here, results on the generation of nanoporous thin films using diblock copolymers are presented. By varying the copolymer molecular weight, pore diameters ranging from 14 to 50 nm have been produced.

2. Experimental

Asymmetric diblock copolymers of polystyrene and

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poly(methylmethacrylate), denoted by P(S-*b*-MM), were prepared by anionic synthetic routes. The molecular weights of the copolymers and the polydispersities, indicated in parentheses, were 4.2×10^4 (1.04), 7.3×10^4 (1.06), 7.7×10^4 (1.07), 8.3×10^4 (1.06), 8.5×10^4 (1.05), 1.03×10^5 (1.03), 1.78×10^5 (1.04) and 2.95×10^5(1.05). These copolymers are designated as 42K, 73K, 77K, 83K, 85K, 103K, 178K and 295K, respectively. The volume fraction of PMMA in each copolymer was 0.3. Consequently, the morphology of the copolymer in the bulk consists of cylindrical microdomains of PMMA in a PS matrix.

Surfaces with balanced interfacial interactions to PS and PMMA were prepared in two ways. In one case, as described previously [10,11], hydroxy-terminated random copolymers of S and MMA, prepared by a nitroxide mediated living free radical synthesis containing an S fraction of 0.58, were spin coated onto the native oxide layer of a Si wafer. At this composition, the interactions between the random copolymer and PS or PMMA are balanced. At other compositions, there are preferential interactions with ether PS (>0.58) or PMMA (<0.58). The random copolymer film was heated to 170°C for 72 h under vacuum, allowing the hydroxy end groups to diffuse and react with the oxide layer, anchoring the random copolymer to the substrate. Random copolymer not attached to the surface was removed by rinsing with toluene, leaving a ~6 nm film of anchored P(S-*r*-MMA). In the second case [12], the Si substrate was passivated by dipping the wafer into an aqueous (17% w/v) solution of hydrofluoric acid for ~2 min. The substrate was then rinsed thoroughly with de-ionized water to hydrogen passivate the surface. Films of P(S-*b*-MMA), ~30 nm in thickness, were spin coated from toluene solutions onto each of these surfaces and heated to 170°C under vacuum for 48 h to orient the cylindrical domains normal to the surface.

Smooth, ~1 μm thick films of P(S-*b*-MMA) were prepared by spin coating 10% (w/v) solutions of the copolymer in toluene onto a Si wafer. A thin layer of poly(dimethyl siloxane) (PDMS), was spin coated on top of the P(S-*b*-MMA). The PDMS layer acted as a buffer layer between the P(S-*b*-MMA) and the upper electrode, providing a layer that conforms to the surface of the upper electrode, ensuring that the surface of the copolymer remained smooth. An aluminized Kapton film (50.8 μm thick) served as the upper electrode. To prevent electrical shorting, the Kapton side was placed facing the PDMS layer. For P(S-*b*-MMA) with molecular weights less than 103,000 g mol^{-1}, the films were annealed at 175°C for 14 h under an electric field strength of 30 V μm^{-1}. For higher molecular weight P(S-*b*-MMA), the samples were annealed at 185°C for 20 h under slightly higher field strengths (up to 40 V μm^{-1}). After cooling the samples to room temperature under the applied field, the voltage was removed and the upper electrode was simply peeled away. The PDMS layer was removed by rinsing with hexane. This left a P(S-*b*-MMA) film with a smooth surface with the cylindrical microdomains oriented normal to the surface.

Both thin and thick films were exposed to deep ultraviolet radiation using a low pressure mercury–UV lamp with a dosage of 25 J cm^{-2}. This crosslinked the PS matrix and degraded the PMMA cylindrical microdomains [17,18]. Samples were then rinsed with acetic acid and deionized water to remove the degradation products. Atomic force microscopy measurements were performed using a Digital Instruments Nanoscope III in the tapping mode.

3. Results and discussion

Shown in Fig. 1 are phase contrast AFM images of P(S-*b*-MMA) thin films prepared on substrates to which P(S-*r*-MMA) was anchored. Previous studies [10,11] have shown this surface to have balanced interfacial interactions with both blocks, which causes the cylindrical microdomains to orient normal to the surface. The images show an increase in the domain size and an increase in the center-to-center distance between the cylindrical microdomains with increasing molecular weight of the copolymer. The molecular weight dependence of the domain sizes will be discussed later. However, the lateral ordering of the domains degrades with increasing molecular weight. For the 295K P(S-*b*-MMA), the lateral ordering of the microdomains is lost.

These results illustrate a competition between the kinetics of the microphase separation and the kinetics associated

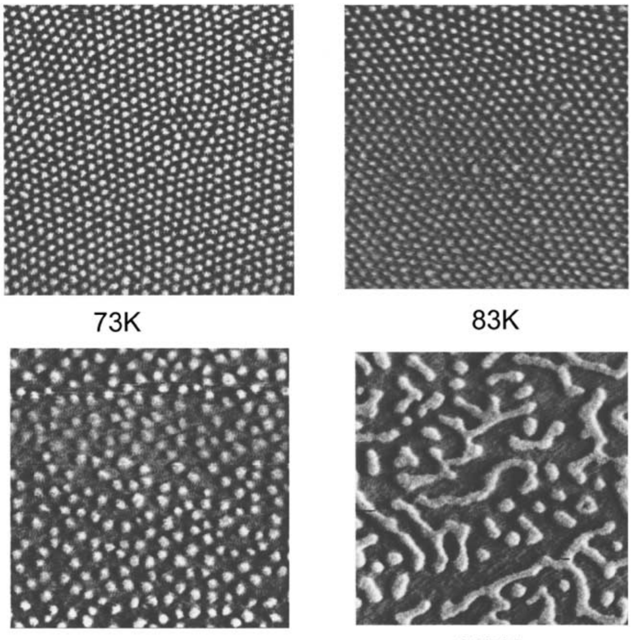
73K
83K
103K
295K

Fig. 1. Phase contrast AFM images (1 μm × 1 μm) of P(S-*b*-MMA) with the cylindrical microdomains oriented normal to the film surface as a function of the indicated molecular weight. Interfacial interactions of the substrate were balanced by anchoring a random copolymer.

with ordering of the microdomains normal to the surface. While χ is not dependent on molecular weight, the product χN increases with molecular weight and the copolymer is in the strong segregation regime. Consequently, with increasing N the driving force for phase separation increases. Microphase separation is a local process requiring only short-range motions of the chains. After microphase separation, the orientation of the microdomains normal to the surface occurs slowly, as this requires coordinated motions of many chains. This diffusive process becomes progressively slower with increasing N. Thus, with increasing molecular weight, the films are trapped in a non-equilibrium state, which is reflected in lost or poor ordering.

Similar results are observed for P(S-*b*-MMA) on the passivated Si substrates. Shown in Fig. 2 are the results for the 73K and 295K copolymers. For the lower molecular weight P(S-*b*-MMA), results identical to those for the copolymer on the neutral, random brush were found. Well-defined cylindrical microdomains oriented normal to the surface are observed. For the 295K P(S-*b*-MMA), the ordering observed on the passivated surface is much better than that seen on the neutral brush surface. This may be associated with the penetration of the copolymer into the brush to the underlying oxide layer, which is not possible here. However, substantial disorder is still evident.

Electric field alignment of cylindrical microdomains occurs readily in thin films with the cylindrical microdomains spanning the entire film thickness [3,4]. However, an inherent problem with this method has been that the film conforms to the surface of the rough upper electrode due, more than likely, to the electrostatic pressure at the air–polymer interface [19]. Recent studies of Lin et al. [20] have shown that the electrostatic pressure can be substantially reduced by replacing air with a dielectric medium that closely matches the polymer. PDMS is ideally suited for this purpose since its dielectric constant is 2.93, which is between that of PS (2.5) and PMMA (3.6). In addition, PDMS is fluid and, hence, can easily conform to the surface of the upper electrode. Optical microscopy, X-ray reflectivity and neutron scattering studies indicate that PDMS and P(S-*b*-MMA) are immiscible. Thus, PDMS can act simply as a dielectric layer that conforms to the upper electrode surface, allowing the applied field to act only on the copolymer microdomains. In all cases, after removal of the upper electrode and rinsing with hexane to remove the PDMS, the surface of the copolymer film was found to be smooth.

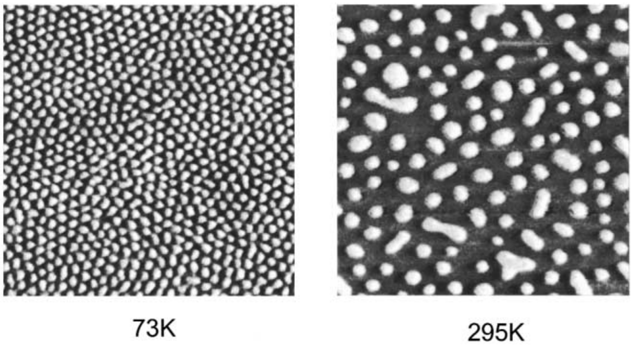
73K 295K

Fig. 2. Same as Fig. 1 only the substrates were hydrogen passivated Si wafers. Images are 1 μm × 1 μm.

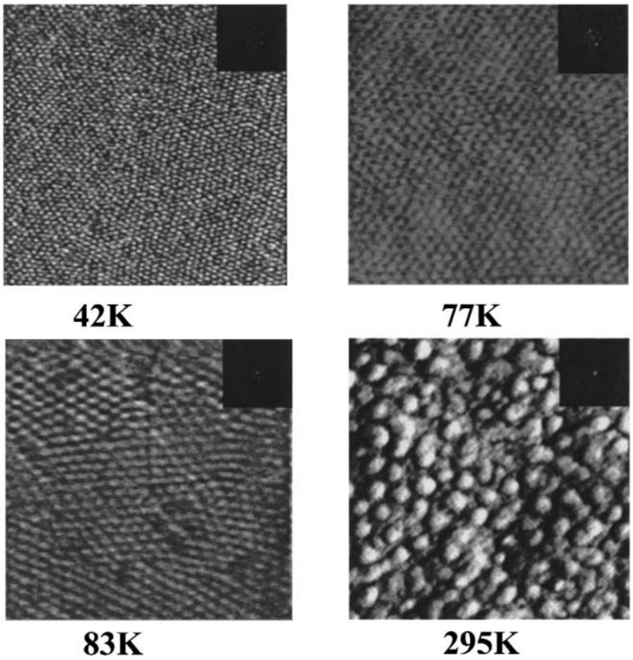
42K 77K 83K 295K

Fig. 3. Phase contrast images of P(S-*b*-MMA) films oriented in an electric field. The insets are fast Fourier Transforms of the AFM images. Any deviations of the FFTs from circular symmetry are scanning artifacts. The FFTs cover a wavevector range ($2\pi/d$, where d is the Bragg spacing) of $\pm 0.785\ \text{nm}^{-1}$. The molecular weights of the copolymers are indicated. Images are 1 μm × 1 μm.

Shown in Fig. 3 are the AFM phase images of films of P(S-*b*-MMA), aligned with an electric field as a function of molecular weight. An orientation of the microdomains normal to the film surface is seen in all cases. Thus, the applied external field is sufficient to overcome interfacial interactions and any kinetic barriers hampering the alignment of the microdomains normal to the surface, even for the high molecular weight copolymer. The insets show the Fast Fourier Transform (FFT) of a well-ordered region of the AFM image. The six-spot pattern is characteristic of hexagonal close packing of the cylindrical microdomains. An FFT of a larger area yields a circular pattern, which is characteristic of grains of the hexagonally packed cylinders arranged randomly on the surface. With increasing molecular weight, the diameter of the six-point pattern in the FFT decreases as would be expected with the increase in both the diameter and the center-to-center separation distance of the PMMA cylinders.

Shown in Fig. 4 is the lattice spacing characteristic of the center-to-center separation distance of the cylindrical domains as a function of the number of segments in the copolymers. The data shown were taken from the experiments on both thin and thick films. In the strong segregation

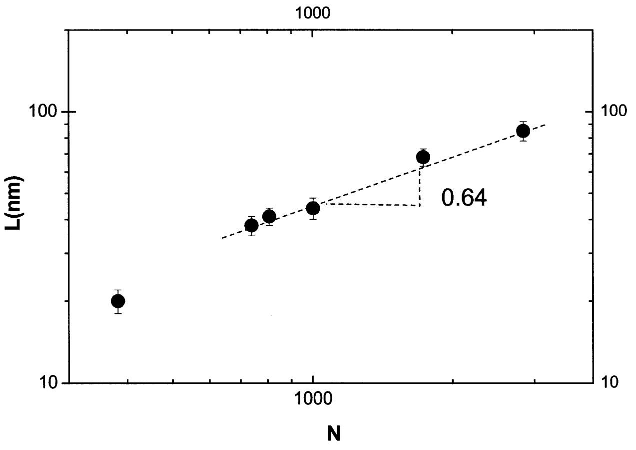

Fig. 4. The lattice period measured from the AFM images as a function of the number of segments in the copolymer.

regime, L_0 should vary as $N^{2/3}$. For the higher molecular weight P(S-*b*-MMA) ($N > 800$) this regime is approached and the data yield a power law exponent of 0.64. This result, while expected, shows that the kinetic barrier associated with the microdomain orientation can be overcome. Thus, the variation in the molecular weight of the copolymer provides a very simple means of changing the size scale of the nanoscopic domains. For the copolymers studied the cylindrical microdomain diameters changed from 14 to 50 nm with the lattice period varying from 24 to 89 nm, respectively. An alternative approach to achieving similar control over the size of the microdomains and their separation distance is by the addition of homopolymers. While this approach is equally easy, as will be reported elsewhere [21], the demands placed on the mixtures, in terms of preferential segregation to surfaces and interfaces due to molecular weight differences or specific interfacial interactions (however, slight), are much more stringent. The major disadvantage to the pure copolymer approach is that a new block copolymer must be synthesized to change the size scale. This, however, given the advances in nitroxide mediated synthesis, is no longer an impediment.

The laterally ordered arrays of the cylindrical copolymer microdomains have a large number of end-use applications as templates to transfer structures to the underlying substrate [2,5,22], as scaffolds for support of inorganic nanostructures [4,23], or as separation media [24]. Each of these applications require the removal of the minor component and a crosslinking of the matrix. For P(S-*b*-MMA), a single procedure has been described [3]. Shown in Fig. 5 are a series of AFM tapping mode images of thin films of P(S-*b*-MMA) oriented in an electric field, exposed to deep UV radiation and washed with acetic acid and deionized water to remove the degradation by-products. Ordered hexagonal arrays of closed-packed pores in a cross-linked PS matrix are seen in each image. The lattice constants for the arrays of pores are identical to those of the parent copolymer film, indicating that the initial morphology of the copolymer has been retained. Independent X-ray scattering and electron microscopy results support this finding.

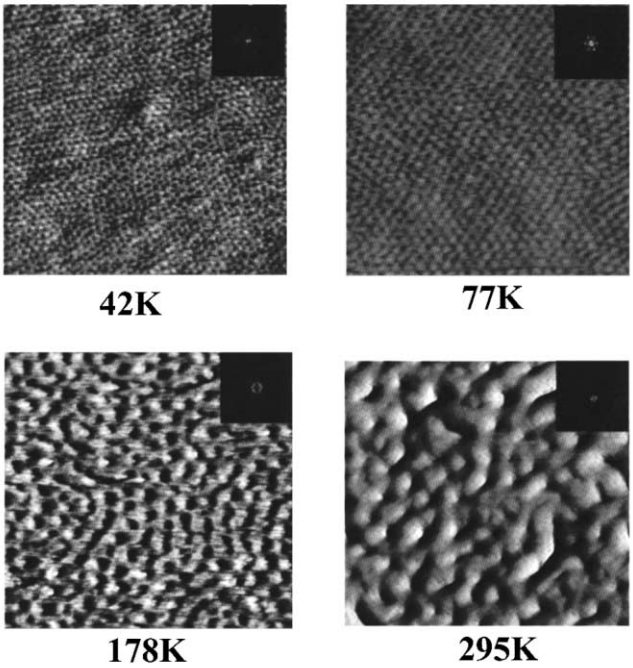

Fig. 5. Phase contrast images of arrays of nanopores produced from electric field aligned copolymers after exposure to keep UV radiation and washing with acetic acid. Images are 0.5 μm × 0.5 μm. The insets are fast Fourier Transforms of the AFM images. Any deviations of the FFTs from circular symmetry are scanning artifacts. The FFTs cover a wavevector range ($2\pi/d$, where d is the Bragg spacing) of $\pm 0.785\ \mathrm{nm}^{-1}$. The molecular weights of the copolymers are indicated. Images are 1 μm × 1 μm.

In conclusion, this study has shown that the microdomain morphology of diblock copolymers can be oriented normal to the surface over a broad range of molecular weights. This has led to a unique means of controlling the size scale nanopores in thin films. Arrays of hexagonally close packed pores with diameters, ranging from 14 to 50 nm and separation distances from 24 to 89 nm, respectively, have been achieved by standard photolithographic procedures. Both controlled interfacial interactions and applied external fields can be used to achieve the domain alignment. In the case of an applied electric field, a method has been shown by which a smooth surface can be achieved.

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