Observed Surface Energy Effects in Confined Diblock Copolymers

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By using thin layers of random copolymer, we have varied the specificity of block-wall interactions for films of diblock copolymer confined between parallel walls. For highly specific interactions (bare walls), one block component segregates to both interfaces, and the frustration due to incommensuration between film thickness and the diblock's bulk period is accommodated by the formation of layers parallel to the walls with perturbed period. In contrast, reduced specific interactions (random-copolymer-coated walls) allow the frustration to be accommodated by perpendicular ordering of the diblock, such that both block components are present at the walls.

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Frustration is a common element to commensurate-incommensurate transitions in adsorbed gases and charge density waves, to spin glasses, and to modulated structures. In each case, competing interactions drive the system toward at least two imcompatible structures. Thin films of symmetric diblock copolymers confined between two hard, parallel walls represent model systems in which frustration effects may be studied, where the competition is between bulk interactions, which drive the formation of lamellae with a natural period L_0, and surface interactions, which lead to segregation of the components to interfaces [1–9].

Symmetric diblock copolymers consist of polymer chains of equal volume covalently connected at one end. Because the blocks of the copolymer are usually immiscible, phase separation occurs. But unlike conventional mixtures, where macroscopic domains may grow, the connectivity of the diblock copolymer chains restricts phase separation to chain dimensions, typically tens of nanometers. In the case of symmetric diblock copolymers, lamellar microdomains are formed with a characteristic period of L_0 [10]. Perturbations from this spacing result in enthalpic and entropic penalties in the free energy. In thin films, preferential interactions between the blocks and the substrate and the blocks and air cause the microdomains to orient parallel to the interfaces, resulting in a multilayered structure. Two types of multilayers may occur: *a symmetric* film exists if the same block segregates to both interfaces upon annealing [11], while an *antisymmetric* film exists if each interface adsorbs a different component [12]. Incommensuration between the film thickness and natural period occurs if the as-cast film thickness $t \neq nL_0$ for a symmetric system or $t \neq (n + \frac{1}{2})L_0$ for an antisymmetric system. In unconfined films, this is accommodated through the formation of terraces of step height L_0 at the free surface, allowing the preferred block(s) to be present at both interfaces while preserving the bulk equilibrium period.

By confining films between two rigid surfaces prior to annealing, terrace formation is suppressed [5,8] and the development of the period L_0 for parallel multilayers is frustrated. There are two obvious lamellar orientations for identical confining walls, with the equilibrium orientation arising from the minimization of interfacial and distortion energies. If the affinity of one block for the walls dominates the energy required to stretch or compress the chains, an integral number of *parallel* lamellae should form for all film thicknesses t, but with a perturbed period $L \neq L_0$ for thickness $t \neq nL_0$. As thickness is increased, L oscillates about L_0 with period L_0. The maximum excursions in L/L_0 should decrease as thickness is increased because the mismatch between t and nL_0 is distributed among more layers. We recently reported neutron reflectivity (NR) results for diblock copolymer films of deuterated polystyrene (*d*-PS) and poly(methyl methacrylate) (PMMA) confined between rigid walls which were known to preferentially adsorb PMMA [5]. The data support this picture of strongly preferential surface interactions, with parallel lamellae at all measured thicknesses and periodic variations in L; qualitatively similar results have been found for another diblock copolymer system [8].

On the other hand, if there is no preferential adsorption at all, the lowest energy structure should be one with lamellae oriented *perpendicular* to the walls; in this way L_0 may be achieved for any thickness. In the intermediate case of *some* preferential attraction, energetic considerations imply perpendicular lamellae near half-integral values of t/L_0 (regions of maximum frustration), with parallel lamellae at other thicknesses. A number of theoretical approaches show cyclic variations in L as a function of t [2,6,7]. In an extension of the work of Turner [2],

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periodic cycling between perpendicular and parallel orientations is also predicted [4]; numerical simulations yield a similar result [7,9]. For the symmetric case, these models have as relevant parameters: (1) the difference in interfacial tensions between the two blocks and the walls, normalized by the block-block interfacial tension; and (2) incommensuration L/L_0 necessary to span an arbitrary thickness, $t = nL$.

In this Letter, we have attempted to reduce preferential adsorption by coating the confining walls with a random copolymer composed of the two block components. A monomer of one component is attracted to others of the same type but repelled by those of the other type (the latter being the mechanism for microphase separation). As a result, a surface composed of an equal mixture of monomers should be less apt to induce segregation of one component over the other; variation of the fraction of each component incorporated into the random copolymer should continuously vary the selectivity of the surface field. The microstructure of such a system has been investigated using NR, to probe structure normal to the confining walls; small angle neutron scattering (SANS), recently shown to be an excellent probe of in-plane structure for films of less than 100 nm thickness [13]; and transmission electron microscopy (TEM).

The samples with reduced surface interactions consisted of three distinct polymer layers, each made by spin casting, confined between rigid walls. For neutron scattering, the middle layer was a symmetric diblock copolymer of *d*-PS and PMMA, with weight average molecular weight $M_W = 8.0 \times 10^4$, polydispersity 1.04, and *d*-PS volume fraction $\phi_S = 0.51$ (Polymer Laboratories). For TEM, the middle film was a normal-styrene/methyl methacrylate diblock, with $M_W = 10^5$, $\phi_S = 0.52$, and polydispersity 1.1. On either side of the diblock was a random poly(styrene-*r*-methyl methacrylate) copolymer layer, denoted P(S-*r*-MMA), prepared by free radical synthesis with $\phi_S = 0.53$ and $M_W = 1.7 \times 10^5$. Finally, the rigid upper surface consisted of 1–2 μm of vapor-deposited SiO_x $(1 \leq x \leq 2)$.

Samples with walls which preferentially adsorb one component were also prepared. These consisted of the diblock film deposited directly on silicon and covered with a PMMA buffer layer ($M_W = 4.8 \times 10^5$) prior to SiO_x deposition. (As discussed previously [5], the PMMA layer was necessary to prevent the SiO_x layer from interfering with the ordering of the diblock.) Both walls are known to adsorb PMMA in these samples.

Because frustration effects are expected to be larger for thinner films, the neutron scattering samples were made with thicknesses in the range $t = 1.4L_0$–$3.2L_0$, with $L_0 \approx 30$ nm; they were then annealed for periods of 115 to 140 h at 175 °C *in vacuo*. TEM samples were made near $t = 2.5L_0$ and $t = 3.0L_0$ and annealed for 144 h at 190 °C.

All measurements were performed at room temperature on the quenched films, well below the glass transition temperatures of the polymers. The neutron reflectivity measurements were performed on the IBM/UMINN/NIST reflectometer at the Cold Neutron Research Facility (CNRF) at NIST. The SANS measurements were performed at the CNRF using both 30-m instruments. For TEM, the walls were removed in a two-step process. First, the SiO_x overlayer was etched away by immersion in 50% aqueous hydrofluoric acid solution for periods of 1–10 min. The polymer film was then scored into a grid pattern and removed by slow immersion in KOH solution (pH = 11–13) at 80–90 °C; when carefully done, the film slowly detaches from the substrate as the native oxide is etched. The sections were collected onto TEM grids and the PS stained by exposure to RuO_4 vapors for 10–15 min. These sections provide a "top-down" view of the film. Low-dose TEM was performed on a Jeol 200CX microscope using 100 kV accelerating voltage.

Figures 1(a) and 1(b) compare neutron reflectivity profiles $R_{kz,0}$ measured for the films with strongly preferential and less preferential walls. The reflectivities differ strikingly. For the first series, first- and third-order Bragg peaks exist for all values of t/L_0; this indicates that well-developed order exists for all thicknesses. Second-order reflections are absent due to symmetry. By contrast, the second series shows up to three reflection orders, the

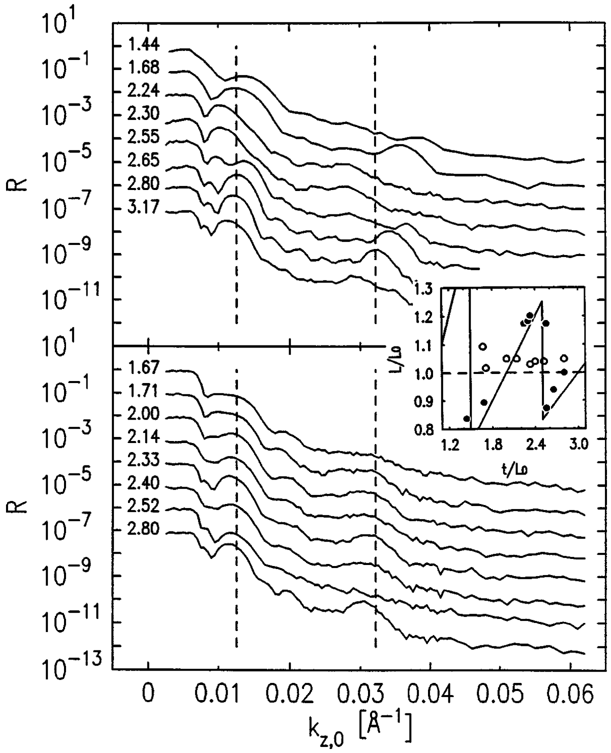

FIG. 1. NR profiles for confined diblock copolymer films between SiO_x/PMMA surfaces (top) and P(S-*r*-MMA) surfaces (bottom) with reduced thicknesses t/L_0 as indicated. The dashed line indicates first- and third-order Bragg peaks for multilayers with the bulk period L_0. The inset shows lamellar period calculated from the first-order peak position k_1, $L \approx \pi/k_1$, as a function of reduced film thickness t/L_0 for the first (●) and second (○) sets of films.

notable exception being $t/L_0 = 2.52$, where only a first-order reflection is seen. The positions of the Bragg peaks differ between series as well. Both the first- and third-order peaks in the first series show significant and systematic variations with thickness. A further feature is the presence of "split" first- and third-order Bragg peaks for $t/L_0 = 2.55$, where the split peaks also follow the trends just described. This behavior is qualitatively the same as that seen for samples of greater thickness, $t/L_0 = 5-7$ [5]. In contrast, the second series shows no apparent peak movement as a function of thickness; both first- and third-order peaks appear at approximately the values expected for parallel lamellar structure with the bulk spacing L_0.

The inset of Fig. 1 demonstrates these trends more clearly, where the first-order Bragg peak positions have been used to calculate L. For the PMMA/SiO$_x$ wall series, the derived L values clearly follow the qualitative predictions of the phenomenological model [4] for strong adsorption of one species to both interfaces: expansion of lamellae below $t/L_0 = 2.33$, coexisting expanded and contracted lamellae at $t/L_0 = 2.55$, and a sudden contraction for larger thicknesses. This is consistent with a transition from $n = 2$ to $n = 3$ layers near the half-integral point. In contrast to this, the period for the system with P(S-*r*-MMA) walls is nearly constant at $L = 30.9$ nm ($\approx L_0$). This counters our simple reasoning above, in which parallel order should be seen only near integral thicknesses if preferential block-wall interactions have been sufficiently reduced. But we note that the overall parallel order in these films is consistently less than in the first series, as seen by the reduced intensity of the Bragg peaks relative to the first [(10–40)%] for all thicknesses. The reduced intensity suggests that some of the material in these films is ordered in directions other than parallel to the walls. Especially suggestive is the absence of the third-order peak for $t/L_0 = 2.52$, indicating that parallel order is reduced for this highly frustrated film thickness relative to thicker and thinner films.

In an effort to determine if frustration induces some other lamellar orientation, we performed SANS measurements on the random wall $t/L_0 = 2.52$ and 2.80 films. The SANS measurements were performed by placing the wafers normal to the incident beam, such that the neutrons entered through the back of the Si substrate [13]. In this geometry, SANS probes scattering length density correlations parallel to the confining walls, i.e., perpendicular to the direction examined in reflectivity. In both cases, two-dimensional, azimuthally symmetric scattering patterns were obtained in approximately 30 min.

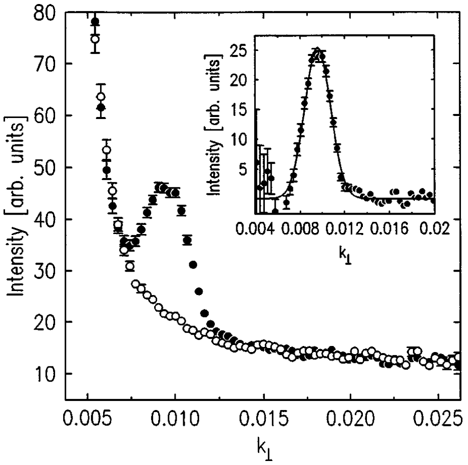

FIG. 2. Azimuthally averaged SANS patterns for films between P(S-*r*-MMA) surfaces for $t/L_0 \approx 2.5$ (•) and $t/L_0 \approx$ (∘). The inset shows the subtraction of the second set from the first.

In Fig. 2, the azimuthally averaged SANS patterns are shown. The $t/L_0 = 2.52$ film exhibits a single, well-defined peak indicative of in-plane order, while the $t/L_0 = 2.80$ film shows no such peak. The diffuse background for both samples is virtually identical and due overwhelmingly to the Si wafer. The difference between the $t/L_0 = 2.80$ data and the $t/L_0 = 2.52$ data is shown in the inset. A Gaussian fit to the peak gives as the maximum $k_{\mathrm{SANS}} = 0.0096$ Å^{-1}, corresponding to a period $d = 32.7$ nm, close to that of the bulk. The width of the peak, $\Delta k = 0.0012$ Å^{-1}, is resolution limited; this implies that the correlations giving rise to this scattering must extend over length scales of at least a few hundred nanometers. These SNAS results are most easily explained by a lamellar structure which is oriented perpendicular to the walls.

The indications of weak parallel order from NR and perpendicular order from SANS imply coexistence of lamellae of these orientations in the $t/L_0 = 2.52$ film. But more complicated structures could be present, such as interconnected and disordered regions. The simplest model for coexistence, one where different areas of film exhibit either perpendicular or parallel morphologies, can be ruled out, since L should still vary with t for the parallel domains, while the NR results show that L is approximately constant with thickness. Moreover, the presence of a significant second-order reflection at $k_{z,0} \approx 0.02$ Å^{-1} in the NR data for all films in this series other than $t/L_0 = 2.52$ shows that the structure normal to the walls does not consist of symmetric layers with alternating scattering length; i.e., the three-dimensional morphology is probably more complex than symmetric lamellae. To better determine the microscopic structure, a local technique must be employed. For this we have used plan-view TEM on films prepared as described above.

Figure 3 shows a micrograph of a diblock copolymer film confined between P(S-*r*-MMA)-coated walls viewed normal to the confinement surfaces; this film has thickness $t/L_0 \approx 2.5$, a thickness of maximal frustration. In the micrograph, the PMMA appears as bright regions and the PS as dark regions. The apparent asymmetry in the sizes of the regions is due to radiation-induced thinning of the PMMA under the electron beam. The perpendicular orientation fills the entire field of view, and, in fact, occupied all of the sections of the film inspected. It is clear that, while the entire film appears to be laterally microphase separated, it does *not* possess well-developed perpendicular order in the form of large lamellar grains. In addition to lamellae-like stripes, there are regions of several tens of nanometers in extent consisting of "dots," stripe ends, and undifferentiated areas. Plan-view TEM of films with $t/L_0 \approx 2.8$, nearer an integral number of layers, show no signs of perpendicular lamellae. This confirms the SANS results described above. Plan-view TEM on strong-adsorption samples (PMMA and native SiO_x walls) with $t/L_0 \approx 2.5$ and 3.0 show no signs of lamellae normal to the confining surfaces; cross-sectional studies on similar samples (prepared on an Ultem plastic substrate) show well-developed parallel order, as expected from our NR results.

The lack of true long-range lamellar order, the existence of nonlamellar regions, and the approximately constant $L \approx L_0$ from NR all suggest that the effects on film structure due to the P(S-*r*-MMA)-covered walls is more complicated than the phenomenological model [4] would suggest. Possible frustration effects include both partially disordered films as well as interconnected or channel structures [14]. A true three-dimensional understanding of the structure of these films requires a detailed investigation using both plan-view and cross-sectional TEM for a wide range of film thicknesses. While this is beyond the scope of the current work, we have begun cross-sectional microscopy on diblock copolymer films confined between random copolymers. In particular, the film shown in Fig. 3 was embedded in epoxy and cross sectioned; the resulting micrographs suggest a mixed state perpendicular near at least one wall but parallel in the interior of the film (we are unable to identify the microstructure from these preliminary results).

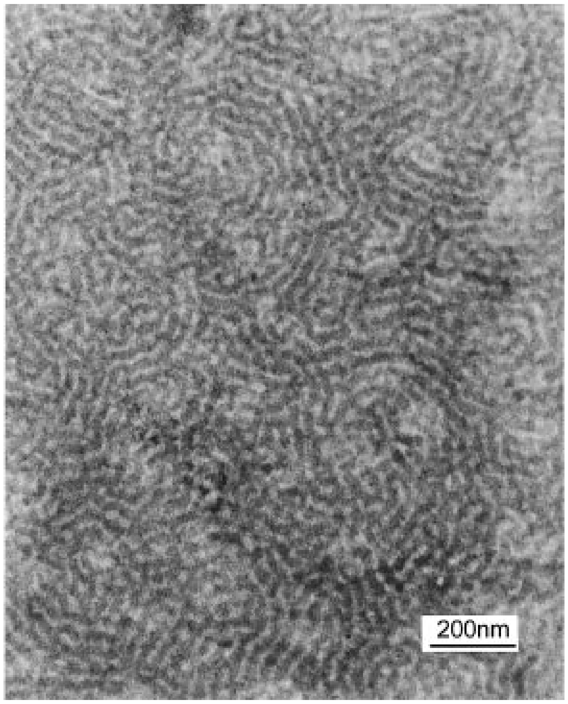

FIG. 3. Plan-view TEM of $t/L_0 \approx 2.5$ film annealed between P(S-*r*-MMA) surfaces after removal from confinement.

In conclusion, we have shown that the relative interactions between the blocks and the confining walls strongly influence the manner in which a diblock copolymer responds to applied frustration. In the case of strongly preferential adsorption of one block to the walls, the lamellar microdomains are always oriented parallel to the interfaces and frustration results in perturbation of the lamellar period. As the interactions between the blocks and the walls become less specific, frustration between the film thickness and natural period can result in ordering perpendicular to the interfaces. Random copolymers placed at the block copolymer film interfaces provided an inexpensive, direct means to controllably vary the interfacial energy and thus "tune" the copolymer film microdomain orientation. By incorporating different functional groups within random copolymers such tunability might be extended to adsorption processes in complex fluids, polymer mixtures, or membranes.

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[1] K. R. Shull, Macromolecules **25**, 2122 (1992).

[2] M. S. Turner, Phys. Rev. Lett. **69**, 1788 (1992).

[3] M. Kikuchi and K. Binder, Europhys. Lett. **21**, 427 (1993).

[4] D. G. Walton, G. J. Kellogg, A. M. Mayes, P. Lambooy, and T. P. Russell, Macromolecules **27**, 6225 (1994).

[5] P. Lambooy, T. P. Russell, G. J. Kellogg, A. M. Mayes, P. D. Gallagher, and S. K. Satija, Phys. Rev. Lett. **72**, 2899 (1994).

[6] M. Kikuchi and K. Binder, J. Chem. Phys. **101**, 3367 (1994).

[7] G. Brown and A. Chakrabarti, J. Chem. Phys. **102**, 1440 (1995).

[8] N. Koneripalli, N. Singh, R. Levicky, F. S. Bates, P. D. Gallagher, and S. K. Satija, Macromolecules **28**, 2897 (1995).

[9] A. C. Balazs (private communication).

[10] F. S. Bates and G. H. Frederickson, Annu. Rev. Phys. Chem. **41**, 525 (1990).

[11] T. P. Russell, G. Coulon, V. R. Deline, and D. C. Miller, Macromolecules **22**, 4600 (1989).

[12] G. Coulon, T. P. Russell, V. R. Deline, and P. F. Green, Macromolecules **22**, 2581 (1989).

[13] T. P. Russell, P. Lambooy, J. G. Barker, P. D. Gallagher, S. K. Satija, G. J. Kellogg, and A. M. Mayes, Macromolecules **28**, 787 (1995).

[14] E. L. Thomas, D. M. Anderson, C. S. Henkee, and D. Hoffman, Nature (London) **334**, 598 (1988).