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Equilibrium Orientation of Confined Diblock Copolymer Films

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ABSTRACT: Using a two-dimensional Scheutjens and Fleer self-consistent field calculation, we determine the equilibrium morphology of thin films of symmetric AB diblock copolymers confined between hard, smooth plates. A lamellar phase is established with the stripes either perpendicular or parallel to the walls. With neutral walls, the perpendicular orientation is stabilized by the nematic ordering of the monomers, which arises from the orientational constraint imposed by the walls. When the substrates are composed of pure A monomer (thus repulsive to B), there are transitions from strained parallel conformations, which wet the substrates with A polymer, to distorted perpendicular configurations as the film thickness is varied. It is possible that the removal of one of the walls (the usual experimental scenario of thin films spun cast onto a substrate) can still lead to spontaneous and robust pattern formation on the scale of tens of nanometers.

Introduction

The regular patterns formed by diblock copolymers can potentially be used as templates in fabricating optoelectronic devices with features in the tens of nanometers scale. Diblock copolymers, composed of a linear block of A chemically linked to the end of a linear block of B, form a variety of structures when A and B are thermodynamically incompatible. When the blocks are similar in molecular weight and stiffness, the chains microsegregate into a lamellar structure.[1,2] The bulk forms a layered material, with A-rich domains separated by B-rich regions. The junction between the different blocks lies at the AB interface, and the respective blocks stretch into the A and B domains, thereby forming an ABBA repeat sequence (see Figure 1a). The domains can be aligned in the bulk through the application of an external shear.[3] Once aligned, the domains can be microtomed to expose ordered, alternating A and B stripes with a well-defined separation. The stripe width can be tuned by cutting the sample at an oblique angle and by controlling the molecular weight of the copolymer.[4−6] If A and B are chosen so that a metallic compound preferentially wets one of the stripes, the metal can be deposited onto the polymer substrate in a highly controlled manner. This system of alternating polymeric and metallic stripes, whose features are an order of magnitude smaller than typically achieved through photolithography, should exhibit unique optical or electronic properties that can be harnessed for novel applications.

This procedure relies on the thermodynamic behavior of copolymers in the bulk; an alternative procedure relies on the thermodynamic properties of copolymers in thin films.[7,8] When a dilute solution of copolymer is spun onto an appropriate substrate, a dense, disordered polymer film is produced. When the film is annealed, the copolymers microsegregate in the presence of the polymer−substrate interface and the polymer−vacuum interface. In addition to the morphology of the separated domains, the orientation of the domains is controlled by kinetics and thermodynamics. We make no further comment on the role of kinetics in the formation of the aligned domains, although this may be a serious omission.[9] When the lamellar planes are aligned parallel to the substrate, there is no contrast to be exploited at the free surface for creating ordered domains of deposited conductor. However, when the domains are *perpendicular* to the substrate, a striped pattern is presented at the free surface. The striped pattern is often disordered in experimental systems[7,8] but may be ordered through the application of an external electric field.[10]

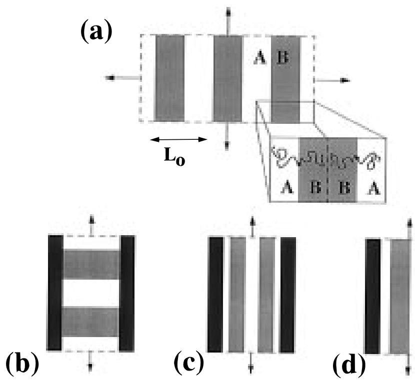

Figure 1. Schematic. (a) In the bulk, the copolymers arrange themselves in an ABBA repeat pattern with a periodicity L_0. The copolymers stretch out normal to the direction of the composition modulation. (b) When the copolymers are confined between flat plates, the composition modulation can establish itself perpendicular to the plates. The copolymers then stretch out along the walls. (c) The composition modulation may also align itself with the plates. Here, the composition is symmetric; that is, an integral number of repeat sequences fit in the gap (two shown here), and the plates are covered with the same type of material. (d) Here, parallel layers are formed, but only one and a half layers are accommodated in the gap. This morphology is asymmetric.

In this paper, we use a two-dimensional self-consistent field (SCF) model[11,12] to determine the equilibrium orientation of the lamellar planes when a melt of symmetric diblocks is confined between two impenetrable surfaces. This scenario models experiments in which the polymers are localized between two rigid plates.[8,13,14] This study is also relevant to the situation where the diblocks are spun cast onto one solid surface. Here, the solid forms one wall, while the air−polymer interface forms another boundary. Through the SCF calculations, we determine how the thickness of the film (plate separation) and the relative strength of the monomer−wall interactions affect the structure of the

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confined diblock film. In particular, we calculate which orientation has the smallest cost in free energy per unit wall area. We then compare our findings with the experimental data[8] and scaling predictions.[15−17] The findings allow us to isolate experimental conditions that affect the morphology of the film and provide guidelines for tailoring the system to yield the desired structures.

Earlier studies have revealed that the overall orientation of the films is controlled by two kinds of effects: those arising from the local perturbation of the polymer layer at the interfaces[15] and that arising from distortion of the lamellar order throughout the layer.[16,17] First, we discuss the interfacial effects. Of these, the easiest to understand is the *wetting* effect. Unless the substrate is chosen with care, it will prefer to wet with, for example, component A over component B. This effect drives the lamellae toward being parallel to the substrate.[18] The next surface effect favors the perpendicular orientation. With perpendicular lamellar planes, the copolymer chains are stretched out along the substrate. To obtain a (fixed) average extension per monomer in the bulk, a bias must be applied to each step of the copolymer's random walk. Enforcing this bias incurs a fixed cost in free energy for each monomer on the chain. The entropic stretching energy of the copolymer chains arises from each of these small costs. The necessary bias is smaller, however, whenever the chain encounters the substrate, since steps across the wall are forbidden. Looking at the monomers as rigid rods, the rods must lie in the plane of the wall if they are in the wall's immediate vicinity. That is, the wall imparts a nematic order to the nearby monomer segments. Thus, the substrate facilitates the average alignment and extension of the chains. There is no benefit from this effect when the chains are stretched perpendicularly to the surface, *i.e.*, when the domains are parallel to the substrate.[15] The last local surface effect is determined by the surface concentration of chain ends. Chain ends are easier to pack at a hard surface than segments in the middle of the chain, and thus their presence at an interface lowers the interfacial tension.[19−21] When the layers are parallel to the surface, the surface density of free ends is considerably enhanced over the average density of free ends, and when the layers are perpendicular to the substrate, the surface density of free ends is only slightly greater than average.[15,22] Thus, this effect favors the parallel orientation.

Apart from these local surface effects, distortion of the lamellar order throughout the film influences the orientation of the domains. The distortion may arise from a mismatch in the bulk lamellar spacing and the thickness of the cast film. When the thickness of the film is between nL_0 and $(n + {}^1/_2)L_0$, where L_0 is the periodicity of bulk lamellae, the film may form n parallel lamellae that are slightly stretched, or $n + {}^1/_2$ parallel lamellae that are slightly compressed,[16] each case costing in free energy. Alternatively, the mismatch in film thickness may be relaxed by the creation of island or hole defects at the free surface of the film.[23] Here, the film thickness is not uniform: in some areas of the film the thickness is nL while, in other areas, the thickness is $(n + {}^1/_2)L$, when the surface tension of A is matched to B's. The system can be described as the coexistence of two phases (island-phase and hole-phase) with the restriction that the total amount of polymer is conserved. The free energy cost in this case comes from the boundary between the islands and holes. When the lamellae are aligned perpendicularly, however, there is no frustration due to the thickness of the film, and consequently, there is no free energy penalty associated with the film thickness.[17]

In experiments of PS-PMMA diblock copolymers,[8] these ideas were exploited to create perpendicular films. Incommensurate film thicknesses were chosen, and relaxation through the creation of islands was suppressed through depositing a rigid silicon oxide layer on top of the film. Thus, the film was confined between two flat, rigid substrates. To control the surface interactions, a buffer layer of symmetric PS-PMMA random copolymer was deposited at both substrates. In such a system, with nearly neutral wetting interactions and incommensurability of parallel lamellae locked in, the technologically interesting perpendicular orientation should occur. Interestingly, in this experimental system, the perpendicular orientation occurs at a commensurate film thickness, while the parallel morphology arises when the thickness is moved away from commensurability. Below, we confirm the findings of the experimental studies on the PS-PMMA system and show that these results are consistent with the incomplete neutralization of the substrate by the random copolymer. Our major conclusion is that the technologically interesting perpendicular orientation can occur in equilibrium even when the substrates are chosen to preferentially wet with a single component.

Lattice SCF

Our SCF method is based on the lattice model of Scheutjens and Fleer, which is a mature numerical technique that describes many-component polymeric systems at thermal equilibrium. The details of the model are put forth in ref 11, and we describe them only briefly here.

We consider a molten layer of pure diblock copolymers trapped between two infinite, smooth, parallel plates. Finding the proper statistical weight, n_c, for a copolymer chain to assume the conformation c in the presence all the other chains is a formidable problem. The process is complicated by the physical constraint that most polymers are nearly incompressible, so to a good approximation the n_c's specify a state that completely occupies the lattice.

Self-consistent field theories break this problem up into two much simpler halves. In dense layers, each copolymer encounters its neighbors much more often than itself. In the absence of any other interactions, going from monomer to monomer along the chain, the copolymer quickly "forgets" its conformation. Thus, without incompatibility between A and B monomers, the copolymers adopt conformations resembling random walks. We apply an external potential, $U(r)$, to these ideal chains. The potential U depends upon position, r, as well upon as the type of monomer. It is a fairly simple problem (at least numerically and on a lattice) to determine the single-chain statistics of the copolymers in the field U. The single-chain statistics are given in terms of the unnormalized probabilities $G(r,r';n,1)$, the statistical weight attributed to finding the nth monomer on a copolymer at the position r given that the first monomer on the chain is located at r'. Similarly, $G(r,r';N,n)$ can be calculated: this is the unnormalized probability to find the nth monomer at r if the last monomer on the chain is located at r'.

Once, if $G(r,r';n,1)$ and $G(r,r';N,n)$ are known, it is a fairly simple matter to calculate $\phi_A(r)$ and $\phi_B(r)$, the volume fraction of monomers A and B throughout space.

The SCF calculation is then complete when U is chosen (through an iterative procedure) such that $\phi_A(r) + \phi_B(r) = 1$, and U satisfies the self-consistency condition

$$U_A(r) = \alpha(r) + \chi\langle\phi_B(r)\rangle + \delta(r - r_{surf})\chi_{AS} \qquad (1)$$

where U_A is the potential for A monomers, χ is the Flory–Huggins mixing parameters for A and B monomers, and U_B is found by switching A for B in the above. The notation $\langle\,\rangle$ stands for the "contact fraction" sum over nearest neighbors on the lattice: $\langle f(r)\rangle = f(r) + \Sigma_{r'=nn} f(r')$. The potential $\alpha(r)$ does not depend on the type of monomer and enforces incompressibility in the self-consistent solution. The last term controls the specific interaction of A monomers and the substrate. For neutral substrates, $\chi_{AS} = \chi_{BS}$.

Defining the chain weighting factor, $G(r) = \Sigma_{r'} G(r,r';N,1)$, the free energy density at the site r is given by[11]

$$F(r) = \ln G(r) + {}^1\!/_2\chi\phi_A(r)\langle\phi_B(r)\rangle + {}^1\!/_2\chi\phi_B(r)\langle\phi_A(r)\rangle \qquad (2)$$

When r is adjacent to a wall, the appropriate surface interaction must be added in eq 2.

To describe a system in which lamellae are oriented parallel to the walls, this model may be executed in a single spatial direction, z, the direction normal to the substrates.[24] However, when the lamellae orient perpendicularly to the substrate, variations along (x-direction) and normal (z-direction) to the walls must be accommodated.[25] Therefore, we implement this model in two spatial directions on a cubic lattice with mesh size a, and we assume that all quantities are translationally invariant in the third (y) direction.[12]

Symmetric Diblocks and Neutral Walls

We consider a melt of diblock copolymers, with $N/2$ A monomers per chain and $N/2$ B monomers, with $\chi = 0.1$ fixed for all of our calculations. The wall interactions are neutralized by the choice $\chi_{AS} = \chi_{BS} = 0$. Initially, we consider $N = 150$. The lattice we consider is a cubic lattice with L sites in the z-direction and L_x sites in the x-direction. Impenetrable substrates exist at lattice sites with $z = 0$ and $z = L + 1$. Periodic boundary conditions are imposed in the x-direction.

We form n parallel lamellae for various values of the plate separation L[26] and determine $F^n_{\|}(L)$, the average free energy per unit volume in the system. We employ the bulk lamellar phase as the reference state from which the free energy is calculated.[27] Thus, $F^n_{\|}(L)$ gives the free energy associated with disturbing the "natural" lamellar phase. The free energy per unit substrate area (interfacial tension) is given by

$$\gamma^n_{\|}(L) = F^n_{\|}(L)L \qquad (3)$$

Figure 2 shows $\gamma^n_{\|}(L)$ for N=150 with n=$^1/_2$, 1, and $^3/_2$. When the plate separation is near 19 lattice units (the bulk repeat spacing for diblocks of this molecular weight and χ), the distortion energy is minimized when a single complete ABBA layer spans the system. When $L \approx {}^{19}/_2$, a half layer of AB fits between the walls with minimal distortion, and when $L \approx 19(^3/_2)$, one and a half layers fit between the substrates.

If the rigid surface at $z = L + 1$ is removed, then $\gamma^n_{\|}(L)$ must be a convex function of L for thermodynamic stability. Suppose both A and B have the same interfacial tension with air. Then, if a film of these diblocks with a thickness $^{19}/_2 < L < 19$ is spun onto a solid substrate, we expect a coexistence between morphologies with $^1/_2$ and 1 complete layers. That is, the incommensurability of the film thickness can be relaxed by forming terraces at the free surface. On the other hand, when both surfaces are rigid, there can be no such coexistence. In this case, we instead find a transition from $n = {}^1/_2$ to $n = 1$ at $L \approx 12$ and a transition from $n = 1$ to $n = {}^3/_2$ at $L \approx 23$ (see Figure 2), in agreement with previous theoretical treatments.[9,16,17,24]

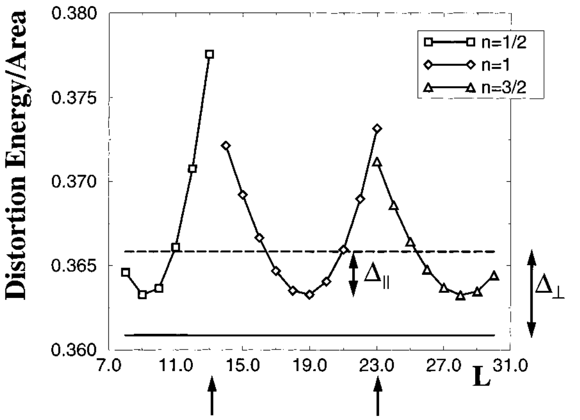

Figure 2. $N = 150$, Parallel vs Perpendicular. Here we show the distortion free energy per unit area to form $n = {}^1/_2$, $n = 1$, and $n = {}^3/_2$ layers at various plate separations for $N = 150$. $L_0 \approx 19$, where $n = 1$ has its minimal distortion energy. At $L = 14$, there is a discontinuous transition between the stretched $n = {}^1/_2$ layer and the compressed $n = 1$ layer. Similarly at $L = 24$ there is a coexistence of states with $n = 1$ and $n = {}^3/_2$. The solid line indicates the distortion free energy for the perpendicular orientation, and the dashed line indicates the distortion free energy of a melt of neutral homopolymer of molecular weight $N = 150$. The arrows indicate the thicknesses at which the perpendicular orientation is maximally stabilized.

When lamellae are formed in the perpendicular orientation,[28] the lateral system size, L_x, determines the periodicity of the lamellae in our calculations. At each plate separation L, we are careful to determine the value of L_x that minimizes the free energy per unit volume. When a full lamella is accommodated from $x = 0$ to $x = L_x$, this free energy is minimized with $L_x \approx 19$, the bulk lamellar repeat spacing. That is, confinement between the plates does not affect the spacing of the lamellae in the perpendicular orientation, as has been pointed out.[8,17]

We define $\gamma_{\perp}(L)$ as in the parallel case and show a comparison between the orientations in Figure 2. The free energy per unit area for perpendicular lamellae does not depend on the surface separation, as we expect. The perpendicular orientation is actually composed of two regions: one near the interfaces and another in the middle of the film. Near the interfaces, the chains encounter the constraint of a hard wall, but in the middle of the film the chains are essentially in their bulk state. Increasing L merely increases the size of the middle (bulklike) layer and thus does not affect the surface energy $\gamma_{\perp}(L)$.

Significantly, $\gamma_{\|} > \gamma_{\perp}$, at all plate separations L.[25] Therefore, the perpendicular orientation is the true equilibrium orientation of this film.[15] The minimal difference in surface energies for the two orientations is on the order of 1%, which is large enough to affect engineered systems. The perpendicular orientation is still the equilibrium orientation when the upper surface is removed (provided A and B have the same surface tension with air). The basic conclusion is that when care is taken to neutralize the wetting preference of the substrate, the perpendicular orientation is the thermodynamically favored orientation *at all plate separations*.

The dashed line in Figure 2 indicates the free energy cost per unit area, γ, when $\chi = 0$.[29] Thus, γ gives the interfacial tension when the gap is filled with a homopolymer with $N = 150$. γ arises entirely from entropy: the otherwise Gaussian chains are forbidden to cross the substrate at a cost on the order of kT for each monomer in contact with the wall.[30] We use γ as a baseline against which we can compare $\gamma_\perp$ and $\gamma_\parallel$. As we see, $\gamma_\perp$ and $\gamma_\parallel$ differ from γ by only a small amount. That is, the major contribution to both $\gamma_\perp$ and $\gamma_\parallel$ is purely entropic in origin and arises from the hard wall constraint.

Interestingly, the unstrained parallel films have a lower surface energy than an unstructured melt at the same molecular weight. The diblock films have an enrichment of free ends in the vicinity of the substrate, and this lowers the free energy cost to form the interface at the substrate. We define $\Delta_\parallel = \gamma - \gamma_\parallel^n(nL_0)$, the reduction in interfacial tension for unstrained films of thickness $^1/_2L_0$, L_0, and $^3/_2L_0$. We determine the minimum distortion energy by fitting a cubic to $\gamma_\parallel^n$ in the vicinity of the minima. We define $\Delta_\perp$ similarly: $\Delta_\perp = \gamma - \gamma_\perp$. Here, the nematic interaction causes the perpendicularly oriented film to have a lower surface tension than the unstructured melt. Finally, we define the quantity $\Delta = \Delta_\perp - \Delta_\parallel = \gamma_\parallel^n(nL_0) - \gamma_\perp$, which gives a measure of how strongly the perpendicular orientation is stabilized relative to the unstrained parallel orientations.

When the surface is neutral, a specific scaling form for the dependence of Δ is available:[15]

$$\Delta \approx c_\perp N^{-2/3} - c_\parallel N^{-8/9} \tag{4}$$

where $c_\perp$ and $c_\parallel$ are positive constants of order unity. When $\Delta > 0$, the perpendicular orientation is thermodynamically stable.

The positive contribution from the perpendicular orientation arises from the extended diblock chains coming into contact with the wall. These stretched-out chains are under tension, and the wall lowers the tension for each extended monomer it encounters by a factor of order unity. In the bulk, the elastic energy per chain is L_0^2/a^2N, so that the elastic energy density is L_0^2/a^5N^2. Thus, the elastic energy stored in the surface layer a thick is L_0^2/a^4N^2. This stress is relieved by a factor of order unity, so we arrive at

$$\gamma_\perp \sim \gamma - \frac{L_0^2}{a^4N^2} \tag{5}$$

In the strong segregation limit, $L_0 \sim N^{2/3}$,[4-6,22] so we arrive at the first term in eq 4.

The second term in eq 4 arises from the free end density per unit area of parallel lamellae. The vicinity of the impenetrable substrate is similar to the vicinity of the AA midplane interface in the bulk.[15,30] The edges of adjacent lamellae interpenetrate on a length scale given by $\xi \approx N^{4/9}L_0$.[31] The end density per unit midplane area, $\epsilon(z)$, is a function of the distance to the midplane, z:[22]

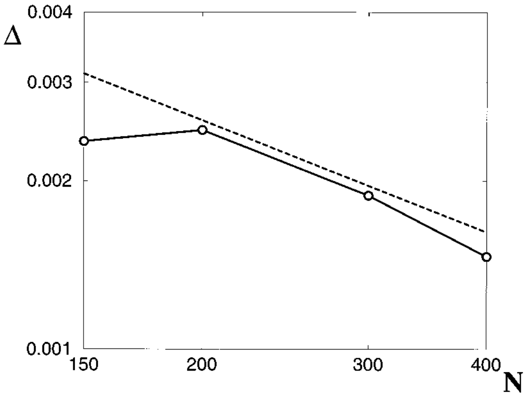

Figure 3. $\Delta(N)$. $\Delta(N) = \Delta_\parallel(N) - \Delta_\perp(N)$ is plotted against N on log−log axes. A reference power law ($\Delta \approx N^{-2/3}$) is shown.

$$\epsilon(z) \approx N^{-1}(L_0/z)^{1/2} \quad \text{for} \quad z \ll L_0 \tag{6}$$

The divergence in $\epsilon(z)$ at the midplane is cut off when z is on the order of ξ. Thus, the midplane density of free ends is $\epsilon(\xi) \approx N^{-8/9}$. Up to a factor of order unity, this is also the areal density of free ends near the substrate, since the effect of the wall may be replaced with a reflection symmetry when the wall is neutral.[30] Each of these free ends lowers the interfacial free energy by an amount on the scale of kT.[19-21] Thus, we arrive at the second term in eq 4.

Figure 3 shows Δ determined numerically from our SCF calculations. There is fair agreement with the leading molecular weight dependence given in eq 4. We note that we have calculations available for less than half a decade in molecular weight, and scaling over several orders of magnitude is needed to accurately determine the scaling form of Δ. Nonetheless, it is clear that the perpendicular orientation is the equilibrium orientation at all plate separations that we have examined, given the proviso that the surfaces are exactly neutral.[32]

Symmetric Preferential Walls

Providing neutral substrates is in principle possible either by adjusting the surface chemistry of the substrates or by carefully tuning the properties of the copolymer components A and B. In practice, however, it is difficult to establish neutral surfaces. Thus, we repeat the above calculations with the stipulation that $\chi_{AS} = 0$ and $\chi_{BS} = \chi$. In effect, we evaluate the A homopolymer as a candidate prelayer for the same experiments as those carried out in ref 8.

Figure 4 shows the results of this calculation. The asymmetric parallel films (dashed lines) with 0.5 and 1.5 lamellae expose a layer of B monomers to the substrate and hence increase the free energy due to the extra B-surface contacts at the substrate. Symmetric parallel layers (solid line), however, are able to coat each substrate with A polymer. When the film thickness is near $L_0 = 19$, the symmetric parallel situation is clearly the most favorable. However, when the thickness is either $^1/_2L_0 \approx 9$ or $^3/_2L_0 \approx 28$, the perpendicular morphology (thick line) is the most favored. When the thickness is equal to these fractions of L_0, the symmetric parallel morphologies with 1 and 2 lamellae are maximally strained. Also, the perpendicular orientation is stabilized over the antisymmetric morphology with either $^1/_2$ or $^3/_2$ layers by the nematic surface effect.

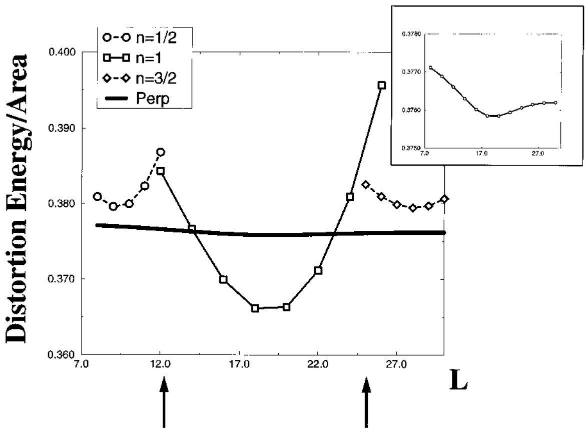

Figure 4. Symmetric preferential walls. Here, $N = 150$, and the substrate is repulsive to B monomers ($\chi_{BS} = \chi$). The antisymmetric films with $n = {}^1/_2$ (○) and $n = {}^3/_2$ (◇) expose a layer of B fluid to the wall, while the film with $n = 1$ (□) wets both substrates with A fluid and hence has a much smaller free energy when $L \approx L_0$. The thick, solid curve shows the distortion penalty for the perpendicular orientation and is shown in more detail in the inset. Note that there is a marked minimum in the interfacial tension when the perpendicular film has a thickness near L_0. The parallel orientation with $n = 1$ is the lowest in free energy only when L is near L_0. The arrows indicate the film thicknesses at which the perpendicular orientation is maximally stabilized.

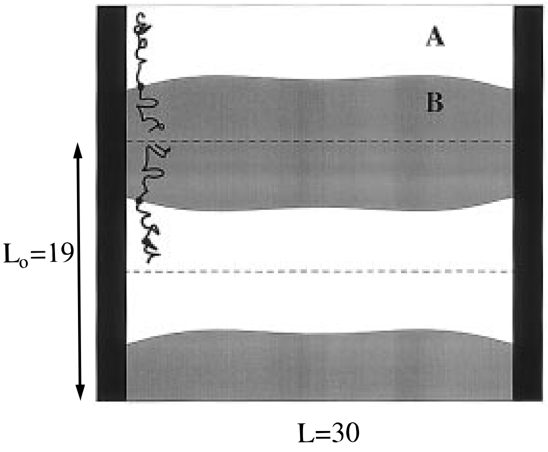

Figure 5. AB interface from SCF calculation. Here we show the interface between A and B domains according to our SCF calculations. $N = 150$, and the substrates repulse B with $\chi_{BS} = \chi$. The plate separation is $L = 30$, and in Figure 4, we see that this distorted perpendicular orientation is the lowest free energy state. We show the typical conformation of the copolymer chains schematically. The AB interface encounters the substrate, with the A domains partially spreading to cover more of the substrate and the B domains contracting to avoid contacts with the substrate. The oscillations of the AB interface from each surface interfere constructively when $L \approx L_0$.

Thus, we expect that when the prelayer is so asymmetric as to be pure A homopolymer, frustration due to confinement can again produce suitably perpendicular films.

When the perpendicular morphology is favored with preferential walls (for example at $L = 30$ in Figure 4), the AB interface between the diblocks is distorted. Figure 5 reveals the shape of the AB interface as calculated in our 2D SCF formalism. We note that the interface exhibits interesting oscillations. The range of these oscillations is predicted to be on the scale of L.[35] The oscillations are due to the fact that the A domains spread to cover more of the substrate and the B domains contract to avoid contact with the surfaces. Thus, when the film thickness is near L_0 there is constructive interference between the oscillations coming from each surface, and indeed the free energy profile for the perpendicular morphology reflects this (inset to Figure 4). There is a pronounced minimum in the interaction near L_0.

Discussion

A general method for neutralizing the substrate interactions was successfully demonstrated in ref 8. A prelayer of compositionally symmetric random copolymer was applied at both the upper and lower substrate. The random copolymer interacts with the A and B blocks as if it were a homopolymer C whose monomers are effectively half A and half B.[33,34] That is, $\chi_{AC} = \chi_{BC}$, so that a surface coated with this statistical copolymer is exactly neutral. In fact, this method suggests a means of producing a tunable substrate: when C has a fractional A content of f, the $\chi_{AC} = f^2\chi$ and $\chi_{BC} = (1 - f)^2\chi$.[8,17,33,34]

In ref 8, the perpendicular orientation is observed when the film thickness is constrained to be $2.52L_0$. This corresponds to a film thickness with maximal distortion for films with either two or three full lamellae and corresponds to a film with $n = 2.5$ undistorted layers. From the above calculations, we expect that the competition between 2.5 parallel lamellae and perpendicular lamellae is won by the perpendicular orientation, as is in fact seen experimentally.

When the film thickness is increased to $2.8L_0$, the parallel morphology occurs experimentally. However, this film thickness has nearly the maximal strain between layers with 2.5 and 3 lamellae. Thus, we expect the perpendicular morphology to be more likely to form at this film thickness if the surfaces were exactly neutralized. This is, however, contrary to the experimental results.

If the random copolymer prelayer is not exactly symmetric in A and B, the prelayer could show a preference for adsorbing, say, A. Also, the prelayer could rearrange itself to present more B than A to the lamella it is directly in contact with. The worst case scenario for both effects is that the wall is composed entirely of A monomers. This corresponds to the maximal asymmetry in the random copolymer C and to the maximal extent to which monomers on C could be rearranged in the surface layer.

Figure 4 recapitulates the experimental result. When the film thickness is $[(2n + 1)/2]L_0$, the perpendicular orientation is favored (for example, when $L_0 \approx 9$ and $L_0 \approx 27$). When the film thickness is moved closer to nL_0, the symmetric parallel orientation becomes the stable orientation. Thus, the experimental results are consistent with a nonzero surface interaction.

The interaction may in fact be tuned by controlling the composition of the random copolymer layer. When the perpendicular state is observed in an experiment at both integral and half-integral multiples of L_0, then the surface has been sufficiently neutralized. With such a neutralizing surface preparation (as in Figure 2), choosing L to be halfway between $[(2n + 1)/2]L_0$ and nL_0 (in other words, when the thickness is chosen to be $L = [(2n + 1)/4]L_0$), the layers with $n/2$ and $(n + 1)/2$ parallel layers are maximally strained, and the perpendicular orientation is stabilized. In Figure 2, the arrows at $L \approx 14$ and $L \approx 23$ mark the film thicknesses satisfying this criterion. The resulting film will be sufficiently separated in free energy from the nearby parallel orientations that they will exhibit good ordering. Clearly, the random copolymer layer exploited in ref 8 does not satisfy this condition. When the film thickness was set to $2.8L_0 \approx (2\cdot 5 + 1)/4L_0$, a well ordered parallel morphology was produced, which can never happen when the walls are properly neutralized.

However, the random copolymer layer used in the experiment was very nearly symmetric in composition, so it is difficult to understand how large surface interactions arise in the system. One possibility is that, while the random copolymer layer was overall symmetric in composition, the individual random copolymer chains displayed a large *chemical* dispersity. In experiments evaluating the interface-toughening ability of random copolymers at an immiscible AB interface,[36] it is found that random copolymers can provide a far tougher interface than is possible if the chains were really characterized by a single 50−50 composition.[37] The current speculation is that an imbalance of reactivity ratios results in a composition creep during the synthesis of the random copolymer. If this is the case in this experiment, then the random copolymer layer may show structure, with chains with a majority of A segregating toward the substrates, leaving a relatively rich B layer in contact with the diblock film. Thus, unless the composition and the chemical dispersity of the random copolymer layer is tuned finely, the surface layers could show a wetting preference.

When the surface is enriched fully with a single monomer, say type A, we determined that the incommensurability and the nematic effects can destabilize the parallel morphology, producing perpendicular films. We stress that the surface layer must be impenetrable for this to work. If the surface were penetrable, for example the surface of a molten A homopolymer layer of molecular weight $N/2$, then the interfacial tensions near the substrate in the vicinity of the AB junction cannot support the perpendicular morphology. The interfacial tension between the A domain and the substrate vanishes. The interfacial tension between the B domain and the substrate, $\gamma_B = \gamma_{AB}$, the interfacial tension at the AB lamellar interface. Mechanical stability of the perpendicular lamellae is assured by Young's law only when the AB interface is parallel to the substrate.

If the substrate were impenetrable however, $\gamma_B \approx \chi$, while $\gamma_{AB} \approx X^{1/2}$, and the layer may yet be stable. Thus, if a homopolymer prelayer is applied, it should be of such a large molecular weight that it remains glassy during the annealing of the diblock film. Alternatively, the surface layer could be a self-assembled monolayer end-functionalized with A monomer, or the homopolymer layer could be cross-linked densely enough to prevent interpenetration with the diblock layers.

Conclusion

Using a numerical model for the system of ref 8, we have systematically explored how the equilibrium film morphology is affected by incommensurate film thicknesses and an imbalance in the surface interaction A and B monomers. When the surfaces are smooth, rigid, and neutral, the lamellar order always establishes itself perpendicularly to the confining walls. When the surface is made entirely out of A monomers, the experimentally observed transition between perpendicular and parallel morphologies is recapitulated. The results provide guidelines for fabricating the technologically useful perpendicular orientation. In particular, it suffices in experiments of the types executed in ref 8 to choose the neutralizing prelayer to be a high molecular weight homopolymer A, rather than a statistical copolymer. Also, the film thickness should be chosen so that a half-integral number of unstrained lamellae fit in the gap. Taken together, these criteria will facilitate the fabrication of polymer surfaces that can be decorated with well-defined domains of metallic compounds, and thus they may prove useful in novel optical or electronic applications.

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References and Notes

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(26) To induce the parallel morphology to appear, we force the self-consistent potential U to be translationally invariant in the x-direction. Then, the converged solution also displays this invariance, so there is a composition modulation only in the z-direction.
(27) To determine the properties of the bulk lamellar phase, we replace the confining substrates with periodic boundaries and apply eq 2. The free energy given in eq 2 takes a uniformly mixed state as its zero.
(28) To induce the perpendicualar morphology of the lamellae, we implement periodic boundary conditions in both the x- and z-directions and choose the self-consistent potential to be invariant in the z-direction. Once we have a converged solution in these circumstances, we relax the constraint on U, thus allowing variations in the z-direction. Also, we impose hard wall boundary conditions at $z = 0$ and $z = L + 1$. We then recalculate the self-consistent potential, U, thus arriving at a state in which the lamellae are perpendicular to the substrates.
(29) With $\chi = 0$, and with hard wall conditions in the z-direction, the free energy given by eq 2 is calculated. The appropriate reference state in this case is not the lamellar microphase

but rather an ideal melt of homopolymers. Then, $\gamma = F/L$ is calculated.

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