A Free Energy Model for Confined Diblock Copolymers

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Introduction

The nature of the microphase separation transition in diblock copolymer systems has been studied extensively, both theoretically[1-4] and experimentally.[5-7] It is well-known that symmetric A-B diblock copolymers (composed of nearly equal fractions of A and B segments) form alternating lamellar structures if the copolymer molecular weight is sufficiently high. In thin films the lamellae are experimentally found to orient parallel to the substrate due to surface energy differences between the A and B blocks or to preferential interactions of the blocks with the substrate.[8-11] In cases where one block segregates preferentially to both surfaces, a symmetric film structure is produced with a thickness nL_0, where L_0 is the bulk equilibrium lamellar period and n is an integer. If the initial film thickness does not conform to nL_0, islands or holes are observed on the surface with a step height of L_0. The formation and growth of these surface topology characteristics have been studied[12,13] along with their relation to the internal organization process of the copolymer.[14]

Recent experiments on copolymer films confined between two hard parallel surfaces have demonstrated that confinement suppresses step formation and results in a lamellar period, L, that is perturbed from L_0 when the plate separation $D \neq nL_0$.[15,16] Confinement of copolymer melts has also been treated theoretically.[17-19] Turner[18] developed a phenomenological free energy model for the strong segregation limit which considers symmetric and antisymmetric lamellar morphologies organized parallel to the confining surfaces. Antisymmetric film structures were predicted to be favored for D values approaching $(n + 1/2)L_0$ since, in this regime, the entropic penalty associated with chain deformation is larger than the energetic penalty of having the B block adjacent to one of the substrates. Kikuchi and Binder[19] performed Monte Carlo simulations that incorporate a surface field which is repulsive to one of the blocks. Different orientations were reported on the basis of the relationship between the bulk equilibrium lamellar period L_0 and the film thickness D. For cases where L_0 and D are compatible, a horizontal orientation is indicated. For cases where L_0 and D are not compatible, a vertical orientation or a coexistence of the two orientations is observed. In a one-dimensional self-consistent field treatment, Shull[17] predicted a lamellar orientation parallel to the confining substrates in both the weak and strong segregation regimes. Layers closest to the walls were calculated to be thinner than half the layer thickness in the center of the film. With varying film thicknesses, the transition between n and $n + 1$ layers was shown to be continuous for $n = 1$ and discontinuous for $n > 1$. Alternate orientations of the lamellar microdomains were not considered in this treatment, however.

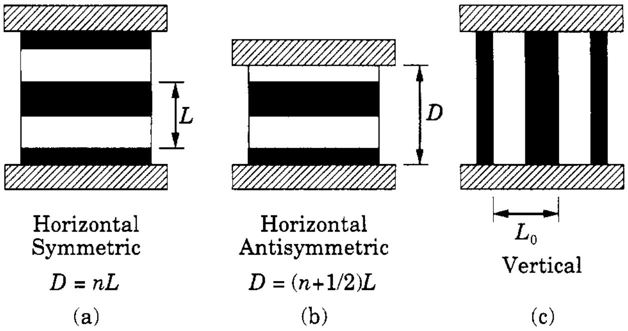

Figure 1. Schematic illustration of lamellar morphologies for copolymer systems confined between two parallel substrates. (a) A horizontal symmetric morphology with the lower energy block adjacent to both of the substrates. The number of layers, n, and the lamellar period, L, depend on the plate separation, D, such that $D = nL$. (b) A horizontal antisymmetric morphology with each block adjacent to one of the substrates. There are a half-integral number of layers such that $D = (n + 1/2)L$. (c) A vertical lamellar morphology where the bulk equilibrium lamellar period, L_0, is realized.

In this paper, the treatment of Turner is extended to include the possibility of a vertical orientation of the lamellar morphology. A free energy model is constructed for confined diblock copolymers organized normal to the walls and compared to the symmetric and antisymmetric horizontal cases. The vertical orientation is shown to be favored over both horizontal structures in a limited range of film thicknesses that depends on the material parameters of the confined structure.

Model Description

For simplicity, the model assumes that the copolymer is compositionally symmetric, with A and B blocks having an equal number of segments $N/2$, each of persistence length a. The model is valid for a system well within the ordered regime, i.e. the strong segregation limit.

The driving force for microphase separation in bulk copolymer systems is easily demonstrated through a phenomenological free energy model that balances the decrease in interfacial energy from segregating the A and B blocks with the entropic penalty for deforming the chains from their disordered state conformation. The resulting bulk free energy, F, is approximated by[3]

$$\frac{F}{kT} = \frac{3p}{8Na^2}L^2 + \frac{2pNa}{L}\sqrt{\frac{\chi}{6}} \tag{1}$$

where p is the number of copolymer chains in the system, χ is the Flory-Huggins segmental interaction parameter that quantifies the net A-B segmental repulsion, and L is the lamellar period. Minimization of eq 1 with respect to L gives the bulk equilibrium lamellar period as

$$L_0 = 2\left(\frac{1}{3}\sqrt{\frac{\chi}{6}}\right)^{1/3} N^{2/3}a \tag{2}$$

Equation 2 correctly predicts the experimentally observed scaling[5-7] of the lamellar period with copolymer molecular weight, $L_0 \sim N^{2/3}$. The corresponding bulk equilibrium free energy is given by

$$\frac{F_0}{kT} = \frac{3p}{2}\left(\frac{\chi}{2}\right)^{1/3} N^{1/3} \tag{3}$$

Turner's model of a block copolymer system confined between infinite, parallel plates extends this bulk free energy model with the addition of surface interaction terms.[18] His system is defined such that $\gamma_{AS} \le \gamma_{BS}$, where γ_{AS} and γ_{BS} are the A block/substrate and B block/substrate interfacial tensions, respectively. The free energy of a symmetric system, in which the A block is adjacent to both substrates (Figure 1a), and the free energy of an antisymmetric system, in which each block is adjacent to one of the substrates (Figure 1b), are approximated by

$$\frac{F_h}{F_0} = \frac{1}{3}\left\{\lambda^2 + \frac{2}{\lambda} + \frac{1}{m\lambda}\left[2\Gamma + \delta\left(\frac{1-(-1)^{2m}}{2}\right)\right]\right\} \qquad (4)$$

where $m = n$ for a horizontal symmetric morphology and $m = n + {}^1/_2$ for a horizontal antisymmetric morphology. The normalized period λ is given as

$$\lambda = L/L_0 \qquad (5)$$

and Γ and δ are defined as

$$\Gamma = \gamma_{AS}/\gamma_{AB} \qquad (6)$$

and

$$\delta = \frac{\gamma_{BS} - \gamma_{AS}}{\gamma_{AB}} \qquad (7)$$

where γ_{AB} is the interfacial tension between the A and B blocks.

In the vertical morphology (Figure 1c), the imposed thickness constraint acts perpendicular to the lamellar ordering, and unless $D < L_0/2$, the bulk equilibrium period L_0 is realized. The key to analyzing the vertical morphology is to recognize that the amount of interface between each copolymer block and the substrate is identical to the horizontal antisymmetric case studied by Turner. Since the sample volume is fixed by the amount of copolymer present, assuming a constant monomer density leads to a plate separation that can be defined as $D = mL$, where both m and L are the values that would be realized by the *horizontal* system. By direct analogy to Turner's free energy expression in eq 4, the free energy of the vertical morphology is expressed as

$$\frac{F_v}{F_0} = \frac{1}{3}\left[3 + \frac{1}{m\lambda}(2\Gamma + \delta)\right] \qquad (8)$$

The horizontal free energy eq 4 and the vertical free energy eq 8 are shown in Figure 2 for $\delta = 0.15$. The vertical morphology is favored over the horizontal morphology when $F_v < F_h$. By subtracting eq 8 from eq 4, a vertical morphology is found to be favored over a horizontal *antisymmetric* morphology when

$$\lambda^3 - 3\lambda + 2 > 0 \qquad (9)$$

which is realized for *all* λ, except at $\lambda = 1$ where the two morphologies are degenerate. The vertical morphology is favored over a horizontal *symmetric* morphology when

$$\lambda^3 - 3\lambda + 2 - \frac{\delta}{n} > 0 \qquad (10)$$

which is realized for λ in the regions $\lambda < \lambda_-$ and $\lambda > \lambda_+$, where λ_- and λ_+ are the two positive roots of eq 10 and $\lambda_+ > \lambda_-$. The two morphologies are degenerate at $\lambda = \lambda_-$ and $\lambda = \lambda_+$.

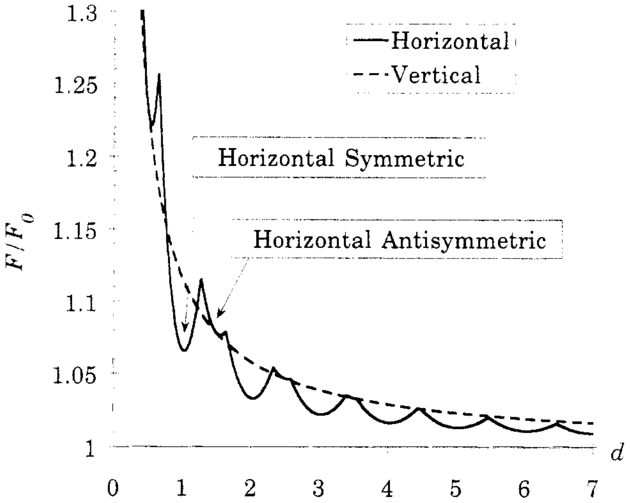

Figure 2. Free energy of the horizontal (eq 4) and vertical (eq 8) morphologies for $\delta = 0.15$ as a function of the reduced plate separation, $d = D/L_0$. Note that the vertical morphology is always favored over the horizontal antisymmetric morphology.

The change in the lamellar period (with corresponding chain deformation) is limited to less than half of the bulk equilibrium period. This restriction arises from the fact that further deformation would be accompanied by a change in the number of lamellae, n:

$$-\frac{1}{2} < n(\lambda - 1) < \frac{1}{2} \qquad (11)$$

The combination of eqs 10 and 11 leads to a critical number of layers

$$n_{\pm} = \left[\left[\frac{3 + \sqrt{9 \pm 8\delta}}{8\delta}\right]\right] \qquad (12)$$

where n_+ and n_- are for chains expanded and contracted from their bulk equilibrium conformation, respectively, and $[[x]]$ denotes the greatest integer less than or equal to x. Above this critical number of layers, a horizontal symmetric morphology is always favored, and below it, a horizontal symmetric or vertical morphology is favored, depending on the value of λ as in eq 10. Equation 12 can be rewritten to examine the critical values of δ as a function of the number of layers as

$$\delta_{\pm} = \frac{6n \pm 1}{8n^2} \qquad (13)$$

Subtracting the lower bound given in eq 13 from the higher yields

$$\delta_+ - \delta_- = 1/4n^2 \qquad (14)$$

Thus, the range over which the morphology depends on chain conformation reaches a maximum of ${}^1/_4$ at $n = 1$ and vanishes for large values of n. These results are shown in Figure 3. Note that for $\delta = 0.15$, the case in Figure 2, $n_+ = 5$ and $n_- = 4$, indicating that for contracted chains, a horizontal symmetric morphology is expected for $n > 4$ layers, while for expanded chains, only a horizontal symmetric morphology persists for $n > 5$ layers.

Figure 4 shows the lamellar period as a function of the sample thickness for $\delta = 0.15$. Note that wherever the vertical morphology is favored, $\lambda = 1$. Figure 4 indicates that the period is confined between two envelopes. The vertical/horizontal envelope limits λ for values below the critical n where both vertical and horizontal symmetric morphologies are expected. In this region, λ is limited to values $\lambda_- \le \lambda \le \lambda_+$. The horizontal envelope limits λ for values above the critical n where only the horizontal

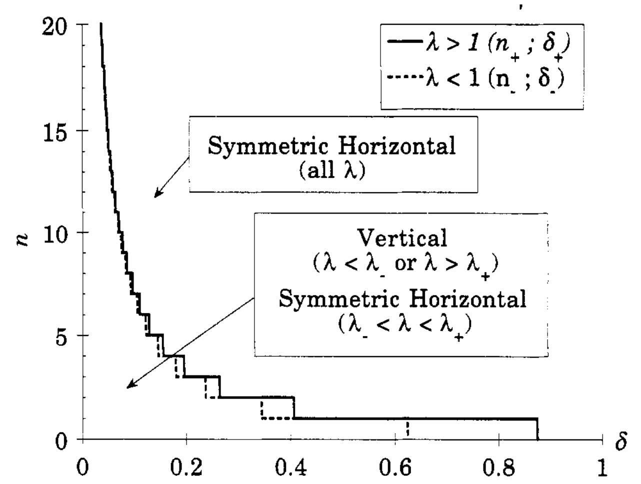

Figure 3. Critical number of layers (critical values of δ), above which only a symmetric horizontal morphology is found, and below which a symmetric horizontal or vertical morphology is found.

symmetric morphology is predicted. In this region, λ is limited to values dictated by eq 11. Recent experimental results on confined films of poly(styrene-*b*-methyl methacrylate)[15] and poly(styrene-*b*-isoprene)[16] quantitatively demonstrate this variation of λ with film thickness.

As shown in eq 10, the region over which the vertical morphology is favored depends directly on δ. Hence it would be useful in testing these predictions to have some means to tune this value experimentally. Equation 7 shows that δ can be varied by either changing the chemical structure of the A and B blocks or by tailoring the substrates to modify the surface interaction parameters. The latter can be realized by incorporating a thin layer of A/B random copolymer between the substrates and the diblock. If the fraction of the A monomer in the random copolymer is ϕ, the interfacial tensions between the substrates and the two blocks can be approximated by

$$\gamma_{AS} = (1 - \phi)\gamma_{AB} \tag{15}$$

and

$$\gamma_{BS} = \phi\gamma_{AB} \tag{16}$$

The previously imposed condition that $\gamma_{AS} \leq \gamma_{BS}$ now reduces to $\phi \geq {}^1/_2$. Combination of eqs 15 and 16 with eq 7 leads to a new relationship for δ:

$$\delta = 2\phi - 1 \tag{17}$$

By incorporating a random A/B copolymer "buffer" layer between the substrates and the diblock, the presence of a vertical morphology would depend solely on the fraction of A in the random copolymer. One interesting case to consider is a random copolymer comprised of 50% A block. In this case $\delta = 0$ and eq 10 reduces to the same expression as eq 9. Thus the vertical morphology is favored for all values of λ except for $\lambda = 1$, where the vertical and horizontal symmetric morphologies are equally probable. Using this approach, we have recently been successful in inducing orientation of lamellar microdomains normal to the confining walls. These results will be reported in a separate article shortly.

Dissimilar Substrates

The condition of identical confining surfaces can easily be relaxed by defining two chemically distinct substrates such that $\delta_1 \leq \delta_2$ and rewriting eq 4 as

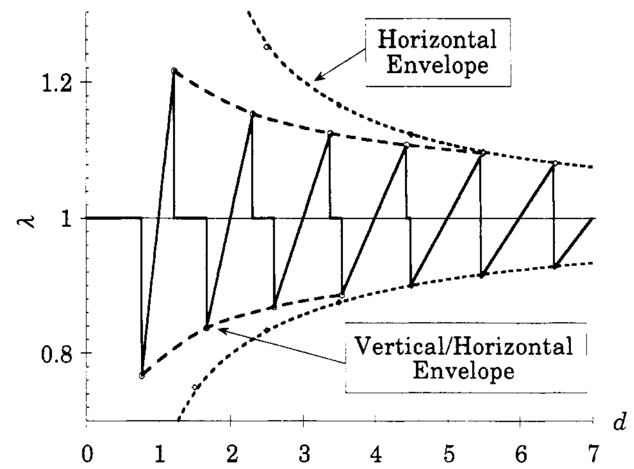

Figure 4. Reduced lamellar period, λ, as a function of reduced plate separation, $d = D/L_0$, for $\delta = 0.15$. Wherever the vertical morphology is favored, the bulk equilibrium lamellar period, L_0, is realized, thus $\lambda = 1$.

$$\frac{F_h}{F_0} = \frac{1}{3}\left\{\lambda^2 + \frac{2}{\lambda} + \frac{1}{m\lambda}\left[\Gamma_1 + \Gamma_2 + \delta_k\left(\frac{1-(-1)^{2m}}{2}\right)\right]\right\} \tag{18}$$

where *k* is the index of the substrate which is adjacent to the B block for the antisymmetric horizontal case, and by rewriting eq 8 as

$$\frac{F_v}{F_0} = \frac{1}{3}\left\{3 + \frac{1}{m\lambda}\left[\left(\Gamma_1 + \frac{\delta_1}{2}\right) + \left(\Gamma_2 + \frac{\delta_2}{2}\right)\right]\right\} \tag{19}$$

Following the method detailed above for identical substrates, the vertical morphology is found to be favored over a horizontal antisymmetric morphology for *dissimilar* substrates when

$$\lambda^3 - 3\lambda + 2 + (-1)^k\frac{\delta_2 - \delta_1}{2n + 1} > 0 \tag{20}$$

which is realized for all λ, when $k = 1$. When $k = 2$, however, there exists a region where the horizontal antisymmetric morphology is favored over the vertical morphology. The vertical morphology is favored over a horizontal symmetric morphology when

$$\lambda^3 - 3\lambda + 2 - \frac{\delta_1 + \delta_2}{2n} > 0 \tag{21}$$

which occurs over a limited regime, analogous to the case of identical substrates.

Conclusions

It was shown that for diblock copolymer films confined between two infinite, parallel plates, a vertical morphology is possible where the lamellar period of the bulk is realized. A critical number of layers was derived, below which the morphology can be either vertical or horizontal symmetric, depending on the extent of chain deformation. Above this critical number of layers, only a horizontal symmetric morphology is predicted. The fact that a horizontal symmetric morphology is favored for thicker films is not surprising, since in this case, any chain deformation can be distributed over many layers, thus effectively eliminating the entropic penalty that stabilizes the vertical morphology. It has also been shown that the horizontal antisymmetric morphology predicted by Turner[18] is never favored when the two confining substrates are chemically identical but that it is metastable whenever the vertical morphology is anticipated. When the two substrates are dissimilar, however, there exists a limited regime over which the antisymmetric morphology can be realized.

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