

Immiscibility of large and small symmetric diblock copolymers

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We examine binary mixtures of large and small symmetric AB diblock copolymers using self-consistent field theory. In accord with experiment, we find that when the ratio of their polymerization indexes exceeds about 1:5, they become immiscible producing a coexistence between long- and short-period lamellar phases. As in experiment, the short-period phase contains few large diblocks, but the long-period one contains a substantial volume fraction of small diblocks. © 1995 American Institute of Physics.

One of the most straightforward and commercially viable approaches of producing new materials and tailoring their characteristics is achieved by blending different atomic and/or molecular species to form a single homogeneous material. By varying the composition of the blend, it is possible to control the properties of the material, such as its strength, weight, flexibility, and durability. Not only does blending often produce superior materials, it is also a very economical process. The materials that result from it, such as metallic alloys and various plastics, are components in many of the commercial products that we encounter in everyday life. As commercial uses develop for block copolymer materials, it is inevitable that blending will become increasingly important in controlling their properties.

A particularly relevant issue when producing a blend is the miscibility of its components. For metals¹ and plastics,² there exists a rather thorough understanding of what causes the components to become immiscible and phase separate. At present, little is known regarding the conditions that lead to macrophase separation in block copolymer blends. The need for such an understanding is clear, and, accordingly, the study of copolymer blends has seen a rapid growth in the last couple of years. Most of this work has focused on binary AB diblock copolymer melts. One of the more intriguing results emerging from this work is that diblocks of similar composition but dissimilar molecular weights phase separate. This result has been demonstrated for both lamella-forming diblocks³ and sphere-forming ones.⁴ Theoretical work^{5,6} has so far failed to explain this phenomenon, suggesting that it may occur due to a nonequilibrium effect.

In this Letter, we use self-consistent field theory (SCFT)⁷ to examine the miscibility of two lamella-forming AB diblock copolymers with different polymerization indexes. The small and large diblocks are composed of N_s and N_l segments, respectively. Both species are symmetric with equal numbers of A and B segments. We define the A and B segments to have equal volumes, $1/\rho_0$, and we assume that they have equal segment lengths, a . The immiscibility between A and B segments is controlled through the Flory–Huggins parameter, χ . The application of the SCFT to a diblock/homopolymer blend is described in Ref. 8 and is easily generalized to the present binary diblock system.

Previous work^{5,6} on symmetric diblock blends used the

strong-segregation theory (SST),⁹ which is the zero-temperature limit of the SCFT. According to the SST, these blends are completely miscible and always produce a single lamellar phase. The Helmholtz free energy, F , of this phase is given by

$$\frac{N_l F}{k_B T \rho_0 V} = \frac{\pi^2 D^2}{32 a^2 N_l} \frac{\alpha + (1 - \alpha) q_l^3}{[\alpha + (1 - \alpha) q_l]^3} + \frac{2 a N_l}{D} \left(\frac{\chi}{6} \right)^{1/2}, \quad (1)$$

where $\alpha \equiv N_s/N_l$, q_l is the number fraction of the large diblocks, and D is the lamellar spacing. The first term in Eq. (1) results from the entropic stretching energy of the copolymers,^{10–12} and the second term is due to the interfacial tension between A- and B-rich domains.⁵ Minimizing F with respect to D gives the equilibrium spacing,

$$\frac{D}{a N_l^{1/2}} = 2 \left(\frac{8 \chi N_l}{3 \pi^4} \right)^{1/6} \frac{\alpha + (1 - \alpha) q_l}{[\alpha + (1 - \alpha) q_l^3]^{1/3}}. \quad (2)$$

Substituting this back into Eq. (1) gives

$$\frac{N_l F}{k_B T \rho_0 V} = \frac{3}{4} \left(\frac{\pi^2 \chi N_l}{3} \right)^{1/3} \frac{[\alpha + (1 - \alpha) q_l^3]^{1/3}}{\alpha + (1 - \alpha) q_l}. \quad (3)$$

If one plots F in terms of the volume fraction of the short diblock, ϕ_s , using the relation

$$q_l = \alpha(1 - \phi_s)/[\phi_s + \alpha(1 - \phi_s)], \quad (4)$$

one finds that its curvature is strictly positive (i.e., $d^2 F/d\phi_s^2 > 0$) for all values of α . This implies that large and small diblocks will never phase separate,¹³ contrary to experiment.

As we demonstrate below, this disagreement is a consequence of the SST, which assumes that the copolymers have their junctions located on infinitely narrow interfaces with their blocks extending outward along straight paths. When we examine this system using SCFT, which allows a finite width in the distribution of junctions and fluctuations in the trajectories of copolymers, macrophase separation does occur in excellent agreement with experiment. Below, we present the phase behavior of the SCFT in terms of the three coordinates, χN_l , $\alpha \equiv N_s/N_l$, and ϕ_s . In order to visualize the phase diagram, we present various two-dimensional slices through it.

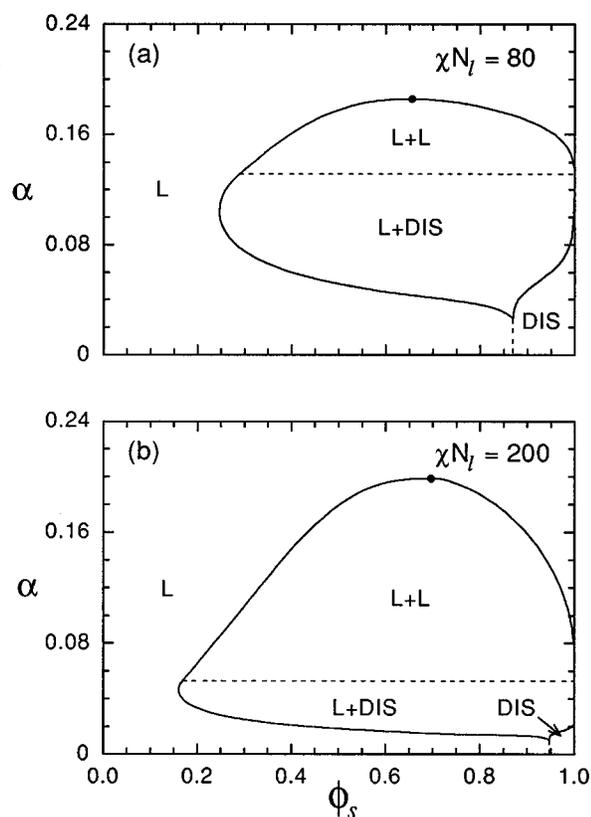


FIG. 1. Slices through the phase diagram at constant χN_l plot in terms of $\alpha \equiv N_s/N_l$ and the volume fraction of small diblocks, ϕ_s . Dots denote critical points below which the lamellar (L) phase separates into two coexisting lamellar (L+L) phases. The L+DIS coexistence region occurs when the short-period L phase disorders. Binodals and continuous transitions are denoted with solid and dashed lines, respectively.

To begin, we show slices through the phase diagram in Fig. 1 with χN_l held fixed at 80 and 200. When α is close to one, the large and small diblocks are completely miscible and form a single lamellar (L) phase. However, at $\alpha \sim 0.2$, critical points are encountered below which the melt separates into two coexisting lamellar (L+L) phases, a long-period one rich in large copolymers and a short-period one of mostly small copolymers. As α decreases, the short-period lamellar phase disorders via a continuous second-order transition at $\chi N_l \alpha \approx 10.495$ producing a L+DIS coexistence region. As α is reduced further, the entropy of mixing causes the L+DIS region to diminish eventually producing a tricritical point and then a continuous transition separating the L and DIS phases. For $\alpha \approx 0$, entropy of mixing tends to distribute the small copolymers uniformly throughout the melt. Thus, the “dilution” approximation¹⁴ becomes valid, and, therefore, the continuous transition is located at $\chi N_l(1-\phi_s) \approx 10.495$. In reality, fluctuations will cause the continuous transitions to become first-order producing small biphasic windows¹⁴ like the one reported in Ref. 15.

In Fig. 2 are slices through the phase diagram with α fixed at 0.10 and 0.04. At large χN_l , the melt can separate into coexisting lamellar (L+L) phases. Consistent with experimental observations,³ the long-period lamellar phase contains typically 15% to 35% small diblocks by volume,

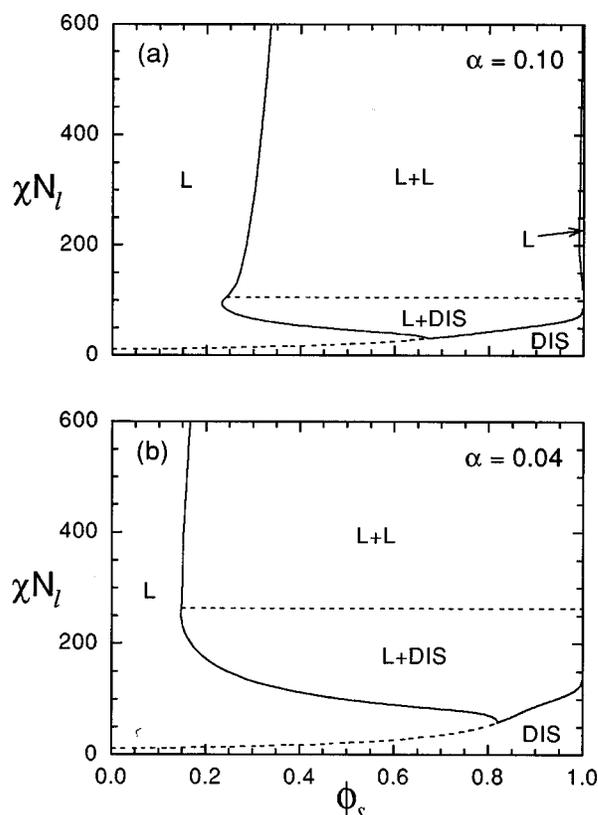


FIG. 2. Slices through the phase diagram similar to those in Fig. 1, but for constant α .

whereas very few large copolymers are found in the short-period phase. For $\alpha=0.04$, the short-period phase is so pure that its region of stability is not visible on the scale of Fig. 2(b). As χN_l increases, the long-period phase is able to solubilize more of the short copolymers, thus, reducing the size of the L+L region. Eventually, this region must disappear in accordance with the prediction of the SST. However, we find that χN_l must become extremely large, probably on the order of 10^4 , before this occurs. Approaching the weak-segregation limit, the short-period lamellar phase disorders at $\chi N_l \alpha \approx 10.495$ resulting in the L+DIS region. As χN_l decreases further, entropy of mixing again causes the L+DIS region to shrink producing a triple point followed by a critical line that terminates at $\chi N_l = 10.495$ and $\phi_s = 0$.

Although the SST is not sufficient to produce the regions of negative curvature in the free energy that lead to macrophase separation, it does predict the lamellar spacing, D , reasonably well. This is demonstrated in Fig. 3. There we plot D vs ϕ_s for $\chi N_l = 200$ at $\alpha = 0.25$ and 0.10. The SCFT results are shown with solid lines. For $\alpha = 0.10$, a two-phase region occurs for $\phi_s = 0.286$ to 0.990 in which two lamellar phases coexist with periods $D/aN_l^{1/2} = 1.437$ and 0.526. In this region, we have plotted the period of the single metastable phase with a dotted line. The dashed lines in Fig. 3 show the results using SST [i.e., Eq. (2)]. The SST does well considering that for the small diblocks χN_s is only 50 and 20 when $\alpha = 0.25$ and 0.10, respectively. Despite the slight

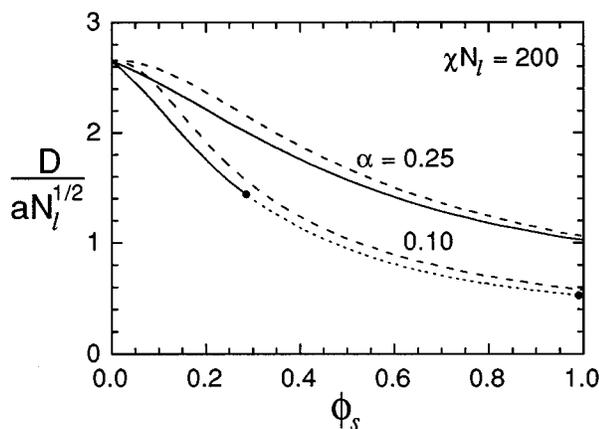


FIG. 3. Lamellar spacing, D , vs the volume fraction of small copolymers, ϕ_s , plotted for $\chi N_l=200$ and $\alpha=0.25$ and 0.10 . Results using SCFT and SST are shown with solid and dashed lines, respectively. A dotted line is used in the region where SCFT predicts macrophase separation.

flaw¹² in Ref. 5, the period they obtained using SST behaves similarly to Eq. (2), and their conclusion still holds that the SST produces an improved functional form for the lamellar spacing over $D \sim \chi^{1/6} N_n^{2/3}$ suggested by Ref. 16, where $N_n = N_l(\alpha + (1-\alpha)q_l)$ is the number-averaged polymerization.

In Fig. 4, we show profiles of the A -monomer density, $\phi_A(z)$, for the two coexisting lamellar phases at $\chi N_l=200$ and $\alpha=0.10$. The short-period phase in Fig. 4(a), contains just 1.0% large diblocks by volume. Their contribution to $\phi_A(z)$ is greatest in the middle of the A -rich lamellae but even there the contribution is only 0.015. For the long-period phase in Fig. 4(b), there is a significant contribution to $\phi_A(z)$ due to the small copolymers. We show it using a dashed line. As found previously by both SCFT¹⁷ and experimental measurements,¹⁸ the short A blocks are preferentially located near the interfaces. The dotted line shows the prediction of the SST^{6,10} demonstrating that it inaccurately predicts the monomer profiles even at this high degree of segregation. When we increased χN_l by an order of magnitude, we find the SST is still inaccurate in this regard.

In summary, we have theoretically predicted the phase separation observed in blends of symmetric AB diblocks. The details of our calculation agree well with the available experimental results.³ Small and large diblocks are completely miscible if the ratio of their molecular weights is no greater than about 1:5. As this ratio is exceeded, the blend can phase separate into two distinct lamellar (L+L) phases or coexisting lamellar and disordered (L+DIS) phases. We find asymmetric solubility of the minority species, i.e., typically the small-copolymer-rich phase is nearly pure whereas the large-copolymer-rich phase contains a substantial amount of small diblocks. In this latter case, we find that the small diblocks are preferentially located near the interfaces as found experimentally.¹⁸ Although, we find the SST poorly approximates the free energy and the monomer distributions of the SCFT, it does provide a good analytic expression for the lamellar spacing, Eq. (2), which should prove to be more accurate than the empirical one proposed by Ref. 16. Although, the behavior described here is for two lamella-

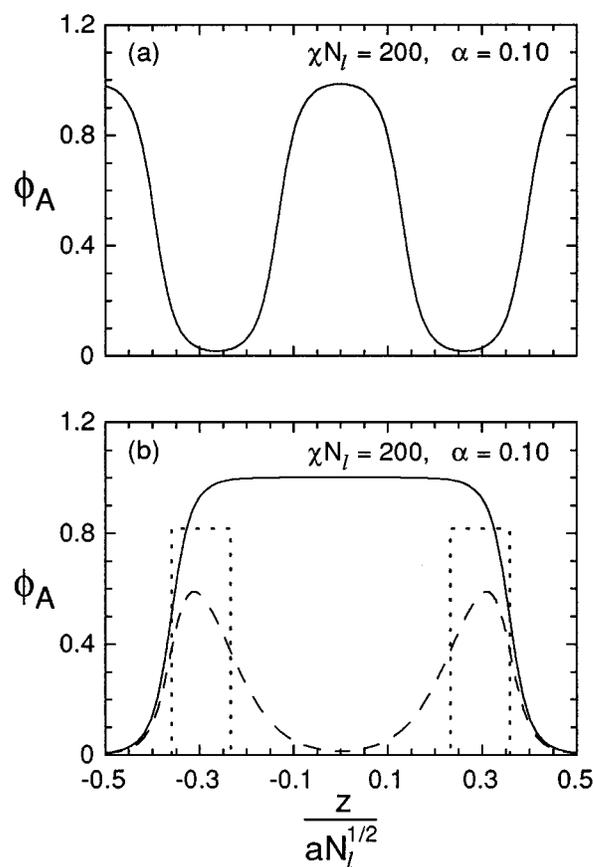


FIG. 4. Profiles of the A -monomer density, $\phi_A(z)$, for the (a) short- and (b) long-period lamellar phases coexisting at $\chi N_l=200$, $\alpha=0.10$, and $\phi_s=0.286$ to 0.990 . In case (b), the contribution due to the short copolymers as predicted by the SCFT and SST is plotted with dashed and dotted lines, respectively.

forming diblocks, we expect analogous behavior for other diblock pairs having equal A -monomer fractions but different molecular weights as experiments⁴ have already indicated.

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¹²Because Ref. 5 treats the large blocks improperly in the region occupied by the small blocks, they obtain an incorrect expression for the stretching energy in Eq. (1).

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