Lamellar Phase of a Symmetric Triblock Copolymer

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ABSTRACT: We study the lamellar phase formed by symmetric ABA triblock copolymers with degree of polymerization N and A monomer fraction f. Employing a mean-field, lattice formalism, we calculate the fraction of copolymers which bridge the B-rich lamellae. This fraction is found to be significant, although it is strictly bounded above by $1/2$ within the formalism. Once the lamellar phase is strongly segregated, the fraction of bridges decreases slowly with increasing N, increasing Flory parameter χ, and decreasing f. In the strong-segregation limit, the lamellar spacing D is found to scale as $D \sim N^a \chi^b$ with $a = 0.68$ and $b = 0.19$. The interfacial width ξ does not scale as a power of N but does scale with χ as $\xi \sim \chi^c$, where $c = -0.51$. Both D and ξ are nearly independent of f.

1. Introduction

Copolymer melts exhibit a rich variety of structured phases when the different copolymer blocks are incompatible. Of the many copolymer architectures studied, most work has concentrated on the simple diblock. Recently, the linear triblock has also been studied. Most of this work[1-7] has focused on the symmetric triblocks in which the two end blocks are identical.

Mayes and Olvera de la Cruz[8,9] have calculated the phase diagram of the ABA triblock copolymer system. Their results show that the phase diagram is very similar to that calculated for the simpler AB diblock copolymer system,[10-13] with both systems exhibiting lamellar, hexagonal, and cubic phases in the same sequence. Experiments have supported this.[1-4] This result is not too surprising since cutting the triblock in the middle produces two diblocks. The entropy gained from doing this is thought to be small,[1,2,14] so that the free energy of triblocks in a particular phase is nearly the same as that of twice as many diblocks of half the length in their analogous phase. Consequently, the phase diagram remains much the same.

In this paper, we concentrate on the lamellar phase of the triblock system. In both the ABA triblock and AB diblock systems, this phase occurs when the fraction of A monomer content of the copolymer, f, is about one-half. There are many similarities between the lamellar phases of these two systems. Theoretical evidence suggests that, in the strong-segregation limit, the lamellar spacing, D, scales with respect to N, the degree of polymerization, and χ, the Flory–Huggins parameter, as $D(N,\chi) \sim N^a \chi^b$, where the exponents a and b are the same for both copolymer systems.[14,15] This is supported by experiment.[1,16,17] Both theory[10,11,15,18-21] and experiment[3,16,22-25] agree that $a \approx 2/3$. (Two notable exceptions are the experiments in refs 1 and 26, which both find $a \approx 4/5$.) The value of the second exponent is not as well established. Most theoretical[10,11,18,19,27] determinations of b agree on the value of $1/6$, whereas the limited experimental measurements[22,28] obtain $1/3$. One should also expect the interface between lamellae to have the same profile and width, ξ, in the triblock and diblock systems.[14] Thus, in the strong-segregation limit, we expect $\xi(N,\chi) \sim \chi^c$, where $c \approx -1/2$.[10,18,19]

There is one notable difference between a system of ABA triblocks and the system of AB diblocks formed by

cutting the triblocks in half. In the former, there is a distinction between those conformations in which the two A blocks of a given triblock are located in different A-rich lamellae, forming bridges between them, and those in which they are located in the same lamella, forming loops. Presumably, the presence of the bridges alters the mechanical properties of the triblock melt from that of the diblock.[5-7] A recent experiment[2] comparing triblock and diblock melts has detected some difference in their dynamical mechanical properties which is attributed to this effect.

We calculate the ratio of bridges to loops as a function of N, χ, and f using a lattice model which is solved within a mean-field approximation. The use of a lattice should have no qualitative effect on the results provided that the lamellar spacing is large compared with the lattice spacing, which is taken to be the average Kuhn length of the monomers. Mean-field theory should be adequate for such systems because the effect of fluctuations is small except for temperatures extremely close to the transition temperature between disordered and lamellar phases.[29,30] In the process of calculating the desired ratio, it is necessary to calculate the equilibrium lamellar spacing. We take the opportunity, therefore, to examine the scaling properties of this spacing in both the strong- and weak-segregation limits and that of the width of the A/B interface.

2. Theory

The monodisperse copolymer melts which we study contain symmetric ABA triblocks in which each end block consists of N_A A monomers and the central block consists of N_B B monomers. Hence, the degree of polymerization is $N = 2N_A + N_B$, the A block fraction is $f = 2N_A/N$, and the symmetry parameter introduced by Mayes and Olvera de la Cruz[8,9] is $\tau = 0.5$. We label the monomers of each copolymer sequentially, $s = 1, 2, 3, ..., N$, and treat the two ends of the copolymer as distinguishable. We later correct the entropy for the fact that the copolymers are symmetric and thus indistinguishable under the transformation $s \rightarrow N + 1 - s$.

We follow closely the lattice-model formalism of Scheutjens and Fleer.[31,32] The copolymers are placed on a lattice of coordination number z, with each lattice site being occupied by one monomer (*i.e.*, the melt is treated as incompressible). Periodic boundary conditions are applied to the lattice. Because we expect these symmetric copolymers to form a lamellar phase,[8] we divide the lattice into layers labeled by $i = 1, 2, 3, ..., M$. Each layer

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consists of L lattice sites, and thus the lattice has a total of LM sites. For a site in layer i, the fraction of its nearest-neighbor sites in layer $i + \delta$ is given by λ_δ (*e.g.*, for the fcc lattice we employ with layers in the (111) direction, $z = 12$, $\lambda_0 = {}^1/_2$, $\lambda_1 = \lambda_{-1} = {}^1/_4$, and all other $\lambda_\delta = 0$.)

In the Scheutjens–Fleer formalism, individual copolymer configurations are grouped according to the layers in which their monomers occur. The configuration group $c = \{i_1, i_2, ..., i_N\}$ is the set of all copolymer configurations in which the sth monomer occurs in layer i_s for $s = 1, 2, 3, ..., N$. Note that this grouping precludes the investigation of phases with concentration variations in more than one direction, as in cubic and hexagonal phases. It is convenient to define a few quantities in order to develop this formalism. Let $\gamma(s)$ specify the type, A or B, of the sth monomer and $k(s,c)$ specify the layer in which this monomer appears when in configuration group c. The related function, $\Delta(s,c) \equiv k(s+1,c) - k(s,c)$, specifies how a copolymer in configuration group c steps between the layers. Lastly, we define

$$r_{i,\alpha,c} = \sum_{s=1}^{N} \delta_{\alpha,\gamma(s)} \delta_{i,k(s,c)} \qquad (1)$$

where $\delta_{a,b}$ is the Kronecker delta so that $r_{i,\alpha,c}$ is the number of α monomers found in layer i from a copolymer which is in configuration group c.

The total number of copolymer configurations in group c, including those in which the copolymer intersects itself, is given by

$$\Omega_c = Lz^{N-1} \prod_{s=1}^{N-1} \lambda_{\Delta(s,c)} \equiv Lz^{N-1} \omega_c \qquad (2)$$

Let n_c be the number of copolymers on the lattice which belong to configuration group c. For each configuration of the lattice there corresponds a set of these numbers, $\{n_c\}$, such that $\sum_c n_c = LM/N$, the total number of copolymers. The number of lattice configurations which correspond to a particular set $\{n_c\}$ is approximately

$$\Omega(\{n_c\}) = \left(\prod_c \frac{\Omega_c^{n_c}}{n_c!} \right) \left(\frac{L!}{L^L} \right)^M \left(\frac{1}{2} \right)^{LM/N} \qquad (3)$$

The first factor is the number of lattice configurations if one lifts the restriction of single occupancy per lattice site. The second factor is a mean-field correction for this lifting of the single occupancy constraint.[31,33] Finally, the last factor accounts for the inversion symmetry of the copolymer.

With the number of configurations corresponding to a given set $\{n_c\}$ at hand, we now need an expression for the internal energy of such a configuration. We will assume nearest-neighbor interactions only and characterize their strength by the usual Flory–Huggins parameter,

$$\chi \equiv \frac{z}{2k_BT} (2u_{AB} - (u_{AA} + u_{BB})) \qquad (4)$$

where $u_{\alpha\beta}$ is the nearest-neighbor interaction between monomers α and β. In the mean-field approximation, the internal energy, $U(\{n_c\})$, of each lattice configuration in the set $\{n_c\}$ is given by

$$\frac{U(\{n_c\})}{LMk_BT} = \frac{\chi}{M} \sum_{i=1}^{M} \phi_{i,A} \langle \phi_{i,B} \rangle = \frac{\chi}{M} \sum_{i=1}^{M} \langle \phi_{i,A} \rangle \phi_{i,B} \qquad (5)$$

where

$$\phi_{i,\alpha} \equiv \frac{1}{L} \sum_c n_c r_{i,\alpha,c} \qquad (6)$$

is the fraction of sites in layer i occupied by α monomers and

$$\langle \phi_{i,\alpha} \rangle \equiv \sum_{\delta=-1}^{1} \lambda_\delta \phi_{i+\delta,\alpha} \qquad (7)$$

is the average number of nearest neighbors of a site in layer i which are occupied by α monomers.

The partition function within the above mean-field approximations is

$$Z = \sum_{\{n_c\}} \Omega(\{n_c\}) \exp(-U(\{n_c\})/k_BT) \qquad (8)$$

where the sum is over all sets $\{n_c\}$ which satisfy the constraints $\sum_\alpha \phi_{i,\alpha} = 1$ for all i. In the thermodynamic limit, the largest term completely dominates the sum and all the other terms can be ignored. The set $\{n_c\}$ corresponding to this dominant term are the equilibrium values of the n_c's. Maximizing the summand in eq 8 with respect to the n_c's subject to the above constraints, we find these equilibrium values to be

$$\frac{n_c}{L} = \omega_c \prod_{i=1}^{M} (P_{i,A})^{r_{i,A,c}} (P_{i,B})^{r_{i,B,c}} \qquad (9)$$

$$= \omega_c \prod_{s=1}^{N} P_{k(s,c),\gamma(s)} \qquad (10)$$

where the Boltzmann weight,

$$P_{i,\alpha} \equiv \exp(m_i + \chi \langle \phi_{i,\alpha} \rangle) \qquad (11)$$

is called the *free-segment probability* of component α in layer i. For each layer i, there is a Lagrange multiplier m_i, which is adjusted to satisfy the incompressibility constraint $\phi_{i,A} + \phi_{i,B} = 1$. Several constant factors have been adsorbed into these multipliers.

The task now is to obtain a self-consistent set of equations for the free-segment probabilities. This is done as follows. The free-segment probabilities depend upon $\phi_{i,\alpha}$, the fraction of sites in layer i occupied by monomers of type α. This, in turn, can be expressed in terms of $\phi_{i,s}$, the fraction of sites in layer i occupied by monomers numbered s, because the architecture of the copolymers, embodied in $\gamma(s)$, is known:

$$\phi_{i,\alpha} = \sum_{s=1}^{N} \phi_{i,s} \delta_{\alpha,\gamma(s)} \qquad (12)$$

For the particular case of symmetric triblocks studied here,

$$\gamma(s) = B, \quad fN/2 + 1 \le s \le N(1 - f/2)$$
$$= A, \quad \text{otherwise} \qquad (13)$$

The fraction of sites in layer i occupied by monomers s can be written

$$\phi_{i,s} = \frac{1}{L} \sum_c n_c \delta_{i,k(s,c)} \qquad (14)$$

which, on substitution of eq 10, becomes

$$\phi_{i,s} = \sum_c \omega_c \prod_{t=1}^{N} P_{k(t,c),\gamma(t)} \delta_{i,k(s,c)} \qquad (15)$$

Equations 11–15 constitute the desired set of self-consistent equations.

The step of calculating $\phi_{i,s}$ from $P_{i,\alpha}$, eq 15, is simplified by introducing the intermediate functions

$$p(i,s) \equiv \sum_d \omega_d \prod_{t=1}^{s} P_{k(t,d),\gamma(t)} \delta_{i,k(s,d)} \qquad (16)$$

which are denoted *end-segment probabilities* as they are the relative probabilities that polymers of s monomers will have their last segment in layer i. Here the configurations of a polymer of length s are labeled by the index d just as those of length N are labeled by c, and the definition of ω_d is completely analogous to that of ω_c, eq 2. To proceed, we break the product over monomers t from 1 to N in eq 15 into products from 1 to s and from s to N and use the fact that, on ignoring overlaps, the configurations of that part of the polymer from segments 1 to s are independent of the configuration of segments s to N. The result of this operation is

$$\phi_{i,s} = \frac{p(i,s)\, p(i,N+1-s)}{P_{i,\gamma(s)}} \qquad (17)$$

By similarly decomposing the configurations of a polymer of length s into those from 1 to $s - 1$ and those of the last segment s, one obtains from the definition of $p(i,s)$, eq 16, a recursion relation from which they can all be calculated from $p(i,1) = P_{i,A}$:

$$p(i,s) = P_{i,\gamma(s)} \sum_{\delta=-1}^{1} \lambda_\delta p(i+\delta,s-1) \qquad (18)$$

for $s = 2, 3, ..., N$.

Once a solution of the self-consistent set of equations is found, the free energy, $F = U - k_B T \ln \Omega$, corresponding to that solution is evaluated using eqs 3 and 5. The logarithm of $\Omega(\{n_c\})$ can be simplified using the expressions for n_c, eq 9, and for $\phi_{i,\alpha}$, eq 6, and the constraint $\sum_c n_c = LM/N$. After simplifying, we obtain

$$\frac{F}{LMk_BT} = \frac{1}{M} \sum_{i=1}^{M} \{m_i - \chi\phi_{i,A}\langle\phi_{i,B}\rangle\} + \chi + 1 - \ln z +$$
$$\frac{1}{N}(\ln 2z - 1) \quad (19)$$

We look for solutions that correspond to a lamellar phase. Because this phase is spatially periodic with wavelength D, it is not necessary to determine the densities on all M layers of the system, but only on D of them. By taking advantage of the reflection symmetry of the lamellar phase, one need not calculate all D values, but only about half of them. There are two slightly different ways of doing this. If D is even, one can consider solutions in which the plane of symmetry either is at plane $D/2 + 1$ or is in between planes $D/2$ and $D/2 + 1$. Similarly, there are two solutions for D odd. Not surprisingly, the free energies of the two possibilities are almost the same. (We find the free energies to be equal to within 1 part in 10^{10}.) Our procedure ignores lamellar phases with a wavelength which is incommensurate with the lattice spacing. However, when the true wavelength is a large number of lattice spacings, we do not expect the differences between lamellar phases with an incommensurate wavelength and a nearby commensurate wavelength to be significant. Figure 1 shows as a dotted line the A monomer profile, $\phi_{i,A}$, in the lamellar phase for a polymer with $N = 2000$ and $f = 0.5$ at $\chi = 0.05$.

Having determined the equilibrium wavelength of the lamellar phase, we turn to the calculation of the fraction of B blocks that form bridges across the B-rich lamellae. To do so, it is useful to determine the *anisotropy factors*,
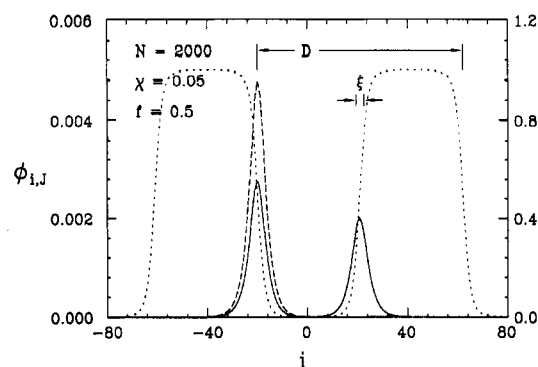

Figure 1. Shown with a dashed line is the concentration of junctions, $\phi_{i,J}$, at a single A/B interface. The solid line shows the distribution of the junctions connected to them by the B blocks of the copolymers. The dotted line shows the A monomer concentration profile, $\phi_{i,A}$.

$g_{i,s,\delta}$, which are defined as follows.[33] If the sth monomer of a polymer is in the ith layer, then the probability that the $(s + 1)$th monomer occurs in a given nearest-neighbor site in the $(i + \delta)$th layer is defined to be $g_{i,s,\delta}/z$. As this probability would be $1/z$ if the polymer followed an unbiased random walk, the $g_{i,s,\delta}$ expresses the deviation of the polymer configuration from this reference. These factors can be expressed in terms of previously defined quantities:

$$g_{i,s,\delta} = P_{i,\gamma(s)} p(i+\delta,N-s)/p(i,N+1-s) \qquad (20)$$

From their definition, it is clear that the anisotropy factors must satisfy the normalization conditions

$$\sum_{\delta=-1}^{1} z\lambda_\delta \frac{g_{i,s,\delta}}{z} = 1 \qquad (21)$$

and from eqs 18 and 20 and the symmetry $\gamma(s) = \gamma(N-s+1)$, it is easy to verify that this is so. Now, given a distribution, $d(i,s)$, of s segments from a given set of copolymers, the distribution of the $(s + 1)$th segments from the same set of copolymers is

$$d(i,s+1) = \sum_{\delta=-1}^{1} \lambda_\delta g_{i-\delta,s,\delta} d(i-\delta,s) \qquad (22)$$

Because the approximation treats the copolymers as random walks in a field, the distribution of the $(s + 2)$th monomers depends solely upon $d(i,s+1)$. Hence, eq 22 can be used iteratively to calculate the distribution of the $(s + n)$th monomers belonging to the copolymers whose distribution of sth monomers was $d(i,s)$.

To calculate the ratio of bridges to loops, we first calculate the distribution of the A–B junction at $s = N_A + 1$, ϕ_{i,N_A+1}, which is a spatially periodic function of i with wavelength D that peaks at each interface. To focus on the distribution at a single interface located at i_0, we define

$$\bar\phi_{i,N_A+1} \equiv 0, \quad -\infty < i < i_0 - w$$
$$\equiv \phi_{i,N_A+1}, \quad i_0 - w \leq i \leq i_0 + w$$
$$\equiv 0, \quad i_0 + w < i < +\infty \qquad (23)$$

where w is chosen to be much larger than the natural width of the peak but smaller than the wavelength. We choose $w = D/4$, but its precise value is unimportant. The function $\bar\phi_{i,N_A+1}$ is shown in Figure 1 as a dashed line. With this function as an initial distribution, $d(i,N_A+1)$, we use eq 22 to determine the distribution of the other copolymer junctions, $d(i,N_A+N_B)$. This distribution, shown by the solid line in Figure 1, has two peaks; one is centered at i_0 and represents the fraction of junctions which loop back

to the original interface, and a second, smaller peak represents those polymers which bridge the B-rich region. From the areas under these two peaks, the fractions of loops and bridges, ν_L and ν_B, are obtained.

3. Results

The results we present are obtained using a face-centered cubic lattice in which the layers form normal to the (111) direction. For comparison, we have also employed a simple-cubic lattice. We find, in agreement with Roe,[34] no qualitative differences and only minor quantitative differences between results from the two lattices. We choose to work with the fcc lattice as it is a close-packed lattice with a large coordination number.

Because we use a lattice, the lamellar phase undergoes numerous transitions at which the spacing D changes discretely as N, χ, and f are varied. As one would expect, we find that these transitions occur sequentially with D increasing or decreasing by one. Our results deal with a reasonably large range of periods ($D \sim 20$–120) and thus a large number of such transitions. To reduce the number of these transitions to be located, we ignore all phases in which D is odd. This reduces the number of transitions by half but doubles the size of the discontinuities at the transitions. Nonetheless, these discontinuities are small and we obtain results which vary smoothly with the change of parameters. As noted earlier, there are two solutions for a given lamellar spacing which have essentially the same free energies, so that it is somewhat arbitrary which solution we work with. We choose that with plane of symmetry between $i = D/2$ and $D/2 + 1$ as this contains one less unknown density to be determined.

The profile shown in Figure 1 for $N = 2000$, $\chi = 0.05$, and $f = 0.5$ corresponds to a strongly segregated melt with well-defined A-rich ($\phi_{i,A} \approx 1$) and B-rich ($\phi_{i,A} \approx 0$) lamellae. The A/B interfaces ($\phi_{i,A} \approx 0.5$) are narrow and can be fit well to the usual form[10,18,19]

$$\phi_{i,A} \approx \frac{1}{2}\left(1 \pm \tanh\left(\frac{i - i_0}{\xi}\right)\right) \tag{24}$$

where i_0 and ξ are fitting parameters. One interprets i_0 as the position of the A/B interface and ξ as its width. Figure 1 shows the dimensions of this interfacial width ($\xi = 3.10$) and the lamellar spacing ($D = 82$) in relation to the profile.

As noted earlier, Figure 1 also shows with a solid line the distribution of polymers with both A–B junctions at $i \approx -20$, thus forming loops, and of polymers with one A–B junction at $i \approx -20$ and the other at $i \approx 20$, thus forming bridges. The peak at $i \approx 20$, corresponding to bridges, is smaller than the one at $i \approx -20$, corresponding to loops. This will always be the case in the approximation employed in which the copolymers perform a random walk in a field that is symmetric about the midplane of the B-rich lamellae. Thus, if a random walk performed by a B block reaches this midplane, it has, by symmetry, an equal chance of terminating at either neighboring A/B interface and thus has an equal chance of forming a loop or a bridge. However, there are random walks that do not reach the midplane, and these must form loops. Hence, there are more loops than bridges.

Figure 2 shows the variation with N of the fraction of bridges, ν_B, for fixed χ and f. For the chosen value of these parameters, the transition from the disordered to the lamellar phase occurs at $N = 368$. At the transition, ν_B is small, reflecting the fact that, in the weak-segregation limit, the B block can wander readily into the A-rich regions. With increasing N, the A-rich lamellae become less
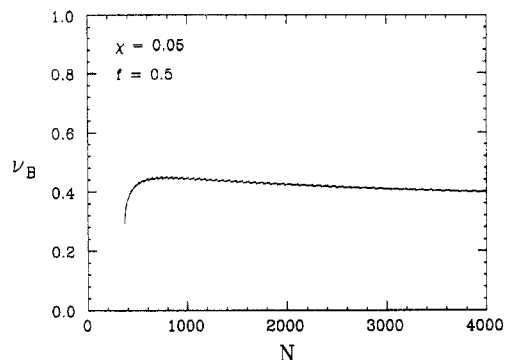

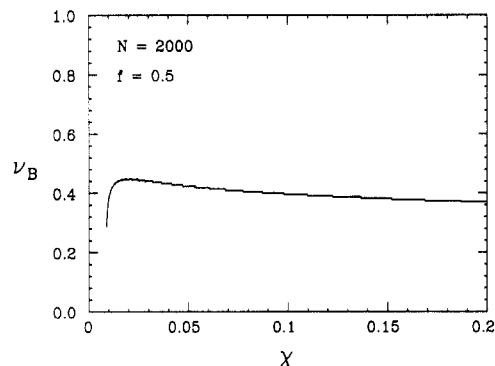**Figure 2.** Fraction of copolymers which form bridges versus the degree of polymerization.

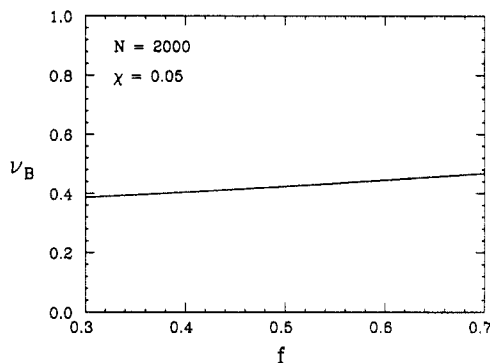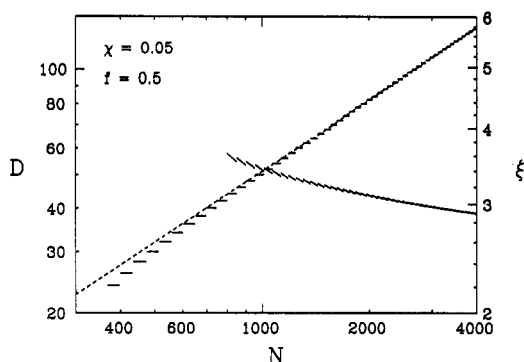**Figure 3.** Fraction of copolymers which form bridges versus the Flory–Huggins parameter.

Figure 4. Fraction of copolymers which form bridges versus the A monomer content of the copolymers.
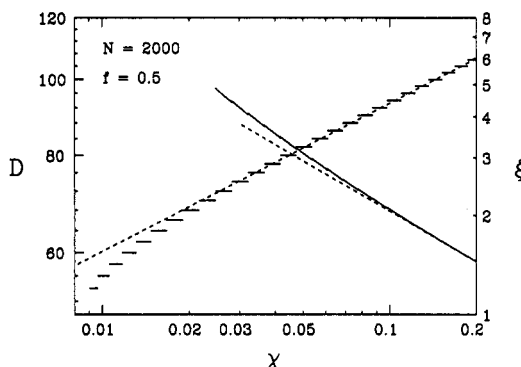
penetrable to the B blocks, causing them to form more bridges. Thus ν_B increases initially. However, there is an opposite trend due to the fact that as N increases, the width of the lamellae which must be traversed by the B block also increases. This decreases ν_B. For large N, this is the dominant factor. The discontinuities in ν_B which occur when the equilibrium spacing changes discontinuously are visible in the figure.

The dependence of ν_B on χ is shown in Figure 3 and is similar to that shown in Figure 2. In this case, the order–disorder transition occurs at $\chi = 0.00903$. Again as one goes from weak to strong segregation, ν_B begins at a small value, reaches a maximum, and then decreases slowly. One may note that, in the case of strong segregation, the regions of constant D have nearly zero slope, illustrating that χ has little direct effect on ν_B, so that its decrease is due to the increase of the lamellar period.

Figure 4 shows the variation of ν_B with f at fixed N and χ. In this case, ν_B increases slowly and monotonically with f. This results from the fact that the period is very insensitive to f; in this particular case, there is not a single transition in the period over the range of f plotted. Thus,

Figure 5. log–log plot of the lamellar spacing and the interfacial width versus the degree of polymerization. The dashed line is the fit $D \approx 0.466N^{0.68}$.

Figure 6. log–log plot of the lamellar spacing and the interfacial width versus the Flory–Huggins parameter. The dashed lines are the fits $D \approx 144.5\chi^{0.19}$ and $\xi \approx 0.637\chi^{-0.51}$. At the transition, $\chi = 0.00903$.

as f increases, the width of the A-rich lamellae increases and that of the B-rich lamellae decreases. The latter favors bridges and accounts for the increase.

We calculated both D and ξ as a function of N for fixed χ and f. The results are shown on the log–log plot in Figure 5. We find that the lamellar spacing exhibits power-law growth, $D \sim N^a$, for fixed χ in the strong-segregation limit. Our best fit, shown with a dashed line, gives $a = 0.68$. The interfacial width decreases very slowly with increasing N. The decrease is slower than a power law. In Figure 6, D and ξ are plotted as a function of χ for fixed N and f. Again for strong segregation, the lamellar spacing exhibits power-law growth, $D \sim \chi^b$ for fixed N with $b = 0.19$, but here the interfacial width also obeys power-law behavior, $\xi \sim \chi^c$ with $c = -0.51$. Because b differed significantly from what we expected,[10,18,19] $1/6$ we also tried a fit for $N = 1000$ but obtain the same exponent of 0.19. We note that both D and ξ were found to be nearly independent of f.

4. Discussion

Our results indicate that the fraction of bridges is comparable to the fraction of loops, although the former must be less than the latter, as we noted earlier. We find that typically 0.4 of the copolymers form bridges for $N\chi \sim 100$. The fraction of bridges reaches a maximum just as the melt becomes moderately segregated and decreases slowly with increasing segregation (i.e., increasing N and χ). Increasing f alone causes the width of the B-rich lamellae to decrease and therefore increases the fraction of bridges.

In the strong-segregation limit, we found that the lamellar spacing scaled with N and χ as $D(N,\chi) \sim N^a\chi^b$ with $a = 0.68$ and $b = 0.19$. We believe that these exponents would be unchanged had we worked with a diblock

copolymer melt. We find that D is only very weakly dependent on f, a result which agrees with ref 18. Our result for the exponent a is only slightly larger than the commonly quoted value of $2/3$. Our value of b falls in the range of other theoretical results.

In the weak-segregation limit, we find that the lamellar period D increases more rapidly with N than the $N^{2/3}$ behavior of the strong-segregation limit (see the small-N regime of Figure 5). This is in agreement with refs 11, 19, 20, 35, and 36. We do not claim that D exhibits a power-law behavior in this limit, but we can see that a fit to $D \sim N^{4/5}$ would be reasonably good. This may explain why some experiments have measured such a value[1,23,26] rather than the $2/3$ appropriate to the strong-segregation limit. Similarly, Figure 6 shows that if data close to the disorder-order transition were used to obtain the exponent b giving the scaling behavior of D with χ, a value which is larger than that for the strong-segregation limit would result. This is in accord with the measurement of Hashimoto et al.,[22,28] who obtained $1/3$ for b, a result larger than those obtained theoretically for the strong-segregation limit.

We expect the interfacial width to scale the same way as in diblock copolymer melts, and our results support this. We find that ξ is nearly independent of N, as is observed experimentally.[16,24] We also found it to be nearly independent of f. Finally, we observe that ξ scales with χ as $\xi \sim \chi^c$ with $c = -0.51$, in agreement with the theoretical value[10,18] of $-1/2$.

We located the transition from the disordered to lamellar phase for a polymer of $N = 2000$ and $f = 0.5$ to occur at $\chi = 0.00903$ ($N\chi = 18.06$) and for the polymer of $N = 368$ and $f = 0.5$ to occur at $\chi = 0.05$ ($N\chi = 18.40$). The transitions are found to be second order. We note that the locations of both transitions agree well with the mean-field phase diagram in ref 9. This reference also suggests the location we have calculated would actually be a spinodal line and that cubic and hexagonal phases would exist in very narrow regions between the disordered and lamellar phases. Our approach limits us from exploring this possibility. In any event, when fluctuations are taken into account, these phases are believed to be unstable and the disorder–lamellar transition to become weakly first order.[30]

Within the description of the mean-field approximation, there is no segregation of A and B monomers in the disordered phase, and the copolymers are described by random walks with their radius of gyration, measured in lattice spacings, given by $R_G = N^{1/2}$. Near the order-disorder transition, the lamellar phase is very weakly segregated (i.e., $\phi_{i,A} \approx f$) and the copolymers are only slightly perturbed from their Gaussian configurations. Consequently, the lamellar spacing, $D_c(N,\chi_c(N))$, at the transition $\chi_c(N)$ is approximately R_G.[10] For $f = 0.5$, we find that $D_c(N,\chi_c(N)) \approx 1.2N^{1/2}$. As stressed by others,[19,37] this does not imply that $D(N,\chi)$ at fixed χ scales as $N^{1/2}$ in the weak-segregation limit near the transition as has sometimes been assumed.[9,21,26,38] Once the transition occurs, increasing N increases the segregation, causing the polymers to stretch.[8,26] Therefore D increases faster than $N^{1/2}$. For diblocks, refs 11, 19, and 36 find that $D(N,\chi) \sim N^{0.95}$ for fixed χ near the transition.

In many theories, such as the continuum self-consistent field theories used in refs 11, 19, and 36, the exponents a and b in the relation $D(N,\chi) \sim N^a\chi^b$ are not independent because χ enters the theory only in the combination χN. This implies that at the transition to the lamellar phase $N\chi_c(N)$ is constant and that the fraction of loops and bridges depends only on χN. Further, D is given by a scaling relation $D(N,\chi) = N^{1/2}d(\chi N)$, which implies that

$a - b = 1/2$.[11] Because the self-consistent formalism we employ is not a continuum but a lattice theory, these relations are only satisfied approximately. Hence we find $a - b = 0.49$ and $N\chi_c(N)$ to vary slightly with N. The fraction of bridges we obtain, shown in Figures 2 and 3, while clearly having a similar dependence on χ and N are not given by the same function of the variable χN.

Experiment[38] confirms that fluctuations can usually be ignored in copolymer melts. The one place they cannot be ignored is near the order–disorder transition. Due to them, the transition moves to larger values of χN,[8,13,39] and in the disordered phase somewhat before the transition occurs, the copolymers stretch from their Gaussian configurations.[26] This behavior has been reproduced by both simulation[40] and a Hartree approach to the fluctuations.[39] The crossover in the disordered phase from Gaussian to stretched coils occurs in the vicinity of the mean-field (or "classical"[13]) spinodal line. (This crossover is not a phase transition, as suggested by ref 26.) Thus, the classical spinodal line appears to separate the disordered phase into a region in which the melt is unstructured and another in which there is short-range order and the copolymers are stretched.

References and Notes

(1) Hadziioannou, G.; Skoulios, A. *Macromolecules* **1982**, *15*, 258.
(2) Gehlsen, M. D.; Almdal, K.; Bates, F. S. *Macromolecules* **1992**, *25*, 939.
(3) Richards, R. W.; Thomason, J. L. *Macromolecules* **1983**, *16*, 982.
(4) Mori, K.; Tanaka, H.; Hashimoto, T. *Macromolecules* **1987**, *20*, 381.
(5) Milner, S. T.; Witten, T. A. *Macromolecules* **1992**, *25*, 5495.
(6) Zhulina, E. B.; Halperin, A. *Macromolecules* **1991**, *25*, 5730. These authors also note that loops from different A-rich lamellae which reach to the midplane of the B-rich lamellae are likely to be entangled and therefore to behave structurally much like bridges.
(7) Ghijsels, A.; Raadsen, J. *Pure Appl. Chem.* **1980**, *52*, 1359. Hansen, P. J.; Williams, M. C. *Polym. Eng. Sci.* **1987**, *27*, 586.
(8) Mayes, A. M.; Olvera de la Cruz, M. *J. Chem. Phys.* **1991**, *95*, 4670.
(9) Mayes, A. M.; Olvera de la Cruz, M. *J. Chem. Phys.* **1989**, *91*, 7228.
(10) Ohta, T.; Kawasaki, K. *Macromolecules* **1986**, *19*, 2621.
(11) Vavasour, J. D.; Whitemore, M. D. *Macromolecules* **1992**, *25*, 5477.
(12) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(13) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *87*, 697.
(14) Helfand, E.; Wasserman, Z. R. In *Developments in Block Copolymers—1*; Goodman, I., Ed.; Applied Science: London, 1982.
(15) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1976**, *9*, 879.
(16) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1237.
(17) Hashimoto, T.; Shibayama, M.; Fujimura, M.; Kawai, H. In *Block Polymer Science and Technology*; Meier, D. J., Ed.; MMI Press: Chur, 1983.
(18) Semenov, A. N. *Sov. Phys.—JETP (Engl. Transl.)* **1985**, *61*, 733.
(19) Shull, K. R. *Macromolecules* **1992**, *25*, 2122.
(20) McMullen, W. E. *Macromolecules* **1993**, *26*, 1027, 1798.
(21) Oono, Y.; Bahiana, M. *J. Phys.: Condens. Matter* **1989**, *1*, 5297.
(22) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1983**, *16*, 1093.
(23) Hashimoto, T. *Macromolecules* **1982**, *15*, 1548.
(24) Hashimoto, T.; Fujimura, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1660.
(25) Matsushita, Y.; Mori, K.; Saguchi, R.; Nakao, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1990**, *23*, 4313.
(26) Almdal, K.; Rosedale, J. H.; Bates, F. S.; Wignall, G. D.; Fredrickson, G. H. *Phys. Rev. Lett.* **1990**, *65*, 1112.
(27) Reference 25 points out that the theory in ref 15 predicts the exponent $b = 1/7$.
(28) Hashimoto, T.; Ijichi, Y.; Fetters, L. J. *J. Chem. Phys.* **1988**, *89*, 2463. In this work, the temperature interval $(T_c - T)$ over which measurements were made is such that T_c/T was approximately 1.3. Figure 6 suggests that in order for the exponent b to attain its value in the strong-segregation limit, temperatures $T_c/T > 5$ need to be sampled.
(29) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(30) The major effect of the fluctuations is to cause the transition to the lamellar phase to be first order in contrast to the mean-field prediction of a continuous transition. Brazovsky, S. A. *Zh. Eksp. Teor. Fiz.* **1975**, *68*, 175 [*Sov. Phys.—JETP (Engl. Transl.)* **1975** *41*, 85].
(31) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619; *Macromolecules* **1985**, *18*, 1882.
(32) Theodorous, D. N. *Macromolecules* **1988**, *21*, 1422. *Inter alia*, this paper applies the formalism of ref 31 to the interface between the disordered phase of triblocks and vacuum.
(33) Helfand, E. *J. Chem. Phys.* **1975**, *63*, 2192; *Macromolecules* **1976**, *9*, 307.
(34) Roe, R. J. *J. Chem. Phys.* **1974**, *60*, 4192.
(35) Somes, R. A.; Terentjev, E. M.; Petschek, R. G. *Macromolecules* **1993**, *26*, 3344.
(36) Shull, K. R.; Mayes, A. M.; Russell, T. P. *Macromolecules* **1993**, *36*, 3929.
(37) Helfand, E. *Macromolecules* **1975**, *8*, 552.
(38) Bates, F. S.; Rosedale, J. H.; Fredrickson, G. H. *J. Chem. Phys.* **1990**, *92*, 6255.
(39) Barrat, J.-L.; Fredrickson, G. H. *J. Chem. Phys.* **1991**, *95*, 1281.
(40) Fried, H.; Binder, K. *Europhys. Lett.* **1991**, *16*, 237.