Conformationally Asymmetric Block Copolymers

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ABSTRACT: The standard parameters controlling AB diblock copolymer phase behavior are \(\chi N\) and \(f_A\), where \(\chi\) is an A-B segment interaction parameter, \(N\) is the overall degree of polymerization, and \(f_A\) is the volume fraction of the A block. Recently, it has been recognized that the ratio of the A and B statistical segment lengths \(a_A/a_B\) also represents another important parameter. Here, we theoretically examine the effects of this latter parameter on the phase behavior using the standard Gaussian chain model. Calculations are performed using both self-consistent field theory (SCFT) and strong segregation theory (SST). The ratio \(a_A/a_B\) is shown to have strong effects on order–order phase boundaries. Furthermore, it significantly affects the relative stability of the complex phases. In particular, it enhances the metastability of the perforated lamellar phase and may actually cause it to become an equilibrium structure. We also illustrate that varying \(a_A/a_B\) produces large changes in the relative domain spacings at order–order phase boundaries, which could strongly affect the kinetics of these transitions. © 1997 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 35: 945–952, 1997

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INTRODUCTION

The AB diblock architecture provides the model system for examining microphase separation in block copolymer melts.1–3 This simple architecture consists of two chemically distinct blocks, A and B, with one end from each covalently bonded together. Only two quantities are required to characterize this macromolecule: its total number of segments \(N\) and the fraction \(f_A\) of those that belong to the A block. (Because melts can be treated as incompressible, we conveniently define segments based on a common fixed volume, \(1/\rho_0\).) This system is further simplified because the interactions between A and B segments can be well represented by a standard Flory–Huggins enthalpy with a strength controlled by a single parameter, \(\chi\). Although the effects of more general interactions, compressibility, and polydispersity have not been thoroughly examined for block copolymer melts, they are expected to be small relative to the effects of conformational asymmetry examined below.1

The product \(\chi N\) dictates the degree to which the A and B blocks segregate. When \(\chi N \approx 10\), entropy dominates the enthalpic penalty of mixing A and B segments, resulting in a disordered phase. However when \(\chi N\) is increased, the A and B blocks become immiscible causing an order–disorder transition (ODT), where the unlike blocks separate. Because these blocks are chemically joined, the A and B domains remain microscopic, and consequently, ordered periodic structures are produced. The composition \(f_A\) of the diblock controls the geometry of the resulting microstructure; the various documented geometries...
minority blocks become so short that they unbind from their domains producing a disordered phase. Just prior to this disordered phase, theory predicts that the spherical domains of the $S$ phase reorder into a close-packed arrangement, which we denote as the $S_{cp}$ phase.

The physics of microphase separation involves the interfacial tension between $A$ and $B$ domains and the entropic penalty of stretching the polymers so as to maintain a uniform segment density. The latter penalty occurs because fewer conformations are available to a “coarse-grained” segment as it becomes stretched. Assuming Gaussian or random-walk statistics, the entropy loss that results when the ends of a segment are stretched to a distance $\ell$ is proportional to $(\ell/a)^2$, where $a$ is the statistical segment length. While the interfacial tension favors large domain sizes, the entropic stretching penalty favors small ones; the competition sets the equilibrium domain size.

Figure 1. Illustrations of block copolymer microstructures showing the domains occupied by the minority component blocks. The majority component blocks fill the remaining space within the structures.

are shown in Figure 1. At nearly symmetric compositions (i.e., $f_A \approx \frac{1}{2}$), the $A$ and $B$ domains form alternating layers, the lamellar ($L$) phase. Slightly off symmetry, complex structures have been observed. They include a perforated lamellar ($PL$) phase, where the thin minority component layers of a lamellar structure each exhibit an hexagonal array of passages through which the majority component layers are connected. [A modulated lamellar phase has been proposed, but the evidence for it is inconclusive and, furthermore, it goes against our present understanding of microstructural selection; calculations by Yeung et al. suggest that the experiments can be explained by an instability developing in the $L$ phase.] Another reported complex phase is a bicontinuous structure with $Ia\overline{3}d$ space-group symmetry, denoted the gyroid ($G$), where the minority component domain forms two interweaving threefold coordinated lattices. [A similar structure, but with $Pn\overline{3}m$ symmetry and two fourfold coordinated lattices, referred to as the ordered bicontinuous double diamond ($D$) phase has been reported in the past, but it is now thought to have been a misidentified $G$ phase.] Beyond the complex structures, a cylinder ($C$) phase occurs where the minority component forms hexagonally packed cylinders, and then a spherical ($S$) phase occurs where the minority component forms spheres arranged on a body-centered cubic lattice. At very high molecular asymmetries (i.e., $f_A \rightarrow 0$ or 1), the minority blocks become so short that they unbind from their domains producing a disordered phase. Just prior to this disordered phase, theory predicts that the spherical domains of the $S$ phase reorder into a close-packed arrangement, which we denote as the $S_{cp}$ phase.

Theoretical calculations generally assume that the $A$ and $B$ segments are conformationally symmetric; that is, they have equal statistical lengths, $a_A$ and $a_B$, respectively. Because the geometry of the microstructure involves a competition between the stretching penalties of $A$ and $B$ blocks, conformational asymmetry can have a profound influence on the phase boundaries. Despite the fact that experiments have demonstrated such effects, conformational asymmetry has received little theoretical attention. There are two notable studies—one by Helfand and Wasserman and another by Vavasour and Whitmore. Both used self-consistent field theory (SCFT) supplemented with a unit cell approximation (UCA). Because of the UCA, these studies were unable to treat complex phases. Furthermore, the former calculation implemented a narrow interface approximation (NIA), which restricted its validity to strongly segregated melts. Nevertheless, these calculations demonstrated that conformational asymmetry has a significant influence on order–order transitions (OOTs). Reference 14 also suggested that the asymmetry suppresses the usual mean-field critical point and produces narrow windows of first-order transitions between the disordered state and various ordered structures analogous to fluctuation effects, but this conclu-
sion has now been attributed to numerical inaccuracies.19

In this article we calculate a series of phase diagrams for varying degrees of conformational asymmetry and provide a more complete assessment of its effects on phase behavior. These calculations are based on the SCFT without implementing either the UCA or NIA. As a result, our phase diagrams are more accurate than the ones in refs. 13 and 14, and furthermore, they account for the complex phase behavior. Therefore, we are able to examine how the delicate balance in free energies among the complex phases is affected by conformational asymmetry. The influence of conformational asymmetry on domain spacings is also examined. A number of these SCFT calculations are supplemented with ones based on the strong segregation theory (SST) of Semenov.20

**PHASE DIAGRAMS**

The method for evaluating the free energy of an arbitrary periodically ordered microstructure using the full SCFT was introduced in ref. 21. Although that reference outlines the procedure for conformationally symmetric diblocks \( (\alpha_A = \alpha_B) \), the generalization to asymmetric diblocks \( (\alpha_A \neq \alpha_B) \) is straightforward.14 Comparing the free energies of the structures illustrated in Figure 1 produces the phase diagrams shown in Figure 2. We performed our calculations for three values of \( \alpha_A/\alpha_B = 1.0, 1.5, \) and 2.0, ranging from totally symmetric to a degree of asymmetry bordering on the limit of experimental accessibility. It is not surprising that the arrangement of the classical phases is unaffected by the introduction of conformational asymmetry. However, it is impossible to anticipate the effect on the complex phase behavior because these phases differ so slightly in free energy. As it turns out, the gyroid structure remains the only stable complex phase over the parameter space examined in Figure 2. For some of the higher degrees of segregation, we experienced two types of numerical difficulty in evaluating the free energy of the complex phases: either too many Fourier terms were required to accurately represent the spatially dependent quantities or convergence problems occurred when solving the self-consistent field equations. In these instances, we have extrapolated the phase boundaries using dashed curves.

The most obvious effect of the conformational asymmetry is to shift the phase boundaries. This is best illustrated in Figure 3. There we restrict our attention to the classical structures and plot the locations of the \( L/C, C/S, \) and \( S/\text{disordered} \) boundaries as a function of conformational asymmetry at fixed degrees of segregation, \( \chi_N = 30, 60, \) and \( \infty \). For the finite degrees of segregation the full SCFT is used, and for the infinite-segregation limit the SST described in the Appendix is used. In the limit of \( \chi_N \to \infty \), the \( S/\text{disordered} \) boundary approaches \( f_A = 0 \) squeezing out the disordered phase. For the finite degrees of segregation, we show results from the SCFT calculation of Vavassour and Whitmore,14,22 which implemented the UCA. Generally, the inaccuracies introduced by
A-rich cylinders in a B-rich matrix. This tendency causes the OOTs to shift towards larger A block volume fractions $f_A$. To explain why the effect on the ODT is small, we must recognize that the ODT occurs primarily because the minority blocks pull free of their domains causing the spherical phase to disorder. When A blocks form the spherical domains, the energy binding them to their domain relative to the thermal energy is approximately $\chi N f_A$. Because this quantity does not involve the statistical segment lengths, the ODT is relatively unaffected by the conformational asymmetry.

Figure 3. Mean-field phase boundaries between the $L$ (lamellar), $C$ (cylindrical), $S$ (spherical), and disordered phases as a function of conformational asymmetry. Solid, dashed, and dotted curves denote the boundaries for $\chi N = 30$, 60, and $\infty$, respectively. In the later case, the $S$/disordered phase boundary coincides with $f_A = 0$. For comparison, results from Refs. 14 and 22 are shown with solid and open circles for $\chi N = 30$ and 60, respectively. The dimensionless quantity $(a_A - a_B) / (a_A + a_B)$ used here to measure conformational asymmetry is convenient because it is zero for $a_A = a_B$ and its magnitude is invariant under the interchange of labels, i.e., $A \leftrightarrow B$.

The relative stability of the complex phases is illustrated in Figure 4. In all instances, the double diamond ($D$) phase is least unstable along the $C/G$ phase boundary. Following that boundary, we plot its excess free energy $\Delta F_D$ as a function of $\chi N$ for several values of $a_A/a_B$ in Figure 4(a). Although conformational asymmetry, in general, enhances the stability of the $D$ phase, it still remains rather unstable. However, the situation is much different for the $PL$ phase. This phase is always found to be least unstable along the $L/G$ boundary, consistent with where $PL$ is observed experimentally. Therefore, that is the path along which its excess free energy $\Delta F_{PL}$ is plotted in Figure 4(b). In this case, conformational asymmetry greatly enhances the stability of the $PL$ phase when the minority block possesses the shorter statistical segment length. With A blocks
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The $G$ structure is best able to meet these requirements and is therefore stable. Based on results where homopolymer is added to diblock microstructures, the $PL$ is unstable because its majority domain suffers from high degrees of packing frustration whereas the $D$ phase is unstable because of packing frustration in its minority domain. This is consistent with our present findings. Reducing the stretching penalty and, therefore, packing frustration in the majority domain by increasing the relative segment length of the majority component lowers $D_{FD}$. Conversely, increasing the segment length of the minority component relative to that of the majority component lowers $D_{FPL}$. Actually, $D_{FD}$ is also reduced by decreasing the relative segment length of the minority component, but this occurs because of the shift in the $C/G$ phase boundary. When the $C/G$ transition shifts to a higher minority component fraction, the $D$ structure is better able to produce uniform domains with CMC-like interfaces; this is evident from ref. 28 where CMC along the $C/G$ phase boundary and (b) excess free energy of the $PL$ phase along the $L/G$ boundary for several degrees of conformational asymmetry. Here we assume that the $A$ blocks form the minority component domains. Note that $D_{FD}$ and $D_{FPL}$ are plotted on different scales.

Figure 4. Excess free energy of the $D$ phase $\Delta F_D$ along the $C/G$ phase boundary and (b) excess free energy of the PL phase $\Delta F_{PL}$ along the $L/G$ boundary for several degrees of conformational asymmetry. Here we assume that the $A$ blocks form the minority component domains. Note that $\Delta F_D$ and $\Delta F_{PL}$ are plotted on different scales.

Experimentalists often use either small-angle x-ray or neutron scattering (SAXS or SANS) to identify ordered phases. The magnitude of the principle scattering vector $q^*$ provides a measure of the domain spacing $D^* = 2\pi/q^*$, and the higher order reflections are used to identify the space-group symmetry of the microstructure. In general, discontinuities in $D^*$ occur at the OOTs, although measuring them can be difficult because metastability of the phases can prevent the accurate determination of a transition. From diblock systems exhibiting reasonably small hystereses, it is evident that these discontinuities in $D^*$ are typically small (e.g., 1 or 2%), but in some cases large discontinuities (on the order of 10%) have been reported. In instances where phase transitions occur epitaxially, these discontinuities are presumably important to the kinetics; a poor match in $q^*$ will hinder the epitaxial growth of the stable state. Below, we show that conformational asymmetry can produce large $q^*$ (or equivalently large $D^*$) discontinuities.

In an earlier publication, we explained that complex phase selection involves choosing a structure with $A$- and $B$-rich domains which are uniform in thickness (so as to minimize packing frustration) and with an interfacial surface of nearly constant mean curvature (CMC) (so as to minimize interfacial energy). The $G$ structure is best able to meet these requirements and is therefore stable. Based on results where homopolymer is added to diblock microstructures, the $PL$ is unstable because its majority domain suffers from high degrees of packing frustration whereas the $D$ phase is unstable because of packing frustration in its minority domain. This is consistent with our present findings. Reducing the stretching penalty and, therefore, packing frustration in the majority domain by increasing the relative segment length of the majority component lowers $D_{FD}$. Conversely, increasing the segment length of the minority component relative to that of the majority component lowers $D_{FPL}$. Actually, $D_{FD}$ is also reduced by decreasing the relative segment length of the minority component, but this occurs because of the shift in the $C/G$ phase boundary. When the $C/G$ transition shifts to a higher minority component fraction, the $D$ structure is better able to produce uniform domains with CMC-like interfaces; this is evident from ref. 28 where CMC surfaces with the symmetry of the $D$ phase are generated for several volume fractions of the minority domain.

DOMAIN SPACINGS

Experimentalists often use either small-angle x-ray or neutron scattering (SAXS or SANS) to identify ordered phases. The magnitude of the principle scattering vector $q^*$ provides a measure of the domain spacing $D^* = 2\pi/q^*$, and the higher order reflections are used to identify the space-group symmetry of the microstructure. In general, discontinuities in $D^*$ occur at the OOTs, although measuring them can be difficult because metastability of the phases can prevent the accurate determination of a transition. From diblock systems exhibiting reasonably small hystereses, it is evident that these discontinuities in $D^*$ are typically small (e.g., 1 or 2%), but in some cases large discontinuities (on the order of 10%) have been reported. In instances where phase transitions occur epitaxially, these discontinuities are presumably important to the kinetics; a poor match in $q^*$ will hinder the epitaxial growth of the stable state. Below, we show that conformational asymmetry can produce large $q^*$ (or equivalently large $D^*$) discontinuities.

In Figure 5, the variation in domain spacing $D^*$ with the diblock composition $f_A$ is plotted at fixed $xN$ for both conformationally symmetric ($a_A/a_B = 1.0$) and asymmetric ($a_A/a_B = 1.5$) mole-
As mentioned earlier, this causes the disordered phase to occur for highly asymmetric diblock compositions. Figure 5(a) demonstrates that the discontinuities in $D^*$ are small for $a_A/a_B = 1.0$. As $a_A/a_B$ increases, the discontinuities on the $f_A < \frac{1}{2}$ side of the phase diagram initially decrease, then switch sign, and eventually increase in size. Nevertheless, for experimentally relevant $a_A/a_B$, they remain relatively small. However, on the other side of the phase diagram $f_A > \frac{1}{2}$, increasing $a_A/a_B$ causes the discontinuities to become large. This is consistent with the conditions under which large discontinuities were reported experimentally.23

Figure 5. Domain spacings $D^*$ as a function of the A block volume fraction $f_A$ for conformationally (a) symmetric and (b) asymmetric diblock copolymers. Solid curves are calculated for $\chi N = 30$ and 60 using SCFT, and the dashed curve represents the SST prediction for $\chi N = 60$. Domain spacings are defined as $D^* = 2\pi/q^*$, where $q^*$ is the magnitude of the principle scattering vector. (The quantity $a = [f_A a_A^2 + (1 - f_A) a_B^2]^{1/2}$ is an averaged segment length.) Discontinuous jumps in $D^*$ occur at each order–order phase transition. In this calculation, the $S_{cp}$ phase is ignored; when it is included, the domain spacing at the $S/S_{cp}$ transition simply adjusts so as to keep the volume of the Wigner–Seitz unit cell approximately constant.

Discontinuities in $D^*$ are evident at each order–order transition. At the lower degree of segregation $\chi N = 30$, the sequence of ordered phases is $S \rightarrow C \rightarrow G \rightarrow L \rightarrow G \rightarrow C \rightarrow S$ as $f_A$ increases, and at $\chi N = 60$, we have assumed that it is $S \rightarrow C \rightarrow L \rightarrow C \rightarrow S$. For the sake of simplicity we have ignored $S_{vp}$, and at $\chi N = 60$ we have not accounted for the complex phases because we cannot evaluate their free energies there. Nevertheless, all the complex phases are likely unstable or nearly so at this high degree of segregation.1,5,25 For comparison, we provide the SST prediction (see the Appendix) at $\chi N = 60$ using dotted curves; as usual the SST represents the domain spacing well even though some of its underlying assumptions are far from satisfied.31 The rise in $D^*$ near the ODT as calculated with the SCFT occurs because the short minority blocks are poorly anchored to their spherical domains and consequently pull free, swelling the majority domain. As mentioned earlier, this causes the disordered phase to occur for highly asymmetric diblock compositions. Figure 5(a) demonstrates that the discontinuities in $D^*$ are small for $a_A/a_B = 1.0$. As $a_A/a_B$ increases, the discontinuities on the $f_A < \frac{1}{2}$ side of the phase diagram initially decrease, then switch sign, and eventually increase in size. Nevertheless, for experimentally relevant $a_A/a_B$, they remain relatively small. However, on the other side of the phase diagram $f_A > \frac{1}{2}$, increasing $a_A/a_B$ causes the discontinuities to become large. This is consistent with the conditions under which large discontinuities were reported experimentally.23

SUMMARY

We have examined the effects of conformational asymmetry on the phase behavior of diblock copolymer melts. Over the region of our study, we find that conformational asymmetry has little effect on the topology of the mean-field phase diagram reported earlier in ref. 1. The arrangement of the classical lamellar (L), cylindrical (C), and spherical (S) phases is unchanged. Furthermore, the narrow regions of close-packed spheres ($S_{cp}$) remain along the edge of the ODT, and the gyroid (G) phase remains stable between the L and C phases. The most notable result of conformational asymmetry is to shift the order–order transitions towards compositions richer in the segments possessing the longer statistical length, which is consistent with experiment.2,12 The asymmetry also has important effects on complex phase behavior. In general, it reduces the instability of the D phase, but not to a large degree. On the other hand, the instability of the perforated lamellar (PL) phase can be greatly reduced by choosing the majority segments to have the longer statistical length. In fact, the results indicate that the PL phase may become stable at intermediate degrees of segregation. The implication of such a result is that the topology of the complex phase region may vary between chemically distinct diblock systems simply due to the inherent differences in their conformational asymmetry. In addition, we found that conformational asymmetry strongly affects the relative domain spacing between structures along their boundaries, which presumably will affect the kinetics of epitaxially driven transitions.32

We are grateful to M. D. Whitmore and J. D. Vavasour for supplying results from their SCFT calculations. This work has benefited from our discussions with D. A.
and the geometry of the microstructure. The first of the two terms, which is a rather involved calculation were presented earlier by Helfand and Wasserman.\textsuperscript{17} The remaining two coefficients are straightforward to calculate\textsuperscript{25} when the standard unit cell approximation (UCA)\textsuperscript{16} is implemented and exclusion zones are ignored. It has been demonstrated that the inaccuracy due to ignoring exclusion zones is absolutely negligible.\textsuperscript{34}

With the UCA, the \( L \) phase is treated exactly, but for the \( C \) and \( S \) phases the Wigner–Seitz unit cells are replaced by circular and spherical cells, respectively, of radius \( R \). Given these approximations and assuming that the \( A \) blocks form the minority component domains,

\[
F = \frac{\mathcal{F}_{\text{el}}}{nk_BT} + \alpha^A \left( \frac{R}{aN^{1/2}} \right)^2 + \alpha^B \left( \frac{R}{aN^{1/2}} \right)^2 + \beta(\chi N)^{1/2} \left( \frac{R}{aN^{1/2}} \right)^{-1}
\]

where \( n \) is the total number of molecules, \( R \) is a measure of the domain size, \( a = \frac{f_A d_A^2}{R} + (1 - f_A) d_B^2 \), and the coefficients, \( \alpha^A, \alpha^B, \) and \( \beta \), are quantities that depend on the molecular composition \( f_A \), the conformational asymmetry \( a_A/a_B \), and the geometry of the microstructure. The first two terms, \( \mathcal{F}_{\text{el}}^A \) and \( \mathcal{F}_{\text{el}}^B \), account for entropic losses from stretching the \( A \) and \( B \) blocks, respectively. They are proportional to \( R^2 \) because the chains are assumed to be Gaussian. The last term, \( \mathcal{F}_{\text{int}} \), represents the interfacial energy and is proportional to the interfacial area which in turn is proportional to \( R^{-1} \). Minimizing this free energy amounts to balancing entropic stretching energy against interfacial energy (i.e., \( 2 \mathcal{F}_{\text{el}}^A + 2 \mathcal{F}_{\text{el}}^B = \mathcal{F}_{\text{int}} \)).

This determines the equilibrium domain size, which exhibits the well established scaling form,

\[
R = a \left( \frac{\beta}{2(\alpha^A + \alpha^B)} \right)^{1/3} \chi^{1/6} N^{2/3}
\]

With that, the free energy expression reduces to

\[
F = \frac{3}{2} (2(\alpha^A + \alpha^B) \beta^2 \chi N)^{1/3}
\]

Below, we provide the coefficients, \( \alpha^A, \alpha^B, \) and \( \beta \), for each of the classical phases. The coefficient, \( \beta \), requires the evaluation of the \( A/B \) interfacial tension, which is a rather involved calculation when the \( A \) and \( B \) segments are conformationally asymmetric. However, results for this cal-

\[
\alpha^A = \begin{cases} \pi^2 f_A^3 / 8 & \text{for } L \\ \pi^2 (1 - f_A)^3 (3 + f_A^{1/2}) / 16 (1 - f_A)^2 & \text{for } C \\ 3\pi^2 (1 - f_A)^3 (6 + 3f_A^{1/3} + f_A^{2/3}) / 80 (1 - f_A)^2 & \text{for } S \end{cases}
\]

\[
\alpha^B = \begin{cases} \pi^2 f_A / 8 & \text{for } L \\ \pi^2 (1 - f_A)^3 (3 + f_A^{1/2}) / 16 (1 - f_A)^2 & \text{for } C \\ 3\pi^2 (1 - f_A)^3 (6 + 3f_A^{1/3} + f_A^{2/3}) / 80 (1 - f_A)^2 & \text{for } S \end{cases}
\]

\[
\beta = \begin{cases} 1 / 6^{1/2} g(f_A, a_A/a_B) & \text{for } L \\ 2f_A^{1/2} / 6^{1/2} g(f_A, a_A/a_B) & \text{for } C \\ 3f_A^{2/3} / 6^{1/2} g(f_A, a_A/a_B) & \text{for } S \end{cases}
\]
where

\[ g(f, \gamma) = \frac{1 + \gamma}{2(1 - f + f \gamma^2)^{1/2}} \left[ 1 + \frac{1}{3} \frac{1 - \gamma}{1 + \gamma} \right] \]  

(8)

By equating the volumes of the approximate and actual Wigner–Seitz unit cells, the principle domain spacings are calculated to be

\[ D^* = \begin{cases} 
2R, & \text{for } L \\
(3\pi^2/4)^{1/6}R, & \text{for } C \\
(8\pi^2/9)^{1/6}R, & \text{for } S 
\end{cases} \]  

(9)

**REFERENCES AND NOTES**