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Self-Consistent Theory of Block Copolymer Blends: Selective Solvent

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ABSTRACT: We present a theoretical study of the lamellar microphase of block copolymer/selective solvent blends in which the solvent is good for one block and either good or near-Θ for the other. The calculations used numerical solutions to the equations of the self-consistent mean-field theory of polymer blends. Two types of systems were studied. In the first, all pure-component densities were taken to be equal, as were the two Kuhn statistical lengths, and the solvent was idealized as being athermal for one of the blocks. In the other type, realistic values for these parameters were used; calculations were carried out for the particular case of PS-*b*-PBD/styrene. We examined the dependence of the lamellar thickness on molecular weight, overall concentration, and Flory interaction parameters, and we discuss the solvent and polymer density profiles. We compare the predictions for blends with selective solvents with previous ones for nonselective solvent cases, and we compare the idealized systems with real systems. The theory predicts some significant differences between the idealized and real systems.

1. Introduction

The microphase behavior of block copolymers and block copolymer blends remains the object of continued experimental[1–24] and theoretical[25–47] study. Conceptually, one can consider at least three related aspects of the problem. The first is that of understanding which of the possible microphases is the equilibrium one for a given system, e.g., refs 11, 15, 21, 22, 33, 34, 36, 37, 40, 46, and 47. The second aspect is the details of a given microphase, such as the dependence of the microdomain thickness on molecular weight and overall concentrations, or the distribution of each component within the microdomains, e.g., refs 5–7, 15, 18, 20, 23, 24, 30–33, 39, and 40. Underlying both of these aspects is the further question of the degree to which theoretical results for idealized model systems apply to real systems. By model systems, we mean in this paper ones in which the pure-component densities of all components, $\rho_{0\kappa}$, are equal, as are all Kuhn statistical lengths, b_κ, and the solvents are specified either as athermal or as "good" but without quantitatively relating the solvent quality to real systems.

The work reported here addresses the second and third of these aspects: we study the lamellar microphase of diblock copolymer/selective solvent blends, through numerical solutions to the equations of the self-consistent mean-field theory.[41,42] Our goals are, first, to compare the predictions for model copolymer/selective solvent systems with predictions for model copolymer/nonselective solvent systems and, second, to compare results for model systems with those using realistic system characteristics. For this purpose, we chose a particular system and used experimentally determined values of pure-component densities, Kuhn statistical lengths, and Flory interaction parameters.

The numerical calculations provide the most complete mean-field treatment of these systems, without making assumptions about the width of the interphase regions or shapes of the density distributions. However, our approach neglects fluctuation[37] and equation of state effects[48] and the effects of swelling by good solvents.[49] The first and last of these are likely to be important in systems near the MST, especially for those with low polymer concentrations. Even within these limitations, quantitative comparison with experiment relies on the precision of the measured Flory parameters and the degree to which they are independent of composition and molecular weights.

Since we assume that layers are the equilibrium structure, we have attempted to limit attention to systems in which this assumption is valid. Within our approach, this is difficult to do in a rigorous and consistent theory, because mean-field theory predicts that virtually all systems undergo microphase transitions to cylinders and spheres as the MST is approached. For example, for model copolymer systems, Leibler's RPA theory predicted these transistions for all cases except for perfectly symmetric copolymers, $f_A = f_B = 0.5$, where f_A and f_B are the volume fractions of the A and B blocks of the molecules.[34] Whitmore and Vavasour found the same result for model copolymer/neutral solvent blends.[47] Furthermore, fluctuation effects appear to broaden the lamellar region near the MST by only a few percent.[37] On the other hand, it is generally accepted that, at least away from the MST, lamellae should be stable over a composition range of approximately $0.35 \lesssim f_A \lesssim 0.65$. Theories of copolymers and copolymer/solvent blends in the strong segregation regime agree with this result.[33,36,46,47]

The approach we took to restrict ourselves to systems which are lamellar had two aspects. First, we considered only solvents which are good for one block of the copolymer and either good or near-Θ for the other, avoiding highly selective solvents. Second, we carried out a limited set of self-consistent calculations for cylinders as well as lamellae and compared their free energies, following the approach of ref 47. The results implied that, for the systems we chose, the layered structure was the equilibrium one as long as $f_A \simeq f_B$. As discussed in section 3 below, the resulting density profiles and this conclusion are consistent with the phase diagram shown by Birshtein and Zhulina for the strong segregation limit.[46] However, we did not compare these competing morphologies right to the MST and so did not rule out the possibility that mean-field theory would predict a microphase change just before reaching the disordered phase.

We also verified that, at least within our formalism, the systems we chose did not macrophase separate. This was done following the procedure described by Hong and Noolandi but using the full self-consistent calculations for the free energy of the microphase rather than a fourth-order expansion.[43]

Since one of our goals is to compare copolymer/selective solvent blends with copolymer/nonselective solvent blends,

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it is appropriate to summarize briefly the findings of ref 45, in which the latter were modeled using the same approach we used here. The first set of calculations of ref 45 considered model systems (as described above) with symmetric copolymers, $f_A = f_B = 0.5$. The solvent was perfectly nonselective, with $\chi_{SA} = \chi_{SB}$, and ranging in value from 0 to 0.3. The results of these calculations turned out to be nearly independent of the actual values of χ_{SA} and χ_{SB}, as long as they were equal. The order-disorder transition occurred very hear $\bar{\phi}_c\chi_{AB}Z_C \simeq 10.5$, and so to a first approximation this product played a role similar to that played by $\chi_{AB}Z_C$ for diblock copolymers. This is consistent with the dilution approximation, in which the dominant effect of the neutral solvent is simply a reduction of χ_{AB} to an effective value of $\chi_{eff} = \bar{\phi}_c\chi_{AB}$. Having found that the results were nearly independent of χ_{SA} in such blends, a systematic series of calculations was performed assuming athermal solvents; i.e., $\chi_{SA} = \chi_{SB} = 0$. The effects of the three remaining characteristics were investigated, with their values ranging over

$$0.05 \le \chi_{AB} \le 0.3$$

$$100 \le Z_C \le 2000$$

$$0.1 \le \bar{\phi}_c \le 0.9 \tag{1}$$

With these choices, the value of $\bar{\phi}_c\chi_{AB}Z_C$ varied from 12 to over 400, i.e., from near the MST to well into the strong segregation regime.

One set of results of these calculations consisted of the dependences of the equilibrium domain (layer) thickness, d, on these quantities, which were found to be stronger near the MST than in the strong segregation regime. In units of the Kuhn length, b, this was expressed as

$$d/b \propto [\chi_{AB}]^p[Z_C]^q[\bar{\phi}_c]^r \tag{2}$$

with

$$p \simeq 1/3 \qquad q \simeq 0.8 \qquad r \simeq 0.4 \tag{3}$$

in the weak segregation regime and

$$p \simeq 0.2 \qquad q \simeq 0.7 \qquad r \simeq 0.2 \tag{4}$$

in the strong segregation regime. The prediction that the scaling is stronger in the weak segregation regime is in agreement with at least one recent set of experiments.[24]

Two series of density profiles for these model systems were also shown. In the first, $Z_C = 200$ and $\chi_{AB} = 0.2$, and $\bar{\phi}_c$ was varied from 0.2 to 0.9. In the second, $Z_C = 1200$ and $\chi_{AB} = 0.1$, and $\bar{\phi}_c$ was varied from 0.1 to 0.8. In both of these, the systems ranged from near the MST to the strong segregation regime. Of particular interest was the fact that, in all cases, the solvent profile, $\phi_S(x)$, was almost uniform, with excesses in the interphase regions of at most 0.04. The nonuniformity in the solvent density tended to be largest for small Z_C and for volume fractions on the order of $\bar{\phi}_c \simeq 0.5$.

In the second type of system treated in ref 45, the assumptions of the model calculations were eliminated, and values for the χ parameters, Kuhn lengths, and monomer volumes were taken from experiments. The system chosen was PS-*b*-PI/TOL, for which the calculated polymer density profiles had been presented earlier.[41] Toluene is almost perfectly nonselective, with $\chi_{PS-TOL} = 0.44$ and $\chi_{PI-TOL} = 0.40$. Two sets of density profiles were shown, one in the strong ($\bar{\phi}_c\chi_{PS-PI}Z_C \simeq 80$) and one in the relatively weak ($\bar{\phi}_c\chi_{PS-PI}Z_C \simeq 20$) segregation regime. As in the model system calculations, each solvent profile had a small maximum in the interphase region. In slight contrast with the model systems, the solvent density in the PS subdomain exceeded that in the PI subdomain by an amount which was comparable to the excess in the interphase, reflecting the small differences in the two solvent-polymer interaction parameters.

In this paper, we again report two sets of calculations. In the first, we use model systems with interaction parameters $\chi_{SA} = 0$, as in ref 45, and $\chi_{SB} = \chi_{AB}$, ranging up to 0.3 as before. These solvents are athermal for the A blocks and good but not as good for the B blocks. We compare the predicted dependence of the lamellar thickness on Z_C, χ_{AB}, and $\bar{\phi}_c$ for the model selective and nonselective solvent cases. For the second set of calculations, we chose a system with realistic interaction parameters. A convenient one turned out to be PS-*b*-PBD/styrene, which was studied earlier in the context of interfacial tension.[50] In this case we consider the variations in lamellar thickness with Z_C and $\bar{\phi}_c$, leaving the three χ parameters constant, and compare with the model calculations. We also present a series of density profiles for this case.

2. Formalism

Our goal is to calculate the equilibrium domain thickness, polymer and solvent concentration profiles, and free energy density of each blend, using the formalism and procedure which are fully described in refs 45 and 47. A given blend is specified by the overall volume fractions $\bar{\phi}_c$ and $\bar{\phi}_s = 1 - \bar{\phi}_c$ and the characteristics of the polymer and solvent molecules. The polymers are specified by their total degrees of polymerization, Z_C, the degrees of polymerization of each block, Z_{cA} and $Z_{cB} = Z_C - Z_{cA}$, the two Kuhn statistical lengths b_A and b_B, and the bulk densities ρ_{0A} and ρ_{0B}. The solvent molecules are specified by the bulk density ρ_{0S}. Each ordered microphase is represented by a set of lattice vectors and an associated unit cell of volume Ω.

The starting point of the theoretical treatment used here is an expression for the partition function in which the polymers are modeled as flexible space curves, each with an associated Weiner weight. The interactions are modeled by Flory parameters χ_{AB}, χ_{SA}, and χ_{SB} which are defined using the solvent for the reference density, but also including gradient terms which are incorporated using finite range parameters denoted $\sigma_{\kappa\kappa'}$. In principle, there is a unique value of $\sigma_{\kappa\kappa'}$ for each pair of components. However, since the theory implies only that their magnitudes should be comparable with the size of the monomers and also since sample calculations indicate that the specific values make little difference to the results,[50,51] we chose them all to be the same, equal to the geometric mean of the Kuhn lengths, as in the work on copolymer/neutral solvent blends.

The partition function is transformed into a functional integral of a free energy functional, which is evaluated approximately by the saddle-point method. This requires the minimization of the free energy functional, subject to constraints. One of the constraints that is imposed is that of incompressibility, i.e., $\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) + \phi_S(\mathbf{r}) = 1$ everywhere. The result of this minimization is a set of self-consistent equations for these volume fractions and associated potentials $\omega_\kappa(\mathbf{r})$ and an expression for the free energy.

For each polymer component p, p = A or B, we solve the diffusion equation for periodic polymer distribution functions, denoted $\tilde{Q}_p(\mathbf{r},\tau|\mathbf{r}')$ in ref 45, subject to appropriate initial conditions. The corresponding local volume fractions are calculated via convolutions such as

$$\phi_A(\mathbf{r}) = \frac{\bar{\phi}_A}{Z_A Q_C} \int_0^{Z_A} d\tau\, q_A(\mathbf{r},\tau) \int_\Omega d\mathbf{r}'\, \bar{Q}_A(\mathbf{r}, Z_A - \tau | \mathbf{r}') \times q_B(\mathbf{r}', Z_B) \quad (5)$$

where

$$q_p(\mathbf{r},t) = \int_\Omega d\mathbf{r}'\, \bar{Q}_p(\mathbf{r},\tau|\mathbf{r}') \quad (6)$$

and

$$Q_C = \frac{1}{\Omega}\int_\Omega d\mathbf{r}\, q_A(\mathbf{r},Z_A)\, q_B(\mathbf{r},Z_B) \quad (7)$$

The local solvent volume fraction is calculated from the incompressibility condition.

The periodic potentials $\omega_p(\mathbf{r})$ which appear in the diffusion equation are functions of the three reduced densities $\phi_\kappa(\mathbf{r})$, and so the problem must be solved self-consistently. This must be done for each structure and assumed lattice constant, e.g., domain thickness. The reduced free energy per unit volume, relative to a uniform melt, is calculated from the converged solutions via

$$\frac{\Delta F}{\rho_{0S} k_B T} = \frac{1}{\Omega}\int_\Omega d\mathbf{r} \left\{ \chi_{SA}\left[\phi_S(\mathbf{r})\,\phi_A(\mathbf{r}) - \bar{\phi}_S\bar{\phi}_A - \frac{\sigma^2}{6}\nabla\phi_S(\mathbf{r})\cdot\nabla\phi_A(\mathbf{r})\right] + \chi_{SB}\left[\phi_S(\mathbf{r})\,\phi_B(\mathbf{r}) - \bar{\phi}_S\bar{\phi}_B - \frac{\sigma^2}{6}\nabla\phi_S(\mathbf{r})\cdot\nabla\phi_B(\mathbf{r})\right] + \chi_{AB}\left[\phi_A(\mathbf{r})\,\phi_B(\mathbf{r}) - \bar{\phi}_A\bar{\phi}_B - \frac{\sigma^2}{6}\nabla\phi_A(\mathbf{r})\cdot\nabla\phi_B(\mathbf{r})\right] + \ln\left(\frac{\phi_S(\mathbf{r})}{\bar{\phi}_S}\right) - \frac{\rho_{0A}}{\rho_{0S}}\omega_A(\mathbf{r})\,\phi_A(\mathbf{r}) - \frac{\rho_{0B}}{\rho_{0S}}\omega_B(\mathbf{r})\,\phi_B(\mathbf{r}) \right\} - \frac{\bar{\phi}_C}{r_C}\ln(Q_C) \quad (8)$$

Here k_B is Boltzmann's constant, and T is the temperature. Also appearing in eq 8 is r_C which is given by

$$r_C = r_A + r_B \quad (9)$$

where $r_p = Z_p\rho_{0S}/\rho_{0p}$ for p = A or B.

In the layered structure, the problem is one-dimensional with period d; hence, we needed to solve for the functions $\bar{Q}_p(x,\tau|x')$ and $q_p(x,\tau)$ in the spatial interval $[0,d]$ and for $\tau \epsilon [0,Z_p]$. In order to identify each equilibrium domain thickness, we needed to find the value which minimized ΔF for each system, which we did by performing a set self-consistent calculations throughout a range of d, until the minimum in ΔF was located. For the cylinders, we followed a similar procedure, but with the hexagonal unit cell approximated by a cylinder.

On the basis of the precision in our solutions to the modified diffusion equation and the attained convergence, we estimate that the density profiles profiles are converged to about six significant figures. We also estimate that the calculated values of d are located to about ±0.1 (in units of the Kuhn length) which is more accurate than was attained in ref 45.[53]

3. Results

3.1. Model Systems. We begin with the model system, i.e., the solvent is athermal for the A blocks so $\chi_{SA} = 0$; we set $\chi_{SB} = \chi_{AB}$, and all reference densities and the two Kuhn lengths are equal. We also assume that the copolymers are symmetric, $Z_{cA} = Z_{cB}$.

Figures 1–3 show the dependence of the equilibrium domain thickness, d, on Z_C, $\bar{\phi}_c$, and χ_{AB}. Figures 1 and 2 were calculated with $\chi_{AB} = 0.1$ and can be compared directly with Figures 5 and 4 of ref 45, respectively. Figure 3 was calculated for the same degrees of polymerization and volume fractions as in Figure 6 of ref 45 and can be compared directly with it. The calculations cover Z_C ranging from 200 to 2000, $\bar{\phi}_c$ ranging from 0.2 to 0.8 or 0.9, and χ_{AB} ranging from 0.05 to 0.3. With these choices, we explore from the weak to the strong segregation regimes, with $\chi_{AB}Z_C$ reaching in excess of 150.

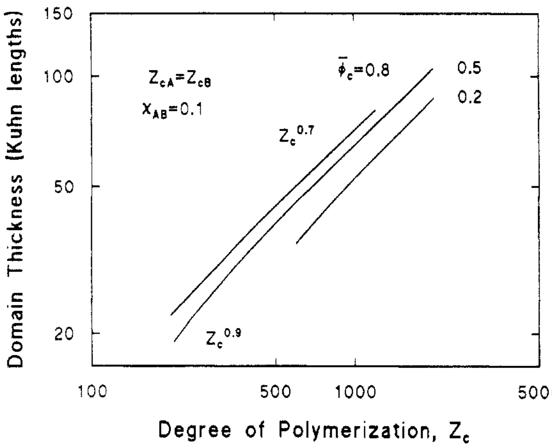

Figure 1. Equilibrium domain thickness, d, in units of the Kuhn statistical length, as a function of the copolymer degree of polymerization, Z_C, for three values of copolymer volume fraction $\bar{\phi}_c$ and for $\chi_{AB} = 0.1$. In the weak segregation regime, d varies approximately as $d \propto [Z_C]^{0.9}$, but the dependence weakens slightly in the strong segregation regime, approaching $d \propto [Z_C]^{0.7}$.

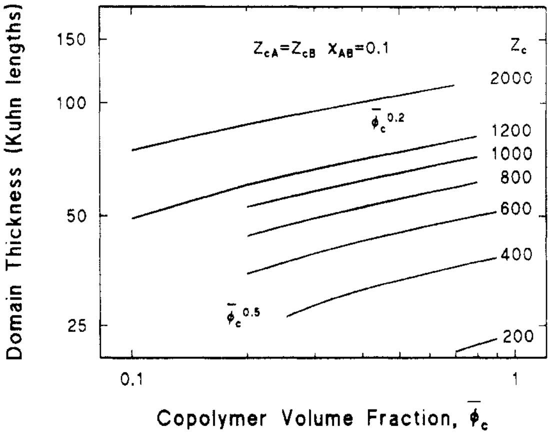

Figure 2. Equilibrium domain thickness, d, as a function of the overall copolymer volume fraction, $\bar{\phi}_c$, for $\chi_{AB} = 0.1$ and different degrees of polymerization Z_C. The lower left-hand corner of the diagram corresponds to the weak segregation regime. Here the curve for $Z_C = 400$ terminates at the value of $\bar{\phi}_c$ which corresponds to the MST. In this region, d scales approximately as $d \propto [\bar{\phi}_c]^r$, with r approaching 0.5. Moving to higher copolymer content or higher Z_C corresponds to the strong segregation regime, where the dependence of d on $\bar{\phi}_c$ weakens to $d \propto [\bar{\phi}_c]^{0.2}$.

As found for the neutral solvent case, the results can be summarized approximately by the power law relationships given by eq 2, with values of the exponents which vary from the weak to the strong segregation regimes. We found

$$p \simeq 0.5 \qquad q \simeq 0.9 \qquad r \simeq 0.5 \quad (10)$$

in the weak segregation regime and

$$p \simeq 0.2 \qquad q \simeq 0.7 \qquad r \simeq 0.2 \quad (11)$$

in the strong segregation regime. Although corresponding figures are not shown, the values $p \simeq 0.2$ and $q \simeq 0.7$ were also found for the cases of larger χ_{AB} used in Figure 3. Furthermore, the values for the strong segregation regime are the same as those for the copolymer/neutral solvent blends and nearly the same as those found for

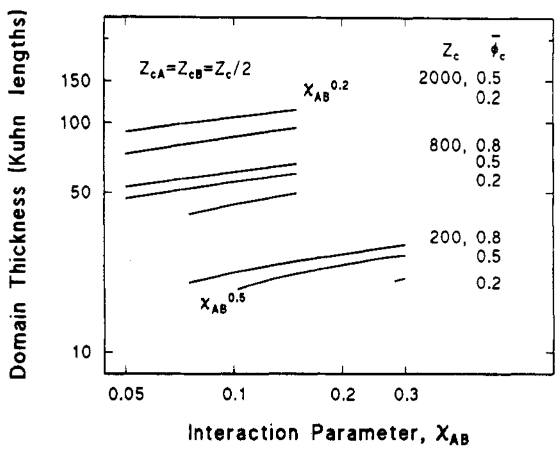

Figure 3. Equilibrium domain thickness, d, as a function of χ_{AB} for three values of the copolymer volume fraction, $\bar{\phi}_c$, and three degrees of polymerization Z_C. Toward the weak segregation limit, d varies approximately as $d \propto [\chi_{AB}]^{0.5}$, but the dependence weakens in the strong segregation regime to $d \propto [\chi_{AB}]^{0.2}$.

copolymers in this regime.[30,33] In the other limit they appear to be slightly larger than the values reported for the neutral solvent case.[45] However, these differences do not reflect differences between the selective and nonselective cases. Rather, they are due to the refinements in the algorithm which have allowed us to perform calculations closer to the MST than was possible in ref 45.[54] In any event, the actual values should not be considered quantitatively significant, because in this regime the fluctuations and, in some cases, swelling effects of good solvent could alter these exponents. The important point is that, for the model systems, the predictions for the scaling are the same for the selective and nonselective solvents, with stronger dependences in the weak segregation regime than in the strong segregation regime.

3.2. PS-*b*-PBD/S Blends. In this section we discuss a system with realistic values of interaction parameters. The particular system we chose was PS-*b*-PBD/S, where S denotes styrene solvent (styrene monomers). For completeness, we also used available numerical values of the other characteristics of this system:[50,55]

$$\chi_{PS\text{-}S} = 0.49 \qquad \chi_{PBD\text{-}S} = 0.29 \qquad \chi_{PS\text{-}PBD} = 0.024$$

$$\rho_{PBD} = 10.6\ \mathrm{nm}^{-3} \qquad \rho_{PS} = 6.07\ \mathrm{nm}^{-3} \qquad \rho_S = 5.25\ \mathrm{nm}^{-3}$$

$$b_{PBD} = 0.68\ \mathrm{nm} \qquad b_{PS} = 0.68\ \mathrm{nm} \tag{12}$$

These χ parameters indicate that the styrene is a selective solvent which is good for the PBD and almost a Θ solvent for the PS. Compared with the model calculations, the difference between χ_{SA} and χ_{SB} is similar (0.2), but the polymer–polymer interaction parameter is much smaller than χ_{SA}, χ_{SB}, or their difference. It should be noted that the particular choice of system is of only secondary importance; the primary goal is to choose a system described by realistic parameter values.

We began by estimating the lamellar ↔ cylindrical microphase boundaries for these blends, carrying out self-consistent calculations for both the lamellar and cylindrical structures as described in ref 47, for blends with $\bar{\phi}_c = 0.5$, with $Z_C = 2500$ in one series of calculations and $Z_C = 1700$ in a second series. In each case, we calculated the equilibrium lattice constant and free energy ΔF for the lamellae and cylinders as a function of Z_{PS}. The results indicated that the L ↔ C microphase boundaries are asymmetric.

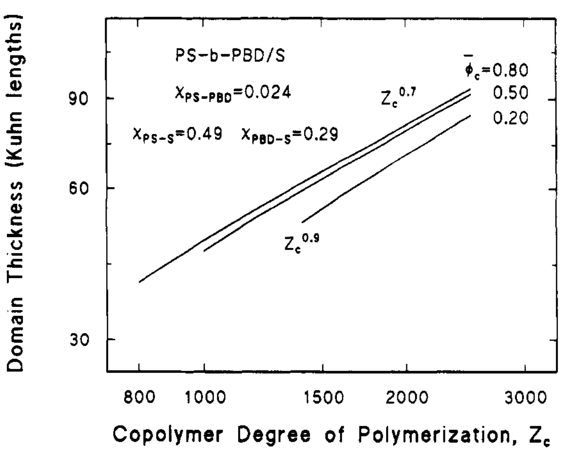

Figure 4. Equilibrium domain thickness, d, as a function of the copolymer degree of polymerization, Z_C, for PS-*b*-PBD/S blends with three different copolymer volume fractions, all with $f_{PS} = f_{PBD} = 0.5$. In the weak segregation regime $q \simeq 0.9$, but the dependence weakens in strong segregation to $q \simeq 0.7$.

In the first case, the lamellae were stable for $425 \lesssim Z_{PS} \lesssim 1000$ or, in terms of the relative volume fractions of each block, $0.26 \lesssim f_{PS} \lesssim 0.55$. For the second case, this narrowed to $330 \lesssim Z_{PS} \lesssim 690$ or $0.30 \lesssim f_{PS} \lesssim 0.55$. Note that the phase boundary on the PS-rich side did not change significantly over this range of Z_C. We concluded that, at least over this range and probably a broader one, these blends would remain lamellar for copolymers satisfying $f_{PS} \simeq f_{PBD} \simeq 0.5$. Furthermore, as we shall see below, the calculations indicate that the solvent concentrations in the two subdomains are nearly equal. In such a case, the results of Birshtein and Zhulina imply that the solvent does not alter the microphase boundaries, at least in the strong segregation regime.[46] For these reasons, we used $f_{PS} = f_{PBD} = 0.5$ in our calculations, recognizing that if we were to carry out the self-consistent calculation very near the order–disorder transition, then we might find a change in the morphology. In passing we note that $f_{PS} = f_{PBD} = 0.5$ corresponds to blocks with rather unequal degrees of polymerization for these copolymers, with $Z_{PS} \simeq 0.36 Z_C$, $Z_{PBD} \simeq 0.64 Z_C$, and $Z_{PBD} \simeq 1.7 Z_{PS}$.

In order to ensure that, at least within our mean-field approach, the microphase separation did not induce macrophase separation in the blends we modeled, we calculated the total free energy density of the blend as a function of concentration,[43] for the case with the largest copolymer degree of polymerization we considered. This free energy density can be written as

$$f(\bar{\phi}_c) = f_{hom} + \Delta f \tag{13}$$

where f_{hom} is the free energy density of a uniform, homogeneous blend relative to a fully demixed homogeneous system, and $\Delta f = \Delta F/V$ with ΔF given by eq 8. In contrast with earlier work,[43] we used the full self-consistent calculations for Δf. We found that, even with the inclusion of Δf, then the curvature of $f(\bar{\phi}_c)$ was positive for all $\bar{\phi}_c$, indicating that the blends would not macrophase separate.

Figures 4 and 5 show the calculated equilibrium domain thickness as a function of copolymer degree of polymerization for three different copolymer volume fractions and as a function of $\bar{\phi}_c$ for four different copolymer degrees of polymerization, respectively. Discussing first the location of the MST, for the case of unequal polymer and solvent pure-component densities, ρ_{0K}, the transition for pure copolymers with $f_A = f_B = 0.5$ is given by a generalization

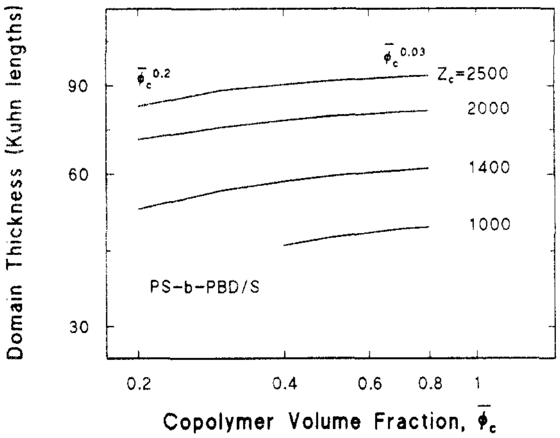

Figure 5. Equilibrium domain thickness, *d*, as a function of the copolymer volume fraction for PS-*b*-PBD/S blends with four different copolymer degrees of polymerization, all with $f_{PS} = f_{PBD} = 0.5$. In the weak segregation regime $p \simeq 0.2$, but the dependence weakens in strong segregation $p \simeq 0.03$.

of the original Leibler criterion[34] of $\chi_{AB}Z_C = 10.5$ to[44]

$$\chi_{AB}r_C = 10.5 \qquad (14)$$

where r_C is given by eq 9. For these PS-*b*-PBD copolymers, and χ parameters defined using ρ_{0S} for the reference density, then $r_C = 0.63Z_C$ and so eq 14 is equivalent to $\chi_{PS\text{-}PBD}Z_C \simeq 16.7$. The addition of solvent tends to destabilize the microphase, shifting the transition to larger values of $\chi_{PS\text{-}PBD}r_C$. Consistent with this picture, we found the transition was at $\chi_{PS\text{-}PBD}r_C = 11.6$ for the $\bar{\phi}_c = 0.8$ blend and at $\chi_{PS\text{-}PBD}r_C = 20$ for the $\bar{\phi}_C = 0.2$ blend. Using $r_C = 0.63Z_C$ and $\chi_{PS\text{-}PBD} = 0.024$, these values translate to $Z_C \simeq 770$ and $Z_C \simeq 1300$ for the two cases, respectively.

It is interesting to contrast this with the effect of neutral solvent. To a good approximation, the effect of neutral solvent is simply to dilute the polymer interactions and shift the transition to $\bar{\phi}_c\chi_{PS\text{-}PBD}r_C = 10.5$ or $\chi_{PS\text{-}PBD}r_C = 10.5/\bar{\phi}_c$. Such an effect would shift the transitions to $\chi r_C = 13$ and 52, rather than 11.6 and 20, respectively. Thus this selective solvent has a significantly weaker tendency to destabilize the microphase than does the neutral solvent.

Returning now to Figure 4, it can be seen that the calculations have been terminated at the low end near values of Z_C corresponding to the MST. The scaling of *d* with Z_C can again be expressed as in eq 2, with the same values of the exponents as in the other cases, i.e., $q \simeq 0.9$ in the weak segregation regime, decreasing to $q \simeq 0.7$ in the strong segregation regime.

There is, however, a significant difference for the dependence of *d* on $\bar{\phi}_c$, seen in Figure 5. Although this can again be described approximately by a power law relationship, in this case the values of the exponent vary from only $r \simeq 0.2$ in the weak segregation regime to $r \simeq 0.03$ in the strong segregation regime. These are smaller than in any of the model calculations, selective or nonselective solvents.

This relatively weak dependence of the domain thickness on $\bar{\phi}_c$ parallels changes in the density profiles, which are shown in Figure 6 for the case $Z_C = 1600$, again for $f_{PS} = f_{PBD} = 0.5$. As in Figures 2 and 3 of ref 45, this figure shows a series of density profiles corresponding to different blend concentrations, ranging from $\bar{\phi}_c = 0.2$ in the first panel to $\bar{\phi}_c = 0.8$ in the last. The first panel clearly corresponds to the weak segregation regime, with relatively small variations in the densities of the two copolymer constituents, $\phi_{PS}(x)$ and $\phi_{PBD}(x)$. As $\bar{\phi}_c$ is increased (successive panels), the polymer density profiles sharpen to an extent, but not as much as in the case of copolymer/neutral solvent blends. For example, in the series of panels of Figure 3 of ref 45, the copolymer profiles sharpen, and the interphase region thins, to a significantly greater extent. It is also accompanied by a greater increase in the domain thickness; i.e., the value of the exponent *r* is larger in the neutral solvent case.

The panels of Figure 6 also show the preferential localization of the solvent in the PBD subdomains. However, the quantitative difference between the solvent densities in the two regions is modest. The difference between the maximum and minimum solvent volume fractions varies from a value of 0.05 for the $\bar{\phi}_c = 0.2$ blend, up to 0.09 for the $\bar{\phi}_c = 0.4$ and 0.5 blends, and back to 0.04 for the $\bar{\phi}_c = 0.8$ blend. In contrast to the copolymer/neutral solvent cases, there was no solvent excess in the interphase regions; instead $\phi_S(x)$ decreased monotonically from the center of one subdomain to the center of the other. This was generally the case in the model calculations as well, except for the larger values of χ_{AB}. For example, for the case of $\chi_{AB} = 0.3$ and $\bar{\phi}_c = 0.5$, $\phi_S(x)$ was nearly constant throughout the favored subdomain with a value of $\phi_S(x) \simeq 0.54$, it increased very slightly in the interphase to $\phi_S(x) \simeq 0.55$, and then it decreased to $\phi_S(x) \simeq 0.44$ in the other subdomain.

Finally, the profiles shown in Figure 6 are consistent with our prediction that, for these blends, even with the solvent, the lamellar structure was stable for $f_{PS} \simeq f_{PBD} \simeq 0.5$. As mentioned above and as argued by Birshtein and Zhulina,[46] if the solvent had been highly localized in one of the subdomains, then for these copolymers the two subdomains would have had quite unequal volumes, and one of the other morphologies would have been stable. For cases in which the solvent densities in the two subdomains are nearly equal, they predicted that the solvent has little effect on the microphase boundaries. For the cases studied here, the solvent densities are almost equal in the two subdomains, and the lamellar structure was generally favored. A shift to at least the cylindrical morphology just before reaching the MST remains a possibility; this would correspond to the homogeneous ↔ lamellar transition being shifted away from the point $f_{PS} = 0.5$.

4. Summary

We have modeled the lamellar structure of copolymer/selective solvent blends, using numerical solutions to the equations of the self-consistent mean-field theory. The approach makes no assumptions regarding the shapes of the density profiles, the degree to which the solvent is preferentially distributed between and within the microdomains, or the width of the interphase regions. However, it does neglect fluctuation and equation of state effects and the effects of swelling by good solvents. We verified that the choices of systems modeled were consistent with the assumption of the lamellar structure, except perhaps very near the MST, and that the systems studied would not macrophase separate. We treated two types of systems, always choosing solvents which are at least as good as Θ solvents for both copolymer blocks. The first type consisted of model systems in which all pure component densities $\rho_{0\kappa}$ and the two Kuhn statistical lengths were equal, and for these cases we used solvents which were athermal for one of the blocks of the copolymers. The second was PS-*b*-PBD/styrene blends, using experimentally determined values for the χ parameters, $\rho_{0\kappa}$, and Kuhn lengths. For this system, the polymer–polymer interaction parameter is much smaller than either of the solvent–polymer interaction parameters or their difference.

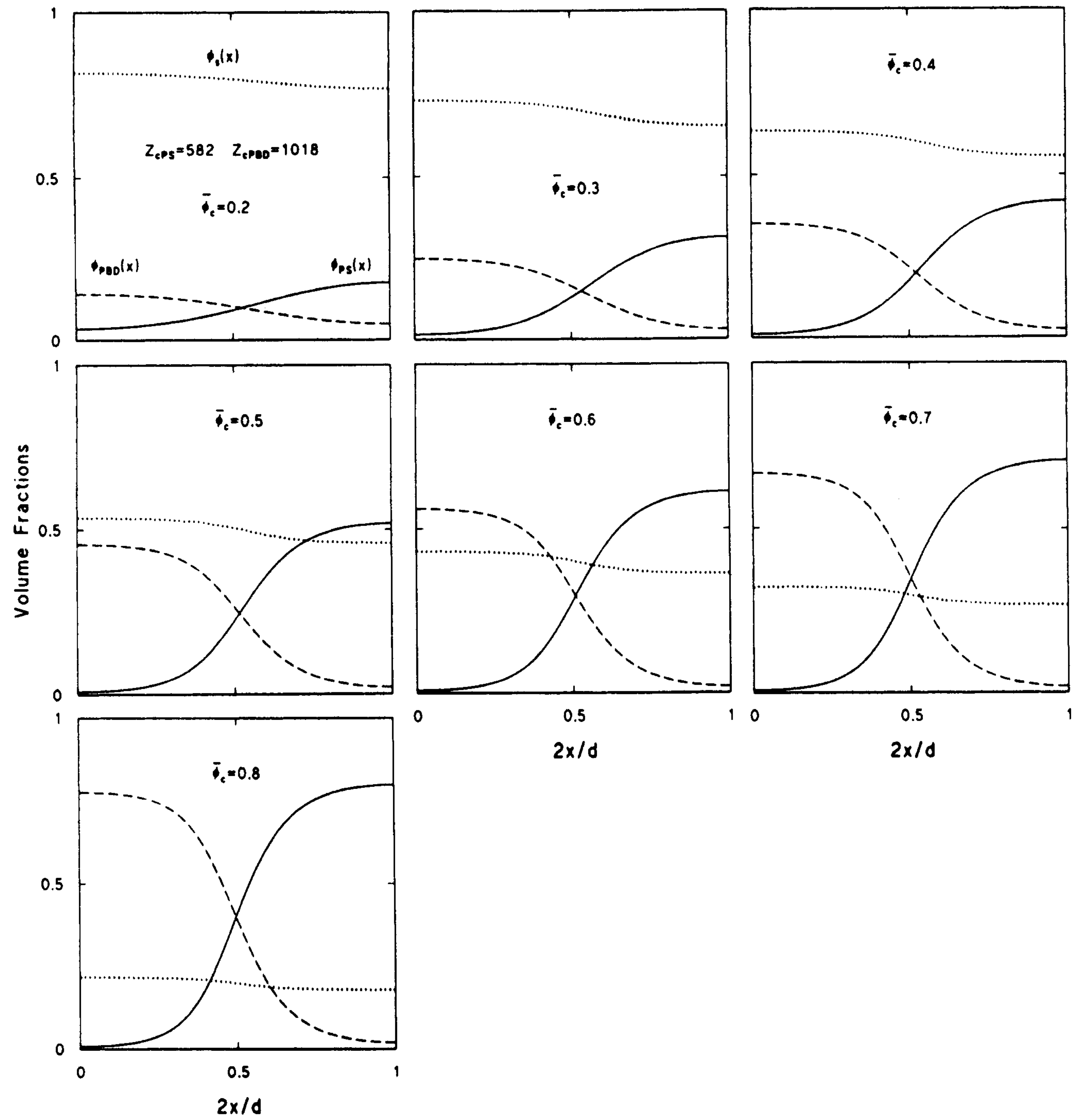

Figure 6. Density profiles for PS-*b*-PBD/S blends corresponding to different overall copolymer volume fractions, $\bar{\phi}_c$, all with Z_C = 1600 and $f_{PS} = f_{PBD} = 0.5$. The first panel corresponds to 20% copolymer volume fraction and is in the weak segregation regime. Successive panels correspond to progressively more copolymer, up to 80% in the last panel. In all cases the solvent is preferentially localized in the PDB subdomain, but the change in $\phi_S(x)$ across the domain is at most 0.09.

In all cases, we found that the solvent was distributed relatively uniformly throughout each subdomain, with a maximum difference between the solvent volume fraction in the centers of the two subdomains of about 0.1. Related to this is our finding that the lamellar microphase was generally stable relative to other morphologies for copolymers with blocks of nearly equal volume fractions, $f_A \simeq f_B \simeq 0.5$, even if, as in the PS-*b*-PBD/styrene blends, this corresponds to disparate block degrees of polymerization, e.g., $Z_{PBD} \simeq 1.7Z_{PS}$. This is consistent with the prediction of Birshtein and Zhulina for the strong segregation regime[46] for cases in which the solvent is nearly equally distributed between the two subdomains.

The addition of solvent tends to destabilize the microphase, shifting the MST to higher values of $\chi_{AB}r_C$ or $\chi_{AB}Z_C$. We found that the effect of the selective solvent can be significantly weaker than for the neutral solvent. For the specific case studied, the MST was shifted to $\chi_{AB}r_C \simeq 20$ for the 20/80 PS-*b*-PBD/styrene blend, whereas the addition of nonselective solvent would have shifted it to $\chi_{AB}r_C \simeq 50$.

The scaling of d with Z_C was the same for all cases, selective and nonselective solvents, model and real systems, as was its scaling with χ_{AB}. In particular, the values of the corresponding exponents were larger in the weak segregation regime than in the strong segregation regime. The scaling with copolymer volume fraction was the same for the two sets of model calculations, selective and nonselective solvents, but it was significantly weaker for the PS-*b*-PBD/styrene blends; the calculated values of the exponent were at least a factor of 2 smaller. Even here, the scaling of d with $\bar{\phi}_c$ was stronger in the weak than in the strong segregation regimes. This suggests that the scaling of d with $\bar{Z}_C$ and χ_{AB} is relatively universal, but the scaling of d with $\bar{\phi}_c$ may vary considerably from one system to another.

We end by noting that a quantitative comparison of the results discussed here with experiment would require new experiments. For example, there has been experimental work on the lamellar, cylindrical, and spherical microphases of copolymer/nonselective solvent blends[1,7,8] and on copolymer/selective solvent blends with highly asymmetric copolymers such that the blends adopted either the spherical or cylindrical morphology with or without the solvent.[5,6,10] However, to our knowledge there have not been systematic studies of the lamellar structure of these blends. In particular, such measurements could investigate the degree of universality of scaling laws for d and perhaps the relative concentrations of solvent in each subdomain for real systems.

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