Segment Distributions in Lamellar Diblock Copolymers

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ABSTRACT: Predictions from a self-consistent-field theory of inhomogeneous polymer systems are compared to results obtained from neutron reflectivity studies of ordered lamellar diblock copolymers and their blends with homopolymers. Previously measured distributions of chain ends and junction points in neat diblock copolymers, and of homopolymers in diblock copolymer/homopolymer blends, were found to be in quantitative agreement with theory. By extending the theory to more strongly segregated systems, we show that relatively weak centralization of chain ends within the appropriate domain of a lamellar diblock copolymer is expected in all cases. Agreement between theoretical and experimental values for the interfacial widths between copolymer domains or between immiscible homopolymers is also quantitative, provided that the effects of fluctuations of the interface position are appropriately taken into account.

I. Introduction

Several recent experimental and theoretical advances have contributed significantly to our current understanding of ordered block copolymer systems. Of particular experimental importance has been the realization that thin block copolymer films with exceptional orientational order can be produced by a simple surface ordering process.[1,2] These films, when labeled appropriately with a deuterated component, are ideally suited for neutron reflectivity studies which enable one to probe detailed structural features. Studies of this kind have in fact been used to probe many structural features of block copolymer systems which had previously been inaccessible. These features include the width of the interfacial region between block copolymer domains,[3,4] homopolymer distributions in lamellar diblock copolymer/homopolymer blends,[5] and distributions of chain ends and junction points in block copolymer systems.[6]

Experimental studies such as those mentioned above have provided many insights into the general features of block copolymer systems. Detailed results are, of course, confined to the specific systems which were examined. For this reason the concurrent development of theoretical models which predict the detailed structure of inhomogeneous polymer systems, of which ordered block copolymers are an example, has been an equally important development. The models which we refer to are based on the description of polymer chain statistics in terms of random walks in a perturbing mean field. This mean field must be determined in a self-consistent way, and numerical means are generally required to solve the resulting equations. The fundamental treatment was initially developed by Edwards and applied to the description of a single polymer chain in a solvent.[7] Helfand extended this treatment to polymer/polymer interfaces[8-11] and to diblock copolymers in the strong segregation regime.[12-15] The underlying theoretical treatment is not limited to bulk block copolymers in the strong segregation regime, however, and has recently been extended to the weak segregation regime[16,17] and to surfaces and thin films of block copolymers.[16] Similar theoretical treatments of solvent-containing systems have been developed independently by Scheutjens and Fleer[18,19] and by Hong and Noolandi.[20-23] All of these theories are based on the same fundamental mean-field description of polymer chain statistics, with additional approximation made in some cases.

It is quite clear from the list of references cited above that numerical self-consistent-field (SCF) techniques have found applicability in a wide range of areas in polymer science. Our focus here is on their application to polymer melts, where the predictive power of these theoretical models, as demonstrated by a limited number of comparisons to experimental data, has been encouraging. Adsorption isotherms for A/B diblock copolymers which segregate to the interface between immiscible A and B homopolymers are accurately predicted by the numerical SCF treatment if the χ parameter characterizing the thermodynamic interaction between A and B repeat units is known.[24,25] Comparison of theory to experiment allows one to extract a χ parameter which is found to be independent of the homopolymer molecular weight. The chemical potential of copolymer chains is limited by the formation of micelles in a bulk homopolymer phase. Recent calculations[26] indicate that this limiting chemical potential is also in quantitative agreement with predictions from the numerical SCF theory.

The numerical SCF treatment can be used to predict many properties of practical importance, e.g., the interfacial tension between immiscible blend components (with or without added block copolymer), the surface composition of a miscible polymer blend, etc. The quantities which are of more relevance to the results of recent neutron reflectivity experiments are the volume fraction profiles of a labeled component in a polymer melt. Comparisons between calculated and experimental profiles have so far been limited to the study of an end-adsorbed polymer layer in a polymeric matrix.[27] Reasonable agreement between theory and experiment was demonstrated in this case, but comparison to data from other polymer systems is clearly warranted. Our purpose here is to compare SCF predictions to recent results obtained for the distributions of labeled ends and labeled junction points in a diblock copolymer and to results for the distribution of a labeled homopolymer in a lamellar copolymer/homopolymer blend. We begin with a summary of the SCF equations in the following section. Section III is a comparison of theoretical and experimental results. In section IV we compare detailed theoretical results to theoretical results which are obtained from a narrow interphase approximation. This approximation was developed previously for block copolymer/homopolymer blends[28] and is employed here to evaluate the distribution of end segments in lamellar diblock copolymers. The importance of fluctuations in the interface position as they relate to the measured interfacial width is discussed in section V, and a brief summary of all our results is given in section VI.

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II. Self-Consistent-Field Theory

We consider a binary blend of an A homopolymer of degree of polymerization N_h, with an A/B diblock copolymer of degree of polymerization N_c. These degrees of polymerization are defined in terms of a reference concentration ρ_0, such that the volume of a homopolymer chain is N_h/ρ_0 and the volume of a copolymer chain is N_c/ρ_0. The statistical segment length a_a of an A repeat unit is defined by the requirement that the radius of gyration of an A homopolymer chain is given by $a_a(N_h/6)^{1/2}$. A similar definition holds for a_b, the statistical segment length of a B repeat unit. Note that a_a and a_b are not required to be identical in our treatment. We consider lamellae forming diblock copolymer/homopolymer blends where the composition varies only in a direction normal to the lamellar surfaces. Three polymer chain probability distribution functions, $q_{c1}(z,n)$, $q_{c2}(z,n)$, and $q_h(z,n)$, are the central quantities of the theory. These distribution functions are related to the probability of finding the termination of a chain segment of length n at position z. Chain segments are defined such that they begin from a given end of a chain. Two distribution functions, q_{c1} and q_{c2}, are required to describe the two distinct chain ends of the diblock copolymer, whereas a single distribution function q_h is sufficient for describing the homopolymer. The properties of inhomogeneous polymer systems are described (within the mean-field approximation) by the behavior of the distribution functions in a spatially varying mean field $w(z)$. This behavior is governed by the following modified diffusion equations:[7,9,10,12,13,21,29]

$$\frac{\partial q_{c1}(z,n)}{\partial n} = \frac{a^2(n)}{6}\frac{\partial^2 q_{c1}(z,n)}{\partial z^2} - w(z,n)q_{c1}(z,n) \qquad (1)$$

$$\frac{\partial q_{c2}(z,n)}{\partial n} = \frac{a^2(n)}{6}\frac{\partial^2 q_{c2}(z,n)}{\partial z^2} - w(z,n)q_{c2}(z,n) \qquad (2)$$

$$\frac{\partial q_h(z,n)}{\partial n} = \frac{a_a^2}{6}\frac{\partial^2 q_h(z,n)}{\partial z^2} - w_a(z)\, q_h(z,n) \qquad (3)$$

with the initial condition that all distribution functions are equal to 1 at $n = 0$. The boundary conditions for the distribution functions are determined by the requirement that the lamellar morphology is characterized by the periodicity L, i.e., $q(z,n) = q(z+L,n)$.

The n dependence of a and of w appearing in eqs 1 and 2 is entirely determined by the species (A or B) represented by the nth repeat unit. We consider a diblock copolymer which contains gN_c repeat units of type A followed by $(1-g)N_c$ repeat units of type B. Equation 1 for q_{c1} therefore has $w(z,n) = w_a(z)$ and $a(n) = a_a$ for n ranging from 1 to gN_c and $w(z,n) = w_b(z)$ and $a(n) = a_b$ for n ranging from gN_c to N_c. Similarly, eq 2 for q_{c2} has $w(z,n) = w_b(z)$ and $a(n) = a_b$ for n ranging from 1 to $(1-g)N_c$ and $w(z,n) = w_a(z)$ and $a(n) = a_a$ for n ranging from $(1-g)N_c$ to N_c. The mean fields, w_a for A repeat units and w_b for B repeat units, are given by:

$$w_a(z)/k_BT = \chi\phi_b^2(z) - \phi_c(z)/N_c - \phi_h(z)/N_h - \Delta w(z)/k_BT \qquad (4)$$

$$w_b(z)/k_BT = \chi\phi_a^2(z) - \phi_c(z)/N_c - \phi_h(z)/N_h - \Delta w(z)/k_BT \qquad (5)$$

where ϕ_a and ϕ_b are the local volume fractions of A and B repeat units and χ is the Flory interaction parameter characterizing the thermodynamic interaction between A and B repeat units. The incompressibility constraint is accounted for in the quantity Δw which is given by

$$\Delta w(z)/k_BT = \zeta\{1 - \phi_h(z) - \phi_c(z)\} \qquad (6)$$

Here ζ is a parameter which is inversely proportional to the compressibility of the copolymer melt. Values of ζ for real polymers are high enough so that the results obtained from the mean-field calculations are indistinguishable from the limiting incompressible case corresponding to $\zeta = \infty$.[9,10]

The quantities $\phi_c(n_1{:}n_2,z)$ and $\phi_h(n_1{:}n_2,z)$ are defined as the local contributions to the respective copolymer and homopolymer volume fractions from all portions of a chain from n_1 to n_2. These quantities are given by:

$$\phi_c(n_1{:}n_2,z) = \frac{1}{N_c}\exp\left\{\frac{\mu_c'}{k_BT} - 1\right\}\int_{n_1}^{n_2} q_{c1}(z,n)\, q_{c2}(z,N_c-n)\, dn \qquad (7)$$

$$\phi_h(n_1{:}n_2,z) = \frac{1}{N_h}\exp\left\{\frac{\mu_h'}{k_BT} - 1\right\}\int_{n_1}^{n_2} q_h(z,n)\, q_h(z,N_h-n)\, dn \qquad (8)$$

where μ_h' and μ_c' are closely related to the homopolymer and copolymer chemical potentials. The total local homopolymer and copolymer volume fractions are given by summing over all repeat units;

$$\phi_c(z) = \phi_c(0{:}N_c,z) \qquad (9)$$

$$\phi_h(z) = \phi_h(0{:}N_h,z) \qquad (10)$$

The actual chemical potentials, μ_h for the homopolymer chains and μ_c for the copolymer chains, are obtained by adding the contributions from the "excess" free energy Δw:

$$\mu_h = \mu_h' + \frac{N_h}{L}\int_0^L \phi_h(z)\, \Delta w(z)\, dz \qquad (11)$$

$$\mu_c = \mu_c' + \frac{N_c}{L}\int_0^L \phi_c(z)\, \Delta w(z)\, dz \qquad (12)$$

The overall free energy density f of the system is given by summing the contributions from the copolymer and homopolymer chains;

$$\frac{f}{\rho_0} = \frac{\Psi_h\mu_h}{N_h} + \frac{(1-\Psi_h)\mu_c}{N_c} \qquad (13)$$

where ρ_0 is the concentration of repeat units; i.e., $1/\rho_0$ is the reference volume used to define the degrees of polymerization and the interaction parameter χ. The quantity Ψ_h is the overall homopolymer volume fraction;

$$\Psi_h = \frac{1}{L}\int_0^L \phi_h(z)\, dz \qquad (14)$$

Pure polymers in the absence of thermodynamic interactions characterized by χ serve as the reference state for this free energy density. The free energy density f_0 of a homogeneous blend with respect to this same reference state is given by the familiar regular solution form:

$$\frac{f_0}{\rho_0 k_BT} = \frac{\phi_h \ln \phi_h}{N_h} + \frac{\phi_c \ln \phi_c}{N_c} + \chi\phi_a\phi_b \qquad (15)$$

Numerical methods are generally required to obtain self-consistent solutions to the complete set of mean-field equations listed above. These methods usually involve a transformation of the continuous variables z and n into discrete variables i and j. The treatment outlined here is in fact identical to the lattice treatment of Scheutjens and Fleer[18,19] provided that one uses the appropriate relationship between the lattice spacing and the statistical segment length.[30] We map the mean-field equations onto

Table I. Characterization of the Diblock Copolymers Which Were Studied Experimentally[5,6]

block sequence	M_{total}	M_{PS}	M_{PMMA}	L_{expt} (Å)	L_{thry} (Å)	error (%)
PS–PMMA–dPMMA	70 000	32 000	38 000[a]	293	315	7.5
PS–dPS–PMMA	100 000	40 000[b]	60 000	427	410	4.0
PS–PMMA	91 000	41 000	50 000	375	375	0.0

[a] End-labeled (10% deuterated). [b] Center-labeled (6% deuterated).

a lattice, as described previously[16] and utilize a relaxation method[31] to obtain their self-consistent solution.

III. Comparison of Theory with Experiment

We compare to data from three separate polystyrene/poly(methyl methacrylate) (PS/PMMA) diblock copolymers, the characteristics of which are shown in Table I. Two of these polymers are selectively labeled with deuterium. These copolymers, referred to as the end-labeled and center-labeled copolymers, are actually triblock copolymers where the third block consists of either deuterated PS (dPS) or deuterated PMMA (dPMMA). The end-labeled polymer has a short deuterated PMMA block at the end of the copolymer chain, giving an overall block sequence of PS–PMMA–dPMMA. The center-labeled polymer has a short deuterated PS block between the longer blocks of PS and PMMA, giving a block sequence of PS–dPS–PMMA. The lengths of the deuterated portions correspond to 10% of the total PMMA block for the end-labeled copolymer and 6% of the total PS block for the center-labeled copolymer. A more complete description of these polymers has been given previously, along with a detailed description of the experimental results.[6] In these experiments thin films of the diblock copolymers were cast onto silicon substrates and annealed under vacuum at 160 °C for several days to produce exceptionally well-oriented lamellar thin films. Neutron reflectivity measurements were made on ordered samples which were quenched to room temperature. The third diblock copolymer contains no deuterium but was blended with a deuterated PMMA homopolymer. In this case the volume fraction profile of the labeled homopolymer was probed by neutron reflectivity. Experimental results from this blending experiment have also been reported previously.[5]

The thin films contract in the thickness direction by a certain amount during the quench to room temperature. All distances reported in this work correspond to these contracted films. By assuming that the volume contraction takes place entirely in the thickness direction for these thin films, an estimate of the contraction can be made from the volume thermal expansion coefficients for the polymers. Tabulated values of these coefficients[32] give an expected 5% decrease in the film thickness, and of all associated length scales, during a quench from 160 °C to room temperature. The length scales obtained from the theory are determined by the PS and PMMA statistical segment lengths at the annealing temperature. Use of the volume fraction profile obtained at room temperature is not expected to appreciably affect the validity of our comparison to the theory, since the uncertainty of the segment lengths at 160 °C certainly exceeds 5%.

The measured equilibrium repeat periods of the three block copolymers are listed in Table I, along with the values of the repeat periods obtained by the self-consistent-field theory. For these calculations we have assumed statistical segment lengths of 6.7 Å for monomeric PS repeat units[33] and 7.1 Å for monomeric PMMA repeat units.[34] We have used $\chi = 0.04$ in the calculations, where $1/\rho_0$, the reference volume, corresponds to the volume of a PS monomeric repeat unit. This value for the χ parameter is quite close to the value of 0.037 which has been previously determined by comparison to scattering data in the disordered phase.[35] We emphasize here that the volumes of PS and PMMA monomeric repeat units are not identical. Polystyrene has a room-temperature density of 1.05 g/cm^3 and a molecular weight per monomeric repeat unit of 104. These values give a volume for the PS repeat unit of 165 Å^3. Poly(methyl methacrylate) has a room-temperature density of 1.15 g/cm^3 and a molecular weight per monomeric repeat unit of 100, giving a volume of 144 Å^3 per repeat unit. When the repeat unit for PMMA is redefined so that it has the same volume as a PS monomeric repeat unit, the PMMA statistical segment length becomes 7.5 Å. The difference between the PS and PMMA segment lengths when compared in this fashion is still relatively small, especially when one considers the errors involved in accurately determining these quantities. However, for other copolymer systems it is quite possible that the difference in statistical segment lengths will be more substantial. We have used two separate values of the statistical segment lengths for PS and PMMA (at constant segmental volume) primarily to illustrate the ability of the self-consistent-field theory to account for these differences.

The data in Table I show that the experimentally determined repeat periods of the three block copolymers are reliably reproduced by the self-consistent-field theory for a single set of statistical segment lengths and a single χ parameter. Over any region where the quantity χN varies by only a small amount, the self-consistent-field prediction for the relationship between L, χ, and N_c for symmetric diblock copolymers can be written in the following form:

$$L \propto \chi^{\delta} N_c^{\delta+0.5} \qquad (16)$$

The quantity δ is approximately equal to $^1/_6$ in the strong segregation regime ($\chi N_c > 50$) and increases continuously as χN is decreased.[16,17] A maximum value of $\delta \cong 0.45$ is obtained at $\chi N_c = 10.5$, the mean-field critical point where the amplitude of the composition modulation in the lamellar copolymer microphase vanishes. Because the N_c dependence of L is always stronger than the χ dependence of L, it is difficult to obtain highly accurate values of χ by comparing theoretical and experimental values of the repeat period L. For example, with $\delta = 0.2$ a 10% error in the degree of polymerization N_c translates to a 40% error in the determination of χ. The situation is somewhat better in the weak segregation regime, where with $\delta = 0.45$ a 10% error in N_c gives a 22% error in χ. However, fluctuation effects become important near the order–disorder transition,[36–38] thereby complicating the analysis in this regime. The point which we emphasize here is that the equilibrium repeat periods as determined by the self-consistent-field theory are entirely consistent with the experimental values, given a 10% uncertainty in the homopolymer molecular weight and a value of χ which is consistent with previous experiments.

In principle, the equilibrium repeat period of the copolymer/homopolymer blend can be obtained as a function of the volume fraction of homopolymer in the blend. In practice this is very difficult to accomplish because it requires that self-consistent solutions to the mean-field equations be obtained at different values of L while holding the overall homopolymer volume fraction Ψ_h fixed. The difficulty arises from the fact that Ψ_h is not

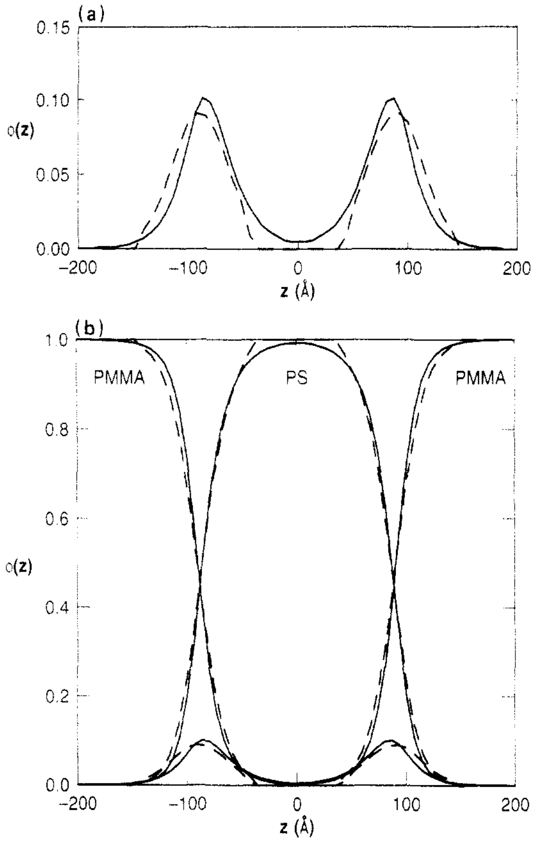

Figure 1. Calculated (—) and experimentally determined (- - -) volume fraction profiles for the labeled portion of the center-labeled diblock copolymer: (a) labeled portions only; (b) labeled portions in addition to the overall PS and PMMA volume fractions.

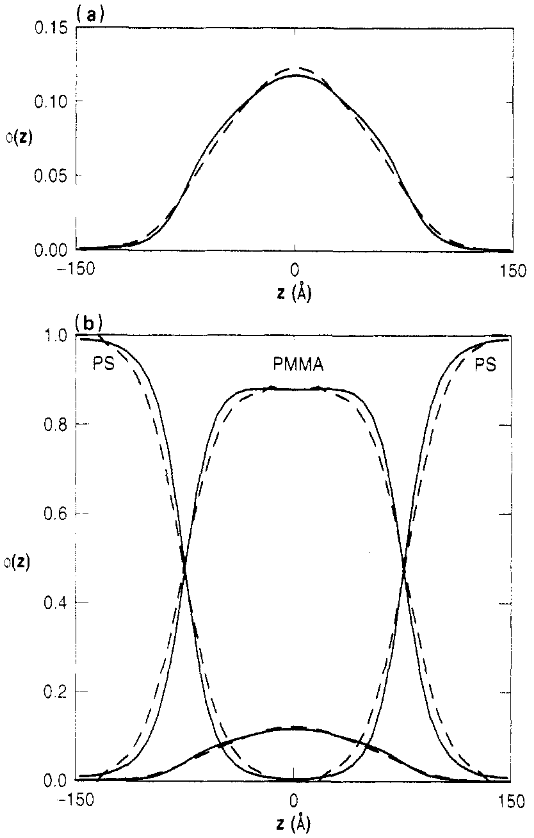

Figure 2. Calculated (—) and experimentally determined (- - -) volume fraction profiles for the labeled portion of the end-labeled diblock copolymer: (a) labeled portions only; (b) labeled portions in addition to the overall PS and PMMA volume fractions.

one of the inputs to the problem. Instead, the prefactors μ_c' and μ_h' which appear in eqs 7 and 8 for the volume fractions are adjusted interatively until the correct value of Ψ_h is obtained. The free energy density is very sensitive to the final value of Ψ_h, so this quantity needs to be obtained quite reproducibly at several values of L in order to obtain the equilibrium repeat period. This complication is not present when determining the equilibrium repeat periods of pure copolymers, and these values are much more easily obtained. In our calculation of the segmental distributions, we fix the periodicity L to the values which were determined experimentally. Analysis of the data in this manner allows us to decouple the small errors in the determination of the equilibrium repeat period from the determination of the segmental distributions in block copolymers with a known repeat period.

Results for the center-labeled and end-labeled polymers are shown in Figures 1 and 2, respectively. In both cases previously described results from the neutron reflectivity experiments[5,6] are compared to the predictions of the SCF theory. Theoretical predictions are obtained by substituting into eq 7 values for n_1 and n_2 which correspond to the labeled portions of the chain. In examining the distributions of the labeled segments, shown in detail in part a of Figures 1 and 2, agreement between theory (solid lines) and experiment (dashed lines) is found to be quite good. The experimentally determined profiles were obtained by calculating reflectivity profiles from an assumed set of volume fraction profiles for labeled and unlabeled segments.[39] These reflectivity profiles are quite sensitive to the assumed distributions, allowing one to determine these distributions with a high degree of accuracy. The agreement between theory and experiment is especially satisfying because the experimental results were obtained without prior knowledge of the theoretical predictions, a statement which also holds for the blend data shown in Figures 3 and 4.

In part b of Figures 1 and 2 we have added the theoretical and experimental curves for the overall PS and PMMA volume fractions. These curves, which have been included in order to illustrate the relative placement of the labeled segments within the lamellar microdomain morphology, are completely specified by the domain sizes and by a parameter w which describes the width of the region between the PS and PMMA domains. Several different definitions of this interfacial width have been used. We use a definition based on the derivative of the volume fraction profile:

$$w \equiv \left|\frac{\partial \phi_{PS}}{\partial z}\right|^{-1}_{\phi_{PS}=0.5} \tag{17}$$

Reflectivity profiles from the labeled copolymers described here are not highly sensitive to the interdomain width. The experimental domain widths shown in Figures 1a and 2a were actually measured in previous experiments on block copolymers of PS and PMMA for which one of the blocks was fully deuterated.[3] The measured widths of 50 Å are slightly larger than the theoretically determined widths of 40 Å. Possible origins of this discrepancy are discussed below in section V on interface fluctuations. Our focus here is instead on the labeled sections of the copolymer chains. Inspection of Figures 1b and 2b shows that the centers of the copolymer chains, i.e., the segments very close to the junction points between PS and PMMA blocks, are essentially confined to a region of width w, whereas the end segments are more evenly distributed throughout the appropriate microdomain.

Results obtained for the distributions of deuterated PMMA homopolymer within the unlabeled PS/PMMA

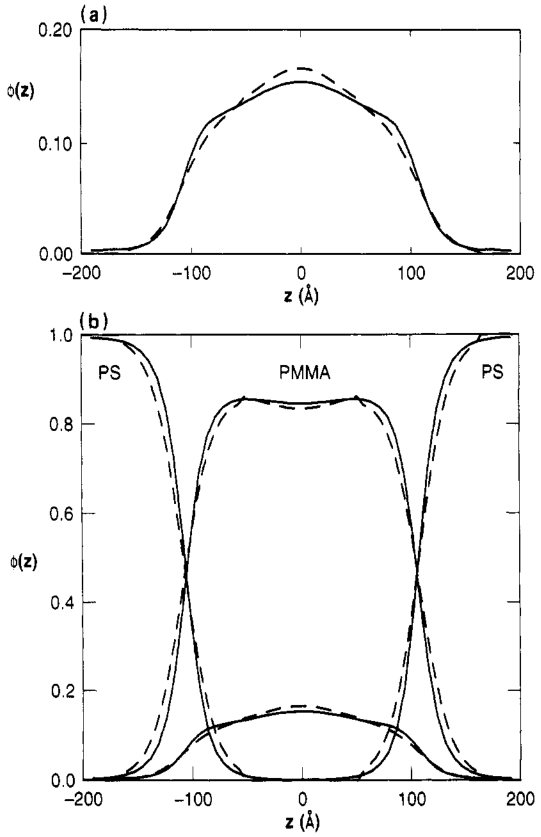

Figure 3. Calculated (—) and experimentally determined (- - -) volume fraction profiles for a PMMA homopolymer with M = 12 000 in the unlabeled diblock copolymer: (a) homopolymer volume fraction; (b) homopolymer volume fraction in addition to the PS and PMMA block volume fractions.

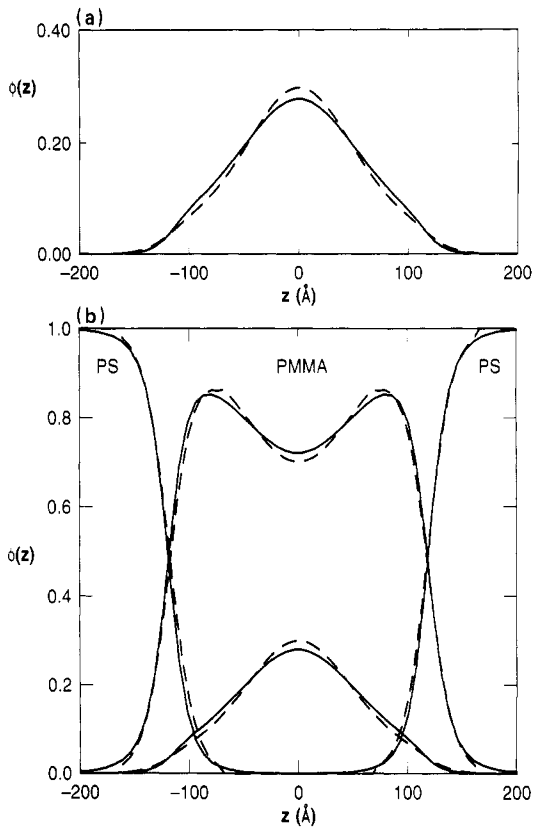

Figure 4. Calculated (—) and experimentally determined (- - -) volume fraction profiles for a PMMA homopolymer with M = 57 000 in the unlabeled diblock copolymer: (a) homopolymer volume fraction; (b) homopolymer volume fraction in addition to the PS and PMMA block volume fractions.

diblock copolymer are shown in Figures 3 and 4. As with Figures 1 and 2, we compare theoretical and experimental results for the labeled segments in part a of each figure and include the overall volume fractions for the PS and PMMA blocks in part b of each figure. Both figures correspond to an overall homopolymer weight fraction in the blend of ~10%. The data in Figure 3 is for a homopolymer with a molecular weight of 12 000, whereas the data in Figure 4 is for a homopolymer with a molecular weight of 57 000.[40] Agreement between the experimental and theoretical results is again quite good. Note that the homopolymer distribution for the low molecular weight copolymers is significantly broader than the distribution of the high molecular weight homopolymer. This result is consistent with a previous theoretical treatment of copolymer/homopolymer blends.[28]

IV. Narrow Interphase Approximation

In the strong segregation regime the repeat period for a lamellar diblock copolymer increases with the $^{2}/_{3}$ power of the molecular weight. At the same time a slight decrease in the interfacial width is expected with increasing molecular weight, because the areal density of junction points in the interfacial region is decreasing.[13,16] As a result the width of the interfacial region relative to the size of the individual domains decreases as one moves further into the strong segregation regime. For highly segregated diblock copolymers the interfacial width can be neglected altogether. In this case the interfacial regions can be treated as planes which act as grafting surfaces for a set of polymer "brushes". An individual domain consists of two opposing polymer brushes attached to these grafting planes. The properties of an individual copolymer domain in the absence of added homopolymer are now completely determined by the domain width normalized by the radius of gyration of the corresponding copolymer block. Many of these properties, for example, the profiles of each of the two blocks, have been calculated previously.[28] These calculations invoke a brush theory[30] which is identical in spirit to the treatment outlined in section II but with the simplifying assumption that the width of the interfacial region between microdomains is completely negligible. Here we refer to this method as the narrow interphase approximation. Brush profiles obtained in this way can of course be divided into contributions from each of the repeat units along a given chain. The distribution of repeat units which are very close to the junction point is coupled to the interfacial width w, as illustrated by the results shown in Figure 3. A δ function distribution for the junction points is therefore obtained from our narrow interphase approximation. The degree of freedom for the placement of individual repeat units increases for repeat units which are further from the junction point. Chain ends have the broadest spatial distribution because they are the repeat units which are the most loosely coupled to the grafting surface. The distribution of chain ends calculated from the narrow interphase approximation is shown in Figure 5 for three values of the normalized domain width, $l_a/R_{g,a}$. Here l_a is the size of the A copolymer domain and $R_{g,a}$ is the unperturbed radius of gyration of the A copolymer block. (The analysis presented here is of course equally valid for the B copolymer block.) Values of χN_c shown at the top of the figure were calculated from the known relationship[16] between χN and L/R_g for symmetric diblock copolymers. For very high values of χN_c ($\chi N_c >$ 200) this relationship is quite accurately given by the

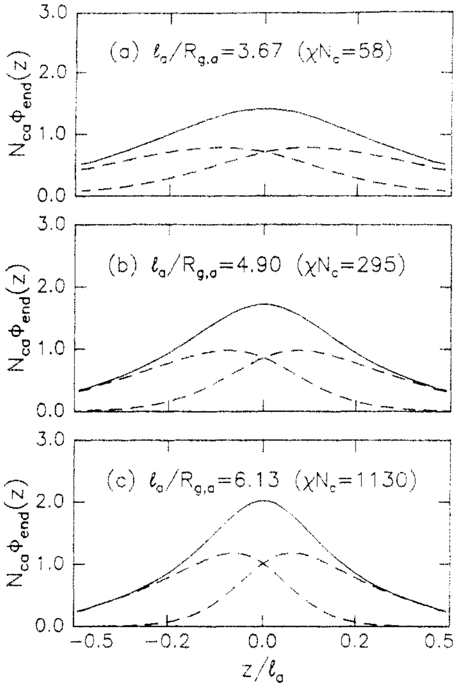

Figure 5. Normalized end segment distribution for ordered diblock copolymers as calculated from the narrow interphase approximation for three different values of the normalized domain thickness $l_a/R_{g,a}$. Contributions from blocks attached to each side of the domain are plotted separately (- - -), as is the overall end segment distribution (—). The corresponding values of χN_c are as indicated.

following scaling relationship derived by Semenov:[41]

$$l_a/R_{g,a} = 1.90(\chi N_c)^{1/6} \tag{18}$$

Note that the ends are not strongly centralized even for $\chi N_c = 1130$, a value which almost certainly exceeds those which one expects to find in real copolymer systems.

In a previous treatment of block copolymer/homopolymer blends utilizing the narrow interphase approximation, it was shown that the homopolymer distribution is nearly independent of the homopolymer molecular weight when this molecular weight exceeds that of the corresponding copolymer block.[28] In this limit the homopolymer profiles are completely specified by Φ_h, the overall homopolymer volume fraction in the domain ($\Phi_h \neq \Psi_h$), and by l_a, the domain width. For sufficiently large domains ($(1-\Phi_h)l_a > 3.2$) the homopolymer volume fraction profiles were found to have the following form:

$$\phi_h(x) = 0.5\left\{\tanh\left(\frac{\Phi_h l_a + 2z}{w_{ol}}\right) + \tanh\left(\frac{\Phi_h l_a - 2z}{w_{ol}}\right)\right\} \tag{19}$$

where w_{ol} is given by

$$w_{ol} = 1.09R_{g,a} + 3.16\left\{\frac{(R_{g,a})^2}{(1-\Phi_h)l_a}\right\} \tag{20}$$

Figure 6 is a comparison of predictions from the narrow interphase approximation (eqs 19 and 20) to predictions obtained from the complete solution to the equations of section II. The values of Φ_h and l_a for this comparison correspond to the system studied experimentally, the results of which are shown in Figure 4. The small differences between the complete detailed solution for the homopolymer profile and the results obtained from the narrow interphase approximation are due primarily to the finite width of the interface. The narrow interphase approximation clearly works quite well in this case, even though χN_c is only equal to about 40 for this copolymer.

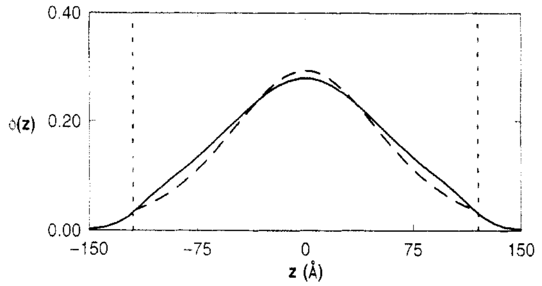

Figure 6. Comparison of the detailed theoretical result for the distribution of the higher molecular weight PMMA homopolymer (—) to the result obtained from eqs 19 and 20 (- - -). Here we have used a_{PMMA} = 7.1 Å, where a_{PMMA} is the PMMA statistical segment length (based on a monomeric PMMA repeat unit).

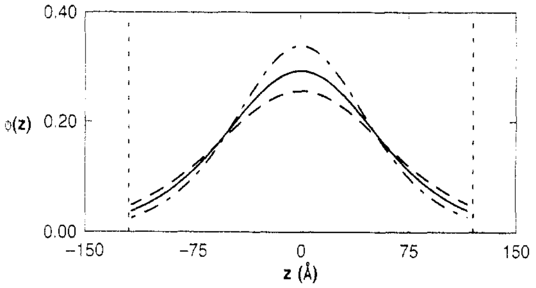

Figure 7. Predictions of eqs 19 and 20 for the distribution of the higher molecular weight PMMA homopolymers for a_{PMMA} = 7.1 (—), 6.4 (- · -), and 7.8 Å (- - -).

The narrow interphase approximation will give an even better description of the homopolymer volume fraction profile at higher values of χN_c, where the interfacial regions are narrower with respect to the domain widths.

One important factor with regard to the homopolymer distributions is that they are quite sensitive to the copolymer radius of gyration, and hence the value chosen for the statistical segment length. This point is illustrated in Figure 7, where the predictions of eqs 19 and 20 are plotted for the same values of Φ_h and l_a. The solid curve corresponds to a statistical segment length of 7.1 Å for a PMMA monomeric repeat unit and is identical to the narrow interphase prediction shown in Figure 6. The two additional curves in Figure 7 correspond to PMMA statistical segment lengths of 7.8 (dashed) and 6.4 Å (dot-dashed). Thus, a 10% error in the statistical segment length can result in uncertainties of the sort shown in Figure 7. Within this uncertainty, the theoretical predictions are in quantitative agreement with the experimental results.

V. Effects of Interface Fluctuations

One area of apparent discrepancy between theory and experiment exists in the values of the interfacial width w. Measured values of this quantity are higher than the values calculated from the SCF treatment. In order to understand this discrepancy as it relates to interdomain widths in block copolymers, we begin with a discussion of the simpler case of immiscible homopolymers, where the apparent discrepancy between theory and experiment also exists. The interfacial width between immiscible homopolymers is itself a very important property, particularly with respect to the mechanical strength of the interface. Adhesion between immiscible polymers is expected to be determined largely by the areal density of entanglements between molecules from opposing phases, a quantity which is very sensitive to the width of the interfacial region. The theoretical value of the interfacial width w_∞ between homopolymers of infinite molecular weight is given by the following formula:[11]

$$w_\infty = 2a'/(6\chi)^{1/2} \tag{21}$$

where a' is an average of the statistical segment lengths for the two homopolymers. For small relative differences between the two segment lengths, this average is simply their arithmetic mean. For the PS/PMMA system with a reference volume equal to the volume of a PS repeat unit, one has $\chi = 0.04$, $a_{\text{PS}} = 6.7$ Å, and $a_{\text{PMMA}} = 7.5$ Å. With these parameters eq 21 gives $w_\infty = 29$ Å. The interfacial width between polymers of finite molecular weight is somewhat greater than w_∞, but this difference is less than 10% for $\chi N > 12$,[42] where measurements of the PS/PMMA interfacial width have been carried out.[3,43] These measurements give an interfacial width between homopolymers of 50 Å, which is considerably larger than the predicted value. This discrepancy can be accounted for by considering the contribution associated with fluctuations in the position of the interface. These fluctuations represent a spatial variation of the average position of the interface. The effective interfacial width, w_{eff}, which is measured experimentally will be given by the convolution of the intrinsic width w with the distribution of interface positions sampled by the measurement.

The theory of interfacial fluctuations was developed primarily to describe capillary waves at the liquid/vapor interface.[44,45] Extension of these ideas to polymeric systems is straightforward. The basic result of these treatments is an expression for $\langle(\Delta z)^2\rangle$, the mean-square displacement of the interface from its average position:

$$\langle(\Delta z)^2\rangle = \frac{k_{\text{B}}T}{2\pi\gamma_{\text{ab}}} \ln\left\{\frac{\lambda_{\max}}{\lambda_{\min}}\right\} \tag{22}$$

where γ_{ab} is the interfacial tension between immiscible homopolymers, and $\lambda_{\min}$ and $\lambda_{\max}$ are the minimum and maximum wavelengths of the fluctuations. Equation 22 can be used to estimate the importance of interfacial fluctuations. The long wavelength cutoff $\lambda_{\max}$ is limited by the lateral coherence length for the neutron reflectivity measurements, which is approximately 1 μm. Here we assume that the annealing time is sufficient for equilibration of all fluctuations with wavelengths below this coherence length. If the long wavelength fluctuations are not equilibrated, due to the high viscosity of the polymers, then $\lambda_{\max}$ will be given instead by the wavelength which has a relaxation time comparable to the experimental annealing time. We expect that the intrinsic interfacial width will provide a good estimate of $\lambda_{\min}$. For small relative differences between the segment lengths the polymer/polymer interfacial tension is given by[11]

$$\gamma_{\text{ab}} = a'\rho_0 k_{\text{B}}T(\chi/6)^{1/2} \tag{23}$$

The interfacial tension between PS and PMMA homopolymers at 170 °C is 2 dyn/cm, as given by eq 23 with $a' = 7.1$ Å, $1/\rho_0 = 165$ Å^3, and $\chi = 0.04$. Substitution of this value for γ into eq 22, with $\lambda_{\max} = 1$ μm and $\lambda_{\min} = 30$ Å, gives $\langle(\Delta z)^2\rangle^{1/2} = 16.8$ Å. Convolution of a Gaussian distribution of interface positions with a step function profile gives an error function profile with an interfacial width (as defined by eq 16) of $\langle 2\pi(\Delta z)^2\rangle^{1/2}$. Thus with these assumptions w_{eff}, the effective interfacial width which is measured in a reflectivity experiment, will be 42 Å, even for an interface which has a negligible intrinsic width w. Note that this value is not extremely sensitive to the values of $\lambda_{\max}$ and $\lambda_{\min}$ which are chosen. For example, changing the ratio $\lambda_{\max}/\lambda_{\min}$ by a factor of 5 results in only a 12% change in $\langle(\Delta z)^2\rangle^{1/2}$. Calculated values for the effective interfacial width are not extremely sensitive to values of w which are significantly less than the minimum value of w_{eff}. We have shown above that taking $w = 0$ gives $w_{\text{eff}} = 42$ Å. Taking $w = 29$ Å gives $w_{\text{eff}} = 51$ Å. Thus, the measured values of the interfacial width for immiscible homopolymers are entirely consistent with the self-consistent-field predictions for the intrinsic interfacial width when the effects of interfacial fluctuations are taken into account.

The situation for ordered diblock copolymer systems is somewhat more complicated. In this case we consider not just a single interface but multiple interfaces which are constrained to be roughly parallel to one another by the connectivity of the block copolymer chains. Typical values for polymer surface tensions are an order of magnitude higher than typical values for the interfacial tension. Because the fluctuation contribution to the interfacial width scales inversely with the relevant interfacial (or surface) tension, the surface of an ordered block copolymer film is quite smooth, as is the film/substrate interface. We are now interested in interfacial fluctuations in a system of polymer chains which are in effect grafted to a flat surface. This general situation has been considered by Fredrickson *et al.*[46] In a grafted chain system a fluctuation in the interface position requires that the chains be stretched laterally over a distance which is comparable to the wavelength of the fluctuation. As a result, fluctuations with wavelengths significantly larger than the copolymer radius of gyration are suppressed. The value of $\lambda_{\max}$ which one must use in eq 22 is therefore significantly less than the lateral coherence length for the neutron reflectivity experiment. The exact value chosen for $\lambda_{\max}$ is somewhat arbitrary, but a reasonable value to choose is the copolymer repeat period, as has been suggested by Semenov.[47] With $\lambda_{\max} = 400$ Å, $\lambda_{\min} = 30$ Å, and $\gamma = 2$ dyn/cm, eq 22 gives $\langle(\Delta z)^2\rangle^{1/2} = 11.1$ Å at 170 °C, which, after multiplication by $(2\pi)^{1/2}$, corresponds to a contribution to the interfacial width of 28 Å. This contribution is added to the intrinsic interfacial width, in quadrature, to give the measured interfacial width. The net effect of the connectivity of the immiscible copolymer blocks is therefore to reduce the fluctuation contribution to the interfacial roughness. This decrease is offset by the greater intrinsic width of the interface as calculated by the numerical SCF treatment. For copolymer interfaces (with $\chi N \cong 50$) we predict $w = 40$ Å and $\langle 2\pi\Delta z^2\rangle^{1/2} = 28$ Å, giving $w_{\text{eff}} = 49$ Å. For homopolymer interfaces we predict $w = 29$ Å and $\langle 2\pi\Delta z^2\rangle^{1/2} = 42$ Å, giving $w_{\text{eff}} = 51$ Å. Both values are in good agreement with results obtained from previous reflectivity experiments.

VI. Summary

We have shown that numerical solution of a set of self-consistent-field equations gives predictions for the structure of ordered diblock copolymer systems which are in very good agreement with results obtained from neutron reflectivity experiments on ordered diblock copolymer films. The spatial distributions of chain ends and of junction points are accurately described by the theory, as are the spatial distributions of added homopolymers. By generalizing the theoretical treatment we predict that chain ends will be distributed throughout the appropriate domain for all experimentally accessible values of χN_c. Centralization of the chain ends within a domain increases somewhat as χN_c is increased, but the increase is not dramatic. We also obtain agreement between measured and theoretical values for interfacial widths within ordered diblock copolymers and for immiscible homopolymers, provided that the effects of interfacial fluctuations are accounted for. Our results provide a confirmation of the ability of numerical self-consistent-field techniques to accurately describe inhomogeneous polymer systems, including those which are difficult or impossible to probe experimentally.

References and Notes

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(39) The quantity directly probed by a neutron reflectivity experiment is the scattering length density b/V, which is a linear combination of the volume fractions for all segment types in the system. When more than two segment types are present, as for example with the PS–PMMA–dPMMA and PS–dPS–PMMA copolymers, additional information must be used to unambiguously relate the scattering length density profile to the appropriate volume fraction profiles. In our case this additional information comes from experiments described in refs 3 and 5, where only two segment types were present.
(40) These molecular weights were determined by size-exclusion chromatography, using normal (nondeuterated) PMMA as a calibrant. The actual molecular weights of the polymers, obtained by taking into account the increased mass of a monomeric repeat unit due to deuteration, are 8% larger than the values reported in the text.
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