Homopolymer Distributions in Lamellar Copolymer/Homopolymer Blends

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ABSTRACT: A quantitative mean-field treatment, based on the representation of polymer chain statistics by probability distribution functions, is applied to lamellar blends of an AB diblock copolymer with an A homopolymer. We work in the strong segregation limit, where the interface between A and B microdomains is narrow and the A homopolymer segregates exclusively to the A domain. Copolymer blocks are modeled as end-adsorbed "brushes" which are anchored to opposing sides of a microdomain. Numerical solution of the mean-field equations can be used to determine homopolymer and copolymer profiles for all blend compositions. For pure diblock copolymers we obtain a simple analytic expression for the width of the overlap region between opposing copolymer brushes. Similar analytic expressions are obtained for the homopolymer distribution in blends for which the homopolymer molecular weight is larger than the molecular weight of the corresponding copolymer block. Numerical solutions to the mean-field equations are given for a set of experimentally studied copolymer/homopolymer blends. Fundamental aspects of lamellar copolymer/homopolymer blends, including those with low molecular weight homopolymers, are discussed in the context of this well-characterized model system.

I. Introduction

The properties of single-component polymeric materials are determined by the structure of the polymer itself. Because the number of available polymeric components is limited, it is often desirable to mix different polymeric components together to form a blend with unique material properties. Properties of miscible blends, where the components mix to form a single phase, are typically given by some average of the properties of the blend components. Properties of immiscible blends, however, are determined not only by the composition of the separate phases but also by the phase morphology. As a result, the properties of an immiscible blend can be dramatically different from the properties of any of the components. Rubber-toughened plastics are a primary example of this type of behavior. Here the toughness of a glassy matrix material is enhanced significantly by the incorporation of a dispersion of rubbery particles which are chemically bound to the matrix phase.[1] The size scale of the blend morphology is critical, as is generally the case with multiphase polymer blends.

Block copolymers are a particularly important class of blend materials since the size scale of phase separation for immiscible polymers is limited by their connectivity along a single polymer chain. Examples include the well-known "thermoplastic elastomers", triblock copolymers consisting of a rubbery central block and glassy end blocks. These materials organize to form glassy spherical or cylindrical microdomains in an elastic matrix phase. Block copolymers also form lamellar and bicontinuous morphologies, depending on the asymmetry of the block copolymer and the strength of the unfavorable thermodynamic interaction between immiscible blocks.[2] When the blocks are highly incompatible, the width of the interphase between microdomains is much less than the size of a microdomain.[3,4] The interphase region in this strong segregation regime therefore defines a two-dimensional "intermaterial dividing surface", the geometry of which characterizes the copolymer morphology.[2]

Junctions between copolymer blocks in the strong segregation limit are constrained to lie on the intermaterial dividing surface. Each domain therefore consists of a set of polymer chains which are tethered to this surface. Properties of ordered block copolymer melts are governed by the properties of these tethered chains, or "brushes". Consider for example a lamellar microdomain morphology formed by an AB diblock copolymer. As shown in Figure 1a, each microdomain consists of a set of opposing polymer brushes. The composition across each domain is constant; the A domain contains only A repeat units and the B domain contains only B repeat units. There is, however, an underlying heterogeneity within each microdomain. This intradomain heterogeneity is due to the structure of the brushes themselves and is not reflected in the composition. Polymer chain ends, for example, must be concentrated near the center of the domain where the two opposing brushes overlap.

Intradomain heterogeneity associated with the brush structure is particularly important with regard to the phase behavior of block copolymer/homopolymer blends. These blends are important in that they represent yet another way in which the morphology, and hence the material properties, can be controlled.[5–7] The character of an individual domain and the shape of the intermaterial dividing surface can both be changed by blending with homopolymer.[8] Consider for example the copolymer/homopolymer blend depicted schematically in Figure 1b, where the homopolymer segregates preferentially to one of the domains. The temperature dependence of rheological properties for a blend where the homopolymer and the miscible copolymer block have dissimilar glass transitions will depend on the distribution of homopolymer across the domain. The qualitative features of the rheological behavior will depend on the geometry of the intermaterial dividing surface, which in turn depends on the preferred mean curvature induced by the presence of the brush structure. This preferred mean curvature is itself a function of the homopolymer distribution, so that all of these blend properties are functions, either directly

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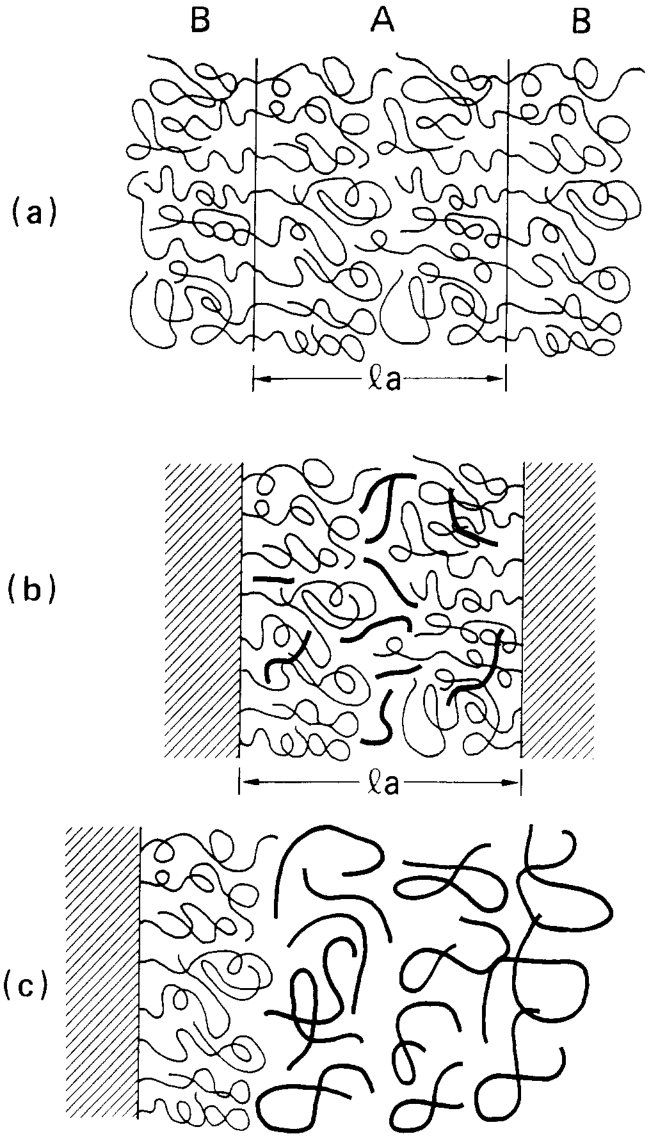

Figure 1. Schematic representations of (a) a pure lamellar diblock copolymer, (b) a single microdomain for a copolymer/homopolymer blend, and (c) a brush/homopolymer interface. Homopolymer chains are indicated by the bold lines, and the quantity l_a represents the width of an A microdomain.

or indirectly, of the homopolymer distribution.

In this paper we use an existing mean-field theory of polymer brushes[9] to calculate the distribution of homopolymer A across the A microdomain of a lamellar AB diblock copolymer in the strong segregation regime. The following section includes a summary of the theoretical treatment. Section III contains a discussion of the predictions for pure lamellar diblock copolymers. These predictions are general and have direct relevance to any lamellar diblock copolymer in the strong segregation regime. Section IV is a discussion of predictions for diblock copolymer/homopolymer blends which exhibit the lamellar morphology. These predictions are placed in the context of homopolystyrene/poly(styrene-*b*-isoprene) blends for which the equilibrium repeat periods have been measured experimentally.[10] The final section is a brief summary of our results.

II. Mean-Field Theory

We consider a single lamellar microdomain containing copolymer blocks with degree of polymerization N_c and a chemically equivalent homopolymer with degree of polymerization N_h. Homopolymer and copolymer profiles are given by the self-consistent solution to a set of mean-field equations. These equations are summarized here, in order to illustrate the basis of the mean-field treatment. Details of the technique are described in a previous treatment of end-adsorbed polymer brushes in polymeric matrices.[9] Each microdomain contains two copolymer brushes which originate from the opposing dividing surfaces on either side of the planar microdomain. Polymer chain statistics are characterized by probability distribution functions, $q(i,j)$, which represent the probability that j repeat units exist between a specified chain end and a repeat unit which is located at i. For systems with a planar geometry such as the lamellar morphology studied here, i represents the distance from one of the two surfaces to which the copolymer brushes are anchored, in units of $\mathbf{a}$, the statistical length of a polymer chain repeat unit. This statistical length is defined such that R_g^c, the unperturbed radius of gyration of the copolymer block, is given by $\mathbf{a}(N_c/6)^{1/2}$. Two different distribution functions are required to describe the copolymer brushes: q_{c1} for the tethered end and q_{c2} for the free end. The homopolymer is fully characterized by a single distribution function q_h, since the two homopolymer chain ends are identical. Connectivitity of the polymer chain repeat units and heterogeneities in the local environment are accounted for in the following recursion relations for the distribution functions:

$$q_{c1}(i,j) = \left\{\frac{1}{6}q_{c1}(i-1,j-1) + \frac{1}{6}q_{c1}(i+1,j-1) + \frac{4}{6}q_{c1}(i,j-1)\right\} \times \exp\{-w(i)/k_BT\} \quad (1)$$

$$q_{c2}(i,j) = \left\{\frac{1}{6}q_{c2}(i-1,j-1) + \frac{1}{6}q_{c2}(i+1,j-1) + \frac{4}{6}q_{c2}(i,j-1)\right\} \times \exp\{-w(i)/k_BT\} \quad (2)$$

$$q_h(i,j) = \left\{\frac{1}{6}q_h(i-1,j-1) + \frac{1}{6}q_h(i+1,j-1) + \frac{4}{6}q_h(i,j-1)\right\} \times \exp\{-w(i)/k_BT\} \quad (3)$$

Gaussian chain statistics are recovered when the local mean-field, $w(i)$, is positionally independent. In this case the distribution function $q(i,j)$ is proportional to $q(i-1,j-1) + q(i+1,j-1) + 4q(i,j-1)$. The ratio 1:1:4 arises because a random walk on a simple cubic lattice has four chances to remain in the same layer and one chance to move into each of the two adjacent layers. A spatially varying mean field biases these probabilities, therby introducing a local distortion to the polymer chain configurations.

The mean field is related to the free energy associated with the placement of a repeat unit in the local environment. In our case all repeat units are identical, and the mean field is the same for all repeat units:

$$\frac{w(i)}{k_BT} = -\frac{\phi_c(i)}{N_c} - \frac{\phi_h(i)}{N_h} + \zeta\{\phi_c(i) + \phi_h(i) - 1\} \quad (4)$$

where $\phi_c(i)$ and $\phi_h(i)$ are the respective local volume fractions of copolymer and homopolymer repeat units. The last term in eq 4 is associated with the incompressibility constraint, with ζ being inversely proportional to the bulk compressibility of the system. We typically use $\zeta = 10$, which gives results equivalent to the incompressible limit of $\zeta = \infty$.

The local copolymer and homopolymer volume fractions are given by summing the contributions from the N repeat units along a chain. A given repeat unit which is removed from one of the chain ends by j repeat units is removed from the other chain end by $N - j$ repeat units. The contribution from this repeat unit to the overall volume fraction is therefore proportional to the product $q(i,j)$

$q(i,N-j)$. Overall polymer volume fractions are obtained from the summation over these product terms

$$\phi_h(i) = A_h \sum_{j=1}^{N_h} q_h(i,j)\, q_h(i,N_h-j) \qquad (5)$$

$$\phi_c(i) = A_c \sum_{j=1}^{N_c} q_{c1}(i,j)\, q_{c2}(i,N_c-j) \qquad (6)$$

where the prefactors A_h and A_c determine the relative amounts of homopolymer and copolymer which are present.

The mean-field equations are closed by including the initial and boundary conditions for the distribution functions. Boundary conditions for each of the distribution functions are $q(0,j) = q(L+1,j) = 0$, because the domain in question extends from $i = 1$ to $i = L$ and the copolymer and homopolymer chains are assumed to be completely immiscible with the adjacent domains. Initial conditions for $j = 0$ are determined by the interactions of the chain ends with the dividing surfaces. The homopolymer chain ends and the free copolymer chain ends have no preferential affinity for the dividing surfaces, such that the initial conditions for q_h and q_{c2} are $q(i,0) = 1$, for $1 < i < L$. Initial conditions for q_{c1} are determined by the condition that all joints between different copolymer blocks exist at $i = 1$ or $i = L$; i.e., $q_{c1}(i,0) = 0$ for all i not equal to 1 or L. An iterative procedure is used to obtain the solution to the mean-field equations,[11] using the same nonzero values for $q_{c1}(1,0)$ and $q_{c1}(L,0)$. The values of $w(i)$ obtained from this calculation are then substituted into eqs 1, 2, and 6, with $q_{c1}(L,0) = 0$, in order to determine $\phi_c^1(i)$, the contribution to the copolymer volume fraction associated with the brush anchored to the dividing surface at $i = 1$. The brush anchored at $i = L$ is characterized by $\phi_c^2(i) = 1 - \phi_h(i)$.

The overall volume fraction of homopolymer in the domain Φ_h, is given by summing the contribution from each layer:

$$\Phi_h = \frac{1}{L}\sum_{i=1}^{L} \phi_h(i) \qquad (7)$$

The mean-field equations set forth in this section are solved by a relaxation method which is described in the appendix of ref 11. The overall homopolymer volume fraction is determined by the specific initial conditions for q_{c1} and by the values of A_h and A_c which are chosen. Different combinations of these parameters can give the same value of Φ_h. The brush profiles themselves, however, are functions only of $\mathbf{a}$, Φ_h, N_c, N_h, and the domain width l_a ($l_a = L\mathbf{a}$). The first four of these parameters are given by known material parameters and by the composition of the blend in question. Homopolymer and brush profiles for a blend with a known composition are therefore obtained from the theory with no adjustable parameters, provided that the domain width is determined independently.

The fundamental approximation made in our approach is the mean-field approximation, where only averaged quantities are considered. Polymer chain connectivity is taken into account through the recursion relationships for q_h, q_{c1}, and q_{c2} (eqs 1–3). These recursion relationships also include the spatially dependent mean field $w(i)$, and it is through this parameter that the effects of all nonbonded repeat units are included. In the most general application of the mean-field theory it is possible to construct a free energy expression from $\Delta w(i)$ and from the prefactors A_h and A_c which appear in the expressions for the volume fractions.[9,11,12] This underlying theory is mathematically identical to the theory of Scheutjens and Fleer,[13,14] although some algebraic manipulation of the mean-field equations is required in order to clearly see this equivalence. The theory is also equivalent to those developed by Helfand and co-workers[4,15–18] and by Hong and Noolandi,[19] provided that the polymer repeat units and the step size of the lattice are defined appropriately.[9] Equivalence to these off-lattice approaches shows that the imposition of a lattice does not affect the results of the calculation.

Minimization of the free energy with respect to the repeat period can be performed in order to predict the equilibrium repeat period. This calculation has recently been carried out for symmetric diblock copolymer melts for the entire thermodynamic regime from the order–disorder transition to the strong segregation regime.[12] Calculation of the equilibrium repeat period for copolymer/homopolymer blends can also be performed, although this calculation is complicated by the need to keep the overall homopolymer volume fraction constant as the repeat period is varied. In addition, many of the results obtained in this manner for copolymer/homopolymer blends are sensitive to the detailed parameters of the system. The narrow interphase approximation is an additional approximation which we have added to the mean-field treatment in order to obtain results which are of more general interest. As a consequence of this approximation, the contribution to the free energy from the interfacial region is no longer appropriately accounted for and we must take the repeat period as an input parameter.

III. Microdomain Properties for Pure Diblock Copolymers

We begin with a discussion of pure diblock copolymer microdomains. As with the copolymer/homopolymer blends, we refer all distances to the radius of gyration of the copolymer block that is compatible with the homopolymer. We do this because the radius of gyration is the fundamental size scale of a polymer chain (or a portion of a polymer chain). The segment length of a repeat unit (equal to the lattice spacing) is an ambiguous reference length because this length is coupled to the definition of a repeat unit. One commonly chooses the monomeric building block as the repeat unit, but there is no fundamental reason why this must be the case. Consider for example the following two combinations of N_c and L: $N_c = 260$, $L = 30$ and $N_c = 1040$, $L = 60$. Brush profiles obtained for these two combinations of N_c and L are identical when plotted against the normalized distance x/l_a, as they are in Figure 2a. The normalized domain width l_a/R_g^c ($=L(6/N_c)^{1/2}$) is equal to 4.56 for both combinations of N_c and L, and it is for this reason that the profiles overlap when plotted against x/l_a. The two combinations of N_c and L actually represent the same copolymer domain. The only difference is that we have defined the molecular weight of a repeat unit to be a factor of 4 greater for $N_c = 260$ than it is for $N_c = 1040$. The statistical segment length, i.e., the end-to-end distance of a repeat unit, scales as the square root of the repeat unit molecular weight and is therefore twice as great for $N_c = 260$ as compared to $N_c = 1040$.

Figure 2a indicates that the profiles are completely specified by l_a/R_g^c and are not affected by lattice artifacts associated with the definition of a repeat unit. This figure also shows that the profiles are independent of the interdomain width when this width is very narrow ($^1/_{30}$ or $^1/_{60}$ of the domain width). Actual interdomain widths are

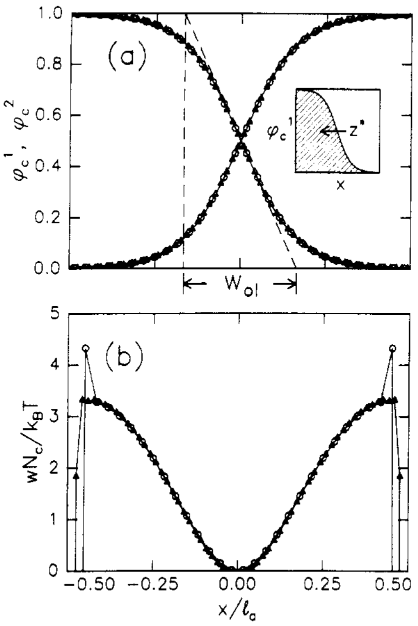

Figure 2. (a) Brush profiles for a pure copolymer domain for which $l_a = 4.56R_g^c$. The inset illustrates the definition of z^*. Data for $N_c = 260$, $L = 30$ (○) and $N_c = 1040$, $L = 60$ (△) are included. (b) Normalized mean fields corresponding to the brush profiles shown in part a. The normalized mean fields for the two values of N_c differ only in the outermost lattice layers.

generally greater than these values but are often still narrow enough so that the results obtained in our "very narrow interface" approximation are relevant.

In many cases a simple hyperbolic tangent form characterizes the brush profiles so that the only unspecified parameter is the brush overlap width w_{ol}. The profile for the brush anchored at $x = 0$ is given by

$$\phi_c^1(x) = 0.5 + 0.5 \tanh(-2x/w_{ol}) \tag{8}$$

The profile for the brush anchored at $x = l_a$ is the mirror image of this profile about $x = 0$:

$$\phi_c^2(x) = 0.5 + 0.5 \tanh(2x/w_{ol}) \tag{9}$$

One can easily show that w_{ol} is equal to the reciprocal of the characteristic slope of the brush profile, as illustrated in Figure 2a:

$$w_{ol} = |d\phi_c^1/dx|^{-1}_{\phi_c^1=0.5} \tag{10}$$

The brush overlap width is an important quantity in that the degree of molecular entanglement between opposing brushes, and hence the mechanical strength of the lamellar structure, is expected to be related to this width.[20]

An insightful comparison can be made between the profiles obtained for brush/brush interfaces (Figure 1a) and those obtained for brush/homopolymer interfaces (Figure 1c). Brush profiles for the brush/homopolymer system have been calculated previously.[9] When the chemical structures of the brush and homopolymer are identical, for example, a polystyrene copolymer brush in a polystyrene homopolymer matrix, the brush profiles are completely specified by the quantities z^*, R_g^c, and N_h/N_c. Here z^*, a measure of the brush thickness, is defined as the area under the brush profile as illustrated in the inset of Figure 2a. One can easily calculate the areal density of copolymer chains at the dividing surface by dividing z^* by the volume of the copolymer brush. The area per junction point at the intermaterial dividing surface is then obtained as the reciprocal of this areal density.

The homopolymer molecular weight dependence of the brush profile is small for $N_h/N_c > 1$. A good approximation to the brush profiles in this regime is obtained by using the asymptotic "dry brush" limit, $N_h/N_c = \infty$. For $z^*/R_g^c > 1.6$, the dry brush profiles are given by the hyperbolic tangent form of eq 8.[9] These brush/homopolymer profiles are therefore completely characterized by the dependence of w_{ol} on z^*, just as the brush/brush profiles are completely characterized by the dependence of w_{ol} on l_a. The properties of brush/brush interfaces can therefore be compared to the properties of dry brush/homopolymer interfaces by comparison of the brush overlap widths for these two types of interfaces.

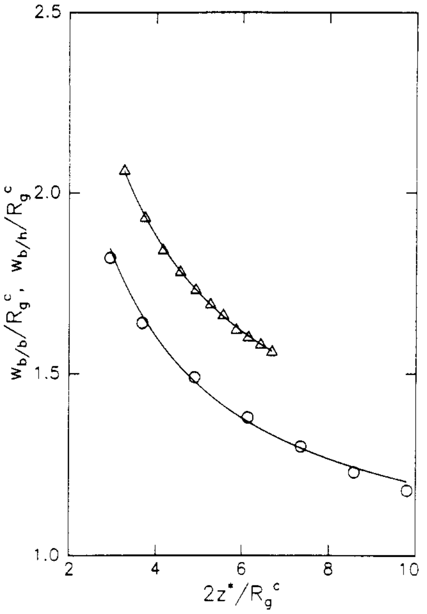

Figure 3. Calculated values of the overlap widths $w_{b/b}$ (○) and $w_{b/h}$ (△) as functions of $2z^*/R_g^c$. The solid lines represent the empirical fits of eqs 11 and 12. Here $w_{b/b}$ characterizes a brush/brush interface such as that found in the center of a pure diblock copolymer microdomain (Figure 1a), and $w_{b/h}$ characterizes the interface between a brush and a high molecular weight homopolymer (Figure 1c).

We define $w_{b/b}$ as the value of w_{ol} for a brush/brush interface in the absence of homopolymer. The quantity $w_{b/h}$ is similarly defined as the value of w_{ol} for a brush/homopolymer interface with $N_h/N_c = \infty$. In the absence of added homopolymer, a given lamellar microdomain consists of two brushes, with $z^* = l_a/2$ for each brush. One therefore has $w_{b/b}(l_a) = w_{b/b}(2z^*)$. Master curves for $w_{b/h}$ and $w_{b/b}$ as a function of $2z^*$ are shown in Figure 3. The solid lines represent the following empirical fits:

$$w_{b/h}/R_g^c = 1.09 + 3.16\{R_g^c/2z^*\} \tag{11}$$

$$w_{b/b}/R_g^c = 0.93 + 2.69\{R_g^c/2z^*\} = 0.85w_{b/h} \tag{12}$$

The 15% difference in the overlap widths for brush/brush and brush/homopolymer interfaces can be attributed to the different constraints placed on the two types of brushes. These constraints are related to the requirement that the volume fractions sum to 1 and are reflected in the spatial dependence of the mean field. The mean field corresponding to the brush/brush profiles of Figure 2a is plotted in Figure 2b, where we again include data for $N_c = 260$, $L = 30$ and $N_c = 1040$, $L = 60$. The derivative of the mean field is negative in the left half of the domain and is positive in the right half of the domain. This result is a straightforward consequence of the requirement that brush chains fill the entire polystyrene domain, so that the brushes are extended toward the domain center.

Extension of the brush anchored at the left side of the domain requires that the mean field decrease with increasing x, whereas extension of the brush anchored at the right side of the domain requires that the mean field decrease with decreasing x. By symmetry, the spatial derivative of w must vanish at $x = 0$, and in this region the local chain configurations are Gaussian. Brush/brush and brush/homopolymer interfaces are in fact similar because in both cases the overlap region consists of nearly Gaussian chains. The relatively small (15%) compression of the brush profile when high molecular weight homopolymer is replaced with an identical brush can be attributed to the fact that an opposing brush is slightly less compliant than a high molecular weight homopolymer. The upturn in the mean field at $x = 0$ is associated with the symmetry constraint and serves to force a given brush back onto itself.

The properties of the mean field at the domain edges are artifacts of the narrow interphase approximation, where the polymer volume fraction is assumed to jump from zero to 1 across a single lattice layer. Modeling the domain boundaries as impenetrable walls in this way introduces a component to the mean field which appears only in the first and second lattice layers, as illustrated by Figure 2b. Strong damping of the wall effects in polymer melts is a manifestation of screening, with the width of a lattice layer representing the screening length. The actual screening length for an amorphous polymer is the limiting straight-line distance between two backbone bonds on adjacent portions of a polymer chain, below which the orientations of the bonds become correlated to one another. Screening lengths for highly flexible polymers such as polystyrene and polyisoprene are approximately 10 Å.[21]

The self-consistent mean-field treatment used to determine the properties of the polymer brushes is valid only for length scales which are larger than the screening length of the polymer melt in question. In this limit the properties are dependent only on the radius of gyration of the polymer and not on the manner in which the screening length, i.e., the lattice spacing, is defined. The mean-field profiles of Figure 2b are indeed independent of L if the distance is scaled by R_g^c, the mean-field is scaled by the volume of a repeat unit, and the outermost points for which the wall effects dominate are neglected. The mean-field profile can therefore be used to determine the manner in which the chain configurations are distorted locally. Inspection of Figure 2b shows that the polymer chains are nearly ideal in the vicinity of the wall ($|x/l_a| > 0.4$); i.e., the derivative of the mean-field vanishes. The central portions of each brush ($0.05 \lesssim |x/l_a| \lesssim 0.35$) are uniformly extended away from the interfaces to which they are anchored, as indicated by the nearly constant slopes of the mean fields in these regions. These effects are both natural consequences of the volume-filling constraint. Uniform extension of the central portions of the brush means that the average distance of a repeat unit from the wall is linearly related to its curvilinear distance from the grafted end. This "strong stretching" assumption is commonly made in scaling theories which describe some of the basic properties of polymer brushes.[22] Chain repeat units are pulled back to the regions near the domain edges ($|x/l_a| > 0.4$) in order to completely fill space there. In these regions the chain statistics are nearly Gaussian and the strong-stretching picture does not apply. Chains are also nearly Gaussian in the overlap region in the center of the microdomain ($|x/l_a| < 0.05$) because of the symmetry condition mentioned above. Detailed results in the wall region are of course affected by our use of the narrow interphase approximation.

It is important to keep in mind that the spatial dependence of w is related to the local distortions of the polymer chains; i.e., it determines the average direction of a vector between adjacent repeat units. Properties which average over all repeat units of a given polymer chain will vary over larger length scales, simply because local effects are included in all polymers which have any of their repeat units immediately adjacent to the wall. For example, the actual gradius of gyration of a polymer chain will be anisotropic when even a small portion of this chain is distorted locally by contact with an impenetrable wall.

IV. Copolymer/Homopolymer Blends

Properties of copolymer/homopolymer blends can be understood in terms of the effects of the homopolymer addition on the properties of the copolymer brushes. Our discussion of these effects will be placed in the context of binary blends of a poly(styrene-*b*-isoprene) (PS/PI) diblock copolymer with various polystyrene homopolymers. The strong unfavorable interaction between styrene and isoprene repeat units assures that essentially all of the PS homopolymer exists in the PS microdomains, as shown schematically in Figure 1b. We are interested in the distribution of PS homopolymer in these domains, so the relevant copolymer brushes are the PS copolymer blocks.

Small-angle X-ray scattering was used to measure the repeat periods for a lamellae forming diblock copolymer and for copolymer/homopolymer blends prepared from this copolymer. Transmission electron microscopy was used to verify that the microdomain morphologies for all of these blends were indeed lamellar and that the copolymer and homopolymer chains did not segregate to distinct macroscopic phases. Details of these experiments have been reported previously.[10] The molecular weights of the PS block and the PI block are 27 000 and 22 000, respectively, giving a PS volume fraction of 51% for the pure block copolymer. The PS block has a degree of polymerization N_c of 260 from which $R_g^c = 44$ Å is obtained from the 6.7-Å statistical segment length for polystyrene.[23] A PS domain width l_a of 197 ± 2 Å is calculated for the pure diblock copolymer from the PS volume fraction and the measured lamellar repeat period of 387 ± 4 Å. This domain width corresponds to $4.48R_g^c$, so the calculated brush profiles for the PS domain of the pure copolymer are equivalent to those shown in Figure 2a, with $l_a = 197$ Å. Use of the narrow interphase approximation is valid in this case, since the domain width is considerably larger than the 20-Å estimated width of the interface between the polystyrene and polyisoprene domains.[3]

Blend compositions are defined by x_{ps}, the weight fraction of PS homopolymer in the blend. Since all of the PS homopolymer can be assumed to segregate to the PS domain in this system, l_a is obtained from the measured repeat period by multiplying by the volume fraction of styrene repeat units in the blend. In addition, Φ_h, the overall volume fraction of homopolymer in the PS microdomain, is related to x_{ps} as

$$\Phi_h = \frac{(M_{cps} + M_{cpi})x_{ps}}{M_{cps} + M_{cpi}x_{ps}} = \frac{49x_{ps}}{27 + 22x_{ps}} \qquad (13)$$

where M_{cps} and M_{cpi} are the respective molecular weights of the styrene and isoprene copolymer blocks. This simple relationship holds because the PS homopolymer and the PS block of the copolymer have identical densities, so the volume fraction of PS homopolymer in the PS domain is equal to the weight fraction of PS homopolymer in the PS domain. Values for Φ_h obtained from eq 13 can then be

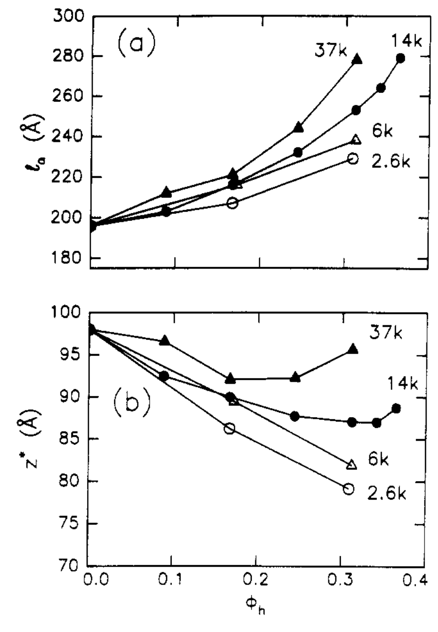

Figure 4. (a) Measured polystyrene domain widths, l_a, as a function of Φ_h for the poly(styrene-*b*-isoprene)/polystyrene blends. The polystyrene block molecular weight is 27 000, and the homopolystyrene molecular weights are as indicated in the figure. (b) Values of z^* for the polystyrene copolymer brushes are derived from Φ_h and l_a according to eq 14. Symbols are as in part a.

used to determine the values of z^* for the PS brushes:

$$z^* = (1 - \Phi_h)l_a/2 \tag{14}$$

Figure 4 shows how l_a and z^* change as the copolymer is blended with increasing amounts of four different PS homopolymers. The highest molecular weight homopolymer used in this study has a molecular weight of 37 000, for which $N_h/N_c = 1.37$. All of the additional blends have $N_h/N_c < 1$. The similarity between brush/brush and brush/homopolymer interfaces for $N_h/N_c > 1$ allows us to obtain quantitative, analytic predictions for the homopolymer distributions. We consider these blends first and follow with a discussion of the qualitative features of the homopolymer distribution for $N_h/N_c < 1$.

Blend Properties for $N_h/N_c > 1$. Figure 5 shows the calculated brush and homopolymer profiles for four blends with $N_h/N_c = 1.37$. Values of Φ_h for these blends range from 0.09 to 0.31. The brush profiles have the hyperbolic tangent form of eqs 8 and 9 and are therefore fully characterized by the overlap width w_{ol}. In the presence of homopolymer, the midpoints of the brushes are offset from the domain center by $l_a\Phi_h/2$. The following relations for the brush profiles can therefore be written:

$$\phi_c^1(x) = 0.5 + 0.5\tanh\left(\frac{-\Phi_h l_a - 2x}{w_{ol}}\right) \tag{15}$$

$$\phi_c^2(x) = 0.5 + 0.5\tanh\left(\frac{-\Phi_h l_a + 2x}{w_{ol}}\right) \tag{16}$$

The homopolymer distribution is obtained from the requirement that the volume fractions sum to 1:

$$\phi_h(x) = 1 - \phi_c^1(x) - \phi_c^2(x) = 0.5\left\{\tanh\left(\frac{\Phi_h l_a + 2x}{w_{ol}}\right) + \tanh\left(\frac{\Phi_h l_a - 2x}{w_{ol}}\right)\right\} \tag{17}$$

The complete homopolymer distribution for $N_h/N_c > 1$ is therefore specified by w_{ol}. Figure 6 is a plot of the theoretically determined variation in w_{ol} with added copolymer for the blends with $N_h/N_c = 1.37$. For $\Phi_h = 0$, w_{ol} is equal to 67 Å as given by eq 12, with $l_a = 192$ Å and $R_g^c = 44$ Å. As Φ_h increases, w_{ol} increases monotonically until it reaches a plateau value of approximately 90 Å. This plateau value, corresponding to the brush/homopolymer overlap width for $N_h/N_c = 1.37$, is 15% higher than the limiting dry brush value obtained for $N_h/N_c = \infty$, indicated by the arrow in Figure 6. This small discrepancy represents the difference in the brush/homopolymer overlap width for $N_h/N_c \cong 1$ as compared to $N_h/N_c = \infty$.

For $N_h/N_c > 1$, the homopolymer chains fit between the copolymer brushes without significantly distorting these brushes. The data for $N_h/N_c = 1.37$, for example, show that z^* is nearly independent of Φ_h and that w_{ol} is always within 15% of the value corresponding to a brush/ho-

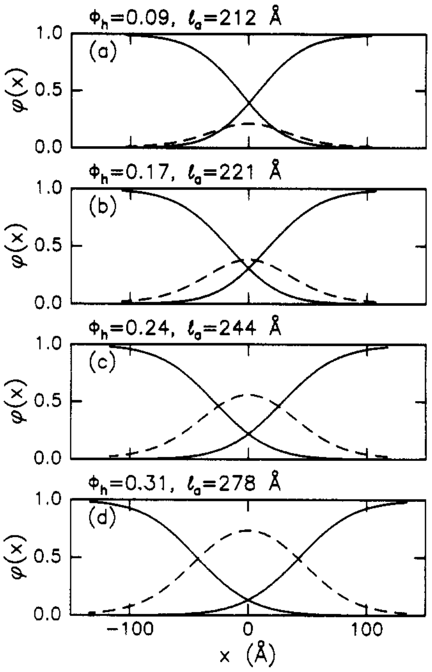

Figure 5. Calculated copolymer (—) and homopolymer (- - -) profiles for four blends with $N_h/N_c = 1.37$ and varying Φ_h. The depth scale shown in part d applies to parts a–c as well.

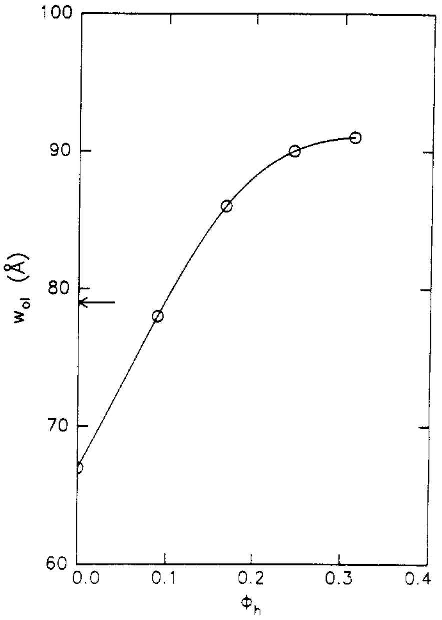

Figure 6. Calculated variation in the brush overlap width with Φ_h for the four blends with $N_h/N_c = 1.37$. The arrow at $w_{ol} = 79$ Å represents $w_{b/h}$, the value for an interface between a single brush and a high molecular weight homopolymer.

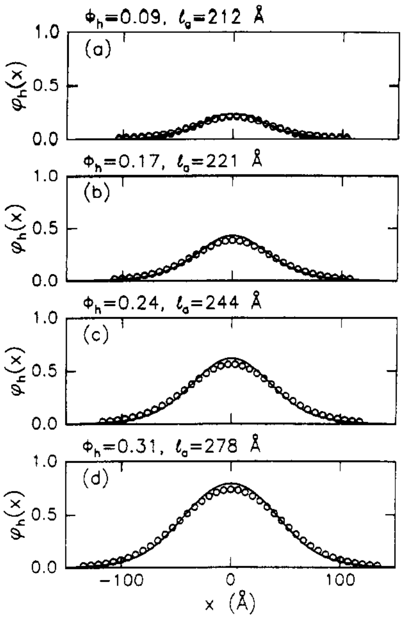

Figure 7. Comparison of the homopolymer profiles as given by the complete solution of the mean-field equations (○) and by eqs 17 and 18 (—) for the four blends with $N_h/N_c = 1.37$. The depth scale shown in part d applies to parts a–c as well.

mopolymer interface in the limit $N_h/N_c = \infty$. These results suggest a very simple method for estimating the distribution of high molecular weight polymers in a lamellar microdomain of width l_a and homopolymer volume fraction Φ_h. This distribution is as given by eq 17, where we use the value of w_{ol} for the brush/homopolymer interface (eq 11). Substitution of eq 14 for z^* into eq 11 gives

$$w_{\mathrm{ol}} \cong 1.09R_g^{\,c} + 3.16\left\{\frac{(R_g^{\,c})^2}{(1-\Phi_h)l_a}\right\} \qquad (18)$$

Equations 17 and 18 can be used to obtain a good approximation for the homopolymer distribution with no adjustable parameters, provided that $N_h/N_c > 1$. An additional requirement for eqs 17 and 18 to give an accurate description of the homopolymer distribution is that $z^*/R_g^{\,c}$ be larger than 1.6, because the hyperbolic tangent form of the brush profile is not valid for smaller values of this quantity. Figure 7 is a comparison of the prediction from eqs 17 and 18 (solid lines) to the detailed solution of the equations set forth in section II (symbols) for the blends with $N_h/N_c = 1.37$. Agreement between the two treatments is quite good.

The preceding analysis indicates that, for $N_h/N_c > 1$, prediction of the homopolymer distribution is very straightforward when Φ_h and l_a are known. However, the possibility of macrophase separation can complicate the determination of Φ_h for blends with homopolymers of high molecular weight. Interactions between opposing polymer brushes are attractive for $N_h/N_c \gg 1$.[9] These attractive interactions are entropic in origin, being associated with the distortion of the homopolymer at the brush/homopolymer interface. (For $N_h/N_c < 1$, these attractive interactions are overwhelmed by repulsive osmotic interactions which scale as $1/N_h$.) When interactions between polymer brushes are attractive, the overall free energy of the system is minimized by exclusion of the homopolymer into a separate, macroscopic phase. In general, there will be a maximum value of Φ_h which decreases with increasing N_h/N_c. When the value of Φ_h as determined by eq 13 is greater than this maximum value, an ordered copolymer phase will coexist with a phase which is rich in homopolymer. For $N_h/N_c < 1$ there is no solubility limit and Φ_h can take on all values. The limit of very high Φ_h corresponds to a dilute solution of disordered micelles, while intermediate Φ_h corresponds to a variety of ordered morphologies.[5,7,8,24] The onset of attractive interactions for increasing values of N_h/N_c describes the equilibrium tendency for these micelles to coalesce into an ordered microdomain morphology. Our analysis of the homopolymer distribution within a lamellar microdomain remains valid in the presence of macrophase separation, provided that the actual value of Φ_h is determined.

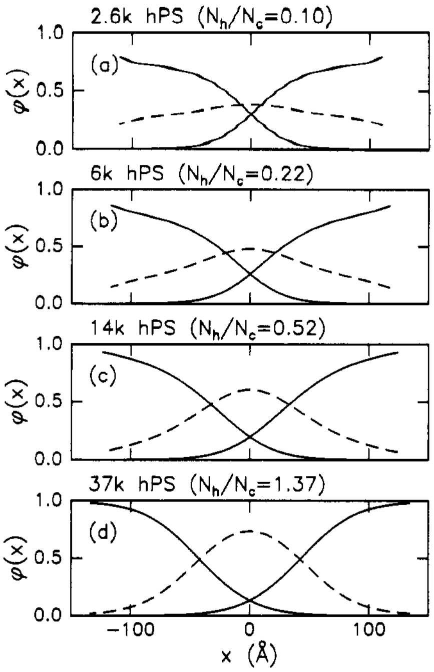

Figure 8. Calculated copolymer (—) and homopolymer (- - -) profiles for four blends with $\Phi_h = 0.31$ and varying N_h/N_c. The depth scale shown in part d applies to parts a–c as well.

Blend Properties for $N_h/N_c < 1$. Brush profiles are sensitive to the homopolymer molecular weight when $N_h/N_c < 1$. The resulting homopolymer profiles also depend on molecular weight and no longer conform to the simple analytic form valid for $N_h/N_c > 1$. Hashimoto et al. realized that such a molecular weight dependence must exist, and they suggested some qualitative forms for these distributions.[5] The most general features of the homopolymer distribution as suggested by these authors are correct, although the sharpness of the homopolymer distribution is underestimated.[10] The molecular weight dependence which we calculate is illustrated in Figure 8 where homopolymer and copolymer distributions are shown for $\Phi_h = 0.31$, with N_h/N_c varying from 0.10 to 1.37. In all cases there is a tendency for the homopolymer chains to collect at the center of the domain, i.e., between the brushes. The maximum slopes of the brush profiles are similar in all cases. Reciprocals of these maximum slopes are 105 Å ($2.4R_g^{\,c}$) for the three profiles with $N_h/N_c < 1$, as compared to 92 Å ($2.1R_g^{\,c}$) for the profile with $N_h/N_c = 1.37$. However, profiles with $N_h/N_c < 1$ are superimposed on a homopolymer background which becomes more diffuse as N_h/N_c decreases. In addition, the values of z^* decrease with decreasing N_h/N_c, as shown by Figure 4b.

Entropic penalties associated with the localization of the homopolymer chains increase with decreasing homopolymer molecular weight and are responsible for the broadening of the homopolymer distribution. Low molecular weight chains penetrate into the brush structure, decreasing the local brush volume fractions. Two complementary effects associated with this homopolymer penetration are responsible for the decrease in z^* which is observed experimentally. Because z^* is an integral of the brush volume fraction, it can remain constant only if the spatial extent of the brush is increased by extending further away from the dividing surface to which it is anchored. The free energy penalty associated with this chain stretching causes z^* to decrease as the brush becomes swollen with low molecular weight homopolymer. In addition, the free energy of an interface between high molecular weight components is decreased by the addition of a lower molecular weight component.[25] Lower interfacial free energies favor a higher interfacial area per chain, i.e., a lower z^*. Figure 8 shows that a decrease in the homopolymer molecular weight is accompanied by an increase in the amount of homopolymer which penetrates to the interface. The decrease in the free energy of this interface, while probably not as important as the increase in the stretching energy, will also contribute to the decrease in z^*.

Swelling of the brush structure by low molecular weight homopolymer often favors the formation of a curved intermaterial dividing surface. The geometry of block copolymer micelles is influenced by this spontaneous curvature.[26-28] as are the geometries of ordered blend morphologies characterized by higher values of Φ_h.[5,8,24] The actual blend geometry is a function both of Φ_h and of N_h/N_c. For $N_h/N_c < 1$, a copolymer characterized by a lamellar morphology for $\Phi_h = 0$ will undergo transitions to morphologies characterized by decreasing radii of curvature as Φ_h is increased.[5,8,24] These transitions occur at moderate values of Φ_h ($\Phi_h \cong 0.4$–0.8) where there is still considerable overlap between brushes originating from different dividing surfaces. Since interactions between overlapping brushes with $N_h/N_c < 1$ are repulsive, the domains are forced to order onto a lattice.

Blends containing symmetric diblock copolymers and having $N_h/N_c \cong 1$ are interesting in that the brush interactions are repulsive, yet there is no spontaneous mean curvature. Macrophase separation is therefore avoided at all values of Φ_h while retaining the lamellar geometry.[29] When Φ_h is low, brushes from neighboring micelles overlap. The resulting repulsive forces cause the micelles to order, such that a well-defined lamellar morphology is formed. Repulsive interactions between micelles decrease with increasing Φ_h and eventually become so weak that the domain width fluctuates until eventually the lamellar micelles are spatially disordered. The magnitude of these fluctuations is determined by the bending modulus of the lamellar micelles[30] and by the details of the repulsive potential. Study of these fluctuations is expected to give useful insights into the nature of the fundamental brush structure.

V. Summary

We have shown that the distribution of homopolymer in a copolymer microdomain is nonuniform, with the maximum in the distribution corresponding to the center of the domain. This maximum is related to the tendency for the homopolymer to segregate to the region between the two copolymer brushes which make up the pure copolymer microdomain. Localization of the homopolymer chains to the domain center is most pronounced for homopolymer molecular weights which are at least as great as the molecular weight of the corresponding copolymer block. The distribution of a high molecular weight homopolymer is independent of molecular weight and is given to a very good approximation by eqs 17 and 18. A similar analytic result exists for the width of the overlap region between opposing brushes in a pure diblock copolymer, as given by eq 12.

The calculated homopolymer distributions have been used to explain the qualitative features of lamellar block copolymer/homopolymer blends. Our general result that the homopolymer segregates preferentially to the center of the domain with which it is compatible is valid for nonlamellar geometries as well. In addition, many of the features discussed here are applicable to systems for which the homopolymer is miscible with one of the copolymer blocks but is not chemically identical with this block. Tailoring the distribution of this dissimilar block may therefore provide a powerful method for altering the material properties. Details of the homopolymer distribution will be depend on the nature of the enthalpic interaction between the homopolymer and the copolymer domain, but the qualitative effects described here will still be observed. These enthalpic effects can easily be included in the theory in order to obtain predictions for any given blend system of interest.

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Registry No. S/I (block copolymer), 105729-79-1; PS (copolymer), 9003-53-6.