Microstructural Characteristics of Strongly-Segregated AXB Triblock Terpolymers Possessing the Lamellar Morphology

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Received June 14, 1993; Revised Manuscript Received November 30, 1993[⊗]

ABSTRACT: While several theoretical formalisms exist which are capable of providing valuable insight into the molecular organization responsible for periodic morphologies in strongly-segregated diblock, triblock, and starblock copolymers possessing A and B monomers, few efforts have specifically addressed materials consisting of more than two different monomer species. In this work, a self-consistent field formalism, based on concepts developed for AB diblock and ABA triblock copolymers, is proposed for strongly-segregated AXB triblock terpolymers. Here, X denotes either a third, chemically dissimilar (C) monomer species or a random (A/B) segment composed of both A and B monomer units. Analytical expressions for the free energy and microdomain periodicity at equilibrium have been obtained for the lamellar morphology in terms of pairwise interaction parameters (χ_{AX} and χ_{BX}), chain length (N), and molecular composition (f_X). The microdomain periodicity of ordered AXB terpolymers is predicted to exhibit the same $N^{2/3}$ scaling behavior as that of AB diblock copolymers and is also found to decrease initially with f_X, suggesting that relatively short midblocks enhance microphase mixing.

Introduction

Molten AB diblock copolymers order into a variety of periodic morphologies when the two contiguous monomer sequences (blocks) are sufficiently incompatible and repulsive A–B interactions dominate. Within this strong-segregation regime, $\chi_{AB}N \gg (\chi_{AB}N)_c$, where χ_{AB} is the Flory–Huggins interaction parameter, N is the number of monomers along the backbone, and the subscripted c refers to the order–disorder transition. Numerous theoretical formalisms have been proposed[1–7] to address the microstructural characteristics of strongly-segregated diblock copolymers, since these materials constitute excellent examples of self-assembled systems and relate directly to short-chain amphiphiles. These formalisms have provided valuable insight into the molecular conformations responsible for observed morphologies and have enabled accurate prediction of microstructural characteristics from homopolymer physical properties.

While most experimental and theoretical efforts have focused on AB diblock and ABA triblock copolymers, microphase ordering has also been observed in a variety of copolymers possessing different molecular architectures (e.g., multiblock,[8,9] starblock,[10,11] and cyclic[12]), as well as in linear AXB terpolymers.[13–24] In the latter, X denotes either a chemically dissimilar monomer species (X = C) or a random segment composed of A and B monomers (X = A/B). Few theoretical efforts[25,26] have specifically addressed the morphologies of ordered ACB terpolymers, even though some of these materials show promise as permselective membranes. Similarly, copolymers possessing an A(A/B)B architecture, in which the A/B segment exhibits properties intermediate to those of the A and B end blocks, have not received extensive theoretical attention[27] despite their similarity to "tapered" block copolymers.[20–24]

Some of the observed ACB[15–19] and A(A/B)B[20,21,24] morphologies (e.g., lamellae with coexisting dispersed spheres/cylinders and an ordered tricontinuous double-diamond) are unique to materials possessing three chemically dissimilar blocks, while others (e.g., alternating lamellae) are analogous to those found in strongly-segregated AB copolymers. In the present work, the self-consistent field (SCF) approach proposed by Semenov[4] is extended to strongly-segregated AXB terpolymers possessing the lamellar morphology (illustrated in Figure 1).

Theoretical Formalism

I. Development for AB Copolymers. In the treatment developed by Semenov,[4] the free energy per unit area (F) of an ordered AB diblock copolymer is derived relative to an ensemble of identical, but disconnected, blocks in the melt.[28] It is divided into three contributions: one from each of the A and B lamellae, which stack in parallel to generate long-range order, and one to account for short-range interactions at each interphase (wherein the block junctions reside at equilibrium). These contributions are denoted as F_A, F_B, and F_{AB}, respectively, and lead to

$$F = F_A + F_B + F_{AB} \tag{1}$$

Semenov[4] envisioned microphase ordering as the analog of electrostatic repulsion and consequently demonstrated that each F_i (i = A or B) could be obtained from

$$F_i = \frac{1}{4a^2}\int_0^{R_i} g(\eta_i)\,d\eta_i \int_0^{\eta_i} E(x,\eta_i)\,dx \tag{2}$$

Here, a is the monomer gyration radius ($= b/\sqrt{6}$, where b is the monomer length) and, in the nomenclature of Zhulina and Halperin,[28] $g(\eta_i)\,d\eta_i$ is the probability distribution associated with finding the unrestricted end of block i (η_i) within the spatial interval $d\eta_i$. Since the blocks are anchored at only one end, they are not uniformly stretched, in which case $E(x,\eta_i)$ accounts for the local tension of block i at monomer distance n along the block. The limits on the integrals in eq 2 correspond to the length of block i ($0 \rightarrow \eta_i$) and the half-width of microdomain i ($0 \rightarrow R_i$), i.e., $R_i = L_i/2$ from Figure 1.

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1994.

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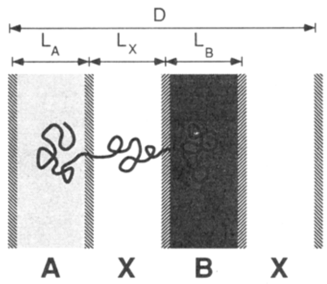

Figure 1. Schematic illustration of the lamellar morphology in a strongly-segregated AXB triblock terpolymer. The distance between block junctions in adjacent (cross-hatched) interphases is denoted L_i, where i = A, X, or B, and the period (D) is equal to $L_A + 2L_X + L_B$. If A and B are highly incompatible, the X midblock will adopt a bridged conformation, as seen here.

Both $E(x,\eta_i)$ and $g(\eta_i)$ are determined from boundary conditions which guarantee constant block mass and uniform volume filling, respectively. The mass constraint on $E(x,\eta_i)$ is given by

$$\int_0^{\eta_i} E^{-1}(x,\eta_i)\,dx = \int_0^{N_i} dn = N_i \qquad (3)$$

where N_i is the number of monomers in block i. Constant density is obtained by requiring that

$$\int_x^{R_i} g(\eta_i)E^{-1}(x,\eta_i)\,d\eta_i = 2 \qquad (4)$$

By solving eqs 2–4, Semenov[4] obtained a closed analytical expression for F_i, namely,

$$F_i = \frac{\pi^2 R_i^{\,3}}{24a^2 N_i^{\,2}} \qquad (5)$$

In the limit of strong segregation, the free-energy contribution reflecting short-range A–B interactions at each interphase (F_{AB}) is derived from the surface tension between adjacent A and B microdomains. A single repeat distance (D) consists of two interphases, in which case

$$F_{AB} = 2a\chi_{AB}^{\,1/2} \qquad (6)$$

Thus, the total free energy of the lamellar morphology, obtained by combining eqs 1, 5, and 6, is

$$F = \frac{\pi^2 R_A^{\,3}}{24a^2 N_A^{\,2}} + \frac{\pi^2 R_B^{\,3}}{24a^2 N_B^{\,2}} + 2a\chi_{AB}^{\,1/2} \qquad (7)$$

Since the melt is presumed to be incompressible, $D = L_A + L_B = 2(R_A + R_B)$. If f_A is defined as N_A/N, then $N_B = N_A(1/f_A - 1)$ and, assuming unit monomer density for both the A and B constituents, $R_B = R_A(1/f_A - 1)$ and $D = 2R_A/f_A$. Substituting these relationships for N_B and R_B into eq 7 and dividing by D yield the free energy per unit volume ($\mathcal{F}$):

$$\mathcal{F} = \frac{\pi^2 R_A^{\,2}}{48a^2 N_A^{\,2}} + \frac{a\chi_{AB}^{\,1/2} f_A}{R_A} \qquad (8)$$

The free-energy function in eq 8 is minimized with respect to R_A to determine R_A* at equilibrium. Upon differentiation and algebraic rearrangement, R_A* can be expressed as

$$R_A^* = 2\left(\frac{3}{\pi^2}\right)^{1/3} a N_A^{\,2/3} f_A^{\,1/3} \chi_{AB}^{\,1/6} \qquad (9)$$

or, in terms of N, the monomer length b, and theequilibrium periodicity D*,

$$D^* = \frac{4}{\sqrt{6}}\left(\frac{3}{\pi^2}\right)^{1/3} b N^{2/3} \chi_{AB}^{\,1/6} \qquad (10)$$

Equation 10 reveals that D* for an equilibrated diblock lamellar morphology scales as $N^{2/3}$ and $\chi_{AB}^{1/6}$ and is independent of molecular composition (i.e., f_A). In addition, the minimum free energy ($\mathcal{F}$*), evaluated at R_A*, is also found to be independent of f_A:

$$\mathcal{F}^* = \frac{1}{4}\left(\frac{9\pi^2 \chi_{AB}}{N^2}\right)^{1/3} \qquad (11)$$

II. Extension to AXB Terpolymers. In the case of an AXB terpolymer possessing alternating, nonmodulating[19] lamellae, the free energy must include the long-range interactions associated with the A, X, and B microdomains, as well as short-range interactions at the AX and BX interphases; viz.,

$$F = F_A + F_X + F_B + F_{AX} + F_{BX} \qquad (12)$$

Some of the expressions derived[4] for AB diblock copolymers are directly applicable in this extension to AXB terpolymers. For instance, the A and B terminal blocks of an AXB material are each anchored at only one end and exhibit the same nonuniform stretching as the blocks of an AB diblock copolymer. Consequently, both F_A and F_B are determined from eq 5. Likewise, the short-range interactions at narrow AX and BX interphases (F_{AX} and F_{BX}, respectively) can each be written in a fashion analogous to eq 6. The only remaining free-energy term that must be included in eq 12 is F_X.

The conformation of the middle X block is dependent on the chemical dissimilarity between the A and B end blocks. When A and B are compatible, the terpolymer behaves as an ABA triblock copolymer, exhibiting both looped and bridged conformations.[28] In the event that midblock looping occurs (or if lamellae form in a binary blend of AX and BX diblock copolymers in which A, B, and X are all strongly incompatible and each copolymer possesses $N_X/2$ monomers), eqs 2–4 can be used to derive F_X if (a) η_X corresponds to the midpoint of the X block (at $N_X/2$) and (b) a factor of 2 is included to account for the two X lamellae/D. In this limit,

$$F_X = \frac{\pi^2 R_X^{\,3}}{3a^2 N_X^{\,2}} \qquad (13a)$$

If, on the other hand, the terminal blocks of an AXB terpolymer are strongly incompatible, the middle X block will be anchored at two different interphases and adopt a bridged, rather than looped, conformation across L_X. Uniformly stretched Gaussian chains of the type addressed by Alexander[29] must be considered in evaluating the free energy of a bridged middle block, in which case F_X for the two X lamellae within D may be written as

$$F_X = \frac{2L_X^{\,3}}{4a^2 N_X^{\,2}} = \frac{4R_X^{\,3}}{a^2 N_X^{\,2}} \qquad (13b)$$

These two expressions for F_X only differ in terms of the numerical coefficient, which is denoted as Ω in the remaining derivation. The total free energy (F in eq 12) is therefore given by

$$F = \frac{\pi^2 R_A{}^3}{24a^2 N_A{}^2} + \frac{\Omega R_X{}^3}{a^2 N_X{}^2} + \frac{\pi^2 R_B{}^3}{24a^2 N_B{}^2} + 2a\chi_{AX}{}^{1/2} + 2a\chi_{BX}{}^{1/2} \tag{14}$$

For the diblock architecture, $N = N_A + N_B$, whereas $N = N_A + N_X + N_B$ for a triblock terpolymer. To express the free energy exclusively in terms of A, ϵ is introduced and defined as N_B/N_A so that $N_X = N_A(1/f_A - 1 - \epsilon)$. Assuming unit monomer density, ϵ also equals R_B/R_A, in which case eq 14 simplifies to

$$F = \frac{R_A{}^3}{a^2 N_A{}^2 f_A}\left[\frac{\pi^2}{24}(f_A + f_A\epsilon) + \Omega(1 - f_A - f_A\epsilon)\right] + 2a(\chi_{AX}{}^{1/2} + \chi_{BX}{}^{1/2}) \tag{15}$$

If $N_X = 0$, $\epsilon = 1/f_A - 1$ and eq 15 reduces to eq 7 for an AB diblock copolymer, recognizing, of course, that $\chi_{AX}{}^{1/2} + \chi_{BX}{}^{1/2}$ must be replaced by $\chi_{AB}{}^{1/2}$. The period for a lamellar AXB terpolymer is, from Figure 1, equal to $L_A + L_B + 2L_X$ or, in terms of R_A, $(2R_A/f_A)(2 - f_A - f_A\epsilon)$. As before, $\mathcal{F}$ is obtained from F/D and can, upon algebraic rearrangement, be expressed as

$$\mathcal{F} = \frac{R_A{}^2}{2a^2 N_A{}^2(2 - f_A - f_A\epsilon)}\left[\Omega + f_A(1 + \epsilon)\left(\frac{\pi^2}{24} - \Omega\right)\right] + \frac{af_A(\chi_{AX}{}^{1/2} + \chi_{BX}{}^{1/2})}{R_A(2 - f_A - f_A\epsilon)} \tag{16}$$

Minimization of $\mathcal{F}$ with respect to R_A and substitution of D for R_A^* yield D^* at equilibrium:

$$D^* = \frac{4}{\sqrt{6}}\left(\frac{3}{\pi^2}\right)^{1/3} bN^{2/3}\psi(\chi_{AX}{}^{1/2} + \chi_{BX}{}^{1/2})^{1/3} \tag{17}$$

where

$$\psi = (2 - f_A - f_A\epsilon)[\Lambda + f_A(1 + \epsilon)(1 - \Lambda)]^{-1/3} \tag{18a}$$

and $\Lambda = 24\Omega/\pi^2$. From earlier discussion regarding ϵ, $\psi \rightarrow 1$ in the limit as $N_X \rightarrow 0$. The same is not true in general as N_A (or N_B) approaches zero, since a bridged X block ($\Omega = 4$) possesses different elastic properties than does a looped block ($\Omega = \pi^2/3$). In some instances, then, it is more desirable to know $\psi(f_X)$ rather than $\psi(f_A)$. Since $f_A = (1 - f_X)/(1 + \epsilon)$, eq 18a can be rewritten as

$$\psi = (1 + f_X)[1 + f_X(\Lambda - 1)]^{-1/3} \tag{18b}$$

A generalized expression for D^* corresponding to a multiblock material possessing m different blocks is provided in Appendix I. Despite the number of midblocks, the microdomain periodicity, like that of an AB diblock copolymer, is predicted to scale as $N^{2/3}$. When midblocks are present, however, D^* is also found to depend on composition and on the pairwise interaction parameters between adjacent blocks. If the periodicities of an AB copolymer and an AXB terpolymer are denoted by D^*_{AB} and D^*_{AXB}, respectively, then eqs 10 and 17 can be combined to yield

$$\frac{D^*_{AXB}}{D^*_{AB}} = \psi\chi_r{}^{1/3} \tag{19}$$

where $\chi_r \equiv (\chi_{AX}{}^{1/2} + \chi_{BX}{}^{1/2})/\chi_{AB}{}^{1/2}$. As before, the minimum free-energy $\mathcal{F}^*$ is readily obtained from eqs 16 and 17; i.e.,

$$\mathcal{F}^* = \frac{1}{4\psi}\left[\frac{9\pi^2}{N^2}(\chi_{AX}{}^{1/2} + \chi_{BX}{}^{1/2})^2\right]^{1/3} \tag{20}$$

Unlike its analog for a diblock copolymer, $\mathcal{F}^*$ is composition-dependent. In the event that $f_X \rightarrow 0$, the AXB terpolymer reduces to an AB diblock copolymer, and eqs 11 and 20 become identical.

Results and Discussion

I. General Case—ACB Terpolymers. Most of the strongly-segregated ACB triblock terpolymers reported in the literature are composed of styrene, a diene (isoprene or butadiene), and either 2-vinylpyridine, 4-vinylpyridine, or (4-vinylbenzyl)dimethylamine monomers. In recent efforts, Mogi et al.[18] have systematically explored the morphologies of symmetric poly[isoprene-*b*-styrene-*b*-(2-vinylpyridine)] (ISP) terpolymers differing in f_S. [Here, *symmetric* implies $\epsilon \approx 1$.] On the basis of their findings, they suggest the following morphological progression with increasing f_S: alternating lamellae of I, S, and P; an ordered tricontinuous double-diamond; dispersed cylinders of I and P on a square lattice; and dispersed spheres of I and P on a body-centered cubic lattice. Additional morphologies have been reported for asymmetric terpolymers.[15-17,19] Production of such well-defined terpolymer series is not, however, trivial due to the accuracy required during synthesis. A theoretical formalism capable of elucidating key molecular-morphological relationships is therefore warranted if an improved understanding of such materials is desired.

Two previous theoretical formalisms have been proposed to address microphase-separated ACB terpolymers in the strong-segregation regime without assuming[16] a hypothetical two-stage microphase-separation scheme to make use of established diblock formalisms (see Appendix II). The first[25] employs confined single-chain (CSC) statistics, a parameterized approach pioneered by Meier[1] and Williams et al.[2] Enthalpic and entropic contributions to the free energy are derived for isolated molecules in the absence of uniform volume filling. The second treatment[26] is an extension of the Kawasaki and Ohta[5] formalism for strongly-segregated diblock copolymers. It considers the effect of long-range concentration fluctuations on the free energy through an expansion in monomer density. Both theories predict that $D^* \sim N^{2/3}$, in agreement with eq 17.

Mogi et al.[30] have also successfully synthesized a series of lamellar ISP terpolymers of varying molecular weight in an attempt to discern the molecular-weight dependence of D^*. Their results from small-angle X-ray scattering (SAXS) reveal at first glance that $D^* \sim \bar{M}_n{}^{0.77}$, and they propose an ansatz based upon the Semenov[4] SCF framework which yields $D^*_{ISP}/D^*_{SP} \approx 1.26$ for ISP terpolymers with $N_I = N_S = N_P$ and $\chi_{IS} = \chi_{SP}$. Note that eq 19 yields $D^*_{ISP}/D^*_{SP} \approx 1.07$ for analogous materials possessing bridged midblocks ($\Omega = 4$) or $D^*_{ISP}/D^*_{SP} \approx 1.12$ if the midblocks loop ($\Omega = \pi^2/3$). In either case, enhanced stretching of the ISP molecules is predicted (but not to the extent suggested by Mogi et al.[30]), with the bridged midblock conformation being more probable since polyisoprene and poly(2-vinylpyridine) are incompatible.[31]

If the periodicities obtained by Mogi et al.[30] are cast in terms of N rather than $\bar{M}_n$ and only copolymers with $\bar{M}_n < 200\,000$ are considered (since it is unlikely that the high-

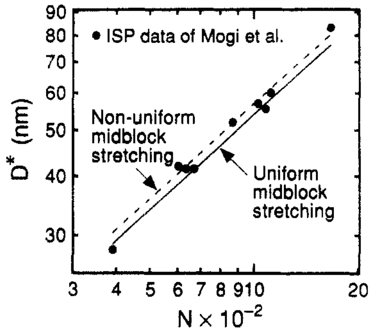

Figure 2. Dependence of microdomain periodicity (D^*) on monomer number (N) in a series of ISP triblock terpolymers exhibiting the lamellar morphology. Predictions displayed for looped and bridged midblock conformations (dashed and solid lines, respectively) compare well with SAXS data (●) from Mogi et al.[30] The lines reflect an $N^{2/3}$ scaling dependence of predicted D^*.

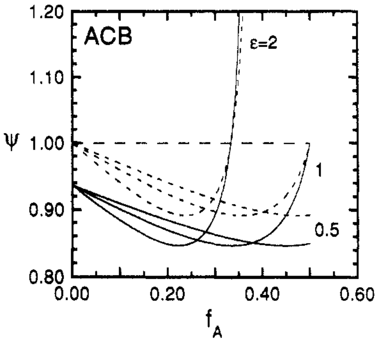

Figure 3. Function ψ presented in terms of f_A for three values of ϵ: 0.5, 1, and 2. The positions of the minima for looped and bridged midblock conformations (dashed and solid lines, respectively) are discerned by minimizing eq 18a, and the f_A yielding $\psi = 1$ correspond to compositions at which the terpolymer reduces to either an AC or BC diblock copolymer.

molecular-weight terpolymers reach equilibrium), we find that $D^* \sim N^{0.71}$. Moreover, if their 36 000 IDP-4 terpolymer is also excluded due to its relatively low $\bar{M}_n$ and deuterated styrene block, the scaling exponent reduces to 0.68. Here, N is obtained from $\Sigma_i N_i'$ (i = I, S, P), where, following Owens et al.,[32] $N_i' = N_i(b_i/b_i')^2$, $b_i' = b_i(\rho_i/\rho')^{1/2}$, and $\rho' = (\rho_I \rho_S \rho_P)^{1/3}$. The monomer lengths ($b_i$) are 0.59 nm (I) and 0.68 nm (S and P), and the monomer densities (ρ_i) are taken as 13800, 10100, and 11000 mol/m^3 for I, S, and P, respectively.[30,32] Calculation of D^* for ISP terpolymers from eqs 17 and 18 requires χ_{IS} and χ_{SP} from strongly-segregated IS[33-35] and SP[36] diblock copolymers. Estimates of $\chi_{IS} \approx 0.12$ and $\chi_{SP} \approx 0.13$ are obtained by first normalizing the I–S and S–P monomer pairs to constant volume (to discern N) and then fitting eq 10 to $D^*(N)$. As is seen in Figure 2, predicted D^* values for the terpolymers compare favorably with experimental data.

Attention is now drawn to some of the details of the present SCF formalism. The function $\psi(f_A)$ in eq 18a, for instance, is plotted for three different ϵ in Figure 3. Although the lamellar morphology has been observed[18] over a relatively narrow composition range ($f_i \approx 0.3$, i = A or B), predictions are presented here for f_A ranging from 0.0 to 0.5. If $f_A = 0.0$ for terpolymers with looped midblocks, $D^*_{ACB} = D^*_{BC}$ (in which case χ_r in eq 19 is referenced with respect to χ_{BC}). As f_A increases, ψ is observed to decrease initially with f_A until it reaches a minimum at $f_A{}^\circ$, which occurs at $(1 + \Lambda/2)[(1 + \epsilon)(\Lambda - 1)]^{-1}$. When the $\psi(f_A)$ curves corresponding to terpolymers with looped midblocks in Figure 3 exceed $f_A{}^\circ$ and again equal unity, the B block is nonexistent and the triblock terpolymer reduces to an AC diblock copolymer (χ_r is referenced to χ_{AC}).

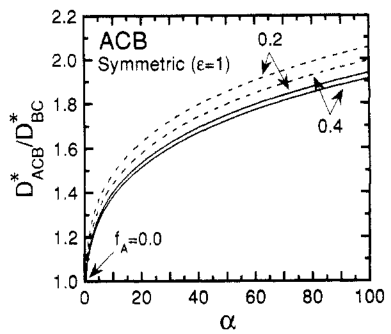

Figure 4. D^*_{ACB}/D^*_{BC} presented as a function of the relative monomer repulsion ratio α for symmetric ACB triblock terpolymers (with $\epsilon = 1$) for f_A = 0.0, 0.2, and 0.4. When f_A = 0.0, terpolymers with looped midblocks (dashed lines) correctly reduce to a BC diblock copolymer, whereas those with bridged midblocks (solid lines) do not. If $f_A > 0.0$, D^*_{ACB}/D^*_{BC} increases with α, corresponding to an increase in molecular stretching with block incompatibility.

The reduced ACB periodicity in eq 19 relies upon both binary interaction parameters (χ_{AC} and χ_{BC}), as well as on molecular composition (see Figure 3). The importance of the interaction parameters can be determined by considering, for the sake of illustration, a symmetric terpolymer architecture (with $\epsilon = 1$) in which the AC and BC interaction parameters are related through α, defined as χ_{AC}/χ_{BC}. This parameter quantifies the relative strength of A–C monomer repulsion. Incorporation of α into eqs 18 and 19 (with reference to a BC diblock) yields

$$\frac{D^*_{ACB}}{D^*_{BC}} = \frac{2(1-f_A)(1+\alpha^{1/2})^{1/3}}{[\Lambda + 2f_A(1-\Lambda)]^{1/3}} \qquad (21)$$

When $f_A = 0$, the A block does not exist, $\alpha = 0$, and $D^*_{ACB}/D^*_{BC} = (\pi^2/3\Omega)^{1/3}$. If the C midblock adopts a looped conformation, $\Omega = \pi^2/3$ and $D^*_{ACB} = D^*_{BC}$. (This is not the case, however, if the midblock is uniformly stretched in a bridged conformation.) If $f_A > 0$, then D^*_{ACB}/D^*_{BC} increases monotonically with α, as seen in Figure 4. Over the entire range of α shown (from 0 to 100), D^*_{ACB}/D^*_{BC} is predicted to increase from unity to approximately 2.0, indicating that ACB molecules of constant N become more highly stretched along the lamellar normal as the chemical dissimilarity (i.e., repulsion) between the A and C monomers increases.

II. Specific Case—A(A/B)B Copolymers. Another family of AXB materials that can be addressed by the formalism developed here includes triblock copolymers in which X = A/B. Hashimoto et al.[20,21] and Gronski et al.[22,23] pioneered the synthesis and microstructural characterization of such materials to gain clearer insights into the effect of monomer sequencing on morphological development in block copolymers. Some general molecular-morphological relationships were reported, but difficulty associated with accurately controlled synthesis often precluded unambiguous studies of such materials. In particular, the existence of a composition gradient across the A/B midblock has been found[24] to affect the ultimate copolymer morphology. Recent synthesis developments[37] employing *sec*-butyllithium and potassium alkoxide cocatalysts in anionic polymerization have provided a significantly better opportunity to produce block copolymers with nontapered A/B blocks. Even with such

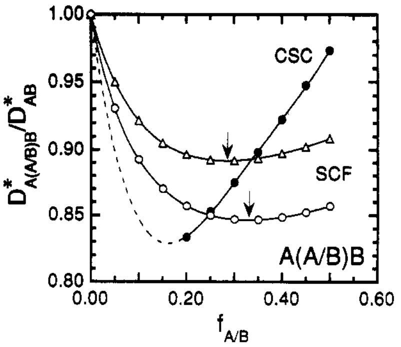

Figure 5. Dependence of $D^*_{A(A/B)B}/D^*_{AB}$ on $f_{A/B}$ for symmetric A(A/B)B triblock copolymers. Predictions obtained within the SCF framework are shown as (△) and (○) for looped and bridged midblock conformations, respectively, while those from a CSC formalism[27] are displayed as (●). In all three cases, $D^*_{A(A/B)B}/D^*_{AB}$ is predicted to decrease from unity (due to enhanced microphase mixing) and reach a minimum at $f_{A/B}^{\circ}$ (arrows).

achievements, a theoretical framework is required to interpret experimental results and elucidate the role of monomer sequencing on morphology in A(A/B)B block copolymers.

To again facilitate predictions, only symmetric copolymers ($\epsilon = 1$) are considered, even though the expressions derived here are applicable to nonsymmetric copolymers as well. The pairwise interaction parameters, $\chi_{A(A/B)}$ and $\chi_{B(A/B)}$, can be related through α as before, but we elect to relate them here through an expression proposed[20,38] for tapered block copolymers, namely,

$$\chi_{\mathrm{eff}} = \chi_{AB}(\omega_A^{(A)} - \omega_A^{(B)})^2 \tag{22}$$

The effective interaction parameter for a diblock copolymer possessing one or more mixed (A/B) blocks is denoted as χ_{eff}, and $\omega_i^{(j)}$ is the fraction of i monomers in the jth block. Equation 22 can therefore be used to determine the effective interaction parameters in an A(A/B)B copolymer with pure A and B terminal blocks:

$$\chi_{A(A/B)} = \chi_{AB}(1 - \omega)^2 \tag{23a}$$

$$\chi_{B(A/B)} = \chi_{AB}\omega^2 \tag{23b}$$

where ω denotes $\omega_A^{(A/B)}$. Since the role of the A/B block is of principal interest in this section, substitution of these expressions into eqs 18b and 19 (referenced to χ_{AB}) yields $\chi_r = 1$ and

$$\frac{D^*_{A(A/B)B}}{D^*_{AB}} = (1 + f_{A/B})[1 + f_{A/B}(\Lambda - 1)]^{-1/3} \tag{24}$$

Figure 5 is a graphical representation of eq 24, along with previous predictions obtained from the CSC formalism[27] (which also predicts $D^* \sim N^{2/3}$). The CSC predictions in Figure 5 correspond to a molecular weight of 200 000 and *imply* that a minimum exists between $f_{A/B} = 0$ (pure AB diblock) and $f_{A/B} \approx 0.2$ (three-microphase morphology). As pointed out earlier, a minimum in microdomain periodicity is predicted at $f_{A/B}^{\circ}$ with the present formalism. Differentiation of eq 24 with respect to $f_{A/B}$ reveals that $f_{A/B}^{\circ} = 0.33$ for a bridged A/B midblock. Predictions from the CSC and SCF formalisms both indicate that chemical incorporation of an A/B segment between the terminal blocks of an AB diblock copolymer initially promotes microphase mixing, followed by an increase in block stretching at higher $f_{A/B}$. This predicted trend is certainly amenable to experimental verification.

At sufficiently high $f_{A/B}$, the condition of strong segregation may not be met, resulting in microphase dissolution or some other critical phenomenon.[39]

The predictions presented here for ACB triblock terpolymers and A(A/B)B triblock copolymers are strictly valid for the lamellar morphology. A rich variety of nonlamellar morphologies have also been experimentally observed[15-21,24] in such materials and should be considered in future theoretical efforts.

Conclusions

The SCF formalism developed by Semenov[4] for strongly-segregated AB diblock copolymers has been extended here to include AXB triblock terpolymers, where X denotes either a chemically dissimilar C block or a random A/B segment. As with diblock copolymers, the microdomain periodicity is predicted to scale as $N^{2/3}$ for both material families, in agreement with complementary theoretical treatments.[25-27] The microdomain periodicity of the ACB design is also sensitive to (i) the pairwise interaction parameters between the A–C and B–C blocks and (ii) molecular composition. The periodicity of an A(A/B)B triblock copolymer relative to that of the parent AB diblock copolymer is only dependent on molecular composition and is predicted to decrease initially with $f_{A/B}$ due to enhanced microphase mixing. The predictive capability of the formalism derived here should assist in elucidating molecular-morphology relationships in triblock terpolymers and may prove useful in the design of specialty terpolymers for applications in which the chemical functionality of a third monomer species is desired within a thermoplastic elastomer.

Acknowledgment. We thank the College of Engineering (NCSU) for the provision of funding, Dr. S. T. Milner (Exxon) for an illuminating discussion, and one of the reviewers for insightful comments.

Appendix I. Generalization to Multicomponent Multiblock Materials

The theoretical development presented in the text specifically addresses AXB triblock terpolymers in the strong-segregation regime. However, the principles employed here can be generalized to include linear multiblock copolymers composed of *m* chemically dissimilar blocks which do not loop. As before, we assume equal monomer gyration radii (a) and unit monomer densities so that the free energy per unit volume can be written as

$$\mathcal{F} = \frac{1}{D}\left[\frac{\pi^2 R_o^3}{24a^2N_o^2} + \frac{\pi^2 R_m^3}{24a^2N_m^2} + \sum_{i=0}^{m-2}\frac{4R_i^3}{a^2N_i^2} + 2a\Big(\sum_{\substack{\text{all jk pairs}\\ j\neq k}} \delta_{jk}\chi_{jk}^{1/2}\Big)\right] \tag{AI.1}$$

where the subscripts o and m denote the terminal blocks, the index i is over all middle (i.e., nonterminal) blocks, $D = L_o + L_m + 2\sum_{i=0}^{m-2} L_i$, and δ_{ij} is related to the Kronecker delta, equal to 1 if the j and k microdomains are adjacent (and j–k monomer interactions exist) or 0 if they are not. If ϵ_i is defined as N_i/N_o ($=R_i/R_o$), then $N_i = \epsilon_i N_o$, $N_m = N_o[(1/f_o) - 1 - \sum_{i=0}^{m-2}\epsilon_i]$, and $D = (2R_o/f_o)(1 + f_o\sum_{i=0}^{m-2}\epsilon_i)$. Note that these ϵ_i are defined relative to the $m - 2$ middle blocks rather than to the terminal (m) block (as in the text) and that $\epsilon_0 = 0$. Substitution of these relationships into eq AI.1, followed by minimization of $\mathcal{F}$ with respect to R_o and subsequent algebraic rearrangement, yields

$$D^* = \frac{4}{\sqrt{6}}\left(\frac{3}{\pi^2}\right)^{1/3} bN^{2/3}\Big(\sum_{\substack{\text{all jk pairs}\\ \text{j}\neq\text{k}}} \delta_{\text{jk}}\chi_{\text{jk}}{}^{1/2}\Big)^{1/3} \times \frac{(1 + f_{\text{o}}\sum_{\text{i}=0}^{m-2}\epsilon_{\text{i}})}{\left[1 + \left(\frac{96}{\pi^2} - 1\right)f_{\text{o}}\sum_{\text{i}=0}^{m-2}\epsilon_{\text{i}}\right]^{1/3}} \qquad \text{(AI.2)}$$

These relationships are only valid in the limits of thermodynamic equilibrium and strong segregation. It is doubtful whether both of these conditions could be realistically met at large m.

Appendix II. Stepwise Microphase Ordering in AXB Terpolymers

Shibayama et al.[16] have employed SAXS to investigate the morphologies found in strongly-segregated poly[styrene-*b*-(4-vinylbenzyl)dimethylamine-*b*-isoprene] triblock terpolymers. In an effort to compare their observed microstructural characteristics with theoretical predictions, they proposed a sequential, or "stepwise", microphase-separation scheme which permitted them use of established theories developed solely for ordered diblock copolymers. Here we explore the validity of such an approach. The equilibrium periodicity for an ACB terpolymer in the present work is given by eqs 17 and 18 in the text. If the terpolymer is conceptualized as a linear combination of AC and BC diblock copolymers, then the corresponding microdomain period (D'_{ACB}) consists of $D^*_{\text{AC}} + D^*_{\text{BC}}$, in which case eq 10 yields

$$D'_{\text{ACB}} = 4\left(\frac{3}{\pi^2}\right)^{1/3} a(N_{\text{AC}}{}^{2/3}\chi_{\text{AC}}{}^{1/6} + N_{\text{BC}}{}^{2/3}\chi_{\text{BC}}{}^{1/6}) \qquad \text{(AII.1)}$$

It can be readily shown that $N_{\text{AC}} = N_{\text{A}} + N_{\text{C}} = N(1 - f_{\text{A}}\epsilon)$ and $N_{\text{BC}} = N_{\text{B}} + N_{\text{C}} = N(1 - f_{\text{A}})$. Substitution of these relationships into eq AII.1 results in the following expression for D'_{ACB}:

$$D'_{\text{ACB}} = 4\left(\frac{3}{\pi^2}\right)^{1/3} aN^{2/3} \times [\chi_{\text{AC}}{}^{1/6}(1 - f_{\text{A}}\epsilon)^{2/3} + \chi_{\text{BC}}{}^{1/6}(1 - f_{\text{A}})^{2/3}] \qquad \text{(AII.2)}$$

The ratio of D^*_{ACB} (eqs 17 and 18a) to D'_{ACB} (eq AII.2) can therefore be written as

$$\frac{D^*_{\text{ACB}}}{D'_{\text{ACB}}} = (\chi_{\text{AC}}{}^{1/2} + \chi_{\text{BC}}{}^{1/2})^{1/3}(2 - f_{\text{A}} - f_{\text{A}}\epsilon)/ \{[\chi_{\text{AC}}{}^{1/6}(1 - f_{\text{A}}\epsilon)^{2/3} + \chi_{\text{BC}}{}^{1/6}(1 - f_{\text{A}})^{2/3}] \times [\Lambda + f_{\text{A}}(1 + \epsilon)(1 - \Lambda)]^{1/3}\} \qquad \text{(AII.3)}$$

If the terpolymer molecule is symmetric ($\epsilon = 1$) and if $\alpha \equiv \chi_{\text{AC}}/\chi_{\text{BC}}$, then eq AII.3 simplifies to

$$\frac{D^*_{\text{ACB}}}{D'_{\text{ACB}}} = \frac{2(1 + \alpha^{1/2})^{1/3}}{1 + \alpha^{1/6}}\left[\frac{1 - f_{\text{A}}}{\Lambda + 2f_{\text{A}}(1 - \Lambda)}\right]^{1/3} \qquad \text{(AII.4)}$$

The expressions derived here for $D^*_{\text{ACB}}/D'_{\text{ACB}}$ are not, in general, equal to unity. More specifically, eq AII.4 yields $D^*_{\text{ACB}}/D'_{\text{ACB}} < 1$ for all permissible values of f_{A} greater than zero. Thus, the stepwise microphase-ordering assumption[16] is not rigorously valid.

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