Effect of Looping on the Microstructure of Linear Multiblock Copolymers

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ABSTRACT: The molecular characteristics responsible for observed equilibrium morphologies in microphase-separated diblock copolymers are now well understood. However, additional factors must be taken into consideration when block copolymers possessing more complex architectures are designed. In the case of linear $(AB)_n$ multiblock copolymers, the backbone consists of two terminal blocks with only one junction each and $2n - 2$ middle blocks, each possessing two junction sites. While the two terminal blocks are anchored at one end only, the middle blocks are fixed at both ends. A middle block can assume either an extended conformation, in which case its two block junctions reside in different interphases, or a looped conformation, in which both junctions are found in the same interphase. The present work addresses the effect of looping on the free energy and microstructure of such $(AB)_n$ multiblock copolymers. Looping statistics are generated here as a function of the number of AB block pairs (n) and are incorporated directly as conformational constraints into a confined single-chain formalism. Predictions for the free-energy minimum, along with microstructural dimensions such as the periodicity, are provided as functions of the number of block pairs and the number of looping events per molecule.

Introduction

Diblock copolymers consist of two contiguous sequences (blocks) of chemically-dissimilar monomers (A and B) which are covalently bonded together. When the blocks are sufficiently incompatible, these materials undergo self-assembly and order into a periodic microstructural network. Theoretical[1-3] and experimental[4-6] evidence indicates that the microphase-separation transition from a disordered state to a well-ordered microstructure occurs when $\chi_{AB}N \approx 10.5$ in nearly symmetric copolymers (neglecting fluctuation effects), where χ_{AB} is the Flory–Huggins interaction parameter characterizing the A–B monomer repulsions and N is the number of monomers in the copolymer. Within the strong-segregation limit ($\chi_{AB}N \gg 10.5$), the blocks of these molecules reside in separate microdomains, thereby forcing the molecules to stretch along the axis normal to the interphase which divides the microphase cores.[7-16] While the morphologies that have been observed to date in pure diblock copolymers continue to fascinate researchers in terms of phase behavior, molecular packing, and curvature constraints,[17,18] the diblock architecture is the *simplest* block copolymer design capable of forming an established microstructure.

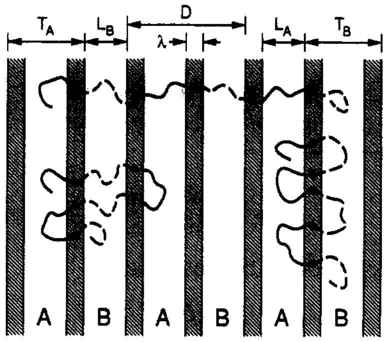

Figure 1. Schematic illustration of the lamellar morphology postulated for microphase-separated $(AB)_n$ multiblock copolymers with nearly equal molar compositions in the strong-segregation limit. In this case, $n = 3$. Microdomain regions and cores (T_i and L_i, respectively, where i = A or B) are labeled, along with the periodicity (D) and the cross-hatched interphases (λ). The top conformation corresponds to a fully extended $(AB)_3$ molecule, for which $m = 0$ and $L_{mol} = 5D/2$. In the lower left depiction, $m = 2$ and $L_{mol} = D$. The lower right one portrays the fully-looped conformation, in which $m = 4$ and $L_{mol} = D/2$. Note that m is bounded by 0 and $2n - 2$ for these molecules.

Several theoretical studies have sought to elucidate both the phase behavior and morphological characteristics of more complex molecular architectures. Only linear $(AB)_n$ multiblock copolymers, an example of which is depicted in Figure 1, are considered in this work. Krause[19] first addressed the phase behavior of such materials and predicted that an increase in the number of AB block pairs (n) reduces the driving force for microphase separation in copolymers of equal molecular weight. Benoit and Hadziioannou[20] extended the mean-field formalism of Leibler[1] to several different multiblock architectures and obtained predictions for the order–disorder transition (ODT) in the weak-segregation limit, along with microstructural dimensions such as the microdomain periodicity, as functions of n for symmetric $(AB)_n$ copolymers. More recent efforts by Kavassalis and Whitmore[21] have employed the functional integral methods developed by Hong and Noolandi[22] to examine the phase behavior of both symmetric and asymmetric linear multiblock molecules. Predictions from the latter two theories[20,21] are found to be in very good quantitative agreement.

An attempt[23] to model the free energy and microstructure of microphase-separated $(AB)_n$ copolymers in the strong-segregation limit using the confined single-chain approach originally proposed by Meier[10] and Williams and co-workers[13,14,24] has revealed that, in addition to the molecular architecture, block looping can have a significant impact on the equilibrium morphologies of these materials. Predictions for fully-looped molecules have been found to

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agree very well with those obtained from the Benoit and Hadziioannou[20] formalism, which explicitly assigns a Gaussian conformation to the blocks. However, results from the confined-chain theory[23] for non-looped blocks are considerably different, thereby suggesting that block looping must be considered in modeling $(AB)_n$ morphologies.

The objectives of the present work are two-fold: (i) develop the statistics necessary to describe the block looping distribution as a function of n and (ii) incorporate these statistics into the confined-chain model proposed earlier for either fully-extended or fully-looped $(AB)_n$ molecules so that conformation–microstructure relationships can be established.

Thermodynamic Theory

The model proposed here is an extension of the statistical thermodynamic formalism initially developed by Meier[10] and Williams and co-workers.[13,24] It implicitly assumes that the equilibrium morphology of a microphase-separated block copolymer can be represented by a single copolymer chain confined within a postulated morphology in microdomain space. As in previous efforts in this spirit, only the lamellar morphology, illustrated in Figure 1, is considered here. To facilitate model development, this section is divided into two subsections, with one dedicated to looping statistics and the other to the free-energy formalism.

1. Looping Statistics. Looping effects can be completely disregarded in diblock copolymers, since both blocks share a single junction and no driving force exists for the free end of either block to enter back into the junction-occupied interphase. In a triblock copolymer, however, the middle block is capable of looping,[25] in which case the molecule may assume either an extended or a looped conformation. However, as the number of blocks, or block pairs (n), in an $(AB)_n$ copolymer increases, the number of potential looping events increases significantly, as does the number of possible molecular conformations. Before developing the statistics associated with specific looping occurrences, we establish the upper and lower limits on looping within an $(AB)_n$ molecule.

Consider first the case of a fully-extended molecule. Here, *fully-extended* denotes the conformation in which every junction resides in a *different* interphase. This limit reflects a single conformation and can be expressed by $m = 0$, where m is the number of block loops along the copolymer backbone. Likewise, exactly one conformation exists for the case wherein all of the middle blocks loop back upon themselves such that every block junction resides in the *same* interphase. Since the two terminal blocks cannot participate in looping, the value assigned to m in this *fully-looped* limit is $2n - 2$. Both of these limits have been discussed in detail previously, with the maximum looping condition referred to as the sequential diblock approximation (SDA).[23] The focus of the present work is to elucidate the looping probability distribution as a function of n between these two limits and subsequently incorporate this n-dependent distribution into the confined-chain thermodynamic model.

Table I
Parameters of the Distribution Function Required To Generate the Looping Statistics Employed Here

n	m	σ	$X_{\sigma m}$	X_m
1	0	1	1	1
2	0	3	1	1
	1	2	2	2
	2	1	1	1
3	0	5	1	1
	1	4	2	4
		3	2	
	2	3	4	6
		2	2	
	3	2	4	4
	4	1	1	1
4	0	7	1	1
	1	6	2	6
		5	2	
		4	2	
	2	5	6	15
		4	4	
		3	5	
	3	4	8	20
		3	10	
		2	2	
	4	3	9	15
		2	6	
	5	2	6	6
	6	1	1	1

The total number of possible looping events a symmetric $(AB)_n$ molecule can assume is $2^{2(n-1)}$. Specific conformations dependent on the number of loops (m) are discriminated here by their lateral expanse, or projection along the axis normal to the lamellae, which is denoted by L_{mol} (see the caption of Figure 1 for examples when $n = 3$). Note that L_{mol} is more sensitive to the variety of permissible conformations than the end-to-end distance of the $(AB)_n$ molecule, which can be extracted from a one-dimensional random-walk analysis. Since L_{mol} has dimensions of length, we choose to normalize it with respect to a length characteristic of an AB block pair (l_o) in this statistical analysis. The resulting parameter is denoted as σ, where

$$\sigma \equiv L_{\mathrm{mol}}/l_o \tag{1}$$

The number of times m occurs for a given L_{mol} is given by $X_{\sigma m}$, which satisfies the condition that

$$\sum_{m=0}^{2n-2} \sum_{\sigma=1}^{2n-1} X_{\sigma m}(n) = 2^{2(n-1)} \tag{2}$$

Values of $X_{\sigma m}(n)$ can be obtained by tallying the number of conformations for any given $(AB)_n$ architecture and are tabulated in Table I for $1 \leq n \leq 4$.

Two points regarding the distribution $X_{\sigma m}$ warrant discussion. First, if the summation over σ in eq 2 is performed at constant values of m, the resulting function (X_m) conforms to a binomial distribution (see Table I). This relationship is particularly useful in ascertaining the average number of looping events ($\langle m \rangle$). Values of $\langle m \rangle$ for a specific n in an $(AB)_n$ molecule are rigorously obtained from

$$\langle m \rangle(n) = \sum_{m=0}^{2n-2} \sum_{\sigma=1}^{2n-1} \frac{X_{\sigma m}(n) m}{2^{2(n-1)}} \tag{3}$$

This expression can be solved numerically by employing the values listed in Table I. Alternatively, recognizing that $X_m(m)$ for any n is represented by a binomial distribution leads directly to the relationship[26] $\langle m \rangle = n - 1$. If eq 2 is summed over m at constant σ, a different distribution (X_σ) arises which reflects the populations of molecular conformations possessing an expanse of L_{mol}. When $n \geq 3$, different values of m yield the same value of σ (Table I), indicating degeneracy. The functional relationship of $X_\sigma(\sigma)$, presented relative to the total number of looping events for a particular n in Figure 2, reveals that the maximum in this distribution decreases and broadens asymmetrically as n increases from unity.

With the functional relationship of $X_{\sigma m}(n)$ established, we now consider the molecular conformations associated

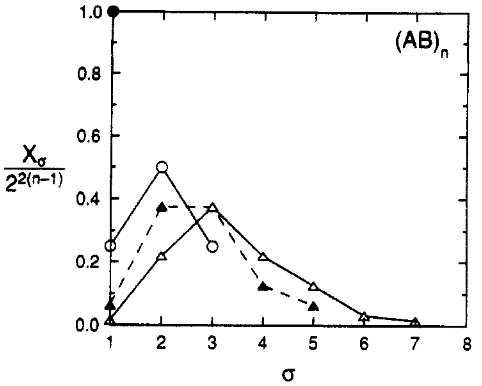

Figure 2. Conformational probability distribution function (X_σ) normalized with respect to the total number of looping events and presented as a function of σ for four values of n: 1 (●), 2 (○), 3 (▲), and 4 (△). This function reflects discrete summations of $X_{\sigma m}$ which have been grouped together to represent a specific molecular projection (L_{mol}) along the lamellar normal. This distribution clearly decreases and broadens asymmetrically as n increases from unity.

with this probability function. Meier[10] has shown that terminal blocks and extended middle blocks along L_{mol} obey space-filling criteria based on the approach to uniform core density. No data are, however, available regarding the properties of looped blocks in multiblock copolymers. An assumption previously[23] implemented is that the conformational properties of a looped middle block are similar to those of a terminal block with only one end anchored in an interphase.[27] While one might expect that this assumption should be valid only for relatively long blocks, Balsara et al.[28] have demonstrated that a similar approximation, namely that of a Gaussian chain mimicking the looped middle block in micelle-forming triblock copolymers, is accurate to within a few percent even for small block lengths. Invoking our assumption here leads to an explicit expression for L_{mol}, viz.,

$$L_{\text{mol}} = \frac{\sigma}{2}(L_A + L_B + 2\lambda) \tag{4}$$

where L_i (i = A or B) denotes the ith microdomain core and λ denotes the interphase, both shown schematically in Figure 1. This expression implies that the characteristic dimension of an AB block pair (l_o in eq 1) is equal to $L_A/2 + L_B/2 + \lambda$ and that the dimensionless coefficient σ corresponds to the number of different interphases traversed by the copolymer molecule (whether it is extended or looped). From eq 4 and Table I, σ is found to be a function of n, bounded by 1 (when $m = 2n - 2$) and $2n - 1$ (when $m = 0$). Average values of $\sigma(n)$ are obtained in a manner similar to that shown in eq 3:

$$\langle\sigma\rangle(n) = \sum_{m=0}^{2n-2}\sum_{\sigma=1}^{2n-1}\frac{X_{\sigma m}(n)\sigma}{2^{2(n-1)}} \tag{5}$$

These $\langle\sigma\rangle$ can also be derived directly from $\langle m\rangle$, differing by only 2.5% from those obtained by eq 5 when values of σ become degenerate ($n \geq 3$). The functional relationships of both $\langle m\rangle(n)$ and $\langle\sigma\rangle(n)$ are presented in Figure 3. As expected, $\langle m\rangle = n - 1$, whereas the function $\langle\sigma\rangle(n)$ can be accurately approximated when $n > 1$ by

$$\langle\sigma\rangle \approx 2(n-1)^{1/2} \tag{6}$$

The exponent in eq 6 arises from the random-walk behavior associated with block looping (see Appendix). When n is relatively small (excluding $n = 1$, for which looping cannot occur), eq 6 reflects the inability of the two terminal blocks to loop. At large n, the terminal blocks are negligible relative to the $2n - 2$ middle blocks, and eq 6 effectively scales as $n^{1/2}$. Values of $\langle\sigma\rangle$ are also provided for asymmetric $(AB)_nA$ molecules in Figure 3 to discern the accuracy of eq 6, but only symmetric molecules are considered throughout the remainder of this work. Once $\langle\sigma\rangle$ is determined, $\langle L_{\text{mol}}\rangle$ is obtained directly from eq 4.

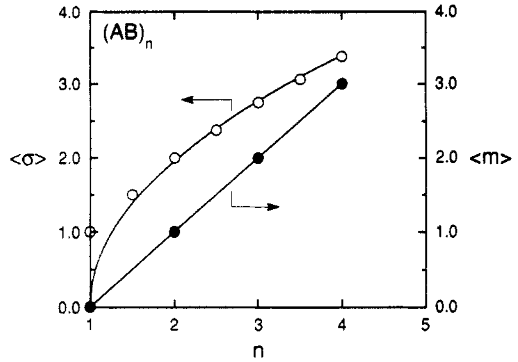

Figure 3. Functional relationships of $\langle\sigma\rangle(n)$ (○) and $\langle m\rangle(n)$ (●) for n varying from 1 to 4. Values corresponding to nonintegral n are obtained from asymmetric $(AB)_nA$ architectures, but only symmetric $(AB)_n$ molecules are considered in the thermodynamic formalism. It is clear from the curve fits (solid lines) that $\langle m\rangle = n - 1$, whereas $\langle\sigma\rangle(n > 1)$ is described by a power-law function which reflects random-walk behavior (see eq 6).

2. Free-Energy Formalism. If Δg is the difference in molar free energy between the microphase-separated and analogous homogeneous states of a block copolymer (at equal molecular composition, weight, and architecture), then equilibrium is achieved when Δg is minimized with respect to each region in microdomain space:

$$(\partial\Delta g/\partial A_i) = 0 \qquad (i = 1, 2, 3, ..., k) \tag{7}$$

where A_i is a measure of the ith region and k is the number of regions that must be included in the minimization (see, for instance, Figure 1). As pointed out earlier,[23] assumptions based on similarity principles and on the conservation of junctions within interphases reduce k to 2 for monomolecular $(AB)_n$ copolymers. Decomposing the minimized free-energy function into its enthalpic (Δh) and entropic (Δs) contributions yields

$$\Delta g_{\text{min}} = (\Delta h - T\Delta s)_{\text{min}} \tag{8}$$

where T is the value of the absolute temperature (298 K). Conditions yielding only negative Δg_{min} values are presented here, as they are presumed to correspond to microphase-separated morphologies in the strong-segregation limit.

The enthalpy (Δh) can be written in terms of a modified Flory[29] equation as

$$\Delta h = -v\Delta\delta_{AB}^{2}\left[\Phi_A\Phi_B - \frac{f}{8}(1 + \pi^2\tau)\right] \tag{9}$$

Here, v is the total molar volume, which assuming incompressibility is equal to $v_A + v_B$. Individual v_i (i = A or B) are determined from W_iM/ρ_i, where W_i and ρ_i are the weight fraction and mass density, respectively, of component i in the copolymer and M is the molecular weight of the system. The volume-fraction composition of each component in the copolymer molecule is denoted as Φ_i, and $\Delta\delta_{AB}$ is the difference in solubility parameters (δ) between components A and B. Bulk properties (δ_i and ρ_i) are readily available in the literature for a variety of homopolymers, and the ones employed here are the same as those used previously.[23] Note that W_i and Φ_i refer to component i in the copolymer and not to block i (compositions on a block basis can be determined by dividing either W_i or Φ_i by n).

The term containing f in eq 9 corresponds to the heat of mixing arising from all of the different interphase regions traversed by an $(AB)_n$ molecule. This contribution to Δh requires the molar volume of mixed material, which is given by fv in eq 9. By definition, f is the total volume fraction of interphase material and is calculated from

$$f = \sigma f_{AB} \tag{10}$$

where f_{AB} is the volume fraction corresponding to one interphase region, given by

$$f_{AB} = \lambda / L_{mol} \tag{11}$$

Since L_{mol} is a function of m, it follows that f_{AB} is also dependent on the number of loops a multiblock molecule possesses. The microstructural periodicity D ($=L_A + L_B + 2\lambda$ from Figure 1) is related to L_{mol} by $D = 2L_{mol}/\sigma$, which implies that f is equal to $2\lambda/D$ and is independent of m. Consequently, this formalism predicts that the enthalpic contribution to Δg does *not* depend on the looping conformation of an $(AB)_n$ molecule. The term multiplied by f in eq 9 arises from the average composition product of the interphase region, assuming a symmetric sigmoidal interphase composition profile,[23] and τ is a dimensionless long-range interaction parameter ($=t^2/6\lambda^2$, where t is approximately 0.6 nm).[10]

In previous presentations of this confined chain model, the entropic function (Δs) in eq 8 has been typically divided into three contributions reflecting (i) the restriction of the block junctions to interphase regions, (ii) confinement of block i to T_i (see Figure 1), and (iii) block deformation accompanying confinement. The details of the individual contributions to Δs, which are based both on probabilities derived from solution of the diffusion equation in a parallel-plate geometry in the absence of a potential field and on elasticity theory, have been provided earlier by Meier[10] and Henderson and Williams[13] for diblock copolymers and elsewhere[23] for fully extended $(AB)_n$ multiblock copolymers. Here, all of the contributions to Δs are combined into a single expression given by

$$\Delta s = \sigma R \ln f_{AB} + \frac{(\sigma + 1)R}{2} \sum_{i=A,B} \ln \left\{ \frac{2}{\pi} e^{-\zeta_i^{(1)}} \sin \zeta_i^{(2)} \times \left[2p_1 + (1 - p_1)\left(1 - \cos \frac{\pi\lambda}{T_i}\right)\right]\right\} - \frac{3}{2}[\alpha_i^2 - 1 - p_1 \ln \alpha_i^2] \tag{12}$$

where R is the gas constant, $\zeta_i^{(1)} = \pi^2 \langle r_i^2 \rangle / 6T_i^2$, and $\zeta_i^{(2)} = \pi\lambda/2T_i$. The fraction of terminal or looped blocks, p_1, is written as

$$p_1 = \frac{1 + m/2}{n} \tag{13}$$

An assumption implicit in eq 13 which accounts for the $m/2$ term is that the m loops along the $(AB)_n$ molecule can occur with equal probability among the A and B blocks. Note that when $m = 0$ (no looping), $p_1 = 1/n$, $\sigma = 2n - 1$, and eq 12 reduces to the one previously put forth for fully-extended linear multiblock copolymers. If, on the other hand, $m = 2n - 2$ (fully looped), $p_1 = 1$, $\sigma = 1$, and eq 12 reduces to the correct form for a pseudo-diblock copolymer.

The microdomain dimensions employed explicitly in eq 12 are written in terms of the two dimensionless minimization parameters β ($=\lambda/T_A$) and Γ ($=T_A^2/\langle r_A^2 \rangle_o$). Unperturbed rms end-to-end distances ($\langle r_i^2 \rangle_o^{1/2}$) are estimated from $K_i(W_iM/n)^{1/2}$, where K_i is the Kuhn segment length (values of which have been reported previously). In accord with eq 7, Δg is minimized with respect to β and Γ. The minimization is performed numerically, and λ and T_A are obtained directly from the values of β and Γ, respectively. Values of the expansion coefficient α_A in eq 12 are determined from Γ by its relationships to $\langle r_A^2 \rangle_o$ (through $\langle r_A^2 \rangle / \langle r_A^2 \rangle_o$) and by the conditions established for minimizing deviations from uniform core density. These conditions[10] are written in the general form $T_i^2 = C_k \langle r_i^2 \rangle$, where C_k is a series of coefficients, each of which depends on the number of anchored block junctions (k) a block possesses. Values of C_k are 2.0 (when $k = 1$) and 1.5 (when $k = 2$). The corresponding expression for $\alpha_A^2(\Gamma)$ is

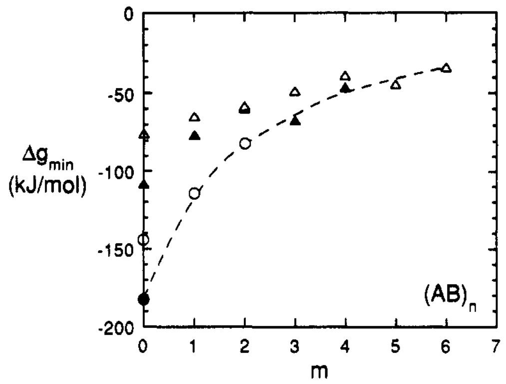

Figure 4. Predicted Δg_{min} presented as a function of m for the four values of n employed in Figure 2. Values of Δg_{min} for $m = 0$ correspond to fully-extended molecular conformations, while the dashed line is a guide for the eye, connecting the Δg_{min} evaluated for fully-looped molecules. The magnitude of Δg_{min} becomes less dependent on m as n increases. The symbols used here are the same as those in Figure 2, and the molecular characteristics of these hypothetical constant-length copolymers are held constant at $M = 200\,000$ and $W_A = 0.50$.

$$\alpha_A^2 = \Gamma / \bar{C} \tag{14}$$

where $\bar{C} \equiv \sum_k p_k C_k$. Equation 14 indicates that $\bar{C}$ is given as an arithmetic mean with respect to p_k; it can also be calculated as a geometric mean with only minor differences in the model predictions. If the relationship developed by Meier[10] for the conservation of junctions within an interphase is utilized, T_B is obtained from

$$T_B = \alpha_B \bar{C}^{1/2} \langle r_B^2 \rangle_o^{1/2} \tag{15}$$

where $\alpha_B = \alpha_A \xi_{AB} (W_B/W_A)^{1/2}$ and $\xi_{AB} = (\rho_A K_A)/(\rho_B K_B)$. The periodicity D is subsequently given by $T_A + T_B - 2\lambda$.

Results and Discussion

In this section, we present some of the predictions obtained from this formalism. Unless otherwise specified, the molar composition (W_A) will be held constant at 0.50 throughout the following predictions, and the total molecular weight (M) will be maintained at 200 000. All of these predictions relate to constant-length copolymers, in which M is held constant and, as n is increased, the block lengths decrease.

The functional relationship of $\Delta g_{min}(m)$ is shown in Figure 4 for four values of n. Since m assumes multiple values when $n \geq 3$ (see Table I), values of σ needed in the free-energy minimization are obtained by appropriately weighting each σ by $X_{\sigma m}$ for a given m. For instance, when $n = 4$ and $m = 3$, σ is obtained from [(4)(8) + (3)(10) + (2)(2)]/20. As described earlier[23] and seen here, values of m are bound by $m = 0$ (no looping) and $m = 2n - 2$ (fully looped). At constant m, Δg_{min} is predicted to become more positive as the number of block pairs increases, in agreement with the entire genre of models[19–21,23] devoted to $(AB)_n$ copolymers. If n is held constant, Δg_{min} tends to

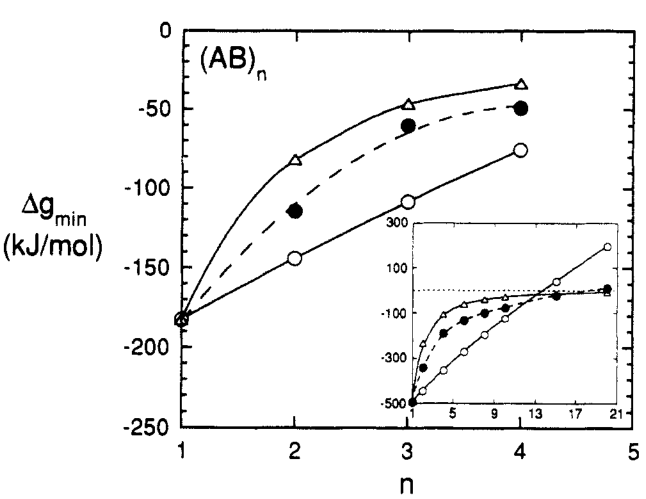

Figure 5. Functional relationship of $\Delta g_{\min}(n)$ for three different molecular conformations. The fully-extended conformation, given by $m = 0$, is denoted by ○, whereas the fully-looped condition ($m = 2n - 2$) is shown as △. Predicted $\Delta g_{\min}$ for the most probable conformation, corresponding to the average extent of looping ($\langle m \rangle$), are presented as ●. Solid and dashed lines are drawn from a cubic-spline algorithm as guides for the eye. The inset follows the same format as above for predicted $\Delta g_{\min}(n)$ when M is increased to 500 000. Note that the three curves in this case cross when n is increased sufficiently.

become more positive as the middle blocks of the molecule assume a looped conformation (m increases), thereby reflecting the entropic penalty associated with block looping. The features of this apparent trend are dependent on n. For instance, when $n = 2$, $\Delta g_{\min}$ increases abruptly as m goes from $m = 0$ ($\Delta g_{\min} = -144$ kJ/mol) to $m = 2$ ($\Delta g_{\min} = -82$ kJ/mol). The variation in $\Delta g_{\min}$ is less pronounced, only +42 kJ/mol, between $m = 0$ and $m = 6$ in the case when $n = 4$. This trend observed in Figure 4 suggests that middle-block looping is not thermodynamically favored in copolymers with few blocks but approaches the same energy state (and becomes more favorable) as fully-extended multiblock molecules at large n. This point is discussed further below.

Another representation of these observations is provided in Figure 5, in which $\Delta g_{\min}(n)$ is presented for the two conformational extremes, $m = 0$ and $m = 2n - 2$ (both obtained from Table I). Also shown is the function $\Delta g_{\min}(n)$ evaluated at $\langle m \rangle$, wherein $\langle m \rangle$ is determined from eq 3. As n is increased from unity, these three relationships are noticeably different, reflecting the probabilities associated with the middle blocks looping back upon themselves (see Figure 2). However, as n is increased further within the range $1 \leq n \leq 4$, predicted $\Delta g_{\min}|_{m=0}$, $\Delta g_{\min}|_{m=2n-2}$, and $\Delta g_{\min}|_{m=\langle m \rangle}$ become comparable in magnitude.

At larger n, all three $\Delta g_{\min}$ curves in Figure 5 approach or exceed zero, thereby making functional comparisons difficult. If M is increased, though, $\Delta g_{\min}$ can be determined over a broader range of n for the three cases of m discussed above. The inset in Figure 5 illustrates the $\Delta g_{\min}(n)$ relationships up to $n = 20$ when $M = 500\,000$. Predicted $\Delta g_{\min}|_{m=\langle m \rangle}$ in this case rely on eq 6 for $\langle \sigma \rangle$ and employ the relationship $\langle m \rangle = n - 1$. At low values of n, the three curves appear similar to the ones obtained when $M = 200\,000$, with the $\Delta g_{\min}|_{m=0}$ curve being the most negative and, by inference, the most energetically favored. At larger n, however, the curves are observed to cross, and the predicted $\Delta g_{\min}|_{m=2n-2}$ function eventually becomes the most negative of the three. These predictions indicate that, at equilibrium, looping is not preferred in $(AB)_n$ molecules of few blocks, but becomes increasingly more favored as n increases.

Both Figures 4 and 5 clearly demonstrate that the $\Delta g_{\min}$ values predicted in this work are dependent on m. Consider a multiblock copolymer permitted to undergo microphase separation under quiescent conditions, from a concentrated solution for example. Each microdomain will consist of molecules possessing a variety of conformations. Rigorous calculation of the physical properties exhibited by the copolymer therefore requires proper weighting of each possible conformation with its associated free energy to produce a thermodynamic ensemble average. Rather than choose this more complicated approach, we have elected to probe the effect of conformational differences on the free-energy function for any given n and examine consequent variations in predicted physical properties. As n becomes large, though, the properties of a microphase-separated $(AB)_n$ copolymer are expected to coincide with those corresponding to the most probable degree of looping ($\langle m \rangle$).

In this work, we have selected to identify the various conformations an $(AB)_n$ molecule is capable of assuming, assign a corresponding probability distribution function to these conformations, and then ascertain the minimum free energy for a given set of molecular parameters, now including block looping criteria. Another approach that has been taken by ten Brinke and Hadziioannou[30] and more recently by Balsara et al.[28] in their efforts to model micellization of BAB triblock copolymers (in which the middle A block loops back into the core-corona interphase) is to derive an analytical expression for the free-energy of looping per looped block (g_{loop}). In both cases, this expression on a molar basis takes the form

$$g_{\text{loop}} = a_1 RT \ln (a_2 N_A) \tag{16}$$

where N_A is the degree of polymerization of the looping block ($= W_A M / n m_A$ in the present study, where m_A is the monomer mass of component A). The prefactors a_1 and a_2 differ between the two micelle models, with ten Brinke and Hadziioannou[30] estimating a_1 to be approximately $^3/_2$ and $a_2 = 1$ from chain cyclization considerations. Balsara et al.[28] suggests that $a_1 = {}^1/_2$ and $a_2 = \pi\chi_{AB}$ on the basis of diffusion arguments. For either micelle model,[28,30] though, eq 16 indicates that $g_{\text{loop}} \propto \ln N_A$, assuming χ_{AB} is invariant at a given T. Regrettably, no comparison can be made with predicted $\Delta g_{\min}(m)$ from the present model, since an expression for g_{loop} is not directly attainable here.

Microstructural dimensions, such as the periodicity (D), are also functions of m. Figure 6 illustrates this point, as $D(m)$ is presented for the same values of n utilized in Figure 4. As n increases at constant m, D is observed to decrease, in accord with a reduction in block length. When n is held constant, D increases with m. This feature is attributed to the necessity of uniformly filling microdomain space. Microdomains containing looped blocks must be able to accommodate blocks whose junctions reside in one interphase along with those whose ends are anchored in the opposing interphase. Lamellae incorporating only extended middle blocks would be faced with a different space-filling dilemma due to the fact that the blocks must span the entire microdomain core (L_i, where i = A or B, in Figure 1) so that their junctions reside in separate interphases. The extent of block stretching accompanying this expansion, along with the free energy of deformation, is reduced when the cores contract, thereby resulting in both smaller L_i and D, as in Figure 6. This behavior has been experimentally observed[31] in a series of neat variable-

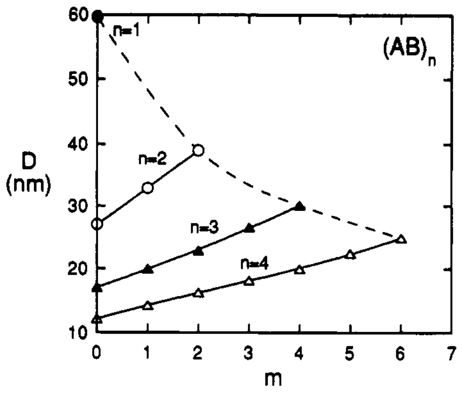

Figure 6. Predictions for the microstructural periodicity (D) as a function of m for the values of n provided in Figure 2. D is predicted to increase with m at constant n and decrease with n at constant m. The dashed line is drawn as a guide for the eye and connects the $D(n)$ which correspond to fully-looped molecular conformations. The symbols employed here are the same as those in Figure 2.

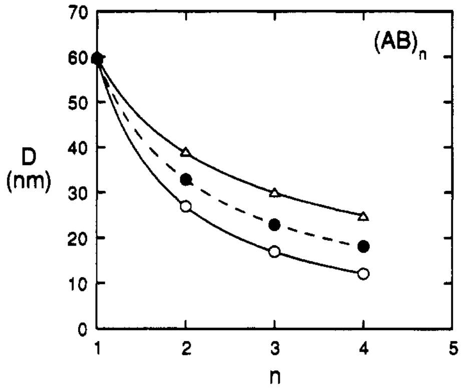

Figure 7. Predicted $D(n)$ for the cases of $m = 0$ (○), $m = 2n - 2$ (△), and $m = \langle m \rangle$ (●), as described in the caption of Figure 5. Each of these functions is found to exhibit a power-law relationship (shown by the solid and dashed lines), with scaling exponents equal to -1.15, -0.66, and -0.86, respectively.

length (AB)$_n$ copolymers consisting of polystyrene and polyisoprene, in which the block lengths are approximately constant while n increases from 1 to 4. The relationship between D and m at constant n is therefore a direct measure of the conformation of the middle blocks. While not exactly linear, the slopes $(\partial D/\partial m)_n$ seen in Figure 6 become less positive as n increases.

A representation similar to that shown for $\Delta g_{\min}$ in Figure 5 is provided in Figure 7 for $D(n)$ evaluated at $m = 0$, $m = 2n - 2$, and $m = \langle m \rangle$. Values of D corresponding to fully-extended block conformations are given by the lower curve, while the fully-looped condition corresponds to the upper curve. Scaling relationships taking the form of $D|_{m=0} \sim n^{-1.15}$ and $D|_{m=2n-2} \sim n^{-0.66}$ are observed and have been previously[23] compared with predictions from the Benoit and Hadziioannou[20] model. In the present work, $D|_{m=\langle m \rangle}$ is predicted to scale as $n^{-0.86}$. This scaling relationship is in excellent agreement with recent experimental data obtained[32] with transmission electron microscopy and small-angle X-ray scattering on a series of well-defined (AB)$_n$ multiblock copolymers composed of polystyrene and polyisoprene, each possessing a constant overall molecular weight (120 000) and n varying from 1 to 4.

Another relationship which provides valuable information on the extent of block stretching along the lamellar normal is the variation of D with respect to M. This scaling relationship typically takes the form of $D \sim M^b$. A value of $b = 0.5$ would correspond to a polymer possessing random (Gaussian) chain statistics, whereas $b \rightarrow 1$ indicates that the material is in an extended chain conformation (in which $\langle r_i^2 \rangle^{1/2} = K_i M_i$). For diblock copolymers, b has been shown both experimentally[7-9] and theoretically[10-16] to equal approximately 0.67 in the strong-segregation limit. Recent theoretical efforts by Melenkevitz and Muthukumar[33] suggest that a crossover regime exists between the weak-segregation limit (where $\chi_{AB}N \approx 10.5$ and $b \approx 0.50$) and the strong-segregation limit ($\chi_{AB}N \approx 100$ and $b \approx 0.67$), wherein the scaling exponent assumes a value of 0.72. The possibility that these postulated (AB)$_n$ copolymers belong in this crossover regime is not considered here. Earlier predictions for $D(M,n)|_{m=0}$ have indicated that the M^b scaling behavior is retained when n increases from unity.[23,32] A similar analysis has been performed on predicted $D(M,n)|_{m=\langle m \rangle}$ and reveals comparable results in which $b(n)$ increases to 0.79 when $n = 4$. This scaling behavior indicates that as n increases in the multiblock architecture, an (AB)$_n$ molecule assuming the most probable looping conformation is predicted to be stretched further along the lamellar normal than its diblock analogue.

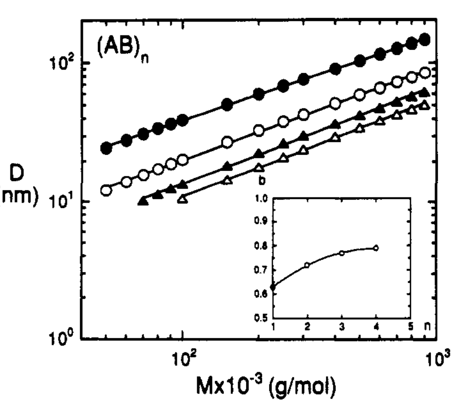

Figure 8. Variation of D with the overall molecular weight (M) for four values of n: 1 (●), 2 (○), 3 (▲), and 4 (△). In all cases, $m = \langle m \rangle$. As observed earlier[23] for the case of $m = 0$, $D \sim M^b$ for all four n (solid lines). The function $b(n)$ is provided in the inset and clearly reveals that b increases with n (the solid line is a guide for the eye). This behavior suggests that (AB)$_n$ molecules, while even looped to a finite extent, are more stretched along the lamellar normal than their diblock analogues.

Conclusions

Looping statistics which describe the variety of block conformations possible in linear (AB)$_n$ copolymers have been developed. As n increases, the total number of looping events increases as $2^{2(n-1)}$, with the average equal to $n - 1$. These statistics are cast into a conformational format on the basis of the projection of the molecule along the lamellar normal and are subsequently incorporated directly into a confined single-chain thermodynamic model for (AB)$_n$ molecules in the strong-segregation limit. Predictions for the minimized free-energy function indicate that looping is not highly favored in low-n molecules but becomes increasingly more favored as n becomes large. The microstructural periodicity is also dependent on both m and n, decreasing with n at constant m and increasing with m at constant n. Two important scaling relationships have been identified for constant-length copolymers possessing the most probable looping conformations ($\langle m \rangle$), namely, $D \sim n^{-0.86}$ and $D(n) \sim M^b$. The former is in excellent agreement with experimental data presented elsewhere.[32] In the latter $b = b(n)$, where b increases from about 0.63 ($n = 1$) to 0.79 ($n = 4$).

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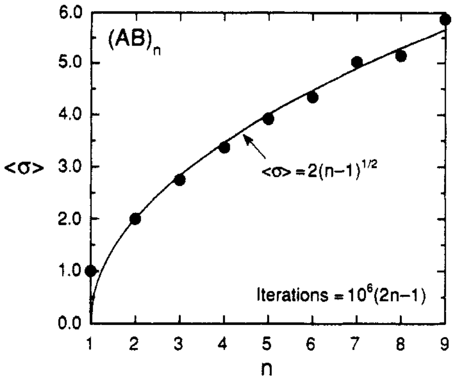

Figure 9. One-dimensional random-walk simulations of $\langle\sigma\rangle$ (●) presented as a function of n. The simulations employed l_o (eq 1) as the segmental length and $2n - 1$ as the number of such segments per copolymer molecule. The solid line corresponds to eq 6 in the text and is valid for $(AB)_n$ molecules which are capable of looping ($n \geq 2$).

Appendix. Random-Walk Behavior of Multiblock Copolymers

The values of $\langle\sigma\rangle$ presented as a function of n in Figure 3 were obtained by appropriately weighting σ and $X_{\sigma m}$ in Table I. As pointed out earlier, though, $\langle\sigma\rangle$ can be obtained from a random-walk analysis, since it is analogous to the end-to-end distance of a chain macromolecule if the segmental length is chosen as l_o (see eq 1). The corresponding number of such segments in an $(AB)_n$ molecule is $2n - 1$. According to this picture, the point at which the molecule is permitted to pivot (to form a loop) is centered within a microdomain core and *not* at a junction site. One-dimensional random-walk simulations, in which the number of iterations for a given n was $10^6(2n - 1)$, have been performed for copolymers possessing values of n up to 9, with $\langle\sigma\rangle$ determined from the molecular projection along the walk axis. The results of this analysis are provided in Figure 9 and compare favorably with the analytical function presented in eq 6 when $n > 1$. Note than random-walk behavior is expected to become increasingly more apparent at large n but is observed even when n is small.

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