Notes

Effect of Chain Persistence Length on the Moduli of Block Copolymer Films

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Introduction

Interfacial layers formed by amphiphilic molecules are widely used as stabilizers of immiscible liquid mixtures. Diblock copolymers, the macromolecular analogue of small molecule surfactants, are similarly used to stabilize incompatible polymer blends. Understanding the relationship between copolymer properties and the self-assembled interfacial layer characteristics is important, since these control the type, size, and polydispersity of the stable domains.[1−9]

Interfacial layers of flexible diblock copolymers (where the persistence lengths of both blocks are of the same order as the monomer size) at the interface between immiscible liquids[1,2] or homopolymers[3−6] have been thoroughly examined. The layer characteristics are controlled by a balance between the entropy of the two blocks and the strength of the interactions between them.[1−9]

Not all polymer chains are flexible. Moreover, the chain stiffness may vary in different environments. (For example, the persistence length of a polyelectrolyte in water depends on salinity.) Qualitatively, one expects the behavior of stiff chains to resemble that of flexible chains. The persistence length will simply rescale the chain dimensions and entropic penalty, as shown in Figure 1. However, recent studies of stiff copolymers either in bulk or in a selective solvent[10−14] indicate that the phase diagram of copolymers that contain a rigid block is not similar to that of flexible chains. For example, Matsen[11] calculates that the order−disorder transition shifts toward the disordered state with increasing molecular rigidity, while Radzilowski and Stupp[13] find that the aggregates formed by rod−coil chains are much smaller than those of their flexible counterparts, thereby indicating much smaller aggregation numbers. The effect of the chain persistence length must therefore be more than to rescale the chain dimensions.

How does the chain persistence length affect the interfacial characteristics of diblock copolymer layers at the interface between immiscible homopolymers? Although some aspects of the phase diagram of copolymers containing stiff blocks are known,[10−14] they do not relate directly to the interfacial parameters, such as the layer bending moduli. In this paper we explicitly calculate the interfacial properties of films composed of diblock copolymers where one block is flexible, as a function of the other block's rigidity. Naively, one would assume that increasing the stiffness of a block (while keeping the overall chain contour length constant) will lead to an increase in interfacial stiffness. This will translate to an increase in the bending modulus (resistance to bending) and a decrease in the Gaussian modulus (resistance to saddle splay). This is consistent with the analogy between chains, the chain persistence length, and changing the chain asymmetry or the ratio of the two block molecular weights.[4] However, contrary to this expectation, we find that increasing the chain stiffness leads to a maximum in the bending modulus; beyond a critical value, the layer resistance to bending decreases with chain stiffness to values *below* those of the fully flexible diblock. The effect of stiffness on the Gaussian modulus is found to depend on the diblock composition; in some cases the Gaussian modulus decreases monotonically with stiffness, thereby indicating increasing resistance to saddle formation. However, at a certain range of copolymer composition the Gaussian modulus may go through a minimum. In such blocks, the resistance to saddle formation may decrease to values significantly below those of the flexible chains.

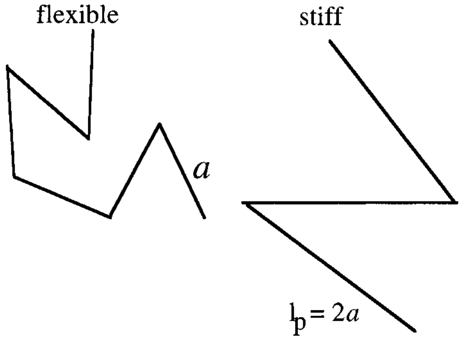

Figure 1. Effect of chain stiffness on an ideal chain. The chain contour length is given by Na, where N is the number of monomers and a a monomer size (in this figure $N = 6$). The number of random walk steps, ν, defines the effective chain molecular weight and is equal to Na/l_p, where l_p is the chain stiffness. The chain radius of gyration, R_g, is proportional to $\nu^{1/2}l_p$, and the entropic penalty for stretching the chain to an arbitrary length scales as $1/R_g^2$.

In short, we find that increasing the chain stiffness may lead to formation of very flexible layers whose resistance to any form of bending is relatively low. This result is extremely intriguing, since the high stiffness of diblock copolymer layers remains one of the major obstacles to their utilization.

Model and Results

The moduli of interfacial layers can be defined through an expansion of the energy in terms of c_1 and c_2, the dimensionless local curvatures,[15]

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$$F = \mathbf{F_0} + \frac{1}{2}\mathbf{K}\{(c_1 + c_2 - 2c_0)^2 + \bar{\mathbf{K}}c_1c_2 \tag{1a}$$

which reduces, in the case of cylindrical interfaces where $c_1 = 0$ and $c_2 = c$, to

$$F_{\text{cyl}} = (\mathbf{F_0} + 2\mathbf{K}{c_0}^2) - 2\mathbf{K}cc_0 + \frac{1}{2}\mathbf{K}c^2 \tag{1b}$$

for spherical interfaces where $c_1 = c_2 = c$

$$F_{\text{sph}} = (\mathbf{F_0} + 2\mathbf{K}{c_0}^2) - 4\mathbf{K}cc_0 + (2\mathbf{K} + \bar{\mathbf{K}})c^2 \tag{1c}$$

and, for a symmetric saddle where $c_1 = -c_2 = c$

$$F_{\text{sad}} = (\mathbf{F_0} + 2\mathbf{K}{c_0}^2) - \bar{\mathbf{K}}c^2 \tag{1d}$$

$\mathbf{K}$ and $\bar{\mathbf{K}}$ are the mean and Gaussian bending moduli, respectively. c_0 is the spontaneous, or preferred, curvature.[15] The first term in eq 1a defines the energy of a flat film. The second term accounts for the energetic penalty associated with a curvature that is not the optimal one, c_0. The third term accounts for the interface bending stiffness.

The Helfrich formulation is convenient, providing that the phenomenological parameters $\mathbf{F_0}$, $\mathbf{K}$, $\bar{\mathbf{K}}$, and c_0 are known. To derive these as a function of the copolymer properties, a molecular model for copolymers at interfaces is required. In the strong segregation limit where the two blocks are highly incompatible, such a model is readily available:[1-5] The chains are driven to the interface by the incompatibility between the two blocks, which is manifested in an interfacial energy. Their packing at the interface forces them to stretch in the direction perpendicular to the surface, which leads to surface saturation at some finite surface density.

Using either rigorous[16,17] or scaling arguments,[12] we can calculate the stretching energy required to extend a chain to an end-to-end length h as[18]

$$F \approx \frac{3h^2}{4l_\text{p}aN} \tag{2}$$

Here l_p is the chain persistence length,[17] a is a molecular (bond or segment) length scale,[17] and N is the number of segments in the chain. Implicit in eq 2 is the assumption that the chain contour length aN is much larger than either the persistence length, l_p, or h, the end-to-end distance. In the limit of fully flexible chains where l_p is of order a, eq 2 reduces to the familiar flexible chain expression. All energies are given in units of kT, where k is the Boltzmann costant and T the temperature. In all subsequent discussions, length scales are always given in units of a.

Now examine a diblock copolymer AB at the interface between incompatible homopolymers. The free energy of an AB diblock copolymer at an interface is given by the stretching penalty of both blocks and the interfacial energy

$$F_{\text{AB}} = F(N_\text{A},l_\text{A},h_\text{A}) + F(N_\text{B},l_\text{B},h_\text{B}) + \gamma\Sigma \tag{3}$$

where (N_i, l_i, h_i) are the molecular weight, persistence length, and end-to-end distance of block i (A or B). γ is the surface tension between the A and B chains and Σ the interfacial area per copolymer, and $F(N_i,l_i,h_i)$ is given by eq 2, using the parameters of block i. We neglect the interfacial energy between the A block layer and the A homopolymer and the B block layer and the B homopolymer. For simplicity, we also assume that the monomer length of both blocks is the same, a, and that the stretching deformation of each block is small so that eq 2 applies.[18] We also assume that both blocks form a molten layer, which means that no solvent (or homopolymer) penetrates into the copolymer layer. This allows us to relate the thickness of the block layer, h_i, to the geometry of the interface. For example, the energy of a cylindrical layer can be written[2-5]

$$F_{\text{AB}}^{\text{cyl}} \approx \gamma\Sigma + \frac{3\nu}{4\Sigma^2} + \frac{3c}{4\Sigma^3}\left(\frac{{N_\text{A}}^2}{l_\text{A}} - \frac{{N_\text{B}}^2}{l_\text{B}}\right) + \frac{15c^2}{16\Sigma^4}\left(\frac{{N_\text{A}}^3}{l_\text{A}} - \frac{{N_\text{B}}^3}{l_\text{B}}\right) \tag{4}$$

where $\nu = (N_\text{A}/l_\text{A} + N_\text{B}/l_\text{B})$, the overall number of persistence lengths in a copolymer chain. The effective asymmetry of the copolymer can be defined as the ratio between the number of A block units, N_A/l_A, to the number of B block units, N_B/l_B. We will limit our discussion to systems where this ratio is moderate, since it is well-known that surface layers formed by highly asymmetric copolymers are unstable compared to micelles.[2,3] Since the interfacial layer is self-assembled, the surface area per chain, Σ, adjusts in response to the interfacial curvature. Minimization with respect to Σ and expanding to second order in curvature yields the energy of a cylindrical or a spherical layer, respectively:

$$F_{\text{AB}}^{\text{cyl}} \approx \left(\frac{3}{2}\right)^{4/3}\gamma^{2/3}\nu + c\frac{\gamma\left(\frac{{N_\text{A}}^2}{l_\text{A}} - \frac{{N_\text{B}}^2}{l_\text{B}}\right)}{2\nu} + c^2\frac{\gamma^{4/3}}{4\cdot 12^{1/3}\nu^{7/3}}\left(\frac{2{N_\text{A}}^4}{{l_\text{A}}^2} + \frac{2{N_\text{B}}^4}{{l_\text{B}}^2} + \frac{N_\text{A}N_\text{B}(5{N_\text{A}}^2 + 5{N_\text{B}}^2 + 6N_\text{A}N_\text{B})}{l_\text{A}l_\text{B}}\right) \tag{5a}$$

$$F_{\text{AB}}^{\text{sph}} \approx 3\left(\frac{3}{2}\right)^{4/3}\gamma^{2/3}\nu + c\,\frac{\gamma\left(\frac{{N_\text{A}}^2}{l_\text{A}} - \frac{{N_\text{B}}^2}{l_\text{B}}\right)}{\nu} + c^2\frac{\gamma^{4/3}}{3\cdot 12^{1/3}\nu^{7/3}}\left(\frac{4{N_\text{A}}^4}{{l_\text{A}}^2} + \frac{4{N_\text{B}}^4}{{l_\text{B}}^2} + \frac{N_\text{A}N_\text{B}(13{N_\text{A}}^2 + 13{N_\text{B}}^2 + 18N_\text{A}N_\text{B})}{l_\text{A}l_\text{B}}\right) \tag{5b}$$

Comparing these expressions to the Helfrich interfacial energy (eq 1) gives us the layer moduli as a function of the copolymer parameters:

$$\mathbf{K} = \frac{\gamma^{4/3}}{2\cdot 12^{1/3}\nu^{7/3}}\left(\frac{2{N_\text{A}}^4}{{l_\text{A}}^2} + \frac{2{N_\text{B}}^4}{{l_\text{B}}^2} + \frac{N_\text{A}N_\text{B}(5{N_\text{A}}^2 + 5{N_\text{B}}^2 + 6N_\text{A}N_\text{B})}{l_\text{A}l_\text{B}}\right) \tag{6a}$$

$$\bar{\mathbf{K}} = -\frac{2^{1/3}\gamma^{4/3}}{3^{4/3}\nu^{7/3}}\left(\frac{{N_\text{A}}^4}{{l_\text{A}}^2} + \frac{{N_\text{B}}^4}{{l_\text{B}}^2} + \frac{N_\text{A}N_\text{B}({N_\text{A}}^2 + {N_\text{B}}^2)}{l_\text{A}l_\text{B}}\right) \tag{6b}$$

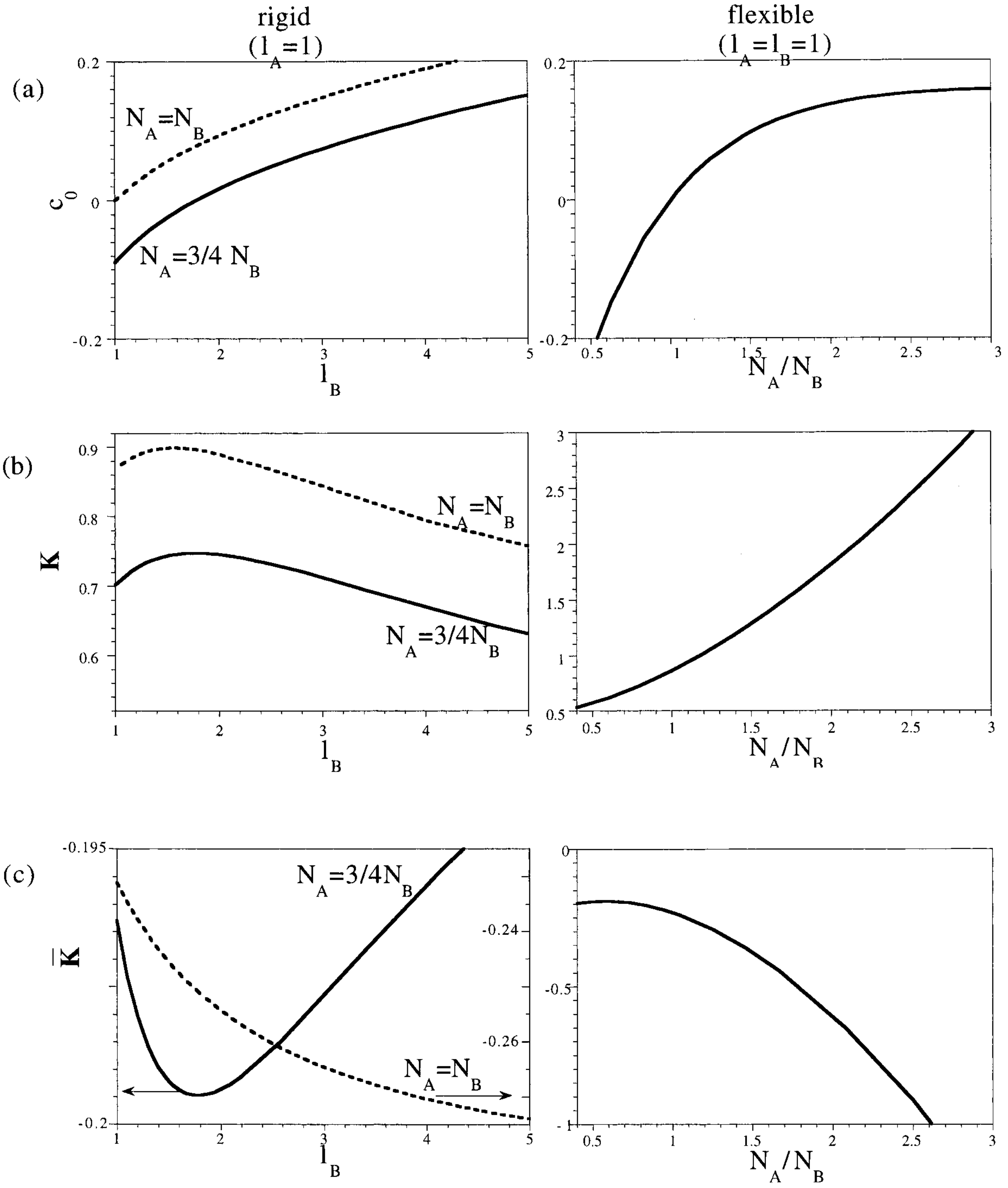

Figure 2. Effect of chain asymmetry and rigidity of the interfacial moduli. Defining the effective chain asymmetry as the ratio between the number of "steps" in each block, $\epsilon = (N_A/l_A)/(N_B/l_B)$, the asymmetry of flexible chains where $l_A = l_B = 1$ is equal to N_A/N_B. For rigid chains where N_A/N_B is fixed and $l_A = 1$, $\epsilon \sim l_B$. Since highly asymmetric chains form micelles rather than interfacial layers,[1-6] we concentrate on relatively symmetrical chains where ϵ is of order unity. (A) Effect of chain rigidity and asymmetry of the spontaneous curvature, for both rigid and flexible chains. $l_A = 1$ for the rigid chain. (B) Effect of chain rigidity and asymmetry of the mean bending modulus, for both rigid and flexible chains. $l_A = 1$ for the rigid chain. (C) Effect of chain rigidity and asymmetry of the Gaussian (saddle-splay) modulus, for both rigid and flexible chains. $l_A = 1$ for the rigid chain.

$$c_0 = \left(\frac{3}{2\gamma}\right)^{1/3} \nu^{4/3} \times \frac{\dfrac{N_A^{\,2}}{l_A} - \dfrac{N_B^{\,2}}{l_B}}{\dfrac{2N_A^{\,4}}{l_A^{\,2}} + \dfrac{2N_B^{\,4}}{l_B^{\,2}} + \dfrac{N_A N_B(5N_A^{\,2} + 5N_B^{\,2} + 6N_A N_B)}{l_A l_B}} \tag{6c}$$

As may be expected, the mean bending modulus is always positive, thereby indicating an inherent resistance to bending. The Gaussian modulus is always negative, which means that saddle-type deformations are unfavorable.[14] The spontaneous curvature may be either negative or positive, depending on the ratio of the block lengths and rigidities. In the limit of flexible chains ($l_A = l_B = 1$) these expressions reduce to the expected values.[3-5] Since these expression are rather messy, let us examine in detail specific cases.

In Figure 2a the spontaneous curvature is plotted as a function of the B chain rigidity for two types of copolymer chains and compared to the spontaneous curvature of a flexible copolymer. A negative value of c_0 indicates preferential curvature of the interface toward the A block, zero denotes a flat (lamellar) layer, and a positive value indicates curvature toward the B block. In copolymers where both blocks are flexible ($l_B = 1$), the spontaneous curvature is proportional to the molecular weight difference between the two blocks.[2-5] Therefore, for a given A block molecular weight, the spontaneous curvature of a copolymer where $l_A = l_B = 1$ increases with N_B.

The effective molecular weight ratio of a rigid copolymer is defined as $\epsilon = (N_A/l_A)/(N_B/l_B)$. ϵ of a flexible chain is equal to N_A/N_B, while that of a given stiff chain where N_A/N_B is fixed and $l_A = 1$, $\epsilon \sim l_B$. We see in Figure 2a that, indeed, the spontaneous curvature increases with ϵ both for the flexible and for the rigid chains. Quantitatively, $c_0 = 0$ not when $\epsilon = 1$ but when (eq 6c) $N_A/\sqrt{l_A} = N_B/\sqrt{l_B}$.

In Figure 2b we compare the mean bending modulus **K** of a rigid copolymer to that of a flexible one. Unlike the spontaneous curvature case, we see qualitative differences between the dependence of the stiff and flexible chain modulus on the effective molecular weight ratio. In the flexible chain system reducing the molecular weight of the B block (thereby increasing ϵ) leads to a monotonic increase in the layer's bending modulus. However, in the rigid copolymer **K** varies nonmonotonically with ϵ (namely, l_B), first increasing and then decreasing. The Gaussian modulus of a rigid chain (Figure 1c) displays an even more curious behavior: it decreases monotonically with the rigid chain ϵ for the symmetrical chains but, in the nonsymmetrical case, passes through a minimum and then increases up to some limit value at high l_B. The flexible chain's Gaussian modulus decreases with decreasing B chain length.

To determine the regime where nonmonotonic behavior may occur, we minimize the three moduli (eq 6) with respect to the persistence length of the B block (taking $l_A = 1$). We find that the spontaneous curvature always increases (monotonically) with chain rigidity. However, for a wide range of copolymer compositions (N_A/N_B) both bending moduli display an extremum point, as shown in Figure 3.

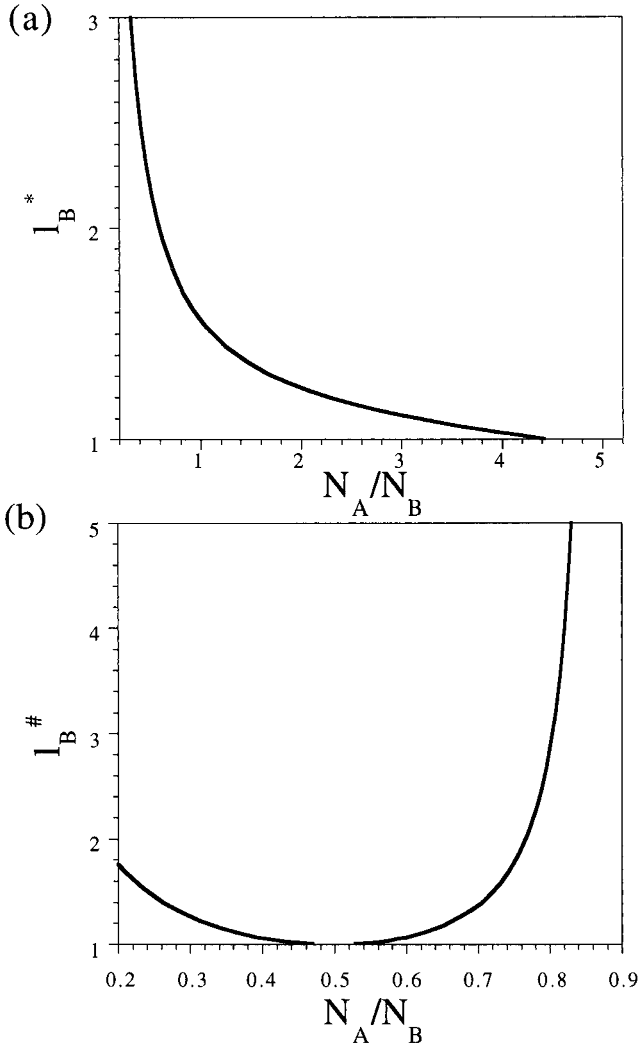

Figure 3. Effect of chain asymmetry, N_A/N_B, on the persistence length of the bending moduli at the extremum point. $l_A = 1$. Note that, due to our definition where the monomer size is 1, l_B cannot be smaller than unity. (A) l^*_B is the persistence length for which **K** is maximal. Obtained from the solution of $\partial \mathbf{K}/\partial l_B = 0$. (B) $l^\#_B$ is the persistence length for which $\bar{\mathbf{K}}$ is minimal. Obtained from the solution of $\partial \mathbf{K}/\partial l_B = 0$.

Discussion and Conclusions

We present here a simple model for the moduli of diblock copolymer films in the strong segregation limit, as a function of the blocks' persistence length. We find that the effect of the chain persistence length is more significant than a simple rescaling of the molecular weight.

The nonmonotonic dependence of the bending moduli on the chain rigidity can be explained when we consider the effect of chain stiffness on the interfacial layer. Increasing the persistence length of one block (at a constant molecular weight) reduces the stretching energy penalty of that block associated with the packing at the interface. This leads to an increased surface density and a concurrent increase in the resistance to bending. However, the bending stiffness of the rigid block *decreases* with chain rigidity.[19] The competition between the two trends leads to the nonmonotonic behavior observed.

How do the moduli affect the phases formed? Consider a mixture of incompatible homopolymers, stabilized by an appropriate copolymer. In the limit where there is an excess of both homopolymers, the emulsion droplet size will be inversely proportional to the spontaneous curvature. The sign of the spontaneous curvature will determine which homopolymer is encapsulated and which is the dispersed phase. As the copolymer concentration increases, one of the homopolymers will become depleted, in which case the droplets will become constrained. Both the domain size and size distribution (polydispersity) will be determined then by the bending moduli.[2] Also significant is the fact that, in some regimes, increasing the chain rigidity significantly reduces the bending moduli, thereby reducing the penalty for interfacial bending and for the formation of saddles. This means that the blend domains would become less rigid and may deform easily when under external fields such as shear.

The analysis provided here also applies to copolymer bilayers. For a spherical bilayer, one may write the energy as

$$F^{\mathrm{bi}}_{\mathrm{sph}} \approx F_{\mathrm{sph}}(c) + F_{\mathrm{sph}}(-c) = 2(\mathbf{F_0} + 2\mathbf{K}{c_0}^2) + 2(2\mathbf{K} + \bar{\mathbf{K}})c^2 \quad (7)$$

neglecting the shift in curvature due to the bilayer thickness.[5] Small values of **K** and $\bar{\mathbf{K}}$, when compared to kT, thereby indicate the possibility of stable vesicle formation.[5]

In conclusion, we find that the bending moduli of copolymer chains containing a stiff block differ qualitatively, as well as quantitatively, from those of copolymers where both blocks are flexible. In the limit of high chain stiffness, both the Gaussian and saddle moduli may be considerably reduced. We would like to emphasize that our analysis is valid only for chains where the chain persistence length is much smaller than the contour length (i.e., Gaussian chains) and in the limit of low stretching. Also, we neglect the effect of chain persistence length on the interfacial tension between the two blocks. As shown by Semenov,[20] both the interfacial width and tension depend on the block persistence length. However, for the rigidities used here ($l_b \leq 5a$) the change in the surface tension[20] is less than 1% and can therefore be neglected.

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(18) The full form of eq 2 is $F \approx 3(h - R_0)^2/4l_paN$, where R_0, which scales as $(Nl_pa)^{1/2}$, is the unperturbed chain end-to-end radius. This expression is based on the view of the polymer chain as an entropic spring,[15,17] so that $(h - R_0)$ is the perturbation of the chain rest length. In this discussion we assume that $h \gg R_0$ so that only the leading term remains. Like any spring model, eq 2 breaks down at high perturbation[16] when h approaches the chain's contour length. This translates to the condition[1−5] that $\gamma/N \ll 1$, which is reasonable for most high molecular weight chains.
(19) The mean bending modulus of N long chains anchored by one end onto a curved surface at a constant surface area per chain Σ (i.e., "brush") scales inversely with the persistence length: $\mathbf{K} = 25N^3/3\Sigma l_p$.
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