Elastic Constants for Random Block Copolymers in the Strong Segregation Limit: Effects of Sequence Distribution

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ABSTRACT: We consider the quasi-static mechanical response of microphase-segregated A–B random block copolymers to compressive strains in the strong segregation limit. Our analytical calculations show that the elastic constant that describes this response exhibits a nonmonotonic dependence on the fraction of blocks of type A (for a given degree of blockiness). Furthermore, the magnitude of the elastic constant is extremely sensitive to the disorder correlations along the copolymer backbones. The physical origin of the variation of the elastic constant with block sequence distribution and the size and stiffness of the blocks is discussed.

I. Introduction

In many technological applications the processing of complex fluids, such as polymers, is an important step. Complex molecules often form fluid phases that are not ordered on the atomic scale but exhibit order on the mesoscopic scale (e.g., ref 1). The processing of such materials involves the deformation of these mesoscopic structures. Hence, understanding the mechanical behavior of the mesoscopic structures formed by complex fluids under appropriate conditions is an issue of some practical consequence. Several fundamentally important questions also need to be addressed in order to pursue an understanding of the mechanical behavior of such materials. As such, there has been considerable recent interest in investigating these issues.[2,3]

One of the best examples of a system that is fluid-like on atomic length scales but is structured at mesoscopic scales is provided by block copolymers with incompatible blocks. In recent years, model block copolymers with well-defined architectures have been studied extensively by both theorists and experimentalists.[1,4–13] Specific examples of architectures that have been studied include diblock and triblock copolymers, graft copolymers, alternating multiblock copolymers, and, most recently, random block copolymers. These materials undergo a microphase separation transition, or order–disorder transition, leading to the formation of inhomogeneous composition patterns. The transition occurs because the incompatible blocks segregate to form microdomains. Among the different chain architectures, the phase diagram of diblock copolymers has been the most extensively studied (e.g., refs 1, 5, 7, and 8). For this system, it is now well established that there are large-amplitude composition fluctuations prior to the transition to an ordered phase. For simple diblocks the length scale that characterizes these spatial flucutations remains essentially constant as one passes through the transition. At lower temperatures, microdomains composed of strongly stretched chains are formed. This regime is referred to as the strong segregation limit (SSL). For carefully prepared samples of diblock copolymers the phase diagram exhibits a rich variety of ordered structures. Lamellar, hexagonal arrays of cylinders, body centered cubic arrays of spheres, and ordered bicontinuous double diamond phases have been observed for diblock copolymers with well-defined architectures.[1,5,7] More recently, Frederickson et al.[13,14] have considered the phase behavior of copolymers with ill-defined architectures. Specifically, they have considered model random block copolymers. These materials (e.g., polyurethanes and SBR rubber) are of great practical importance. They are also of much theoretical interest because they constitute a class of materials wherein a quenched disorder is carried by the fluid whose statistical properties are of interest. Fredrickson et al.[13,14] have carried out a mean field analysis for melts of random block copolymers. They predict a very rich phase diagram which includes an isotropic Lifshitz point and various liquid and ordered phases.

As we have noted, the ordered domains that are formed when the blocks are sufficiently incompatible are on the mesoscopic scale. At the atomic level, amorphous block copolymer materials are not ordered. Consider deforming such a fluid. Clearly, there are at least two important time scales that are relevant. The first is the relaxation time associated with segmental motion, and the second pertains to the relaxation of the mesoscopic ordered structures. The latter process occurs on much longer time scales. As such, it is easy to envisage situations wherein deformations are carried out over time scales that exceed the segmental (or internal stress) relaxation time, while being of too short a duration for relaxation of the domain structure. This is precisely the reason why microstructured fluids possess a measurable elastic modulus and seem to respond in a solid-like fashion over certain time scales. It is this quasi-static mechanical behavior that will concern us in this paper.

The quasi-static mechanical behavior of the lamellar microstructure of diblock copolymers has been considered very recently by two groups of authors.[2,3] Amundson and Helfand[2] have studied deformation of the lamellar composition pattern in the weak segregation limit (WSL). Wang[3] has considered both the SSL and the WSL for arbitrary deformations. In the present paper, we consider similar issues for random block copolymers. Specifically, in this paper we shall focus our attention on lamellar microphases of random block copolymers in the SSL. Furthermore, we shall restrict attention to the quasi-static response of these materials to small compressive strains. Our results show that the response is a strong function of the block sequence distribution of random copolymers.

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This finding points to the possibility of tailoring the mechanical properties by appropriate modification of conditions used to prepare (synthesize) these random copolymers.

We should note that random block copolymeric materials, such as polyurethanes, rarely self-assemble into lamellar phases with any reasonable degree of long-range order. The structures observed in physical systems likely reflect a local equilibrium with regard to layer spacing and chain conformations but are globally out of equilibrium as regards the large-scale composition pattern. Thus, our calculations for a lamellar phase with perfect long-range order are meaningful only in the sense that they reflect the intrinsic elastic properties of a "grain" within a microphase-segregated material that contains a statistical distribution of grain sizes and orientations. Nevertheless, such intrinsic grain elastic properties are the required input for more ambitious theories that attempt to compute macroscopic elastic properties of disordered, microstructured materials. Moreover, it has proven possible and desirable to impart macroscopic long-range order in model di- and triblock copolymer materials.[15-17] This may also be possible for certain random multiblock copolymers. In such cases, our computed elastic constants will directly reflect the macroscopic quasi-static response normal to the lamellar planes. Finally, it should be noted that we restrict consideration to copolymers with amorphous (noncrystalline) blocks and to temperatures above the glass transitions of the pure block components.

This paper is organized as follows. In section II, we describe how the sequence distributions of our model random block copolymers are specified. We also define our model for the lamellar microphase in the SSL. In section III, our method of calculation is outlined. In section IV, we describe and discuss our results, demonstrating an interesting dependence of the quasi-static mechanical response on the architecture of random block copolymers. Finally, in section V, we make a few concluding remarks and suggest experiments that could test our predictions.

II. Model Specification

We define the architecture of random block copolymers following Fredrickson et al.[13] We consider each chain to be made up of segments of types A and B, with each segment being a prepolymer of length N. We imagine that the linear chains are synthesized by using a coupling agent that can randomly copolymerize the prepolymers. Furthermore, we employ the first-order Markov model[18] to describe the polymerization process. As shown by Fredrickson et al.,[13] this implies that the block sequence distribution can be described in terms of two statistical quantities. One parameter that is necessary is the average volume fraction of A blocks (f) that make up the chains. However, this is not sufficient, and the following 2 × 2 matrix of conditional reaction probabilities is also required to define the chain architecture:

$$\mathbf{P} = \begin{pmatrix} p_{AA} & p_{AB} \\ p_{BA} & p_{BB} \end{pmatrix} \qquad (1)$$

where p_{IJ} is the conditional probability that a segment of type J is followed by one of type I. These conditional probabilities are directly related to the kinetics of the different coupling reactions. As noted by Fredrickson et al.,[13] conservation of probabilities and the fact that f and p_{IJ} must be independent of position along the chain demands that only one of the four probabilities in eq 1 is independent. We choose this one independent measure of the matrix $\mathbf{p}$ to be its only nontrivial eigenvalue, λ.

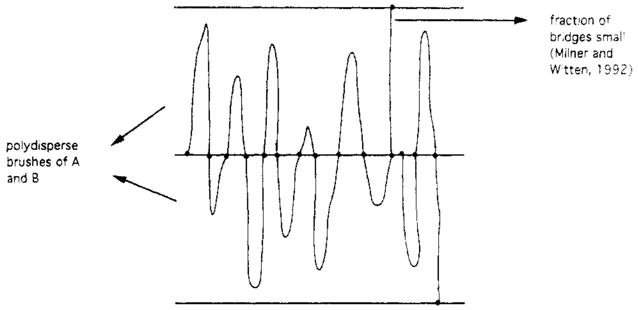

Figure 1. Schematic representation of a grain of random block copolymers in the SSL. Note the distribution of lengths of the bridges and loops.

Specifically,

$$\lambda = p_{AA} + p_{BB} - 1 \qquad (2)$$

Thus, f and λ define the chain architecture and are determined uniquely in terms of the reactivity ratios.[18] Physically, f is a measure of the probability of finding a segment of type A at an arbitrary location on the chain. As has been noted in previous studies,[13,14,19,20] λ measures the strength of chemical correlations along the chain. Equation 2 makes clear that λ can acquire values between -1 and $+1$. It is easy to see that $\lambda = -1$ corresponds to an alternating multiblock copolymer, while $\lambda = +1$ corresponds to a mixture of two homopolymers of A and B. When $\lambda = 0$ there are no chemical correlations along the chain, and we shall refer to this case as an ideal random block copolymer. Our study will focus on how the quasi-static mechanical response of random block copolymers to compressive strains depends upon f and λ.

We now describe our picture of the local structure of the lamellar microdomains in the SSL. Our model is similar to that employed many years ago by Helfand and Wasserman[21] and by Semenov[22] for diblock copolymers. We consider the regions of A and B to be separated by a thin interface wherein the junction points of the A and B blocks lie. Each region is made up of strongly stretched loops and bridges of A- and B-type segments. Figure 1 illustrates this picture of a "grain" in the SSL. The essential difference between the model for diblock copolymers and that for random block copolymers is that in our case each region is made up of loops that have a distribution of lengths. This distribution of loop lengths is a consequence of having a random architecture and, as we shall see, is completely determined by f and λ. Note that having a distribution of loop lengths implies that the chains fill space less densely compared to monodisperse loops.

Before we proceed with our calculation of the quasi-static response, we note that the presence of bridges will be ignored in our analysis. This approximation is based on work done by Milner and Witten[23] on telechelic chains. These authors have shown that at equilibrium and for small compressive deformations the fraction of bridges is very small. Thus, we ignore the bridges in carrying out our simple analytical calculations. With this approximation, each region of the lamellar domain may be described as a polydisperse brush,[24,25] with each loop being equivalent to two stretched chains.

Our calculation will now proceed in the standard Helfand–Wasserman–Semenov way. We shall calculate the equilibrium properties by balancing the interfacial free energy with the elastic free energy of the two *polydisperse* brushes. We shall then obtain the quasi-static response to a small compressive strain by expanding

$$\mathrm{B - (A - A - A \ldots\ldots A)_l - B}$$

Figure 2. Configuration for calculating $P_A(l)$.

$$\mathrm{A - (B - B - B \ldots\ldots\ldots B)_n - A}$$

Figure 3. Configuration for calculating $P_B(n)$.

the equilibrium free energy in powers of the deformation. For small compressive deformations, we expect the response to be simply Hookean. We shall examine the corresponding elastic constant's dependence upon block sequence distribution.

III. Method of Calculation

As we have noted, the first step in our calculation involves obtaining the equilibrium free energy by balancing the elastic free energy of the polydisperse brushes that compromise the A- and B-rich regions with the interfacial energy. The brush free energies depend upon the specific distribution of loop lengths in the A- and B-rich regions. Thus, it is appropriate to first obtain the "molecular weight distributions" that characterize our brushes.

The polydispersity of the A brush is obtained by calculating the probability associated with finding a "run" of A segments at an arbitrary location on the chain. This is easily obtained by calculating the probability associated with the existence of the sequence shown in Figure 2 at an arbitrary location on the chain. The probability of finding a sequence of l consecutive A blocks, $P_A(l)$, is

$$P_A(l) = (1-f)p_{AB}(p_{AA})^{l-1}p_{BA} \tag{3}$$

Using conservation of probabilities, eq 3 can be rewritten purely in terms of f and λ as follows:

$$P_A(l) = \alpha_A \eta_A^{\,l-1} \tag{4}$$

where

$$\begin{aligned} \alpha_A &= (1-f)^2(1-\lambda)^2 f \\ \eta_A &= f(1-\lambda) + \lambda \end{aligned} \tag{5}$$

Note that since each segment of A is comprised of N monomers, eqs 4 and 5 define the probability of finding a sequence of lN monomers of A at an arbitrary location on the chain.

The polydispersity of the B brush is specified by calculating the probability associated with finding a sequence of n consecutive B blocks at an arbitrary location on the chain. This corresponds to the probability of finding the configuration shown in Figure 3 and is easily obtained to be

$$P_B(n) = f(1-p_{AA})(p_{BB})^{n-1}(1-p_{BB}) \tag{6}$$

In terms of f and λ eq 6 reads

$$P_B(n) = \alpha_B \eta_B^{\,n-1} \tag{7}$$

where

$$\begin{aligned} \alpha_B &= f^2(1-f)(1-\lambda)^2 \\ \eta_B &= f(\lambda-1) + 1 \end{aligned} \tag{8}$$

Although we shall carry out calculations with the exact discrete distributions of loop lengths represented by eqs 4 and 7, certain physical issues are easier to illustrate by using expressions that result from a continuum approximation to these distributions. The continuum versions of eqs 4 and 7 read as follows:

$$\begin{aligned} P_A(l) &= \mu_A \exp[-\zeta_A l] \\ \mu_A &= \frac{(1-f)^2(1-\lambda)^2 f}{f(1-\lambda)+\lambda} \\ \zeta_A &= |\ln \eta_A| \end{aligned} \tag{9}$$

$$\begin{aligned} P_B(n) &= \mu_B \exp[-\zeta_B n] \\ \mu_B &= \frac{f^2(1-f)(1-\lambda)^2}{f(\lambda-1)+1} \\ \zeta_B &= |\ln \eta_B| \end{aligned} \tag{10}$$

Note that if the continuum distribution is employed, the average loop lengths of A and B blocks (in units of number of monomers) is N/ζ_A and N/ζ_B, respectively. This result will prove useful later to illustrate certain physical issues.

Having defined the polydispersity of our brushes, we now proceed to calculate the elastic free energies of the A and B brushes. We carry out this calculation following the prescription of Milner et al.,[24] who developed explicit expressions for the free energy of a polydisperse brush. To use the results derived by these authors, we need to calculate the number of chains per unit area with degree of polymerization greater than m. This quantity is easily calculated for both the A and B regions of the grain by using eqs 4 and 7 (analogously, eqs 9 and 10 for the continuum distribution). Following Milner et al.,[24] we denote these quantities by $\bar{\sigma}$. $\bar{\sigma}_A(m)$ and $\bar{\sigma}_B(m)$ are given by the following expressions when the discrete distribution is employed.

$$\begin{aligned} \bar{\sigma}_A(m) &= \frac{1}{\Sigma}\eta_A^{2m} \\ \bar{\sigma}_B(m) &= \frac{1}{\Sigma}\eta_B^{2m} \end{aligned} \tag{11}$$

In eq 11, m refers to the number of segments of A or B; the actual length measured in number of monomer units is mN, and we note that $2mN$ monomers are involved in each loop. Furthermore, Σ denotes the area per chain (half-loop) at the interface. If the continuum distribution is employed, the analog of eq 11 is

$$\begin{aligned} \bar{\sigma}_A(m) &= \frac{1}{\Sigma}\exp[-2\zeta_A m] \\ \bar{\sigma}_B(m) &= \frac{1}{\Sigma}\exp[-2\zeta_B m] \end{aligned} \tag{12}$$

We now use formulas provided by Milner et al.[24] to calculate the free energies of the A and B brushes. Performing this calculation obtains the following expressions for the brush free energies per chain:

$$\begin{aligned} f_A &= \frac{\pi^2}{24}\frac{1}{\Sigma^2}N\frac{\eta_A^6}{1-\eta_A^6}\frac{\upsilon_A^2}{b_A^2}k_BT \\ f_B &= \frac{\pi^2}{24}\frac{1}{\Sigma^2}N\frac{\eta_B^6}{1-\eta_B^6}\frac{\upsilon_B^2}{b_B^2}k_BT \end{aligned} \tag{13}$$

where υ_i are the monomer volumes, b_i are the statistical segment lengths, and k_BT is the thermal energy.

The free energy per chain for the bilayer is then given by adding the brush free energies to the interfacial energy. This obtains

$$f = \gamma\Sigma + \frac{\pi^2}{24}\frac{Nk_BT}{\Sigma^2}\left[\frac{\upsilon_A^2}{b_A^2}\frac{\eta_A^6}{1-\eta_A^6} + \frac{\upsilon_B^2}{b_B^2}\frac{\eta_B^6}{1-\eta_B^6}\right] \tag{14}$$

where γ is the interfacial tension. To calculate the equilibrium free energy and the bilayer spacing, we minimize eq 14 with respect to Σ. We also enforce incompressibility since we are interested in molten random block copolymers. This procedure yields the following expressions for the bilayer spacing (D_0) and the equilibrium free energy per unit volume ($\bar{f}_0$):

$$D_0 = N^{2/3}\left[\frac{6\upsilon_A\eta_A^6}{1-\eta_A^6} + \frac{6\upsilon_B\eta_B^6}{1-\eta_B^6}\right]\left[\frac{72\gamma}{\pi^2k_BT}\right]\times \left[\frac{6\upsilon_A^2\eta_A^6}{b_A^2(1-\eta_A^6)} + \frac{6\upsilon_B^2\eta_B^6}{b_B^2(1-\eta_B^6)}\right]^{-1/3} \tag{15}$$

$$\bar{f}_0 = \frac{\gamma}{D_0} + \frac{\pi^2}{24}\frac{D_0^2k_BT}{N^2}\left[\frac{\upsilon_A^2}{b_A^2}\frac{\eta_A^6}{1-\eta_A^6} + \frac{\upsilon_B^2}{b_B^2}\frac{\eta_B^6}{1-\eta_B^6}\right]\times \left[\frac{6\upsilon_A\eta_A^6}{1-\eta_A^6} + \frac{6\upsilon_B\eta_B^6}{1-\eta_B^6}\right]^{-3} = \frac{3\gamma}{2D_0} \tag{16}$$

Equations 15 and 16 are obtained by using the exact discrete distribution for the loop lengths. If the continuum analog is employed, one obtains the following equations that correspond to eqs 15 and 16:

$$D_0 = N^{2/3}\left[\frac{\upsilon_A}{\zeta_A} + \frac{\upsilon_B}{\zeta_B}\right]\left[\frac{72\gamma}{\pi^2k_BT}\right]^{1/3}\left[\frac{\upsilon_A^2}{\zeta_Ab_A^2} + \frac{\upsilon_B^2}{\zeta_Bb_B^2}\right]^{-1/3} \tag{17}$$

$$\bar{f}_0 = \frac{\gamma}{D_0} + \frac{\pi^2}{144}\frac{D_0^2k_BT}{N^2}\left[\frac{\upsilon_A^2}{\zeta_Ab_A^2} + \frac{\upsilon_B^2}{\zeta_Bb_B^2}\right]\left[\frac{\upsilon_A}{\zeta_A} + \frac{\upsilon_B}{\zeta_B}\right]^{-3} = \frac{3\gamma}{2D_0} \tag{18}$$

For illustrative purposes, consider eq 17 for the case wherein $\upsilon_A = \upsilon_B = b_A = b_B = 1$. Then, this equation reduces to

$$D_0 = [\langle N_A\rangle + \langle N_B\rangle]^{2/3}\left[\frac{72\gamma}{\pi^2k_BT}\right]^{1/3} \tag{19}$$

where $\langle N_A\rangle$ and $\langle N_B\rangle$ are the number-average lengths of contiguous A and B segments, respectively. This result shows that the bilayer spacing scales with the 2/3 power of the sum of the average chain lengths of the A and B blocks. We note this point for two reasons. First, this result is analogous to the scaling obtained by Helfand[21] for diblock copolymers ($D_0 \sim N^{2/3}$) many years ago. Furthermore, as we shall see in section IV, this point foreshadows the physical interpretation of our numerical results.

We now proceed with the calculation of the elastic constant by expressing the free energy of the deformed grain as an expansion in powers of the deformation, ΔD. For compressive strains that are not too large, we expect the response to be simply Hookean. We obtain the elastic constant that describes this Hookean response from the coefficient of the quadratic term in the free energy expansion. The free energy density of the deformed grain then reads

$$\bar{f}(D_0 + \Delta D) = \bar{f}_0 + \left(\frac{\partial\bar{f}}{\partial D}\right)_{D=D_0} D_0\left(\frac{\Delta D}{D_0}\right) + \frac{1}{2}\left(\frac{\partial^2\bar{f}}{\partial D^2}\right)_{D=D_0} D_0^2\left(\frac{\Delta D}{D_0}\right)^2 + \ldots \tag{20}$$

The second term in the expansion vanishes, and the coefficient of the quadratic term yields the elastic constant. Using eq 16 we obtain the following result for the elastic constant, K:

$$K = \frac{3\gamma^{2/3}}{N^{2/3}}\left[\frac{6\upsilon_A\eta_A^6}{1-\eta_A^6} + \frac{6\upsilon_B\eta_B^6}{1-\eta_B^6}\right]^{-1}\left[\frac{72}{\pi^2k_BT}\right]^{-1/3}\times \left[\frac{6\upsilon_A^2\eta_A^6}{b_A^2(1-\eta_A^6)} + \frac{6\upsilon_B^2\eta_B^6}{b_B^2(1-\eta_B^6)}\right]^{1/3} \tag{21}$$

where we define

$$K = \left(\frac{\partial^2\bar{f}}{\partial D^2}\right)_{D=D_0} D_0^2$$

Use of the continuum distribution leads to the corresponding result

$$K = \frac{3\gamma^{2/3}}{N^{2/3}}\left[\frac{\upsilon_A}{\zeta_A} + \frac{\upsilon_B}{\zeta_B}\right]^{-1}\left[\frac{72}{\pi^2k_BT}\right]^{-1/3}\left[\frac{\upsilon_A^2}{b_A^2\zeta_A} + \frac{\upsilon_B^2}{b_B^2\zeta_B}\right]^{1/3} \tag{22}$$

Examination of eq 21 or 22 shows that there are three parameters that arise naturally. The first is the relative magnitude of the ratio υ_i^2/b_i^2 for the A and B segments. The second is the ratio of monomer volumes, υ_A/υ_B. These two parameters do *not* depend upon the sequence distribution that characterizes the random block copolymer chains. However, they do influence the manner in which the chains pack. The third parameter is the sum of the average block lengths on the A and B segments. Of course, this quantity is directly determined by the chain architecture. In the following section, we present results that show the variation of the elastic constant as a function of these parameters. The physical origin of the results is also discussed.

IV. Results and Discussion

We present results for a reduced elastic constant that is defined in a manner such that only the dependence upon the sequence distribution, the ratio of the monomer sizes, and the ratio of the statistical segment lengths is manifested in the computed results. Specifically, we define the reduced elastic constant, $\bar{K}$, as follows:

$$\bar{K} = K\left[\frac{8N^2\upsilon_Bb_B^2}{3\pi^2k_BT\gamma^2}\right]^{1/3} \tag{23}$$

where υ_B is the monomer volume and b_B is the statistical segment length of the segments of type B. The monomer volume and statistical segment length of the segments of type A will be multiples of υ_B and b_B. We present results for the following four cases: *case 1*, $\upsilon_A/\upsilon_B = b_A/b_B = 1$; *case 2*, $\upsilon_A/\upsilon_B = 1$, $b_A/b_B = 5$; *case 3*, $\upsilon_A/\upsilon_B = 5$, $b_A/b_B = 1$; *case 4*, $\upsilon_A/\upsilon_B = 0.2$, $b_A/b_B = 5$.

We will examine the variation of $\bar{K}$ with f, λ, and the ratio of monomer volumes and statistical segment lengths.

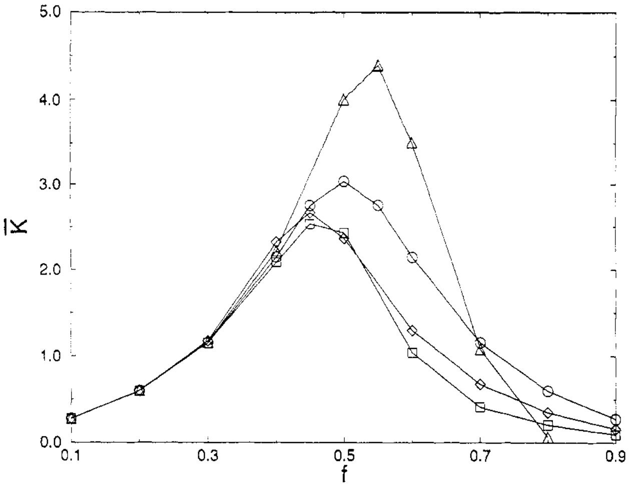

Figure 4. $\bar{K}$ as a function of f for $\lambda = 0$. The symbols denote computed values. The lines are just drawn through these symbols and do not represent any fitted function. Circles correspond to case 1; squares correspond to case 2; diamonds correspond to case 3; triangles correspond to case 4.

We will compute values of the reduced elastic constant over a wide range of values of f and λ. Note, however, that lamellar morphologies may not be formed for all values of these parameters. Consider first the dependence of the elastic constant on f at a fixed value of λ. For illustration purposes, we choose $\lambda = 0$; this corresponds to an ideal random block copolymer. Figure 4 shows our results (obtained using eq 21) for the four cases noted above. The most interesting feature of these results is that the elastic constant exhibits an extremum for all the cases that we have studied. In order to clarify the physical origin of this extremum, consider case 1 wherein the extremum occurs at $f = 0.5$. In this case the ratios of the monomer volumes and statistical segment lengths are fixed at unity and $\lambda = 0$; so $\bar{K}$ depends only on the sequence distribution parameter, f. As we have noted earlier, the elastic constant depends upon the sum of the average lengths of the A and B blocks. This is so because the bilayer spacing depends upon this quantity. For the random block copolymer architectures that we consider, this quantity exhibits an extremum at $f = 0.5$. Since the elastic constant scales with the sum of the average lengths of the A and B blocks, it too exhibits an extremum at $f = 0.5$ for case 1. This result is a direct consequence of the random block architecture of the copolymers. Although we show results only for $\lambda = 0$, it should be clear that an extremum exists for all values of λ except the perfectly alternating case ($\lambda = -1$). Note also that the elastic constant for monodisperse diblock copolymers is independent of f.

The value of f at which the extremum occurs and the magnitude of $\bar{K}$ depend upon the choice of the parameters that reflect the relative monomer sizes and statistical segment lengths of the two blocks. This is so because these quantities influence the way in which the chains pack in the two regions of the grain. This is illustrated in Figure 4. Consider case 2; in this case, the statistical segment length of the A block is 5 times that for the B block while the monomer volumes are the same. We find that for this situation the extremum occurs at $f = 0.45$. The effect of b_A being 5 times larger than b_B on the magnitude of $\bar{K}$ becomes more pronounced at higher values of the fraction of A blocks. Specifically, we see that the elastic constant acquires smaller values compared to case 1. The physical reason for this is that the stiffer A blocks pack with less entropy penalty, leading to a lower elastic constant. Due to the same physical reason, we observe a similar effect for case 3 wherein the monomer size of the A block is larger. For both cases 2 and 3, choosing ratios of monomer sizes and statistical segment lengths different from unity shifts the position of the extremum to lower values of f compared to case 1. However, this is not always true. The location of the extremum can also be shifted to values of f greater than 0.5 by appropriate choice of parameters. This is illustrated by case 4 in Figure 4; here the extremum is located at roughly $f = 0.55$.

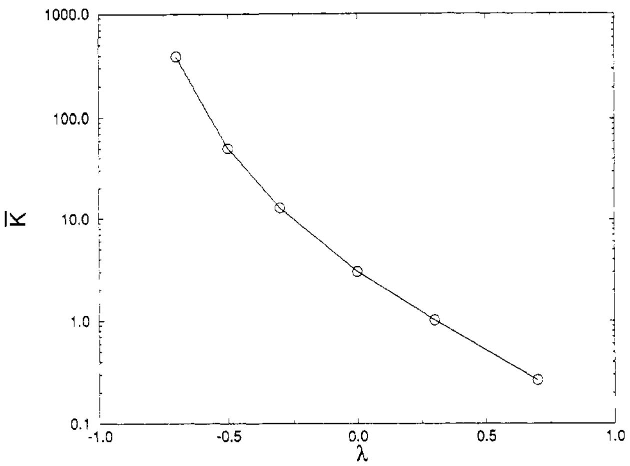

Figure 5. $\bar{K}$ as a function of λ for $f = 0.5$.

It is interesting to see how the elastic constant depends upon the degree of blockiness (as measured by λ) of the random copolymer chains. Figure 5 shows the variation of $\bar{K}$ with λ at a fixed value of the fraction of A blocks ($f = 0.5$). Recall that smaller values of λ correspond to chains that are less blocky. Our results for $\bar{K}$ show a remarkable sensitivity to the degree of blockiness. For λ varying between -0.7 and $+0.7$, the value of the reduced elastic constant changes by 3 orders of magnitude. The less blocky architectures yield higher values for the elastic constant. This behavior can be understood physically by imagining what would happen in the limit of perfectly alternating multiblock copolymers ($\lambda = -1$). In this case, there would be no distribution of loop lengths in the A or B regions since the loop lengths would be exactly the length of each prepolymer. This would lead to small bilayer spacings, and the chains would pack densely in space. The elastic constant of such a grain would be larger than that corresponding to cases wherein there is a distribution of loop lengths (more blocky chains). This is so because the bilayer spacing is larger and the chains pack more sparsely in space when there is a distribution of loop lengths. Thus, our prediction that the elastic constant decreases with λ is physically reasonable. The magnitude of the variation with degree of blockiness is somewhat surprising, however.

V. Concluding Remarks

In this paper we have considered the elastic response to compressive strains of lamellar grains of random block copolymers in the SSL. We have been especially concerned with the dependence of the elastic constant on the chain architecture and other parameters (such as monomer size and statistical segment length) that influence chain packing. Three features of our results are noteworthy. The first pertains to the variation of the elastic constant with the fraction of A blocks for a fixed degree of blockiness. For this situation we find that the elastic constant exhibits a maximum. The extremum occurs because the elastic constant scales with the sum of the average lengths of contiguous A and B blocks. This quantity has an extremum at $f = 0.5$, and so the elastic constant also exhibits an extremum. The location of the extremum, however, can be shifted (from $f = 0.5$) if the A and B blocks have unequal monomer sizes and statistical segment lengths. A second interesting feature of our results relates to how altering the ratio of monomer sizes and statistical segment lengths can change the way that the chains pack, thereby affecting the value of the elastic constant. Our calculations show that situations wherein the chains pack relatively sparsely correspond to low values of the elastic constant. The third interesting feature that we observe is also a consequence of differences in the way that random block copolymers with different sequence distributions pack in the SSL. We find the value of the elastic constant to be strongly dependent on the degree of blockiness of the chain. Chains with a more blocky architecture (larger values of λ) have a greater distribution of loop lengths and thus pack more sparsely in space. This leads to lower elastic constants compared to cases when the architecture is closer to an alternating block copolymer.

The results of our simple calculations indicate that the mechanical properties relevant for the processing of microstructured random block copolymers can be tailored by appropriate choice of the sequence distribution. Note that the sequence distribution is determined by the matrix $\mathbf{p}$, which, in turn, can be manipulated by choosing appropriate chemistry. Given this implication of our predictions and the fact that our results can be directly tested against experiments, we urge experimentalists to measure the elastic response of random block copolymers using dynamical mechanical spectroscopy. We believe that the difficulties associated with carrying out such experiments are primarily related to synthesizing copolymers with known values of f and λ and with aligning the grains.[26] We note, however, that the first difficulty may be somewhat alleviated by the fact that the elastic constant varies substantially with the parameters that define the chain sequence distribution. Since these effects are not small, even with some uncertainty in the parameters that determine the sequence distribution, the trends that we predict should be observable.

We close by noting that we have considered merely one aspect of the mechanical behavior of microphase-segregated random block copolymers. The interesting cases of tensile deformations and behavior in the WSL have not been examined. We hope to return to these issues in a forthcoming sequel.

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