The Bending Modulus of Triblock Copolymer Lamellae: Stress Relaxation via the Bridge-to-Loop Process

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ABSTRACT: We calculate the bending modulus K of microphase-separated di- and triblock copolymer lamellae in the strong segregation limit. We restrict our attention to triblock architectures of the form A–B–A where the two A-blocks have equal size and chemistry. Inside a triblock lamella some of the chains form "bridges" between two A-regions and some form "loops" into the same A-region. The bending modulus K is found to depend on the chain architecture, as well as the bridging fraction, while the compressional modulus does not. We present results for K as a function of f, the total length fraction of A-block. For $f = {}^1/_2$ bridging triblocks are found to have a bending modulus ${}^{13}/_4$ times larger than either (i) those forming loops or (ii) diblocks of half the length. If initially half the triblocks bridge and half loop (at the level of the simplest treatment they have the same energies in a flat layer), the initial ratio of the modulus of a triblock layer to a diblock one is ${}^{17}/_8$. However, after deformation, the modulus (and stress) drops as equilibration of bridges to loops occurs. Since the stress is a function of the bridging fraction, we argue that it may provide a probe of the dynamics of the bridge-to-loop process.

1. Introduction

Under appropriate conditions di- and triblock copolymers are known to self-assemble spontaneously in the melt to form regular liquid crystalline microphases.[1–3] This self-assembly is driven by the immiscibility of the two chemical components of the polymer, denoted A and B. There is a balance between the entropic cost of segregating the components (stretching chains) and the enthalpic cost of mixing them. The A-component (say) may be segregated into close-packed arrays of flat sheets, cylinders, or spheres surrounded by B-rich regions; these are the lamellar, cylindrical, and cubic microphases, respectively. In addition, more exotic bicontinuous phases[4,5] are also known to exist, albeit usually in a relatively small region of the phase diagram. We will consider in what follows only the strong segregation limit[1] (SSL) corresponding to temperatures low enough that the A and B components are strongly segregated (but not so low that they form a glass). In the SSL the phase behavior[6] is sensitive only to f, the total length fraction of A in the copolymer. We study here the lamellar microphase, found for systems which are not too asymmetric $|f - 0.5| \lesssim 0.22$.

We consider two monodisperse copolymer melts: (i) an A–B diblock in which each chain of length N consists of an A-block of N_A monomers joined to a B-block of N_B monomers; (ii) an A–B–A triblock in which one A-block of N_A monomers is joined to each end of a B-block of $2N_B$ monomers, giving a total chain length of $2N$. We choose the architecture of (ii) for convenience; the equality of the two A-blocks means the A-regions contain monodisperse blocks and the treatment is considerably simplified.

In a microphase-separated lamellar layer, a triblock copolymer can adopt one of two conformations. Either it can "bridge" the two exterior A-regions or it can form a "loop" where both its A-blocks lie in the same region; see Figure 1. For a flat (unperturbed) lamella, these two conformations have the same free energy at the level of our treatment and might therefore be expected to be equally distributed (but see discussion in section 5). In section 4 we consider triblock lamellae consisting of only bridges. The linearity of the problem makes the extension to arbitrary bridging fractions trivial.

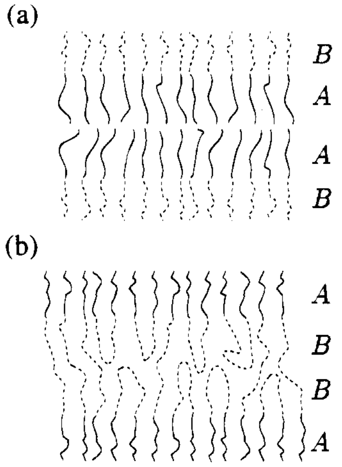

Figure 1. Schematic diagram showing a piece of (a) diblock copolymer bilayer and (b) triblock layer. The A- and B-blocks are shown by solid and dashed lines, respectively. Some of the triblock chains are shown as loops and some as bridges.

We model the chain stretching energy using the Alexander–de Gennes theory of polymer brushes.[7,8] This involves making the simplifying assumption that all chain ends are located *at* the brush exterior. This approximation is a rather good one in the sense that the energies differ from the more sophisticated self-consistent mean field (SCMF) results[6,9] by 20% or less.[10]

There has been much recent interest in the dynamics of microphase-separated copolymers.[11–13] While some theoretical predictions exist,[11,12] the experiments[13] are far from conclusive. One experimental difficulty is synthesizing samples for which the theoretically convenient $N \rightarrow \infty$ limit applies. In the SSL two different dynamic processes have been proposed. The first[11] involves waiting for the A-block (say) of a chain to pass through a neighboring B-block. This moves the center of mass of the chain by one microphase repeat spacing $\sim N^{2/3}$. The large associated energetic barrier is related to the free energy cost of the transient mixed state,

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scaling $\sim N^{2/3}$. Hence for this process $\tau_{\text{step}} \sim \exp[\text{const} \times N^{2/3}]$. The second alternative[12] is a "retraction" motion of the chain end. This motion is very similar to that thought to dominate the dynamics of star polymers[14] and may also be important in the dynamics of adsorbed layers.[15] It involves the chain end retracting inside its tube to within an entanglement length of the A−B interface, unlooping itself from this last entanglement, and finally re-extending into a new tube. This process involves a step size of the order of the tube diameter and is believed to be much slower:[14] $\tau_{\text{step}} \sim \exp[\text{const} \times N]$. Thus for long enough chains the first process should dominate. As we shall see, the present work may help to provide a way of probing this process.

The paper is organized as follows: Section 2 details the method used to calculate the free energy of a curved diblock lamellar monolayer. The elastic and interfacial contributions are detailed in sections 2.1 and 2.2, respectively, and the overall free energy per unit volume $\mathcal{F}^{\text{mon}}$ is presented in section 2.3. In section 3 we construct a diblock bilayer from two monolayers and calculate its moduli by expanding for small curvatures. We argue that these are identical to a triblock layer in which all chains form loops. In section 4 we construct a layer of purely bridging triblock chains. This has one less degree of freedom than the diblock bilayer, where the number of chains in each monolayer can vary independently, resulting in an enhanced bending modulus. Finally, in section 5 we extend our argument to arbitrary bridging fraction and discuss the implications for statics and dynamics.

2. A Diblock Lamellar Monolayer

We first seek to calculate the free energy/curvature relationship for a single A−B diblock monolayer. To this end we consider a strongly segregated layer in three different geometries, described by the variable $d = 1, 2, 3$. For $d = 1$ the layer is flat, $d = 2$ corresponds to a cylindrical shell, and $d = 3$ corresponds to a spherical shell. In sections 3 and 4 we will expand perturbatively for small curvatures, i.e., large radii of curvature. The overall free energy per unit volume $\mathcal{F}_d^{\text{mon}}$ involves the following two terms: (i) F_{el}, the elastic energy of the chains in one unit cell, treated as if its ends were held at the layer surfaces; (ii) F_{AB}, the surface energy of the A−B interface in one unit cell.

The microphase separation itself is driven by the bulk mixing energy which is saved by the nearly complete segregation of the immiscible components. Since this term is a constant, we omit it from our definition of the free energy. In what follows we adopt a system of units in which the monomer size $b = 1$ and $k_BT = 1$. We use the formalism of ref 6 even though we choose to employ the Alexander−de Gennes approximation. We also restrict our attention to the SSL in which the chains are all extended over a distance which is large compared to their unperturbed radii of gyration. Throughout we neglect corrections due to fluctuations.

2.1. Elastic Energy of the Segregated Layer.

In this section we calculate F_{el}, the elastic free energy density of the polymer brushlike chains in the three different geometries mentioned above. In order to do this, we need to calculate the free energy of a molten, highly stretched polymer brush. For $d = 1$ the brush is treated as if it were grafted to two flat surfaces, separated by $R_b - R_a$, and the unit cell is a unit area of this brush. For $d = 2$ the brush is modeled as if it were attached to two concentric cylindrical surfaces, of radii R_a and R_b, with the unit cell being one unit length of this cylindrical shell. For $d = 3$ it is treated as if it were attached to two concentric spherical surfaces, of radii R_a and R_b. Here the unit cell is a single spherical shell. In the present work we will not need to employ the case $d = 3$ but it is nonetheless natural to include it.

In each of these cases the block which resides closest to the interior surface of the unit cell is denoted A, without loss of generality. Thus the interior block has length $N_A = fN$ and the exterior $N_B = (1 - f)N$.

If the nth segment of a chain is found at position $\mathbf{r}$, the chain stretching field $\mathbf{E} = \mathrm{d}\mathbf{r}/\mathrm{d}n$ describes the local extension of a given chain. In calculating the elastic free energy of a chain, we use the ideal result that when a piece of chain with ΔN monomers is extended over a distance Δr the elastic free energy is[16] $\Delta F = (k\Delta N/2)(\Delta r/\Delta N)^2$ where $k = {}^3\!/_2$ for a Gaussian chain in 3-D. Hence the elastic free energy of the chains in one unit cell is just the sum of the contributions from all monomers on all chains

$$F_{\text{el}} = \frac{k}{2} Q \int_{R_a}^{R_b} \mathrm{d}r\, E(r) \tag{1}$$

where Q is the number of chains per unit cell and r is the radial coordinate, varying between the radii of the inner and outer surfaces of the monolayer. There are two further constraints: (i) the melt is incompressible and (ii) each chain must expend exactly N monomers in traveling from $r = R_a$ to $r = R_b$. These two constraints are

$$\frac{Q}{E(r)} = d\nu_d r^{d-1} \tag{2a}$$

and

$$\int_{R_a}^{R_b} \frac{\mathrm{d}r}{E(r)} = N \tag{2b}$$

respectively where ν_d is given by[17]

$$\nu_d = \begin{cases} 1 & \text{for } d = 1 \\ \pi & \text{for } d = 2 \\ 4\pi/3 & \text{for } d = 3 \end{cases} \tag{3}$$

Combining these constraints, we find

$$E(r) = \frac{Q}{d\nu_d} r^{1-d} \tag{4}$$

and

$$\nu_d(R_b^{\,d} - R_a^{\,d}) = QN \tag{5}$$

Equation 5 equates the total unit cell volume to the product of the number of the chains per cell and the volume per chain. Substituting these results into (1), we find the free energy per unit cell

$$F_{\text{el}} = \frac{kQ^2}{2d\nu_d} m_d(R_b, R_a) \tag{6}$$

where

$$m_d(R_b, R_a) = \begin{cases} R_b - R_a & \text{for } d = 1 \\ \log(R_b/R_a) & \text{for } d = 2 \\ 1/R_a - 1/R_b & \text{for } d = 3 \end{cases} \tag{7}$$

2.2. A–B Interfacial Energy. There is also a contribution to the free energy due to mixing of A and B near the A–B interface, which is located at $r = R_{AB}$. The interfacial region is predicted[6] to be a narrow shell with an associated dimensionless surface tension $\gamma_{AB} = \chi^{1/2}$, where χ is the usual Flory parameter describing the interaction energy between the A and B components. The contribution to the free energy of one unit cell due to the A–B interfacial energy is therefore

$$F_{AB} = d\nu_d \gamma_{AB} R_{AB}{}^{d-1} \tag{8}$$

where R_{AB} can be expressed in terms of R_a and R_b according to $\nu_d(R_{AB}{}^d - R_a{}^d) = QfN$ by using a chain contour/vooume fraction argument analogous to (2b) and (5). Using (5) we find

$$R_{AB} = (fR_b{}^d + (1-f)R_a{}^d)^{1/d} \tag{9}$$

Additional corrections to the surface tension, for example due to fluctuations or to the loss of entropy with confinement of the A–B junction points at the interface,[6] enter only as higher order corrections in the long chain limit and so we omit them here.

2.3. Total Free Energy. The total free energy per unit volume $\mathscr{F}_d^{mon}$ follows by summing F_{el} and F_{AB} and dividing by the volume of the monolayer $\nu_d(R_b{}^d - R_a{}^d)$

$$\mathscr{F}_d^{mon} = \frac{F_{el} + F_{AB}}{\nu_d(R_b{}^d - R_a{}^d)} \tag{10}$$

Minimization of the energy density of a flat monolayer $\mathscr{F}_1^{mon}$ with respect to the layer thickness $\Delta R = R_b - R_a$ gives the equilibrium thickness h

$$h = (\gamma_{AB} N^2/k)^{1/3} \tag{11}$$

and energy density μ

$$\mu = \frac{3}{2}\left(\frac{k\gamma_{AB}{}^2}{N^2}\right)^{1/3} \tag{12}$$

of an equilibrium flat monolayer. Rescaling with respect to this length according to $z_a = R_a/h$ and $z_b = R_b/h$, we have

$$\mathscr{F}_d^{mon}[z_b,z_a,f] = \mu\left(\frac{1}{3d}(z_b{}^d - z_a{}^d)m_d(z_b,z_a) + \frac{2d[fz_b{}^d + (1-f)z_a{}^d]^{(d-1)/d}}{3(z_b{}^d - z_a{}^d)}\right) \tag{13}$$

3. The Diblock Lamellar Phase

The free energy density of a diblock lamellar phase is equal to the free energy density of an ABBA (or BAAB) bilayer $\mathscr{F}_d^{bi}$. This is constructed from two monolayers by weighting them by their respective volume fractions. The dimensionless radii of the inner and outer surfaces of the bilayer are z_i and z_o respectively, with the junction between the two monolayers being found at z. Using (13), $\mathscr{F}_d^{bi}$ is given by

$$\mathscr{F}_d^{bi} = ((z_o{}^d - z^d)\mathscr{F}_d^{mon}[z_o,z,f] + (z^d - z_i{}^d)\mathscr{F}_d^{mon}[z,z_i,1-f])/(z_o{}^d - z_i{}^d) \tag{14}$$

Since we are interested in small deformations from the flat state, we now choose to expand the inner and outer bilayer radii perturbatively in powers of the curvature $c \equiv 1/z$ with a view to extracting the bending modulus.

$$z_i = z - 1 - [\eta_i^{(1)}c = \eta_i^{(2)}c^2 + O(c^3)] \tag{15a}$$

$$z_0 = z + 1 + [\eta_o^{(1)}c + \eta_o^{(2)}c^2 + O(c^3)] \tag{15b}$$

where we recall that c is a dimensionless curvature, in units of $1/h$.

We can calculate the bending modulus from the $d = 2$ unit cell. Expanding $\mathscr{F}_2^{bi}$ in powers of c and minimizing with respect to $\{\eta_i^{(1)},\eta_o^{(1)}\}$ and then $\{\eta_i^{(2)},\eta_o^{(2)}\}$ using *Mathematica*, we find

$$\eta_i^{(1)} = -\eta_o^{(1)} = (2f-1)/6 \tag{16a}$$

$$\eta_i^{(2)} = \eta_o^{(2)} = (3+f)(f-1)/18 \tag{16b}$$

where the relationships $\eta_i^{(1)} = -\eta_o^{(1)}$ and $\eta_i^{(2)} = \eta_o^{(2)}$ are required on symmetry grounds: The change in bilayer thickness must be even in c and the ratio of the change in the two monolayer thicknesses must be odd in c.

The expansion of the free energy density is

$$\mathscr{F}_2^{bi} = \mu\left(1 + \frac{4f(1-f)}{9}c^2 + O(c^4)\right) \tag{17}$$

from which we may extract a dimensionless bending modulus. Taking care to re-insert two powers of h (the curvature is in units of $1/h$), we have

$$K_{bi} = \frac{8\mu h^2 f(1-f)}{9} \tag{18}$$

where h (eq 11) and μ (eq 12) are known (given $\gamma_{AB} = \chi^{1/2}$ and $k = {}^3/_2$) and we recall that our units of energy and length are k_BT and the monomer size b, respectively. We will find that the bending modulus of a triblock lamella comprised entirely of loops has the same scaling as (18).

The compressional modulus can be extracted from $\mathscr{F}_1^{mon}$ (eq 13) by writing $z_a = z$ and $z_b = z + 1 + \epsilon$ with $\epsilon \ll 1$, and expanding $\mathscr{F}_1^{mon}$ in powers of ϵ

$$\mathscr{F}_1^{mon} = \mu(1 + \epsilon^2 + O(\epsilon^4)) \tag{19}$$

from which we extract a dimensionless compressional modulus

$$B = 2\mu \tag{20}$$

We will find that the compressional modulus of a triblock layer has the same scaling as (20), independent of the fraction of loops to bridges.

4. Triblock Lamellar Phases: The Hypothetical Case Where All Chains Form Bridges

In this section we will restrict our attention to triblock layers made up entirely of bridging chains. In section 5 we will extend this to layers with arbitrary bridging fractions. The free energy density $\mathscr{F}_d^{bridge}$ is constructed from two *hypothetical* monolayers, as before, except that in this case we require them to have equal volumes: The bridging chains are continuous and are symmetric about their Nth monomer. In this section we calculate perturbatively the response of such a triblock lamella to a small deformation. The radii of the inner and outer surfaces of the triblock layer, in units of h (eq 11), are z_i and z_o, respectively, with the junction between the two hypothetical monolayers located at z. Hence the "equal volume" constraint analogous to (5) is

$$z_o^d - z^d = z^d - z_i^d \tag{21}$$

Using (13) $\mathcal{F}_d^{\mathrm{bridge}}$ is given by

$$\mathcal{F}_d^{\mathrm{bridge}} = \frac{1}{2}(\mathcal{F}_d^{\mathrm{mon}}[z_o,z,f] + \mathcal{F}_d^{\mathrm{mon}}[z,z_i,1-f]) \tag{22}$$

With a view of extracting the bending modulus, we expand the inner and outer bilayer radii perturbatively in powers of the curvature $c \equiv 1/y$ according to (15), as before. We consider the $d = 2$ unit cell and expand $\mathcal{F}_2^{\mathrm{bridge}}$ in powers of c. At the corresponding stage in section 3, we proceeded by minimizing with respect to $\{\eta_i,\eta_o\}$ at each order but now we may only minimize with respect to one of these η_i (say), the other being fixed by the equal volume constraint (21). We find

$$\eta_i^{(1)} = -\eta_o^{(1)} = 1/2 \tag{23a}$$

$$\eta_i^{(2)} = \eta_o^{(2)} = -1/8 \tag{23b}$$

The expansion of the free energy density is

$$\mathcal{F}_2^{\mathrm{bridge}} = \mu\left(1 + \frac{4 - 3f^2}{9}c^2 + O(c^4)\right) \tag{24}$$

from which we extract a dimensionless bending modulus.

$$K_{\mathrm{bridge}} = \frac{2\mu h^2(4 - 3f^2)}{9} \tag{25}$$

This result seems to imply that the bending modulus is finite in the limits $f \to 0, 1$. In fact our model assumes an interfacial tension γ_{AB} which is independent of the number of monomers in the short block, i.e., f. This approximation fails when the block becomes very short,[6] $N_i \lesssim \chi^{-1/2}$. Formally therefore K_{bridge} actually vanishes in the limits $f \to 0, 1$ but we need not worry about this as (i) the equilibrium phase is no longer lamellar for such values of f and (ii) in the SSL the crossover regime has vanishingly small $O(1/N)$ extent along the f axis.

The compressional modulus of a triblock lamella can be extracted from the flat $d = 1$ unit cell in a similar way to (19). It has the same scaling as (20) and is independent of the bridging fraction, i.e., is the same for loops and bridges. This is natural: If the triblock chains are cut exactly in half, the compressional modulus is unaffected.

The bending modulus for triblock layers comprised entirely of loops scales identically to K_{bi} (eq 18) at the level of our treatment. This also is unsurprising since a triblock loop (but *not* a bridge) can be cut exactly in half without affecting the bending modulus.

5. Triblock Lamellar Phases: The Extension to General Bridging Fractions

Inside a triblock layer some chains may form loops and some may form bridges. We define the bridging fraction p to be the fraction of chains forming bridges. Superposition gives the bending modulus of a triblock monolayer with arbitrary bridging fraction; see Figure 2.

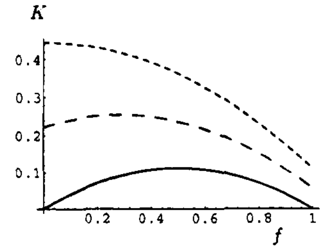

Figure 2. Plot of the bending moduli K_{tri} of the triblock phase (dashed lines) and K_{bi} of the diblock phase (solid line) in dimensionless units of μh^2 (see text) as a function of the asymmetry parameter $f = N_A/N$. The A-blocks are found at the ends of the triblock chain, which has total length $2N$, twice that of the diblock. For the triblock phase two different bridging fractions are shown. The upper dashed curve is for the hypothetical case where all chains form bridges ($p = 1$) while the lower is for half-loops and half-bridges ($p = 1/2$), which may be more applicable for flat layers at equilibrium.

$$K_{\mathrm{tri}} = pK_{\mathrm{bridge}} + (1 - p)K_{\mathrm{bi}} \tag{26}$$

At the level of the Alexander–de Gennes treatment, the free energies of a loop and a bridge in a flat layer are identical.[18-20] Thus we might insert $p = 1/2$. For this value of p and the special case of $f = 1/2$ we find $K_{\mathrm{tri}}/K_{\mathrm{bi}} = 17/8$. This ratio has a maximum of $K_{\mathrm{tri}}/K_{\mathrm{bi}} = 2.83$ for $f = 0.28$ (for $f < 0.28$ we would lose the lamellar phase). However, the response to deformation of a triblock layer is not purely a static problem. To see this, note that K_{tri} is a monotonic increasing function of p. Therefore if we apply a fixed deformation to the layer, the stress can partially relax via equilibration of bridges to loops. This occurs when the A-blocks of a bridging chain pass through the neighboring B-block, forming a loop in the process.[12] This process is highly reminiscent of the first mechanism[11] discussed in section 1 for the motion of microphase-separated *diblock* chains. In fact the time scales for the triblock bridge-to-loop process and the corresponding diffusive step of a diblock chain should be rather similar. Experimentally it may be possible to apply a deformation to a thin triblock layer[21] (possibly by an atomic force machine) and then measure the stress relaxation. The precise relationship between stress and bridging fraction depends on the experimental geometry and the copolymer–surrounding phase interfacial tensions. These interfacial tensions should be small: If they are too large (i.e., $\gg\gamma_{AB}$), the stress may be dominated by the interfacial contribution and hence be rather insensitive to changes in the modulus K. To calculate the precise dependence of the stress on the bridging fraction, a calculation based on the formalism of ref 22 may be appropriate.

Finally, we emphasize that there may be many additional slow relaxation processes at work in the microphase-separated copolymer systems. These include the starlike retraction mechanism and others discussed in ref 12. However, in the strict $N \to \infty$ SSL the bridge-to-loop jumping process (and its diblock analogue[11]) is thought to dominate the very long time stress relaxation.

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References and Notes

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(18) However, within the SCMF picture it is thought that loops are preferred over bridges.[19,20] By relaxing the Alexander–de Gennes constraint that all loops just reach the midplane between neighboring monolayers, we reduce the energy density by a factor of order 20% of μ. Using (12), this equates to $\sim (\chi N)^{1/3} k_B T$ per chain, which might be several $k_B T$. However, we argue that our treatment remains appropriate since (i) p is arbitrary, (ii) there is no firm evidence for this excess of loops over bridges, and (iii) the ratio of loops to bridges can be controlled by "doping" one A-block, creating an A–B–A* triblock where χ_{AA^*} may be chosen to enhance and control the bridging fraction. (In the limit where χ_{AA^*} is large, the A- and A*-blocks phase separate into neighboring monolayers.) The extension of the present calculation to A–B–A* architecture is straightforward.

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