Microphase Separation of Block Copolymer Rings

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ABSTRACT: Phase segregation properties of ring block copolymers are discussed using the theory of Leibler, ignoring the topological constraints specific to ring polymers. We find that the ordering properties of ring diblocks are similar to those of linear copolymers with a reduced chemical length N. For a melt of symmetric diblock rings, there is microphase separation for a demixing interaction larger than $(\chi N)^* = 17.8$; this is about 1.7 times that required for segregation of linear diblocks with the same structure. The wavelength of the ordering mode is about 0.67 of that for the equivalent linear diblock melt. Deep into the strongly-segregated state, the wavelength of lamellar domains composed of rings is $2^{-2/3} = 0.63$ times that of linear diblock lamellae with the same N.

Linear block copolymers composed of immiscible monomers have long been known to display microphase separation.[1] Leibler's theory[2] forms the cornerstone of our understanding of this phase transition. Ring diblock copolymers have recently been synthesized in sufficient quantities to examine their microdomain-forming properties.[3] In this paper, extension of Leibler's work to the case of a melt of ring copolymers is presented, along with some comments on the strong-segregation properties of the mesophase. The results are derived using Gaussian chain statistics that ignore the *topological* constraints unique to rings in three dimensions: a correct treatment of the statistical mechanics of even a single ring must respect the constraint that the knot type of the chain is conserved.[4] This is a difficult problem of mathematical physics, and I propose, as a first step, to ignore all topological constraints and to study the properties of "phantom" rings that explore all topological classes. By comparing the results of this study to those for *linear* chains with the same structure, it should be possible, via experiment or computer simulation, to determine whether the topological constraints of real rings strongly affect the static properties of the microphases.

The scaling properties of the microphase separation of ring block copolymers composed of two species of monomers (labeled A and B) are the same as in the linear case: a phase transition is encountered in the ring block copolymer melt for $(\chi N)^* = C$, where C is a constant that depends on the polymer architecture, where χ is the repulsive energy (in units of kT) of adjacent unlike monomers, and where N is the chemical length. The domain size at the transition is on the order of the radius of gyration of the blocks, or $\approx N^{1/2}a$, where a is the monomer length. These scaling results follow from the same considerations as in the linear case: the transition occurs when the entropy cost of confining a block to a particular domain, a cost of order kT, is equal to the enthalpy gain of doing so, of order χN. This confinement entropy is also an estimate for the chain stretching free energy, and thus the chains are nearly unstretched at the transition: the domain size near the phase boundary will be on the order of the "free" chain radius of gyration.

We follow the approach of Leibler[2] of first calculating "phantom" (Gaussian) chain correlations and then using the random-phase approximation (RPA) to compute the effects of the monomer-monomer interactions in the strongly interacting dense system. These interactions (a) force the total monomer volume fraction to be unity everywhere (appropriate to the case of an incompressible melt) and (b) include the repulsive interactions of adjacent *unlike* monomers.

The probability of a Gaussian chain segment of n monomers to have its ends separated a distance $\mathbf{r}$ is[5]

$$L(\mathbf{r},n) = \left(\frac{3}{2\pi a^2 n}\right)^{3/2} \exp\left(\frac{-3r^2}{2a^2 n}\right) \tag{1}$$

The average end-to-end distance squared of an N-monomer chain is thus $\int d^3r\, L(\mathbf{r},N) = Na^2$; the radius of gyration squared is $R^2 = Na^2/6$. The probability of observing monomer n' at $\mathbf{r}'$ for an N-monomer *ring*, given that monomer n is at $\mathbf{r}$, is

$$P(\mathbf{r},\mathbf{r}';n,n') = \frac{L(\mathbf{r}'-\mathbf{r},|n'-n|)\, L(\mathbf{r}-\mathbf{r}',N-|n'-n|)}{L(\mathbf{0},N)} \tag{2}$$

This expression is simply the product of the probabilities of the chain segments from n to n' and from n' back to n (a segment $N - |n'-n|$ monomers long) to stretch from $\mathbf{r}$ to $\mathbf{r}'$ and from $\mathbf{r}'$ back to $\mathbf{r}$, respectively. The denominator, the probability of an open chain forming a loop after N steps, is required for normalization of P, so that the probability of observing monomer n' at any $\mathbf{r}'$ once n and $\mathbf{r}$ are set is unity: $\int d^3r'\, P(\mathbf{r},\mathbf{r}';n,n') = 1$. The Fourier components of P are useful:

$$\tilde{P}(\mathbf{q},\mathbf{q}';n,n') = \int d^3r\, d^3r'\, e^{i(\mathbf{q}\cdot\mathbf{r}+\mathbf{q}'\cdot\mathbf{r}')} P(\mathbf{r},\mathbf{r}';n,n') = (2\pi)^3\delta^3(\mathbf{q}+\mathbf{q}')\, N S_{n,n'}(q) \tag{3}$$

$$S_{n,n'}(q) \equiv N^{-1} \exp(-q^2R^2|\nu - \nu'|(1 - |\nu - \nu'|))$$

where $\nu = n/N$ and $\nu' = n'/N$. The corresponding linear chain result is just $S^L_{n,n'}(q) = N^{-1} \exp(-q^2R^2|\nu - \nu'|)$.

In a melt of such phantom rings, we may compute the two-point function $G_{n,n'}(\mathbf{r},\mathbf{r}')$, the connected correlation of monomers n of any chain and n' of any chain, at positions $\mathbf{r}$ and $\mathbf{r}'$. In terms of the volume fraction operator for monomer n at position $\mathbf{r}$, $\rho_n(\mathbf{r})$, this is

$$G_{n,n'}(\mathbf{r},\mathbf{r}') = \langle \rho_n(\mathbf{r})\, \rho_{n'}(\mathbf{r}')\rangle - \langle \rho_n(\mathbf{r})\rangle\langle \rho_{n'}(\mathbf{r}')\rangle \tag{4}$$

Since the chains are statistically independent, the second term of (4) is just $1/N^2$. The first, two-body term of (4) is composed of two contributions:

$$\langle \rho_n(\mathbf{r})\, \rho_{n'}(\mathbf{r}')\rangle = \frac{1}{N^2} + \frac{a^3}{N} P(\mathbf{r},\mathbf{r}';n,n') \tag{5}$$

The first contribution to (5) is the probability of monomer n of one chain being at $\mathbf{r}$ while monomer n' of

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a *different* chain is at $\mathbf{r}'$; this is independent of the position due to statistical independence of the chains. The second contribution is due to the case that monomers n and n' are on the *same chain*: it is the probability of monomer n of a chain being at $\mathbf{r}$ (which is $1/N$) times the probability that monomer n' of that chain is found at $\mathbf{r}'$. Thus we have

$$G_{n,n'}(\mathbf{r},\mathbf{r}') = \frac{a^3}{N}P(\mathbf{r},\mathbf{r}';n,n') \tag{6}$$

The Fourier transform of this quantity is

$$\tilde{G}_{n,n'}(\mathbf{q},\mathbf{q}') = \int \mathrm{d}^3r\, \mathrm{d}^3r'\, e^{i[\mathbf{q}\cdot\mathbf{r}+\mathbf{q}'\cdot\mathbf{r}']}G_{n,n'}(\mathbf{r},\mathbf{r}') = (2\pi a)^3\delta^3(\mathbf{q}+\mathbf{q}')\, S_{n,n'}(q) \tag{7}$$

The function $S_{n,n'}$ is the contribution to radiation scattering from the n and n' monomers.

From (7) we may easily calculate the scattering from fluctuations in the volume fraction difference of the two types of monomers, once the chain architecture is specified. We study the case of a diblock ring melt, composed of N-monomer rings of which monomers $0 \le n \le fN$ are of type A, and the remainder are of type B. Defining $\phi_I(\mathbf{r})$ to be the volume fraction of monomer type I (=A, B) at $\mathbf{r}$, we observe that the correlation of the I and J volume fractions is

$$G_{IJ}(\mathbf{r},\mathbf{r}') = \langle\phi_I(\mathbf{r})\,\phi_J(\mathbf{r})\rangle - \langle\phi_I(\mathbf{r})\rangle\langle\phi_J(\mathbf{r}')\rangle = \int_{n\in I}\mathrm{d}n \int_{n'\in J}\mathrm{d}n'\, G_{n,n'}(\mathbf{r},\mathbf{r}') \tag{8}$$

The Fourier transforms of these quantities lead to the scattering functions as in (4)–(7):

$$S_{AA}(\mathbf{q}) = N\int_0^f \mathrm{d}\nu \int_0^f \mathrm{d}\nu'\, e^{-x|\nu-\nu'|(1-|\nu-\nu'|)} \tag{9}$$

$$S_{BB}(\mathbf{q}) = N\int_f^1 \mathrm{d}\nu \int_f^1 \mathrm{d}\nu'\, e^{-x|\nu-\nu'|(1-|\nu-\nu'|)}$$

$$S_{AB}(\mathbf{q}) = S_{BA}(\mathbf{q}) = N\int_0^f \mathrm{d}\nu \int_f^1 \mathrm{d}\nu'\, e^{-x|\nu-\nu'|(1-|\nu-\nu'|)}$$

where $x = q^2R^2$ and $R^2 = Na^2/6$. These objects correspond to those calculated by Leibler[2] for linear diblocks.

We may now use Leibler's results to write down the scattering from the A–B concentration difference $\phi(\mathbf{r}) = \phi_A(\mathbf{r}) - \phi_B(\mathbf{r})$ using the RPA, assuming a demixing free energy of the form

$$F_D = \frac{\chi}{a^3}\int \mathrm{d}^3r\, \phi_A(\mathbf{r})\,\phi_B(\mathbf{r}) \tag{10}$$

and incompressibility, i.e., $\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) = 1$. The RPA scattering function is

$$S(\mathbf{q}) \equiv \int\frac{\mathrm{d}^3r}{a^3}(\langle\phi(\mathbf{r})\,\phi(\mathbf{0})\rangle - \langle\phi(\mathbf{r})\rangle\langle\phi(\mathbf{0})\rangle) = \frac{4W(q)}{T(q)-2\chi W(q)} \tag{11}$$

where $W \equiv S_{AA}S_{BB} - S_{AB}^2$ and $T = S_{AA} + S_{BB} + 2S_{AB}$. We see that there is an instability toward demixing, signified by diverging scattering, at the minimum χ^* that solves $T(q^*) - 2\chi^* W(q^*) = 0$. This corresponds to the spinodal point for microphase separation. Since $W \approx N^2$ and $T \approx N$, we have $(\chi N)^* \approx 1$; we expect $(qR)^* \approx 1$, corresponding to a wavelength of order $N^{1/2}a$.

Figure 1 shows the result for $f = {}^1/_2$ comparing the ring and linear symmetric diblock cases: we plot the $\chi = 0$ scattering function $S(q)/N = 4W(q)/NT(q)$. The peak of this function is $2/(\chi N)^*$, and the location of the peak gives

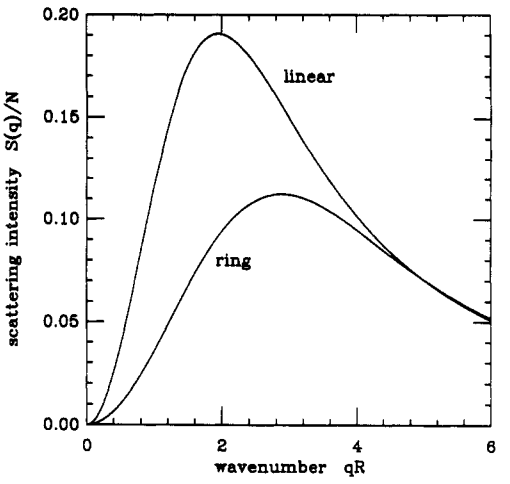

Figure 1. Scattering intensity $S(q)/N$ vs wavenumber qR for ring and linear diblock copolymer melts with $f = {}^1/_2$ and $\chi = 0$. The upper peak is linear chains; the lower peak is rings. The peak of the ring scattering function is at larger wavenumber and is less intense than the corresponding features of the linear chain scattering.

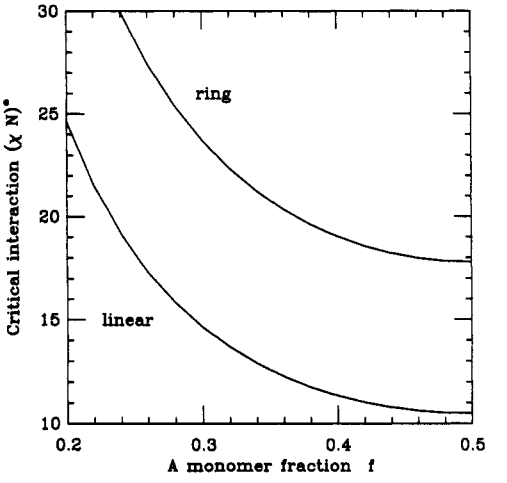

Figure 2. Mean-field spinodal $(\chi N)^*$ vs the fraction f of a chain that is composed of A monomers, for ring and linear diblock melts. For each f, the amount of demixing interaction χ required to make the disordered state unstable for the rings is larger than that required to destabilize disordered linear diblocks with the same N and f.

q^*. In the linear case, we note Leibler's results $(\chi N)^* = 10.5$ and $(qR)^* = 1.95$. The ring diblock result is $(\chi N)^* = 17.8$ and $(qR)^* = 2.88$. The rings require a larger amount of A–B repulsion to segregate than do the equivalent linear molecules. This is due to the fact that the closed topology suppresses concentration fluctuations. The characteristic wavelength for concentration fluctuations is smaller, leading to a larger $(qR)^*$ for rings than for linear chains of the same structure. We note that at small q, the structure factors are rather different due to the constraint that the ring closes. However, at large q, the ring and linear structure factors are asymptotically the same since the short-distance behavior of the chain conformation fluctuations is insensitive to the overall conformation shape. Finally, both structure factors go to zero at $q = 0$, reflecting the fact that long-wavelength concentration fluctuations are suppressed by the chemical connection between the A and B monomers.

It is instructive to compare the symmetric ring results to microphase instabilities in symmetric multiblock copolymer melts, where there are more constraints on the block ends than in the linear diblock case. Benoit and Hadziioannou[6] have carried out RPA calculations for linear molecules with structures $(AB)_n$, where the A and B blocks

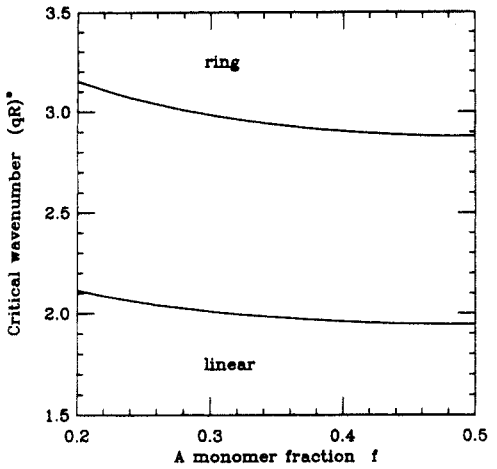

Figure 3. Wavenumber of unstable mode $(qR)^*$ at the spinodal point $(\chi N)^*$ vs fraction f of a chain that is composed of A monomers, for ring and linear diblock copolymers. For each f, the unstable mode of the ring diblocks has a larger wavenumber (shorter wavelength) than that for linear diblocks with the same N and f.

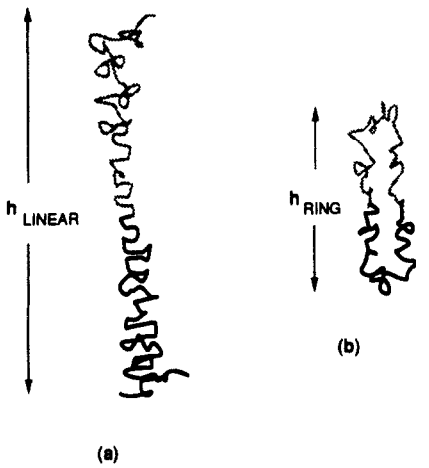

Figure 4. Chain conformations of $f = {}^1/_2$ diblocks in strongly-segregated lamellae. (a) Linear diblock conformation. The N monomers are extended over a distance h. (b) Ring diblock conformation. Two hairpin turns separate two segments of length $N/2$ monomers, which each are extended over a distance h. We may consider the ring lamellae to be made up of linear diblocks of length $N/2$.

are each of chemical length $N/2$. The linear quad-block $(n = 2)$ has a mean-field microphase transition for $(\chi N)^* \approx 12.5$ and $(qR)^* \approx 2.2$; as n is increased, both these quantities increase but approach limiting values for $n \to \infty$ of $(\chi N)^* \approx 15.0$ and $(qR)^* \approx 2.5$. As n is increased, a larger fraction of block ends are constrained by connections to other blocks, resulting in an increase in the repulsion necessary to drive microphase formation. However, we see that the more severe constraints imposed by the diblock ring architecture lead to even larger values of the transition interaction and the ordering wavenumber than for the $n = \infty$ multiblock.

In Figure 2 the mean-field instability point $(\chi N)^*$ is plotted versus f for the diblock ring and for the linear diblock. This critical interaction corresponds to the spinodal for the mesophase, but it should be close to the mean-field phase transition point for $0.7 > f > 0.3$, because, for linear diblocks, the transition is weakly first-order in this range.[2] Figure 3 shows $(qR)^*$ at the spinodal point as a function of f. In mean-field theory, the symmetric case $f = {}^1/_2$ has a critical phase transition at the spinodal point: however, as in the linear chain case, fluctuations are expected to drive this transition to be first order and to shift it to somewhat larger values of χN.[7]

In order to calculate properties of the ordered mesophase, the nonlinear response properties of the diblock ring melt must be analyzed. Near $f = 0.5$, and not too far into the ordered phase, calculations similar to those of Leibler (which take into account contributions to the free energy of up to fourth-order in the A–B concentration difference) could be used. Recent extensions of the mean-field theory to infinite order[8] could be applied to the ring case to study the stability of ordered phases with different domain morphologies (lamellae, rods, spheres, ...). Here we carry out a much simpler computation. For $f = {}^1/_2$ diblocks, we expect lamellar domains. For large $\chi \gg 17.8/N$, there will be strong segregation and strong stretching of the chains in the lamellae. We may carry out a simple calculation of the behavior of the lamellar spacing h, using an approach pioneered by Semenov.[9]

A *linear* diblock in the $f = {}^1/_2$ ring melt under strong-segregation conditions has its junction point strongly confined to an A–B interface, as shown in Figure 4a. We define the distance between successive A–B interfaces as h; the "lattice constant" of the domain pattern is $2h$. The scaling form of the free energy per chain is

$$F(h,N) = \frac{h^2}{2a^2N} + \chi^{1/2}\frac{Na}{h} \tag{12}$$

The first term is the entropy reduction ("stretch free energy cost") required to extend the chains over a characteristic distance h. The latter term is the interfacial free energy. This is simply the strong-segregation surface tension $\chi^{1/2}/a^2$, times the area of A–B interface per chain, Na^3/h. Minimization of (12) with respect to h yields the well-known result $h_{\mathrm{LINEAR}}(N) = \chi^{1/6}N^{2/3}a$.

The strongly-segregated *ring* melt has chains in conformations as shown in Figure 4b. Since the chains are strongly stretched over a distance large compared to the distance they traverse parallel to the interfaces, we may view their conformations as "double hairpins". Since the free energy cost of locating the free end of a chain is of order kT, a negligible fraction of the stretching energy, the free energy of the rings is described by that of a lamellar phase of *linear* chains of length $N/2$. The equilibrium domain size is thus

$$h_{\mathrm{RING}}(N) = 2^{-2/3}h_{\mathrm{LINEAR}}(N) \tag{13}$$

a result dependent only on the scaling behavior of (12).

It should be emphasized that such strong-stretching estimates are valid only when the domain size is rather large compared to the free chain radius, or when $h/R = (\chi N)^{1/6} \gg 1$. For $\chi \approx 0.2$, $h/R > 4$ for $N > 20\,000$: rather large molecular weights are required to observe strongly stretched chains.

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References and Notes

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