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Chain Architecture and Asymmetry in Copolymer Microphases

Scott T. Milner

Corporate Research Science Laboratories, Exxon Research & Engineering Company, Annandale, New Jersey 08801

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For strongly-segregated diblock copolymer microphases, a strong empirical relation exists between the volume fraction of the two species and resulting microphase symmetry.[1] Microphases of spherical domains occur only for rather low volume fractions of the interior species, *i.e.*, quite asymmetric chains ($\phi \approx 0$–0.15); cylindrical domains occur for less asymmetric chains ($\phi \approx 0.15$–0.3), and lamellar phases, for roughly symmetric diblocks ($\phi \approx 0.3$–0.5). This relation appears to persist even when low molecular weight compatible homopolymer is added.[1]

In a variety of potential applications, *e.g.*, microphases used as semipermeable membranes or templates, it would be desirable to control the microphase morphology and volume fraction separately. This paper explores the simultaneous control of volume fraction and microphase symmetry by changing the molecular architecture, in particular by employing various starblock copolymers instead of diblocks.

A useful analogy exists between block copolymers and surfactants, which suggests an approach for designing copolymers disposed to give, for example, cylindrical or spherical microphases with a relatively large volume fraction of the interior species, unobtainable for diblock copolymers. Surfactant molecules with bulky "tails", in particular twin-tailed surfactants, tend to self-assemble into micelles or microphases with the double tail on the outside of a curved (spherical or cylindrical) surface. Simply, an asymmetric architecture for surfactants allows control of micelle and microphase structure by a means other than simply changing the total length of the surfactant tail.

With surfactants, the tails are of low molecular weight, and the interactions between the polar "head groups" and solvent are complex; hence, it is rather difficult to give a microscopic calculation of microphase behavior. In contrast, with long flexible copolymers, one can calculate phase behavior in terms of the interaction parameter between unlike monomers, denoted χ, and elastic parameters of the chains (length and stiffness).

As an illustration of the effect of asymmetric copolymer architecture on phase behavior, consider a melt of "Y polymers", *i.e.*, three-armed stars with two A arms and one B arm.[2] At volume fraction $\phi = {}^1/_2$, the two A arms are half as long as the single B arm. If such a copolymer formed a strongly-segregated lamellar phase, the constraint of constant mass density forces the thickness of the A and B layers to be equal. Hence, the A arms are more strongly stretched than the B arm—the arms are equally extended, but the A arms have a square radius of gyration half that of the B arms.

In fact, a lamellar layer of such a Y polymer would tend to bend so that the A arms resided on the outside of the bend; in this way, the A arms find more volume close to the A–B interface without having to stretch so much. The volume fraction for which the layer has no tendency to bend in either direction can be found by a simple argument, as follows.

The free energy of the Y polymer layer is written as the sum of the free energies of the polymer "brushes" which are its two sides, with twice as many chains per unit area in the A brush as in the B brush. In general, the free energy per chain f of a strongly-stretched curved melt brush has the form[3]

$$f(r) \sim h^2/R^2(1 + c_1h/r + \ldots) \qquad (1)$$

where c_1 is a constant of order unity, h is the thickness of the brush when it is flat, r is the radius of curvature, and R is the radius of gyration of the chains in the brush. The height h is determined by "mass conservation" as $h = V\sigma$, where V is the volume displaced by one block, and σ is the number of blocks per area.

The free energy per copolymer of a curved Y polymer layer then takes the form

$$f_Y(r) \sim h_B^2/R_B^2(1 + c_1h_B/r + \ldots) + 2h_A^2/R_A^2(1 - c_1h_A/r + \ldots) \qquad (2)$$

The layer has no tendency to bend when the coefficient of $1/r$ vanishes; this happens when

$$\frac{V_B^3}{R_B^2} = \frac{16V_A^3}{R_A^2} \qquad (3)$$

Note that the ratio $V_A/R_A^2 \equiv l_A$ is a material parameter independent of chain length, because V_A and R_A^2 are both proportional to chain length. (In fact, it has been argued, and recently shown experimentally, that l_A so defined is proportional to the distance between entanglements in a melt of homopolymer A; that is, the plateau modulus G_∞ is proportional to kT/l_A^3 in such a melt.[4])

If the A and B blocks are elastically identical, then $l_A = l_B$, and the spontaneous curvature of the layer vanishes when $V_B = 4V_A$, *i.e.*, when the volume fraction of B monomers is $\phi = {}^2/_3$. One expects this value of ϕ to occur in the middle of the range of ϕ for which the lamellar phase occurs; for elastically symmetric diblocks, the center of the lamellar phase would have been $\phi = {}^1/_2$, which suggests that the Y polymer architecture shifts the phase boundaries substantially.

Of course, even diblock copolymers may be elastically asymmetric, having different monomer volumes and persistence lengths. In the above example, the factor of 16 in eq 3 would be absent for diblock architecture; then, the volume fraction of B for which spontaneous curvature vanishes is $\phi = 1/[1 + (l_B/l_A)^{1/2}]$, which illustrates the effect of elastic asymmetry on microphase behavior. Suppose that A is more flexible than B; hence, for equal displaced volumes $V_A = V_B$ the A block has a smaller radius of gyration and so $l_A > l_B$. Then $1/[1 + (l_B/l_A)^{1/2}] > {}^1/_2$, and the flexible block, which is harder to extend, is favored on the outside of curved structures.

To proceed further, I employ calculations of copolymer microphase behavior appropriate to the strong segregation limit,[5,6] in which interfaces between A and B monomers are sharp and the A/B interfacial tension is large enough that copolymers become stretched as they seek to reduce the area per chain of A/B contact along the interfaces. I shall generalize the Y polymer to a starblock copolymer with n_A A arms of volume V_A and n_B B arms of volume V_B; the volume fraction of B monomer is $\phi = n_BV_B/(n_AV_A + n_BV_B)$. Then $n_A = n_B = 1$ represents a diblock, $n_A = 2$, $n_B = 1$, a Y polymer, and so forth.

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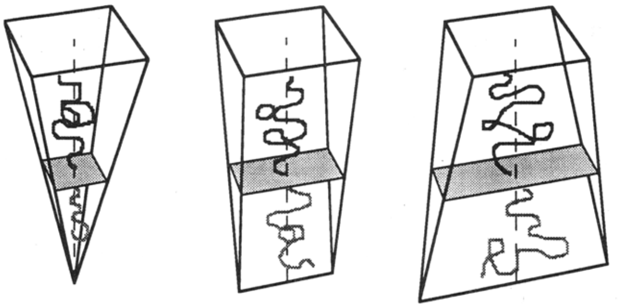

Figure 1. Representative "wedges" for spherical, cylindrical, and bicontinuous phases. The dividing surface is shown shaded, and a diblock conformation, sketched.

The morphology and length scale of microphase separation are then determined by a competition of the interfacial tension and the increase in stretching free energy as the copolymer blocks stretch away from an interface. For a given structure, the lattice constant is found by minimizing the sum of these two free energies. The phase diagram as a function of volume fraction is determined by the crossings of the free energy of different structures (lamellar, ordered bicontinuous double diamond [OBDD], cylindrical, or spherical). In the strong segregation regime the free energy of all the microphases scales the same way with chain length and interfacial tension, so the phase boundaries become independent of χ.

Simple calculations of mesophase behavior (as in this paper) assume a "round" unit cell for the cylindrical and spherical phases, even though such unit cells cannot actually pack space. As a result, the chain conformations are one-dimensional—the blocks stretch along the normal to the A/B interface—and all chains experience the same local geometry. Because these calculations correspond to cylindrical or spherical copolymer micelles, which would have to be deformed to pack space, the free energy so computed is in fact a lower bound.[7]

Such calculations can be performed in a unified way[7] in terms of the cross-sectional area $a(z/R)$ relative to the outer surface as a function of height z in an infinitesimal "wedge" of radius R of the unit cell (see Figure 1). The function $a(z/R)$ is equal to unity for lamellae, z/R for cylinders, and $(z/R)^2$ for spheres.

The location z_d of the "dividing surface" separating the two species is determined by equating the relative volume below z_d to the volume fraction ϕ (the A arms are taken to be on the outside of the bend):

$$v(\beta) \equiv \int_0^{\beta} \mathrm{d}y\, a(y) = \phi v(1), \qquad \beta = z_d/R \tag{4}$$

The surface-tension contribution is just the area of this dividing surface $a(\beta)$ times the surface tension γ (which scales as $\chi^{1/2}$ [8]).

Recently,[7] a serviceable approximation has been found for describing a generic bicontinuous phase, analogous to such "round unit cell" calculations. The local geometry in such a phase, instead of being composed of pie-shaped or conical wedges, is composed of "Gaussian wedges". The outer surface of such a Gaussian wedge is a small piece of a surface of zero mean curvature, which separates the two interpenetrating connected regions in the OBDD phase. The narrow end of the wedge represents a piece of the diamond bond-lattice that is contained inside each of the connected regions. The area function for such a Gaussian wedge is $a(z/R) = 2(z/R) - (z/R)^2$.

Such a calculation for bicontinuous phases is analogous to the conventional round unit cell calculations for spherical and cylindrical phases in that details of the lattice structure are neglected; such calculations cannot distinguish between square and hexagonal packings of cylinders or between different bicontinuous phases. This simple estimate results in a uniformly good approximation to a more detailed calculation of the double-diamond free energy as a function of volume fraction for symmetric diblocks. In the present paper we use this estimate, with a constant prefactor (=0.99) adjusted to give a small stable window or bicontinuous phase between lamellae and cylinders, to examine the dependence of the phase diagram on copolymer architecture and asymmetry.

The stretching energy is calculated by methods developed for polymer brushes.[5,6] The copolymer chains are added one by one, and the work to add each is summed. The height of the layer when the number of chains per area is σ is given by the relation

$$v(\beta + h_A/R) - v(\beta) = \sigma V_A a(\beta)/R \tag{5}$$

where h_A is the height of the growing A layer (a similar equation holds for the B block).

The monomer chemical potential $\mu(\phi)$ (the physical pressure, in an incompressible melt) is a decreasing function of distance from the dividing surface and causes the chains to stretch as their monomers seek regions of lower chemical potential. Under the assumption that there are free ends at all distances from the dividing surface, the chemical potential is quadratic in the distance from the dividing surface. For the inwardly curved parts of the structure, this is exact; for the outwardly curved parts, this assumption leads to an unphysical negative density of free ends[5] but has been shown to give good estimates of stretching free energy even for layers with curvature radii comparable to their thickness.[9]

The work to add an A block is independent of the location of the free end and so may be conveniently taken to be the work to add a block with its conformation very near the dividing surface, simply $V_A\mu(z_d)$. Integrating with respect to coverage then gives[6,7]

$$f_{\mathrm{str}} = \frac{3\pi^2 R^2}{8v(1)}\left[\frac{n_A}{(1-\phi){R_A}^2}\int_0^{1-\beta}\mathrm{d}y\, a(y+\beta)y^2 + \frac{n_B}{\phi {R_B}^2}\int_0^{\beta}\mathrm{d}y\, a(\beta-y)\, y^2\right] \tag{6}$$

The interfacial free energy per chain is

$$f_{\mathrm{int}} = \gamma V a(\beta)/(v(1)\, R) \tag{7}$$

where $V = V_A + V_B$ is the total chain volume.

The total free energy per chains is $f = f_{\mathrm{str}} + f_{\mathrm{int}}$, which is then minimized over R to find the scale of the structure.

We divide all the free energies by a characteristic scale,

$$f_0 = (27\pi^2/32)^{1/3} V^{1/3} \gamma^{2/3} (n_A n_B)^{1/2} (l_A l_B)^{1/6} \tag{8}$$

to give

$$f_{\mathrm{lam}} = [\epsilon(1-\phi) + \phi/\epsilon]^{1/3} \tag{9}$$

$$f_{\mathrm{cyl}} = \left[\frac{2\epsilon\phi(1-\phi^{1/2})^3(3+\phi^{1/2})}{(1-\phi)^2} + \frac{2\phi}{\epsilon}\right]^{1/3} \tag{10}$$

$$f_{\mathrm{sph}} = \left[\frac{27\epsilon\phi^{4/3}(1-\phi^{1/3})^3(\phi^{2/3}+3\phi^{1/3}+6)}{10(1-\phi)^2} + \frac{27\phi}{10\epsilon}\right]^{1/3} \tag{11}$$

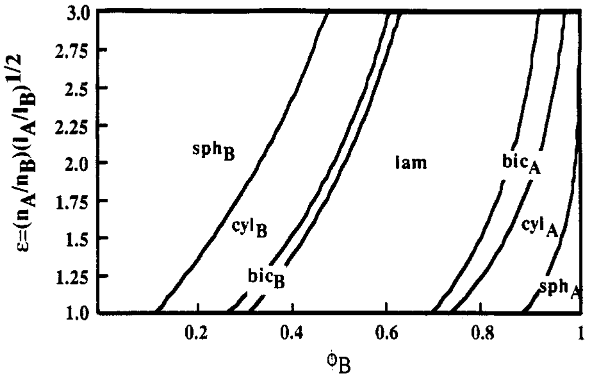

Figure 2. Phase diagram in the strong-segregation limit for star-block copolymers with n_A A arms and n_B B arms (described in text) as a function of the volume fraction of the B monomer.

where $\epsilon \equiv (n_A/n_B)(l_A/l_B)^{1/2}$. Note that the single parameter ϵ describes the effects of both chain architecture and elastic asymmetry in the strong-segregation regime. The "opposite side" of the phase diagram, in which the A arms are on the inside of cylindrical or spherical domains, is obtained by exchanging A and B, *i.e.*, replacing ϕ with $1 - \phi$ and ϵ with $1/\epsilon$.

The corresponding expression for the bicontinuous phase free energy f_{bic} is cumbersome, because the "mass conservation" relation eq 4 is a cubic equation for β in terms of ϕ. Still, the integrals of eq 6 can be performed for $a(y) = 2y - y^2$, eq 4 solved (*e.g.*, numerically), and minimization of $f = f_{str} + f_{int}$ performed, to obtain values of $f_{bic}(\epsilon,\phi)$.

The crossings of these free energy curves determine the phase diagram as function of volume fraction ϕ and asymmetry parameter ϵ, shown in Figure 2. Only values of $\epsilon > 1$ are shown, since the labels A and B may be exchanged. This phase diagram is largely unexplored experimentally, though chemistry does exist to produce such copolymers, and what samples that have been studied so far are consistent with this phase diagram.[2]

The relatively strong dependence of the phase boundaries on the number of arms of each kind is striking. For instance, at constant volume fraction $\phi = 0.4$, and assuming elastically symmetric blocks, diblocks ($n_A = n_B = 1$) would form lamellae, Y polymers ($n_A = 2$) would form cylinders, and "ψ polymers" ($n_A = 3$) would form a spherical phase. Note also that the spherical phase with multiple or flexible arms on the inside of the domains disappears at a finite value of $\epsilon = (60/7)^{1/2} \approx 2.93$.

A different, and more extensively studied, star-block copolymer consists of some number of identical diblock copolymer "arms" with the free ends of the A blocks joined at a point.[10] Such a structure should have a less dramatic effect on the phase diagram in the strong-segregation regime, by the following argument. Unlike the Y polymers, such a star diblock in a given microphase can be viewed as a set of diblocks with the constraint that the free ends of the A blocks are joined together in clusters. Roughly speaking, a constraint on the free end of a chain in a brush affects the free energy by order of kT, which is by assumption small on the scale of the stretching energy. Within a strong-stretching calculation, such a star diblock would have the same phase behavior as its constituent arms.

As a final remark, no firm criterion yet exists for the applicability of strong-stretching calculations other than the formal limit $\chi V \rightarrow \infty$, or equivalently that the stretching energy per *block* $(h/R)^2 \sim (\chi V)^{1/3}$ is much larger than the thermal energy k_BT. Note that, if a sequence of samples were prepared to explore the progression from diblock to Y polymer to ψ polymer at fixed volume fraction and molecular weight, the strong-stretching criterion would be weakened.

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