6782 *Macromolecules* **1993,** *26,* 6782–6788

Self-Assembly of Linear Block Copolymers. Relative Stability of Hyperbolic Phases

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Received July 27, 1992; Revised Manuscript Received June 11, 1993®

ABSTRACT: A simple model is described for the chain entropy of strongly segregated linear diblock copolymers which involves a generalization of rubber elasticity theory to *curved* as well as stretched rubberlike materials. The theory admits calculation of the chain entropy contribution to the free energy of any copolymer microdomain geometry, as a function of the effective surface tension at the domain boundaries (between strongly segregated blocks) and the geometry of the domains. In the absence of global packing constraints, the theory predicts the formation of hyperbolic interfaces (which include bicontinuous microdomain geometries) between the segregated blocks for a significant range of molecular concentrations, as well as the standard lamellar, cylindrical, and spherical geometries. Once the relevant global constraints for pure copolymer systems are imposed, planar, cylindrical and spherical phases dominate, due to the severe geometrical limitations required for uniform space filling by the assembled diblock molecules. The analysis suggests that the formation of exotic hyperbolic phases, such as bicontinuous or mesh mesostructures, requires the relaxation of global constraints.

Introduction

The degree and form of mesostructure in copolymer systems depends on the interaction energy between the various components. The simplest copolymer systems are made of diblock molecules, consisting of two grafted "blocks" of chemically distinct polymers. If the distinct blocks are immiscible, the molecules may self-assemble spontaneously to form strikingly regular structures.[1]

The physical origins of the self-assembly process have been identified, and the gross features that lead to structure formation are well-documented at a theoretical level.[2–7] Most of the observed phenomena seemed to be understood for diblock (AB) copolymers: as the volume fraction of the major component (say A) changes from 50% to 100%, the geometry of the A and B regions varies from alternating planes of A and B, followed by cylinders of B in a continuous matrix of A, to spheres of B in A.

The situation has changed dramatically with the discovery of more exotic bicontinuous[8,9] and "mesh"[10,11] microphase structures in solvent-free copolymer melts. The bicontinuous ("OBDD" or "tetrapod") phase apparently consists of interpenetrating diamond networks of one component, separated by the other moiety.[8,9] This phase has been observed in both diblock copolymers of both linear and star architectures, whose block compositions are intermediate to those which lead to lamellar and hexagonal phases. The interfaces in this phase are periodic saddle-shaped surfaces related to the classical infinite periodic minimal surface of primitive cubic symmetry, the D-surface.[8] The "mesh" phase consists of parallel stacks of lamellae, linked by catenoidal tunnels. In both the "mesh" and bicontinuous "strut" phases, the interfaces are predominantly saddle-shaped, adopting a *hyperbolic* surface geometry.[16] Theoretical understanding of the relative stability of these hyperbolic phases is limited to date; local calculations suggest that saddle-shaped interfaces are favorable in diblock copolymer melts when the blocks have nearly equal dimensions (radii of gyration, segment lengths), compared with planar, cylindrical, or spherical interfaces.[10,12–15]

In fact, similar architectures are well-known in a wide range of surfactant–water mixtures, where they too are formed at compositions intermediate to those required for formation of lamellar and hexagonal phases, as in block copolymers.[16] This apparent universality suggests that some features of surfactant self-assembly may be successfully applied to copolymer aggregation. In particular, we can exploit the relation between the global shape of the microphases and the local molecular geometry. Clearly, the molecular shape of copolymer molecules is not fixed, rather it depends on the molecular composition. We assume here that the shape can be deduced by maximizing the entropy of the diblocks. Extending standard results from rubber elasticity theory to include the possibility of curvature as well as uniaxial stretch deformations, we derive a simple equation for the molecular entropy as a function of the microdomain geometry. Maximization of this expression leads to "preferred" or "spontaneous" curvatures (borrowing from the terminology of surfactant self-assembly), which the copolymer aggregates would adopt in the absence of further constraints. This geometry is *locally* optimal. However, the *global* requirements of uniform space filling may constrain the system. We analyze both of these constraints for the simplest system, which contains only linear diblock copolymer molecules of identical architecture. In this case, it is assumed that all the molecules in the self-assembled aggregate are deformed into an average shape characteristic of the microdomain geometry.

Any attempt to predict the optimal microdomain geometry is hampered by our inability to draw up a complete catalogue of surface form. Understanding of the variety of *global* surfaces is far from complete, and we cannot begin to derive a partition function which covers all possibilities. However, the full spectrum of *local* surface form can be realized by characterizing a surface in terms of its curvatures. Surface curvatures are related to the more intuitive notion of curvature of a planar curve as follows. The intersection of a plane containing the normal vector to the surface at a point and the surface is a normal section to the surface, which is a planar curve. As the plane is rotated about the axis defined by the normal vector, a family of planar curves are traced out. The "normal curvature" of any of these sections is equal to the inverse of the radius of the circle of best fit to the normal section. The maximum and minimum values of the normal curvatures of this family of curves are defined to be the

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® Abstract published in *Advance ACS Abstracts,* October 15, 1993.

0024-9297/93/2226-6782$04.00/0

principal curvatures of the surface at that point, denoted k_1 and k_2. Conventionally, we talk about the mean (H) and Gaussian (K) curvatures of a surface at a point, defined by the relations

$$H = (k_1 + k_2)/2; \qquad K = k_1k_2 \tag{1}$$

The broadest local classification of surfaces encompasses the three geometric classes: hyperbolic (saddle-shaped, negative Gaussian curvature, e.g. minimal surfaces), parabolic (zero Gaussian curvature, e.g. cylinders, planes), and elliptic (positive Gaussian curvature, e.g. spheres). Within each class, an infinity of surface structures occur. For example, ellipsoids are also elliptic surfaces, and Delaunay surfaces of revolution are parabolic. We confine our analysis to "homogeneous" surfaces, whose curvatures are constant everywhere on the surface. This approximation amounts to choosing spheres, planes, and cylinders only as structural candidates in the elliptic and parabolic geometrical classes, respectively. No hyperbolic surface of constant curvatures can be embedded in three-dimensional Euclidean space. We have argued elsewhere that the most nearly-homogeneous global realizations of hyperbolic interfaces involve mesh or bicontinuous strut geometries.[16]

Theory

Consider the aggregation properties of copolymers consisting of two blocks joined to form a linear diblock molecule. Assume that the two moieties—A and B—prefer total segregation from each other; they are immiscible, so the interface between A and B microphases is infinitely thin. (The Flory interaction parameter between A and B moieties, χ, is large.) Assume further that no interdigitation of the chains occurs.

An intuitive picture of the origin of curved interfaces in copolymer melts runs as follows. It is known that the copolymer molecules aggregate to form A and B regions whose densities are constant within each region (and close to the bulk density of each moiety). Thus, where the natural radius of gyration of A chains differs from that of the B chains, the copolymer molecules cannot form parallel planar layers of alternating A and B moieties while maintaining their preferred radii of gyration: the larger blocks can aggregate to form lamellae of uniform density, whereas the smaller blocks cannot (Figure 1a). If some stretching of the larger block (or compression of the smaller block) occurs perpendicular to the planar interface, close packing at uniform density can be achieved due to the accompanying decrease in the chain cross-sectional area (or, under compression, an increase), with equal cross-sectional areas for both A and B blocks at the AB interface (Figure 1b). Certainly, some alteration of cross-sectional area must occur to conserve the packing density of the chains.

This elongation/compression deformation results in a decrease of the chain entropy in the deformed blocks since these blocks have lost their original isotropic conformation. Some of this lost entropy can be restored by curving the interface, so that the effective stretch of the blocks is reduced (Figure 1c). The preferred (local) geometry is expected to be that which minimizes the net entropy loss of the stretching and bending deformations.

The statistical thermodynamics of polymer stretching has been thoroughly analyzed within the context of rubber elasticity theory.[17] We now derive the curvature contribution to the configurational entropy.

The cross-sectional area of each block at a distance x from the AB interface is equal to the area of the surface formed by parallel transport from that portion of the interface occupied by a single AB diblock molecule (Figure 2).

It is known from differential geometry that this area is equal to[16]

$$a_0(1 + 2H\xi + K\xi^2) \tag{2}$$

where a_0 is the interfacial area per molecule, ξ is the distance from the interface, and H and K denote the mean and Gaussian curvatures of the A–B interface, respectively.

Thus, the volume occupied by a slab of polymer of thickness ℓ from the interface and area a_0 measured at the interface is approximately

$$V = \int_0^\ell a_0(1 + 2H\xi + K\xi^2)\,\mathrm{d}\xi \tag{3}$$

where H and K now denote the average values of the mean and Gaussian curvatures over the interface.

Assume (for now) that the x, y axes are oriented parallel to the principal axes of curvature k_1 and k_2. If the chains are stretched by a factor of β along the z-axis (normal to the A–B interface), the affine transformation of the chain ends after stretching and bending about the x- and y-axes follows directly from the parallel surface construction, fixing the chain volumes. If the Cartesian coordinates of a chain end in its undeformed configuration is (x, y, z) and (x', y', z') denotes the coordinates of the end after stretching and ($x \rightarrow \beta^{-1/2}x$, $y \rightarrow \beta^{-1/2}y$, $z \rightarrow \beta z$) and (x'', y'', z'') the coordinates following stretching and bending, then

$$\begin{aligned} x'' &= x\beta_i^{-1/2} \pm k_1\beta_i^{1/2}zx \\ y'' &= y\beta_i^{-1/2} \pm k_2\beta_i^{1/2}zy \\ z'' &= \beta_i z \mp H\beta_i^2z^2 - \frac{K}{3}\beta_i^3z^3 \end{aligned} \tag{4}$$

These equations are accurate provided the curvatures of the interface (H and K) vary little compared with the area occupied by a single chain at the interface. The resulting expression for the free energy of the diblock as a function of the stretching and bending deformations is a straightforward generalization of rubber elasticity theory,[17] which gives a relative entropy change per chain at a temperature T of

$$S = -\frac{kT}{2}\left(\left(\frac{x''}{x}\right)^2 + \left(\frac{y''}{y}\right)^2 + \left(\frac{z''}{z}\right)^2 - 3\right)$$

In terms of the interfacial curvatures, the relative entropy of an i chain (i = A or B) as a function of the stretch and curvatures is then determined by the affine transformation defining stretching plus bending deformations (eq 4):

$$\Delta S_i = -kT\left\{\frac{1}{2\beta_i}[(k_1\gamma_i + 1)^2 + (k_2\gamma_i + 1)^2] + \frac{\beta_i^2}{2}\left[\left(1 + H\gamma_i + \frac{K\gamma_i^2}{3}\right)^{-2}\right]\right\} \tag{5}$$

where γ_i is equal to the stretched length of the ith block, $\beta_i(M_i/3)^{1/2}$. Note that the linear terms in the curvatures, k_1, k_2 and H, are positive if the interface is curved away from the i block domain, and negative otherwise.

The equation encapsulates the "frustration" inherent in copolymer self-assembly. The first bending term is minimized for each block when the interface is spherical—curved toward that block—of radius equal to the perpendicular radius of gyration of the block. The second

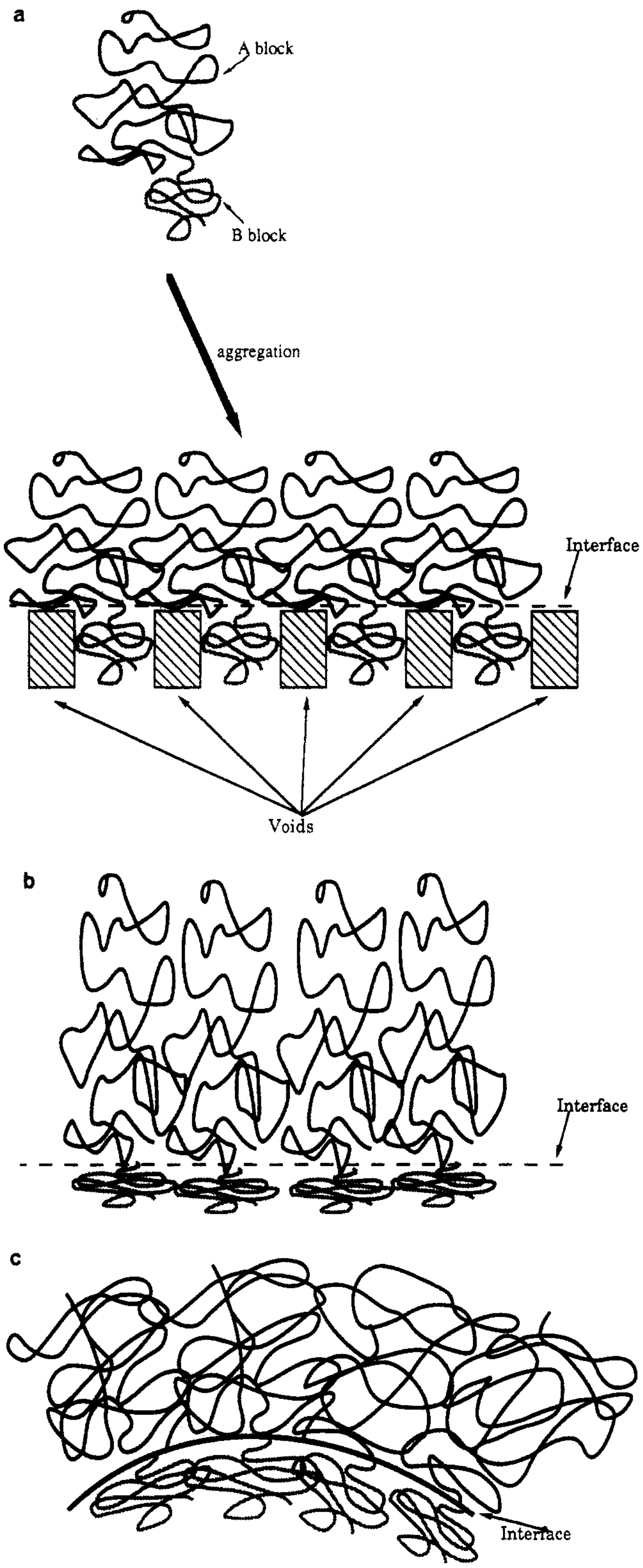

Figure 1. (a) Aggregation of linear diblocks of differing volume per block. In the absence of molecular deformation, the smaller block cannot aggregate at uniform density. (b) A uniaxial stretch/compression at constant volume of the bulkier/smaller block leads to uniform density aggregates. (c) Curvature of the interface allows the chains to restore some of their entropy lost under the stretching deformation.

term favors curvatures *away* from that block. The geometry of the preferred structure in a diblock assembly is further complicated by the fact that there are generically two different length scales in the system, γ_A and γ_B.

Equation 5 has been derived under the assumption that the Cartesian x- and y-axes are parallel to the principal directions of the curved interface. This assumption needs to be relaxed, in which case the curvature of the interface along the x- and y-axes are no longer the principal curvatures (k_1 and k_2, respectively), but the normal curvatures, k_{n_1} and k_{n_2}:

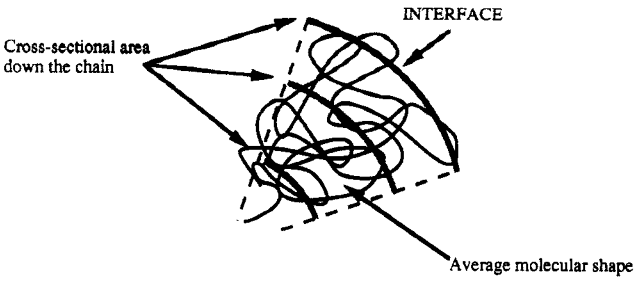

Figure 2. The variation of cross-sectional area along a molecular chain as a function of the interfacial curvatures.

$$k_{n_1} = k_1 \cos^2 \alpha + k_2 \sin^2 \alpha$$

$$k_{n_2} = k_2 \cos^2 \alpha + k_1 \sin^2 \alpha \qquad (6)$$

where α is the angle between the principal directions and the (x, y) coordinate axes.[18] If this angle is arbitrary (corresponding to no preferred orientation of the polymer blocks about the normal to the interface with respect to principal directions along the interface), eq 5 becomes

$$\frac{\Delta S_i}{kT} = -\left\{\frac{1}{2\beta_i}\left[(k_1\gamma_i + 1)^2 + (k_2\gamma_i + 1)^2 - \frac{(k_1\gamma_i - k_2\gamma_i)^2}{4}\right]\right\} - \frac{\beta_i^2}{2}\left(1 + H\gamma_i + \frac{K\gamma^2}{3}\right)^2 \qquad (7)$$

Local Results

Maximization of the entropy with respect to the principal curvatures alone gives the preferred local geometry. For convenience, we adopt γ (referring to the *larger* block) as our length scale and fix the magnitude of the stretch factor, β. Optimization of the molecular entropy with respect to the dimensionless curvatures $k_1\gamma$ and $k_2\gamma$ is straightforward under the assumption that $k_1\gamma$, $k_2\gamma \ll 1$ (small bending). To linear order in the curvatures, we obtain:

$$k_1\gamma = -\frac{AB(C+1)}{(A^2 + C)} \text{ and } k_2\gamma = -\frac{A^2B(C+1) + B}{C} \qquad (8)$$

where

$$A \equiv \frac{(\alpha^3 - 1)}{4\beta} - \frac{\beta^2}{12}(4(1 + \alpha^6) - 9(1 - \alpha^4))$$

$$B \equiv \frac{(\alpha - 1)}{\beta} + \left(\frac{\alpha^4 - 1}{2}\right)\beta^2$$

$$C \equiv \frac{3}{4\beta}(1 + \alpha^3) + \frac{3\beta^2}{4}(1 - \alpha^4); \qquad \alpha \equiv \left(\frac{\Phi_A}{1 - \Phi_A}\right)^{1/2}$$

and Φ_A is the volume fraction of the smaller block.

The magnitude of the entropy depends on the value of the stretch factor β, which cannot be optimized analytically. However, eq 8 can be calculated as a function of β, yielding the curvature of the A–B interface. Where the blocks are of equal volume ($\alpha = 1$) (and equal segment length), the optimal geometry consists of planar interfaces, as expected ($k_1\gamma = k_2\gamma = 0$). As one of the blocks increases its volume relative to the other block, $k_1\gamma$ and $k_2\gamma$ take on opposite signs, indicating the local preference for hyperbolic (saddle-

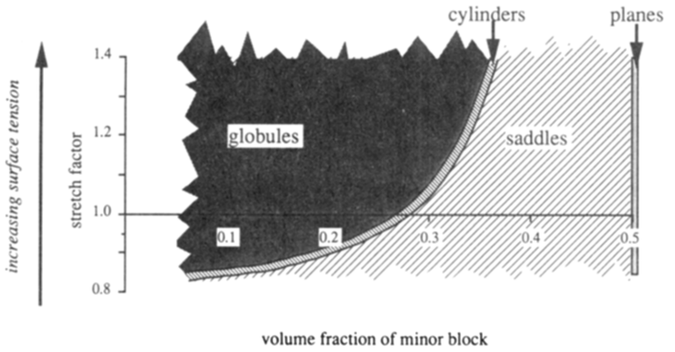

Figure 3. Regions of stability of elliptic globules (both principal curvatures of the same sign), parabolic cylinders (one vanishing curvature), hyperbola (both curvatures of opposite sign), and planes (both curvatures equal to zero).

shaped) interfaces. The extent of this hyperbolic geometry depends on the stretch factor. Roughly speaking, for low "surface tension" between the moieties (lower χ-parameters), this geometry extends from 50% up to about 70% by volume of the larger block ($\beta = 1$), shrinking to less than 10% of the composition range for more strongly segregated diblocks.

As the diblock become increasingly asymmetric, the interface becomes less hyperbolic, until one of the curvatures vanishes, at which point a parabolic geometry is preferred, such as cylinders. Beyond this critical point, elliptic geometries are preferred, leading to ellipsoids of the minor component, embedded in a continuous matrix of the larger block. This "phase diagram" is plotted in Figure 3.

These results suggest that the presence of hyperbolic interfaces in diblock copolymer assemblies is expected, provided the preferred local geometries can be extended throughout space. The preferred curvatures within the hyperbolic region of the phase diagram are interesting, and deserve closer analysis. The evolution of the locally preferred Gaussian and mean curvatures are plotted in Figure 4 for $\beta = 1$.

At a certain composition, the Gaussian curvature attains a minimum value, while the mean curvature exhibits a maximum within the region. This behavior suggests that the *topology* of the interface—which is dependent on the Gaussian curvature—is likely to vary throughout the hyperbolic region, becoming more complex as the Gaussian curvature becomes more negative. We have argued elsewhere that the most homogeneous hyperbolic geometries are those of the square and hexagonal mesh surfaces (genus 2) or the cubic genus 3 triply periodic minimal surfaces ("strut" surfaces).[16] The preferred variation of Gaussian curvature could be realized by the phase sequence mesh → strut → mesh with increasing molecular asymmetry, although more detailed calculations are necessary before more definitive conclusions can be drawn.

Global Calculations

In order to compute the relative stability in the presence of global constraints, some further analysis is required. For computational reasons, it is most convenient to express the stretch parameter for both A and B blocks β_i in terms of the width of a single layer of the ith block, t_i, and a "shape parameter", s_i. This parameter has been widely used to characterize the molecular shapes of surfactant molecules, and has proved to be useful in modeling surfactant self-assembly. We define this shape parameter in terms of the dimensions of the blocks: $s_i = M_i/\sigma_i t_i$, where σ_i denotes the area per molecule at the interface. In terms of the local curvatures of the interface: $s \equiv 1 + Ht_i + Kt_i^2/3$.[19] If σ_0 is the area *in the absence of stretching*, the stretch factor can then be written as $\beta_i = \sigma_0 s_i t_i/M_i$. Since the ratio of the block volume to the width of the block layer without any stretching, $(M_i/3)^{1/2}$, is σ_0, we obtain $\beta_i = 3^{1/2} s_i t_i/M_i^{1/2}$ and $\gamma_i = s_i t_i$.

A realistic expression for the relative free energy per diblock molecule must include a surface energy term, which we treat phenomenologically, introducing a surface tension (in units of kT per unit area), τ. Including entropic and surface energy terms gives the following approximate expression for the free energy change accompanying the deformation per diblock:

$$\frac{\Delta F}{kT} = \frac{\tau M_i}{s_i t_i} + \sum_{i=\mathrm{A}}^{\beta}\Bigg\{\Bigg\{\frac{\alpha_i}{2 s_i t_i}\Bigg\}\Bigg[(s_i k_1 t_i + 1)^2 + \left(s_i\left(\frac{k_1}{k_2}\right)k_1 t_i + 1\right)^2 - \frac{1}{4}(s_i k_1 t_i)^2\left(1 - \frac{k_2}{k_1}\right)^2\Bigg] + \frac{(s_i t_i)^2}{2\alpha_i^2}\left[1 + s_i H t_i + \frac{s_i^2 K t_i^2}{3}\right]\Bigg\} \tag{9}$$

where $\alpha_i \equiv (M_i/3)^{1/2} = \gamma_i/\beta_i$. The complete expression for diblock molecules is given by noting that the curvatures are of opposite sign with respect to each block and inserting appropriate scaling for the different blocks:

$$\frac{M_\mathrm{A}}{M_\mathrm{B}} = \frac{\Phi_\mathrm{A}}{\Phi_\mathrm{B}} \text{ and } \frac{t_\mathrm{A}}{t_\mathrm{B}} = \left(\frac{M_\mathrm{A}}{M_\mathrm{B}}\right)^{1/2}$$

The characteristics of the B block can be expressed in terms of the A block and the composition:

$$\frac{s_\mathrm{B}}{s_\mathrm{A}} = \frac{M_\mathrm{B}}{t_\mathrm{B}}\frac{M_\mathrm{A}}{t_\mathrm{A}} = \left(\frac{\Phi_\mathrm{B}}{\Phi_\mathrm{A}}\right)^{1/2}\frac{s_\mathrm{B}}{s_\mathrm{A}} = \frac{M_\mathrm{B}}{t_\mathrm{B}}\frac{M_\mathrm{A}}{t_\mathrm{A}} = \left(\frac{\Phi_\mathrm{B}}{\Phi_\mathrm{A}}\right)^{1/2} \text{ and } s_\mathrm{B} t_\mathrm{B} = s_\mathrm{A} t_\mathrm{A}\frac{\Phi_\mathrm{B}}{\Phi_\mathrm{A}}$$

The free energy per molecule can now be expressed in terms of the composition, the shape parameters, the surface tension, and interfacial curvatures:

$$\left(\frac{\Delta F}{NkT}\right)_\mathrm{AB} = \frac{\tau M_\mathrm{A}}{s_\mathrm{A} t_\mathrm{A}} + \frac{\alpha_\mathrm{A}}{2 s_\mathrm{A} t_\mathrm{A}}\Bigg\{\Bigg[(s_\mathrm{A}(k_1 t_\mathrm{A}) + 1)^2 + \left(s_\mathrm{A}\left(\frac{k_2}{k_1}\right)(k_1 t_\mathrm{A}) + 1\right)^2 - \frac{1}{4}(s_\mathrm{A}(k_1 t_\mathrm{A}))^2\left(1 - \frac{k_2}{k_1}\right)\Bigg] + \left(\frac{\Phi_\mathrm{A}}{\Phi_\mathrm{B}}\right)^{1/2}\Bigg[\left(1 - \frac{\Phi_\mathrm{B}}{\Phi_\mathrm{A}}s_\mathrm{A}(k_1 t_\mathrm{A})\right)^2 + \left(1 - \frac{\Phi_\mathrm{B}}{\Phi_\mathrm{A}}s_\mathrm{A}(k_1 t_\mathrm{A})\frac{k_2}{k_1}\right)^2 - \frac{1}{4}\left(\frac{\Phi_\mathrm{B}}{\Phi_\mathrm{A}}s_\mathrm{A}(k_1 t_\mathrm{A})\right)^2\left(1 - \frac{k_2}{k_1}\right)^2\Bigg]\Bigg\} + \frac{(s_\mathrm{A} t_\mathrm{A})^2}{2\alpha_\mathrm{A}^2}\Bigg\{\Bigg(1 + s_\mathrm{A}(H t_\mathrm{A}) + s_\mathrm{A}^2\frac{(K t_\mathrm{A}^2)}{3}\Bigg)^{-2} + \left(\frac{\Phi_\mathrm{B}}{\Phi_\mathrm{A}}\right)\Bigg(1 - \frac{\Phi_\mathrm{B}}{\Phi_\mathrm{A}}s_\mathrm{A}(H t_\mathrm{A}) + \left(\frac{\Phi_\mathrm{B}}{\Phi_\mathrm{A}}s_\mathrm{A}\right)^2\frac{(K t_\mathrm{A}^2)}{3}\Bigg)^{-2}\Bigg\} \tag{10}$$

Equation 10 has the form

$$\frac{\Delta F}{NkT} = \frac{c_1}{t_\mathrm{A}} + \frac{c_2}{t_\mathrm{A}} + c_3 t_\mathrm{A}^2 \tag{11}$$

c_1, c_2, and c_3 involve the surface tension, τ, molecular composition, Φ_A, and the geometric parameters $s_\mathrm{A}(k_1 t_\mathrm{A})$ and k_2/k_1, all of which are characteristic of the geometry of the curved interface.

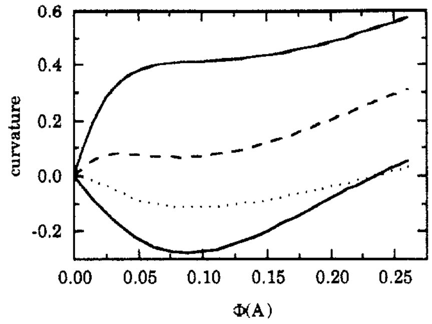

Figure 4. The variation of the principal curvatures (solid lines), the Gaussian curvature (dotted line), and the mean curvature (dashed line) as a function of the molecular composition for $\beta = 1$.

Table I. Geometric Data for Homogeneous Surfaces (Constant Curvatures) within the Parabolic, Elliptic, and Hyperbolic Geometric Classes, Assuming Block A Is the Smaller Block

surface	k_1t_A	k_2/k_1	Ht_A	Kt_A	s_A
planes	0	1	0	0	1
cylinders	-1	0	-1/2	0	1/2
spheres	-1	1	-1	1	1/3
saddles	-1	$3 - 6s_A$	$3s_A - 2$	$3 - 6s_A$	$s_A = 0.50 - 0.02\Phi_A + 1.09\Phi_A{}^2 - 3.97\Phi_A{}^3 + 6.40\Phi_A{}^4$ ($\Phi_A < 0.5$) $s_A = 48.3 - 304.7\Phi_A + 726.5\Phi_A{}^2 - 769.2\Phi_A{}^3 + 308.6\Phi_A{}^4$ ($\Phi_A > 0.5$)

Minimization of the free energy as a function of the A-block thickness, t_A, yields

$$t_{\min} = \left(\frac{c_1 + c_2}{2c_3}\right)^{1/3} \tag{12}$$

The relative stability of the various microphase geometries as a function of molecular composition can be determined numerically by inserting the values of the composition, and the geometric parameters relevant to the geometry under consideration into the expression for c_1, c_2, and c_3. The optimal thickness, $t_{\min}$ is calculated from eq 12 and inserted in eq 10 to give the free energy.

Global Geometric Data

The relevant geometric data for homogeneous elliptic, parabolic and hyperbolic forms are collected in Table I. The details of the entries for hyperbolic surfaces are discussed in the Appendix. The magnitudes of the variables c_1, c_2, and c_3 can be calculated from the relevant entries in Table I. The resulting relative free energies can then be computed as a function of the diblock composition using eq 10 and 12.

Laminar Interfaces

These calculations can be generalized to cover a broader range of aggregate geometries by considering multilayer "laminations" of various geometries. Instead of a single interface of hydrobolic, parabolic, or elliptic geometry, a lamination consists of a stack of parallel sheets, lining the imaginary surface. Thus, a lamination of the sphere results in an onionlike liposome. A "double lamination" of the D-surface—a triply periodic minimal surface which divides space into two equivalent intertwined diamond labyrinths—yields the bicontinuous morphology characteristic of the OBDD or tetrapod phase. This lamination results in two interpenetrating networks consisting of A blocks, separated by a continuum of B blocks.

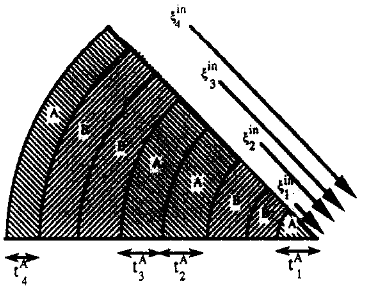

Figure 5. Local geometry of a multilayered lamination of a curved interface.

Suppose, without loss of generality, that the innermost block (i.e. the block with the highest curvatures) in the laminar collective consists of the A moiety of the diblock molecule. If the number of laminations is even, the outermost block is also the A moiety. The local structure consists of diblock molecular aggregates, stacked end-to-end (Figure 5).

In order to minimize the interfacial area between different blocks, the stacking sequence is expected to be AB BA AB BA, rather than AB AB AB. The relative volumes of diblocks in each lamina (ϕ_1, ϕ_2, ϕ_3, from innermost to the outermost block) are free to vary; they will be set by minimization of the collective free energy. Consider the yth interface separating A and B blocks. This interface splits space into two regions. The volume fraction of the inner region is given by $\Phi_y^{in} = \sum_{i=1}^{y-1}\phi_i + \phi_y\Phi_k$, where k = A if y is an odd number, and k = B otherwise. Note that $\sum_{i=1}^{n}\phi_i = 1$.

For laminations of spheres, cylinders, planes, or saddles, the shape parameter of the entire inner volume to one side of this interface (s_y^{in}) is given by the relevant entry in Table I (where Φ_A is replaced by Φ_y^{in} in the case of saddles). Similarly, the values of the dimensionless curvatures $(H\xi)_y^{in}$, $(K\xi)_y^{in}$ and $(k_1\xi)_y^{in}$, $(k_2\xi)_y^{in}$, where ξ^{in} denotes the distance from the yth-interface to a center of curvature can be read from Table I.

The width of the yth A-block layer (t_y^A) is related to the width of the entire inner region (ξ_y^{in}) and the mean and Gaussian curvatures of the yth A–B interface (H_y and K_y, respectively) by standard equations derived from the differential geometry of parallel surfaces:

$$\frac{t_y^A\left(1 + (-1)^{y+1}H_y t_y^A + \frac{1}{3}K_y (t_y^A)^2\right)}{\xi_y^{in}\left(1 + H_y\xi_y^{in} + \frac{1}{3}K_y(\xi_y^{in})^2\right)} = \frac{\phi_y\Phi_A}{\Phi_y^{in}} \tag{13}$$

This equation can be rewritten as a cubic polynomial:

$$\frac{1}{3}K_y(\xi_y^{in})^2\left(\frac{t_y^A}{\xi_y^{in}}\right)^3 + (-1)^{y+1}H_y\xi_y^{in}\left(\frac{t_y^A}{\xi_y^{in}}\right)^2 + \left(\frac{t_y^A}{\xi_y^{in}}\right) = \frac{\phi_y\Phi_k}{\Phi_y^{in}}s_y^{in} \tag{14}$$

Equation 14 can be solved for (t_y^A/ξ_y^{in}) assuming laminar stacks of spheres, planes, cylinders, and saddles with the help of Table I.

The shape parameter of A block molecules in the yth layer is given by

$$s_y^A = 1 + (-1)^{y+1}H_y\xi_y^{in}\left(\frac{t_y^A}{\xi_y^{in}}\right) + \frac{1}{3}K_y(\xi_y^{in})^2\left(\frac{t_y^A}{\xi_y^{in}}\right)^2 \tag{15}$$

The values of $k_1t_y^A$ and k_2/k_1 are equal to the relevant values of k_1t_A and k_2/k_1 (Table I) multiplied by t_y^A/ξ_y^{in}. The entropic contribution to the relative free energy of the yth layer is given by:

$$
\begin{aligned}
\left(\frac{\Delta F}{Nkt}\right)_y = \frac{\tau M_{\mathrm{A}}}{s_y^{\mathrm{A}} t_y^{\mathrm{A}}} + \frac{\alpha_{\mathrm{A}}}{2 s_y^{\mathrm{A}} t_y^{\mathrm{A}}}\Bigg\{\Bigg[\Bigg(s_y^{\mathrm{A}}\bigg(k_1\xi_y^{\mathrm{in}}\bigg(\frac{t_y^{\mathrm{A}}}{\xi_y^{\mathrm{in}}}\bigg)\bigg)+1\Bigg)^2 + \\
\Bigg(s_y^{\mathrm{A}}\bigg(\frac{k_2}{k_1}\bigg)\bigg(k_1\xi_y^{\mathrm{in}}\bigg(\frac{t_y^{\mathrm{A}}}{\xi_y^{\mathrm{in}}}\bigg)\bigg)+1\Bigg)^2 - \\
\frac{1}{4}\Bigg(s_y^{\mathrm{A}}\bigg(k_1\xi_y^{\mathrm{in}}\bigg(\frac{t_y^{\mathrm{A}}}{\xi_y^{\mathrm{in}}}\bigg)\bigg)\Bigg)^2\bigg(1-\frac{k_2}{k_1}\bigg)^2\Bigg] + \\
\bigg(\frac{\Phi_{\mathrm{A}}}{\Phi_{\mathrm{B}}}\bigg)^{1/2}\Bigg[\Bigg(1-\frac{\Phi_{\mathrm{B}}}{\Phi_{\mathrm{A}}}s_y^{\mathrm{A}}\bigg(k_1\xi_y^{\mathrm{in}}\bigg(\frac{t_y^{\mathrm{A}}}{\xi_y^{\mathrm{in}}}\bigg)\bigg)\Bigg)^2 + \\
\Bigg(1-\frac{\Phi_{\mathrm{B}}}{\Phi_{\mathrm{A}}}s_y^{\mathrm{A}}\bigg(k_1\xi_y^{\mathrm{in}}\bigg(\frac{t_y^{\mathrm{A}}}{\xi_y^{\mathrm{in}}}\bigg)\bigg)\frac{k_2}{k_1}\Bigg)^2 - \\
\frac{1}{4}\Bigg(\frac{\Phi_{\mathrm{B}}}{\Phi_{\mathrm{A}}}s_y^{\mathrm{A}}\bigg(k_1\xi_y^{\mathrm{in}}\bigg(\frac{t_y^{\mathrm{A}}}{\xi_y^{\mathrm{in}}}\bigg)\bigg)\Bigg)^2\bigg(1-\frac{k_2}{k_1}\bigg)^{-2}\Bigg]\Bigg\} + \\
\frac{(s_y^{\mathrm{A}} t_y^{\mathrm{A}})^2}{2\alpha_{\mathrm{A}}^2}\Bigg\{\Bigg(\bigg(1+s_y^{\mathrm{A}}\bigg(H\xi_y^{\mathrm{in}}\bigg(\frac{t_y^{\mathrm{A}}}{\xi_y^{\mathrm{in}}}\bigg)\bigg) + \\
(s_y^{\mathrm{A}})^2\frac{\bigg(K(\xi_y^{\mathrm{in}})^2\bigg(\frac{t_y^{\mathrm{A}}}{\xi_y^{\mathrm{in}}}\bigg)^2\bigg)}{3}\Bigg)^{-2} + \\
\bigg(\frac{\Phi_{\mathrm{B}}}{\Phi_{\mathrm{A}}}\bigg)\Bigg(1-\frac{\Phi_{\mathrm{B}}}{\Phi_{\mathrm{A}}}s_y^{\mathrm{A}}\bigg(H\xi_y^{\mathrm{in}}\bigg(\frac{t_y^{\mathrm{A}}}{\xi_y^{\mathrm{in}}}\bigg)\bigg) + \\
\bigg(\frac{\Phi_{\mathrm{B}}}{\Phi_{\mathrm{A}}}s_y^{\mathrm{A}}\bigg)^2\frac{\bigg(K(\xi_y^{\mathrm{in}})^2\bigg(\frac{t_y^{\mathrm{A}}}{\xi_y^{\mathrm{in}}}\bigg)^2\bigg)}{3}\Bigg)^{-2}\Bigg\}
\end{aligned}
\tag{16}
$$

Although eq 16 appears formidable, it is no more than the analogue of eq 10 with the lengths scaled by the width of the yth layer. The complete expression for the entropic contributions to the free energy is given by

$$
\frac{F}{Nk_{\mathrm{B}}T} = \sum_{i=1}^{n}\left[\frac{c_1{}^i}{t_y^{\mathrm{A}}} + \frac{c_2{}^i}{t_y^{\mathrm{A}}} + c_3{}^i(t_y^{\mathrm{A}})^2\right] \tag{17}
$$

where $c_1{}^i$, $c_2{}^i$, and $c_3{}^i$ are given by the relevant expressions in eq 16, related to c_1, c_2, and c_3 found from eqs 10 and 11. The most favorable state for a lamination of n layers can be found with elliptic, parabolic, and hyperbolic geometries by inserting $\sum_{i=1}^{n} c_1{}^i, c_2{}^i, c_3{}^i$ in place of c_1, c_2, and c_3 in eq 11.

Results

The free energy curves are shown in Figure 6a,b,c for scaled surface tensions of 0, 20, and 50 for spheres, cylinders, planes, and hyperbolic structures. The results for laminae are reported only for the case of a two-layer lamination (a "bilayer") on a hyperbolic surface. (In the other cases, the results differ little from those for single layers.)

The most noticeable difference between these results and the relative stabilities expected in the absence of global constraints is the virtual disappearance of the hyperbolic phase. Under the global constraints imposed by the copolymer system, hyperbolic monolayers are very unstable relative to the other geometries. The lamination calculation for bilayers suggests that the free energy is minimized for equal volume fractions within each lamination ($\phi_1 = \phi_2 = 1/2$). By symmetry then, the mean curvature at the midlayer of the B region vanishes, and the structure can be described by a minimal surface. This geometry is of similar stability to the spherical and cylindrical phases when the minor block occupies about 35% of the molecular volume. In contrast to the local calculations, the stability of this symmetric bicontinuous phase is further reduced at low surface tensions.

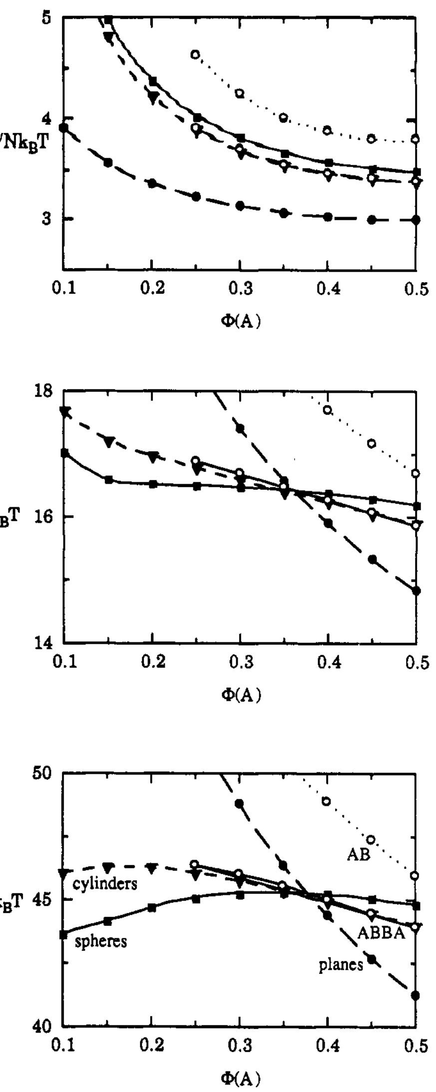

Figure 6. Relative free energies of linear diblock aggregates as a function of molecular composition. From top to bottom the curves are for scaled surface tensions of 0, 20, and 50, respectively. The curves are computed for spheres (filled squares), cylinders (filled nablas), planes (filled circles), hyperbolic monolayers (open circles, dotted curve), and hyperbolic bilayers (open circles, full curve). The last case is found by summing over a two-layer lamination.

Conclusions

It is clear from these calculations that the formation of hyperbolic copolymer phases is theoretically favorable, at least in the absence of global constraints. In practical terms, this suggests that hyperbolic phases—be they bicontinuous "strut" or "mesh" (also known as "lamellar catenoid"[10]) phases—can be induced in a system by addition of extra components, such as neutral solvents or homopolymers. These added components play the microscopic role of "fillers", so that the copolymer diblocks are able to adopt their (local) preferred geometry, which is indeed hyperbolic over a wide variety of diblock molecular compositions.

The global geometry of these hyperbolic phases is dependent on the relative bending energies of mesh and bicontinuous phases, which depends on their relative homogeneities. Recent calculations suggest that the triply-periodic minimal surface known as the "D-surface" is an optimal bicontinuous form for a monodisperse system, which consists exclusively of a single copolymer architecture. The D-surface has a lower bending energy than other triply periodic minimal surfaces. Further, its "global homogeneity" is superior to other surfaces, with the narrowest distribution of tunnel radii (X. Zhang and S. T. Hyde, in preparation). In both reports of a bicontinuous phase in diblock (linear and star) copolymers, it has been suggested that the structure consists of two interpenetrating diamond networks of A blocks, separated by a continuous matrix of B blocks (where B is the larger component).[11,12] Such a proposal is equivalent to one layer of AB molecules on either side of the D-surface (with the free B block ends on the minimal surface). This geometry is thus a reasonable one for monodisperse systems. However, developments in related surfactant-water systems suggest to us that other global geometries will be found in the future. The most likely candidates are the triply-periodic surfaces known as the gyroid and P-surfaces, as well as rhombohedral distortions of these surfaces. A wide variety of more exotic forms are available. Ironically, since these other mesh and strut architectures are less homogeneous, their formation may require a polydisperse distribution of molecules. In principle then, we expect hyperbolic phases to be relatively common in "dirty" systems, such as those formed industrially. This may be one area of science which does not profit from careful laboratory studies of monodisperse systems alone.

Acknowledgment. We express our thanks to Prof. Hashimoto and Dr. Hasegawa of Kyoto University for their support for this project. While the shortcomings of this analysis are our own, their profound understanding of copolymer self-assembly has helped us immeasurably. We are also very grateful to Prof. Kawasaki, of Kyushu University, for a critical reading of this manuscript. One of us (S.T.H.) thanks the Australian Government for a Japan-Australian DITAC grant.

Appendix

The geometric relations for homogeneous hyperbolic interfaces can be derived from the theory of parallel surfaces. Under the assumption of homogeneity, the inner and outer volumes created by the surface can be densely filled (without overlap) by one-parameter families of parallel surfaces swept out on either side of the interface. Thus, if the radius of curvature of the subvolume created on one side of the hyperbolic interface is t, the area of the parallel surface displaced from the interface by distance t is zero. We use the equations expressing the shape parameter in terms of the interfacial curvatures and describe the radius of curvature as the distance from the surface at which the area of a parallel surface to the interface vanishes:

$$s_A = 1 + Ht_A + \frac{Kt_A^2}{3} \text{ and } 1 + 2Ht_A + Kt_A^2 = 0 \qquad \text{(A.1)}$$

Since one of the radii of curvature is equal to the thickness, $k_1 t_A = -1$. These equations imply

$$Ht_A = 3s_A - 2; \quad Kt_A = 3 - 6s_A; \quad \frac{k_2}{k_1} = 3 - 6s_A \qquad \text{(A.2)}$$

Since the interface is saddle-shaped, the outer thickness, t_B, must be equal to the outer radius of curvature of the interface, $1/k_2$:

$$s_B = 1 - Ht_B + \frac{Kt_B^2}{3}; \quad 1 - 2Ht_B + Kt_B^2 = 0 \qquad \text{(A.3)}$$

The composition can then be related to the shape parameters of both blocks:

$$\Phi_B = \frac{s_B}{s_B + s_A}$$

which means that

$$\Phi = \frac{s_A}{s_A + \dfrac{3s_A - 4/3}{(6s_A - 3)^2}} \qquad \text{(A.4)}$$

This can be inverted to give the approximate equations listed in Table I, found by least-squares quartic-polynomial fitting to eq A.4. Two fits have been made, one for $\Phi < 1/2$, another for $\Phi > 1/2$.

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