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Stability of a Catenoid-Lamellar Phase for Strongly Stretched Block Copolymers

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Block copolymers are fascinating materials that are capable of forming spatially periodic structures on the 100-Å scale, whose symmetry properties and lattice constants can be tailored by controlled synthesis.[1] In spite of extensive study for several decades, however, the phase diagram of even the simplest block copolymer melt, a flexible diblock copolymer, is not fully understood.[2] Indeed, as recently as 1986 a new equilibrium phase [the ordered-bicontinuous-double-diamond (OBDD) phase] was definitively identified[3,4] in styrene–isoprene diblock copolymers.

The OBDD phase belongs to the space group *Pn*3*m* and its unit cell is believed to be bisected by a connected triply periodic area-minimizing surface[5–7] that has approximately constant mean curvature (CMC). This bicontinuous phase, which is found at copolymer compositions intermediate between those for which lamellar and cylindrical phases are observed, had not been anticipated theoretically. After its discovery, Anderson and Thomas[7] used the method of Ohta and Kawasaki[8] to estimate the free energy of the OBDD structure but were not successful in predicting its stability relative to cylinders and lamellae. They found, however, that the degree of metastability was minimized in the composition range where the structure is observed. Furthermore, their work suggests that other classes of area-minimizing structures could be candidates for equilibrium microphases in block copolymers.[9]

Recently, Almdal et al.[10] presented small-angle neutron scattering and rheological data on a poly(ethylenepropylene)–poly(ethylethylene) (PEP–PEE) diblock copolymer with a nominal composition of 35% PEE. They convincingly demonstrated the existence of four different phases (in a one-component sample!) that can be accessed by changing temperature. One of the new phases they observed was produced by heating a shear-oriented lamellar phase. Curiously, the original long-range-ordered lamellar structure was recovered on subsequent cooling. Among the structures proposed for this new phase was a monocontinuous, catenoid-lamellar assembly, in which the lamellae of the minor component (PEE) are perforated by catenoid-like tubes of PEP (Figure 1a). The experiments, however, were not able to establish the symmetry of the tube packing in the perforated planes. Unlike other catenoid-lamellar structures that have been proposed in block copolymers and microemulsions,[6,11] only one of the components is three-dimensionally continuous (PEP) in the structure of ref 10.

The experiments on PEP–PEE were carried out in a temperature range in which the copolymer chains are stretched,[12] but the asymptotic (low temperature–large molecular weight) scaling forms for the lattice constants and radii of gyration are not achieved. Accurate estimation of the free energy for the catenoid-lamellar (CL) structure in this regime is complicated by such incomplete chain deformation and by the necessity of including the effects of order parameter fluctuations.[13,14] However, we can easily estimate the free energy of the CL structure in the so-called "strong-segregation limit" (SSL) of low temperature and high molecular weight. This calculation should indicate whether the new phase suggested by Almdal et al. can be found in more typical systems with less compatible blocks, e.g., styrene–butadiene diblock copolymers. Moreover, it will serve as a benchmark calculation of the free energy for an area-minimizing microphase in which the principal radii of curvature have mixed signs. The present paper reports on such a calculation.

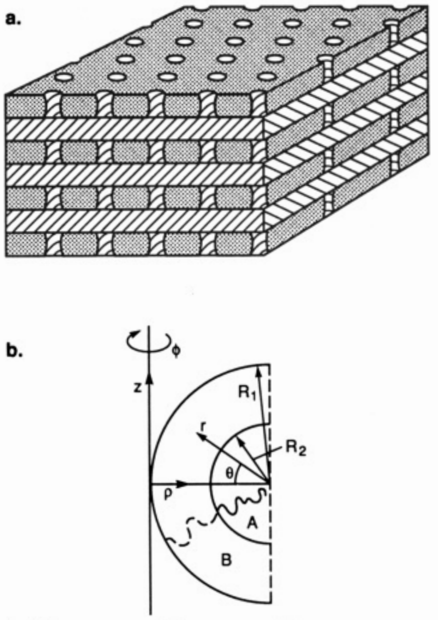

Figure 1. (a) Structure of the catenoid-lamellar phase proposed in ref 10. The minor component (dotted) is perforated by catenoid-like tubes (of the major component) that bridge lamellae. We expect that the tubes are packed hexagonally within the lamellae, although neither this packing nor the registry of the tube lattices in successive lamellar layers has been established experimentally. (b) Spherical approximation for the Wigner–Seitz cell of the catenoid-lamellar phase. The cell is defined as the body of revolution about the z axis of the region bounded by the circular arc of radius R_1. The portion of the cell occupied by A monomers is the half-torus bounded by the circular arc of radius R_2. We employ both the cylindrical coordinate system (ρ,ϕ,z) and the orthogonal system (r,θ,ϕ) in the present calculations.

We employ the conventional AB diblock copolymer used in the literature:[13–15] each chain consists of N monomers, Nf of them being of type A. The A and B monomers are taken to be the same size and shape, with volume v and statistical segment length b; hence, f is also the volume fraction of component A. Effects associated with structural asymmetries will be considered elsewhere. To simplify the subsequent analysis we shall restrict consideration to $f \le {}^1/_2$ (A is the minority component) and exploit symmetry under interchange of A and B to obtain expressions for $f > {}^1/_2$. Furthermore, the energetics of A–B contacts will be described by the conventional Flory χ parameter.

In the above model, the order–disorder transition (for $f \approx {}^1/_2$) occurs at[13,15] $\chi N \sim 10$. Here we shall be concerned with the SSL, which corresponds to $\chi N \gg 10$. Under such conditions, the interfaces between A and B microdomains are narrow,[16] of characteristic width $b\chi^{-1/2}$, while the microdomain period scales asymptotically for $\chi N \rightarrow \infty$ as[17] $b\chi^{1/6}N^{2/3}$, indicating substantial chain deformation normal to the interfaces.

In the present paper we employ the method of Semenov[17] to estimate the free energy of the postulated CL phase in the SSL and compare it with the free energies of the lamel-

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lar, cylindrical, and spherical phases, already calculated in ref 17. Semenov demonstrated that a simple analytical treatment is possible for $\chi N \rightarrow \infty$, where the Schrödinger-like equation describing copolymer configurations[16] reduces to a classical evolution equation.[17,18] For consistency with Semenov's calculations, we make a spherical approximation for the Wigner–Seitz cell of the CL phase. This cell corresponds to the body of revolution (about the z axis) shown in Figure 1b. Replicas of the cell are to be stacked vertically (along z) to build up the quasi-long-ranged lamellar order and in the (ρ,ϕ) plane to densely pack the "catenoids" (hexagonally). It should be noted that the A–B interface in Figure 1b is *toroidal*, i.e., not of CMC. A CMC surface, such as the catenoid, would possess less interfacial area per unit volume, but at the expense of more chain deformation (and deformation nonuniform in θ).[9] In the absence of more detailed structural information about the CL phase, we feel that the spherical approximation is justified.

The SSL free energy of the body of revolution in Figure 1b can be easily estimated by following Semenov.[17] In the SSL, the free energy per Wigner–Seitz cell, F, can be decomposed into contributions from the A "core" region, the B "corona" region, and the interfacial region as $F = F_A + F_B + F_I$. The interfacial contribution is simply the product of the interfacial tension, $\gamma \sim k_B T \chi^{1/2} b^{-2}$ (composition independent), with the area of the interface of revolution in Figure 1b:

$$F_I = 2\gamma\pi R_2(\pi R_1 - 2R_2) \tag{1}$$

To facilitate the calculation of the core and corona energies, we note that the differential volume of revolution for a shell of thickness dr located at r in Figure 1b is

$$dV = 2\pi(\pi R_1 r - 2r^2)\,dr \equiv S_{CL}(r)\,dr \tag{2}$$

In the *core* region, the elastic (stretch) free energy can be computed *exactly*, provided that there is no "dead zone", i.e., (finite) region where A-block ends are found with zero probability.[19,20] We shall see below that the condition for a dead zone to exist is[21] $R_2/R_1 > \pi/4 \approx 0.785$. However, in the composition range of interest ($f \le {}^1/_2$) it can be easily shown that $R_2/R_1 \le 0.626$ (see after eq 10). Hence, there is no dead zone to contend with and our subsequent calculation of the core elastic energy is exact. Proceeding, we note that $S_{CL}(r)$ given by eq 2 can be decomposed as

$$S_{CL}(r) = \frac{\pi R_1}{L} S_2(r) - S_3(r) \tag{3}$$

where $S_2(r) = 2\pi r L$ and $S_3(r) = 4\pi r^2$ are the surface areas of radius-r cylinders (with length L and neglecting ends) and spheres, respectively. Because of the linearity of the integral equation in ref 17 that determines the distribution of A ends in the core, the end distribution function for the CL phase, $g_{CL}(r)$, is related to those for cylinders and spheres as in eq 3, $g_{CL}(r) = (\pi R_1/L)g_2(r) - g_3(r)$. It follows that the core free energy is similarly related to those for cylinders and spheres:

$$F_{A,CL} = (\pi R_1/L)F_{A,2} - F_{A,3} \tag{4}$$

Substituting Semenov's results for the cylinder and sphere core energies, we find

$$F_{A,CL} = \frac{k_B T \pi^3 R_1^{\,5} \alpha^4(\pi - 4\alpha/5)}{16 b^2 N^2 f^2 v} \tag{5}$$

where $\alpha \equiv R_2/R_1$. Finally, to test for a dead zone we insert the formulae for $g_2(r)$ and $g_3(r)$ derived in ref 17 into the above expression for $g_{CL}(r)$. It is easily verified that this end density is nonnegative provided that $\alpha < \pi/4$.

In the corona (B) region, we assume the existence of a dead zone and adopt the approximation of Semenov, namely, constrain the B-block ends to lie at the outer circular arc of radius R_1 in Figure 1b. As the B region is predominantly of negative mean curvature for $f < {}^1/_2$, this should be an adequate approximation.[20] We note that the corona free energy calculated in this manner is an upper bound (but presumably a close one) to the elastic energy of the B region in Figure 1b. However, because of the spherical approximation to the Wigner–Seitz cell it is difficult to say whether our estimate is a rigorous upper bound to the corona energy in the actual CL structure.

Proceeding with the calculation of the corona free energy, it follows that

$$F_{B,CL} = \frac{3Q k_B T}{2b^2} \int_{R_2}^{R_1} dr \left[\frac{dr}{dn}\right] \tag{6}$$

where the number of chains in the cell is denoted Q and dr/dn is the local rate of chain deformation at r. These quantities are obtained by demanding that the corona be filled at the uniform melt density; hence

$$Q = \frac{\pi(3\pi - 4)R_1^{\,3}}{3vN} \tag{7}$$

$$\frac{dr}{dn} = \frac{vQ}{S_{CL}(r)} \tag{8}$$

Performing the integral in eq 6, we obtain

$$F_{B,CL} = \frac{k_B T(3\pi - 4)^2 R_1^{\,5}}{12 b^2 v N^2} \ln\left[\frac{\pi/\alpha - 2}{\pi - 2}\right] \tag{9}$$

It remains to collect the three free energy contributions, divide by the cell volume $\int_0^{R_1} dr\, S_{CL}(r)$ to obtain a free energy density, and then minimize with respect to R_1. This minimization is to be done at fixed $\alpha = R_2/R_1$, since R_2 must be chosen to ensure that the core volume fraction is identically f. The latter constraint leads to $\alpha = \alpha(f)$ being given as the physical root of

$$4\alpha^3 - 3\pi\alpha^2 + (3\pi - 4)f = 0 \tag{10}$$

which has the limits $\alpha(0) = 0$, $\alpha(0.5) = 0.62604$. After minimization, the free energy density of the CL phase is conveniently expressed in units of the lamellar phase free energy density, since the latter is composition independent.[17] Hence, we define $G_{CL} = F_{CL}/F_1$, where F_1 is the lamellar free energy given in ref 17. Our final result can be written in the form

$$G_{CL}(f) = 3\left[\frac{4\alpha(\pi - 2\alpha)}{\pi(3\pi - 4)}\right]^{2/3} W^{1/3} \tag{11}$$

where

$$W(f) = \frac{\pi^2\alpha^4(\pi - 4\alpha/5)}{8f^2(3\pi - 4)} + \frac{3\pi - 4}{6\pi} \ln\left[\frac{\pi/\alpha - 2}{\pi - 2}\right] \tag{12}$$

To assess the stability of the CL phase, it is necessary to express the free energies of the other microphases in units of F_1 as $G_i = F_i/F_1$, $i = 1, 2, 3$. From ref 17 we have for lamellae, cylinders, and spheres, respectively

$$G_1 = 1 \tag{13}$$

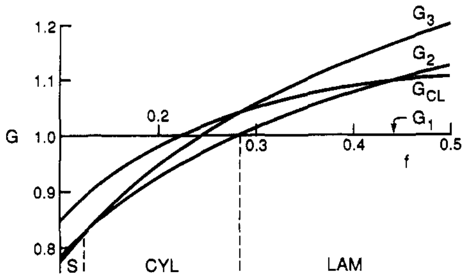

Figure 2. Reduced free energies of the cylindrical (G_2), spherical (G_3), and catenoid-lamellar (G_{CL}) phases. The lamellar phase has a free energy of unity in the energy units employed. The vertical dashed lines at $f = 0.12$ and $f = 0.28$ denote the boundaries between regions of sphere and cylinder stability and cylinder and lamellae stability, respectively.

$$G_2(f) = \frac{2^{2/3} f^{1/3}}{\pi}\left[\frac{\pi^3}{2} + 3\pi \ln (1/f)\right]^{1/3} \tag{14}$$

$$G_3(f) = \frac{3(2f)^{1/3}}{\pi}\left[\frac{\pi^3}{20} + \frac{2\pi}{3}(1 - f^{1/3})\right]^{1/3} \tag{15}$$

These composition-dependent functions are plotted in Figure 2. As was found previously by Semenov,[17] the lamellar phase is lowest in free energy in the composition range $0.28 < f \leq 0.5$, while the cylindrical phase wins out in the range $0.12 < f < 0.28$, and spheres are the lowest free energy structure for $f < 0.12$. The catenoid-lamellar phase has no region of absolute stability in our approximate calculation but is lower in free energy than either spheres or cylinders for $0.44 < f \leq 0.5$. At $f = 0.35$, where Almdal et al.[10] found experimental evidence for the CL phase, our calculations suggest that the CL phase should be metastable with respect to both cylinders and lamellae in the strong-segregation limit (SSL) ($\chi N \rightarrow \infty$). The experimental finding that the CL phase transforms to lamellae on cooling (χ increasing) is consistent with this prediction. In further support of our result is the fact that there have been no identifications of the bulk CL phase in SSL systems, in spite of decades of morphological studies on block copolymers.

From the present results we cannot draw conclusions about the weak-segregation regime ($\chi N \sim 10$) which the authors of ref 10 were investigating. It is not inconceivable that the subtle fluctuation effects that dominate block copolymer systems in this regime could conspire to promote stability of the CL phase near the order–disorder transition, but shut off well below the transition. Explicit demonstration of such an effect represents a formidable challenge to theorists and experimentalists alike.

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(21) It is interesting that the structure shown in Figure 1b, having principal radii of curvature of mixed sign in the "core" (A) region, has no dead zone for $f \leq {}^1/_2$ ($R_2/R_1 \leq 0.626$). Although the *mean curvature* is negative for some θ in the case of ${}^1/_2 < R_2/R_1 < 0.626$, the end density is everywhere positive for $R_2/R_1 < \pi/4$.