Communications to the Editor

Microphases of a Diblock Copolymer with Conformational Asymmetry

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Diblock copolymer melts have received much attention not only because they are of commercial importance but also because they are an extremely well-characterized system which exhibits self-assembly. The simplest phases which these systems display are the lamellar phase in which the two monomers separate into A-rich and B-rich lamellae, the hexagonal phase in which the minority component forms cylinders which pack into a hexagonal array, and the cubic phase in which the minority component forms spheres arranged in a body-centered-cubic structure.[1] Recently, a gyroid phase has been observed[2] in which the minority component forms two three-coordination lattices which interpenetrate and are mirror images of one another. This phase is understood theoretically[3] and is expected to be stable. There have also been numerous observations of an ordered, bicontinuous, double-diamond phase[4–6] in which the minority component forms two separate interpenetrating diamond lattices, but there is some doubt regarding its stability in the diblock system.[7] A monocontinuous catenoid-lamellar phase, in which the minority component lamellae are perforated by holes arranged hexagonally within the layers and staggered between adjacent layers, has been observed,[4,8] as well as a bicontinuous catenoid-lamellar phase.[5]

Monodisperse diblock melts are particularly convenient to study because they are characterized by only a few parameters. If one assumes the system to be incompressible, then it is specified by the Flory–Huggins parameter measuring the incompatibility between unlike monomers χ, the degree of polymerization N, the volume fraction of A-type monomers f, the Kuhn length of A monomers a_A, and that of B monomers a_B. In fact, within mean-field theory, the phase behavior depends only upon the three quantities, χN, f, and a_A/a_B.[9,10] Here we have defined, without loss of generality,[11] the A and B monomers such that their respective volumes, $1/\rho_{0A}$ and $1/\rho_{0B}$, are equal.

Most theoretical work to date has considered the special situation in which $a_A/a_B = 1$. For this case, Leibler[1] used the random-phase approximation to show that the order–disorder transition occurs only between the disordered and cubic phases except at a critical point, $\chi N = 10.495$ and $f = 0.5$, at which the melt makes a transition from the disordered to lamellar phase. More recent results employing the self-consistent-field theory agree with this.[3,10] It is known that when fluctuations are taken into account, the mean-field critical point vanishes and first-order transitions can take place directly from the disordered phase to either the lamellar or hexagonal phase.[12] Vavasour and Whitmore[10] have claimed recently that, even within mean-field theory, such windows of direct transitions occur when the ratio of Kuhn lengths, a_A/a_B, deviates sufficiently from unity.

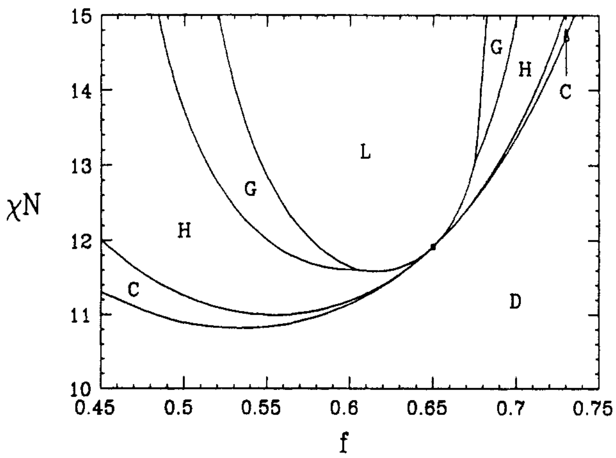

Figure 1. Phase diagram showing regions of stability for the disordered (D), lamellar (L), gyroid (G), hexagonal (H), and cubic (C) phases. All transitions are first order except at the critical point, which is marked by a dot.

Within the self-consistent-field theory employed in refs 3, 9, and 10, one obtains an analytic expression for the free energy of the disordered phase. The free energy of the lamellar phase is obtained after solving a one-dimensional modified diffusion equation. To obtain that of the hexagonal and cubic phases, one is required to solve two- and three-dimensional equations, respectively, which presents a challenging numerical problem. Vavasour and Whitmore[9,10] circumvent it by introducing an approximation which turns the equations for the hexagonal and cubic phases into one-dimensional ones. In this paper, we report the results of an exact solution of the equations and demonstrate that the windows calculated in ref 10 are a consequence either of their approximation or of numerical inaccuracy.

The method by which we solve the modified diffusion equation in higher dimensions is described in our previous work in which we calculate the phase diagram for $a_A/a_B = 1$.[3] Here we obtain the phase diagram for $a_A/a_B = \sqrt{10}$, the asymmetry for which Vavasour and Whitmore found, between $f = 0.61$ and 0.675, windows of first-order transitions from the disordered phase to either hexagonal or lamellar phases. Our calculation yields a transition to the lamellar phase only at the single point $\chi N = 11.92$ and $f = 0.650$ at which the transition is continuous. Otherwise, we find first-order transitions only to the cubic phases. The phase diagram is shown in Figure 1. Our method allows us to calculate free energies very accurately in the weak-segregation limit (a part in 10^9). In turn, this permits the calculation of phase boundaries with numerical errors smaller than the line width in Figure 1. This accuracy strictly limits the possibility of direct transitions to the hexagonal phases to the interval $f = 0.64$–0.66, and we find no reason to suspect that they occur at all. We conclude that an asymmetry in the Kuhn lengths does not change the topology of the mean-field phase diagram, and

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the evidence in ref 10 that it does so can be attributed either to the approximation employed or to an incorrect assessment of numerical accuracy.[13]

Our phase diagram includes regions of stability of the gyroid phase. This is the same phase we located earlier for equal Kuhn lengths.[3] In refs 9 and 10 such a phase was not sought as the approach employed does not permit it. Similarly, the other phases noted above cannot be found by this method. Our approach does permit us to calculate the free energy of the double-diamond, monocontinuous and bicontinuous catenoid-lamellar phases. As in our earlier work, we find them to be only metastable.

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(13) We have been informed by the authors of ref 10 that their numerical accuracy may be less than initially estimated and that this alone might explain the discrepancy between their results and ours. They are currently examining this possibility.