Macromolecules **1991,** *24,* 3975-3976 **3975**

Equilibrium Domain Spacing in Weakly Segregated Block Copolymers

In disordered block copolymer melts the chemical junction between A and B blocks causes composition fluctuations to be localized, resulting in a peak in the scattering intensity at wave vectors of some finite magnitude k^*. In the disordered state, copolymer chains obey random-walk statistics, and one finds $k^* \sim 1/N^{1/2}$, where N is the number of statistical segments per chain. As temperature is decreased, or molecular weight is increased keeping temperature constant, an increasing net repulsion between A and B blocks drives a local segregation to A-rich and B-rich domains, which arrange periodically. The first Bragg reflection of the ordered microdomain morphology is identified with the peak in the disordered state scattering intensity. On further lowering T or increasing N, the primary peak is observed to shift gradually to lower k values as the copolymer chains stretch to decrease the A-B interphase.[1-4] This increase in domain spacing differs with theoretical predictions for copolymers in weak segregation.[5,6]

Leibler[5] analyzed the disorder-order transition for diblock copolymer melts in the weak segregation limit, where the interphase between A and B domains is diffuse. The free energy for a given morphology is written as an order parameter expansion in terms of composition fluctuations of wavelength $2\pi/k^*$

$$(F - F_0)N/kT = [Q(x^*) - 2\chi N]\rho^2 - \alpha\rho^3 + \beta\rho^4 \qquad (1)$$

where χ is the Flory interaction parameter ($\sim 1/T$), $x = k^2N^2/6$ (l is the statistical segment length), and ρ is the amplitude of the primary composition harmonic. The functions $Q(x^*)$, α, and β are computed from the intrachain correlations particular to a copolymer composition and architecture.[5] By minimization of the free energy with respect to ρ, the analysis predicts the disorder-order transition at some value $(\chi N)_t$ where $F = F_0$.

In his analysis, Leibler assumes that the peak of the primary reflection remains stationary at x^*. This assumption requires k^* to be independent of temperature and to vary with molecular weight as $k^* \sim 1/N^{1/2}$, counter to experimental observations.[1-4] This discrepancy motivated us to reexamine Leibler's approach to determine whether the disordered state value for x^* minimizes the free energy expansion in eq 1 above $(\chi N)_t$. A simple modification to the analysis is required in which the ordered phase free energy must satisfy the conditions:

$$F(\rho x^*)/\partial\rho = 0$$

$$F(\rho,x^*)/\partial x^* = 0$$

In our analysis, the minimization with respect to x^* was performed numerically.

Variations in x^* can also be studied in the context of a multiple-harmonic approximation described in a recent study.[7] In this case the computed free energy expansion is minimized with respect to the amplitudes of multiple-composition harmonics, related to the primary and higher order Bragg reflections, and the value of x^*. Since the wave vectors of higher order Bragg peaks are ratios of k^*, any shift in k^* will produce a shift of all the ordered phase reflections. By knowing how k^* varies with temperature, the composition profile of the evolving morphology can be described once the phase shifts of the higher order harmonics are determined.[8] In this study, we model the composition profile for a lamellar microphase as

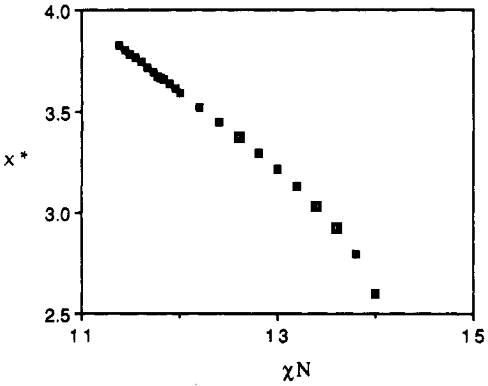

Figure 1. Predicted shift in x^* for lamellar morphology with $f = 0.4$.

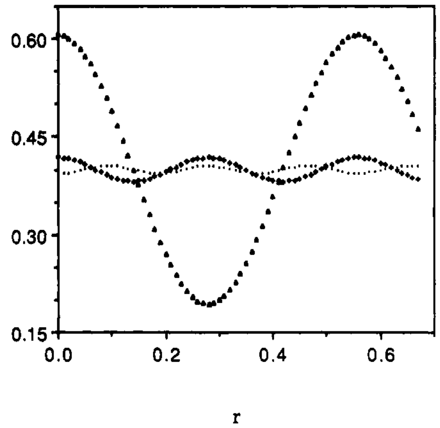

Figure 2. Composition harmonics for $f = 0.4$ at $\chi N = 13$.

$$\rho(r) = f + \rho_1 \cos(k^*r) + \rho_2 \cos(2k^*r) + \rho_3 \cos(3k^*r + \pi) + \rho_4 \cos(4k^*r + \pi)$$

where f is the A block fraction of the copolymer, and ρ_2, ρ_3, and ρ_4 are the amplitudes of the higher order composition harmonics.

Within the present approach, the value of x^* remains constant for $\chi N < (\chi N)_t$. As χN increases above the transition, however, the free energy in eq 1 is not minimized by the disordered state value of x^*. Instead, the peak shifts continuously to lower k values. This result indicates that the copolymer chains stretch even in weak segregation to lessen A-B contacts.

Figure 1 shows the predicted value of x^* as a funtion of χN for a lamellar structure of composition $f = 0.4$. The results were obtained by minimizing a four-harmonic free energy expansion with respect to x^*; results from the single-harmonic expansion in eq 1 are nearly identical, however. In this figure the value of x^* appears to decrease linearly over a significant range in χN with a slope of $\Delta x^*/\Delta\chi N \simeq -0.37$. We find this value in qualitative agreement with the experimental results of Owens et al.[1] for a styrene-isoprene copolymer with $f \simeq 0.4$. When we replotted data for d vs T as x^* vs χN using the authors' values for N, l, and $\chi(T)$, a best straight line fit gave $\Delta x^*/\Delta\chi N \simeq -0.31$, which compares well with Figure 1. At higher χN values, however, x^* in Figure 1 drops rapidly and the free energy grows arbitrarily large, signaling a breakdown of the analysis.

The higher order peaks provide an indication of the degree of order in the microdomain structure. In the multiple-harmonic analysis, the shift in k^* is accompanied

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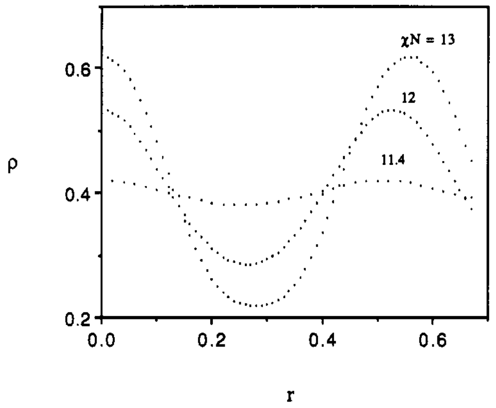

Figure 3. Evolution of lamellar composition profile for $f = 0.4$.

by an increase in the degree of order. For example, when the free energy is minimized in x^*, the predicted amplitudes of the $2k^*$, $3k^*$, and $4k^*$ harmonics for $f = 0.4$ and $\chi N = 13$ increase by 25, 23, and 34% over their values when the free energy is evaluated at x^* in the disordered phase. The primary amplitude, by comparison, increases by only 8%. In Figures 2 and 3 the computed amplitudes are plotted as a function of distance $r = 2\pi R/x^{*1/2}$, where $R^2 = Nl^2/6$. The amplitudes are superimposed in Figure 2 for $\chi N = 13$ and summed in Figure 3. (For clarity purposes, the $4k^*$ harmonic is omitted in Figure 2, being much smaller than the amplitude of the primary oscillation.) Figure 3 shows the evolving composition profile as a function of χN for $f = 0.4$. With increasing χN, the B-rich domains appear to broaden due to the compositional asymmetry of the diblocks. As the difference in the mean compositions of the A-rich and B-rich regions becomes larger, the domain spacing increases and the interface sharpens to further reduce the number of A–B contacts. The k^* values in this figure fall within the range where x^* varies linearly with χN in Figure 1.

Changes in domain periodicity were studied in the body-centered cubic and hexagonal structures, minimizing the single-harmonic free energy expansion in eq 1 with respect to x^*. Typical results are shown in Figure 4 for cylinders at $f = 0.3$. For these morphologies the decrease in x^* as a function of χN again appears to be linear over a large range in χN and then drops rapidly as the limits of the analysis are exceeded. The analysis also suggests that the copolymer chains deform more gradually for these higher dimensional structures.

Recently, we studied variations in x^* within a Hartree analysis of the disorder–order transition.[9] In the Hartree analysis, fluctuations are found to influence the system in the disordered phase, prior to the transition.[10] Including x^* variations, shifts in the peak position are predicted in the disordered phase.[9] Several experimental groups have reported shifts in k^* in the disordered region upon approaching $(\chi N)_t$ by decreasing T or increasing N.[1,4,11] Other studies, however, found $k^* \sim T^0$ above the transition temperature.[2] Further experimental studies that address this issue are warranted.

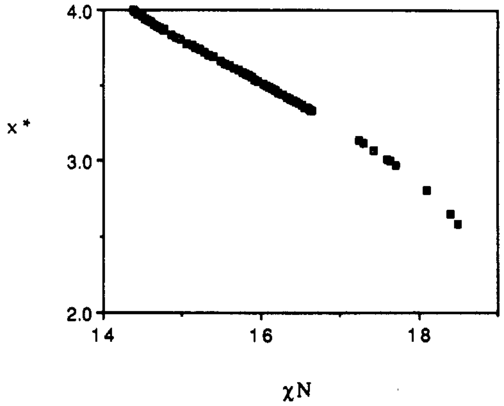

Figure 4. Predicted shift in x^* for hexagonal morphology with $f = 0.3$.

Acknowledgment. This work was supported by the National Science Foundation through the Northwestern University Materials Research Center, Grant No. DMR 8821571, and PYI Grant No. DMR-9057764.

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Received April 18, 1991