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Compressibility of Two Polymer Blend Mixtures

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ABSTRACT: Small-angle neutron scattering measurements have been performed on two polymer blend systems under pressure. Deuterated polystyrene (PSD)/poly(vinyl methyl ether) (PVME) and PSD/poly(butyl methacrylate) (PBMA) blends have been investigated over a range of temperatures and pressures. For the PSD/PVME blend, three compositions were investigated, whereas for the PSD/PBMA system, only one composition was measured. It was found that pressure has the effect of enhancing miscibility for both blends. Our PSD/PVME measurements have shown strong pressure effects on the scattered intensity but no weakening of the composition dependence of the Flory–Huggins χ parameter under applied pressure; this eliminates compressibility as a possible cause for the origin of the composition dependence of χ in this blend system. Moreover, both the entropic part, C, and the enthalpic part, D, of the χ parameter ($\chi = C + D/T$, where T is absolute temperature) were found to depend on pressure.

Introduction

Blending is often used to control the physical properties of polymeric materials. Some polymer blends mix homogeneously and phase separate upon heating (at the so-called lower critical spinodal temperature or LCST) or upon cooling (at the upper critical spinodal temperature or UCST).[1] The deuterated polystyrene (PSD)/poly(vinyl methyl ether) (PVME) LCST blend system has been extensively investigated[2] using small-angle neutron scattering (SANS). The Flory–Huggins χ parameter representing the basic monomer–monomer interactions which drive the thermodynamics of phase separation has been shown to depend on temperature, polymer molecular weight, and volume fraction. The goal of our investigations is to quantify the effect of pressure on the phase decomposition of PSD/PVME blends. It has been argued in the literature[3–9] that the LCST branch of the phase diagram is due to compressibility effects (i.e., to the existence of "free volume"). It should be noted that specific interactions (hydrogen bonding, for example) could also be at the origin of the LCST behavior. Most equation-of-state models focus on free volume without worrying too much about its possible origin at the molecular level. Actually, one could look at specific interactions as an increasing source of free volume with increasing temperature and/or decreasing pressure. The aim of our study is to test some of these ideas and to bring about a better understanding of the effect of pressure on macromolecular mixture thermodynamics. For instance, we would like to test the idea that compressibility may be the origin of the observed composition dependence of χ for PSD/PVME. The PSD/poly(butyl methacrylate) (PBMA) blend system has recently been shown to phase separate upon both heating and cooling;[10] i.e., it is characterized by a miscibility gap between the UCST and the LCST. The effect of pressure on this miscibility gap has also been investigated here.

One previous investigation[11,12] on pressurized polymer blend mixtures had used a single composition and focused on tests of equation-of-state models. For instance, their investigation of the PSD/PVME blend came to the conclusion that while the entropic part (C) of the Flory–Huggins χ parameter ($\chi = C + D/T$, where T is absolute temperature) increased with pressure, the enthalpic part (D) did not vary with pressure. Our experiments also probed the effect of pressure on the composition dependence of χ. Another recent investigation[13] used small-angle X-ray scattering to investigate polystyrene–polyisoprene diblock copolymer (UCST) melts under pressure.

Experiments

For the PSD/PVME experiments, deuterated polystyrene of typical molecular weight (M_w = 188 000, M_w/M_n = 1.02) has been purchased from Polymer Laboratories and poly(vinyl methyl ether) was cationically synthesized, fractionated, and characterized by gel permeation chromatography for its molecular weight (M_w = 201 000, M_w/M_n = 1.49). A set of three samples appropriate for small-angle neutron scattering and corresponding to PSD compositions of 10%, 30%, and 50% (weight fractions) were then prepared using common methods (blending in toluene solution, solvent evaporation, drying, melt pressing into 1.2-mm-thick wafers). For the PSD/PBMA experiments, deuterated polystyrene of low molecular weight was also purchased from Polymer Laboratories (M_w = 10 000, M_w/M_n = 1.03) and poly(n-butyl methacrylate) was synthesized (free-radical polymerization) and characterized for its molecular weight (M_w = 34 000, M_w/M_n = 1.96). Here, only one composition (10% PSD weight fraction) was investigated. Blend samples were dried and kept in a vacuum oven before the experiment in order to avoid moisture.

Small-angle neutron scattering measurements were performed on the NG3 30-m instrument at the National Institute of Standards and Technology, Cold Neutron Research Facility. A wavelength of 5 Å and a wavelength spread of 15% were used along with appropriate sample-to-detector distances (7 m for the PSD/PVME samples and 2.5 m for the PSD/PBMA sample) and tight collimation in order to minimize resolution effects. In-situ pressure measurements were performed using a hydraulic pressure cell with a stainless steel body and where the sample is confined inside an O-ring and in between two sapphire windows. The pressurizing (brake) fluid compresses the 1.2-mm-thick sample through the O-ring up to high pressures (about 100 MPa). Even though the neutron beam diameter was 9.5 mm, the O-ring size (diameter) used was 17 mm in order to make sure that no brake fluid would ever be in the neutron beam. A wide scattering wavenumber (Q) region was measured for the above-mentioned samples, for a range of temperatures, and for four pressures (up to 81.6 MPa which corresponds to 12 000 psi). Note that, for notation convenience, we are referring to the atmospheric pressure condition (14.7 psi) as 100 kPa. Temperature scans

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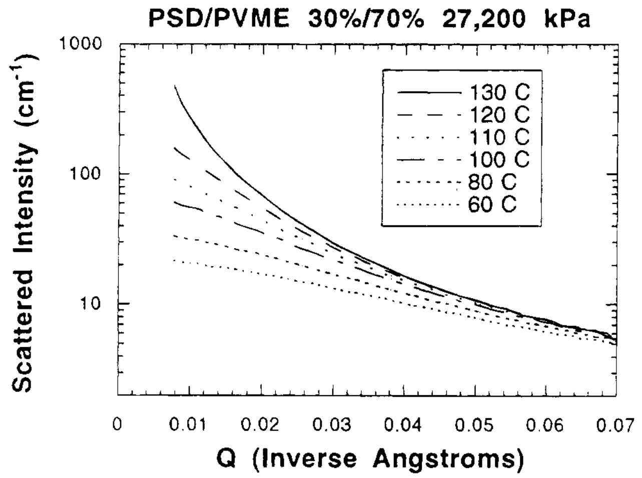

Figure 1. Radially averaged SANS intensity for a PSD/PVME sample (30/70) measured at a pressure of 27.2 MPa and for temperatures between 60 and 130 °C. A typical scattered intensity increase is observed when the spinodal temperature is approached. Qualitatively, similar curves are obtained for other pressures and other sample compositions.

were performed at fixed pressure. Because the pressure was set manually, it drifted slightly with temperature (at 81.6 MPa, pressure increases of order 10% were observed for temperature increases of 100 °C).

SANS data were corrected for background, radially averaged, and presented in the form of an absolute cross section $I(Q)$ using secondary standards. Zimm plots ($I^{-1}(Q) = I^{-1}(0) + BQ^2$) of the reduced data were used to extract an intercept $I^{-1}(0)$ and a slope B which could yield a correlation length. Note that, according to the incompressible random-phase approximation (RPA),[14-17] the intercept $I^{-1}(0)$ is related to the Flory–Huggins χ parameter, while the slope B is related to a correlation length or effective radius of gyration for polymer chains.

Results and Discussion

Upon increasing temperature for fixed pressure, the scattered intensity increases for the PSD/PVME system because the spinodal line is approached from the single-phase region. Figure 1 shows typical scattering curves; other samples and different pressures give similar curves.

Variation of the intercept of the Zimm plot $I^{-1}(0)$ (inverse of the forward scattered intensity) with inverse temperature T^{-1} (in absolute units) for the 50/50 PSD/PVME sample is shown in Figure 2 for four pressures. This variation remains linear at higher pressures but with a pressure-dependent slope and intercept (see Table 1). Assuming the incompressible RPA formalism, $I(0)$ can be related to χ as follows:

$$I^{-1}(0) = k_n^{-2}\{(N_A\phi_A v_A)^{-1} + (N_B\phi_B v_B)^{-1} - 2\chi_{AB}/v_0\} \qquad (1)$$

where k_n^2 is the contrast factor, N_A, ϕ_A, and v_A are the degree of polymerization, volume fraction, and molar volume for component A (say, PSD, for example), and v_0 is a reference volume. The interaction parameter χ_{AB} varies with temperature as $\chi_{AB} = C + D/T$. Figure 2 shows that the intercept C and slope D are pressure-dependent. It is sometimes argued that C represents an entropic quantity and D an enthalpic contribution, although these two quantities have remained empirical so far. Some equation-of-state models such as that due to Sanchez–Lacombe[4] assume that only C is pressure-dependent.

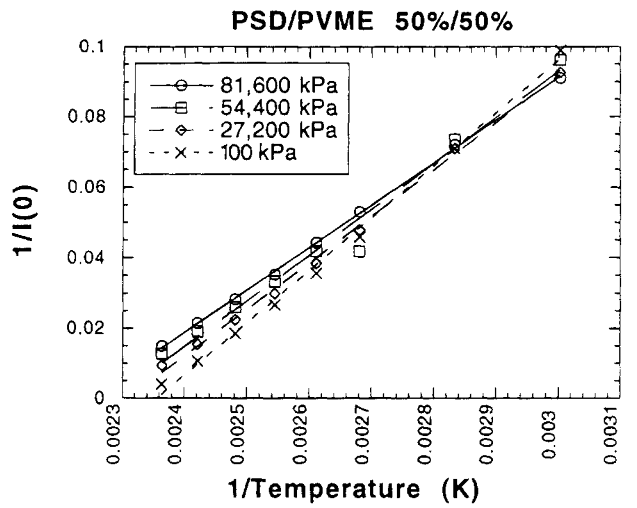

Figure 2. Variation of $I^{-1}(0)$ (inverse of the forward scattered intensity) with inverse temperature T^{-1} for the 50/50 PSD/PVME sample measured at four pressures. $I(0)$ was obtained using a Zimm plot ($1/I(Q)$ vs Q^2) of the reduced SANS data.

Table 1. Intercept and Slope for the Variation of $I^{-1}(0)$ ($I(0)$ is the Forward Scattering Intensity) with Inverse Temperature T^{-1} (Where T is in Degrees Kelvin) for the PSD/PVME Blend

PSD composition (%)	pressure (MPa)	intercept (cm)	slope (cm K)
10	0.1	−0.210	82
	27.2	−0.196	77
	54.4	−0.187	75
	81.6	−0.143	58
30	0	−0.266	105
	27.2	−0.232	92
	54.4	−0.218	89
	81.6	−0.213	88
50	0	−0.351	149
	27.2	−0.306	132
	54.4	−0.298	130
	81.6	−0.271	121

It should be emphasized that the incompressible RPA formalism is not appropriate to describe blend mixtures that are obviously compressible. An RPA formalism has been developed for compressible polymer mixtures;[5,18] this approach requires the use of the monomer–monomer interaction potentials W_{AA} and W_{BB}, which can be obtained from *PVT* measurements on pure components.[19-21] The third potential W_{AB} is harder to estimate and could be obtained from fits to the experimental data. The three-component RPA approach[5,18] considers free volume as the third component, the fraction of which can be estimated from an equation of state such as from the Sanchez–Lacombe model.[4] A number of other equation-of-state models exist. The equation of state requires an initial estimate of the intermonomer interaction potentials and yields a free-volume fraction, whereas the three-component RPA uses the free-volume fraction to yield a better estimate of the intermonomer interaction potentials. These two sets of equations should be solved self-consistently (until the solution converges) and will be the subject of future investigations.

For this PSD/PVME system, the effect of pressure is to raise the spinodal line to higher temperatures by "damping" the concentration fluctuations that mark the onset of spinodal decomposition. Figure 3 shows that this process saturates for the higher pressures and is more dramatic at the highest temperatures. For instance, a sample can be taken into the spinodal phase

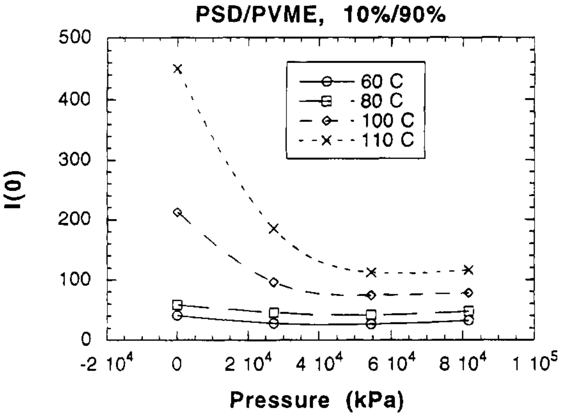

Figure 3. Variation of the forward scattered intensity $I(0)$ with pressure for the 10/90 PSD/PVME sample at four temperatures. Spline fit lines are included as a guide for the eye.

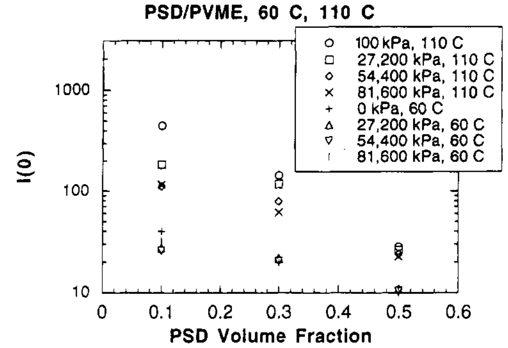

Figure 4. Variation of the forward scattered intensity $I(0)$ with PSD/PVME sample composition for two measurement temperatures (60 and 110 °C).

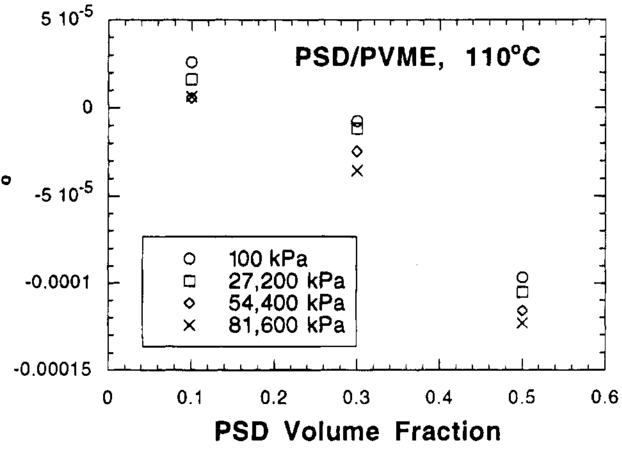

Figure 5. Variation of the rescaled Flory–Huggins χ/v_0 parameter with PSD/PVME sample composition at 110 °C.

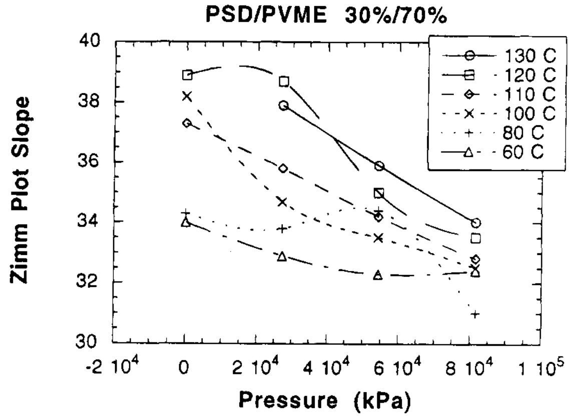

Figure 6. Variation of the Zimm plot slope B (obtained from $I^{-1}(Q) = I^{-1}(0) + BQ^2$) with pressure for the 30/70 PSD/PVME sample measured at various temperatures.

region (as evidenced by a time-dependent increase of the scattered intensity) by raising temperature and then back into the one-phase region by applying pressure. Because pressure can be changed rapidly, spinodal decomposition can be "controlled" at will. Using a long sample–detector distance (13 m) and wavelength (12 Å), it was possible to take the 50% PSD/PVME sample into and out of the spinodal region many times; a careful iterative pressure change strategy (adjusting pressure while looking at real-time SANS data on the imaging screen) allowed us to observe the spinodal ring which quickly (within a couple of minutes) merged with the direct beam. To our knowledge, this is the first observation of a spinodal ring by the SANS technique for a strongly-interacting blend system (as the PSD/PVME). With temperature variation alone, this would not have been possible because the phase separation kinetics are faster than the temperature response of the heating/cooling system.

The free-volume concept has been used in a number of theories[4–9] in order to model compressibility in polymers. Our results and those reported previously[11] are confirming the important role of free volume in the thermodynamics of LCST systems. Some free-volume approaches also predicted that compressibility is the origin of the composition dependence of the Flory–Huggins χ (experimentally observed to be linear for PSD/PVME[2]), i.e., that this composition dependence will weaken at high pressures. In order to test this prediction, we used the incompressible RPA formula (eq 1) with constant (pressure-independent) molar volumes, to obtain χ parameters from values of $I(0)$. The only justification for using an incompressible RPA approach on an obviously compressible system is that the previously reported composition dependence of χ was obtained[2] from scattered intensities using the same incompressible RPA formula. Even though pressure has strong effects on the composition dependence of $I(0)$ (shown in Figure 4), its effect on χ is a pure downward translation (shown in Figure 5) with no observable weakening (i.e., no change in slope). Adding slight molar volume contractions (say, 10% over our measured pressure range) in the incompressible RPA formula (in v_A and v_B) used to obtain χ does not change this conclusion. Our results help eliminate compressibility effects as a possible origin for the composition dependence of χ in PSD/PVME. Other remaining possible candidates include dissimilarity in monomer sizes and shapes, nonrandom mixing, chain fluctuations, etc. The values of the χ parameters reported in Figure 5 are obviously not reliable because they ignore free-volume effects. Even though the values for 10% PSD composition are positive ($\chi/v_0 = 2.58 \times 10^{-5}$ for 0 MPa and 110 °C, for example), they are still well below the values at the spinodal temperature ($\chi_s/v_0 = 3.3 \times 10^{-5}$) which is estimated to be around 130 °C for the 10% PSD composition and at atmospheric pressure.

Even though the slope B of the Zimm plots obtained from $I^{-1}(Q) = I^{-1}(0) + BQ^2$ shows erratic variation with pressure, the downward trends are clear (Figure 6 shows some data and a cubic spline fit that has been included to emphasize the level of imprecision). Note that the slope B which determines the square of the correlation length cannot be simply associated with the square of the radius of gyration as in the incompressible

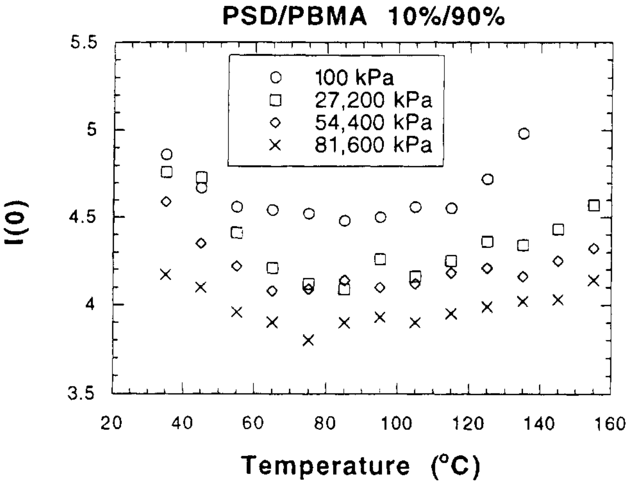

Figure 7. Variation of the forward scattered intensity $I(0)$ with temperature for the 10/90 PSD/PBMA sample and for varying pressure. The upturn in this variation is characteristic of a miscibility gap.

RPA because of fluctuation effects close to the spinodal line. The variation of this "effective" R_g with pressure for PSD/PVME was reported to be linear by Janssen et al.[12] and agrees with our estimate reported in Figure 6. The compressible RPA approach[5,18] with a free-volume component included can predict a strong decrease of the "apparent" radius of gyration with pressure[5] which is due to equation-of-state (free-volume) effects. *PVT* measurements[21] on a PSD/PVME blend have been reported and show that densification effects are small (on the order of 1%).

There are two main differences between the PSD/PVME and the PSD/PBMA blend systems. First, the PSD/PVME phase diagram (temperature *vs* composition) is skewed with a minimum located at low PSD compositions (around 20% for our molecular weights), whereas this is not the case for the PSD/PBMA diagram. Increasing composition (10%, 30%, and 50%) for the PSD/PVME system leads farther away from the spinodal line, while for the PSD/PBMA system, increasing composition (up to 40%) leads closer to the spinodal line.[10] The second main difference between the two polymer systems stems from the fact that, for the PSD/PBMA mixture, the forward scattered intensity $I(0)$ first decreases with temperature and then increases at high temperatures. The upturn characteristic of a miscibility gap remains even at higher pressures. As seen from Figure 7, the effect of pressure is higher at high temperatures and the location of the miscibility gap (temperature where $I(0)$ is minimum) does not seem to vary with pressure. Due to the close proximity of the glass–rubber transition temperature T_g of PSD (which goes up with pressure), the effect of pressure of the UCST branch of the phase diagram cannot be isolated. Separate measurements of T_g for the PSD/PBMA blend system under pressure could yield a better understanding of how monomers pack locally as well as give a handle on separating T_g from UCST contributions. It can only be stated that the forward scattered intensity decreases with increasing pressure for all the measured temperatures (between 35 and 135 °C); this is interpreted as enhanced miscibility. Using the incompressible RPA formula, the χ parameter is here also obtained from $I(0)$ and seen to decrease with pressure (Figure 8). Moreover, pressure has the effect of decreasing the Zimm plot slope for PSD/PBMA as it did for PSD/PVME.

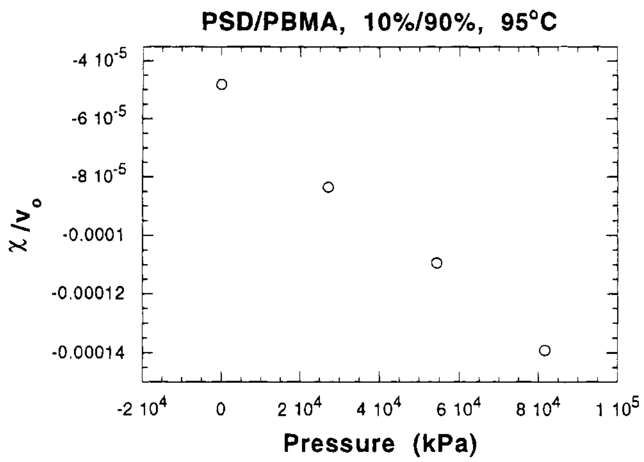

Figure 8. Variation of the rescaled Flory–Huggins χ/v_0 parameter with pressure for the PSD/PBMA sample at 95 °C.

Pressure is an important factor in the understanding of polymer blend thermodynamics as well as in the practical aspect of the polymer processing (blend mixing, injection molding, etc.). Our investigations constitute an initial effort in quantifying pressure effects for two polymer blend systems. Future pressure studies are expected to include pure UCST blend systems, diblock copolymer melts, and polymer solutions.

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References and Notes

(1) De Gennes, P.-G *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(2) Han, C. C.; Bauer, B. J.; Clark, J. C.; Muroga, Y.; Matsushita, Y.; Okada, M.; Tran-Cong, Q.; Chang, T.; Sanchez, I. *Polymer* **1988**, *29*, 2002.
(3) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(4) Sanchez, I. C.; Lacombe, R. H. *Macromolecules* **1978**, *11*, 1145.
(5) Sanchez, I. C.; Bidkar, U. *Macromolecules* **1995**, *28*, 3963.
(6) Dudowicz, J.; Freed, K. F. *Macromolecules* **1991**, *24*, 5112.
(7) Lipson, J. E.; Brazhik, P. K. *J. Chem. Phys.* **1993**, *98*, 8178.
(8) Kumar, S. *Macromolecules* **1994**, *27*, 260.
(9) Yeung, C.; Desai, R. C.; Shi, A.; Noolandi, J. *Phys. Rev. Lett.* **1994**, *72*, 1834.
(10) Hammouda, B.; Bauer, B. J.; Russell, T. *Macromolecules* **1994**, *27*, 2357.
(11) Janssen, S.; Schwahn, D.; Mortensen, K.; Springer, T. *Macromolecules* **1993**, *26*, 5587.
(12) Janssen, S.; Schwahn, D.; Springer, T.; Mortensen, K. *Macromolecules* **1995**, *28*, 2555.
(13) Hajduk, D. A. Morphological Transitions in Block Copolymers. Ph.D. Thesis, Princeton University, Princeton, NJ, 1994.
(14) De Gennes, P.-G. *J. Phys. (Fr.)* **1970**, *31*, 235.
(15) Benoit, H.; Wu, W. L.; Benmouna, M.; Bauer, B.; Lapp, A. *Macromolecules* **1985**, *18*, 986.
(16) Akcasu, A. Z.; Tombakoglu, M. *Macromolecules* **1990**, *23*, 607.
(17) Hammouda, B. *Adv. Polym. Sci.* **1993**, *106*, 87.
(18) Hammouda, B. *J. Non-Cryst. Solids* **1994**, *172*, 927.
(19) Sanchez, I. C.; Panayiotou, C. G. In *Models and Phase Equilibria Calculations*; Sandler, S., Eds.; Marcel Dekker: New York, 1993.
(20) Rodgers, P. A. *J. Appl. Polym. Sci.* **1993**, *48*, 1061.
(21) Ougizawa, T.; Dee, G. T.; Walsh, D. J. *Macromolecules* **1991**, *24*, 3834.

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