Small-Angle Neutron Scattering from Deuterated Polystyrene/Poly(butyl methacrylate) Homopolymer Blend Mixtures

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Introduction. Small-angle neutron scattering (SANS) has been used to investigate a number of polymer blend mixtures[1-9] over the past few years. Using the random-phase approximation[10-15] (RPA) to interpret the SANS data, the segmental interaction parameter, χ, has been obtained and spinodal lines (marking the limit of miscibility) have been mapped out. Some polymer blends such as polystyrene/poly(vinyl methyl ether)[4] phase separate upon heating, i.e., are characterized by a lower critical "solution" temperature (LCST), while others such as poly(vinylethylene)/poly(ethylethylene)[6] phase separate upon cooling, i.e., are characterized by an upper critical "solution" temperature (UCST). Note that the LCST and UCST terminology is often used even for polymer mixtures with no solvent.

A miscibility gap has been observed for the first time in a copolymer melt by Russell et al.,[16,17] who reported the existence of both an upper order-to-disorder transition temperature (UODT) and a lower disorder-to-order transition temperature (LDOT) for a symmetric diblock copolymer of PSD-*b*-PBMA. Using copolymer molecular weights between 2.6×10^4 and 1.7×10^5, small-angle X-ray scattering measurements between 40 and 300 °C showed the existence of both transitions and their shift with molecular weight. The experiments reported here describe SANS measurements performed on a homopolymer mixture of the same material (PSD/PBMA) with lower molecular weights. The objective of these experiments was to determine whether a miscibility gap also existed for this homopolymer mixture and to investigate the temperature and composition dependences of the χ parameter. Use of the lower molecular weights for the homopolymer mixtures stems from the fact that the RPA-predicted stability limit for symmetric diblock copolymers (the Russell et al. case[16,17]) corresponds to $\chi N = 10.5$, whereas for symmetric homopolymer mixtures (our case), it corresponds to $\chi N = 2$, with N being the degree of polymerization.

Experiments. We first experimented with blend mixtures of PSD ($M_w = 2.7 \times 10^4$) and PBMA ($M_w = 1.88 \times 10^4$) for PSD compositions up to 50%. However, these samples were not suitable for SANS measurements because they were opaque (indicating immiscibility) at ambient temperature. Consequently, mixtures of PSD ($M_w = 1.04 \times 10^4$ and $M_n = 5.02 \times 10^3$), purchased from Polymer Laboratories, and PBMA ($M_w = 1.88 \times 10^4$ and $M_n = 9.6 \times 10^3$), which was synthesized in our laboratory, were investigated. Four compositions corresponding to 10%, 25%, 40%, and 50% PSD weight fractions were made. Standard methods were used for preparing the samples (dissolving the appropriate amounts of homopolymers in toluene, drying under vacuum, and then melt pressing to obtain 1-mm-thick disks). Since the 50% by weight PSD composition specimen was opaque, the SANS measurements focused on the remaining three samples which were annealed at 85 °C for 1 h before being cooled down slowly to ambient temperature. SANS measurements were performed on the NG3 30-m SANS instrument at the National Institute of Standards and Technology (NIST) with a wavelength of 5 Å, a wavelength spread of 15%, a source-to-sample distance of 11.67 m (to minimize resolution effects), a sample-to-detector distance of 2.5 m, a source aperture diameter of 5 cm, and a sample aperture diameter of 0.635 cm. Using a computer-controlled heating block, SANS measurements were made on heating from 25 to 125 °C and on cooling from 135 to 35 °C in 20 °C increments. This was done to insure reproducibility of the results. For instance, if a bubble developed in the sample, the trends upon heating and upon cooling would be widely different. Typical SANS corrections (empty quartz cell scattering and blocked beam contribution) were performed, and the scattered intensity was converted to an "absolute" macroscopic cross section (units of cm^{-1}) using a 1-mm-thick water sample (of known cross section) as an intensity standard.

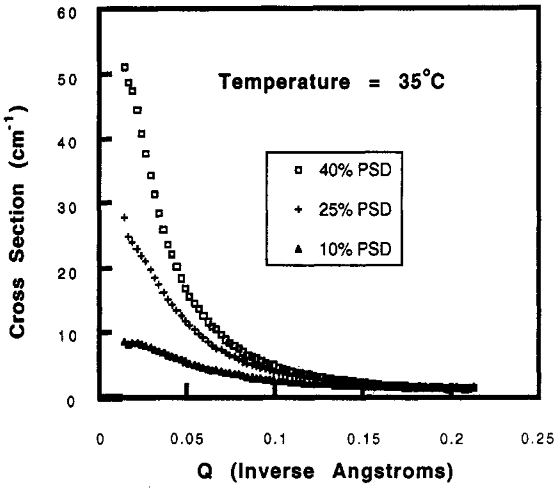

Figure 1. Variation of the SANS cross section with wavenumber for the three PSD/PBMA compositions (10%, 25%, 40% PSD) measured at 35 °C.

Results and Discussion. The scattering profiles for the three PSD/PBMA mixtures are shown as a function of wavenumber, Q, in Figure 1. The scattering at low Q (for example, at $Q = 0.0314$ Å^{-1}) exhibits an unusual temperature dependence characterized by a minimum at intermediate temperatures as shown in Figure 2a–c. Increasing the temperature results in an initial decrease followed by an increase of the low-Q intensity. These results are characteristic of a miscibility gap between an UCST and a LCST. With the exception of the drop in intensity at 25 °C, the trends are quite clear. For the 25 °C measurements, the samples are near or below the glass–rubber transition temperature of the mixture. In addition, the drop in intensity at 135 °C for the 40% PSD sample is due to the fact that the sample is well into the spinodal region as indicated by its opacity. It is interesting to note that the location of the minimum in the variation of the low-Q intensity with temperature depends on composition (minimum is located around 90 °C for 10% PSD, around 80 °C for 25% PSD, and around 70 °C for 40% PSD).

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According to the compressible RPA formalism (so-called de Gennes formula), the absolute scattering cross section $\mathrm{d}\Sigma(Q)/\mathrm{d}\Omega$ is given by:

$$\mathrm{d}\Sigma(Q)/\mathrm{d}\Omega = (b_{\mathrm{PBMA}}/V_{\mathrm{PBMA}} - b_{\mathrm{PSD}}/V_{\mathrm{PSD}})^2 S(Q)$$

and

$$S^{-1}(Q) = [N_{\mathrm{PBMA}}\phi_{\mathrm{PBMA}}V_{\mathrm{PBMA}}P_{\mathrm{PBMA}}(Q)]^{-1} + [N_{\mathrm{PSD}}\phi_{\mathrm{PSD}}V_{\mathrm{PSD}}P_{\mathrm{PSD}}(Q)]^{-1} - 2\chi_{\mathrm{PBMA/PSD}}/V_0$$

where b is the neutron scattering length, N is the degree of polymerization, ϕ is the volume fraction, V is the molar volume, and $P(Q)$ is the usual Debye function for Gaussian coils for each of the two components (PBMA and PSD). V_0 represents a reference "cell" volume (usually taken to be $V_0 = (V_A V_B)^{1/2}$), and $\chi_{\mathrm{PBMA/PSD}}$ is the segmental interaction parameter. SANS data for each temperature and composition were fit to this functional form with three floating parameters: a Q-independent background, an average statistical segment length a_{av}, and the rescaled Flory–Huggins parameter $\chi_{\mathrm{PBMA/PSD}}/V_0$. The individual segment lengths are estimated as $a_{\mathrm{PBMA}} = a_{\mathrm{av}}(V_{\mathrm{PBMA}}/V_0)^{1/2}$ and $a_{\mathrm{PSD}} = a_{\mathrm{av}}(V_{\mathrm{PSD}}/V_0)^{1/2}$. This coupling of the two segment lengths is usual and was done in order to reduce the number of floating parameters. All fits were reasonable and resulted in low residual values. The resulting values of $\chi_{\mathrm{PBMA/PSD}}/V_0$ are shown in Figure 2a–c.

The RPA predictions for the value of χ at the spinodal line are obtained for $S^{-1}(Q) = 0$ and are equal to $\chi_s/V_0 = 5.9 \times 10^{-4}$ for 10% PSD, 2.6×10^{-4} for 25% PSD, and 1.8×10^{-4} for 40% PSD, respectively. Results of our fits for $\chi_{\mathrm{PBMA/PSD}}/V_0$ are well below the values for the first two compositions. For the third composition, the RPA prediction is clearly slightly above the result of the fit for $\chi_{\mathrm{PBMA/PSD}}/V_0$ at 125 °C so that the spinodal line was crossed between 125 and 135 °C. It should be noted that the RPA predictions should be taken with caution due to well-known shortcomings of the RPA (mean field, linear response, incompressible mixtures) especially for low molecular weight blends like the ones measured here and close to the spinodal line. Because of the proximity of the glass–rubber transition temperature for PSD, there is no hope of reaching the UCST by cooling down below ambient temperature.

The results reported here support the observations made by Russell et al.[16,17] on diblock copolymers; i.e., the χ parameter is positive for all the measured temperatures and exhibits a minimum at a temperature value that is dependent on composition (which is the signature of a miscibility gap between an UCST and a LCST). A similar miscibility gap was observed by Ougizawa and Inoue[18] for a mixture of two random copolymers of styrene with acrylonitrile and butadiene.

A number of "free volume" models[19-21] have been developed to explain miscibility gaps in polymer solutions.[22-23] However, to our knowledge, no model exists for polymer blend mixtures. The common feature of the existing models[19-21] is an increase of the compressibility with temperature, i.e., an increase of the free volume (considered to be a third component added to the polymer and solvent components). This brings about the existence of an LCST and therefore can describe an upturn (decrease and then an increase) in the low-Q scattered intensity. Efforts are being made to extend these models to polymer blends.

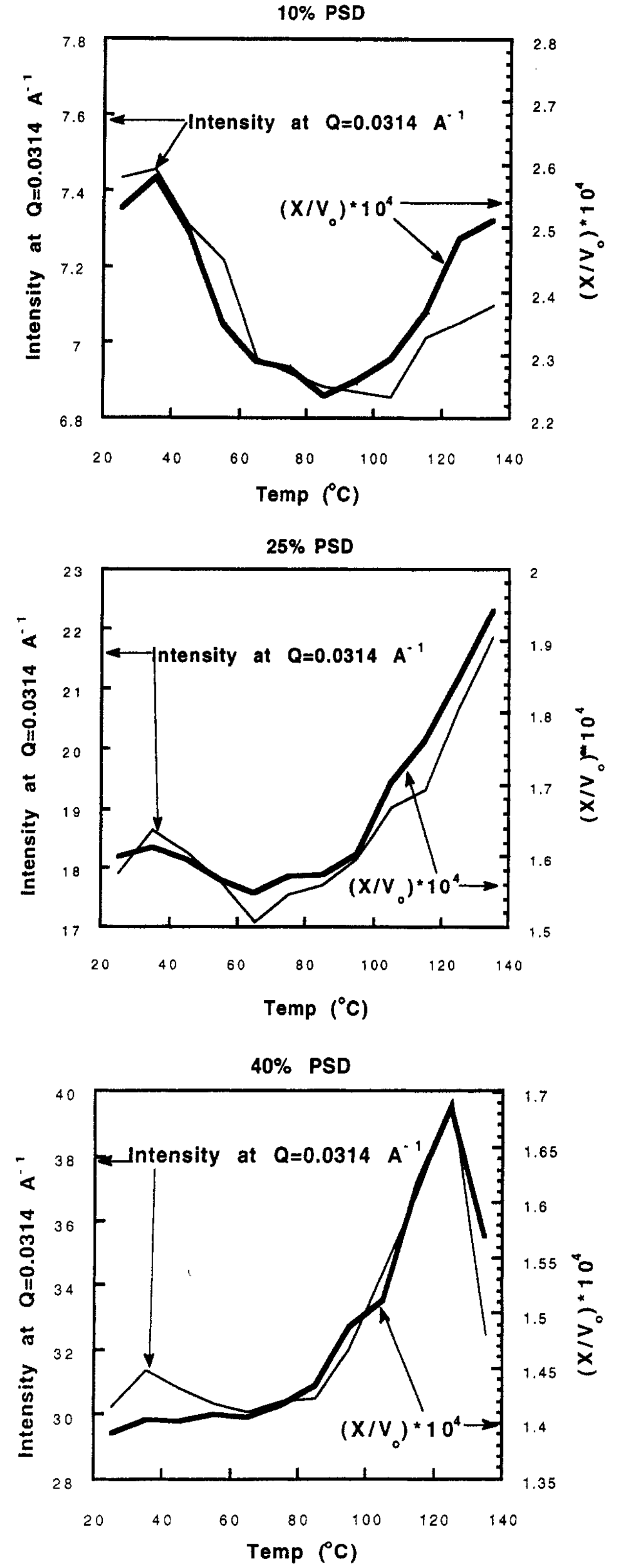

Figure 2. Variation of the low-Q intensity (cross section) measured at $Q = 0.0314$ Å^{-1} and of the rescaled χ parameter ($\chi_{\mathrm{PBMA/PSD}}/V_0$) with temperature for the PSD/PBMA blend with (a) 10% PSD composition, (b) 25% PSD composition, and (c) 40% PSD composition.

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