Communications to the Editor

Synchrotron SAXS Investigation of the Interaction Parameter in a Novel Polymer Blend

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There is an on-going interest in polymer blends spurred by an expanding range of technological applications.[1−3] A wealth of experimental and theoretical information is rapidly advancing our understanding of the factor governing blend miscibility.[4−7] Advanced probes such as small-angle neutron scatttering (SANS) are becoming a routine technique to extract quantitative information such as chain dimension (radius of gyration, R_g) and the Flory−Huggins interaction parameter (χ).[8−9] A peculiar phase behavior of polymer blends is an entropy-driven, lower critical solution temperature (LCST), a phenomenon in which the mixture phase separates upon heating.[5] This is basically the consequence of the vanishingly small combinatorial entropy of mixing, which requires specific attractive interaction, and/or packing events to occur for the blend to be miscible.[9−11] *Subtle higher* order molecular structures such as size and shape of the monomers, tacticity, and isomer structure are therefore of paramount importance in controlling the miscibility of the mixture.[9−11] A well-known example is isotopic substitution, which can shift the critical temperature by orders of magnitude.[12] The purpose of this paper is 2-fold: (i) to report a novel miscible polymer blend that is convenient for experimental and theoretical study and (ii) to demonstrate the merit of synchrotron small-angle X-ray scattering to measure the Flory−Huggins interaction parameter.[13−14] For samples with sufficient electron density contrast, synchrotron radiation has important advantages over SANS: no isotopic labeling is necessary; the highly collimated synchrotron beam and high photon flux allow ultra high resolution experiments (q better than 10^{-3} Å^{-1}), fast data collection (a few seconds), and dynamic measurements in real time.[15] These types of SAXS studies would be further advanced using the new generation of synchrotron facilities such as the Advanced Photon Source (APS) at the Argonne National Laboratory.

We report on the phase behavior of poly(cyclohexyl acrylate) (PCHA) with poly(2-bromostyrene) (P2BrS). We use differential scanning calorimetry (DSC) to determine the state of miscibility (i.e., presence of a single glass transition) and cloud points to locate the LCST. Finally, we determine χ by fitting the de Gennes random phase approximation (RPA)[16] formalism to the SAXS coherent cross section

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Table 1. Sample Characteristics

sample	M_w	M_w/M_n	density (g/cm^3)	molar vol (cm^3/mol)
PCHA	150 640	1.3	1.104[a]	140
P2BrS	60 900	1.7	1.550[a]	116

[a] Measured in a density gradient column at 20 °C.

Sample. Poly(cyclohexyl acrylate) (PCHA) was prepared from cyclohexyl acrylate (Polysciences, Inc.) in benzene solution at 333K using 2,2-azobis(isobutyronitrile) as the initiator. Poly(2-bromostyrene) was obtained from Polysciences, Inc. The molecular weight was determined by size exclusion chromatography on a Waters 840 with three microstyrogel column sets (10^3, 10^4, and 10^5 Å). Five monodisperse polystyrene materials were used for the molecular weight calibration using tetrahydrofuran as the elution solvent. Table 1 summarizes the characteristics of the samples.

Dynamic Scanning Calorimetry (DSC). Blends at different compositions were prepared by co-dissolution in toluene (2 wt %) followed by precipitation in methanol. They were then dried in a vacuum oven at 373 K for 24 h to remove any residual solvent. The thermal measurements were obtained on a Seiko DSC Model 220C. The sample was annealed in the DSC pan at 423 K for 30 min and then cooled down at a rate of 10 °C/min. The glass transition temperature (T_g) was determined as the temperature of the midpoint of the heat capacity change.

Cloud Point Determination. We located the cloud point of a 50/50 blend by light scattering using a He−Ne laser (λ = 6328 Å). Thin polymer films (about 50−70 μm) were cast from a 2 wt % toluene solution onto a glass plate. The films were further annealed at 373 K under vacuum for 12 h. The sample was heated at a rate of 0.1 °C/min and the total forward scattered intensity measured as a function of temperature. The cloud point was determined as the temperature at which the forward light scattering intensity increased sharply.

Small Angle X-ray Scattering (SAXS). We performed the experiments at the Exxon X10A Beamline, National Synchrotron Light Source, Brookhaven National Laboratory, using a two-dimensional position-sensitive detector (MAR image plate, 16 bits). The X-ray beam was monochromatized at 7.2 keV (λ = 1.711 Å) and focused at the detector position with a sample-to-detector distance of 2.2 m. This configuration covered a q-range from 0.005 to 0.1 Å^{-1}. Typical photon flux in this set up is $>10^{10}$ photons/s covering a sample area ~0.1 mm × 0.1 mm. We used kapton films to cast thin polymer films (~0.1 mm) from a 2 wt % toluene solution. These films were further dried at 373 K under vacuum for 12 h. A 50/50 composition along with an empty cell were simultaneously mounted in a translatable Y-Z oven (temperature range 298−493 K controlled within 0.1 °C) with a kapton window through which the X-ray beam passes. The data were corrected for sample and

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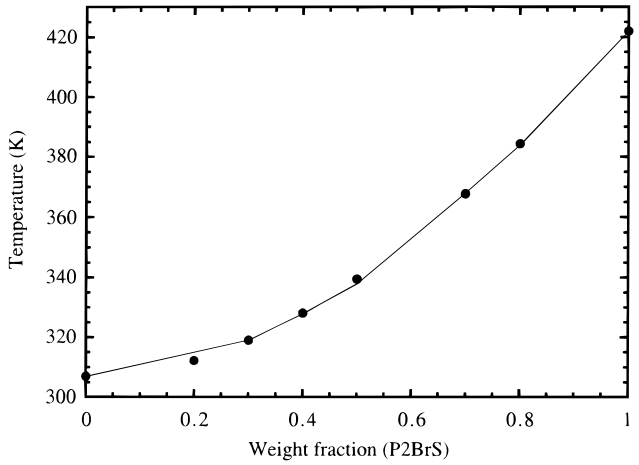

Figure 1. Glass transition temperature of PCHA/P2BrS as a function of composition. The line represents eq 1.

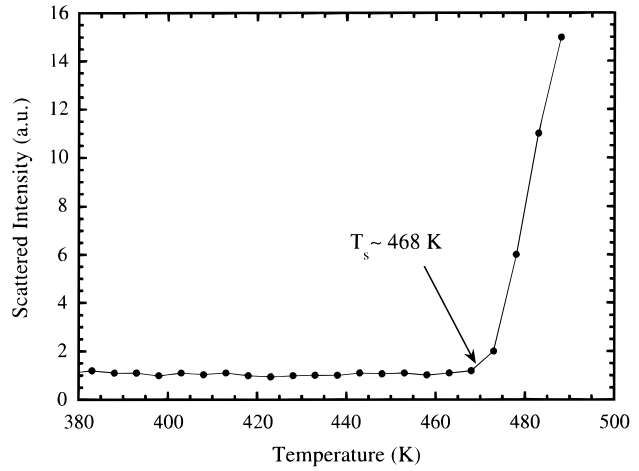

Figure 2. Cloud point determination of the spinodal temperature for a 50/50 blend of PCHA/P2BrS.

kapton attenuation, empty cell scattering, and background scattering and then circularly averaged over a q range of 0.005 to 0.1 Å^{-1}. The data were finally placed on an absolute cross section ($d\Sigma(q)/d\Omega$, cm^{-1}) using a secondary standard from the Oak Ridge National Laboratory (S-2907).

Figure 1 shows the glass transition temperatures of PCHA/P2BrS as a function of composition. The blend is *miscible* at all compositions and temperature less than 423 K as evidenced by the single compositionally-dependent glass transition temperature.[17] The T_g dependence can be represented as

$$T_g = w_1 T_{g1} + \frac{0.72 w_2}{w_1 + 0.72 w_2} T_{g2} \qquad (1)$$

where w_i and T_{gi} are the weight fraction and glass transition of PCHA and P2BrS.

Figure 2 displays the forward light scattering intensity of a 50/50 blend as a function of temperature (372 K ≤ T ≤ 493 K). The location of the spinodal temperature is characterized by a sharp upturn in the scattered intensity around 468 ± 4 K.

Shown in Figure 3 is the SAXS coherent cross section $d\Sigma(q)/d\Omega$ (cm^{-1}) of the same composition (50/50 blend) measured at different temperature. As expected, the low-q intensity, which reflects the concentration fluctuation in the blend, increases with temperatures. The insert displays the Ornstein-Zernike plot, $(d\Sigma(q)/d\Omega)^{-1}$

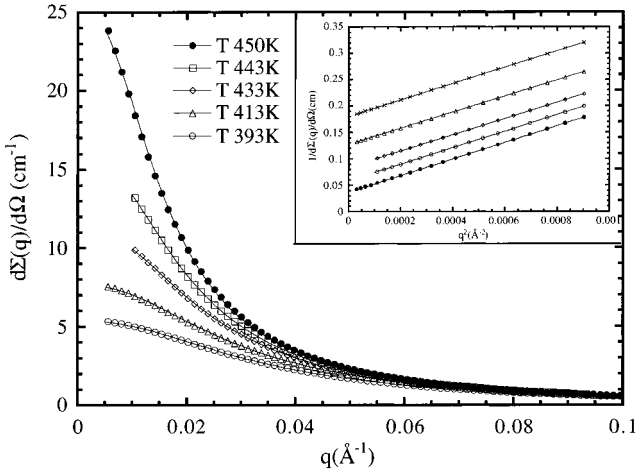

Figure 3. Coherent SAXS cross section (cm^{-1}) for a 50/50 blend of PCHA/P2BrS at different temperatures. Solid lines are fit to the RPA eq 2. Insert is the Ornstein−Zernike plot of the low-q data. The straight lines are linear least-squares fits of the data.

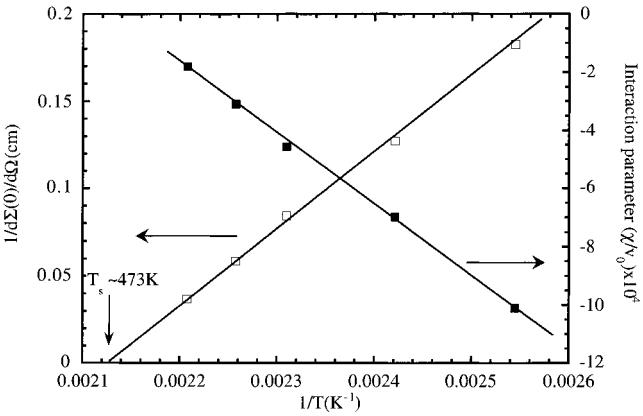

Figure 4. Reciprocal zero wavenumber cross section $d\Sigma(0)/d\Omega$ and the Flory−Huggins χ parameter vs $1/T$ for a 50/50 blend of PCHA/P2BrS. The straight lines are linear least-squares fits of the data.

vs q^2, in the low q-range between 0.005 and 0.02 Å^{-1}. The change in temperature results in a parallel shift of the data with a positive intercept characteristic of a single phase. The data are linear down to $q = 0.005$ Å^{-1} and can be safely extrapolated to $q \to 0$. A plot of the reciprocal of $d\Sigma(q \to 0)/d\Omega$ vs 1/T enables an estimate of the location of the spinodal, where $d\Sigma(0)/d\Omega \to 0$. The results are displayed in Figure 4 (left side) with a spinodal temperature around $T_s \sim 473$ K. The agreement between this value and the cloud point measurement is gratifying. Note also the mean field behavior[5] of the blend in the temperature range between 393 K to 453 K where $(d\Sigma(0)/d\Omega)^{-1} \propto 1/T$.

The binary interaction parameter (χ) can be obtained via the de Gennes random phase approximation (RPA).[16] The RPA provides an expression for the total structure factor, $S(q)$, of a homogeneous blend as

$$\frac{1}{S(q)} = \frac{1}{v_1 N_{n,1} \phi_1 S_D(x_1)} + \frac{1}{v_2 N_{n,2} \phi_2 S_D(x_2)} - \frac{2\chi}{v_0} \qquad (2)$$

where ϕ_i, v_i, and $N_{n,i}$ are the volume fraction, the monomer volume, and the number-average degree of polymerization of the component i. χ is the binary interaction parameter per monomer unit, and v_0 a reference volume often taken as $v_0 = (v_1 v_2)^{1/2}$. $S_D(x)$ denotes the weight-averaged Debye function for polydisperse chains[18]

$$S_D(x_i) = \frac{2}{x_i^2}\left[x_i - 1 + \left(\frac{h_i}{h_i + x_i}\right)^{h_i}\right] \quad (3)$$

where

$$x_i = \frac{q^2 N_{n,i} b_i^2}{6} \quad (4)$$

and

$$h_i = \left[\frac{N_{w,i}}{N_{n,i}} - 1\right]^{-1} \quad (5)$$

b_i and $N_{w,i}$ denote the statistical segment length and the weight-average degree of polymerization of the component i.

The structure factor $S(q)$, is related to the coherent cross section through[13,14]

$$\frac{d\Sigma(q)}{d\Omega} = k_e S(q) \quad (6)$$

where

$$k_e = N\sigma_{TH}\left(\frac{e_1}{v_1} - \frac{e_2}{v_2}\right)^2 \quad (7)$$

is the contrast factor. N, σ_{TH}, and e_i, are, respectively, the Avogadro number, the differential Thomson scattering cross section of the electron,[19] and the number of electrons in the i monomer. The expression in the bracket denotes the electron density difference between the two monomers. Although we can obtained χ through the temperature dependence of $d\Sigma(0)/d\Omega$,[9] we choose to fit eq 2 to the scattering cross section defined in eq 6 to extract χ. A single statistical segment length b and a base-line value were the two extra adjustable parameters used in the fitting procedure. Figure 4 (right side) shows the reciprocal temperature dependence of χ/v_o obtained from the fit. The linear dependence of χ/v_0, as a function of $1/T$ can be represented by

$$\frac{\chi}{v_0} = 0.0052 - \frac{2.44}{T} \quad (8)$$

The interaction parameter is negative over the temperature range studied (372 K $\leq T \leq$ 373 K), and its absolute value decreases with temperature, a characteristic of a miscible blend exhibiting a LCST.

In summary, synchrotron SAXS is a powerfull technique to investigate the thermodynamic of polymer blends. The Flory−Huggins χ parameter was succesfully determined from the absolute coherent SAXS cross section in a novel blend of poly(cyclohexyl acrylate) and poly(2-bromostyrene).

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