Analysis

Neutron Cloud Poinds and Concentration Fluctuations of Polymer Blends

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SUMMARY
        Cloud points were observed in the blends of deuterated polystyrene (PSD) and hydrogeneous poly (vinyl methyl ether) (PVME) by means of temperature scanning Small Angle Neutron Scattering (SANS) technique. The scattering function in the miscible region can be described by the random phase approximation results calculated by de Gennes. This scattering function can also be expressed in the Ornstein–Zernike form in the small q region. A correlation length and spinodal point can then be determined from this critical fluctuation approach.

INTRODUCTION
        The phase diagram of polymer blends is traditionally studied by the light scattering cloud point measurement. Transmitted or scattered light is normally used for this purpose, the intensity of which abruptly changes at the vicinity of the phase transition temperature. We have previously studied PSD/PVME blends (1) by this conventional light scattering technique and it was found that the lower critical solution temperature (LCST) is about 40°C higher than that for hydrogeneous polystyrene PSH/PVME. However, there is one disadvantage in the light scattering technique. Because of the long wavelength involved one may not be able to detect the onset of transition from a stable to a metastable phase. This may be important if the polydispersity of polymers affects the phase separation phenomena. Small angle x-ray (SAXS) or neutron scattering (SANS) techniques are alternative since they are associated with radiation having appreciably shorter wavelengths. SANS is appropriate for PSD/PVME blends to detect the "neutron cloud point" which is the onset of phase transition in this case. This is because that the scattering contrast between PSD and PVME is appreciably high. Furthermore, this technique allows one to obtain information about molecular parameters, such as the Flory–Huggins interaction parameter (χ) and the correlation length (ξ) in the miscible regions of the blend system.
        In this paper, we explore the feasibility of the neutron cloud point measurements and discuss the critical concentration fluctuation of PSD/PVME blends.

EXPERIMENTAL
        The system investigated were blends of deuterated polystyrene (PSD) and poly (vinyl methyl ether) (PVME). The characteristics of these components are listed in Table 1. Samples for SANS experiments were prepared by dissolving the components in toluene and casting them into films, followed by drying in vacuum for a week at 70°C and then for 24

hours at 110°C in order to remove the residual solvent. The dried samples were compression molded at 80°C into discs of 19 mm in diameter and 1.7 mm in thicknesses.

Table 1. The characteristics of the blend component (PSD purchased from Polymer Laboratories, Stowe, OH and PVME from Scientific Polymer Products, Webster, NY).

Component	M_w	M_w	M_w/M_w
PSD	255,000	–	1.08
PVME	99,000	46,500	2.13

The experiments were performed using the SANS facility at the National Bureau of Standards, Washington, DC, which has a two-dimensional position sensitive detector. The incident beam was monochromatized by a velocity selector and had an average wavelength (λ) of 6Å. A focusing collimation system was used to obtain the lower limit of the scattering vector (q) of 0.005Å^{-1}, where $q = \dfrac{4\pi}{\lambda} \sin(\theta/2)$ and θ is the scattering angle. The sample was mounted in a brass cell covered with copper shims of 0.025 mm thickness in order to enhance heat conductivity.

The scattered intensity was collected over the two-dimensional detector pixels ($0.005\text{Å}^{-1} \leq q \leq 0.12\text{Å}^{-1}$) and the dark current intensity due to electronic noise and room background was subtracted. There is no need for further detector response correction in this case. Samples were heated at a rate of 1°C/min and total intensities were recorded as a function of temperature. Phase separation was characterized by an upturn in total scattered intensity with temperature increase as shown in Fig. 1. The intersection of straight lines drawn through portions of the curve below and above the break was taken as the neutron cloud point.

The sample temperatures for both SANS and LS experiments were carefully calibrated in terms of a copper-constantan thermocouple.

The absolute intensity calibration was done using a dry silica gel sample as a secondary standard, which was calibrated in terms of a vanadium standard (2).

RESULTS AND DISCUSSIONS

The scattering function, I(q,T), of a miscible polymer blends has been calculated by de Gennes (3) based on the "Random Phase Approximation." This can be written as

$$\frac{K}{I(q,T)} = \frac{1}{Y_A g_A(Y_A,q)\Phi_A} + \frac{1}{Y_B g_B(Y_A,q)\Phi_B} - 2\chi(\Phi,T) \qquad (1)$$

where Y_i is the reduced degree of polymerization with respect to the unit cell volume, K is a constant, depends on the scattering geometry and the scattering lengths of monomers, Φ is the volume fraction, χ is the Flory-Huggins interaction parameter, $g_N(Y_N,q)$ is the Debye scattering function.

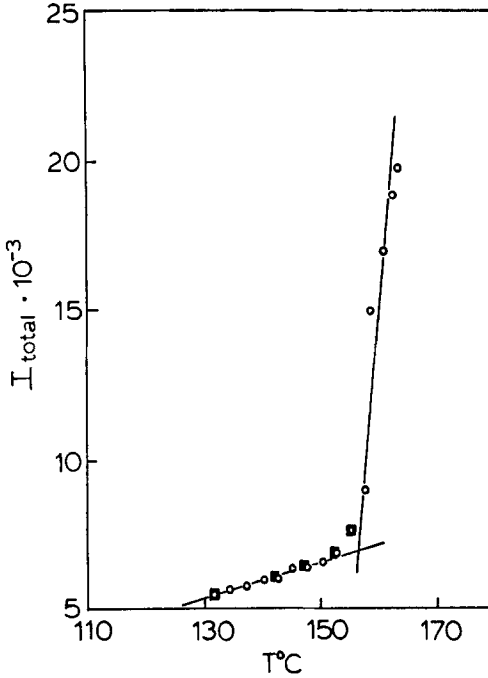The polymer chains in the blend are assumed to remain Gaussian, and at small q, eq. (1) can be written as:

Figure 1. Experimental $I_{tot}(T)$ (in open circle) and calculated $I_{tot}(T)$ (in solid square) at various temperature for wt% 50/50 PSD/PVME blend. Solid lines are drawn through portions of experimental points to determine the neutron cloud point, T_{cp}^{N}.

$$\frac{K}{I(q,T)} = 2[\chi_s(\Phi) - \chi(\Phi,T)] + \frac{q^2 b^2}{18} \frac{1}{\Phi_A \Phi_B} \tag{2}$$

where

$$b = [\Phi_A \Phi_B \left(\frac{b_A^2}{\Phi_A} + \frac{b_B^2}{\Phi_B} \right)]^{1/2} \tag{3}$$

and b_i is the statistical segment length of i, χ_s denotes the interaction parameter at the spinodal point. Eq. (2) can be written in a Lorentzian or Ornstein-Zernike form (4)

$$\frac{I(q,T)}{I(o,T)} = \frac{1}{1+q^2 \xi(T)^2} \tag{4}$$

with

$$\xi(T) = \frac{b}{6} \left\{ \Phi_A \Phi_B [\chi_s(\Phi) - \chi(\Phi,T)] \right\}^{-1/2} \tag{5}$$

This $\xi(T)$ may be interpreted as the concentration correlation length at temperature T.

The scattering function of PSD/PVME with 50/50 weight percent is shown in Fig. 2 for several different temperatures. Before we go into data analysis for correlation length, we would like to discuss the integrated intensity and cloud point study.
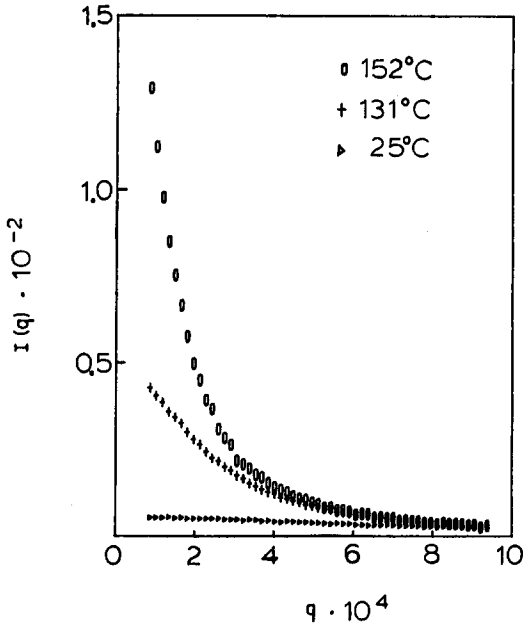
Figure 2. Scattered intensity as a function of q for the above blend at various temperatures.

The total scattered intensity as a function of temperature in the miscible regions is experimentally determined by

$$I_{td}(T) \propto \int_{q_{min}}^{q_{max}} I(q,T) \, 2 \, \Pi \, q \, d \, q$$

which can be integrated to yield:

$$= 2\Pi \frac{I(o,T)}{\xi^2(T)} \ln \left\{ \frac{Cos[tan^{-1}(\xi q_{min})]}{Cos[tan^{-1}(\xi q_{max})]} \right\} \tag{6}$$

where q_{min} and q_{max} are the lowest and highest limits of the scattering vector in our SANS geometry. From both eq. (2) and eq. (5) $I(0,T)$ and $\xi^2(T)$ terms can be cancelled out and lead eq. (7) to the following:

$$I_{tot}(T) \propto \ln \left\{ \frac{Cos[tan^{-1}(\xi q_{min})]}{Cos[tan^{-1}(\xi q_{max}(]} \right\} = F(\xi) \tag{7}$$

The correlation length was obtained from the $I(q,T)^{-1}$ vs q^2 plot as shown in Fig. 3 according to eq. 4. The extracted ξ's at various temperature are listed in Table II. It should be noted that the correlation length increases with increasing temperature. We can calculate $I_{tot}(T)$ from the experimental correlation length by using eq. 7 as shown in Table III. By matching $I_{tot}(T=132°C)$ as the reference point,
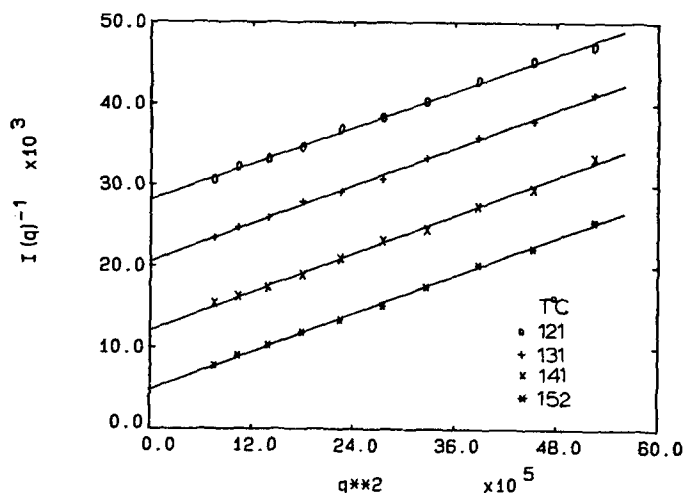
Figure 3. Inverse intensity vs q^2 plots for the above blend at various temperatures.

Table 2. Correlation length at various temperature for two different compositions.

PSD/PVME	50/50	PSD/PVME	80/20
Temp (°C)	ξ (Å)	Temp (°C)	ξ (Å)
121	36.5 ± 0.5	121	34.8 ± 1.0
131	43.6 ± 0.6	131	36.4 ± 0.6
136	50.6 ± 1.2	136	40.3 ± 1.1
141	57.4 ± 1.2	141	41.5 ± 0.9
147	68.2 ± 1.2	147	47.5 ± 0.8
152	90.6 ± 2.2	152	52.8 ± 1.1
157	135.6 ± 4.8	157	55.4 ± 1.1
		162	70.9 ± 1.5

Table 3. Calculated I_{tot} from eq. (7) and experimental I_{tot} for PSD/PVME 50/50.

Temp.	F (ξ)	I_{tot} 10^{-3} (calc)	I_{tot} 10^{-3} (expt)
132	5.42	5.5*	5.5*
142	5.95	6.0	6.1
147	6.28	6.4	6.4
149	6.70	6.6	6.7
152	6.80	6.9	6.9
155	7.50	7.6	7.6

*reference point

it is clear that the data analysis schemes we have used so far are definitely consistent. The total intensity (counts) of scattered neutron before the onset of the phase separation has an insignificant increase.

From eq. (5) we know that ξ diverges at the spinodal point (T_s). Recently, Schelten et al. used this correlation length approach to obtain the spinodal points (T_s) and described the phenomena of critical fluctuations for PSD/PVME blends (5). We have used the same technique to determine T_s which is shown in Fig. 4. These values together with the neutron cloud point T_{cp}^N are listed in Table IV. It is noted that the neutron cloud points are consistent with the light cloud points. Although the cloud points are lower than the corresponding spinodal points as we expected, T_s (160.0°C) for wt % 50/50 PSD/PVME sample is closer to the T_{cp}^N (156.0°C), but the T_s (176.0°C) for wt % 80/20 PSD/PVME sample is significantly higher than T_{cp}^N (168.5°C). This is because the critical composition for this LCST system is around 30% of PSD. The 80/20 sample is farther away from the critical composition. Further studies of T_s from the correlation length approach, together with T_{cp}^N will be reported as a function of composition. The phenomena of critical fluctuations at various compositions as well as temperature and composition dependence of χ for this particular system will also be discussed in the forthcoming paper (6).
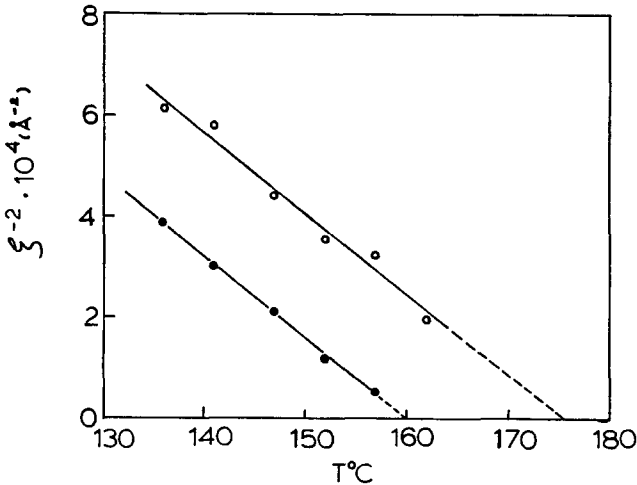

Figure 4.   Inverse square correlation length, ξ^{-2} as a function of T for 50/50 (in solid circle) and 80/20 (in open circle) blends. Spinodal temperature is obtained at $\xi^{-2} \to 0$.

Table 4. The neutron, light cloud points and the spinodal temperatures for wt% 50/50 and 80/20 blends.

Wt%	T_{cp}^{L} °C	T_{cp}^{N} °C	T_{sp} °C
50/50	157.0	156.0	160.0
80/20	171.0	168.5	176.0

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