

Small angle neutron scattering from deuterated polystyrene/poly(vinylmethyl ether)/protonated polystyrene ternary polymer blends

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Small angle neutron scattering measurements were performed on a ternary blend of deuterated polystyrene (PSD), poly(vinylmethyl ether) (PVME) and protonated polystyrene (PSH) for sample temperatures ranging from ambient to 160°C (close to the spinodal decomposition temperature). The extension of de Gennes' random phase approximation formula for the structure factor to three components was used to analyse the data. Two of the Flory-Huggins interaction parameters were obtained from the published literature ($\chi_{\text{PSD/PSH}}$ and $\chi_{\text{PSD/PVME}}$) and the third, $\chi_{\text{PSH/PVME}}$, was extracted from fits to the SANS data. Two different samples corresponding to the same PVME composition but different PSH/PSD fractions gave similar dependences: $\chi_{\text{PSH/PVME}}/v_0 = 10.3 \times 10^{-4} - 0.422/T$ and $\chi_{\text{PSH/PVME}}/v_0 = 10.6 \times 10^{-4} - 0.436/T$, where T is the absolute temperature. Plots of χ versus $1/T$ show a uniform shift of around 20°C (downward in temperature) in going from the PSD/PVME to the PSH/PVME blends.

(Keywords: small angle neutron scattering; ternary polymer blends; polystyrene blends; poly(vinylmethyl ether); random phase approximation; Flory-Huggins interaction parameter)

Introduction

The small angle neutron scattering (SANS) technique has proven to be very valuable for the determination of the Flory-Huggins interaction parameter (χ) in binary polymers. This method, which requires that one of the components of the mixture be deuterated, measures the χ parameter for partially deuterated mixtures. Blends of deuterated polystyrene (PSD) and poly(vinylmethyl ether) (PVME), for instance, have been extensively investigated^{1,2} and temperature, molecular weight and composition dependences of χ have been obtained. The χ parameter for protonated polystyrene (PSH) and PVME is also a quantity of interest to the polymer community. In some instances, such as for the interpretation of light scattering data, one has to either approximate $\chi_{\text{PSH/PVME}}$ by $\chi_{\text{PSD/PVME}}$ and introduce uncertainties (20°C shifts of the cloud point for deuterated and non-deuterated blends have been observed³) or use PSD even if it is not required.

The purpose of this paper is to measure $\chi_{\text{PSH/PVME}}$ from a ternary mixture of PSD/PVME/PSH by SANS. The random phase approximation (RPA) model for ternary homopolymer mixtures is used to analyse the data. Previously measured values of the other interaction parameters $\chi_{\text{PSD/PVME}}$ and $\chi_{\text{PSH/PSD}}$ are used in analysing the data in order to reduce the number of unknown parameters.

RPA theory for a ternary homopolymer mixture

The RPA formalism^{4,5} has turned out to be a major research tool to extract χ parameters in polymer blends. So far, it has worked surprisingly well, considering the crude assumptions involved. RPA has, recently, been extended to multicomponent polymer mixtures^{6,7} such

as homopolymer and/or copolymer blends. In its matrix form⁷, it is simply stated as:

$$S^{-1}(Q) = S_0^{-1}(Q) + V(Q) \quad (1)$$

where $S_0(Q)$ and $S(Q)$ are the static structure factor matrices for the 'bare' and the interacting systems, respectively, and $V(Q)$ is an interaction parameter matrix. This formalism is general and can describe any combination of homopolymer/copolymer mixtures of various architectures (linear, star branched, polymer combs, etc.).

When applied to a ternary incompressible mixture of homopolymers (A, B, C) and assuming that component C is the reference species, sometimes termed the 'matrix' component, then one has to deal with 2×2 matrices for components A and B only:

$$S_{AA}^0(Q) = N_A \phi_A v_A P_A(Q) \quad (2)$$

$$S_{BB}^0(Q) = N_B \phi_B v_B P_B(Q) \quad (3)$$

$$S_{AB}^0(Q) = 0 \quad (4)$$

and the third component, C, enters only through:

$$V_{AA}(Q) = 1/S_{CC}^0(Q) - 2\chi_{AC}/v_0 \quad (5)$$

$$V_{BB}(Q) = 1/S_{CC}^0(Q) - 2\chi_{BC}/v_0 \quad (6)$$

$$V_{AB}(Q) = 1/S_{CC}^0(Q) + \chi_{AB}/v_0 - \chi_{AC}/v_0 - \chi_{BC}/v_0 \quad (7)$$

where N , ϕ and v are the degree of polymerization, volume fraction and monomeric volume, respectively. As customary, v_0 is defined as the volume of the reference lattice cell. If the results are reported in terms of χ/v_0 (as done here), the value of v_0 does not need to be specified. The single-chain structure factors, $P(Q)$ values, are usually taken to be Debye functions:

$$P_A(Q) = 2[\exp(-Q^2 R_{gA}^2) - 1 + Q^2 R_{gA}^2]/Q^4 R_{gA}^4 \quad (8)$$

Table 1 Sample characteristics

Sample	Volume fractions		
	ϕ_{PSD}^a	ϕ_{PVME}^b	ϕ_{PSH}^c
1	0.484	0.516	0.000
2	0.360	0.511	0.129
3	0.238	0.506	0.256

^a PSD: $M_w = 1.95 \times 10^5$ g mol⁻¹; $M_w/M_n = 1.02$; $N = 1741$; $v = 100$ cm³ mol⁻¹

^b PSH: $M_w = 1.90 \times 10^5$ g mol⁻¹; $M_w/M_n = 1.04$; $N = 1827$; $v = 100$ cm³ mol⁻¹

^c PVME: $M_w = 1.59 \times 10^5$ g mol⁻¹; $M_w/M_n = 1.30$; $N = 2741$; $v = 55.4$ cm³ mol⁻¹

$$(b_{\text{PSD}}/v_{\text{PSD}} - b_{\text{PSH}}/v_{\text{PSH}})^2 = 4.16 \times 10^{-3} \text{ mol cm}^{-4}$$

$$(b_{\text{PSH}}/v_{\text{PSH}} - b_{\text{PVME}}/v_{\text{PVME}})^2 = 1.79 \times 10^{-4} \text{ mol cm}^{-4}$$

$$(b_{\text{PSD}}/v_{\text{PSD}} - b_{\text{PVME}}/v_{\text{PVME}})^2 = 6.07 \times 10^{-3} \text{ mol cm}^{-4}$$

and the radius of gyration is given in terms of the statistical length a_A as $R_{gA}^2 = N_A a_A^2 / 6$. Partial structure factors can be obtained as:

$$S_{AA}(Q) = S_{AA}^0(1 + V_{BB}S_{BB}^0) / [(1 + V_{AA}S_{AA}^0)(1 + V_{BB}S_{BB}^0) - V_{AB}^2 S_{AA}^0 S_{BB}^0] \quad (9)$$

$$S_{BB}(Q) = S_{BB}^0(1 + V_{AA}S_{AA}^0) / [(1 + V_{AA}S_{AA}^0)(1 + V_{BB}S_{BB}^0) - V_{AB}^2 S_{AA}^0 S_{BB}^0] \quad (10)$$

$$S_{AB}(Q) = -S_{AA}^0 V_{AB} S_{BB}^0 / [(1 + V_{AA}S_{AA}^0)(1 + V_{BB}S_{BB}^0) - V_{AB}^2 S_{AA}^0 S_{BB}^0] \quad (11)$$

where the Q dependence has been dropped for convenience. Note that the spinodal point is reached when the denominator of the partial structure factors vanishes.

The neutron scattered intensity (macroscopic differential scattering cross-section $d\Sigma(Q)/d\Omega$) is given by:

$$\begin{aligned} d\Sigma(Q)/d\Omega &= \mathbf{B}^T \mathbf{S}(Q) \mathbf{B} \\ &= (b_A/v_A - b_C/v_C)^2 S_{AA}(Q) \\ &\quad + (b_B/v_B - b_C/v_C)^2 S_{BB}(Q) \\ &\quad + 2(b_A/v_A - b_C/v_C) \\ &\quad \times (b_B/v_B - b_C/v_C) S_{AB}(Q) \end{aligned} \quad (12)$$

where the b s are the monomeric scattering lengths for the different components. Note that, due to the incompressibility assumption, this result is independent of the contrast between components A and B.

Experimental

The molecular weights and polydispersity of the polymers used are given in *Table 1*. The polymer blends were made by dissolving the components at the desired composition in toluene and then casting a film of the blend. The cast films were dried in a vacuum oven to remove the toluene and then melt pressed into a shape suitable for neutron scattering (0.8 mm \times 14 mm discs). Data from a set of three samples are reported here. The compositions (volume fractions) are given in *Table 1*. Sample 1 (containing no PSH) was included in order to reproduce the previously obtained results from binary PSD/PVME blends and in order to refine the temperature dependence of $\chi_{\text{PSD}/\text{PVME}}$ for the molecular weights used here. Samples 2 and 3 keep the PVME

composition constant for convenience in estimating the coefficients that enter into the composition dependence of χ .

Measurements were made on the NIST 8 m SANS instrument with 0.9 nm wavelength and at temperatures ranging from 60 to 160°C (the upper limit is close to the spinodal temperature of the blend). Data were corrected for empty cell scattering, beam blocked background, incoherent scattering and transmission and then rescaled to obtain an absolute cross-section $d\Sigma(Q)/d\Omega$ using a silica gel sample with calibrated scattering cross-section. *Figure 1* shows data corrected for sample 3 for temperatures between 135°C and 160°C.

Data treatment and discussion

A non-linear least-squares fit of the three-component RPA model was made to the data using the parameters shown in *Table 1*. In order to reduce the number of floating parameters, a single monomer segment length a_{av} was used with the following assumption:

$$a_i = a_{av}(v_i/v_o)^{1/2} \quad i = A, B, C \quad (13)$$

Also, the following temperature dependences of the χ/v_o parameters were used:

$$\chi_{\text{PSD}/\text{PSH}}/v_o = -2.9 \times 10^{-6} + 0.0020/T \quad (14)$$

$$\chi_{\text{PSD}/\text{PVME}}/v_o = 9.73 \times 10^{-4} - 0.416/T \quad (15)$$

where T is in K. $\chi_{\text{PSD}/\text{PSH}}/v_o$ was obtained from reference 8 and $\chi_{\text{PSD}/\text{PVME}}/v_o$ was the result of fits to the data taken from sample 1 which show good agreement with previously reported results². It should be noted that the value of χ/v_o for PSH/PSD is about two orders of magnitude smaller than that for PSD/PVME. Consequently, the data analysis is not very sensitive to slight variation of $\chi_{\text{PSD}/\text{PSH}}/v_o$. The remaining unknown parameters which were obtained from analysis of the data were: a background level (small compared to $d\Sigma(Q)/d\Omega$), a_{av} and $\chi_{\text{PSH}/\text{PVME}}/v_o$.

It is interesting to see that the reduced SANS data do not follow the intuitive trend that one expects based on previous binary blends experiments, i.e. the scattered intensity at low Q does not necessarily increase with increasing temperature. In fact, the low Q intensity initially decreases with increasing temperature for sample 3 (*Figure 2*) before increasing close to the spinodal temperature. This can be understood in the framework of the three-component RPA as an interplay of the

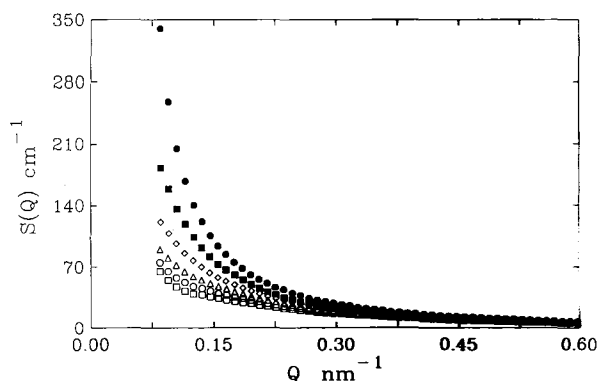


Figure 1 SANS data from sample 3 for temperatures between 135°C and 160°C. Temperature (°C): (□) 135; (○) 140; (△) 145; (◇) 150; (■) 155; (●) 160

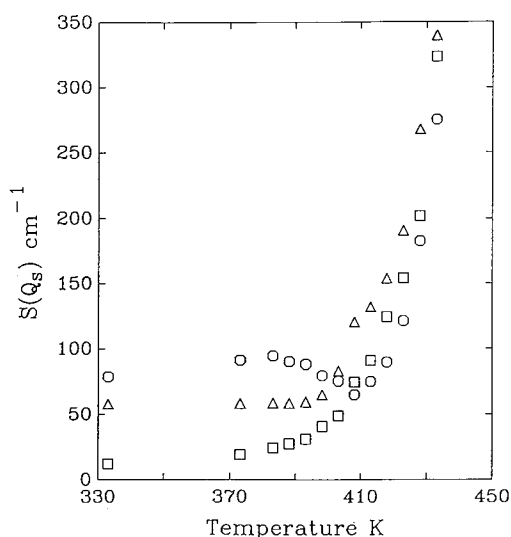


Figure 2 Low Q intensity ($Q_s = 0.085 \text{ nm}^{-1}$) for samples 1 (\square), 2 (\triangle) and 3 (\circ) with increasing temperature

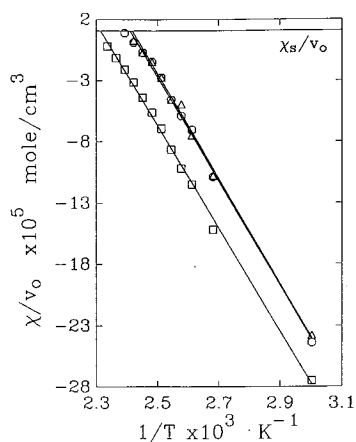


Figure 3 Variations of $\chi_{\text{PSD/PVME}}/v_0$ (obtained from sample 1) and $\chi_{\text{PSH/PVME}}/v_0$ (obtained from samples 2 and 3). Symbols as in Figure 2

various terms in $d\Sigma(Q)/d\Omega$. This behaviour is obtained even when all three χ s are of the form $A + B/T$.

Results of the fits showed that $\chi_{\text{PSH/PVME}}/v_0$ has the

following temperature dependence:

$$\chi_{\text{PSH/PVME}}/v_0 = 10.3 \times 10^{-4} - 0.422/T \text{ for sample 2} \quad (16)$$

$$\chi_{\text{PSH/PVME}}/v_0 = 10.6 \times 10^{-4} - 0.436/T \text{ for sample 3} \quad (17)$$

We have used the same $\chi_{\text{PSD/PVME}}/v_0$ and $\chi_{\text{PSD/PSH}}/v_0$ for samples 2 and 3 (that have the same PVME content but different PSD/PSH ratios). This appears to be a valid assumption since the $\chi_{\text{PSH/PVME}}/v_0$ values obtained show that the spinodal temperature for the PSH/PVME system is 20°C lower than that of PSD/PVME, in agreement with cloud point measurements³. Figure 3 shows that the temperature dependences of $\chi_{\text{PSD/PVME}}/v_0$ and $\chi_{\text{PSH/PVME}}/v_0$ are parallel indicating that deuteration brings about a uniform shift in the spinodal temperature.

A more systematic SANS study to measure the composition dependence of $\chi_{\text{PSH/PVME}}/v_0$ is currently underway on PSD/PVME/PSH samples with a wider range of compositions (varying the PVME content as well as the relative amounts of PSD/PSH). These investigations will, hopefully, yield the full composition dependence of $\chi_{\text{PSH/PVME}}$ in ternary blends and its extrapolated value for binary (PSH/PVME) blends.

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