

Small angle neutron scattering from polymer blends in the dilute concentration limit

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Small angle neutron scattering has been used to study the radius of gyration and thermodynamics of dilute blends of deuterated polystyrene (PSD) in a strongly interacting matrix of poly(vinylmethylether) (PVME) and in a weakly interacting matrix of protonated polystyrene (PSH). The PSD chain is found to be slightly expanded in the PVME matrix over the PSH matrix with the radius of gyration for PSD being 123 Å in PVME vs 115 Å in PSH. The Flory interaction parameter, χ/v_0 , for the PSD/PVME blend is found to be in approximate agreement with an extrapolation of data from studies of χ/v_0 for PSD/PVME at high concentration to the dilute concentrations studied in this work. The concentration dependence of χ/v_0 is close to linear and shows no strong change in slope down to $\phi=0.02$, the lowest concentration studied in this work. Analysis of the temperature dependence of χ/v_0 and the second virial coefficient, A_2 indicates that phase separation should occur for PSD/PVME in the range of 200 °C for a sample with $\phi_{\text{PSD}} \cong 5\%$.

INTRODUCTION

Small angle neutron scattering (SANS) has proven to be one of the most powerful techniques for studying the interactions and conformation of polymer chains both in solutions and the bulk in recent years.¹⁻¹⁶ Early work concentrated on adapting the analysis developed historically for light scattering to SANS. These studies typically involved measuring the scattering from dilute labeled (deuterated) chains in a matrix of unlabeled (protonated) chains or solvent. The goal was to measure the radius of gyration, molecular weight and the Flory interaction parameter, χ , (or the second virial coefficient, A_2).¹⁻¹⁶ Typically the data analysis was done using the classical cross plot technique developed by Zimm.¹⁷ More recently, techniques based on the random phase approximation (RPA) by de Gennes have allowed analysis of bulk polymer systems with high concentrations of labeled chains.^{8,9-11,14-16,18}

In this work we will discuss data from a dilute blend of deuterated polystyrene (PSD) in a poly(vinylmethylether) (PVME) matrix where there are strong interactions between the components. PSD/PVME is a lower critical solution temperature blend where phase separation occurs on heating. The data obtained in the dilute concentration regime will be compared to that obtained at high concentration by other workers.

THEORY

The classical Zimm equation gives the scattering from a dilute mixture of a polymer in a solvent to be^{8,12,17,21}

$$\frac{k_n \phi_a}{I(\mathbf{q})} = \frac{1}{\langle N_a \rangle_n v_a \langle P_a(\mathbf{q}) \rangle_w} + 2A_2 \phi_a, \quad (1)$$

where $I(\mathbf{q})$ is the measured scattered intensity, $\langle P_a(\mathbf{q}) \rangle_w$ is the weight average single particle form factor for species a , ϕ_a is the volume fraction of the dilute polymer, $\langle N_a \rangle_n$ is the number average degree of polymerization of polymer a , v_a is the specific volume of polymer a , A_2 is the second virial coefficient, and k_n is the contrast factor for neutrons. k_n is equal to

$$k_n = N_A \left(\frac{b_a}{v_a} - \frac{b_b}{v_b} \right)^2, \quad (2)$$

where N_A is Avogadro's number and b_i is the neutron scattering length for species i in the mixture. The second virial coefficient is given by

$$A_2 = \left[\frac{1}{2 \langle N_b \rangle_n v_b \langle P_b(\mathbf{q}) \rangle_w} - \frac{\chi}{v_0} \right], \quad (3)$$

where χ is the Flory interaction parameter between components a and b and v_0 is the reference volume of the lattice (usually $v_0 = \sqrt{v_a v_b}$). In general the Zimm equation has been used for polymer-solvent systems where $P(\mathbf{q})$ for the solvent has negligible \mathbf{q} dependence in the \mathbf{q} range of interest for polymers and hence $P_b(\mathbf{q})$ is ignored.

For polymer chains with a Zimm-Shultz molecular weight distribution^{20,21} $\langle P(\mathbf{q}) \rangle_w$ is given by²²

$$\langle P(\mathbf{q}) \rangle_w = \frac{2}{\langle x \rangle_n^2} \left[\langle x \rangle_n - 1 + \left(\frac{h}{h + \langle x \rangle_n} \right)^h \right], \quad (4a)$$

where

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$$h = \frac{1}{\left(\frac{\langle N \rangle_w}{\langle N \rangle_n} - 1\right)}, \quad (4b)$$

$$\langle x \rangle_n = \langle N \rangle_n l^2 q^2 / 6 = \langle R_g^2 \rangle_n q^2. \quad (4c)$$

$\langle N \rangle_w$ and $\langle N \rangle_n$ are the weight and number average degrees of polymerization, l is the statistical segment length, and \mathbf{q} is the scattering vector [$\mathbf{q} = (4\pi/\lambda) \sin(\theta/2)$, where λ is the neutron wavelength and θ is the scattering angle], $\langle R_g^2 \rangle_n$ is the number average square of the radius of gyration. At small \mathbf{q} , $\langle P(\mathbf{q}) \rangle_w$ can be expanded to give

$$\langle P(\mathbf{q}) \rangle_w \cong \frac{\langle N \rangle_w}{\langle N \rangle_n} \left(1 - \frac{1}{3} \frac{\langle N \rangle_z}{\langle N \rangle_n} \langle x \rangle_n \right), \quad (5a)$$

where

$$\frac{\langle N \rangle_z}{\langle N \rangle_n} = \frac{h+2}{h} \quad (5b)$$

and $\langle N \rangle_z$ is the z average degree of polymerization. In the limit of a monodisperse molecular weight distribution ($\langle N \rangle_w = \langle N \rangle_n = N$) Eq. (4a) becomes the Debye function²³

$$P(q) = \frac{2}{x^2} [\exp(-x) - 1 + x], \quad (6)$$

where $x = (Nl^2/6)q^2$. By combining Eqs. (5a) and (1) and taking the limit $\mathbf{q} \rightarrow 0$ Eq. (7) is obtained,

$$\frac{k_n \phi_a}{I(0)} = \frac{1}{\langle N_a \rangle_n v_a} + 2A_2 \phi_a. \quad (7)$$

This allows the determination of the weight average molecular weight and the second virial coefficient from a plot of $\phi_a/I(\mathbf{q}=0)$ vs ϕ_a which is part of the classical Zimm analysis. The second part of the standard Zimm analysis is performed by taking the limit $\phi \rightarrow 0$ for Eq. (1) which after rearrangement gives

$$\lim_{\phi_a \rightarrow 0} \left[\frac{I(\mathbf{q})}{\phi_a} \right] = k_n \langle N_a \rangle_n v_a \langle P_a(\mathbf{q}) \rangle_w. \quad (8)$$

This also allows determination of the weight average molecular weight at $\mathbf{q}=0$ and the size of the molecule from the slope of a plot of $\lim_{\phi_a \rightarrow 0} [\phi_a/I(\mathbf{q})]$ vs q^2 [Eq. (5a)] or by fitting

the entire functional form for $P(\mathbf{q})$ to the data.

de Gennes has developed an expression for the total coherent scattering from a binary (miscible) mixture of polymers using the random phase approximation.^{15,18} The total scattering is given by

$$\frac{k_n}{I(\mathbf{q})} = \frac{1}{\langle N_a \rangle_n v_a \phi_a \langle P_a(\mathbf{q}) \rangle_w} + \frac{1}{\langle N_b \rangle_n v_b \phi_b \langle P_b(\mathbf{q}) \rangle_w} - 2 \frac{\chi}{v_0}. \quad (9)$$

Equation (9) can also be recast in the form used by Zimm

TABLE I. (a) Sample characteristics. (b) Sample compositions (volume fraction).

	(a)		
	N_w/N_n	N_w	N_n
PSD	1.02	1805	1770
PVME	1.66	6853	4128
PSH	1.04	1824	1754
	(b)		
	PSH matrix	PVME matrix	
ϕ_{PSD}		ϕ_{PSD}	
0.018 19		0.019 35	
0.038 31		0.037 81	
0.054 35		0.055 64	

$$\frac{k_n \phi_a}{I(\mathbf{q})} = \frac{1}{\langle N_a \rangle_n v_a \langle P_a(\mathbf{q}) \rangle_w} + 2 \phi_a \left[\frac{1}{2 \phi_b \langle N_b \rangle_n v_b \langle P_b(\mathbf{q}) \rangle_w} - \frac{\chi}{v_0} \right]. \quad (10)$$

When component a is dilute ($\phi_b \rightarrow 1$) Eq. (10) is identical to Eq. (1). In this work Eq. (1)–(10) will be used to analyze SANS data from strongly interacting blends of PSD and PVME polymers to extract the interaction parameter, molecular weight, and radius of gyration (or equivalently, the statistical segment length) as a function of composition and temperature in the dilute PSD regime. The two approaches of using the full RPA theory vs Zimm analysis are equivalent in the limit of dilute labeled polymer and we will use aspects of both types of analysis to examine the data.

EXPERIMENT

The poly(vinylmethylether) was cationically polymerized in toluene using boron trifluoride-ethyl ether complex as the catalyst. The PVME was then fractionated using toluene as the solvent and hexane as the nonsolvent. The details of the synthesis and fractionation procedure have been described elsewhere.²⁴ The molecular weight of the PVME was determined using gel permeation chromatography (GPC) with Mark–Houwink–Sakurada parameters for PVME from the literature.²⁴ The polystyrene and deuterated polystyrene were purchased from Polymer Labs, Inc. and the molecular weights were determined by the manufacturer using GPC.²⁵ The samples for neutron scattering were prepared by dissolving the PSD and PVME in toluene and then allowing the solution to evaporate in a Teflon petridish and form a thin film. This film was then dried in vacuum to remove the remaining toluene. Sample compositions and characteristics are given in Table I. The film was pressed into a SANS sample holder using a hydraulic press at 120 °C. The scattering experiment was carried out as a function of temperature at the NIST Cold Neutron Research Facility using the 30 m NIST-NG7 SANS spectrometer.^{25,26} The data were corrected for scattering from the empty cell, matrix background scattering, detector dark current and sensitivity, sample transmission and thickness, placed on an absolute scale using a calibrated secondary standard and circularly averaged to produce the $I(\mathbf{q})$ vs \mathbf{q} plots. The matrix background scattering correction involves subtracting the scattering from the pure PSH or

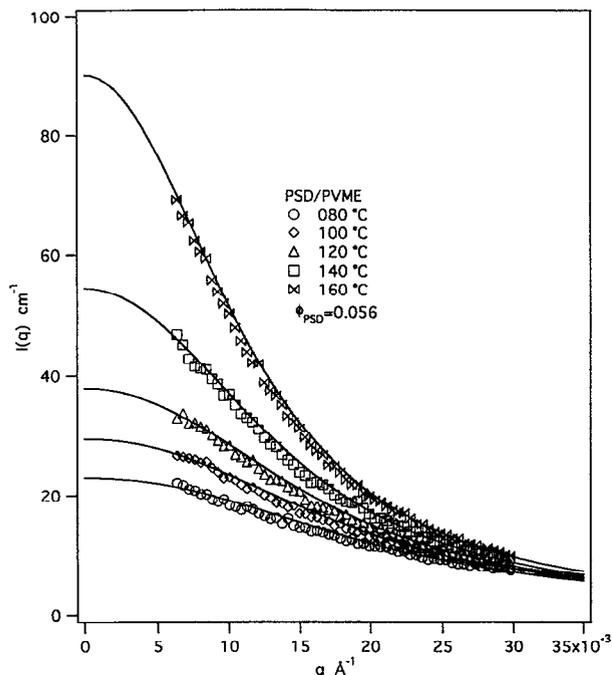


FIG. 1. SANS curves as a function of temperature for $\phi_{\text{PSD}}=0.056$ PSD/PVME blend.

PVME scattering (weighted by the composition of PSH or PVME) from each sample. The scattering from the hydrogenated matrix is largely incoherent and is equivalent to the subtraction of the pure solvent scattering in traditional light scattering.

RESULTS AND DISCUSSION

Figure 1 shows typical SANS data for the highest concentration PSD/PVME sample ($\phi_{\text{PSD}}=0.056$) as a function of temperature. The data show an increase in the scattering as a function of temperature as expected because of an increase in growth of the critical fluctuations as the phase boundary is approached. Rather than plot the data in a typical Zimm plot, the data at each temperature was extrapolated to the limit of zero concentration at every value of \mathbf{q} using the equation

$$\frac{\phi_{\text{PSD}}}{I(\mathbf{q})} = B + A \phi_{\text{PSD}}, \quad (11)$$

where the intercept, $B = \lim_{\phi_{\text{PSD}} \rightarrow 0} [\phi_{\text{PSD}}/I(\mathbf{q})]$ is the limiting zero concentration scattering.

This is identical to one of the steps in the classical Zimm analysis except with the use of a computer it is easy to extend the extrapolation to encompass the entire \mathbf{q} range covered by the experiment rather than just the small \mathbf{q} region. By calculating $\lim_{\phi_{\text{PSD}} \rightarrow 0} [\phi_{\text{PSD}}/I(\mathbf{q})]$ over the entire \mathbf{q} range,

Eq. (4a) for $P(\mathbf{q})$ [in combination with Eq. (8)] can then be fit to the data using a nonlinear least squares algorithm to obtain $I(\mathbf{q}=0)$ and R_g [from $P(\mathbf{q})$] rather than resorting to

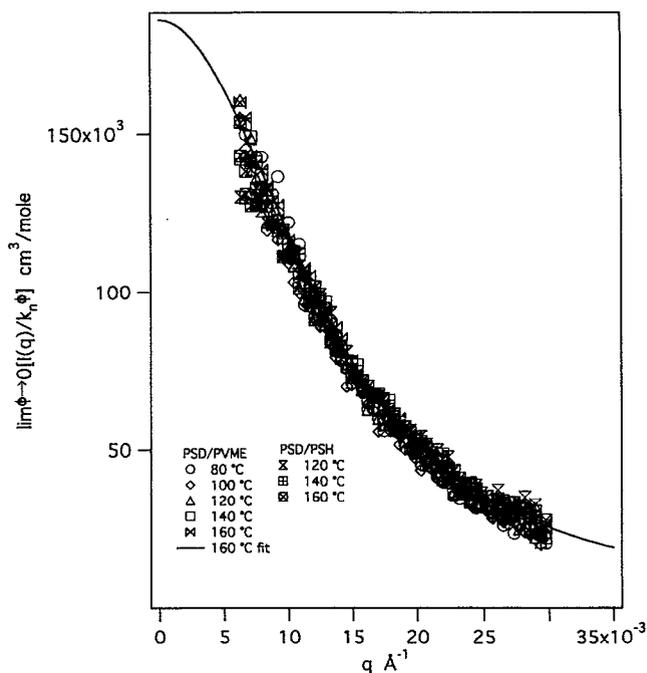


FIG. 2. $\lim_{\phi_{\text{PSD}} \rightarrow 0} [\phi_{\text{PSD}}/I(\mathbf{q})]$ vs \mathbf{q} SANS scattering curves for all samples.

linearizing $P(\mathbf{q})$ by expansion. This type of analysis provides the benefit of utilizing the data obtained at all \mathbf{q} vectors studied in the experiment without the small \mathbf{q} limit imposed by expanding $P(\mathbf{q})$ at $\mathbf{q}R_g < 1$.

Figure 2 shows all the zero concentration extrapolated scattering curves as a function of temperature for all the PSD/PVME and PSD/PSH samples. The data have been normalized by the contrast factor k_n so all the curves collapse together. The curves are all overlapping but small systematic changes in the statistical step length obtained by fitting the data to Eq. (8) are found and will be discussed later. The solid line is a typical fit of Eq. (8) to the data (for the highest temperature PSD/PVME sample, $T=160$ °C. To fit the data Eq. (4a) was used for $P(\mathbf{q})$ with l_{PSD} and N_{PSD} as the floating parameters [note that in the limit of zero PSD concentration the step length and molecular weight of the matrix PVME (l_{PVME} and N_{PVME}) are not important]. An average value of $N_{\text{PSD}}=1720$ was obtained from all the data which is in good agreement with the molecular weight obtained from the manufacturer ($N_{\text{PSD}}=1760$). The values for R_g (calculated from $R_g = N^{1/2}l/\sqrt{6}$) and l_{PSD} obtained from the fits are given in Table II. The average value of R_g is 115 Å for the PSH matrix which corresponds to l_{PSD} of 6.8 Å, in agreement with previous work.¹⁵ The average value of R_g in the PVME matrix is 123 Å ($l_{\text{PSD}}=7.3$ Å), somewhat larger than in the PSH matrix. The data analysis was also performed with the molecular weight of the PSD held fixed. This gave qualitatively identical results only with somewhat more scatter in the R_g values.

Figure 3 is a plot of R_g^{PSD} as a function of temperature $\lim_{\phi \rightarrow 0}$ for both the PSD/PVME and PSD/PSH systems. The straight lines through the data are linear least squares fits. Although a

TABLE II. Step length and degree of polymerization of the PSD chain in PVME and PSH matrices from zero concentration extrapolated scattering data.

Temperature	PVME matrix			PSH matrix		
	$R_{g\text{PSD}}$ (Å)	l_{PSD} (Å)	$N_{n\text{PSD}}^a$	$R_{g\text{PSD}}$ (Å)	l_{PSD} (Å)	$N_{n\text{PSD}}^a$
80 °C	124.4	7.35	1900
100 °C	125.6	7.42	1730
120 °C	124.1	7.33	1790	113.3	6.69	1581
140 °C	122.4	7.23	1825	115.6	6.83	1667
160 °C	118.2	6.98	1819	116.1	6.86	1627

^aAverage of all samples $N_n = 1720$.

definite trend seems to be present with the PSD/PSH having a positive slope and the PSD/PVME having a negative slope, a critical review of the data indicates that all the observed variation is approximately within the error bars from the fit of Eq. (4a) to the data. It is interesting to note that the two lines fit to the data intersect at a temperature of about $T = 182$ °C, which is in the range of the extrapolated spinodal temperature for the highest concentration sample, possibly implying that after phase separation of the PSD from the PSD/PVME blend the R_g is equivalent to that measured in the PSD/PSH blend. Other workers have studied the temperature dependence of the chain end-to-end distance, $\langle r^2 \rangle_0^{1/2}$, for PS and have generally found a negative value of $d \ln \langle r^2 \rangle_0 / dT$ from intrinsic viscosity measurements in theta solvents and positive values from force-temperature measurements.²⁷⁻³¹ Another recently reported neutron study concluded that no discernible temperature dependence for the size of the chain could be measured.^{32,45} It is interesting that the numbers for $d \ln \langle r^2 \rangle_0 / dT$ for PS are not in agreement from the different measurements and even vary in sign.

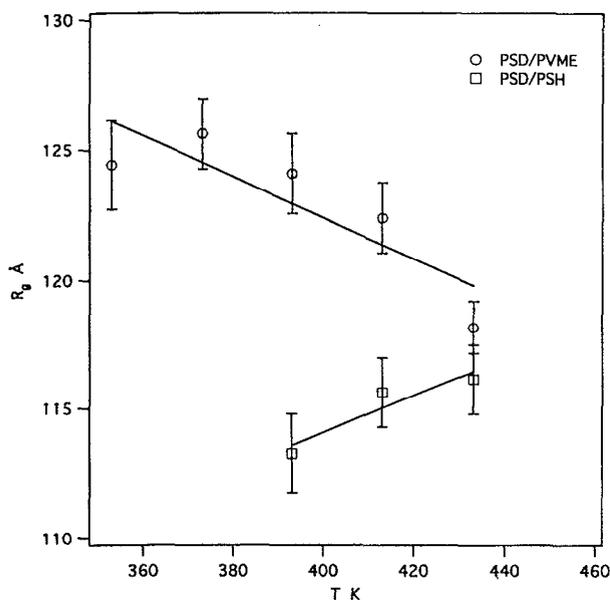


FIG. 3. $R_{g\text{PSD}}^{\lim_{\phi \rightarrow 0}}$ vs temperature for the PSD/PSH and PSD/PVME blends.

If one takes the trends observed in the SANS data presented in this work as being valid then the decrease in $R_{g\text{PSD}}$ with increasing temperature is consistent with the PVME becoming a poorer solvent for PSD as the temperature increases. If the temperature coefficients of PSD in the different matrices are calculated from the data the values obtained are $d \ln \langle r^2 \rangle_0 / dT$ for PSD in PVME = $-6 \pm 5 \times 10^{-4} \text{ K}^{-1}$ and $+6 \pm 4 \times 10^{-4} \text{ K}^{-1}$ for PSD in PSH. These numbers are in general about an order of magnitude smaller than obtained from force-temperature or intrinsic viscosity measurements and it would be difficult to argue decisively that they are significantly different than zero. Although no large changes in $R_{g\text{PSD}}$ as a function of temperature are seen a small average expansion of PSD in PVME is observed with the average value of $R_{g\text{PSD}}$ being about 7% larger in a PVME matrix than in PSH. A much larger change in R_g for a Monte Carlo simulation of dilute polymer blends has been reported by Sariban and Binder where the dilute chain is observed to collapse on the order of 50% for the longest chains as the phase separation transition is approached.³³ Classical Flory theory for chain expansion for a polymer coil in a good solvent should predict that a small expansion of the coil in PSD/PVME at low temperatures since χ/v_0 is negative which gives rise to a favorable free energy of mixing (PVME is a good polymeric solvent at low temperatures).³⁴ This effect should be small (although no attempt has been made to calculate it) since the entropy of mixing is very small due to the high molecular weight of the PVME. A recent calculation predicts a swelling effect in blends when the components have differing monomer sizes and may explain the effects measured in this work.³⁵

An alternative method to fit the data were to use Eq. (9) at all concentrations and temperatures with l and χ/v_0 as the fitting parameters ($v_{\text{PSH}} = 99.5$, $v_{\text{PSD}} = 100.4$, $v_{\text{PVME}} = 55.5$, $v_0 = 99.8$ for PSD/PSH, $v_0 = 74.7 \text{ cm}^3/\text{mol}$ for PSD/PVME). Because of the values of l_a and l_b are strongly coupled in Eq. (9) the values of $R_{g\text{PSD}}$ for PSD and PVME matrices cannot be varied independently. Instead an average value of the statistical segment length, l_{ave}^2/v_0 , is used where^{11,15}

$$\frac{l_{\text{ave}}^2}{v_0} = \phi_a \phi_b \left[\frac{\langle N_a \rangle_z}{\langle N_a \rangle_w} \frac{l_a^2}{v_a \phi_a} + \frac{\langle N_b \rangle_z}{\langle N_b \rangle_w} \frac{l_b^2}{v_b \phi_b} \right]. \quad (12)$$

Only the PSD/PVME data are shown because this system is known to show a strong temperature dependence of χ/v_0 . The PSD/PSH system is thought to have a small positive value of χ/v_0 (Ref. 7) but for the molecular weights used in this experiment measurement of χ/v_0 is difficult and cannot discern between the reported value and zero. It is important to point out that the value of χ/v_0 for PSD/PVME obtained from the fit of Eq. (9) to the data are not necessarily the same χ/v_0 as is normally used in the classical Flory-Huggins free energy of mixing because of the possible composition dependence of χ/v_0 . This composition dependence means that there are derivatives of χ/v_0 with respect to ϕ [i.e., $(\partial \chi/v_0 / \partial \phi)$ and $(\partial^2 \chi/v_0 / \partial \phi^2)$] present in the value of χ/v_0 obtained from Eq. (9). Consequently χ/v_0 is sometimes referred to as the "effective" interaction parameter χ_{eff}/v_0 or the "scattering" interaction parameter. If the functional form

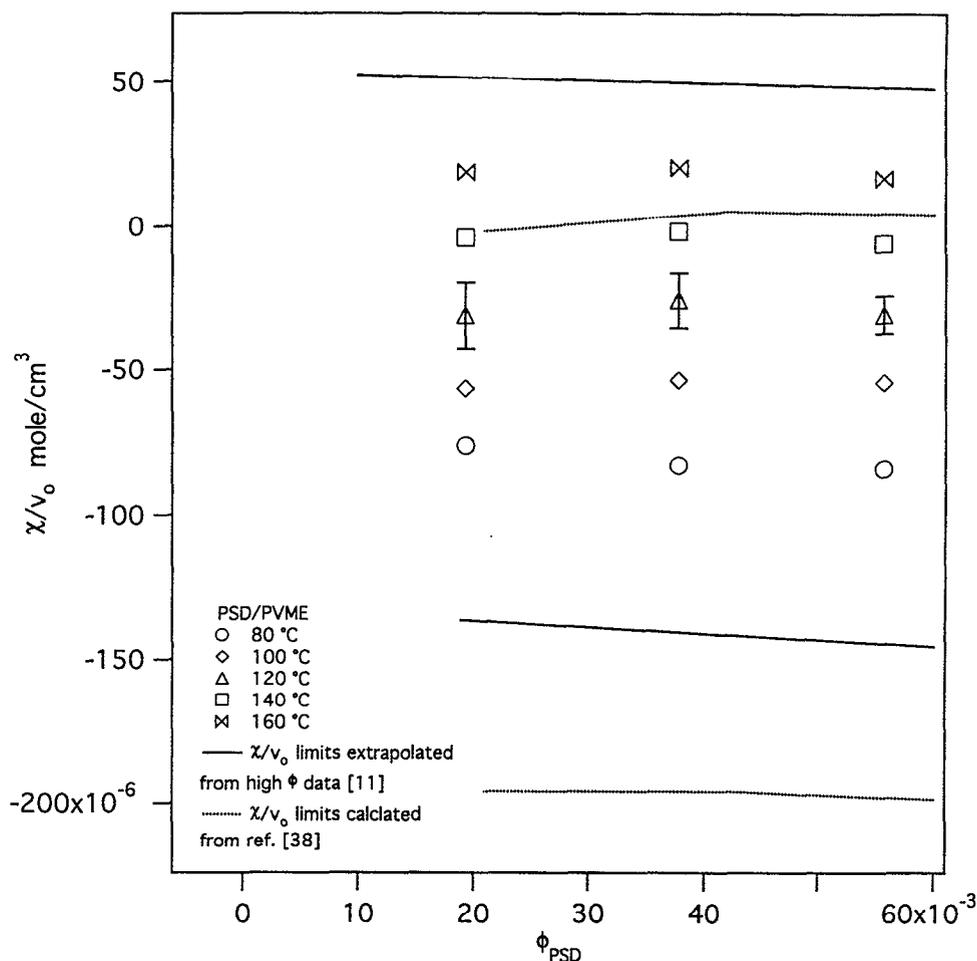
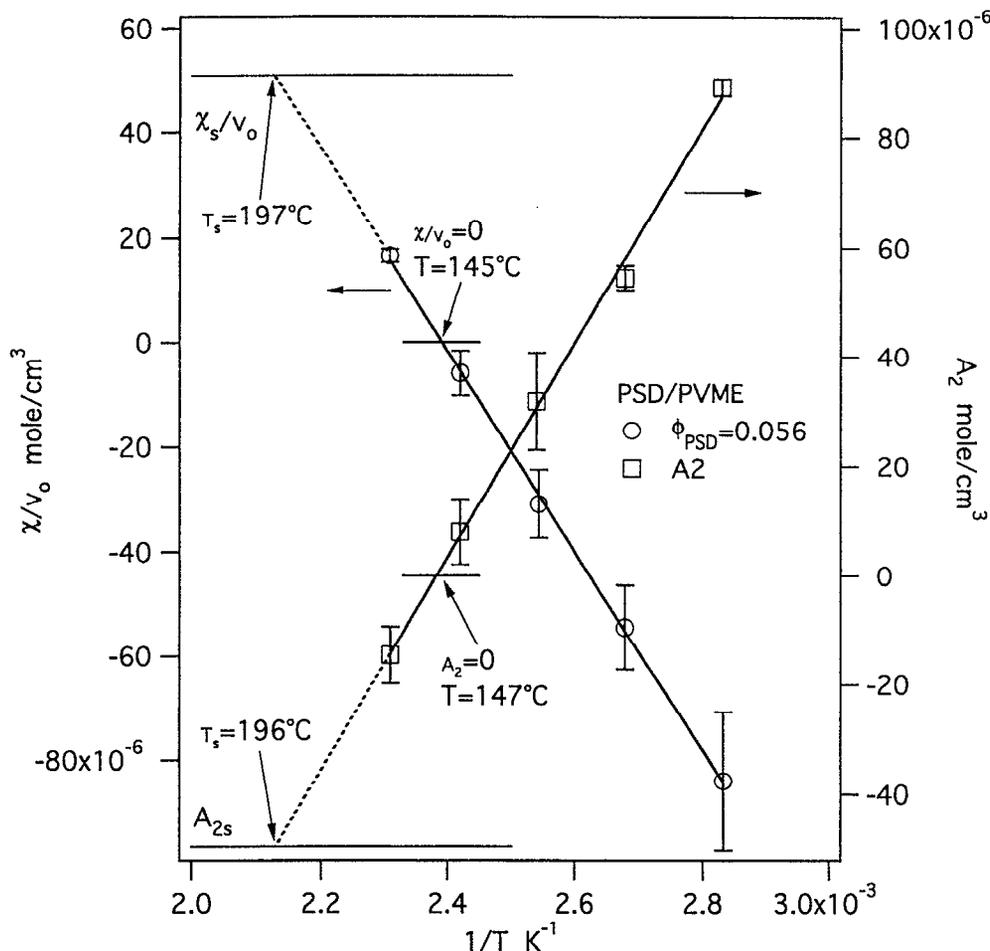


FIG. 4. χ/v_0 vs ϕ for the PSD/PVME blends.

of χ/v_0 is known it is possible to integrate χ/v_0 vs ϕ twice to obtain the value of χ/v_0 used in the Flory-Huggins free energy.¹¹ The overlap concentration, ϕ^* , can be estimated by calculating the monomer concentration in a polymer coil using the measured R_g as the radius of the region of space in which monomers are distributed. For the PSD in the PVME matrix, ϕ^* is about 0.035 (volume fraction) which is about in the middle of the concentrations studied in this work. There were no large changes observed in $R_{g\text{PSD}}$ when the concentration went below ϕ^* from the fit of Eq. (9) to the data and no large swelling effects (as found in low molecular weight solvents) are observed at low temperatures where the PVME matrix corresponds to a "good" polymeric solvent (positive A_2).

Figure 4 is a plot of χ/v_0 for PSD/PVME as a function of concentration for different temperatures. The lines in the figure are calculated from a four parameter model for the composition and temperature dependence of χ/v_0 at 80 and 160 °C for the PSD/PVME blend from Ref. 11. The data in this study fall within the bounds calculated from Ref. 11 and the agreement is remarkably good considering the fits obtained in Ref. 11 were for the concentration range

$\phi_{\text{PSD}}=0.10-0.80$ averaged over different molecular weight(s) and should not be expected to exactly match the samples and concentrations examined in this work. In the composition range studied in this work there is essentially no composition dependence of χ/v_0 . This is in contrast to the high concentration range where a significant composition dependence is observed.¹¹ Recent work by Dudowicz and Freed³⁶⁻³⁸ used a generalized lattice model which includes monomer structure and compressibility to calculate thermodynamic parameters for polymer blends, including χ_{eff} . The effects of monomer structure and compressibility can result in a complex composition dependency of χ_{eff} and explain the almost linear dependence of χ_{eff} on ϕ for PS/PVME as being due mostly to the difference in monomer structure between PS and PVME.³⁶ This work, when extended to lower concentrations, predicts little concentration dependence in χ/v_0 at dilute concentration as observed in this paper and agrees reasonably well on the magnitude of χ/v_0 observed in this work.³⁸ In some of the recent theoretical work the effect of compressibility has been added by using a three component model with a small component of voids.³⁹⁻⁴¹ The effective interaction parameter measured using a two component


 FIG. 5. χ/v_0 vs $1/T$ and A_2 vs $1/T$ for the PSD/PVME blends.

model, such as done in this work, then has contributions from three interaction parameters ($\chi_{\text{polymerA-holes}}$, $\chi_{\text{polymerB-holes}}$, $\chi_{\text{polymerA-polymerB}}$). While the polymer-polymer interaction parameter ($\chi_{\text{polymerA-polymerB}}$) may be independent of composition, the *effective* two component interaction parameter obtained by fitting a two component model to the data exhibit a dependence on composition. In general, this dependence is approximately parabolic, an effect which is not observed in this work.

Figure 5 shows the temperature dependence of χ/v_0 for the highest concentration sample PSD/PVME ($\phi_{\text{PSD}}=0.056$). The scattered intensity at \mathbf{q} equals zero diverges at the spinodal line (theoretically the scattered intensity equals infinity) and χ_s/v_0 can be calculated from Eq. (9) by taking $\lim_{q \rightarrow 0} [k_n/I(\mathbf{q})]$ which gives

$$\frac{\chi_s}{v_0} = \frac{1}{2} \left[\frac{1}{\langle N_a \rangle_w v_a \phi_a} + \frac{1}{\langle N_b \rangle_w v_b \phi_b} \right]. \quad (13)$$

The χ_s/v_0 for the highest concentration sample is plotted as a horizontal line in Fig. 5. This shows that even at 160 °C the samples were still in the single phase region. The straight line through the χ/v_0 data in Fig. 5 is linear least squares fit to the data with the form

$$\frac{\chi_s}{v_0} = A + \frac{B}{T}, \quad (14)$$

where A and B are constants. By extrapolating Eq. (15) to the point where $\chi/v_0 = \chi_s/v_0$ the spinodal temperature, T_s , can be obtained. For the highest concentration PSD sample the spinodal temperature obtained was $T_s = 197$ °C. The values for A , B , and T_s are given in Table III. This value T_s of is significantly higher than observed in other studies of the PS/PVME system because of the dilute PSD concentration. The critical point for the blend in this work should be in the temperature range of 155 °C ($\pm 10^\circ$) and a composition of about $\phi_{\text{PVME}} = 0.15-0.25$ based on the fact that the χ/v_0 val-

 TABLE III. Extrapolated spinodal temperatures for PSD/PVME and fit parameters for the temperature dependence of χ/v_0 ($\chi/v_0 = A + B/T$).

ϕ_{PSD}	T_s (°C)	A^a	B^b
0.019 35	345	4.42×10^{-4}	-0.185
0.037 81	217	4.76×10^{-4}	-0.197
0.055 64	197	4.57×10^{-4}	-0.191

^amol/cm³.

^bK mol/cm³.

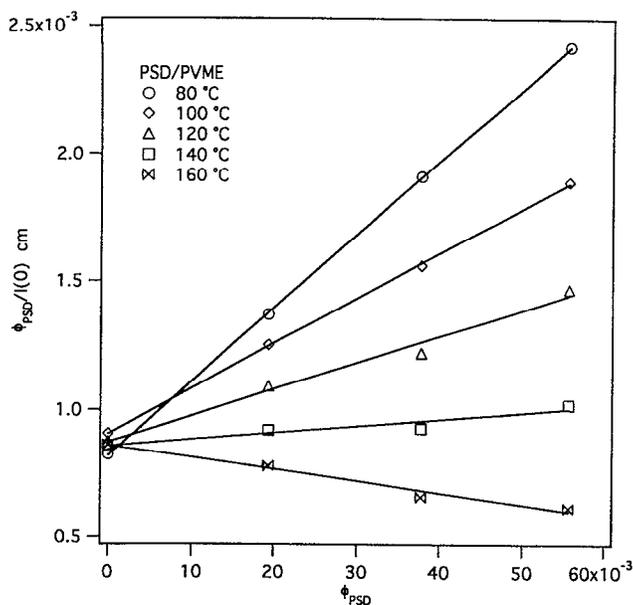


FIG. 6. $\phi_{\text{PSD}}/I(0)$ vs ϕ_{PSD} for different temperatures for the PSD/PVME blends.

ues obtained here compare favorably with other studies.^{11,15} The temperatures where χ/v_0 and A_2 equal zero are also indicated in Fig. 5 which correspond to the temperatures where the solution behaves athermally and ideally, respectively. The temperatures 145 and 147 °C, respectively, are quite close together which is reasonable for a polymer blend. For a low molecular solution they are generally expected to be further apart.

The $\phi/I(0)$ data obtained from the fit of Eq. (9) is plotted as a function of concentration for different temperatures in Fig. 6. From the slope of this plot a value of the second virial coefficient was obtained using Eq. (7). The values of A_2 are given in Table IV. The value of A_2 could also be calculated from the value of χ/v_0 obtained from the fit of Eq. (9) for each composition and temperature using Eq. (3), but because there was no significant composition dependence of χ/v_0 for PSD/PVME in the concentration range studied in this work (Fig. 4) the value of A_2 obtained by averaging over all the compositions at a given temperature from the slope of the lines in Fig. 6 is more meaningful. The temperature dependence of A_2 is plotted in Fig. 5 using the right-hand axis

TABLE IV. Second virial coefficient as a function of temperature for PSD/PVME blends.

Temperature	A_2^*
80 °C	8.91×10^{-5}
100 °C	5.45×10^{-5}
120 °C	3.19×10^{-5}
140 °C	8.10×10^{-6}
160 °C	-1.44×10^{-5}

*mol/cm³.

for A_2 . χ/v_0 and A_2 mirror each other as function of temperature and a critical value of A_2 for phase separation can be defined as

$$A_{2s} = -\frac{1}{2\langle N_a \rangle_w v_a \phi_a}, \quad (15)$$

which is plotted as a horizontal line in Fig. 5 ($\phi_{\text{PSD}}=0.056$). The intersection of the extrapolated fit of A_2 to the value of A_{2s} gives a temperature of phase separation of 196 °C which is in agreement with the value of T_s obtained from χ/v_0 . The temperature at which $A_2=0$, the theta temperature, for the PSD/PVME blend occurs at 147 °C. This is at only a slightly higher temperature than when $\chi/v_0=0$ ($T=145$ °C). In polymer blends the theta point ($A_2=0$) and the point where the blend behaves athermally are expected to be closer together than in a low molecular weight solution due to the low entropy of mixing. Other researchers have observed a dependence of A_2 on the molecular weight of the matrix chain, where both chains are the same species except for labeling (i.e., PSD in PSH) (Ref. 42,43) and analyzed the data in terms of the classical equation for the swelling of a chain in a good solvent.³⁴ It would be interesting to extend the single chain swelling analysis to the system studied here, where the matrix is a "good" polymeric solvent for the dilute species.

CONCLUSIONS

Deuterated polystyrene has been examined by SANS in two different matrices [protonated polystyrene and poly(vinylmethylether) in the limit of dilute concentration]. The single chain scattering curves obtained by extrapolation to zero concentration have been fit using a modified Debye function (accounting for polydispersity) and the value of the radius of gyration, $R_{g\text{PSD}}$, examined as a function of temperature. A small difference in the average value of $R_{g\text{PSD}}$ for PSD in PSH vs PSD in PVME is observed with PSD/PVME being about 7% larger. A trend in the data suggests an increase in $R_{g\text{PSD}}$ with increasing temperature for PSD/PSH while $R_{g\text{PSD}}$ decreases with temperature in PSD/PVME, although this temperature dependence is within the error bars for the data. The data for PSD/PVME has also been analyzed to extract values of χ/v_0 (and equivalently A_2) as a function of temperature. The values of χ/v_0 obtained in the dilute limit are in reasonable agreement with those previously published at high concentration. The concentration dependence of χ/v_0 is close to linear over the concentration range studied and shows no strong change in slope down to $\phi=0.02$, the lowest concentration studied in this work. This is different than predictions made by theories where a strong temperature dependence of the "effective" interaction parameter (as measured in this work) is predicted due to compressibility effects. The temperature dependence of χ/v_0 and A_2 indicate that phase separation will occur in the range of 200 °C for PSD/PVME which is consistent with the phase diagram measured by other researchers.

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