niques can be almost covered by extrapolation of high-pressure measurements.[8]

Finally, the fit of eq 1 to the Brillouin shift f_B at high pressures is ambiguous, because the measurements above 330 bar are in the range where $\omega_B\tau \gg 1$ and ω_0 is not precisely known.[13]

Note Added: After this paper was submitted for publication one other reference on the pressure dependence of the hypersonic attenuation in poly(dimethylsiloxane) appeared.[14] The reported shift of the hypersonic loss maximum at elevated pressure to higher temperature is in agreement with the present results on poly[(phenylmethyl)siloxane]. We also received a preprint by Wang and Fischer,[15] who provide a theoretical framework for the determination of the longitudinal compliance using both light scattering techniques.

Acknowledgment. We gratefully acknowledge the financial support of the Deutsche Forschungsgemeinschaft (D.F.G.) and E. Lükkeville for making the high-pressure cell. Thanks are also due to I. Schiller for typing the manuscript.

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Neutron-Scattering Investigation of the Interaction between Components in Concentrated, Miscible, Amorphous Polymer Blends

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ABSTRACT: Small-angle neutron-scattering (SANS) experiments were performed to investigate the composition and temperature dependence of the interaction between components in the amorphous miscible blend of deuterated poly(styrene) and poly(*o*-chlorostyrene). Recent neutron-scattering theories[1,2] were modified by using an enthalpy-corrected Flory–Huggins theory and an empirical interaction function. The measured interaction function was found to be composition and temperature independent. The results of this investigation are compared to previous theoretical[2-4] and experimental data[2-4,38] on the blends of hydrogenated poly(styrene) and poly(*o*-chlorostyrene).

Introduction

The miscible amorphous blend of poly(styrene) (PS) with poly(*o*-chlorostyrene) (POCS) has been a subject of considerable investigation, primarily due to the large molar mass dependence of the phase diagram[3-5] and the positive heat of mixing measured for this blend system.[3] The heat of mixing results indicate that the PS/POCS blend has no net attractive interactions,[5] yet the system is miscible. In that instance, McMaster has shown that the system can exhibit UCST and LCST behavior,[6] although experimental conditions usually prevent observation of the UCST phase boundary. In a previous study, Zacharius et al.[5] concluded that the experimental evidence pointed to the existence of a critical double point (CDP) for the PS/POCS blend system.

Figure 1 shows the Flory equation of state calculated temperature dependence of the interaction function $\chi_{12}(T)$ for the system of indicated molecular weight poly(styrenes) mixed with M_w 100 000 POCS.[3] This figure illustrates the typical behavior of $\chi_{12}(T)$ for blend components that show no net attractive interactions. The critical value of the interaction between the components, χ_c, is indicated in Figure 1 by the solid horizontal lines. The $\chi_{12}(T)$ curve is assumed to be independent of molecular weight and χ_c is given as

$$\chi_c = (r_1^{-1/2} + r_2^{-1/2})^2/2$$

where r_1 and r_2 are the degrees of polymerization for each blend component. If the blend exists in a state where χ_c is larger than the minima in the $\chi_{12}(T)$ curve, a UCST and LCST will be found at temperatures where $\chi_c = \chi_{12}(T)$. Increasing either component's r value decreases χ_c until, eventually, the critical value coincides with the minima of the $\chi_{12}(T)$ curve. The UCST and LCST then merge in a critical double point. Figure 2 represents the phase diagram as a function of molecular weight resulting from the situation described above.

The critical double point hypothesis put forth by Zacharius et al. requires that the interaction function between components be independent of composition. In this study,

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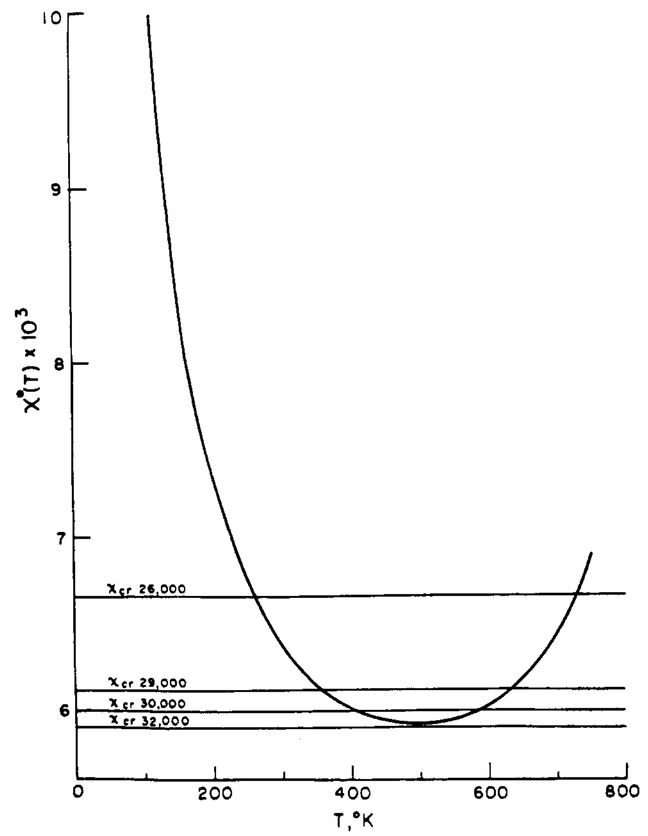

Figure 1. Temperature-dependent interaction parameter, χ_{12}, calculated from the Flory equation of state theory for the blend of PSH (various molecular weights) and POCS (100 000). This plot corresponds to the simulated spinodals in Figure 2 where $X_{23} = 0.011$. The horizontal lines represent the critical value of the interaction function for PSH having the indicated molecular weight. Figure by permission of ref 4.

we will examine the validity of this assumption by utilizing small-angle neutron-scattering (SANS) techniques to measure the temperature and composition dependence of the PS/POCS interaction function. The SANS experiments will allow determination of the interaction function from concentrated, miscible, binary blends of deuterated poly(styrene) (PSD) with POCS. Use of the isotopically labeled analogue of poly(styrene) in the blend greatly enhance the contrast between the components, experimentally allowing for more precise determination of the interaction function of the blend.

Thermodynamics of Polymer–Polymer Blending

The starting equation for molecular theories of polymer–polymer mixing is the Flory–Huggins–Staverman[7–9] expression for the free energy of mixing which is developed in a manner to be independent of any model of molecular mixing.[10] For a binary mixture of polymer components the free energy, $\Delta G^m/NRT$, is given by[11,12]

$$\Delta G^m/NRT = (\phi_A/r_A) \ln \phi_A + (\phi_B/r_B) \ln \phi_B + \Gamma \qquad (1)$$

where $N = n_A r_A + n_B r_B$, and RT is defined as usual. n_A, r_A, and ϕ_A represent the number of moles, the number of repeat units per chain, and the volume fraction of polymer A, respectively. The enthalpy of mixing, expressed by a semiempirical correction term Γ, is defined as[11,12]

$$\Gamma = g(T,P,\phi)\phi_A\phi_B \qquad (2)$$

where the interaction function, g, is a model-dependent term in eq 2 which will contain concentration, temperature, and molar mass corrections to the free energy function as suggested by some model of mixing.[11,12] Two-component polymer solutions are only binary solutions if both components have monodisperse molecular masses. In the case of two components with narrow distribution molecular masses, the binary approximation is usually valid.

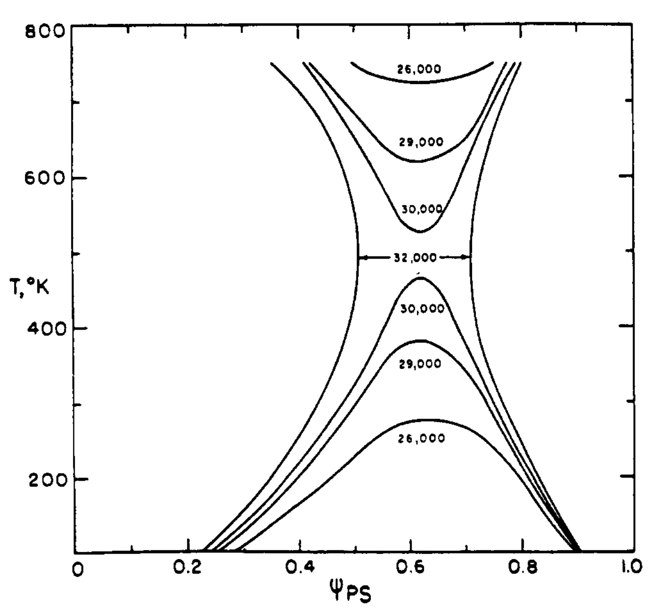

Figure 2. Flory equation of state theory simulated spinodals for the blend of POCS ($M_w = 100 000$) and PSH of various molecular weights, assuming a value of the exchange energy parameter, $X_{23} = 0.011$. Figure by permission of ref 4.

One molecular model that describes the free energy of mixing is the Flory–Huggins lattice model. Previous discussions have determined that the Flory–Huggins model is valid in concentrated regions of uniform segment density,[7,8,14] as is found in concentrated polymer solutions. The major drawback to this lattice model is that the interaction parameter, χ, was assumed to be concentration, temperature, and molar mass independent. The overwhelming evidence is that χ does depend upon these parameters,[11–13,15–19] thereby prompting modification of the Flory–Huggins equation to include an empirical interaction function.[16] For a binary mixture of polymeric components the Flory–Huggins equation is then

$$\Delta G^m/NRT = (\phi_A/y_A) \ln \phi_A + (\phi_B/y_B) \ln \phi_B + \Gamma \qquad (3)$$

where y_A and y_B are the number of lattice sites occupied per chain of components A and B, respectively. The number of lattice sites occupied by component i, y_i, is related to the degree of polymerization of component i, Z_i, by $y_i = Z_i(v_i/v_0)$, where v_i and v_0 are the molecular volumes of monomer i and the lattice cell.

The first two terms of eq 1 and 3 represent the combinatorial entropy of mixing of two homopolymers. The combinatorial entropy terms are proportional to the reciprocal of the number of repeating units (r_A) or the number of lattice sites (y_A) per chain. Therefore, these entropy terms make a very small, negative, contribution to the free energy of mixing. The magnitude and sign of the interaction function will determine the thermodynamic stability of the solution; overall ΔG^m must decrease upon mixing for the solution to be thermodynamically favored. The importance of the interactions between chains in a polymer blend means that the composition, temperature, and molar mass dependence of the interaction function will determine the phase behavior of the mixture.

The binodal line of a phase diagram indicates the separation between regions of thermodynamic stability and metastability. Inside the binodal a concentration fluctuation of sufficient size will cause phase decomposition by a nucleation and growth process. The binodal line is determined by the points where the chemical potential of all components in all phases are equal. For the Flory–Huggins lattice model of mixing of a binary solution the chemical potential is given as

$$\Delta\mu_A/RT = \ln\phi_A + (1 - y_A/y_B)\phi_B + y_A\left[g - \phi_A\left(\frac{\partial g}{\partial\phi_B}\right)\right]\phi_B^2 \quad (4)$$

and the interaction function g is related to the Flory χ by

$$g - \phi_A(\partial g/\partial\phi_B) = \chi \quad (5)$$

If the system shows partial miscibility, then there is a limit of thermodynamic stability (instability to any amplitude concentration fluctuations) called the spinodal.[20] For a binary mixture the spinodal is defined as (following eq 3)

$$\frac{\partial^2(\Delta G^m/NRT)}{\partial\phi_B^2} = \frac{1}{\phi_A y_A} + \frac{1}{\phi_B y_B} + \frac{\partial^2\Gamma}{\partial\phi_B^2} = 0 \quad (6)$$

where the appropriate form of the second derivative of the enthalpy correction term, $\partial^2\Gamma/\partial\varphi_B^2$, is given as

$$\partial^2\Gamma/\partial\phi_B^2 = -2g + 2(1 - 2\phi_B)\partial g/\partial\phi_B + \phi_B(1 - \phi_B)\partial^2 g/\partial\phi_B^2 \quad (7)$$

$\partial^2\Gamma/\partial\phi_B^2$ reduces to the usual Flory–Huggins result of $-2g$ if the interaction function g is assumed to be composition independent.

Interaction Function

Model-dependent forms for the interaction function have been derived from various descriptions of the mixing of polymer components.[7-9,21-25] An empirical expression for g is desired in this study to allow for simple evaluation of any composition and temperature dependence to the interaction function.

Tompa[26] originally suggested an empirical Van Laar concentration-dependent interaction function to explain deviations of experiment from model predictions. The interaction function can be expressed as a polynomial in composition:

$$g = g_0(T) + g_1\phi_B + g_2\phi_B^2 \quad (8)$$

In general all the coefficients g_0, g_1, and g_2 in eq 8 may be temperature dependent, but for the sake of convenience the temperature dependence of g is confined to the $g_0(T)$ term.[12,16] The temperature dependence is then expressed as

$$g_0(T) = g_{01} + g_{02}/T + g_{03}T + g_{04}\ln T \quad (9)$$

The constants g_{03} and g_{04} are usually small, resulting in the usual $1/T$ dependence[16,18] often observed in polymer solutions.[20,27,28] Molecular interpretations of the constants g_0, g_1, and g_2 have been developed[29,30] but Flory concluded that these interpretations go beyond the reliability of the lattice theory[31] and for the purpose of this study no molecular interpretation is required.

Substituting eq 8 and appropriate derivatives into the expression for $\partial^2\Gamma/\partial\phi_B^2$ as provided in eq 7 we obtain

$$\partial^2\Gamma/\partial\phi_B^2 = (2g_1 - 2g_0) + (6g_2 - 6g_1)\phi_B - 12g_2\phi_B^2 \quad (10)$$

Substituting this expression for $\partial^2\Gamma/\partial\phi_B^2$ into eq 6 completes the spinodal expression for the Flory–Huggins lattice model of mixing including an empirical interaction function.

Scattering Theory

The forward scattering due to concentration fluctuations in a homogeneous two-component mixture is related to ΔG^m, the free energy of mixing by[32-34]

$$R(0)^{-1} \sim (\partial^2(\Delta G^m/NRT)/\partial\phi_B^2)_{P,T} \quad (11)$$

where $R(0)$ is the Rayleigh factor at a scattering vector $q = 0$; $q = 4\pi/\lambda \sin\theta/2$ where λ is the wavelength of radiation and θ is the angle between the incident and scattered waves. The Rayleigh factor is defined as

$$R(q) = I_s(q)p^2/I_0V_s \quad (12)$$

where I_0 is the incident intensity and $I_s(q)$ is the intensity of scattered radiation at vector q. p and V_s are the sample-to-detector distance and volume of the scattering element, respectively.

The proportionality constant for eq 11 has been obtained by Scholte[20,27,28] for the small-angle light scattering (SALS), and recently by Hadziioannou, Gilmer, and Stein[1] for the small-angle neutron scattering of concentrated polymeric blends. The proportionality constant for eq 11 allows scattering techniques to be used to probe the free energy function. Scholte[28] developed the SALS equations for the more general Flory–Huggins–Staverman equation (eq 1), whereas the SANS proportionality constant[1] was obtained by assuming the traditional Flory–Huggins equation. Following the derivation of Hadziioannou, Gilmer, and Stein,[1] but utilizing the empirical interaction function form of the Flory–Huggins equation (eq 2 and 6), we obtain

$$\frac{[a_A(v_B/v_A) - a_B]^2}{R(0)v_B} = \frac{1}{Z_A(v_A/v_B)\phi_A} + \frac{1}{Z_B\phi_B} + \partial^2\Gamma/\partial\phi_B^2(v_B/v_0) \quad (13)$$

where $\partial^2\Gamma/\partial\phi_B^2$ has been previously defined in eq 7, a_A and a_B are the scattering lengths per monomer of components A and B, and Z_A and Z_B are the degrees of polymerization of the mixture components. v_A, v_B, and v_0 are the molecular volumes of components A and B and the lattice cell, respectively. For convenience, the lattice cell molecular volume is set equal to the molecular volume of one blend component.

All the constants in eq 13 can be independently determined; therefore, extrapolation of the SANS data to obtain $R_c(0)$ allows for determination of $\partial^2\Gamma/\partial\phi_B^2$ at each experimental composition. The composition dependence of the interaction function, g, is determined in these experiments from the fit of the $\partial^2\Gamma/\partial\phi_B^2$ data according to eq 10. Other model-dependent forms of g, ignored in this study, can be substituted into eq 7 to obtain the appropriate equation, analogous to eq 10.

Neutron scattering has an advantage over other scattering techniques because the contrast between the components of the blend can be artificially enhanced by substitution of one component of the blend with the isotopically labeled analogue. SANS techniques are particularly applicable for the study of amorphous–amorphous miscible blends where the components usually lack sufficient X-ray contrast[36,37] and SALS techniques are hampered by difficulties in clarifying the samples.[1,16]

Experimental Section

Sample Preparation. Narrow molecular weight distribution poly(styrenes) used in this study were synthesized by anionic polymerization by Polymer Laboratories Limited of Shrewsbury, England. The deuterated poly(styrene) (PSD) sample had a weight-average molecular weight M_w 30 500 with a distribution $M_w/M_n = 1.05$, while the hydrogenated poly(styrene) (PSH) had

Table I
Volume Fraction of Components in the PSD/POCS Blends and the Rayleigh Factor at q = 0 Determined from the Least-Squares Polynomial Fit of the SANS Scattering Data

[POCS], vol fraction	$R(0)$, cm^{-1}	10^3(devn), cm^{-1}	[POCS], vol fraction	$R(0)$, cm^{-1}	10^3(devn), cm^{-1}	[POCS], vol fraction	$R(0)$, cm^{-1}	10^3(devn), cm^{-1}
T = 25 °C			T = 125 °C			T = 135 °C		
0.193	29.94	0.9	0.191	32.15	0.9	0.191	29.33	0.9
0.322	48.78	0.2	0.320	54.35	0.2	0.319	50.51	0.2
0.476	55.56	0.2	0.474	55.25	0.2	0.473	56.18	0.2
0.629	38.76	0.2	0.627	38.61	0.2	0.626	37.45	0.2
0.787	22.32	0.9	0.786	21.74	0.9	0.786	20.88	0.9

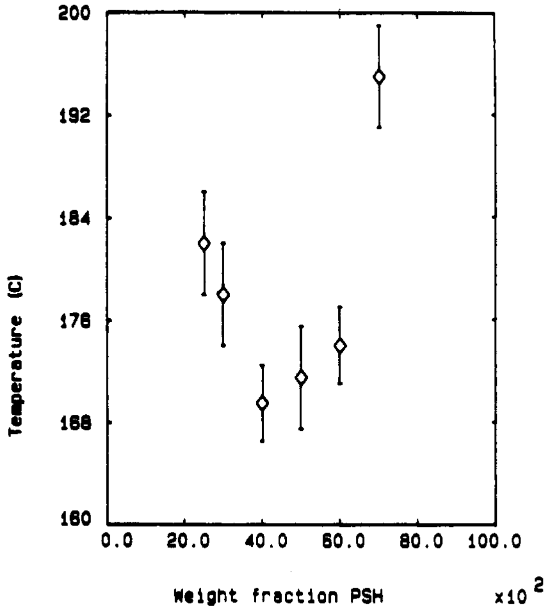

Figure 3. Measured cloud point curve plotted as a function of composition for the blend of PSH (M_w 51 400) and POCS (M_w 65 400). Data points are from heating experiments at 1 °C/min.

a molecular weight M_w 51 400 with a distribution M_w/M_n = 1.06. The narrow molecular weight distribution poly(*o*-chlorostyrene) (POCS) was synthesized by a free-radical polymerization and fractionated by preparative gel permeation chromatography. The synthesis and fractionation have been described elsewhere.[3,38]

The weight-average molecular weight of the POCS fractions were determined from low-angle light scattering on a Chromatix KMX 6 light-scattering apparatus. Gilmer[38] performed a DSC annealing study on blends of PSH and many fractions of the synthesized POCS. As a result of this study we chose the POCS fraction with a molecular weight M_w 61 500 and distribution M_w/M_n = 1.15 for our SANS studies of the interaction parameter. This fraction of the POCS demonstrated miscibility with PSH by DSC even after 10 h of annealing at 160 °C.[38]

Blend samples for all experiments were prepared in the same manner. The blend components were dissolved in benzene (1% w/v) and filtered through a 0.2-μm Teflon Millipore filter. The blends were then freeze-dried for 24 h and dried in a vacuum oven for 2–4 days at 80 °C to remove residual benzene. The blends were prepared in five compositions, listed in Table I.

Cloud Point Determination. In order to obtain an approximate phase diagram for the blend of POCS and PSH, measurements were taken to determine the cloud point temperatures of the blend at various compositions. The blend powder was melt pressed onto a glass slide, its thickness governed by a thin shim around the sample, and a cover slip was placed on top. The pressing temperature ranged from 140 to 150 °C and the 0.3-t pressure was held for 20 min.

Using a temperature programmer connected to a microscope hot stage and a temperature sensor, we heated blends at 1 °C/min to determine the temperature at which the blend became turbid. The scattering was measured at a fixed angle (50°) and the intensity from a photomultiplier tube was recorded on a chart recorder. The cloud point was determined as the temperature at which the intensity suddenly increased.

Small-Angle Neutron Scattering (SANS). In an attempt to minimize any anomalous scattering due to the presence of voids in the final samples, the blend powder was compacted in a KBr pellet press prior to melt pressing. With the blend powder under vacuum (less than 0.5 torr) the force on the KBr press is gradually increased (over a 20-min period) to a final pressure of 8 t. The sample was kept at this pressure for 5 min and then removed from the KBr press.

The sample was then placed in a hole of approximately 13-mm diameter in a metal template. The template was coated with a Teflon spray release agent to aid in removal of the sample after melt pressing. A sandwich was made with the template between Teflon or Mylar sheets which was then placed into a modified Carver C laboratory press. This press allows samples to be under vacuum before and during pressing.[38] The vacuum was maintained at less than 1 torr while the sample was heated to about 5 °C above the glass transition of the particular blend. After temperature equilibration the sample was melt-pressed with a force of 2 t for approximately 25 min. The sample was allowed to cool to 100 °C and removed from the template. The sample was checked for residual strains by looking for birefringence between crossed polars.

Small-angle neutron scattering experiments were performed on the 30-m SANS camera[39] at the National Center for Small Angle Research (Oak Ridge National Laboratory). The incident beam had a wavelength λ = 4.74 Å, with a dispersion in wavelength of 6%. The beam was collimated by a 1.85 cm diameter source slit 7.5 m from the sample. The area detector (64 × 64 cm^2) with 1-cm^2 element size was positioned 12.25 m from the sample in the 20-m evacuated flight path. The data were corrected for instrumental background and incoherent scattering as well as for sample and quartz cell transmissions. Scattering experiments were performed at three temperatures: one below T_g (25 °C), one roughly at T_g (125 °C), and one temperature above the T_g of the blends (135 °C).

The scattering data were normalized for transmission, sample cell scattering, and sensitivity of the detector. The incoherent level for each blend was taken as the volume fraction weighted sum of the incoherent levels of the pure PSD and POCS samples at each temperature. In order to obtain absolute intensity values (Rayleigh ratios) for all scattering experiments, a calibration of the 30-m SANS camera was performed with an irradiated aluminum-4 standard. The value of the zero-angle neutron-scattering intensity for this standard sample is $R(0)$ = 129 ± 10 cm^{-1}. The extrapolation of the SANS data to q = 0 was accomplished by performing a weighted least-squares polynomial fit, as outlined by Bevington,[40] of the $1/R(q)$ vs. q^2 data.

Results

The cloud point curve of the blend of PSH and POCS is shown in Figure 3. This phase diagram indicates that the PSH/POCS blend exhibits lower critical solution (LCST) behavior, confirming the results of previous investigations.[3,38] The cloud point experiment also confirmed a previous DSC annealing study indicating that our blends of PSH/POCS have attained equilibrium miscibility.[38]

Ullman[41] demonstrated that for SANS from a Gaussian coil, a more accurate value of $R(0)$ is obtained if a q^4 dependence is included in the least-squares fit of $R(q)^{-1}$ vs. q^2. This is especially true when data from the large qR_g region (R_g is the radius of gyration of the chain) is included in the fit. Because of the presence of void scattering in the low-q region from our samples, we measured the

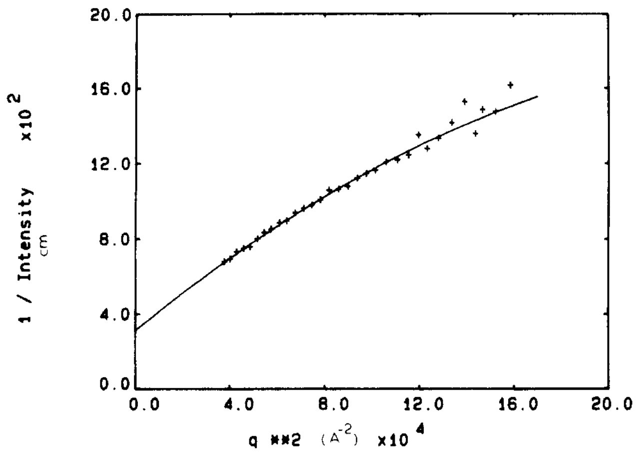

Figure 4. Small-angle neutron-scattering intensity plotted in $R(q)^{-1}$ vs. q^2 form, where $q = 4\pi/\lambda \sin \theta/2$, for a blend of 80 PSD/20 POCS at $T = 125$ °C. Data points are represented by + and the polynomial fit is the solid line.

Table II
Molecular Parameters and Standard Deviations Used in the Calculation of the Second Derivative of the Enthalpy Correction Term in Eq 13 and Temperature-Dependent Parameters Calculated by Use of the Thermal Expansion Coefficient[44]

PSD monomer mol wt	112.20 ± 0.01
POCS monomer mol wt	138.60 ± 0.02
PSD polymer mol wt	30500 ± 1500
POCS polymer mol wt	65400 ± 7000
PSD SANS scattering length × 10^{12}, cm	10.656 ± 0.015
POCS SANS scattering length × 10^{12}, cm	3.662 ± 0.025
PSD	
dρ/dT ($T < T_g$), g cm^3 K^{-1}	-2.65×10^{-4}
dρ/dT ($T > T_g$), g cm^3 K^{-1}	-6.05×10^{-4}
POCS	
dρ/dT ($T < T_g$), g cm^3 K^{-1}	-2.81×10^{-4}
dρ/dT ($T > T_g$), g cm^3 K^{-1}	-6.41×10^{-4}

	25 °C	125 °C	135 °C
PSD gravimetric density,[a] g/cm^3	1.132	1.096	1.090
POCS gravimetric density,[b] g/cm^3	1.246	1.218	1.213
PSD monomer mol vol × 10^{22}, cm^3	1.646	1.700	1.709
POCS monomer mol vol × 10^{22}, cm^3	1.845	1.889	1.897

[a] ±0.01. [b] ±0.02.

scattering from the blends over a qR_g range of 0.8–2.0. The corrected data are fitted to the equation

$$R(q)^{-1} = R(0)^{-1} + b_1q^2 + b_2q^4 \tag{14}$$

where b_1 and b_2 are constants of the fit. Figure 4 shows the corrected SANS data from a PSD/POCS blend plotted in the $R(q)^{-1}$ vs. q^2 form. This plot is typical of all scattering curves and the polynomial fitting allows for extrapolation to the intercept where $R(0)^{-1}$ is obtained. Measured values of $R(0)$ are listed for all samples in Table I.

Table II lists the molecular parameters for PSD and POCS required to calculate the second derivative of the enthalpy correction term, $\partial^2\Gamma/\partial\phi_B^2$, from the SANS experiments according to eq 13. Figure 5 plots $\partial^2\Gamma/\partial\phi_B^2$ calculated from eq 13 against the composition of the blend, for all three experimental temperatures, and these values are reported in Table III. The composition dependence of $\partial^2\Gamma/\partial\phi_B^2$ was fitted to the empirical form given in eq 10 and the interaction parameters g_0, g_1, and g_2 listed in Table III were obtained. The room-temperature calculation of $\partial^2\Gamma/\partial\phi_B^2$ is replotted in Figure 6, along with the weighted least-squares fit of the data according to eq 10. The interaction function, g, can be calculated from the coefficients g_0, g_1, and g_2 according to eq 8, and Figure 7 plots the calculated values of g for all experimental temperatures.

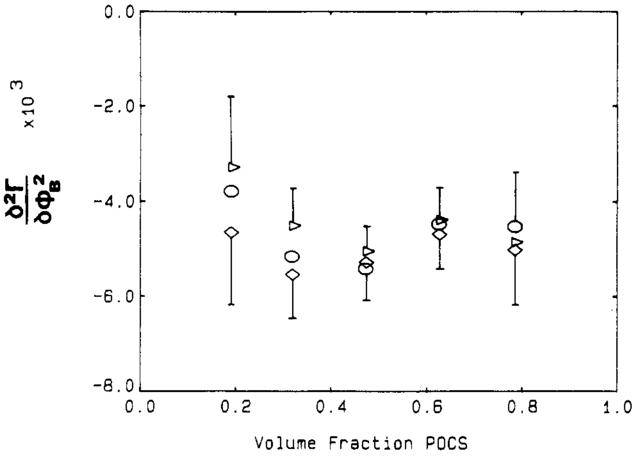

Figure 5. Enthalpy correction term $\partial^2\Gamma/\partial\phi_B^2$ plotted as a function of composition as determined from eq 13. Experimental temperatures are shown as $T = 25$ °C (▷), $T = 125$ °C (◇), and $T = 135$ °C (○).

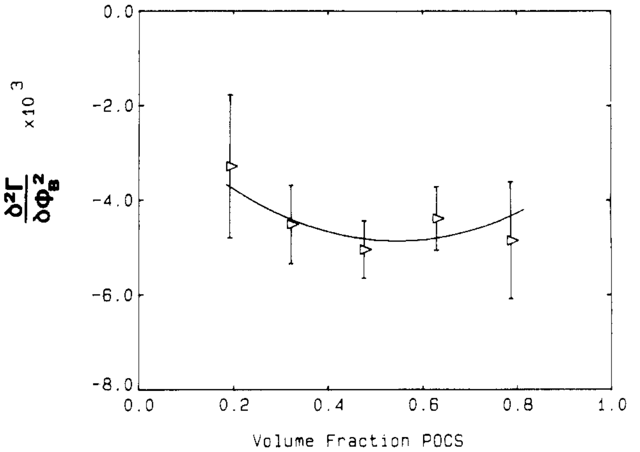

Figure 6. Second derivative of the enthalpy correction term $\partial^2\Gamma/\partial\phi_B^2$ at $T = 25$ °C plotted as a function of composition. The solid line is the polynomial fit of these data according to eq 10; the resulting coefficients are listed in Table III.

Table III
Calculated Values of $\partial^2\Gamma/\partial\phi_B^2$, according to Eq 13 from the Scattering Data Listed in Table I, and Interaction Function Coefficients of Eq 8 Calculated from the Fit of the Preceding Data according to Eq 10

vol fraction		($\partial^2\Gamma/\partial\phi_B^2$)			
PSD	POCS	25 °C	125 °C	135 °C	10^3(devn)
0.80	0.20	−3.28	−4.64	−3.78	1.54
0.68	0.32	−4.51	−5.53	−5.15	0.82
0.52	0.48	−5.04	−5.27	−5.41	0.61
0.37	0.63	−4.38	−4.68	−4.47	0.67
0.21	0.79	−4.85	−5.01	−4.51	1.23

	25 °C	125 °C	135 °C
10^3g_0	1.97	2.56	2.18
10^3g_1	0.90	0.04	0.81
10^3g_2	−0.76	−0.23	−0.97

The error measurements plotted in Figures 5 and 7 propagate from uncertainties in the molecular parameters listed in Table II, and errors resulting from SANS measurements, listed in Table I. The error arising from the scattering measurements is small in comparison to the error uncertainties in the molecular parameters associated with the POCS component of the blend, listed in Table II. The systematic errors plotted in Figures 5 and 7 will affect all data in the same manner.

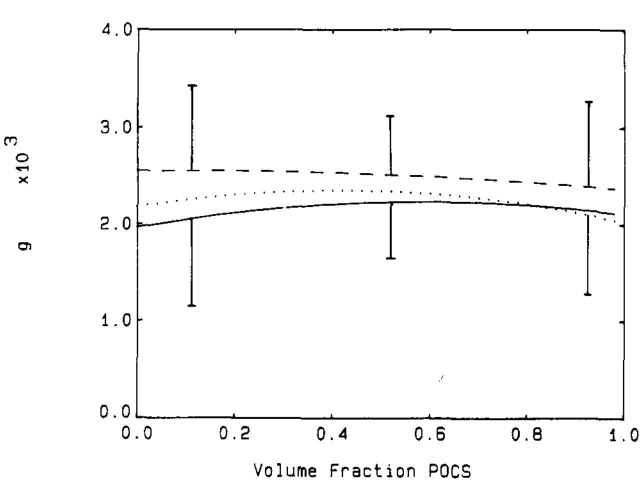

Figure 7. Calculated interaction function, g, according to eq 8 from the coefficients listed in Table III. The solid line T = 25 °C, the dashed line T = 125 °C, and the dotted line T = 135 °C. The errors bars shown arise from deviations in the $\partial^2\Gamma/\partial\phi_B{}^2$ data, as listed in Table III.

Discussion

Utilizing the empirical interaction function (eq 8) and fitting the $\partial^2\Gamma/\partial\phi_B{}^2$ data according to eq 10 allows for critical evaluation of any concentration dependence to the interaction function g. Within experimental error of the measurements, we conclude that the $\partial^2\Gamma/\partial\phi_B{}^2$ data (Figure 5) and the resulting calculation of g (Figure 7) show no composition dependence. This conclusion is also apparent upon examination of the volume fraction weighted fitting parameters g_1 and g_2, of eq 8, listed in Table III. Referring back to eq 7 and 8 the composition independence of g implies that

$$\partial^2\Gamma/\partial\phi_B{}^2 = -2g$$

$$g = g_0(T)$$

The interaction function g is equivalent to $\chi_{12}(T)$ used in the previous studies, and this latter term is plotted in Figure 1.

The critical double point hypothesis presupposes that the interaction between blend components is independent of composition. The vapor sorption measurements were inconclusive,[4,5] but our SANS results verify the composition independence of the interaction function. As mentioned, the sensitivity of the phase diagram to component molar mass is qualitatively explained by the flat shape of the $\chi_{12}(T)$ curve shown in Figure 1. This flat shape, when coincident with the χ_c value for a blend, gives rise to a critical double point.

Zacharius et al. derived a quantitative description of the molar mass effect upon the phase diagram. For a system sufficiently far from the CDP, a small change in critical temperature, T_c to T_{c1} due to a change in degree of polymerization r to r_1, can be expressed as

$$T_{c1} - T_c = \frac{2}{\chi_{12}'(T_c)}\,\frac{r - r_1}{rr_1} \tag{15}$$

The sensitivity of $T_{c1} - T_c$ to $r - r_1$ is determined by the first derivative of the temperature-dependent interaction function, $\chi_{12}'(T_c)$. If $\chi_{12}'(T_c)$ is small, then a small change in the molar mass of either component will result in a large change in the critical temperature.

The temperature dependence of the interaction function we measured by SANS is shown in Figure 7 and the values of g_0 are listed in Table III. Over the range of temperatures of our experiments, the interaction function shows no temperature dependence. This result agrees with the CDP hypothesis and the previous equation of state calculation of $\chi_{12}(T)$.[4] The composition and temperature independence of the interaction function indicates that the PSD/POCS blend forms a miscible blend without any net attractive interactions (i.e., $g > 0$).

Comparison of previous PS/POCS results with measurements taken from a different molecular weight blend of PSD with POCS requires justification. The replacement of one blend component with its labeled analogue has been shown to greatly change the phase diagram, yet have very little effect upon the interaction parameter.[19,42,43] Therefore, the SANS determination of g from the deuterated blend is likely to be an accurate representation of the interaction in the protonated blend. The critical value of the interaction between components is the important parameter in the CDP hypothesis, and our χ_c is only slightly larger than χ_c in the Zacharius et al. study. Also, because of the equal molar volumes of the blend components, and the lack of any net attractive interactions between components, there should be very little excess enthalpy of mixing associated with this blend. Therefore, since g is mostly of an enthalpic nature, there should be little molar mass dependence to the interaction function.

Conclusions

The conclusion from this study and others[4,5] is that the blend of PS (protonated or deuterated) with POCS is an example of a miscible blend with no net attractive interactions. Previous studies of PS/POCS blends have demonstrated that such a system shows unusual phase behavior that can be explained by the critical double point hypothesis. McMaster[6] concluded that the existence of such a system could only occur if the blend components showed similar P–V–T behavior. Accurate values of the P–V–T properties of POCS do not exist, but the P–V–T properties for the POCS component used in the equation of state modeling of a previous study[5] were chosen to be similar to the PS properties.

This study has demonstrated the utility of the SANS technique in obtaining the interaction function from blend components where g was expected to be quite small. With modest accuracy, we were able to measure the composition and temperature dependence of the interaction function from concentrated blends. The use of monodisperse blend components and a measurement technique applicable to binary blends make interpretation of the results straightforward.

Our results showed that the interaction between components was composition and temperature independent, thereby supporting the critical double point hypothesis of Zacharius et al. Our experimental value of the interaction function agreed with the equation of state predictions for this blend,[5] but disagreed with the previous vapor sorption results.[4,5] This disagreement results from the improved accuracy and validity of the SANS technique.

Acknowledgment. We acknowledge the support of the Division of Materials Research of the National Science Foundation and the Materials Research Laboratory of the University of Massachusetts. The SANS measurements were conducted at the National Center for Small Angle Scattering Research at the Oak Ridge National Laboratory, to which we are indebted for the granting of beam time. We particularly appreciate the assistance of Dr. George Wignall in assisting us with these measurements. Appreciation is extended to Professor Julian B. Johnson at the University of Connecticutt for use of the preparative GPC. We are further indebted to Dr. R. Koningsveld for his discussions concerning this work, and to Drs. S. Zacharius, G. ten Brinke, and C. Ryan for their aid in preparing this manuscript.

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Zero-Shear Viscosity of Linear Polymer Solutions over a Wide Range of Concentration

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ABSTRACT: The zero-shear viscosity data of poly(α-methylstyrene) solutions in good, poor, and Θ solvents covering wide ranges of polymer concentration and molecular weight were accumulated and analyzed on the basis of the scaling concept of de Gennes, in comparison with the other theories. The theory was found to be useful for understanding the viscosity behavior in the semidilute region. However, the theory is not applicable if the polymer concentration is higher than $\simeq$0.2 g/mL. The crossover point from the dilute to the semidilute region varies with solvent power.

Introduction

The polymer concentration (C) and molecular weight (M) dependences of the zero-shear viscosity η^0 of linear polymer solutions over a wide range of polymer concentration have been extensively studied.[1-4] Concerning the molecular weight dependence of η^0, it is well established that η^0 is proportional to $M^{3.4}$ if polymer coils are entangled with each other. Concerning the concentration dependence of η^0, however, the problem is more complicated, except in dilute solutions. There are two approaches to the analysis of the polymer concentration dependence of η^0. One is the approach from the dilute-solution side and the other one is the approach from the polymer-melt side.

In dilute solutions, it is well established that the zero-shear viscosity η^0 can be expressed by the expansion form

$$\eta_R{}^0 \equiv \eta_{sp}{}^0/C[\eta] = 1 + k'[\eta]C + ... \qquad (1)$$

in which k' is Huggins' constant and $\eta_{sp}{}^0 = (\eta^0 - \eta_s)/\eta_s$, η_s being the solvent viscosity. That is, $\eta_R{}^0$ is given as a function of $C[\eta]$ in dilute solutions. In more concentrated solutions, too, $C[\eta]$ has been used as an approximate reducing parameter of viscosity. Strictly speaking, however, the superposition of $\eta_R{}^0$ with respect to $C[\eta]$ is not perfect.[5] Utracki and Simha[6,7] proposed that $\eta_R{}^0$ may be expressed in terms of reduced concentration $\tilde{C} \equiv C/\gamma$, where γ is defined by $\gamma \propto k'[\eta]^{-1} \propto M^{-a_1}$. That is

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0024-9297/85/2218-1002$01.50/0