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Synchrotron SAXS Study of Mean Field and Ising Critical Behavior of Poly(2-chlorostyrene)/Polystyrene Blends

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ABSTRACT: Synchrotron small-angle X-ray scattering (SAXS) of poly(2-chlorostyrene)/polystyrene (P2ClS/PS) blends in the immediate neighborhood of the critical mixing point can be achieved by first locating the critical mixing point precisely. By combining a phase volume method with SAXS, the critical mixing point for P2ClS(M_w=2.33×10^5,M_w/M_n=1.19)/PS(M_w=3.7×10^4,M_w/M_n<1.06) in the presence of 22.6 wt% di-*n*-butyl phthalate was found to have a critical weight fraction of PS, $W_{PS,c} = 0.52$. A lower critical mixing temperature T_c = 134.30 °C, where $W_{PS} + W_{P2ClS}$ was set to equal one, could clearly reveal a crossover in the static susceptibility and the correlation length from mean field to Ising-like behavior, with critical exponents γ changing from 1.00 (mean field) to 1.23 (Ising) and ν changing from 0.50 (mean field) to 0.63 (Ising). The crossover occurs at 2.6 K below the critical mixing temperature.

Introduction

In critical phenomena, the second-order phase transition can be examined with great precision and detail using critical binary fluid mixtures in which both components are made up of small molecules. An appropriate choice of the binary fluid mixture with a convenient critical mixing point and stable pure components permits measurements of the critical point behavior in the immediate neighborhood of the critical mixing point. While critical binary fluids are known to exhibit Ising critical properties, blends of high molecular weight and flexible-chain polymers usually show mean field behavior, as predicted by de Gennes.[1] It is therefore intriguing to investigate when the crossover from mean field to Ising behavior occurs as the polymer chains in the blend are shortened. As the width of the Ising range is reciprocally related to the chain length, one approach in the search for the crossover behavior is, indeed, by varying the molecular weight, i.e., the chain length, of one of the two polymer components in the polymer binary mixture (or blend).[2]

The polymer blend poly(vinyl methyl ether)/deuteriopolystyrene (PVME/d-PS)[3,4] has been investigated by neutron scattering and has shown a transition from mean field to Ising behavior at ~2.4 °C below the lower critical solution temperature.[5,6] Bates et al.[7] reported a crossover behavior using a relatively low molecular weight polyisoprene and partially deuterium labeled poly(ethylene–propylene) (PI/partially-d-PEP) blend over a temperature range close to 30 °C above the upper critical solution temperature. From the above two experiments, one can reasonably conclude that the crossover from mean field to Ising critical behavior indeed exists and that the Ising range can be controlled by polymer molecular weight.

In this work, we present synchrotron small-angle X-ray scattering (SAXS) results for a different polymer blend, poly(2-chlorostyrene)/polystyrene (P2ClS/PS) with 22.6 wt % di-*n*-butyl phthalate (DBP) as a plasticizer. The polymer components, poly(2-chlorostyrene) and polystyrene, have a large electron density difference, can be prepared with very narrow molecular weight distributions, and have a range of molecular weights which exhibit critical mixing points at sufficiently low temperatures, so that polymer degradation is not a serious problem. The plasticizer (DBP) is used to adjust (actually to raise) the critical mixing temperature so that the homogeneous melt in the one-phase region is not too viscous. Nevertheless, it should be noted that the addition of a plasticizer changes the polymer blend from a two-component system to a three-component system. By maintaining a constant composition of the plasticizer in the two separate phases, the critical behavior is quasi binary in nature. In a separate experiment,[8] we have demonstrated this condition, which is not a general property for all plasticizers.

In a careful study of the critical behavior of polymer blends, one should have a good knowledge of the thermodynamic state of the polymer mixture, i.e., the coexistence curve. Scattering methods permit us to determine the critical mixing point and the corresponding spinodal temperatures by extrapolation but are not suitable for precise coexistence curve determinations. In this context, we initiated a separate experiment to determine the phase separation temperatures and the volume ratios of the separate phases. By combining the phase separation behavior with synchrotron SAXS results, we know the phase boundary much more precisely and are able to state with confidence and precision how the crossover transition from mean field to Ising critical behavior occurs.

Experimental Section

Materials and Sample Preparation. Polystyrene with weight-average molecular weight M_w = 3.7 × 10^4 and narrow molecular weight distribution M_w/M_n < 1.06 was purchased from Pressure Chemical Co. Poly(2-chlorostyrene) was radically polymerized in toluene and fractionated by the precipitation method using toluene and methanol as the solvent and the precipitant, respectively. M_w and M_w/M_n of P2ClS were determined by gel permeation chromatography to be 2.33 × 10^5 and 1.19. Di-*n*-butyl phthalate (DBP > 99%) was obtained from Tokyo Kasei Kogyo Co. and used without further purification. Films of P2ClS/PS blends with different compositions were prepared according to the procedure described by Kwak et al.[9] Each film of the blend was cut and placed between two small pieces (~20 × 20 mm^2 area and 0.026 mm thick) of Kapton films with a Kapton spacer, whose thickness was 0.066 mm, much greater than the accessible correlation length of this blend even with our refined temperature control (to ±0.02 °C) and scattering

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Table I

		binodal		SAXS		
sample[a]	$W_{\mathrm{P2ClS}}/W_{\mathrm{PS}}$	T_p/°C	T_c/°C	T_s/°C	T_c/°C	T_{sm}/°C
E	48/52	134.30	134.30	134.30	134.30	132.90
A	40/60	134.92		137.20		134.30
B	51/49	134.42		154.60		
C	31/69	140.54		180.50		
D	61/39	139.81		200.00		

[a] Samples contain 22.6 wt % of DBP (e.g., 100 × [$W_{\mathrm{DBP}}/W_{\mathrm{polymer+DBP}}$]). M_w(PS) = 3.7 × 10^4, M_w(P2ClS) = 2.33 × 10^5.

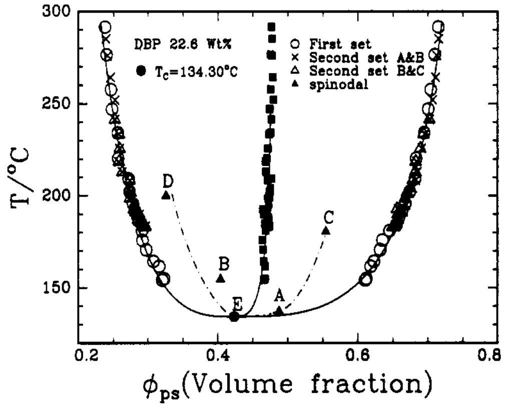

Figure 1. Coexistence curve of P2ClS/PS blends in the presence of 22.6 wt % DBP (M_w(PS) = 3.7 × 10^4, M_w/M_n < 1.06; M_w(P2ClS) = 2.33 × 10^5, M_w/M_n = 1.19). The coexistence curve was determined by a combination of phase volume ratio[8] and SAXS experiments with T_c = 134.30 °C and the critical exponent $\beta \simeq 0.33$ for the coexistence curve. Circles, crosses, and triangles denote the sets of data determined with different initial concentrations. Filled rectangles indicate the midpoints of the coexistence curve and denote the arithmetic mean of the fitting curve of the coexistence curve. $\phi_{\mathrm{PS}} + \phi_{\mathrm{P2ClS}} + \phi_{\mathrm{DBP}} = 1$.

techniques. The polymer blend sample which was sandwiched between the Kapton films was put between two microscope slide glasses, clamped, and then annealed at 80 °C for 12 h. The sandwiched sample was then transferred and fixed on an aluminum sample holder and annealed at 60 °C for at least 1 week before SAXS measurements.

SAXS Measurements. SAXS measurements were carried out at the SUNY X3A2 Beamline,[10] National Synchrotron Light Source, Brookhaven National Laboratory, using a modified Kratky collimator and a one-dimensional Braun detector, Type-OED 50/straight. The X-ray wavelength was set at 0.154 nm. SAXS experiments were performed on five samples of P2ClS/PS blends with different weight fractions of PS, W_{PS}. The sample holder was set in a thermal block which could be controlled to ±0.02 °C over a temperature range from 60 to 215 °C. Each run was collected for a 1000-s period, and all SAXS profiles were corrected for incident X-ray intensity fluctuations, sample and Kapton film attenuations, detector nonlinearity, and stray X-rays.

Results and Discussion

Critical SAXS profiles of P2ClS/PS blend samples were carefully investigated in the neighborhood of the critical mixing point both at and away from the critical composition. The compositions of five P2ClS/PS blend samples are listed in Table I. The composition range of the experiments in its relation with the coexistence curve is shown in Figure 1.

Figure 2 shows typical SAXS profiles of the P2ClS/PS blend at fixed temperatures. The curves have been displaced as shown to show the weak SAXS intensity and asymmetry, both of which increase with increasing temperature. It is also intended to demonstrate the quality of our scattering curves before data analysis. It should be noted that we have not separated the scattering contributions into two parts, i.e., background (noncritical fluctuations) and the critical fluctuations. The background part would be difficult to estimate because of the nature of the lower critical mixing point and the high viscosity of the polymer blend at lower temperatures. However, the effect becomes less severe as the critical mixing point is approached. Figure 3 shows the excess scattered intensity (after background intensity subtraction) of sample E as a function of temperature. From coexistence curve measurements, sample E was estimated to have a composition very close to the critical concentration. It is particularly interesting to note the SAXS profile at 134.30 °C. At this (phase separation) temperature, the scattering curve disappeared. Although the scattering from each domain should be observable in principle during phase separation, the fluctuations in each domain are considered to be negligibly small when compared with the critical scattering of the initial one-phase state because each coexistence phase is located far from the critical mixing point. The intensity of profile 8 (as shown in Figure 3) is weaker than the others, because the large domain size during the initial stages of phase separation could also occur at scattering angles smaller than the accessible small scattering angle range as shown in Figure 3. Furthermore, the uncertainty in the background subtraction should also be more critical, because the scattered intensity has become much weaker. From our SAXS measurements, we could locate the phase separation temperature, in this case the critical solution temperature T_c, to within a few hundredths of a degree. We estimated T_c = 134.30 °C. With T_c = 134.30 °C, we determined a β value of about 0.33 from the coexistence curve of Figure 1. Small variations of T_c, i.e., of the order

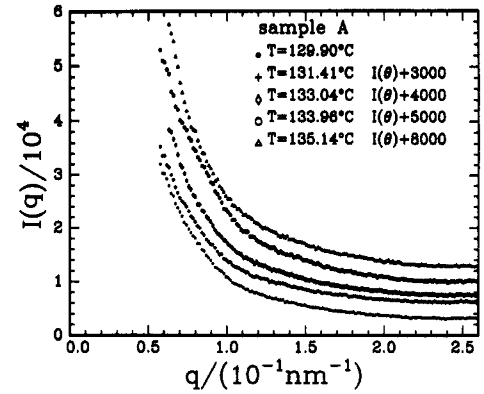

Figure 2. SAXS patterns of sample A at fixed temperatures in the one-phase region. The SAXS intensity $I(q)$ has been corrected for detector nonlinearity, incident intensity variation, and sample attenuation. q is the scattering wave vector.

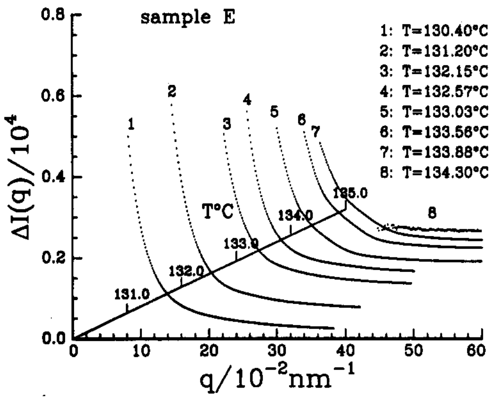

Figure 3. Net SAXS patterns of sample E at fixed temperatures in the one-phase region. The excess SAXS intensity $\Delta I(q)$ (after background intensity subtraction) of sample E as a function of temperature.

of a few tenths of a degree, will not alter the β value appreciably from 0.33. The temperature control was of the order of 0.02 °C. The uncertainty in T_c would be of the order of 0.1 °C. Therefore, we have clearly established an Ising behavior for the critical exponent β of the composition difference $\phi^+ - \phi^-$ between two coexistence phases, i.e., $\phi^+ - \phi^- = \epsilon'^{\beta}(B + B_1\epsilon'^{\Delta})$, with $\Delta = 0.5$, $\epsilon' = (T_c - T)/T_c$, and the B's being the prefactors. In fact, inclusion of the second term $B_1\epsilon'^{\Delta}$ was not essential in fitting the entire coexistence curve covering a temperature range of ~150 °C.

By using the high-quality SAXS data which can be achieved with synchrotron X-rays, we were able to make an Ornstein–Zernike plot in the small-angle range with $0.06 \le q \le 0.14$ nm^{-1} for the data measured at lower temperatures ($T_c - T \ge 3.1$ K), where $\xi q \le 1$. For the data measured at temperatures close to T_c ($T_c - T \le 3.1$ K), we modified our analysis to improve the precision of our determination of $I(0)$ and ξ. First we fitted the excess scattered intensity data by using the scattering factor $S(q)$ based on the de Gennes[1] random phase approximation

$$S^{-1}(q) = (N_A\phi_A)^{-1}f_D^{-1}(q^2R_A^2) + (N_B\phi_B)^{-1}f_D^{-1}(q^2R_B^2) - 2\chi \tag{1}$$

where f_D denotes the Debye structure factor for noninteracting ideal chains

$$f_D = (2/x)[1 - (1 - \exp(-x))/x] \tag{2}$$

with $x = q^2R^2$. The expression of eq 1 remains unchanged by introduction of the quasi binary approximation.

In practice, intensity $I(q) \propto S(q)$ except for a constant factor. If the chain sizes are different, in the small q range eq 1 could be replaced by an approximate expression

$$\begin{aligned} S^{-1}(q) &= (N_A\phi_A)^{-1}(1 - q^2R_A^2/3)^{-1} + (N_B\phi_B)^{-1}(1 - q^2R_B^2/3)^{-1} - 2\chi \\ &= [(N_A\phi_A)^{-1} + (N_B\phi_B)^{-1}](1 + q^2R_g^2/3) - 2\chi \end{aligned} \tag{3}$$

where $\phi_A + \phi_B + \phi_{DBP} = 1$ and the mean radius of gyration R_g is defined by

$$R_g^2 = [(N_A\phi_A)^{-1} + (N_B\phi_B)^{-1}]^{-1}[(R_A^2/N_A\phi_A) + (R_B^2/N_B\phi_B)] \tag{4}$$

Figure 4a shows the fitting curves of eq 3, where R_g and χ are the fitting parameters. The experimental data were measured at temperatures very close to T_c. The symbol Δ of ΔI has been dropped. By extrapolation to $q = 0$, the relative static susceptibility $I(0,T)$ can be determined even though $q\xi \ge 1$. Based on the Ornstein–Zernike (O–Z) relationship

$$I(0,T)/I(q,T) = 1 + q^2\xi^2 \tag{5}$$

We plot the *fitting* results, $I(0,T)/I(q,T)$, vs q^2 over a range of q with $0 \le q \le 0.07$ nm^{-1} as shown in Figure 4b. Least-squares fitting of such SAXS curves in the $0 \le q \le 0.02$ nm^{-1} range has yielded the correlation length ξ for the polymer blend. The results of $I(0,T)$ and ξ at different temperatures for sample E determined directly by employing the O–Z relationship and by the two-step approach are listed in Table II. At temperature distances $T_c - T \ge 3.1$ K, the results obtained from the two different approaches are almost the same within experimental error. However, at temperatures closer to T_c, the relative error due to the use of the O–Z equation was not negligible and could reach 30%. Similar results were reported by Shibayama et al.[11] in the study of a deuterated PS/hydrogenated poly(vinyl methyl ether) blend. The temperature dependence of the relative static susceptibility, $I(0) \propto \epsilon^{-\gamma}$, of sample E is shown in Figure 5, where ϵ_T $(=(T_s - T)/T)$ and T_s are the reduced temperature and the spinodal temperature, respectively; γ is a critical exponent. Here we have relaxed the definition of ϵ to include the spinodal curve instead of only the critical mixing point. In critical phenomena of binary fluids, the reduced temperature is usually defined as $\epsilon'_T = (T_s - T)/T_s$. However, for macromolecules the reduced temperature is preferably defined as $\epsilon_\chi = (\chi_s - \chi)/\chi_s$ (or $(\chi - \chi_s)/\chi_s$). Plots of $I^{-1/\gamma}(0)$ (γ = 1.0 and 1.23) versus T and $1/T$ for sample E are shown in Figure 5a,b and Figure 5c,d, respectively. For a determination of all the characteristic temperatures in the vicinity of the critical mixing point, such as T_{sm}, T_d, T_s, and T_k, the answers were the same in both plots as shown in Figure 5. Hair et al.[12] presented different

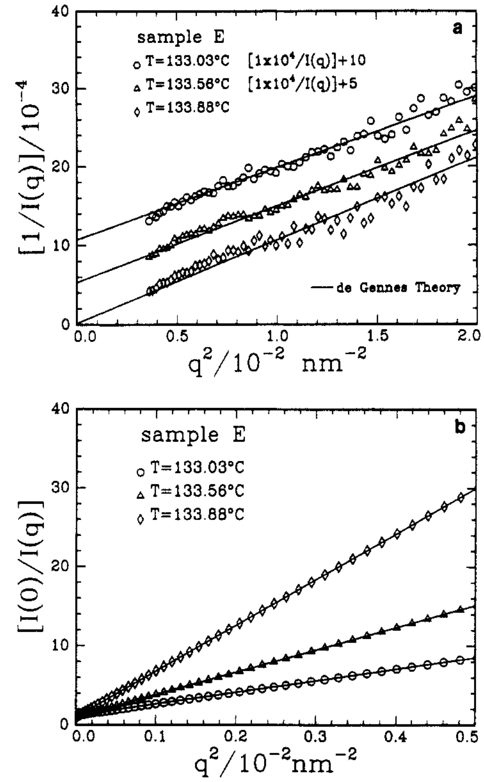

Figure 4. (a) Plots of $I^{-1}(q)$ versus q^2 of sample E. Curve fittings were based on eq 3. (b) Plots of $I(0)/I(q)$ versus q^2 of sample E. $I(q)$'s were determined from fitting curves in (a). Lines are least-squares fittings in the small-angle range with $0 \le q \le 0.07$ nm^{-1}.

Table II

temp/K	$I^{-1}(0)^a/10^{-4}$	$I^{-1}(0)^b/10^{-4}$	ξ^a/nm	ξ^c/nm
399.66	7.55		7.6	
400.66	6.40		8.6	
401.65	5.20		10.0	
402.99	3.86		11.4	
403.24	3.30		12.5	
403.56	3.01		13.1	
403.97	2.50		15.4	
404.35	2.01		17.0	
404.90	1.39	1.38	21.8	21.7
405.3	1.11	1.08	24.6	24.6
405.72	0.880	0.881	30.0	30.1
406.18	0.492	0.721	40.1	35.6
406.22	0.586	0.541	34.7	36.1
406.71	0.267	0.341	55.0	53.2
407.03	0.109	0.181	89.8	74.6

[a] Data determined using the Ornstein–Zernike equation. [b] Data determined from fitting curve based on eq 3. [c] Data determined first from fitting curve based on eq 3 and then at the $q\xi < 1$ region analyzed according to eq 5.

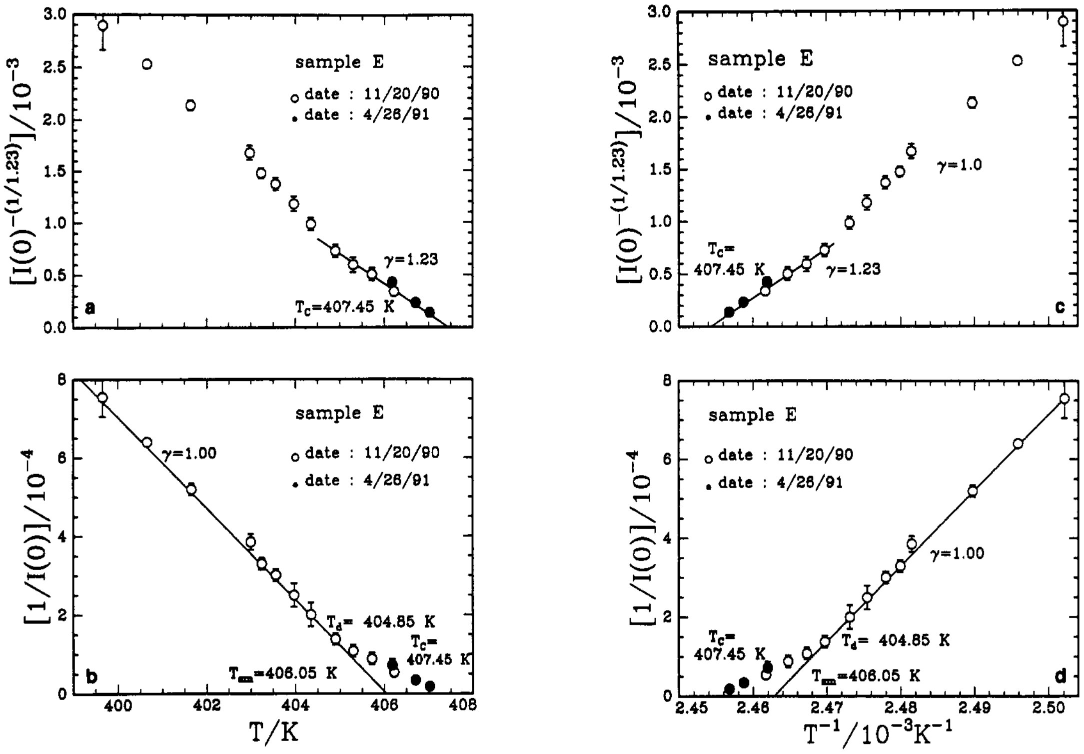

Figure 5. Plots of $I^{-1/\gamma}(0)$ versus temperature T: (a) $\gamma = 1.23$; and (b) $\gamma = 1.00$. Plots of $I^{-1/\gamma}(0)$ versus $1/T$: (c) $\gamma = 1.23$; (d) $\gamma = 1.00$. The plots are used to emphasize the crossover from mean field to Ising behavior in the relative static susceptibility for the polymer blend at the critical solution concentration (sample E). $T_c = 407.45$ K = 134.30 °C. The crossover point is expressed as $T_d = 404.85$ K. The dates show two separate experiments with independent samples.

crossover temperatures T_d obtained in plots of $S^{-1}(0)$ vs $1/T$ and T for low molecular weight deuterated polystyrene/polybutadiene blends. In our case, the difference between ϵ_T and ϵ'_T is small (<3%) in the temperature region of our experiments. Plots a and c of Figure 5 clearly show an Ising regime near the critical mixing point. The mean field regime is demonstrated by plots b and d of Figure 5, with T_{sm} being the hypothetical extrapolated mean field spinodal temperature. In Figure 5 the crossover temperature T_d (=404.85 K) can clearly be identified. In a log–log plot of reciprocal relative susceptibility versus the reduced temperature ϵ_T, as shown in Figure 6a, a critical exponent γ of 1.23 was observed. Similarly, a critical exponent $\nu = 0.63$ in a log–log plot of reciprocal correlation length versus the reduced temperature, as shown in Figure 6b with $\xi \propto \epsilon_T^{-\nu}$, further strengthens the presence of the Ising behavior. A comparison of the log–log plot of reciprocal relative susceptibility and correlation length obtained from the two different approaches versus reduced temperature is shown in Figure 6. In the vicinity of the spinodal temperature the relative error due to the analysis based on the O–Z equation was higher than that measured at lower temperatures. In a log–log plot, the linearity of data points (shown in Figure 6c,d) is not as good as the data determined by using the two-step approach, as shown in Figure 6a,b. The data in this region were plotted on a double-logarithmic scale with $\gamma = 1.23$ (or $\nu = 0.63$), both leading toward a T_s ($\equiv T_c$ here) of 134.30 °C, which is consistent with the critical solution temperature T_c as derived by using the new modified centrifuge apparatus.[8] Thus the composition W_{PS} of 0.52 for sample E could be considered as the critical solution concentration. As listed in Table I, T_{sm} and T_s for the five samples were measured by extrapolating $I^{-1}(0)$ and $I^{-1/1.23}(0)$, respectively, as a function of temperature to zero from the homogeneous region. The binodal curve, which was determined by the centrifuge method, and the spinodal region, as determined by SAXS, as shown in Figure 1 demonstrated the consistency in the two independent sets of experiments. One unique feature of the centrifuge method is that both the coexistence curve and the diameter of the coexistence curve could be determined. The curve fitting was based on the linear diameter approach, ignoring the deviation near the critical point. We were not able to determine the volume fractions of the two phases very near the critical mixing point by this method for the present P2ClS/PS blend because of high viscosity and strong scattering. However, the extrapolated experimental critical solution temperature was very close to the value determined by SAXS. Broseta et al.[13] presented a theory of phase transition for polymer blends in the presence of a good solvent. They pointed out that the critical behavior of a polymer–polymer–good solvent system is different from that of low molecular weight ternary mixtures, and the singularities could be characterized by unrenormalized Ising exponents, i.e., $\beta \simeq 0.325$ for the coexistence curve, $\nu \simeq 0.63$ for the correlation length, and $\gamma \simeq 1.24$ for the susceptibility. The P2ClS–PS–DBP blend can be treated as a concentrated polymer–polymer–good solvent system as DBP is a good solvent for both P2ClS and PS. In the vicinity of the critical mixing point, Ising exponents were indeed observed in this work, in agreement with the theoretical prediction.

Phase separation temperatures T_p of the five samples are also listed in Table I. Figure 7 shows a temperature-dependent plot of $I^{-1}(0)$ for sample A with composition $W_{PS} = 0.60$, which is different from W_{PS} at the critical composition. There is a linear region $333 < T < 406$ K which represents the mean field behavior. It clearly shows that the data measured during the three synchrotron runs were superimposable. The deviation from the mean field behavior is manifested in the inset of Figure 7, where the four data points (three hollow triangles and one hollow circle) reveal the deviation from the mean field manner. The three hollow triangles have been replotted and shows a good linear fitting by assuming different γ values. At

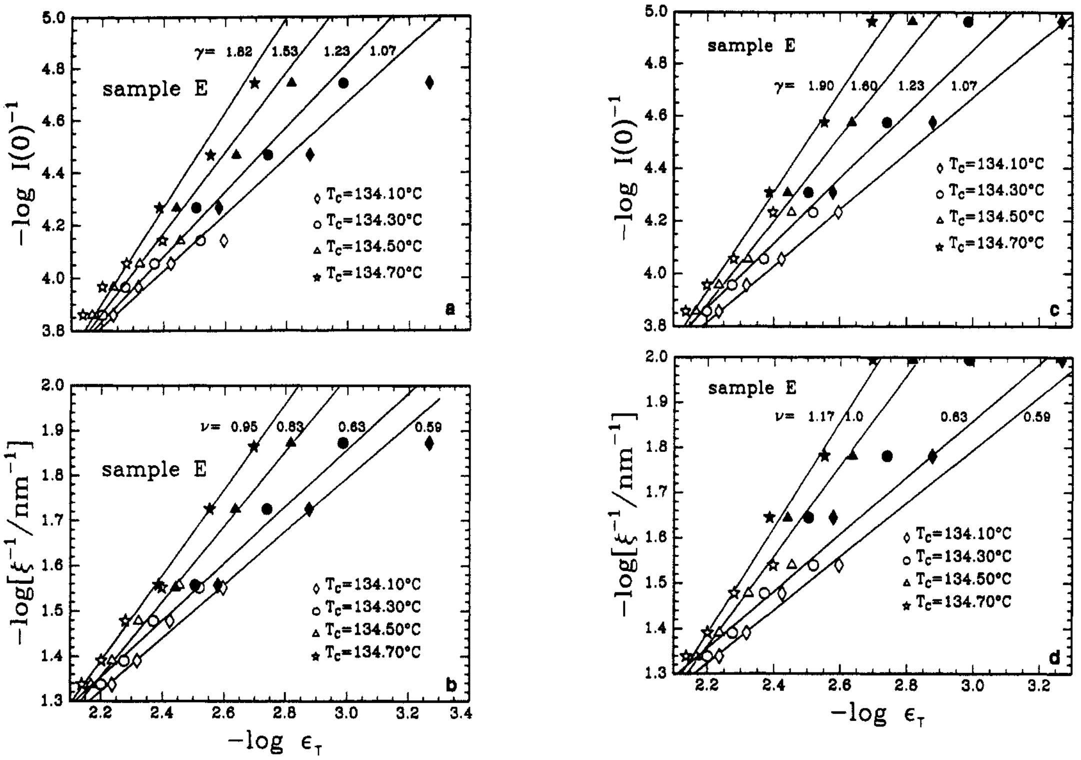

Figure 6. (a) log–log plot of reciprocal relative susceptibility $I^{-1}(0)$ versus the reduced temperature ϵ_T ($=(T_c - T)/T$) using different estimated T_c values. (b) log–log plot of reciprocal correlation length ξ^{-1} versus the reduced temperature ϵ_T ($=(T_c - T)/T$) using different estimated T_c values. (c) log–log plot of reciprocal relative susceptibility $I^{-1}(0)$ versus the reduced temperature ϵ_T ($=(T_c - T)/T$) using different estimated T_c values. (d) log–log plot of reciprocal correlation length ξ^{-1} versus the reduced temperature ϵ_T ($=(T_c - T)/T$) using different estimated T_c values. $T_s = T_c$ at the critical mixing point. In (a) and (b) a two-step fitting approach was used. In (c) and (d) the results were analyzed by using the Ornstein–Zernike equation. Hollow symbols denote sets of data determined on 11/20/90, and filled symbols denote data determined on 4/26/91.

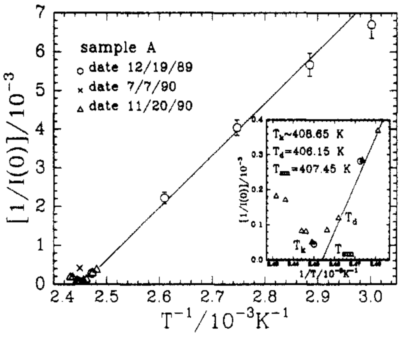

Figure 7. Inverse susceptibility $I^{-1}(0)$ versus inverse temperature T^{-1} for sample A with $W_{PS} = 0.60$. Different symbols denote the dates of measurements.

temperatures higher than T_d, the $I(0)$ value decreases with increasing temperature. Then an abrupt change was observed over a temperature region $T_K \sim 408.65$ K. This type of abrupt change has been reported by Schwahn et al.[5,6] in PVME/d-PS blend studies.

The results of our analysis can be strengthened further by making plots of $\xi^{-1/\nu}$ versus temperature as shown in Figure 8, where the crossover temperature T_d (=404.85 K), the mean field ν value of 0.5, and the Ising ν value of 0.63 are confirmed. We further emphasize the reproducibility of our experiments by showing correlation length results dating back to 11/20/90 as shown in Figure 9. All correlation lengths are consistent with the reduced temperature distance from the spinodal temperature as shown in Figure 9.

From our SAXS results, a crossover in the static susceptibility from the mean field to the Ising-like behavior at 2.6 K below the critical mixing temperature was clearly observed. The reduced temperature ϵ_χ, denoting the crossover region, could be estimated by the Ginzburg criterion, which is defined as $\epsilon_\chi = (\chi_{sm} - \chi_{Td})/\chi_{sm}$, with χ_{sm} and χ_{Td} being the Flory–Huggins interaction parameter at the spinodal temperature, but based on the mean field behavior, and at the crossover temperature, respectively. If both polymers in the blend have different numbers of statistical segments, $N_A \neq N_B$, the $\epsilon_\chi \sim (N_A N_B)^{-1/2}$ can lead to large discrepancies with experimental results. The

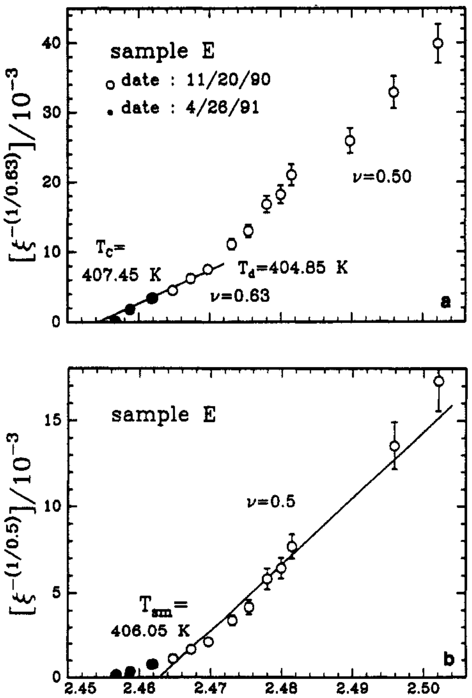

Figure 8. Inverse correlation length $\xi^{-1/\nu}$ versus $1/T$ for sample E: (a) $\nu = 0.63$; (b) $\nu = 0.50$.

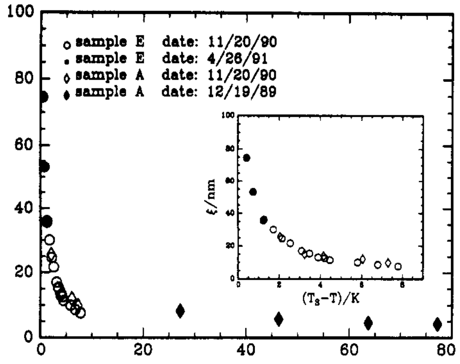

Figure 9. Plot of ξ versus temperature distance from the spinodal temperature for samples A and E.

Table III

	sample			sample	
	E	A		E	A
N_{PS}	356	356	$\chi_{sm}/10^{-3}$ [a]	3.24_5	3.04_9
N_{P2ClS}	1682.3	1682.3	$\chi_{Td}/10^{-3}$ [b]	3.06_8	2.96_8
$R_{g,PS}/10^{-7}$cm	5.75	5.75	$\upsilon_m/10^{-22}$ cm^3	1.79	1.78
$R_{g,P2ClS}/10^{-7}$cm	11.9_9	11.9_9	ϵ_χ [c]	0.055_3	0.026_5
$R_{g,blend}/10^{-7}$ cm	7.55	7.98	$\epsilon_T/10^{-3}$ [d]	2.96_4	3.20_1
T_{sm}/K	406.05	407.45	C [e]	0.56	0.29
T_d/K	404.85	406.15	C [f]	0.030	0.035
ϕ_{PS}	0.423_5	0.483_3			
ϕ_{P2ClS}	0.324_9	0.267_8			

[a] Calculated from the equation $\chi_{sm} = (\upsilon_0/2)[(1/\upsilon_A\phi_A N_A) + (1/\upsilon_B\phi_B N_B)]$. [b] Calculated from the relationship of $\chi(\xi)$ and $\xi(T)$ from SAXS data. [c] Calculated by $\epsilon_\chi = (\chi_{sm} - \chi_{Td})/\chi_{sm}$. [d] Calculated by $\epsilon_T = (T_{sm} - T_d)/T_d$. [e] Calculated for ϵ_χ. [f] Calculated for ϵ_T.

appropriate Ginzburg criterion could be expressed as[7]

$$\epsilon_\chi = C\upsilon_m^{\ 2} \frac{[N_A^{-1}\phi_A^{-3} + N_B^{-1}\phi_B^{-3}]^2}{[N_A^{-1}\phi_A^{-1} + N_B^{-1}\phi_B^{-1}][R_A^{\ 2}N_A^{-1}\phi_A^{-1} + R_B^{\ 2}N_B^{-1}\phi_B^{-1}]^3} \quad (6)$$

where ϕ_A, ϕ_B and R_A, R_B are the volume fractions and the radii of gyration of polymers A and B in the blend, respectively, υ_m is the volume of a chain segment, and C is a *system-independent* constant. In eq 6, we have assumed the effects by DBP to be negligible. The Flory–Huggins parameter can be evaluated from ξ within the framework of the random phase approximation (see Figure 11 caption).[14] From our experimental results we obtained $C = 0.56$ for $\epsilon_\chi = (\chi_{sm} - \chi_{Td})/\chi_{sm} = 0.055_3$ and $C = 0.29$ for $\epsilon_\chi = 0.026_5$ at the two different compositions as denoted by samples E and A, respectively. The actual values used in computing C above are listed in Table III. Along with the published results of Schwahn et al.,[5,6] a similar calculation leads to $C = 0.037$ for $\epsilon_\chi = 0.10$ in the PVME/PS blend system. On the other hand, Bates et al.[7a] presented their results with $\epsilon_\chi = 0.11$ and $C = 0.29 \pm 0.08$ (=0.21[7b]) for a relatively low molecular weight polyisoprene/poly(ethylene–propylene) (PI/PEP) blend. Undoubtedly, eq 6 has reduced the large disparity as shown in $\epsilon_\chi \sim (N_A N_B)^{-1/2}$ to a fairly good agreement with experimental results.

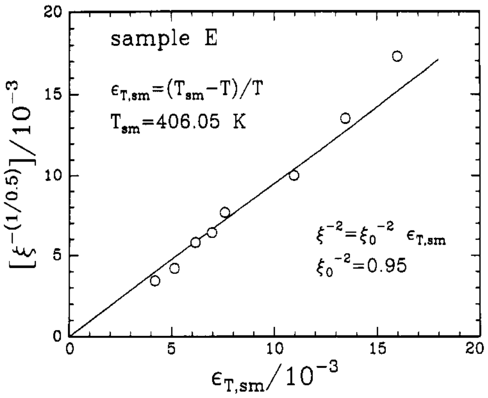

Figure 10. Plot of ξ^{-2} versus reduced temperature $\epsilon_{T,sm} = (T_{sm} - T)/T$.

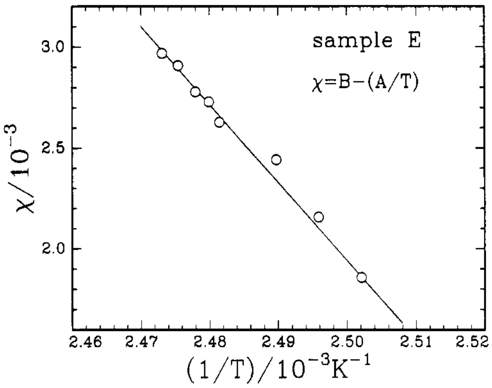

Figure 11. Plot of χ versus $1/T$ in the one-phase region, where χ was calculated from the correlation length measured in the one-phase region using the equation $\chi = \chi_s - (R_g^{\ 2}/6)[(N_A\phi_A)^{-1} + (N_B\phi_B)^{-1}]\xi^{-2}$.

Table IV
Comparison of the Constant *C* Calculated from Equations 6 and 7

	this work			Bates[a] PI2/PEP5	Schwahn[b] PVME/d-PS
	sample E		sample A		
eq used	6	7	6	6	6
ϵ_χ	0.055_3	0.055_3	0.026_5	0.11	0.10
C	0.56	0.87	0.29	0.29 ± 0.08	0.037
$\epsilon_T/10^{-3}$	2.96_4	2.96_4	3.20		
C	0.030	0.047	0.035		

[a] Reference 7. [b] References 5 and 6.

Recently, Hair et al.[12] derived a new form of the Ginzburg criterion as

$$\epsilon_T \sim \upsilon^2 \frac{[N_A^{-1}\phi_c^{-3} + N_B^{-1}(1-\phi_c)^{-3}]^2}{[(N_A\phi_c)^{-1} + N_B^{-1}(1-\phi_c)^{-1} - 2B]^4\xi_0^{\ 6}} \quad (7)$$

where ξ_0 is the bare correlation length, $\xi = \xi_0\epsilon^{-1/2}$. From a plot of ξ^{-2} vs $\epsilon_{T,sm}$ (=$(T_{sm} - T)/T$), as shown in Figure 10, we found $\xi_0 = 1.03$ nm. From a plot of χ vs $1/T$, in the one phase region, as shown in Figure 11, $B = 9.8_6 \times 10^{-2}$. In the derivation of the Ginzburg criterion (eq 7) Hair[12] defined $\epsilon_T = (1 - T_c/T)$. If we calculated $\epsilon_T = (T_{sm} - T_d)/T_d = 2.96_4 \times 10^{-3}$, we found $C = 0.047$. We also used the quasi-binary approximation in eq 7. The values of the constant C calculated from the two different expressions were comparable. If the calculations were performed by using $\epsilon_T = (T_{sm} - T_d)/T_d$ (or $(T_d - T_{sm})/T_d$) in eq 6, $C = 0.030$ and $C = 0.035$ were found for samples E and A, respectively, and if we used $\epsilon_\chi = 0.055_3$ in eq 7 for sample E, we found $C = 0.87$. The constants C calculated from eqs 6 and 7 are listed in Table IV.

The value of the constant C in the Ginzburg criterion depends on how ϵ is defined and computed, i.e., whether we use $\epsilon = \epsilon_\chi = (\chi_{sm} - \chi_{Td})/\chi_{sm}$ or $\epsilon = \epsilon_T = (T_{sm} - T_d)/T_d$. The calculated values of the constant C for sample E from the two different expressions (eqs 6 and 7) are in relatively good agreement with each other, if the same ϵ_χ (or ϵ_T) was employed in eqs 6 and 7. The temperature dependence of χ is normally set as $\chi = -A/T + B$, if the value of constant B is small enough, then B can be neglected and $\epsilon_\chi \sim \epsilon_T$.

However, if the constant B cannot be neglected when compared with A/T, then $\epsilon_\chi \neq \epsilon_T$. Unfortunately, in most cases the constant B cannot be neglected. For instance, in this work we found $B \sim 0.098_6$ and $A/T_{sm} \sim 0.095$ for sample E at $T_{sm} = 406.05$ K, while in the PIP/PEP blend $B \sim 0.0367$ and $A/T \sim 0.082$ at $T_{sm} = 321.25$ K were reported.[7b] Nevertheless, the constant C still exhibits some difference in different polymer blend systems. Thus more experiments are needed to further ascertain the Ginzburg criterion.

Conclusions

In this study, SAXS results clearly reveal a crossover in the static susceptibility and the correlation length from mean field to Ising-like behavior, with critical exponents γ changing from 1.00 to 1.23 and ν changing from 0.50 to 0.63, respectively. The crossover occurs at 2.6 K below the critical temperature. A verification of the Ginzburg criterion has been discussed. On the basis of phase separation measurements by a new modified centrifuge apparatus, $W_{PS} = 0.52$ at the critical composition with $W_{PS} + W_{P2ClS} = 1$ and the effects of DBP ignored. The critical temperature $T_c = 134.3$ °C is consistent between SAXS and independent phase separation measurements.

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