Figure 11. Schematic structure in a lyotropic phase with "blobs of dimension L_p".

of "oriented blobs"; see Figure 11. With a size on the order of L_p, the persistence length, such blobs would “line up“ due to their anisotropic polarizability, meaning that the formation of long-range orientational order would be governed by a Maier–Saupe type potential. Here we are essentially postulating that the excluded volume term in the free energy only has a limited range (on the order of L_p). The excluded volume term would then only tell us something about the local molecular environment and not about long-range orientational order. It is stressed that the explanation given above is speculative and should be treated with due caution.

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References and Notes

(1) Picken, S. J. *Macromolecules* **1989,** *22,* 1766.
(2) Vertogen, G.; de Jeu, W. H. *Thermotropic Liquid Crystals, Fundamentals*; Springer-Verlag, Berlin, 1988.
(3) Sartirana, M.; Marsano, E.; Bianchi, E.; Ciferri, A. *Macromolecules* **1986,** *19,* 1176.
(4) Takase, M.; Krigbaum, W. R. *J. Polym. Sci., Polym. Phys. Ed* **1986,** *24,* 1115.
(5) Bahadur, B. *J. Chim. Phys. Phys.-Chim. Biol.* **1976,** *73,* 255.
(6) Maier, W.; Saupe, A. *Z. Naturforsch.* **1959,** *A14,* 882; *Z. Naturforsch.* **1960,** *A15,* 287.
(7) Ying, Q.; Chu, B. *Makromol. Chem., Rapid Commun.* **1984,** *5,* 785.
(8) Khokhlov, A. R.; Semenov, A. N. *J. Stat. Phys.* **1985,** *38*(1/2), 161.
(9) Odijk, T. *Macromolecules* **1986,** *19,* 2313.
(10) Ten Bosch, A.; Maissa, P.; Sixou, P. *Phys. Lett.* **1983,** *94*(A) 298; *J. Chem. Phys.* **1983,** *79,* 3462; *J. Phys., Lett.* **1983,** *44,* L105.
(11) Warner, M.; Gunn, J. M. F.; Baumgartner, A. *J. Phys. Math. Gen.* **1985,** *18A,* 3007.
(12) *Handbook of Chemistry and Physics*, 55th ed.; CRC Press: Cleveland, 1974.

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Turbidity of Polystyrene in Diethyl Malonate in the One-Phase Region near the Critical Solution Point

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ABSTRACT: We have measured the extinction coefficient of a transmitted beam of monochromatic light through a mixture of polystyrene (molecular weight 1.02×10^5) in diethyl malonate near its upper critical solution point. The resulting turbidity was measured in a reduced temperature region, $10^{-5} < t < 10^{-1}$, where $t = (T - T_c)/T_c$ and T_c is the critical solution temperature, in two samples close to the critical composition. This polymer–solvent system near its critical point exhibits the properties of a near critical binary fluid mixture, and the turbidity can be explained by using an $n = 1$ (Ising) model. When the critical exponents ν and γ were fixed at the values predicted from renormalization group theory, the amplitude ξ_0 of the correlation length was determined to be 1.01 ± 0.08 nm, while the amplitude of the turbidity τ_0 was $(2.00 \pm 0.01) \times 10^{-4}$ cm^{-1}, which are consistent with two-scale-factor universality predictions. The turbidity far from the critical point showed an apparently constant scattering from the polymer solution. Very close to the transition temperature, the system was observed to experience a marked critical slowing with a time constant of 90 min.

Introduction

There are two critical points of interest in studying monodisperse polystyrene in a solvent.[1,2] One occurs at the coil–globule transition corresponding to the Flory Θ temperature and has been explained in terms of the $n = 0$ vector model.[2] The second is a critical solution point that produces a phase separation of the mixture into a polymer-rich phase and a polymer-poor phase, with a critical temperature and composition that depend on the system. This latter critical point has been described[2] by an $n = 1$ (Ising) model in a renormalization group theory.

Modern theories of critical solution points have been very successful in explaining a wide variety of observed phenomena in low molecular weight fluid mixtures[3,4] and, more recently, in polymer–solvent systems near their critical solution point.[5–9] In particular, the critical exponents experimentally measured in polymer–solvent systems agree not only with the experimental values found in low molecular weight binary fluid mixtures but also with the renormalization group predictions for the Ising model (space dimension $d = 3$ and order parameter dimension $n = 1$).[5-9]

Renormalization group theory has been used successfully to relate amplitudes as well as exponents that describe phenomena near a critical solution point. Two-scale-factor universality predicts a universal relationship among the amplitudes B of the coexistence curve, χ_0 of the osmotic compressibility, and ξ_0 of the correlation length. These are defined by

$$\xi = \xi_0 t^{-\nu} \qquad T > T_c \tag{1}$$

$$\phi - \phi_c = B t^{\beta} \qquad T < T_c \tag{2}$$

$$\chi = \chi_0 t^{-\gamma} \qquad T > T_c \tag{3}$$

where ϕ is the volume fraction of one component in the upper or lower phase, ϕ_c is the critical composition, χ is the osmotic compressibility, t is the reduced temperature $t = |T - T_c|/T_c$, and β, ν, and γ are universal critical exponents predicted[10] from the $n = 1$ (Ising) model to be 0.325, 0.63, and 1.241, respectively. It has been shown[11,12] that the amplitudes can be related by

$$R = \xi_0 \left[\frac{B^2}{k_B T_c \chi_0} \right]^{1/3} = 0.65\text{–}0.67 \tag{4}$$

with a predicted[11,12] value of 0.65–0.67 for the three dimensional Ising model. Experiments in liquid–gas systems[13] and small molecular weight liquid mixtures[14,15] have confirmed this value within experimental error. The values of ξ_0 and χ_0 can both be determined by turbidity measurements as described below.

The turbidity τ is the inverse of an effective extinction length and is defined by $\tau = (-1/L) \ln (I_t/I_0)$, where L is the length of the scattering medium and I_t is the transmitted and I_0 the incident light intensity. The turbidity is related to critical phenomena by assuming Ornstein–Zernike scattering,[16,17] which has accurately explained the angular distribution of scattered light near a critical point. A small asymmetry in the forward direction caused Fisher[18] to introduce a critical exponent, η, whose value is small ($\eta = 2 - \gamma/\nu \sim 0.030$), resulting in a negligible effect on the turbidity at the level of current experiments.[15,19] The turbidity can be developed by integrating the light scattered out of the incident beam to give[16]

$$\tau = \tau_0 (1 + t) t^{-\gamma} \left\{ \frac{2a^2 + 2a + 1}{a^3} \ln (1 + 2a) - \frac{2(1 + a)}{a^2} \right\} \tag{5}$$

where

$$\tau_0 = \frac{\pi^3}{\lambda_0^4} \left[\frac{\partial n^2}{\partial \phi} \right]^2 k_B T_c \chi_0 \tag{6}$$

$a = 2k_0^2 \xi^2$, $k_0 = 2\pi n/\lambda_0$, n is the refractive index of the mixture, λ_0 is the vacuum wavelength of the light, and the turbidity amplitude τ_0 is a quantity dependent on the system. Good data close to T_c are crucial in determining ξ_0 which enters in a complicated fashion through a. The compressibility dominates far from T_c, so the turbidity has a simple power law dependence $\tau = 8\tau_0 t^{-\gamma}/3$ for $T \gg T_c$. Close to T_c, the turbidity varies much more slowly and is a function of both τ_0 and ξ_0: $\tau = [\tau_0/(k_0^2 \xi_0^2)] \ln (2a)$ for $T > T_c$. The compressibility amplitude χ_0 can be determined from τ_0 provided measurements of the composition dependence of the refractive index $\partial n^2/\partial \phi$ have been taken. Since these measurements are not available for this polymer system, only the value of τ_0 can be determined from our data.

Hamano et al.[7] have measured the scattered light intensity as a function of angle as well as the turbidity in the system polystyrene (molecular weight 2×10^5) and diethyl malonate over the reduced temperature range $5 \times 10^{-5} < t < 7 \times 10^{-3}$. The angular light scattering was used to determine $\xi_0 = 0.940 \pm 0.007$ nm and $\nu = 0.64$, but they did not correct the data for multiple scattering although they did worry about its effect. Their turbidity data were analyzed by *assuming* these values of ξ_0 and ν to obtain an amplitude equivalent to $\tau_0 = (2.7 \pm 0.1) \times 10^{-4}$ cm^{-1} and $\gamma = 1.22$.

Multiple scattering effects[20] are expected to be small for turbidity measurements though large for angular light scattering measurements in this mixture. When the light scattering was measured as a function of angle, a relatively small amount of multiple scattering can be a significant percentage of the light observed. However, by definition, the turbidity measures all the light scattered from the main beam and having that light scatter more than once is irrelevant provided it does not scatter back into the detector.

The mixture of polystyrene in diethyl malonate is particularly interesting since the two components are closely matched in density and refractive index and because the viscosity is very large (45 cP in $M_w = 1.02 \times 10^5$ polystyrene in diethyl malonate[21]) near the critical solution point. A close density match is important in minimizing gravity effects, while a close refractive index match reduces multiple scattering.[6,7] Measurements in this system have also been made on the coexistence curve,[7,9] dielectric constant,[8] density,[9] viscosity,[21] ultrasonic absorption,[6] relaxation, and spinodal decomposition.[22] However, the amplitude relation predicted by two-scale-factor universality has not been tested since the correlation length has not been measured for the same molecular weight polystyrene for which coexistence curve data are available.

This work describes precise measurements of the turbidity in the one-phase region close to the critical solution point of the polymer–solvent system polystyrene and diethyl malonate. The turbidity data are analyzed for consistency with eq 5, to determine the amplitudes ξ_0 and χ_0, to test the two-scale-factor amplitude ratio R, and to look for effects attributable either to the polymer when far from T_c or to critical slowing down when very close to T_c.

Experimental Methods

The polystyrene used for these measurements was obtained from Toya Soda Manufacturing Co. and had a molecular weight of 1.02×10^5 and a ratio of weight-average to number-average molecular weight of 1.02. It was dried in a vacuum oven for over 2 weeks before being transferred to a drybox for sample preparation.

The diethyl malonate was at least 99% pure as obtained from Aldrich Chemical Co. A 5% aqueous potassium carbonate solution extracted the acids formed by hydrolysis of the ester. The ester was washed with deionized water to remove any potassium carbonate, shaken with sodium sulfate to remove most of the water, filtered to remove the sodium sulfate, and stored over molecular sieves to dry it further.

The sample was prepared[23] to ensure that samples similar to those of Greer et al.[8,9,21] were studied here, so that the amplitudes could be meaningfully combined. This mixture is extremely sensitive to water impurity,[8,9] and thus each cell has a slightly different critical temperature. The effect of impurities on the critical point is principally seen as a shift in the critical temperature, with negligible effects on the critical exponents and critical composition in this experiment.[24,25]

Two cells of different optical path lengths were filled with slightly different compositions of polystyrene ($M_w = 1.02 \times 10^5$) in diethyl malonate. The cells were commercial (Spectrocell) cylindrical cells with a 22-mm diameter and a fill tube that was heated and drawn closed to seal the sample. One cell was made of optical Pyrex with a 1.000-cm optical path length and filled with a 9.469 wt % polystyrene sample. This sample was degassed by a standard freeze-pump-thaw method. The second cell was made of quartz with a 0.389-cm optical path length and filled with a 9.744 wt % polystyrene sample. Both mixtures provided a broad meniscus in the center of the cell at the transition temperature. These compositions should be compared to the critical composition others have found for polystyrene in diethyl malonate of 8.48 wt % for[7] $M_w = 2.0 \times 10^5$, 9.469 wt % for[9] $M_w = 1.07 \times 10^5$, and 8.94 wt % for[26] $M_w = 1.02 \times 10^5$ as used in this experiment.

The temperature of a cell was controlled by immersion in a well-stirred, filtered water bath as done previously.[15] A pair of 5-cm cylindrical tubes with optical glass windows were sealed to the bath light entrance and exit by rubber grommets. These evacuated tubes reduced the distance the light had to travel in the water and provided a thermal insulation for the outside windows that prevented condensation that would otherwise be a problem at the temperatures investigated (≈4 °C). The temperature was controlled with a Tronac PTC-41 controller to ±0.7 mK maximum excursions over an hour and with a long term stability less than 1 mK. The temperature was monitored with a Thermometrics thermistor in a separate AC bridge to an accuracy of ±10 mK and a precision of ±0.2 mK.

The optical system was designed and refined to optimize the precision and accuracy of the light intensity measurements that allowed the turbidity to be determined. The optics has been fully described[15] and was only modified by adding windows on the outside ends of the tubes that acted as windows in the water bath as described above.

The laser beam ($\lambda_0 = 632.8$ nm) was spatially filtered and expanded before a portion was monitored by a reference detector while the transmitted beam was sensed with a photodiode. The main beam traveled through the water bath where the cell was oriented with the laser beam along the cell's cylindrical axis. The cell could be moved out of the beam path to determine the absolute turbidity of the fluid sample. The detection, computer averaging, and experimental procedure are the same as described previously.[15] An improved voltmeter increased the precision of the intensities by a factor of 5, which provided a smaller random error in the turbidity but an accuracy limited by the optical path length determination.

Experimental Results

The procedure of taking intensity measurements with the cell in and out of the beam path corrects for reflected and absorbed light from the bath but not for reflected light from the cell windows. The turbidity due to reflections from the cell windows can be calculated from the refractive indices of the cell windows, water, and the polymer mixture. The refractive index of the polymer solution was measured by a total internal reflection technique and found to be 1.413. Water and the optical glass windows had refractive indices of 1.333 and 1.52, respectively, while the thin (0.389 cm) quartz cell had a refractive index of 1.457. The contribution to the measured turbidity due to the reflectance at normal incidence is then 0.0112 ± 0.0007 cm^{-1} for the 1-cm path length, optical glass cell and 0.0114 ± 0.0005 cm^{-1} for the 0.389 cm quartz cell. The turbidity τ_r due to reflectance from the cell windows is subtracted from the measured turbidity at each temperature to obtain the absolute turbidity τ of the polystyrene-diethyl malonate mixture

$$\tau = -\frac{1}{L} \ln (I_1/I_2) - \tau_r \tag{7}$$

where I_1 and I_2 are the ratios of the transmitted to reference intensities with and without the cell in the beam, respectively. Most of the data were taken with the 1-cm cell, including data far from the critical temperature. This polymer-solvent system has a large amplitude τ_0, which results in measurable scattering another decade in reduced temperature further from T_c than is possible in small molecular weight systems.[15,19]

Because the system has a high τ_0, the turbidity in the cell is very large at the critical point and observation of the phase transition is difficult. Two effects were used to determine the onset of phase separation, which in this system takes a very long time to occur because of the close density match of the components and the high viscosity of the system near T_c. The first was a large increase in the turbidity as the temperature was decreased in small (3-10 mK) steps toward T_c. Since the turbidity changes slowly with temperature close to, but above, T_c, a sudden turbidity increase signals the formation of large concentration fluctuations—the precursor of a second phase. When such an increase was observed, the system was held at the temperature for 1-2 days to look for the second indicator of phase separation: the appearance of macroscopic (1 mm) droplets that would fill the cell. After another day, two liquid phases would be observable separated by a broad meniscus, which appeared to divide the phases equally in our cells. The phase separation process takes a very long time and can easily be missed if data are taken too quickly. What would occur in a few minutes in a small molecular weight system takes hours in this mixture. Thus it was difficult to determine the transition temperature, particularly in the 1-cm path length cell. The transition temperature in this cell was observed to be 4.050 ± 0.003 °C, which is higher than the 3.22 °C observed by Tveekrem et al.[8] but lower than the 7.00 °C determined by Gruner et al.[9] for the same molecular weight polystyrene in diethyl malonate.

Phase separation in the thinner (0.389 cm) cell was easier to observe, and we were able to acquire data close to T_c. The phase separation temperature for the 9.744 wt % polystyrene in this thinner cell was found to be 3.525 ± 0.001 °C. The difference between this phase separation temperature and the critical temperature can be estimated from prior coexistence curve measurements[8] to be 10 mK, assuming the critical composition is 8.94 wt %. The half degree difference in the critical temperature between this sample and the sample used in the 1-cm cell is attributed to trace water impurities.[8,9] Neither sample showed any drift of the critical temperature with time.

The turbidity of the thinner cell was monitored once as a function of time to try to measure the time constants in the system. At this point, the cell temperature was being reduced in 3 mK steps every 24 h. When the temperature was changed to 3.528 °C, a temperature below T_c but above what was observed as the transition temperature, the transmitted light intensity was monitored as a function of time for the next 24 h. The data are shown in Figure 1 as a semilog plot of the dimensionless transmitted light intensity minus the long-time equilibrium value as a function of time. Two exponential decays are seen. The first is a decay with a $1/e$ time constant of 10 min, which we associate with the thermal equilibrium of the cell's fluids. The second decay is much longer with a time constant of 90 min. Such a long time constant is attributed to critical slowing down in the one-phase region.[22,27] The temperature was lowered another 3 mK, and a further 24-h wait was necessary for the fluids to take on the granular appearance characterizing the onset of phase separation. This system is known[22] for

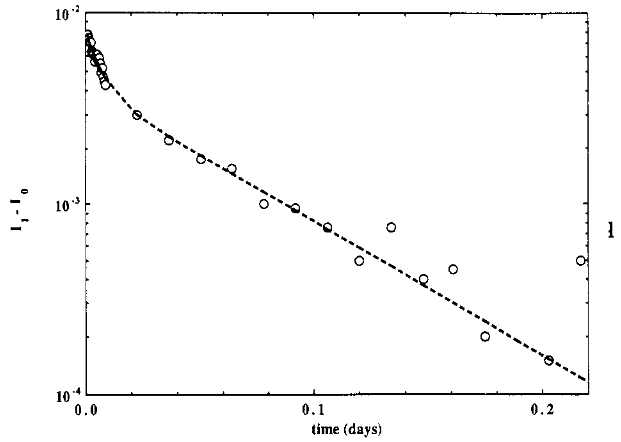

Figure 1. Relaxation of the dimensionless, transmitted light intensity I_1 through a polystyrene–diethyl malonate sample after a 3 mK quench in the one-phase region close to the transition temperature. I_0 is the equilibrium value of the light intensity after 24 h. The data are consistent with a sum of two exponential decays (dashed curve). The short-term time constant of 10 min corresponds to the thermal equilibration, and the long-term time constant of 90 min corresponds to the critical slowing down. The one standard deviation errors for the intensity are 0.0003.

Table I
Absolute Turbidity τ in the One-Phase Region of Polystyrene ($M_w = 1.02 \times 10^5$) in Diethyl Malonate as a Function of Temperature T or Reduced Temperature $t = (T - T_c)/T_c$[a]

T, K	t	τ, cm^{-1}	$\delta\tau$, cm^{-1}
	Run 1		
277.2147	5.3000E-05	3.522	0.016
277.2245	8.8000E-05	3.016	0.009
277.2471	1.7000E-04	2.5	0.004
277.2606	2.1900E-04	2.263	0.005
277.2932	3.3600E-04	1.901	0.003
277.3261	4.5500E-04	1.656	0.002
277.3558	5.6200E-04	1.505	0.003
277.3889	6.8100E-04	1.441	0.002
277.4541	9.1700E-04	1.146	0.002
277.5464	1.2500E-03	0.946	0.002
277.5728	1.3450E-03	0.936	0.002
277.5996	1.4420E-03	0.862	0.002
277.6477	1.6150E-03	0.795	0.002
277.7443	1.9640E-03	0.691	0.002
277.8424	2.3170E-03	0.61	0.002
277.9177	2.5890E-03	0.565	0.002
277.9802	2.8150E-03	0.523	0.002
278.0655	3.1220E-03	0.49	0.002
278.107	3.2720E-03	0.461	0.002
278.212	3.6510E-03	0.42	0.002
278.3379	4.1050E-03	0.379	0.002
278.3614	4.1900E-03	0.372	0.002
278.5561	4.8920E-03	0.324	0.002
278.5623	4.9150E-03	0.329	0.002
278.816	5.8300E-03	0.282	0.002
279.1727	7.1170E-03	0.228	0.002
279.1758	7.1280E-03	0.23	0.002
279.3266	7.6720E-03	0.212	0.002
279.5087	8.3290E-03	0.196	0.002
279.5102	8.3340E-03	0.202	0.002
279.5901	8.6220E-03	0.192	0.002
279.7432	9.1750E-03	0.179	0.002
280.2496	1.1001E-02	0.152	0.002
280.7017	1.2632E-02	0.137	0.002
281.0588	1.3921E-02	0.121	0.002
281.7739	1.6500E-02	0.103	0.002
282.148	1.7850E-02	0.096	0.002
283.6361	2.3218E-02	0.074	0.002
284.9193	2.7847E-02	0.067	0.002
285.2404	2.9006E-02	0.061	0.002
287.0033	3.5365E-02	0.05	0.002
288.107	3.9347E-02	0.045	0.002
305.972	1.0380E-01	0.021	0.001
299.1046	7.9021E-02	0.027	0.001
295.3092	6.5329E-02	0.028	0.001
293.0335	5.7119E-02	0.031	0.001
289.0172	4.2631E-02	0.041	0.001
287.7557	3.8080E-02	0.044	0.001
287.2312	3.6188E-02	0.045	0.001
286.6828	3.4209E-02	0.049	0.001
286.0958	3.2092E-02	0.052	0.001
285.2736	2.9126E-02	0.056	0.001
284.4106	2.6012E-02	0.064	0.001
283.6686	2.3335E-02	0.071	0.001
282.869	2.0451E-02	0.08	0.001
281.3881	1.5109E-02	0.111	0.001
279.4059	7.9580E-03	0.205	0.001
278.5649	4.9240E-03	0.323	0.001
277.9208	2.6000E-03	0.559	0.001
277.3115	4.0200E-04	1.816	0.003
	Run 2		
280.693	1.4486E-02	0.13	0.01
276.736	1.8400E-04	2.473	0.007
276.72	1.2600E-04	2.76	0.007
276.693	2.9000E-05	3.814	0.011
276.732	1.7000E-04	2.497	0.011
276.711	9.4000E-05	2.941	0.011
276.693	2.9000E-05	3.705	0.011
276.688	1.1000E-05	4.098	0.011

[a] T_c is the critical temperature taken as 4.050 °C for the 1-cm cell (run 1) and 3.535 °C for the 0.389-cm cell (run 2).

its slow response in quenches into the two-phase region. We feel that Figure 1 represents the system's one-phase region evolving in time.

The turbidity data are presented in Table I in the order they were taken over an 8-month period. The background turbidity from the cell reflectivity (discussed above) has been subtracted from the experimentally determined turbidity to give the absolute turbidity in units of reciprocal centimeters. The reduced temperature t ranges from 10^{-5} to 10^{-1} and is determined from the experimentally measured critical temperature values for each sample. The error in the turbidity $\delta\tau$ represents the experimental standard deviation propagated from the light intensity measurements and includes the error in the path length determination.

Light scattering in the forward direction is small,[7] and our geometry and aperture sizes should give a negligible multiple scattering contribution to the measured turbidity. The different path length cells were used to see if multiple scattering could be observed in our experiment. Within the experimental uncertainty caused by the critical temperature uncertainty, the turbidity determined in each cell gave the same results as shown in Figure 2.

The almost linear dependence at large t in this figure has a slope of γ corresponding to the domination of the turbidity by the compressibility that results in the $t^{-\gamma}$ power law dependence. The flattening out of τ at reduced temperatures larger than 10^{-1} is due to noncritical light scattering from the polystyrene–solvent system. At small t, the turbidity changes slowly in accordance with eq 5. ξ_0 can be determined from measurements in the region where the turbidity varies slowly at small reduced temperatures through to the steeply sloped region.

Analysis and Discussion

The data shown in Table I can be analyzed by using a properly weighted least-squares fit where the parameters ξ_0, τ_0, ν, γ, and T_c can all be adjusted in eq 5. A properly weighted fit utilizes both the experimental uncertainty in the turbidity $\delta\tau$ given in Table I and the propagated uncertainty in the reduced temperature. The error in the reduced temperature corresponds to the 10 mK

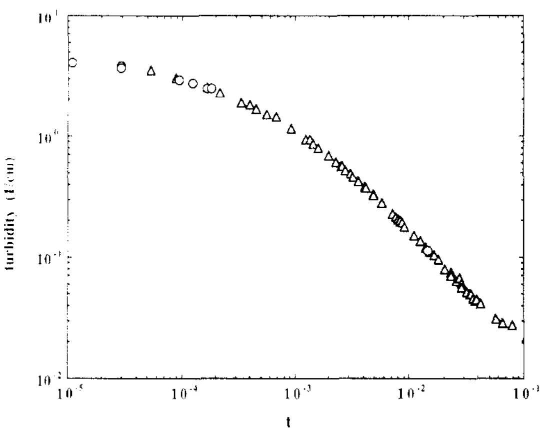

Figure 2. Turbidity in polystyrene ($M_w = 1.02 \times 10^5$) in diethyl malonate as a function of reduced temperature $t = (T - T_c)/T_c$. The circles were taken with the 0.389-cm cell at a composition of 9.744 wt % polystyrene, while the triangles were taken with the 1.000-cm cell at a composition of 9.469%. At small t, the turbidity increases logarithmically and appears flat in this plot. At intermediate temperatures, $10^{-3} < t < 10^{-2}$, the turbidity has a power law dependence on t and appears as a straight line with slope $-\gamma$. An apparently constant background turbidity dominates at large t. The errors in the data are too small to be visible except at very small t, where the error in t is 3.6×10^{-5}.

uncertainty in the critical temperature. A nonlinear fit described in Bevington[28] was used to determine the parameter values. The errors in the parameters take into account the correlated errors[29] in the parameters and are quoted in our results at the 99% confidence interval. Further details about this program will appear elsewhere.[30] In all of the fits reported here, one point at $t = 7.902 \times 10^{-2}$ was omitted from the fits as an outlier.

An additional parameter, τ_b, was added to the right-hand side of eq 5 as a constant, background turbidity that was necessary for this function to fit the data in Table I. This parameter accounted for scattering that was not due to the critical solution point and was presumably caused by the polymer coils in the solvent.[31] We looked for systematic effects in our procedure or apparatus that could account for this apparent background turbidity but could not find any; a background turbidity was certainly not present in small molecular weight fluid mixtures studied with the same apparatus.[15] This background turbidity has not been reported in other measurements of the turbidity in polymer–solvent systems perhaps because no data so far from T_c were obtained and/or because the absolute turbidity was not measured. The light scattering corresponding to the background turbidity is quite evident in the Rayleigh scattering observed in the cell at room temperature (reduced temperature of 0.07). The crossover in the turbidity from critical to noncritical takes place around $t = 8 \times 10^{-2}$ (see Figure 2) which gives an approximate correlation size of 50 Å, a value consistent with the correlation lengths measured in noncritical polymer solutions at this concentration and molecular weight.[31]

The parameters ξ_0, τ_0, ν, γ, and τ_b were varied in the fits of eq 5 to the turbidity data reported in Table I. The critical temperature was allowed to vary within the range determined from observation; however, the other parameters did not change within experimental error, principally because the points close to T_c are not weighted strongly nor does the turbidity change rapidly in this region. The resulting values of the parameters are given in Table II along with the uncertainties in the parameter values at the 99% confidence interval. The data reported in Table I were well explained by an $n = 1$ (Ising) model as shown by the four fits in Table II.

The first two fits allowed the five parameters τ_0, ξ_0, τ_b, ν, and γ to vary freely. When all 67 points were fit by eq 5, the values of the exponents were $\nu = 0.59$ and $\gamma = 1.2$ which are values closer to the $n = 0$ vector model than the $n = 1$ Ising model.[10] However, the contribution from the background light scattering influences the exponents, as seen in the second fit where a range of data closer to T_c was analyzed in the same way as fit 1 and where larger values of the exponents resulted. Because the turbidity has a complicated dependence on the critical exponents and because the background light scattering introduces an additional parameter to the fits, it was not possible to determine the critical exponents from this experiment.

The last two fits in Table II use the exponents fixed at their theoretical values of $\nu = 0.63$ and $\gamma = 1.241$.[10] The reduced range of data closer to T_c were best fit by the parameters in eq 5 havng the values $\tau_0 = (2.00 \pm 0.01) \times 10^{-4}\ \mathrm{cm}^{-1}$, $\xi_0 = (1.01 + 0.08)$ nm, and $\tau_b = (2.1 \pm 0.5) \times 10^{-2}\ \mathrm{cm}^{-1}$. These values do not change significantly when the full range of data are analyzed as shown by the last fit.

Our determination for ξ_0 is larger than that found by Hamano et al.[7] even though we used a smaller molecular weight polystyrene. Debye et al.[32] measured the dispersion of the turbidity in polystyrene and cyclohexane to determine a "molecular force range", which is proportional to the correlation length, for a series of molecular weight polystyrenes. They found this characteristic length to scale approximately as the molecular weight raised to the 0.28 power. If this were also true for polystyrene in diethyl malonate, our smaller molecular weight polystyrene should give a ξ_0 roughly 15% *smaller* than for a $M_w = 2 \times 10^5$ as Hamano et al.[7] used. However, multiple scattering substantially affects angular light scattering measurements.[20] As recently pointed out by Shanks and Sengers,[20] several other small, yet significant, systematic errors occurred in Hamano's data including a gain calibration error and contributions from stray or reflected light so that a precise value for the correlation length amplitude ξ_0 is not clear from Hamano's experiment. Multiple scattering effects in this system would reduce the

Table II
Parameter Values Resulting from Fitting Eq 5 to the Absolute Turbidity Data in Table I[a]

fit	no. of pts	t range	ν	γ	$10^4\tau_0$, cm^{-1}	ξ_0, nm	$10^2\tau_b$, cm^{-1}	χ^2/N
1	67	$10^{-1} \rightarrow 10^{-5}$	0.590 ± 0.005	1.18 ± 0.09	2.95 ± 0.02	1.24 ± 0.5	0.8 ± 0.1	1.21
2	43	$10^{-2} \rightarrow 10^{-5}$	0.617 ± 0.003	1.19 ± 0.77	2.56 ± 0.02	0.99 ± 0.82	1.6 ± 1.0	0.73
3	43	$10^{-2} \rightarrow 10^{-5}$	0.63	1.241	2.00 ± 0.01	1.01 ± 0.08	2.1 ± 0.5	0.69
4	67	$10^{-1} \rightarrow 10^{-5}$	0.63	1.241	2.15 ± 0.01	1.09 ± 0.04	1.2 ± 1.0	1.63

[a] All fits required a constant background turbidity τ_b to account for scattering far from the critical solution temperature T_c. A smaller range of reduced temperature $t = (T - T_c)/T_c$ was used to test the sensitivity of the parameters. Errors on the parameters are at the 99% confidence interval as described in the text. χ^2/N is the reduced χ-squared as defined in ref 28. Fit 3 shows the parameter values giving the best fit to the data.

apparent correlation length.[20] We feel our experiment was less susceptible to these errors because the absolute turbidity was measured.

A crude test of two-scale-factor universality, eq 4, can be done with the results of the analysis of our turbidity data combined with the previous measurement of the coexistence curve[8] in this system. The coexistence curve was measured by a dielectric constant technique and fit to $\epsilon_u - \epsilon_1 = B' t^{\beta}$ where ϵ_u (ϵ_1) is the dielectric constant of the upper (lower) phase and B' is the amplitude determined to be $B' = 2.1 \pm 0.1$ (with $\beta = 0.325$).[8] B' can be related to B in eq 4 by $B = (B'/2)(\partial\phi/\partial\epsilon)$, where $\partial\phi/\partial\epsilon = 0.35$, and $\partial n^2/\partial\phi = 0.47$ can be estimated from the Lorentz–Lorenz relation.[33] In the Lorentz–Lorenz relation we assumed no volume loss on mixing,[33] an effect that could be significant in this system but is as yet unmeasured. Thus, only a crude test of two-scale-factor universality can be done. Since amplitude and exponent values are interrelated in most fits, it is important to compare amplitudes obtained by using a consistent set of exponents which we use as the theoretical Ising model values. Using $\tau_0 = 2.00 \pm 0.01$ cm^{-1} and $\xi_0 = 1.01 \pm 0.08$ nm, we can calculate the value of R in eq 4 as 0.66 ± 0.08 where the error includes the errors in the amplitudes but not the error in neglecting volume loss on mixing in the Lorentz–Lorenz relation.[33] This value is quite consistent with the predicted values[11,12] of 0.65–0.67 and with experimental values others[14,15,19] have found in low molecular weight liquid mixtures.

Summary

From transmitted light intensity data in the one-phase region of polystyrene–diethyl malonate, the turbidity was well determined in the reduced temperature range $10^{-5} < t < 10^{-1}$. A background turbidity was present and was attributed to scattering from the polymer coils. Long-lived relaxation effects are evident in this mixture close to T_c. Although the data could not accurately determine the critical exponents, when the $n = 1$ Ising model values of $\nu = 0.63$ and $\gamma = 1.241$ were used, the best fit to the data close to T_c ($t < 10^{-2}$) gave amplitudes $\xi_0 = 1.01 \pm 0.08$ nm and $\tau_0 = 2.00 \pm 0.01$ cm^{-1}. Two-scale-factor universality was consistent with these amplitudes.

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References and Notes

(1) Kurata, M. *Thermodynamics of Polymer Solutions*; Harwood: New York, 1982.

(2) Williams, C.; Brochard, F.; Frisch, H. L. *Annu. Rev. Phys. Chem.* **1981**, *32*, 433.

(3) Greer, S. C.; Moldover, M. R. *Annu. Rev. Phys. Chem.* **1981**, *32*, 233.

(4) Kumar, A.; Krishnamur, H. R.; Gopal, E. S. R. *Phys. Rep.* **1983**, *98*, 57.

(5) Jacobs, D. T.; Greer, S. C. *Phys. Rev. A* **1981**, *24*, 2075.

(6) Fenner, D. B. *J. Chem. Phys.* **1987**, *87*, 2377.

(7) (a) Hamano, K.; Kuwahara, N.; Nakata, M.; Kaneko, M. *Phys. Lett.* **1977**, *63A*, 121. (b) Hamano, K.; Kuwahara, N.; Nakata, M.; Kaneko, M. *Phys. Rev. A* **1979**, *20*, 1135. (c) Hamano, K.; Kuwahara, N.; Nakata, M.; Kaneko, M. *Phys. Rev. A* **1980**, *21*, 1312.

(8) Tveekrem, J. L.; Greer, S. C.; Jacobs, D. T. *Macromolecules* **1988**, *21*, 147.

(9) Gruner, K.; Greer, S. C. *Macromolecules* **1987**, *20*, 2238.

(10) LeGuillou, J. C.; Zinn-Justin, J. *Phys. Rev. B: Condens. Matter* **1980**, *21*, 3976.

(11) Stauffer, D.; Ferer, M.; Wortis, M. *Phys. Rev. Lett.* **1973**, *29*, 345.

(12) Hohenberg, P. C.; Aharony, A.; Halperin, B. I.; Siggia, E. D. *Phys. Rev. B* **1976**, *13*, 2986.

(13) Sengers, J. V.; Moldover, M. R. *Phys. Lett.* **1973**, *44A*, 261.

(14) Beysens, D.; Bourgou, A.; Calmettes, P. *Phys. Rev. A* **1982**, *26*, 3589.

(15) Jacobs, D. T. *Phys. Rev. A* **1986**, *33*, 2605.

(16) Puglielli, V. G.; Ford, N. C., Jr. *Phys. Rev. Lett.* **1970**, *25*, 143.

(17) Mowery, A. C.; Jacobs, D. T. *Am. J. Phys.* **1983**, *51*, 542.

(18) Fisher, M. E. *J. Math. Phys. (N.Y.)* **1964**, *5*, 944.

(19) Houessou, C.; Guenoun, P.; Gastaud, R.; Perrot, F.; Beysens, D. *Phys. Rev. A* **1985**, *32*, 1818.

(20) Shanks, J. G.; Sengers, J. V. *Phys. Rev. A* **1988**, *38*, 885.

(21) Gruner, K.; Greer, S. C. *Macromolecules*, in press.

(22) Fenner, D. B. *J. Chem. Phys.* **1988**, *88*, 2021.

(23) The components were prepared by Greg Furrow and the samples were filled and sealed by Karen Gruner with the help of John Trembly at the University of Maryland at College Park, MD.

(24) Tveekrem, J. L.; Jacobs, D. T. *Phys. Rev. A* **1983**, *27*, 2773.

(25) Cohn, R. H.; Jacobs, D. T. *J. Chem. Phys.* **1984**, *80*, 856.

(26) This value of ϕ_c differs slightly from that reported in ref 8. For this value, the diameter of the (dielectric constant) coexistence curve reported in ref 8 was linearly extrapolated to the critical temperature and the difference in dielectric constant between the diameter extrapolation and the one-phase value was used to determine ϕ_c. Any volume loss on mixing was neglected.

(27) Fredrickson, G. H. *J. Chem. Phys.* **1986**, *85*, 3556.

(28) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.

(29) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes*; Cambridge: New York, 1986.

(30) Andrews, K. P.; Jacobs, D. T. submitted to *Phys. Acad. Software.*

(31) Wiltzius, P.; Haller, H. R.; Cannell, D. S.; Schaefer, D. W. *Phys. Rev. Lett.* **1983**, *51*, 1183.

(32) Debye, P.; Woermann, D.; Chu, B. *J. Chem. Phys.* **1962**, *36*, 851, 1803.

(33) Andrew, W. V.; Khoo, T. B. K.; Jacobs, D. T. *J. Chem. Phys.* **1986**, *85*, 3985.

Registry No. Polystyrene, 9003-53-6; diethyl malonate, 105-53-3.