Poly(α-methylstyrene) in methylcyclohexane: Densities and viscosities near the liquid–liquid critical point

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We present new measurements of a thermodynamic property, the mass density, and of a transport property, the shear viscosity, of a solution of linear poly(α-methylstyrene), with a number average molecular weight of 32 300, in the solvent methylcyclohexane, in the one and two phase regions within 3 K of the liquid–liquid critical temperature, T_c. Both the density and the viscosity were measured with a magnetic suspension densimeter/rheometer, with precisions of 56 ppm and 4%, respectively. We find no critical anomalies in the density above T_c, the average density below T_c, the viscosity above T_c, or the average viscosity below T_c. The behavior of the difference in density below T_c is consistent with the Ising model. © *2001 American Institute of Physics.*
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I. INTRODUCTION

The nature of critical phenomena in simple fluid systems was elucidated in the 1970's. That fluids, even polymer solutions, belong to the Ising universality class is well established. There remains interest in two aspects of critical phenomena in fluids: (1) the development of a global equation-of-state that unites the critical region with the rest of the phase diagram (the "cross-over" problem),[1] and (2) an understanding of the microscopic origins of the amplitudes of critical anomalies and of the nature of the crossover behavior.[2]

In this paper we address the latter issue, and we contribute to the data available on critical amplitudes in polymer solutions. We present new measurements of a thermodynamic property, the mass density, and of a transport property, the shear viscosity, of a solution of linear poly(α-methylstyrene), with a number average molecular weight of 32 300, in the solvent methylcyclohexane, in the one and two phase regions near the liquid–liquid critical point. We find no critical anomalies in the density above T_c, the average density below T_c, the viscosity above T_c, or the average viscosity below T_c. The behavior of the difference in density below T_c is found to be consistent with the Ising model.

II. THEORY AND PREVIOUS RELATED EXPERIMENTS

A. Density

In the one phase region at $T > T_c$ (where T_c is the critical temperature), we expect a weak cusp in $\rho(t)$,[3] where t is the reduced temperature $(T - T_c)/T_c$, ρ_c is the critical density, and α is the critical exponent with value 0.109.[4]

$$\rho = \rho_c + A_1 t + A_2 t^{1-\alpha} + \cdots, \tag{1}$$

reflecting the critical anomaly in the derivative $(\partial\rho/\partial t)_P$. Many liquid–liquid systems have a measurable $(1-\alpha)$ term,[5,6] but no polymer solution has been found to have a measurable $(1-\alpha)$ term in the density above T_c.[6]

For coexisting liquid phases at $T < T_c$, we expect the difference between the density of the upper phase (ρ_u) and that of the lower phase (ρ_l) to have the form

$$\Delta\rho = \rho_l - \rho_u = Bt^{\beta}[1 + B_1 t^{\Delta} + B_2 t^{2\Delta} + \cdots], \tag{2}$$

where β is a critical exponent with a value of 0.326[4] and Δ is a "correction to scaling exponent" with a value of 0.52.[7] For polymer solutions, the leading coefficient "B" is expected[8,9] to depend on the degree of polymerization N as

$$B = B_0 N^n, \tag{3}$$

where $n = [-(1-\beta)/2] = -0.337$.

The average of coexisting phases (the "diameter" of the coexistence curve) has the form[10,11]

$$\rho_{\text{avg}} = (\rho_l + \rho_u)/2 = \rho_c + Ct + C_1 t^{1-\alpha} + C_2 t^{2\beta} + \cdots, \tag{4}$$

the $(1-\alpha)$ term being a critical anomaly and the 2β term being due to the non-optimal choice of the order parameter. Since $(1-\alpha) = 0.891$ and $2\beta = 0.652$ and both are near one, it can be difficult to sort out these terms in the diameter.[12] No polymer solution has been shown convincingly to have a $(1-\alpha)$ term in the diameter of the coexistence curve.[5,12,13] We note from Eqs. (1) and (4) that $\rho(T)$ and ρ_{avg} will meet at ρ_c if the composition is exactly ρ_c.

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B. Viscosity

For liquid–liquid critical points in the diffusion dynamic universality class, the shear viscosity, η, in the one phase region approaching the critical point is expected to diverge weakly with an exponent y[14]

$$\eta = D(T)t^{-y}[1 + D_1 t^\Delta + D_2 t^{2\Delta} + \cdots], \tag{5}$$

where $y = \nu z_\eta$, ν is the critical exponent for the correlation length, and z_η is the viscosity exponent. From theoretical values $\nu = 0.630 \pm 0.001$[4] and $z_\eta = 0.067 \pm 0.002$,[15] we get $y = 0.042 \pm 0.001$, where the uncertainties are given as one standard deviation. For simple fluids, recent experiments are generally in agreement with the theoretical prediction.[16–20] For polymer solutions, experimental measurements of y have been significantly different from theoretical predictions: $y = 0.028 \pm 0.003$.[21–26] One suggested explanation of the discrepancy for polymer solutions is that polymer solutions belong in a different dynamic universality class because of the asymmetry in the molecular dynamics of the polymer molecules and the solvent molecules.[27,28] Another possible explanation is that the range of asymptotic behavior is very different for polymer solutions. This is again the "crossover" issue discussed above, now with respect to a dynamic property.[29] It has been a continuing theme in the history of critical phenomena for crossover effects to be mistaken for real discrepancies.[30] The issue of range and crossover is related to the question of how to treat the background viscosity of the system. The coefficient D in Eq. (5) includes a temperature dependent background η_B

$$D(T) = \eta_B(T)D_0, \tag{6}$$

where D_0 is a constant and η_B is the background viscosity of the solution in the absence of critical effects. For a polymer solution, η_B is not well-established and many functional forms have been proposed.[23,31]

In the two-phase region, the average of the shear viscosities of the coexisting phases is expected to have the form of Eq. (5).[32] The difference between the viscosities of coexisting phases may be expected to follow the form of Eq. (2), corresponding to the choice of the viscosity as the order parameter.

III. EXPERIMENT

A. Sample preparation

The poly(α-methylstyrene) was obtained from Polymer Source, Inc. (Quebec, Canada). The polymer had been prepared by anionic polymerization, using s-butyl lithium as the initiator. Size exclusion chromatography by Polymer Source showed a unimodal peak with a number average molecular weight $M_n = 32300$, a weight average molecular weight $M_w = 32\,900$, and thus a polydispersity index $PI = 1.02$. The methylcyclohexane (Aldrich Chemical Co., Milwaukee, WI, 99.9% pure) was shipped in a sealed bottle and used without further purification. These were the very same materials used for a study of phase separation temperatures of this mixture.[33] The polymer was allowed to dry in the atmosphere of a high purity dry box for several days, and the solution was prepared in the dry box.

Pruessner *et al.*[33] estimated the critical mass fraction of polymer at this molecular weight to be $m_c = 0.15 \pm 0.02$ and the critical temperature to be 318.3 ± 0.4 K. Furthermore, they observed that for this mass fraction, the liquid–liquid meniscus appeared in the middle of the sample and the phase separation temperature was the highest, indicating that the polydispersity of the sample is low enough for the solution to be treated as a two component system. In this work, we carefully adjusted the mass fraction of polymer in increments of 0.005, checking for equal volumes of coexisting phases at each concentration, and were able to confirm m_c to 0.171 ± 0.005. As we discuss below, our density measurements confirmed m_c to be 0.171 ± 0.002. The sample on which we present measurements consisted of 0.992 g polymer and 4.807 g solvent, giving $m_c = 0.171 \pm 0.002$.

The phase separation temperature, T_p, of this sample was determined by visual observation of meniscus formation in two cooling runs to be 317.72 ± 0.03 K. T_c was determined by a fit to the density data to be 317.722 ± 0.002 K (see below).

B. Density measurement

We measured density with a magnetic suspension densimeter, in which a solenoid is used to suspend a magnetic buoy in the sample, and the current in the solenoid is a measure of the density of the sample.[34–37] A balance of the forces on the buoy leads to the expression

$$\rho = A + BV^2, \tag{7}$$

where ρ is the mass density of the sample fluid in which the buoy is suspended, V is the voltage across a standard resistor in series with the solenoid, and A and B are calibration constants. By suspending a buoy, which had been adjusted to have a density near that of methylcyclohexane, in 11 fluids of known density, we determined $A = 0.7612 \pm 0.0001$ g/cm^3 and $B = 0.1313 \pm 0.0002$ g/(cm^3 volt^2), where the uncertainty is one standard deviation. This calibration sets the *accuracy* of the density measurement at 0.1% for 99% confidence. The inherent *precision* of the density measurement is determined by the resolution, δV, of the voltage (± 0.0002) to be $2B\,\delta V\,V$. At a typical V of 0.3 volts, the precision is thus 16 ppm. The actual reproducibility was limited by sample conditions (see below) to about 56 ppm.

C. Viscosity measurement

The same instrument used for the density measurements can be used for simultaneous viscosity measurements.[34] The buoy is brought into suspension and the density is measured as described above. Then the cell is moved at velocity, v, relative to the suspended buoy; the flow of the sample past the buoy exerts a viscoelastic force on the buoy, which changes the support current (voltage) required to maintain the suspension of the buoy. The balance of the forces on the buoy leads to the relation[38–40]

$$\eta = C(\rho_v - \rho)/v, \tag{8}$$

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where η is the viscosity of the fluid in which the buoy is suspended, C is a calibration constant, ρ_v is the apparent density when the cell is moving at velocity v, and ρ is the density measured when $v = 0$. The calibration of the buoy in eight liquids of known viscosity[41] led to η (Pa s) $= [700 \pm 9] \times 10^{-3}((\rho_v - \rho)/v)$, where ρ and ρ_v are in g/cm^3 and v is in mm/s and the uncertainty in C is given as one standard deviation. The viscosity measurements thus had a calibration accuracy of 4% at a 99% confidence level. The precision of the measurements for this sample was 0.2 mPa s or 4%. The maximum shear rates can be calculated[42] from $3v/2R$, where v is the velocity, and are very low, 0.01–0.2 s^{-1}. The data of Sakai et al.[43] on terminated poly(α-methylstyrene) in α-chloronaphthalene indicated[44] that the viscosity of the polymer solution we study will be independent of shear rate below 10–20 s^{-1}.

D. Temperature measurement and control

The temperature of the sample cell was controlled by circulating a water/ethylene glycol mixture from a controlled bath, past the cell.[34] The temperature at the sample cell was measured by a 5000 Ω thermistor (YSI, Yellow Springs, OH, model 46044) mounted near the sample cell, in series with a 50 KΩ standard resistor (Vishay Intertechnology, Malvern, PA) and a mercury battery.[45] The thermistor was calibrated against a platinum resistance thermometer. The temperature was resolved to 0.2 mK, was accurate to 10 mK, and could be controlled for days with fluctuations of about 2 to 3 mK.

IV. RESULTS AND DISCUSSION

Data were collected on two cooling sequences, runs 1 and 2. The density and the viscosity were measured in both the one- and two-phase regions over a 5 K region around the critical point. In the two-phase region, measurements were made in each phase (upper and lower). The two runs determined T_p for this sample to be 317.72 ± 0.03 K, which is not precisely the same as T_c because the density measurements above T_c do not come to a common point with the average of the densities below T_c (see Fig. 1 and below).

Functions were fitted to the data using a weighted nonlinear least squares routine based on the MatLab (The MathWorks, Natick, MA, version 6) command "fminsearch," weighted by errors in both independent and dependent variables, and including the correlated errors in the fitted parameters.[46,47] All uncertainties are given at the 99% confidence level.

A. Density

For $T > T_c$, at each point we measured the density in the upper part of the sample and in the lower part of the sample and saw no evidence of gravitational sedimentation.[48] The one-phase data are listed in Table I and plotted in Fig. 1. There is an offset of about 30 ppm between runs 1 and 2, but we include both runs in the fit. A high-resolution plot indicates that the first data point from run 2 (at 318.96 K) is an outlier. Omitting that point, the two runs in the one-phase region can be jointly fitted by a straight line for the density, ρ, as a function of temperature, T, in K
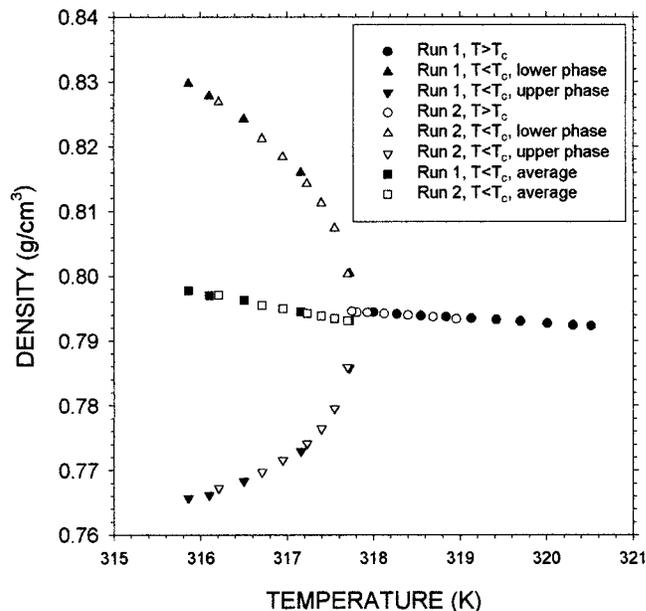

FIG. 1. Mass density as a function of temperature for a solution of linear poly(α-methylstyrene), with a number average molecular weight of 32 300, in the solvent methylcyclohexane, in the one and two phase regions within 3 K of the liquid–liquid critical temperature, T_c.

$$\rho(\text{g/cm}^3) = (1.047 \pm 0.015) - (0.000\,794 \pm 0.000\,048)T. \tag{9}$$

This fit gives a reduced $\chi^2 = 1.0$ and nearly random residuals, assuming a standard deviation for T, $\sigma_T = 0.002$ K and for the density, $\sigma_\rho = 56 \times 10^{-5}$ g/cm^3. Thus within our resolution, there is no evidence of a critical anomaly in the $\rho(T)$ above T_c for poly(α-methylstyrene)+methylcyclohexane.

For $T < T_c$, the data are also listed in Table I. We consider first the difference between coexisting densities, as fitted to Eq. (2). In order to calculate the reduced temperature, $t = (T_c - T)/T_c$, we need to specify T_c. We know (see above) that T_p is 317.72 ± 0.03 K, and that T_c must be higher than T_p. However, the coexistence curve is quite flat, so T_c will be near T_p. We tried fixing T_c at various values and fitting to Eq. (2). Our best fit for the data from both runs is with T_c fixed at 317.722 K and β fixed at 0.326, with two terms in Eq. (2), where $B = 0.320 \pm 0.012$ g/cm^3 and $B_1 = 0.38 \pm 0.25$ are free parameters; in this fit, the first point in run 1 was omitted, the standard deviation in T was taken as 0.002 K, the standard deviation in the density difference was taken as 5×10^{-4} g/cm^3, resulting in a reduced $\chi^2 = 0.7$ and random residuals. Thus the coexistence curve for this polymer solution (like other polymer solutions[49]) is consistent with the predictions of contemporary theory.

We consider now the average of the coexisting densities. We see from Fig. 1 that the average density data do not meet the coexistence curve at the same point as do the data for the density above T_c. This indicates that the sample is not exactly at the critical concentration. Pruessner et al.[33] estimated the critical composition to be $m_c = 0.15 \pm 0.02$; the sample studied here had $m_c = 0.171$. Near T_c, the average density below T_c is lower than the density data above T_c by 0.001 43 g/cm^3, indicating that the sample mass fraction is *higher* than the true critical mass fraction. Our measurements on this

TABLE I. Density and viscosity measurements for a poly(α-methylstyrene), mass fraction=0.171, in methylcyclohexane. Here ρ_u refers to the density in the one-phase region or to the density of the upper phase when two phases are present; ρ_l is the density of the lower of two phases. η_u refers to the viscosity in the one-phase region or to the viscosity of the upper phase when two phases are present; η_l is the viscosity of the lower of two phases.

Run	T (K)	ρ_u (g/cm^3)	ρ_l (g/cm^3)	η_u (mPa s)	η_l (mPa s)
1	320.515	0.792 33		3.8	
	320.305	0.792 45		3.8	
	320.010	0.792 67		3.7	
	319.700	0.793 00		3.8	
	319.420	0.793 30		4.0	
	319.130	0.793 47		4.2	
	318.840	0.793 70		4.2	
	318.550	0.793 87		4.2	
	318.270	0.794 12		4.5	
	318.000	0.794 43		4.7	
	317.720	0.785 79	0.800 42	2.6	7.9
	317.160	0.773 00	0.815 96	1.1	22.9
	316.500	0.768 36	0.824 22	1.1	39.7
	316.100	0.766 22	0.827 82	1.0	48.3
	315.860	0.765 72	0.829 72	0.8	59.7
2	318.960	0.793 38		4.2	
	318.690	0.793 73		4.4	
	318.400	0.793 95		4.5	
	318.125	0.794 21		4.8	
	317.930	0.794 35		4.9	
	317.810	0.794 40		4.9	
	317.750	0.794 54		4.9	
	317.700	0.785 97	0.800 28	2.4	7.6
	317.550	0.779 57	0.807 37	2.1	12.6
	317.395	0.776 44	0.811 26	2.0	16.4
	317.230	0.774 17	0.814 26	1.5	21.2
	316.950	0.771 61	0.818 40	0.8	26.4
	316.710	0.769 78	0.821 22	1.0	31.1
	316.210	0.767 26	0.826 87	0.8	44.6

FIG. 2. Shear viscosity as a function of temperature for a solution of linear poly(α-methylstyrene), with a number average molecular weight of 32 300, in the solvent methylcyclohexane, in the one and two phase regions within 3 K of the liquid–liquid critical temperature, T_c.

Fig. 3 we compare our data for poly(α-methylstyrene) +methylcyclohexane to viscosity measurements for the system polystyrene+cyclohexane[24] ($M_w=4.0\times10^5$) over the same range ($T-T_c \leqslant 3$ K). While the viscosity of poly(α-methylstyrene)+methylcyclohexane is an order of magnitude larger than that of polystyrene+cyclohexane, the behavior over this temperature range is very similar. The viscosity of polystyrene+cyclohexane does show a distinct critical anomaly when data over a larger range ($T-T_c \leqslant 30$ K) are viewed,[24] but that anomaly is not obvious over the range

sample and on an earlier one indicate that a change in mass fraction of 0.005 leads to a change in density of 0.016 g/cm^3, from which we can estimate the true m_c to be 0.0004 lower than 0.171, so the difference is less than the uncertainty in our composition.

The average density below T_c was adequately fitted by a straight line function of the temperature

$$\rho_{\text{avg}}(\text{g/cm}^3) = (\rho_l + \rho_u)/2$$
$$= (1.597 \pm 0.045) - (0.002\,53 \pm 0.000\,14)T,$$
(10)

where the standard deviation in T was taken as 0.002 K, the standard deviation in the density average was taken as 1 $\times 10^{-4}$ g/cm^3, and the reduced $\chi^2 = 1.0$, and the residuals are random. Thus there is no evidence of a critical anomaly in the diameter of the coexistence curve for this system.

B. Viscosity

The viscosity data are listed in Table I and plotted in Figs. 2 and 3. We consider first the behavior above T_c. Figures 2 and 3 show that $\eta(T)$ shows some curvature, but does not show a dramatic anomaly in the viscosity over the range of temperature ($T-T_c \leqslant 3$ K) for which we have data. In
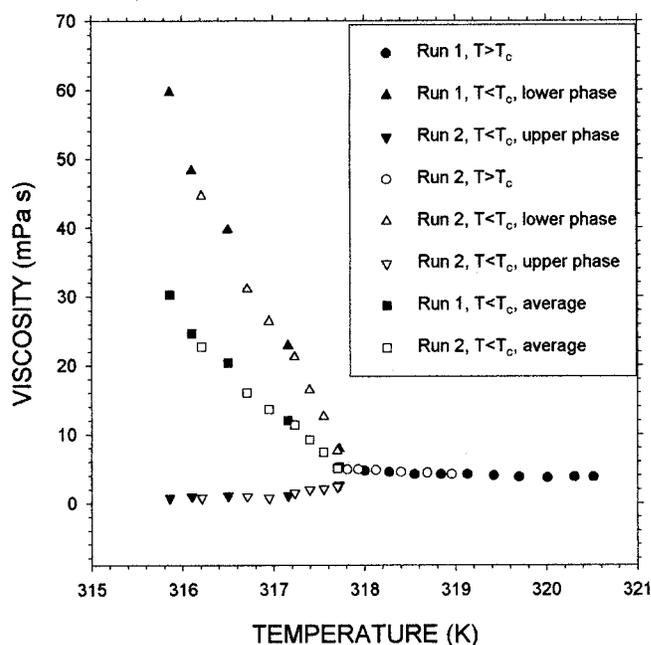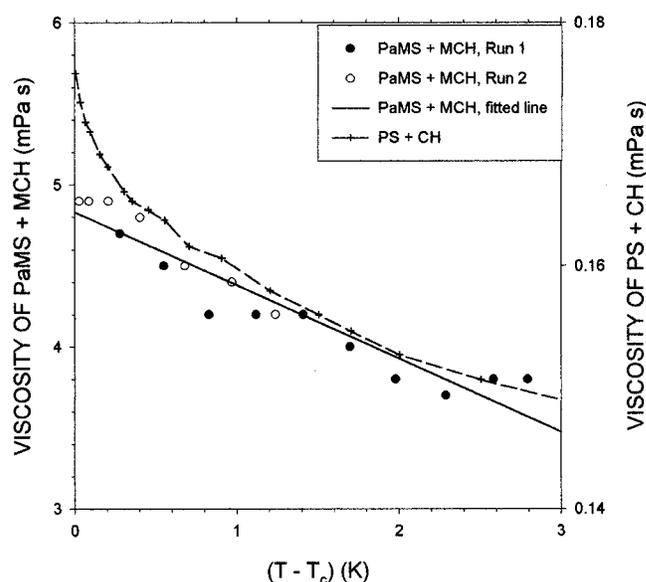

FIG. 3. Shear viscosity for a solution of linear poly(α-methylstyrene) ($M_n = 32\,300$) in methylcyclohexane (PaMS+MCH), in the *one phase* region within 3 K of T_c, as a function of difference of temperature from the critical temperature. Also shown are measurements of the shear viscosity for the system polystyrene+cyclohexane (PS+CH), from Ref. 24.

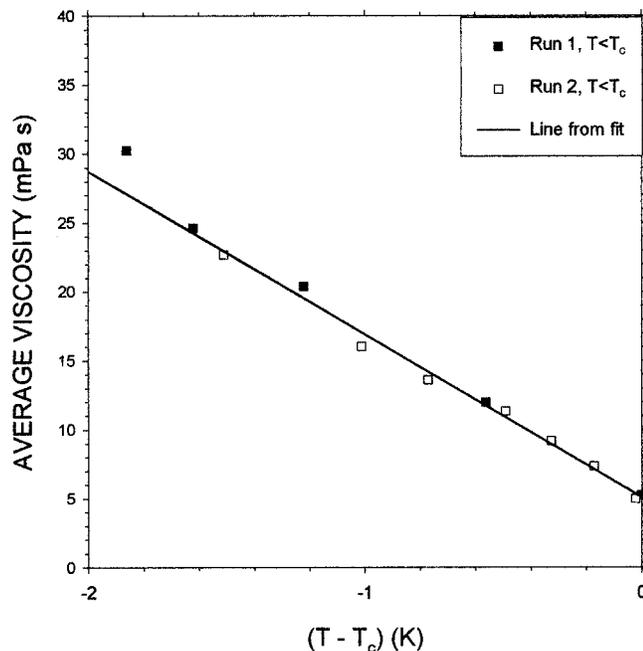FIG. 4. Average shear viscosity of linear poly(α-methylstyrene) (M_n = 32 300) in methylcyclohexane for coexisting phases in the *two phase* region below T_c, as a function of difference of temperature from the critical temperature. Error bars (±0.4 mPa s) are within the size of the plotting symbols. The line is that of the fit discussed in the text.

($T - T_c \lesssim 3$ K). Thus we would expect viscosity measurements on poly(α-methylstyrene)+methylcyclohexane with higher resolution and over a broader temperature range to show behavior very similar to that of polystyrene +cyclohexane. The data we present here do not have enough range or precision to justify an analysis in terms of Eq. (5). We can fit the viscosity above T_c to a straight line in T(K) (taking the uncertainty in T to be 0.002 K and that in η to be 0.2 mPa s) with intercept (145 ± 58 mPa s), slope (-0.44 ± 0.18 mPa s K^{-1}), reduced $\chi^2 = 0.5$. The residuals do show a systematic curvature, suggesting the possible presence of more interesting behavior that is not resolved by our data.

Now we turn to the behavior of the viscosity in the two-phase region below T_c. There are very few published measurements of the viscosities in coexisting liquid phases,[18,32,50,51] and none that we can find for coexisting phases of a polymer in solution. Figure 4 shows an amplification of the measured values of the average viscosity. All 12 points can be fitted by a straight line for η(mPa s) as a function of T(K) (taking the uncertainty in T to be 0.002 K and that in η to be 0.2 mPa s) with intercept (3995 ± 136 mPa s), slope (-12.56 ± 0.43 mPa s K^{-1}), and reduced $\chi^2 = 10$. Dropping the last point in run 1 (315.860 K), the fit improves to reduced $\chi^2 = 3.5$ and random residuals, with intercept (3764 ±159 mPa s) and slope (-11.833 ± 0.502 mPa s K^{-1}). Thus the average viscosity below T_c shows no critical behavior within our range and precision.

The coexistence curve with the viscosity as the ordinate (Fig. 2) is clearly more asymmetric than with the density as the ordinate (Fig. 1), indicating that viscosity is not a good choice for the order parameter. The difference in viscosity between coexisting phases could be fitted to Eq. (2), but

there is no theoretical reason to take an interest in those coefficients at this time. The change of viscosity with temperature is dramatically different in the two phases, as is the case even in some solutions of small molecules.[18]

V. CONCLUSIONS

The behaviors of the density and the viscosity of poly(α-methylstyrene)+methylcyclohexane near the liquid–liquid critical point are remarkably unremarkable. The density above T_c is linear in temperature, showing no evidence of the expected $(1-\alpha)$ term, as we might expect from the lack of a measurable critical term above T_c for either polystyrene+cyclohexane[52] and or polystyrene+diethyl malonate.[23,53] Below T_c, the coexistence curve with the density as the order parameter is quite symmetric. The difference in coexisting densities is consistent with the expected function for the Ising universality class. The diameter of the coexistence curve is linear within our precision, with no evidence of a critical anomaly. Critical anomalies in the diameter have been reported from refractive index measurements on polystyrene+cyclohexane[54] and on polystyrene+methylcyclohexane,[49] but the experiments are not statistically convincing.[12] Thus the amplitudes of these particular critical anomalies seem to be attenuated in polymer solutions as compared to solutions of small molecules.[5] It is known[55,56] that the coefficient of the anomaly in the density above T_c, A_2 in Eq. (1), is related to the amplitude A of the leading anomaly in the heat capacity at constant pressure

$$A_2 = -A\rho_c^2(dT_c/dP)/(1-\alpha), \tag{11}$$

where dT_c/dP is the dependence of the critical temperature on pressure. Thus small values of A or of dT_c/dP could lead to small values of A_2. There are not enough data available on these parameters to determine which determines the small values of A_2 for polymer solutions.[6]

The viscosity above T_c and the mean viscosity below T_c can both be fitted to straight lines as functions of temperature over the rather narrow (±3 K) range of our data, but might show a critical anomaly if data were available over a broader range of temperature and were more precise.

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