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Turbidity of critical solutions of polymethylmethacrylate in 3-octanone

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We have measured the turbidity for a series of solutions of polymethylmethacrylate in 3-octanone (PMMA/3-OCT) with various polymer molecular weights. The obtained correlation length (ξ) and the osmotic compressibility (χ) show power law dependence on both the reduced temperature $\epsilon = (T - T_c)/T_c$ and the degree of polymerization N of the polymer chains, i.e., $\xi \sim N^{0.15} \epsilon^{-0.63}$ and $\chi \sim N^{-0.06} \epsilon^{-1.23}$, with the associated scaling exponents in good agreement with theoretical predictions. When the results of the present experiment are combined with those from an earlier coexistence curve measurement [K.-Q. Xia, X.-Q. An, and W.-G. Shen, J. Chem. Phys. **105**, 6018 (1996)], it is found that the concept of two-scale-factor universality applies to systems consist of the same polymer/solvent pair but with different molecular weights. © *1997 American Institute of Physics.* [S0021-9606(97)51030-0]

I. INTRODUCTION

Polymer solutions near their critical points are known to exhibit power-law dependence on both the reduced temperature and the degree of polymerization N. Thus apart from a system-dependent constant, two scaling exponents fully characterize any thermodynamic property of a polymer solution near its critical point. In a recent coexistence curve measurement,[1] we determined both the temperature exponent and the N exponent for the order parameter. It has long been believed that analogous to those between the temperature exponents, similar scaling laws exist for the N exponents as well,[2,3] and that only two of these exponents are independent, with the one for the correlation length being the most fundamental. The status on the nonclassical value of this exponent (ζ_ν) for the correlation length is, however, far from satisfactory. Early light scattering measurements from solutions of polystyrene (PS) in cyclohexane (CH)[4,5] and in methylcyclohexane (MCH)[6] reported the value of ζ_ν to be around $0.28 \sim 0.29$. A recent critical adsorption measurement[7] in PS/CH also indirectly determined ζ_ν to be around 0.26. Theoretically, de Gennes[8] has predicted $\zeta_\nu \simeq 0.185$ using a nonclassical scaling argument, and Stepanow,[9] in a later renormalization group calculation, has obtained $\zeta_\nu \simeq 0.17$. By proposing a new scaling variable, Sanchez,[3] using coexistence curve data[10] for PS/MCH, obtained $\zeta_\nu = 0.197$. Thus no direct measurement so far has been able to confirm the theoretical predictions for ζ_ν. More direct and precision measurements of the correlation length in polymer solutions are therefore needed in order to resolve this apparent discrepancy. And preferably, the measurements be done for nonpolystyrene systems, so that universality can also be checked.

The correlation length for simple binary liquid mixtures and polymer solutions can be obtained from measured static structure factors in light scattering experiments. However, strong multiple scattering near critical points often complicates the interpretation of the measured intensity angular distribution of the scattered light. Correlation length can also be extracted from turbidity measurements where the effect of multiple scattering is much smaller than it is in angular distribution measurements.[11,12] The turbidity is defined as $\tau = (-1/L)\ln(I_t/I_0)$, where L is the length of the scattering medium, and I_t is the transmitted and I_0 is the incident light intensity. The turbidity τ, the correlation length ξ, and the osmotic compressibility (susceptibility of the polymer solution system) χ are related by an integrated form of the Ornstein–Zernike equation[13,14]

$$\tau = (\pi^3/\lambda_0^4)\left(\frac{\partial n^2}{\partial \phi}\right)^2 k_B T \chi f(\alpha), \tag{1.1}$$

where λ_0 is the wavelength of the light in vacuum, n and ϕ are, respectively, the refractive index and the polymer volume fraction of the solution, k_B is the Boltzmann constant, and T is the absolute temperature. The correlation length enters through the function $f(\alpha)$

$$f(\alpha) = (2\alpha^2 + 2\alpha + 1) \times \ln(1 + \alpha)/\alpha^3 - 2(1 + \alpha)/\alpha^2, \tag{1.2}$$

with $\alpha = 2(2\pi n\xi/\lambda_0)^2$. Note that the correlation length and the osmotic compressibility can be written as power laws of the reduced temperature $\epsilon = (T - T_c)/T_c$ and N, i.e.,

$$\xi = \xi_0 \epsilon^{-\nu} \propto N^{\zeta_\nu} \epsilon^{-\nu}. \tag{1.3}$$

$$\chi = \chi_0 \epsilon^{-\gamma} \propto N^{\zeta_\gamma} \epsilon^{-\gamma}. \tag{1.4}$$

Thus, in principle, the measurements of turbidity will yield four exponents, ν, γ, ζ_ν, and ζ_γ. Combination of the present results with those from our recent coexistence curve measurements for the same system[1] will allow us to test a relation between the related exponents,[3] and therefore the idea of two-scale-factor universality[15,16] (see Sec. III for detailed discussions).

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The rest of this paper is organized as follows. In Sec. II, we describe in detail our turbidity measurements in the single-phase region of the solutions of PMMA in 3-OCT for six different molecular weights of the polymer. The measured results are presented, analyzed, and discussed in Sec. III. Finally, our findings are summarized in Sec. IV.

II. EXPERIMENT

In the present experiment, we used the original samples that were used in our earlier coexistence curve measurements,[1] i.e., the same solutions contained in the same square cells. The sources of materials and the method of sample preparation for these solutions have been detailed in Ref. 1, and will not be described here. Due to the well-known slow drifting of critical temperatures, the T_c's for these samples have been remeasured (using the method described in Ref. 1) just before the turbidity measurements were commenced, and their values are listed in Table II.

The 10 mm pathlength optical square cell were placed in a well-stabilized water bath (temperature fluctuation $\Delta T \leq \pm 2\ mK$), with the temperature control and measurement apparatus exactly those used in the coexistence curve experiment. The sample holder was attached to a precision horizontal translation stage with fine level-adjustment and could be moved vertically. A well-collimated He–Ne laser ($\lambda_0 = 632.8$ nm) was used as the light source. A neutral density filter was placed between the laser and the sample cell to adjust the incident light intensity for measurements conducted at different temperatures, and the filter was aligned to be exactly perpendicular to the incident laser beam so that it does not introduce a shift in the beam position. The detector assembly consisted of a 1 mm diameter aperture, a 632.8 nm interference filter (bandwidth 3 nm), and a photodiode with 1.8 mm² active area. The 1 mm sized aperture together with its 20 cm distance from the cell resulted in a negligible contribution to the detected intensity from scattered lights which include those from multiple scattering. The output voltage of the photodiode, which is proportional to the transmitted light intensity, was first amplified and then measured by a 7-digit voltmeter. We define V_s as the output voltage when the sample cell is in the light path of the laser beam, and V_0 as that when the cell is out of the light path. These two voltages were measured by moving the cell in and out of the laser beam alternatively using the translation stage. These were repeated ten times for each measurement and an average value of V_s/V_0 was obtained. The turbidity was then given by

$$\tau = -\ln(V_s/V_0)/L - \tau_b, \qquad (2.1)$$

where $L = 10$ mm is the light pathlength in the cell, and τ_b is the background turbidity which was determined as follows. The ratio V_s/V_0 was first measured at various temperatures; when the temperature is far away from the critical point, this ratio becomes a constant. The natural logarithm of this constant divided by L was then taken as τ_b. The total uncer-

tainty in τ, including those arising from the measurement of τ_b and the nonlinearity of the detector, was estimated to be about 0.01 cm^{-1}.

III. RESULTS AND DISCUSSION

The turbidity measurements at various temperatures in the one-phase region of the solutions were conducted for each of the six critical samples, with their respective polymer molecular weights being 26 900, 48 600, 95 000, 143 000, 227 000, and 596 000 g/mol. The measured results are listed in Table I. For small α, i.e., large $(T-T_c)$, $f(\alpha)$ approaches its maximum value of 8/3 and Eq. (1.1) becomes[12]

$$\tau = (8/3)(\pi^3/\lambda_0^4)\left(\frac{\partial n^2}{\partial \phi}\right)^2 k_B T \chi_0 \epsilon^{-\gamma}. \qquad (3.1)$$

Thus a log–log plot of τ against ϵ for large $(T-T_c)$ should be a straight line with the slope being the temperature exponent $-\gamma$ of the osmotic compressibility. Following the procedure of Puglielli and Ford,[13] we determined the value of γ for each sample by a least-squares fit in the temperature range of $(T-T_c) \geq 0.5$ K in which the turbidity is linear with ϵ on a log–log scale. Figure 1 shows one example of such a plot for the solution with the PMMA molecular weight being 143 000 g/mol. The line in Fig. 1 represents $\tau = 4.8 \times 10^{-5}\epsilon^{-1.25}$(cm^{-1}). The values of γ for this and for all the other samples are listed in column 3 of Table II. It is seen there that, within the experimental uncertainty, these values all agree well with the theoretical value of 1.24 for the 3-D Ising model.

To analyze the turbidity data in the entire temperature range, the coupling constant $\partial n^2/\partial \phi = 2n(\partial n/\partial \phi)$ must be known. The dependence of the refractive index n on temperature T and on polymer volume fraction ϕ for PMMA/3-OCT can be obtained from our previous work[1]

$$n(T,\phi) = 1.4053 + 0.0912\phi - 4.33\times10^{-4}(T - 40\ ^\circ C). \qquad (3.2)$$

With the help of Eq. (3.2), and by fixing the exponent γ to its experimental values obtained above, we used a three-parameter nonlinear least-squares fitting program to fit Eqs. (1.1)–(1.4) to each of the six sets of turbidity data separately and obtained the values of the exponent ν which are listed in column 4 of Table II. Again, it is seen there that these values of ν agree well with the theoretical value of 0.63 for the 3-D Ising model (the average for the six values of ν is, coincidentally, also 0.63). Having verified that the temperature exponents γ and ν are indeed close to their theoretically expected values, we repeated the above fitting procedures by fixing $\gamma = 1.24$ and $\nu = 0.63$ (i.e., to their respective theoretical 3-D Ising values) for all samples. As the values of amplitudes are known to be sensitively dependent upon the values of exponents in power law fits, using a single value of the exponent allows one to make a meaningful comparison among the amplitudes for different molecular weights.[6] The obtained critical amplitudes χ_0 and ξ_0 from these two-parameter fits are listed in columns 5 and 6 of Table II, respectively. The N exponents are then obtained by fitting

An, Shen, and Xia: Turbidity of critical solutions

TABLE I. Turbidity τ measured in the one-phase region of the PMMA/3-OCT solutions as a function of the relative distance from the respective critical temperatures, for six different molecular weights of the polymer. The total uncertainly in τ was about 0.01 cm^{-1}.

$M = 26\ 900$		$M = 48\ 600$		$M = 95\ 000$	
$(T-T_c)/T_c$	τ (cm^{-1})	$(T-T_c)/T_c$	τ (cm^{-1})	$(T-T_c)/T_c$	τ (cm^{-1})
$1.45e$-2	0.0108	$7.4988e$-3	0.0233	0.0146	0.0111
$9.3760e$-3	0.0163	$5.8541e$-3	0.0305	0.0104	0.0192
$7.6208e$-3	0.0184	$4.2711e$-3	0.0471	$7.0809e$-3	0.0253
$6.0496e$-3	0.0228	$3.1009e$-3	0.0726	$5.6799e$-3	0.0419
$5.2418e$-3	0.0342	$2.7109e$-3	0.0943	$4.5092e$-3	0.0502
$5.0953e$-3	0.0342	$2.3273e$-3	0.1009	$3.3669e$-3	0.0726
$4.2909e$-3	0.0417	$2.0673e$-3	0.1132	$2.4581e$-3	0.1043
$4.2773e$-3	0.0419	$1.9438e$-3	0.1177	$1.8964e$-3	0.1473
$3.2071e$-3	0.0530	$1.6902e$-3	0.1427	$1.6188e$-3	0.1649
$2.4914e$-3	0.0864	$1.5017e$-3	0.1578	$1.3505e$-3	0.1863
$2.0381e$-3	0.1090	$1.3099e$-3	0.1720	$1.0760e$-3	0.2244
$1.7177e$-3	0.1345	$1.1214e$-3	0.2033	$8.1096e$-4	0.2837
$1.3701e$-3	0.1733	$9.3288e$-4	0.2421	$6.2479e$-4	0.3425
$1.0940e$-3	0.2178	$7.3785e$-4	0.2824	$5.3643e$-4	0.3725
$8.8273e$-4	0.2643	$5.5258e$-4	0.3496	$4.5123e$-4	0.4035
$7.4640e$-4	0.3087	$4.2906e$-4	0.4080	$3.5657e$-4	0.4652
$6.7483e$-4	0.3324	$3.0554e$-4	0.4927	$2.6506e$-4	0.5852
$6.4415e$-4	0.3460	$1.7877e$-4	0.6425	$1.7986e$-4	0.6852
$6.1007e$-4	0.3613	$1.0401e$-4	0.8030	$1.1991e$-4	0.8007
$5.6576e$-4	0.3784	$5.5258e$-5	1.0106		
$5.4191e$-4	0.3942	$3.2504e$-5	1.2588		
$5.1123e$-4	0.4103				
$4.7715e$-4	0.4300				
$4.2943e$-4	0.4568				
$3.9535e$-4	0.4756				
$2.5562e$-4	0.6206				
$1.2270e$-4	0.8898				
$1.0225e$-4	1.0361				
$1.9768e$-4	0.7460				
$1.0565e$-4	0.9770				
$9.8838e$-5	0.9967				
$7.1572e$-5	1.1274				
$4.4307e$-5	1.3123				
$3.7490e$-5	1.3831				

$M = 143\ 000$		$M = 227\ 000$		$M = 596\ 000$	
$(T-T_c)/T_c$	τ (cm^{-1})	$(T-T_c)/T_c$	τ (cm^{-1})	$(T-T_c)/T_c$	τ (cm^{-1})
0.0141	$9.1849e$-3	$8.6610e$-3	0.0159	0.0102	0.0112
$6.5268e$-3	0.0243	$5.6882e$-3	0.0334	$7.5986e$-3	0.01903
$4.8649e$-3	0.0361	$4.1129e$-3	0.0524	$6.4274e$-3	0.02242
$4.3852e$-3	0.0396	$3.4356e$-3	0.0680	$5.0582e$-3	0.03039
$3.8839e$-3	0.0540	$2.9084e$-3	0.0837	$4.0624e$-3	0.03958
$3.3949e$-3	0.0601	$7.2481e$-3	0.0197	$3.0298e$-3	0.05585
$2.7048e$-3	0.0859	$4.9005e$-3	0.0397	$2.1811e$-3	0.08078
$2.4572e$-3	0.0909	$3.4356e$-3	0.0602	$2.6027e$-3	0.07002
$2.2189e$-3	0.1073	$2.8992e$-3	0.0706	$3.4910e$-3	0.04652
$1.9961e$-3	0.1175	$2.4120e$-3	0.0850	$1.8558e$-3	0.09775
$1.7733e$-3	0.1278	$2.0963e$-3	0.1105	$1.5955e$-3	0.10882
$1.5319e$-3	0.1409	$1.8388e$-3	0.1214	$1.3975e$-3	0.12753
$1.3988e$-3	0.1608	$1.5967e$-3	0.1297	$1.2080e$-3	0.13893
$1.2688e$-3	0.1826	$1.3240e$-3	0.1479	$1.0184e$-3	0.16082
$1.1760e$-3	0.1881	$1.0665e$-3	0.1809	$8.4021e$-4	0.18588
$1.0305e$-3	0.1950	$8.1522e$-4	0.2030	$6.9027e$-4	0.2102
$9.1295e$-4	0.2346	$6.8037e$-4	0.2210	$5.2619e$-4	0.25211
$8.1082e$-4	0.2404	$5.5165e$-4	0.2503	$3.9606e$-4	0.29138
$7.0560e$-4	0.2610	$4.2293e$-4	0.2901	$2.6592e$-4	0.35573
$5.9110e$-4	0.3034	$3.2180e$-4	0.3265	$1.6974e$-4	0.41605
$4.7659e$-4	0.3608	$2.5437e$-4	0.3820	$1.1599e$-4	0.48026
$3.6208e$-4	0.4112	$1.8082e$-4	0.4445	$4.2435e$-5	0.5702
$2.5067e$-4	0.4995	$1.3362e$-3	0.1437	$2.5461e$-5	0.78602
$1.3617e$-4	0.6561	$1.0788e$-3	0.1852		
$6.8084e$-5	0.8446	$8.2748e$-4	0.2135		

TABLE I. *(Continued.)*

M = 143 000		M = 227 000		M = 596 000	
$(T-T_c)/T_c$	τ (cm^{-1})	$(T-T_c)/T_c$	τ (cm^{-1})	$(T-T_c)/T_c$	τ (cm^{-1})
4.3326e-5	0.9751	6.9570e-4	0.2409		
2.1663e-5	1.1721	6.3134e-4	0.2550		
		5.4552e-4	0.2644		
		5.1488e-4	0.2518		
		4.2600e-4	0.2836		
		3.4632e-4	0.3115		
		4.2906e-5	0.7637		
		1.1952e-4	0.5317		
		9.5007e-5	0.5697		
		4.2906e-5	0.7430		
		7.0489e-5	0.6387		

the respective amplitudes as power laws of the polymer molecular weight M_w which is proportional to N (for PMMA, $N = M_w/100$). In Fig. 2 we show ξ_0 vs M_w in a log–log plot where the solid line is a power-law fit of $\xi_0 = (1.2 \pm 0.2)M_w^{0.15\pm0.02}$(Å). By comparing this with Eq. (1.3), we obtain the exponent $\zeta_\nu = 0.15 \pm 0.02$, which is in good agreement with the renormalization group result 0.17 obtained by Stepanow,[9] and is also in line with those by de Gennes (0.185) and Sanchez (0.197). The exponent ζ_γ can be similarly determined as is shown in Fig. 3 where the solid line represents the fit $\chi_0 = (8.7 \pm 2.6) M_w^{-0.05\pm0.03}$(10^{-8} m^3 J^{-1}). Thus $\zeta_\gamma = -0.05 \pm 0.03$, which is again in line with Stepanow's theoretical value of -0.03. Note that the relative error for ζ_γ is considerably larger than that for ζ_ν, this is due to the very small absolute value of ζ_γ itself. The error bars in Figs. 2 and 3 are 5% of the respective values of ξ_0 and χ_0, these are estimated to be the systematic errors in the measurements of turbidity and

critical temperature, while the uncertainties quoted for ξ_0 and χ_0 in Table II are statistical errors given by the fitting program which did not include contributions by systematic errors.

To estimate the effect of the possible errors in the determined background turbidity τ_b on the extracted exponents, we inserted an additive parameter c on the right side of Eq. (1.1). The value of c was taken as a measure of the error in τ due to the possibly incorrect subtraction of the background τ_b. We then repeated the above fitting procedure which gave ξ_0, χ_0, and c for each of the six solutions. The obtained values of c were smaller than the estimated error of 0.010 cm^{-1} for τ_b for all samples except the one with highest molecular weight ($M_w = 596\,000$ g/mol), which was 0.015 cm^{-1}. This suggests that the background turbidity has been properly determined by the method described in Sec. II. The values of ξ_0 and χ_0 from this new fit were larger than those from the two-parameter fit, but the relative differences were all less than 10% except those for the sample with the highest molecular weight. The relative differences for ξ_0 and χ_0 in that case were 12% and 20%, respectively. The new values of ξ_0 and χ_0 were then used to obtain new values of ζ_ν and ζ_γ, which are 0.17 ± 0.02 and -0.03 ± 0.05, respectively. Therefore, we believe that the value of ζ_ν is between $0.13 \sim 0.19$, and the value of ζ_γ is between $-0.08 \sim 0.02$. It is seen that our ζ_ν supports the predictions of Stepanow, de Gennes, and Sanchez; and that our ζ_γ is consistent with the result of Stepanow. Our result is also consistent with the relation $2\zeta_\nu \approx r$ as pointed out by Sanchez,[3] where r is the exponent on N for the critical polymer volume fraction and its value is generally accepted to be 0.38 ± 0.01.

When combined with our coexistence curve results, the turbidity measurements allow us to test the concept of two-scale-factor university, which states that certain combinations of the critical amplitudes for some thermodynamic properties of a system are the same numerical constants for all systems belonging to the same universality class.[15,16] One example is the ratio R which relates the amplitudes of the order parameter, the correlation length, and the osmotic compressibility[17]
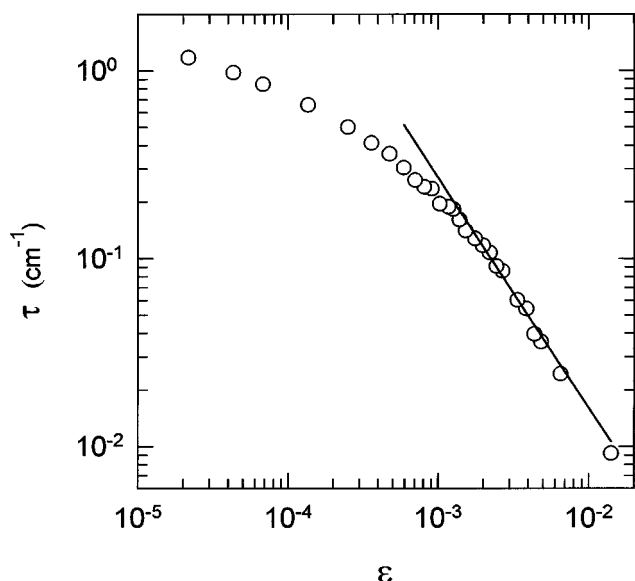

FIG. 1. Measured turbidity versus the reduced temperature for the sample with molecular weight $M = 143\,000$. The solid line is a fit to the portion of data at large $\epsilon = (T-T_c)/T_c$ where the data form a straight line in a log–log scale. The fit gives $\tau = 4.8 \times 10^{-5} \epsilon^{-1.25}$(cm^{-1}).

TABLE II. Molecular weights (M_w), measured critical temperatures (T_c), the temperature exponents γ and ν, and the amplitudes χ_0 and ξ_0, for the osmotic compressibility and correlation length, respectively, the amplitude of the order parameter B, and the universal ratio R as defined by Eq. (3.3), for the six critical samples of PMMA in 3-OCT. The three exponents in the parentheses are here to emphasize that the corresponding amplitudes were obtained by fixing the relevant temperature exponents to the respective theoretical values.

M (g/mol)	T_c (K)	γ	ν	χ_0 (10^{-8} m³/J) ($\gamma = 1.24$)	ξ_0 (Å) ($\nu = 0.63$)	B ($\beta = 0.327$)	R
26 900	293.409	1.23 ± 0.05	0.67 ± 0.03	4.993 ± 0.14	5.203 ± 0.11	1.045	0.58
48 600	307.650	1.21 ± 0.04	0.60 ± 0.03	4.655 ± 0.14	5.778 ± 0.13	0.974	0.61
95 000	316.909	1.23 ± 0.04	0.64 ± 0.03	5.245 ± 0.16	6.255 ± 0.17	0.858	0.58
143 000	323.129	1.25 ± 0.06	0.64 ± 0.03	4.688 ± 0.08	6.586 ± 0.08	0.795	0.60
227 000	326.292	1.26 ± 0.06	0.60 ± 0.03	4.384 ± 0.15	7.619 ± 0.20	0.721	0.66
596 000	333.484	1.21 ± 0.03	0.62 ± 0.03	4.195 ± 0.38	8.195 ± 0.52	0.604	0.62

$$R = \xi_0 \left(\frac{B^2}{k_B T_c \chi_0} \right)^{1/3}, \qquad (3.3)$$

where B is the amplitude of the order parameter defined as

$$\Delta\phi = B\epsilon^\beta \sim N^{\zeta_\beta} \epsilon^\beta. \qquad (3.4)$$

Within an universality class R above is a constant, which means that the length scale ξ_0 is not independent but is universally related to the two independent thermodynamic scales (in this case, B and χ_0). For 3-D Ising model, R has a theoretical value[15,16] of $0.65 \sim 0.67$. On the experimental side, it has been found that $R = 0.68 \sim 0.74$ for three different one-component systems of liquid–gas transitions,[17] and that it ranges from 0.47 to 0.86 for eight different low-molecular-weight binary liquid mixtures.[18,19] In a more recent experiment, Stafford et al.[20] have found $R = 0.66$ for a solution of a single molecular weight polystyrene in diethyl malonate. To our knowledge, R has not been tested by treating polymer solutions containing the same polymer/solvent pair with different molecular weights as different systems.

To calculate the value of R for our data, the amplitude B is needed. Because we obtained our ξ_0 and χ_0 by fixing ν and γ to their theoretical values, for consistency we reanalyzed the results of our coexistence curve measurements[1] for PMMA/3-OCT by fitting Eq. (3.4) to the data with β fixed at its theoretical value of 0.327, the obtained values of B are listed in column 7 of Table II. The relative uncertainty in B, including the errors in the measured refractive index n and that in converting n to the polymer volume fraction ϕ, was estimated to be about 4%. The relative error of R is then estimated to be $\sim 6\%$. The calculated values of R are listed in column 8 of Table II with their average being 0.61 ± 0.03, which is in good agreement with theoretical predictions within experimental uncertainly and also compares well with those from other experiments.

Now we have verified within experimental uncertainty that R is indeed a constant independent of the molecular weight M of the polymer, from Eq. (3.3) it is seen that this is
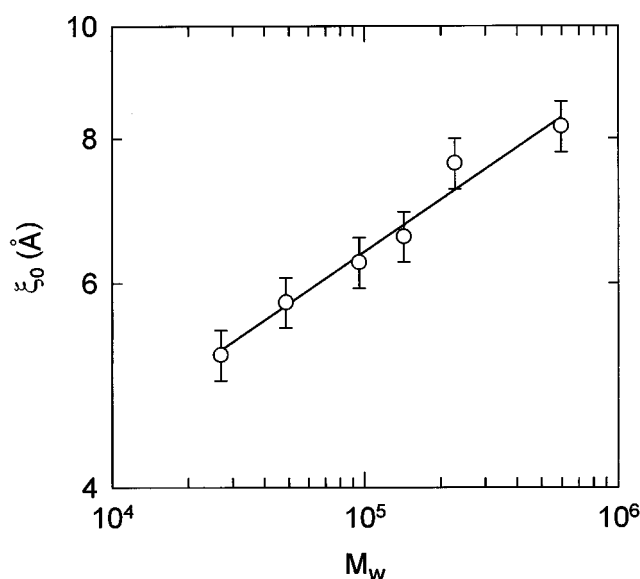

FIG. 2. The critical amplitude ξ_0 for the six samples as a function of molecular weight M on a log–log scale. The solid line represents the power law fit of $\xi_0 = (1.2 \pm 0.2) M_w^{0.15 \pm 0.02}$.
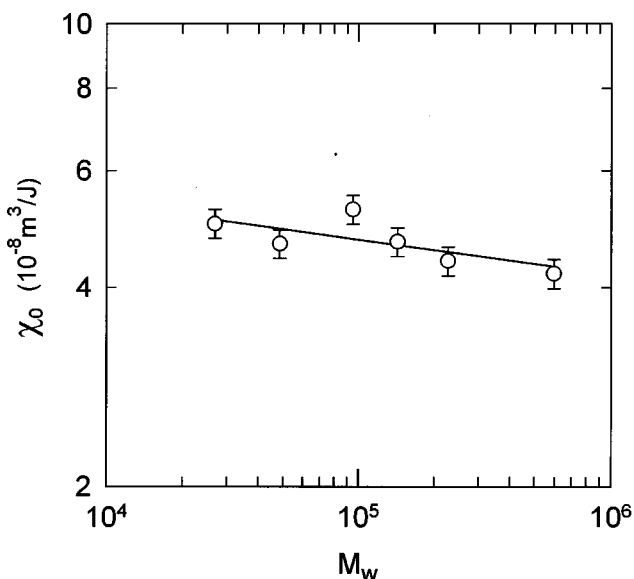

FIG. 3. The critical amplitude χ_0 for the six samples as a function of molecular weight M on a log–log scale. The solid line is a power law fit of $\chi_0 = (8.7 \pm 2.6) M_w^{-0.05 \pm 0.03}$ to the data.

equivalent to requiring a relation among the three N exponents ζ_β, ζ_ν, and ζ_γ, i.e.,

$$(2/3)\zeta_\beta + \zeta_\nu - (1/3)\zeta_\gamma = 0, \tag{3.5}$$

which is analogous[21] to a similar relation for the ϵ exponents $(3\nu = 2\beta + \gamma)$. To check the consistency between our experimentally determined N exponents, we calculated the sum on the left side of Eq. (3.5) by taking $\zeta_\beta = -0.22$ (see Ref. 1), $\zeta_\nu = 0.15$, and $\zeta_\gamma = -0.05$. The result is 0.02 which is smaller than the uncertainties involved in determining the sum. As a comparison, we also calculated the same sum for the system of PS/MCH (using $\zeta_\beta = -0.28$, $\zeta_\nu = -0.28$, and $\zeta_\gamma = 0.03$, as summarized in Ref. 3), which is $0.07 \sim 0.08$. This implies that our results are more consistent with Eq. (3.3) of the two-scale-factor universality hypothesis. The reason may be because the same samples were used in both of our coexistence curve and turbidity measurements, while the three exponents in Ref. 3 were from different studies.

IV. CONCLUSION

We have determined the correlation length (ξ) and the osmotic compressibility (χ) for critical solutions of polyethylmethacrylate (PMMA) in 3-octanone (3-OCT) via turbidity measurements. The experiments were performed for each of six different molecular weights of PMMA. From the experimental ξ and χ, their scaling exponents on the reduced temperature ϵ and on the degree of polymerization N were obtained. The average values of the temperature exponents ($\nu = 0.63$ and $\gamma = 1.23$) were found to be in excellent agreement with their theoretical values according to the 3-D Ising model. The N exponents ($\zeta_\nu \simeq 0.13 \sim 0.19$ and $\zeta_\gamma \simeq -0.08 \sim 0.02$) were found to support those from theoretical calculations,[8,9] and from a recent scaling analysis based on measured coexistence curve data.[3] We note that our ζ_ν is quite different than those from early light scattering experiments,[4–6] and a recent critical adsorption measurement,[7] all of which are more closer to the mean field value of 1/4 than to those predicted by nonclassical theories.

Combining our earlier results from coexistence curve measurements, we found support for the idea of the two-scale-factor universality in that a combination of the critical amplitudes for the correlation length, the osmotic compress-

ibility, and the order parameter is a universal number (R) that is independent of the molecular weights of the individual samples. This is also equivalent to requiring the respective N exponents ζ_ν, ζ_γ, and ζ_β of these three quantities satisfy Eq. (3.5), analogous to that between their corresponding temperature exponents. Furthermore, the universal number R is found to agree with its theoretical value for the 3-D Ising universality class.

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[21] The existence of the corresponding ''sum rules'' for the N exponents analogous to those for the ϵ exponents has been first pointed out by Shinozaki and Nose (Ref. 2), and later shown systematically by Sanchez (Ref. 3). Note that our exponent ζ_β is called b in Ref. 2 and $-b$ in Ref. 3.