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Turbidity measurements and amplitude scaling of critical solutions of polystyrene in methylcyclohexane

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We report turbidity measurements for a series of solutions of polystyrene in methylcyclohexane with varying polymer molecular weights. The obtained correlation length ξ and the osmotic compressibility χ shows power law dependence on both the reduced temperature t ($=|T - T_c|/T_c$) and the molecular weights M_w of the polymers. We find that the relations $\xi_0(1 - \phi_c)^{0.85} \propto M_w^{0.18}$, and $\chi_0(1 - \phi_c)^{-1.20} \propto M_w^{-0.09}$ proposed by An, Jiang, Chen, and Shen [Chem. Phys. Lett. **282**, 403 (1998)] can be used to describe the present experimental results. Moreover, these relations appear to be better suited than a simple scaling for extracting the M_w -exponents. The exponents so obtained are found to be in excellent agreement with theoretical predictions. © 2002 American Institute of Physics. [DOI: 10.1063/1.1494985]

INTRODUCTION

There has been considerable interest recently in the dependence of critical behavior of chain-molecule solutions on the number N of monomer units of the chain-molecules, which is proportional to the molecular weight M_w .^{1–10} It appears that the critical amplitudes of the thermodynamic quantities of the solution either vanish or diverge with M_w , which can be described as

$$\Delta\phi = B|t|^\beta M_w^{-b}|t|^\beta, \quad (1a)$$

$$\chi = \chi_0|t|^{-\gamma} M_w^g|t|^{-\gamma}, \quad (1b)$$

$$\xi = \xi_0|t|^{-\nu} M_w^n|t|^{-\nu}, \quad (1c)$$

$$\phi_c \propto M_w^{-r}, \quad (1d)$$

where $\Delta\phi$ is the volume fraction difference of the two coexisting phases, ξ , and χ are the correlation length and osmotic compressibility, respectively, and T_c is the critical temperature. The exponents β , ν , and γ of the reduced temperature $t = |T - T_c|/T_c$ for these quantities have been well established as universal indices by experiments and theories, and assume the same values as those given by the three-dimensional Ising model. The value of the exponent r for the critical volume fraction ϕ_c is generally accepted to be 0.37–0.38.^{11,12} The coefficients B , ξ_0 , and χ_0 defined in Eq. (1) are the so-called critical amplitudes that depend on M_w . Their M_w -dependence may be characterized by the exponents b , n , and g , which are also believed to be universal. However different theories and experiments seem to yield

different values for these exponents.^{1,6,13} Most of the theories used to explore the exponents started with Flory–Huggins theory and took the limit of $\phi_c \ll 1$. This assumption is valid only in the limit of very large molecular weight, which is difficult to achieve in most practical experiments. And this could be one reason for the discrepancies between different experiments, and between theories and experiments.

Recently, An, Jiang, Chen, and Shen obtained the universal dependence of the critical amplitudes on molar weight for the coexistence curve, correlation length, and osmotic compressibility.¹ The derivations were based on a Landau–Ginsburg–Wilson type model for chain-molecule solutions of both small molecules and polymers, and the results describe well the behavior of these solutions. From Ref. 1, these may be written as

$$B(1 - \phi_c)^{-1.865} \propto M_w^{-b}, \quad b = 0.29, \quad (2a)$$

$$\xi_0(1 - \phi_c)^{0.85} \propto M_w^n, \quad n = 0.18, \quad (2b)$$

$$\chi_0(1 - \phi_c)^{-1.20} \propto M_w^g, \quad g = -0.06. \quad (2c)$$

TABLE I. The molecular weight (M_w), polydispersity (M_w/M_n), critical volume fraction (ϕ_c), and measured critical temperature (T_c) for the eight critical samples of PS in MCH.

M_w (g/mol)	M_w/M_n	ϕ_c	T_c (K)
10 100	1.02	0.204	283.632
30 400	1.02	0.143	304.334
48 800	1.03	0.119	311.997
68 600	1.02	0.104	316.798
97 600	1.03	0.092	319.654
168 000	1.02	0.072	325.117
204 000	1.02	0.070	326.907
330 020	1.04	0.057	329.130

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TABLE II. Turbidity τ measured in the one-phase region of the PS/MCH solutions as a function of the relative distance from the respective critical temperatures for eight different molecular weights of the polymer.

$M_w = 10\ 100\ \text{g/mol}$		$M_w = 30\ 400\ \text{g/mol}$		$M_w = 48\ 800\ \text{g/mol}$	
$(T - T_c)/T_c$	$\tau\ (\text{1/cm})$	$(T - T_c)/T_c$	$\tau\ (\text{1/cm})$	$(T - T_c)/T_c$	$\tau\ (\text{1/cm})$
3.624×10^{-5}	4.141	1.690×10^{-5}	4.912	1.896×10^{-5}	4.207
4.109×10^{-5}	3.981	3.053×10^{-5}	4.212	2.474×10^{-5}	3.923
4.845×10^{-5}	3.764	4.645×10^{-5}	3.721	2.918×10^{-5}	3.707
6.085×10^{-5}	3.477	6.054×10^{-5}	3.417	3.941×10^{-5}	3.407
7.694×10^{-5}	3.180	7.691×10^{-5}	3.134	4.875×10^{-5}	3.169
9.786×10^{-5}	2.877	1.042×10^{-4}	2.762	5.942×10^{-5}	2.976
1.163×10^{-4}	2.676	1.287×10^{-4}	2.533	7.587×10^{-5}	2.764
1.436×10^{-4}	2.429	1.524×10^{-4}	2.322	9.009×10^{-5}	2.581
1.688×10^{-4}	2.234	1.751×10^{-4}	2.168	1.061×10^{-4}	2.434
1.984×10^{-4}	2.051	2.069×10^{-4}	2.000	1.257×10^{-4}	2.264
2.279×10^{-4}	1.901	2.342×10^{-4}	1.876	1.506×10^{-4}	2.110
2.703×10^{-4}	1.729	2.597×10^{-4}	1.775	1.799×10^{-4}	1.947
3.143×10^{-4}	1.594	2.942×10^{-4}	1.664	2.159×10^{-4}	1.791
3.651×10^{-4}	1.449	3.324×10^{-4}	1.551	2.559×10^{-4}	1.643
4.246×10^{-4}	1.316	3.752×10^{-4}	1.444	3.004×10^{-4}	1.514
4.957×10^{-4}	1.181	4.252×10^{-4}	1.337	3.564×10^{-4}	1.373
5.947×10^{-4}	1.041	4.815×10^{-4}	1.231	4.209×10^{-4}	1.246
6.866×10^{-4}	0.926	5.588×10^{-4}	1.119	4.969×10^{-4}	1.111
8.182×10^{-4}	0.815	6.343×10^{-4}	1.015	5.827×10^{-4}	1.001
9.348×10^{-4}	0.711	7.271×10^{-4}	0.919	6.837×10^{-4}	0.886
1.091×10^{-3}	0.614	8.307×10^{-4}	0.821	8.055×10^{-4}	0.789
1.280×10^{-3}	0.523	9.453×10^{-4}	0.738	9.460×10^{-4}	0.693
1.533×10^{-3}	0.434	1.080×10^{-3}	0.653	1.109×10^{-3}	0.614
1.878×10^{-3}	0.349	1.238×10^{-3}	0.588	1.302×10^{-3}	0.544
2.584×10^{-3}	0.253	1.431×10^{-3}	0.516	1.546×10^{-3}	0.461
3.459×10^{-3}	0.173	1.644×10^{-3}	0.453	1.852×10^{-3}	0.388
4.525×10^{-3}	0.137	1.877×10^{-3}	0.394	2.222×10^{-3}	0.322
6.066×10^{-3}	0.087	2.149×10^{-3}	0.345	2.686×10^{-3}	0.256
7.933×10^{-3}	0.063	2.461×10^{-3}	0.305	3.248×10^{-3}	0.211
		3.365×10^{-3}	0.222	3.926×10^{-3}	0.168
		3.802×10^{-3}	0.193	4.768×10^{-3}	0.135
		4.360×10^{-3}	0.164	6.106×10^{-3}	0.108
		5.405×10^{-3}	0.129	7.905×10^{-3}	0.074
		6.547×10^{-3}	0.096	0.0103	0.045
		7.746×10^{-3}	0.080		
		9.092×10^{-3}	0.063		
		0.01061	0.054		
		0.01230	0.046		
$M_w = 68\ 600\ \text{g/mol}$		$M_w = 97\ 600\ \text{g/mol}$		$M_w = 168\ 000\ \text{g/mol}$	
$(T - T_c)/T_c$	$\tau\ (\text{1/cm})$	$(T - T_c)/T_c$	$\tau\ (\text{1/cm})$	$(T - T_c)/T_c$	$\tau\ (\text{1/cm})$
5.524×10^{-5}	2.890	1.663×10^{-5}	4.044	5.686×10^{-6}	4.445
6.226×10^{-5}	2.793	2.307×10^{-5}	3.736	1.297×10^{-5}	3.749
6.664×10^{-5}	2.712	2.916×10^{-5}	3.528	2.068×10^{-5}	3.397
7.322×10^{-5}	2.632	4.134×10^{-5}	3.185	2.583×10^{-5}	3.120
8.506×10^{-5}	2.486	5.544×10^{-5}	2.917	3.440×10^{-5}	2.937
9.515×10^{-5}	2.327	6.849×10^{-5}	2.723	4.468×10^{-5}	2.736
1.136×10^{-4}	2.213	8.989×10^{-5}	2.471	6.096×10^{-5}	2.478
1.324×10^{-4}	2.085	1.092×10^{-4}	2.305	7.553×10^{-5}	2.287
1.495×10^{-4}	1.980	1.270×10^{-4}	2.162	9.010×10^{-5}	2.176
1.662×10^{-4}	1.905	1.529×10^{-4}	2.007	1.068×10^{-4}	2.048
1.912×10^{-4}	1.805	1.849×10^{-4}	1.848	1.240×10^{-4}	1.948
2.144×10^{-4}	1.710	2.235×10^{-4}	1.676	1.467×10^{-4}	1.796
2.438×10^{-4}	1.598	2.667×10^{-4}	1.553	1.724×10^{-4}	1.672
2.802×10^{-4}	1.484	3.119×10^{-4}	1.432	2.041×10^{-4}	1.568
3.162×10^{-4}	1.395	3.725×10^{-4}	1.282	2.379×10^{-4}	1.464
3.587×10^{-4}	1.301	4.446×10^{-4}	1.157	2.769×10^{-4}	1.361
4.131×10^{-4}	1.206	5.288×10^{-4}	1.040	3.236×10^{-4}	1.258
4.780×10^{-4}	1.117	6.250×10^{-4}	0.930	3.802×10^{-4}	1.153
5.552×10^{-4}	1.013	7.420×10^{-4}	0.836	4.419×10^{-4}	1.043
6.513×10^{-4}	0.907	8.781×10^{-4}	0.738	5.152×10^{-4}	0.953
7.723×10^{-4}	0.797	1.047×10^{-3}	0.649	6.129×10^{-4}	0.860
8.978×10^{-4}	0.708	1.242×10^{-3}	0.557	7.329×10^{-4}	0.774
1.043×10^{-3}	0.634	1.473×10^{-3}	0.488	8.602×10^{-4}	0.691

TABLE II. (Continued.)

$M_w = 68\,600$ g/mol		$M_w = 97\,600$ g/mol		$M_w = 168\,000$ g/mol	
1.219×10^{-3}	0.563	1.741×10^{-3}	0.419	1.018×10^{-3}	0.619
1.415×10^{-3}	0.481	2.044×10^{-3}	0.358	1.196×10^{-3}	0.551
1.651×10^{-3}	0.417	2.365×10^{-3}	0.313	1.380×10^{-3}	0.483
1.922×10^{-3}	0.352	2.707×10^{-3}	0.280	1.587×10^{-3}	0.449
2.195×10^{-3}	0.321	3.073×10^{-3}	0.239	1.827×10^{-3}	0.406
2.475×10^{-3}	0.286	3.481×10^{-3}	0.205	2.071×10^{-3}	0.352
2.762×10^{-3}	0.268	4.031×10^{-3}	0.179	2.387×10^{-3}	0.303
3.138×10^{-3}	0.225	4.682×10^{-3}	0.153	2.715×10^{-3}	0.267
3.538×10^{-3}	0.184	5.444×10^{-3}	0.126	3.040×10^{-3}	0.236
3.971×10^{-3}	0.167	6.355×10^{-3}	0.109	3.503×10^{-3}	0.228
4.470×10^{-3}	0.141	7.494×10^{-3}	0.081	3.914×10^{-3}	0.166
5.096×10^{-3}	0.126	8.925×10^{-3}	0.060	4.381×10^{-3}	0.144
5.793×10^{-3}	0.109	0.01111	0.048	4.882×10^{-3}	0.136
6.591×10^{-3}	0.096			5.555×10^{-3}	0.113
7.622×10^{-3}	0.071			6.401×10^{-3}	0.101
8.863×10^{-3}	0.056			7.418×10^{-3}	0.075
0.01050	0.049			8.809×10^{-3}	0.068
				0.0106	0.048
$M_w = 204\,000$ g/mol		$M_w = 320\,020$ g/mol			
$(T - T_c)/T_c$	τ (1/cm)	$(T - T_c)/T_c$	τ (1/cm)		
3.013×10^{-5}	2.856	1.901×10^{-5}	2.770		
4.847×10^{-5}	2.531	2.638×10^{-5}	2.549		
6.510×10^{-5}	2.336	3.571×10^{-5}	2.379		
7.874×10^{-5}	2.134	5.436×10^{-5}	2.108		
9.623×10^{-5}	2.018	7.682×10^{-5}	1.902		
1.218×10^{-4}	1.879	1.014×10^{-4}	1.730		
1.461×10^{-4}	1.733	1.298×10^{-4}	1.580		
1.700×10^{-4}	1.621	1.646×10^{-4}	1.410		
1.964×10^{-4}	1.513	2.019×10^{-4}	1.335		
2.271×10^{-4}	1.402	2.468×10^{-4}	1.217		
2.630×10^{-4}	1.326	3.002×10^{-4}	1.144		
2.962×10^{-4}	1.240	3.714×10^{-4}	0.990		
3.380×10^{-4}	1.187	4.596×10^{-4}	0.903		
3.888×10^{-4}	1.108	5.698×10^{-4}	0.800		
4.578×10^{-4}	1.019	6.931×10^{-4}	0.685		
5.495×10^{-4}	0.905	8.377×10^{-4}	0.620		
6.634×10^{-4}	0.805	1.026×10^{-3}	0.537		
8.011×10^{-4}	0.719	1.251×10^{-3}	0.459		
9.653×10^{-4}	0.651	1.520×10^{-3}	0.404		
1.153×10^{-3}	0.531	1.888×10^{-3}	0.347		
1.373×10^{-3}	0.490	2.349×10^{-3}	0.279		
1.624×10^{-3}	0.427	2.904×10^{-3}	0.249		
1.879×10^{-3}	0.363	3.652×10^{-3}	0.178		
2.200×10^{-3}	0.322	5.452×10^{-3}	0.125		
2.231×10^{-3}	0.294	6.610×10^{-3}	0.093		
2.484×10^{-3}	0.274	7.879×10^{-3}	0.075		
2.498×10^{-3}	0.275	9.766×10^{-3}	0.059		
2.799×10^{-3}	0.258				
2.838×10^{-3}	0.242				
3.142×10^{-3}	0.245				
3.187×10^{-3}	0.195				
3.491×10^{-3}	0.212				
3.584×10^{-3}	0.181				
3.840×10^{-3}	0.195				
4.024×10^{-3}	0.146				
4.233×10^{-3}	0.166				
4.505×10^{-3}	0.134				
4.627×10^{-3}	0.142				
5.027×10^{-3}	0.118				
5.068×10^{-3}	0.122				
5.554×10^{-3}	0.110				
5.611×10^{-3}	0.107				
6.413×10^{-3}	0.090				
7.408×10^{-3}	0.084				

Early light scattering measurements for solutions of polystyrene (PS) in methylcyclohexane (MCH) by Shinozaki *et al.*¹⁴ reported the values of n and g based on Eq. (1) to be 0.28 and 0.08, respectively. But when their data were plotted against molecular weight in \ln – \ln scale, an upward curvature was observed and the value of n was possibly as low as 0.10 for small M_w .^{14,15} Recently, we determined the value of n to be 0.18 ± 0.12 from light-scattering measurements of solutions of PS in MCH,¹² which is significantly smaller than the result of Shinozaki *et al.* However, the osmotic compressibility and the associated index g were not measured in that work. To resolve the discrepancy between our results and those of Shinozaki *et al.* and also to further test the relations (2), we report in this paper the turbidity measurements of solutions of PS in MCH.

EXPERIMENT

Narrowly distributed polystyrene standards were purchased from Polymer Laboratories Ltd. Their weight-average molecular weights M_w and polydispersities M_w/M_n are provided by the manufacture, and are listed in Table I. The solvent methylcyclohexane (99.9%+) was purchased from Aldrich Chemical Co. The polymer was dried with P_2O_5 and the solvent was distilled with metallic sodium. The critical volume fractions of the solutions were determined by adjusting the polymer concentration to achieve equal volumes of the two phases. The results are listed in column 3 of Table I and they are well described by $\phi_c = (6.42 \pm 0.15) M_w^{-0.37 \pm 0.01}$. The critical samples were then flame-sealed in square cells, which are made of optical glass and have a 10 mm pathlength. The critical temperatures were carefully measured and listed in column 4 of Table I. The uncertainty for the measured $(T_c - T)$ was less than 3 mK.

For turbidity measurements, the sample cell was placed in a water bath that has a temperature stability better than ± 2 mK. The cell was attached to a precision horizontal translation stage with fine level-adjustment and could be moved vertically. A collimated He–Ne laser ($\lambda_0 = 632.8$ nm) was used as the light source. For measurements conducted at different temperatures, a neutral density filter was placed between the laser and the sample cell to adjust the incident light intensity so that the photodetector was always working in its most sensitive and linear response region. 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 scatterings. The output voltage of the photodiode, which is proportional to the transmitted light intensity, was first amplified and then measured by a 5-digit voltmeter. We define V_s as the output voltage when the sample cell is in of the light path of the laser beam, and V_0 as that when the cell is out of the light path. 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

$$\tau = (-1/L) \ln(V_s/V_0) - \tau_b, \quad (3)$$

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

RESULTS AND DISCUSSION

Correlation length and osmotic compressibility can be extracted from turbidity measurements. They are related to turbidity by an integrated form of the Ornstein–Zernike equation^{16,17}

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

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

$$f(a) = (2a^2 + 2a + 1) \times \ln(1 + 2a)/a^3 - 2(1 + a)/a^2, \quad (4b)$$

with $a = 2(2\pi n \xi/\lambda_0)^2$, and

$$\xi = \xi_0 t^{-\nu}, \quad (4c)$$

$$\chi = \chi_0 t^{-\gamma}. \quad (4d)$$

Combining Eqs. (4b), (2b), and (2c), the values of ν , γ , ξ_0 , and χ_0 can then be extracted from measured turbidity data.

The turbidity measurements at various temperatures in the one-phase region of the solutions were conducted for each of the eight critical samples as listed in Table I. The measured results are listed in Table II. For small a , i.e., large $(T - T_c)$, $f(a)$ approaches its maximum value of $8/3$ and Eq. (4a) becomes¹⁵

$$\tau = (8/3) (\pi^3/\lambda_0^4) \left(\frac{\partial n^2}{\partial \phi} \right)^2 k_B T \chi_0 t^{-\gamma}. \quad (5)$$

Thus a \ln – \ln plot of τ against t 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,¹⁶ we determined the value of γ for each sample by a least-squares fit in the temperature range of $(T - T_c) > 0.7$ K in which the turbidity is linear with t on a \ln – \ln scale. Figure 1 shows an example of such plots for the solution with $M_w = 97\,600$ g/mol. The line in Fig. 1 represents $\tau = 1.98 \times 10^{-4} t^{-1.23} \text{ (cm}^{-1}\text{)}$. The values of γ for all samples are listed in column 2 of Table III. The error for γ was estimated to be about ± 0.03 , thus these values all agree with the theoretical value of 1.24 predicted for the Ising model within the experimental uncertainty.

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

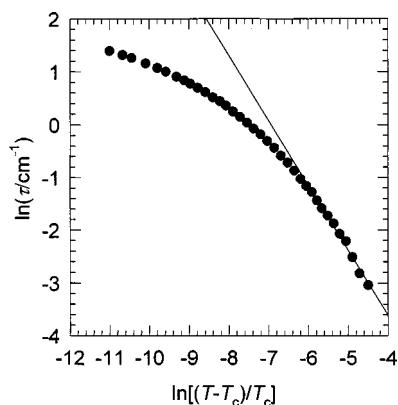


FIG. 1. Ln–ln plot of measured turbidity vs the reduced temperature for the sample with polystyrene molecular weight $M_w = 97\,600$ g/mol. The solid line is a fit to the portion of data for large $t = (T_c - T)/T_c$ in which the data form a straight line in a ln–ln scale. The fit gives $\tau = 1.98 \times 10^{-4} t^{-1.23}$ (cm^{-1}).

known. The dependence of the refractive index n on temperature and on polymer volume fraction for PS/MCH was measured by the method of minimum deviations^{11,18} at various temperatures and volume fractions. The error in the measured refractive index was about ± 0.0001 . A least-squares fit of the results, with a standard deviation less than 0.0002, yields the following relation:

$$n = 1.4336 - 0.000\,530 \times (T - 273.15) + \phi \times [0.1635 + 0.000\,295 \times (T - 273.15)]. \quad (6)$$

With the help of Eq. (6), and by fixing the exponent γ to its experimental values obtained above, we used a three-parameter nonlinear least-squares fitting program to fit Eq. (4) to each of the eight sets of turbidity data separately and obtained the values of ν , ξ_0 , and χ_0 , which are listed in Table III. Again, it is seen that these values of ν agree well with the theoretical value of 0.63 for the Ising model. The calculated values of index η by using $\gamma = (2 - \eta)\nu$ are listed in column 6 of Table III and their average value is 0.041, which also agrees with that reported by Sanchez.³ 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 $\gamma = 1.241$ and $\nu = 0.63$ [i.e., to their respective theoretical three-dimensional (3D) Ising values] for all samples. As the amplitudes are known to be

TABLE III. Temperature exponents and amplitudes for the correlation length and the osmotic compressibility deduced from fitting the measured turbidity to Eq. (1). η is calculated according to $\gamma = (2 - \eta)\nu$.

M_w (g/mol)	γ	ν	ξ_0 (10^{-10} m)	χ_0 (10^{-8} m ³ /J)	η
10 100	1.24	0.64	4.426	3.913	0.053
30 400	1.22	0.63	5.133	4.448	0.058
48 800	1.25	0.64	5.901	3.572	0.025
68 600	1.25	0.64	5.628	3.461	0.053
97 600	1.23	0.63	6.264	4.072	0.041
168 000	1.20	0.60	8.505	5.101	0.013
204 000	1.23	0.63	6.951	3.876	0.049
330 020	1.20	0.61	8.485	4.579	0.038

TABLE IV. The amplitudes ξ_0 , χ_0 , and B for the correlation length, osmotic compressibility, and order parameter, respectively, and the universal ratio R defined in Eq. (7) for the eight samples of PS in MCH. The three t exponents are fixed to their theoretical values when Eq. (1) are used to fit the data to obtain the values of ξ_0 , χ_0 , and B .

M_w (g/mol)	ξ_0 (10^{-10} m)	χ_0 (10^{-8} m ³ /J)	B ($\beta=0.327$)	R
10 100	4.822 ± 0.026	3.973 ± 0.028	1.328	0.68
30 400	5.416 ± 0.024	3.979 ± 0.024	1.108	0.66
48 800	5.973 ± 0.042	3.943 ± 0.029	1.018	0.69
68 600	6.303 ± 0.049	3.787 ± 0.039	0.950	0.70
97 600	6.411 ± 0.020	3.856 ± 0.017	0.880	0.67
168 000	6.922 ± 0.063	3.695 ± 0.05	0.784	0.67
204 000	7.252 ± 0.078	3.678 ± 0.05	0.744	0.68
330 020	7.871 ± 0.080	3.557 ± 0.054	0.663	0.69

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.¹⁵ These two-parameter fits give critical amplitudes ξ_0 and χ_0 and their values are listed in columns 2 and 3 of Table IV.

The above results also afford us the opportunity to test the concept of two-scale-factor universality, which states that certain combinations of the critical amplitudes for some thermodynamic quantities of the system are the same numerical constants for all systems belonging to the same universality class.^{19,20} An example is the ratio R which relates the amplitudes of the order parameter, the correlation length and the osmotic compressibility¹⁹

$$R = \xi_0 (B^2 / 4k_B T_c \chi_0)^{1/3}, \quad (7)$$

where B is the amplitude of the order parameter defined as

$$\Delta \phi = B t^\beta. \quad (8)$$

Within a universality class, R above should be a constant, which means that ξ_0 , B , and χ_0 are not independent but are universally related. For 3D Ising model, R has a theoretical value^{19,20} of 0.65–0.67. On the experimental side, it has been found that $R = 0.68$ –0.74 for three different one-component systems of liquid–gas transitions.²¹ On the other hand, the range of R is found to vary over a relatively large range (0.47–0.86) for low-molecular-weight binary liquid mixtures.^{22,23} For polymer solutions, Stafford, Ploplis, and Jacobs²⁴ found $R = 0.66$ for the solution of a single molecular weight polystyrene in diethyl malonate; and more recently, An, Shen, and Xia²⁵ obtained $R = 0.58$ –0.66 for six molecular weights of polymethylmethacrylate in 3-octanone. To calculate the value of R for the present data, the amplitude B is needed. We calculated the value of B for eight molecular weights using Eq. (2a) and the results summarized in Ref. 1. The values of B and R for the eight systems are listed in columns 4 and 5 of Table IV. The variance of R is seen to be much less than previous results and its average value is 0.68, which is very close to the theoretical value of 0.67.

The values of n and g can be obtained by fitting ξ_0 and χ_0 to Eq. (1) or Eq. (2). In Fig. 2 we show ξ_0 vs M_w in a ln–ln plot where the solid line is the fit of $\xi_0 = (1.32 \pm 0.09) M_w^{0.14 \pm 0.02} (10^{-10} \text{ m})$ with a standard deviation of

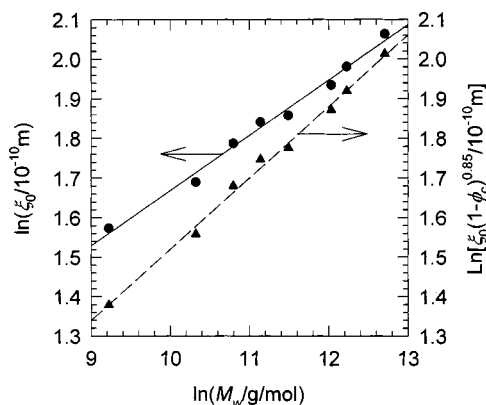


FIG. 2. The critical amplitude ξ_0 for the eight samples as a function of molecular weight M_w on a ln–ln scale. The solid line represents the fit $\xi_0 = 1.32 \times M_w^{0.14} (10^{-10} \text{ m})$ and the dashed line represents $\xi_0 = 1.33 \times (1 - \phi_c)^{0.85} M_w^{0.18} (10^{-10} \text{ m})$.

$0.018(10^{-10} \text{ m})$. By comparing this with Eq. (1b), we obtain the exponent $n = 0.14 \pm 0.02$, which is significantly different from 0.28 and 0.26 obtained from the early light scattering measurements¹⁴ and more recently from a critical absorption measurement⁵ for the same systems of PS/MCH, respectively. However, this is in agreement with the experimental values of (0.15 ± 0.02) and (0.18 ± 0.02) for solutions of polymethylmethacrylate in 3-octanone²⁵ and for PS in MCH,¹³ respectively. It is also consistent with the renormalization group result (0.17) obtained by Stepanow⁴ and significantly departs from the mean field value (0.25). The exponent g can be similarly determined as is shown in Fig. 3 where the solid line is the fit of $\chi_0 = (5.48 \pm 0.36) M_w^{-0.03 \pm 0.02} (10^{-8} \text{ m}^3/\text{J})$ with standard deviation of $0.017(10^{-8} \text{ m}^3/\text{J})$. Thus, $g = -0.03 \pm 0.02$, is again in agreement with Stepanow's theoretical value of -0.03 and with the experimental value (-0.05 ± 0.03) for solutions of polymethylmethacrylate in 3-octanone.²⁵ In Fig. 2 we also show $\xi_0(1 - \phi_c)^{0.85}$ vs M_w in a ln–ln plot where the dashed line represents $\xi_0 = (1.33 \pm 0.09)(1 - \phi_c)^{-0.85} M_w^{0.18 \pm 0.02} (10^{-10} \text{ m})$ with the standard deviation of $0.017(10^{-10} \text{ m})$. In Fig. 3 we also show $\chi_0(1 - \phi_c)^{-1.20}$ vs M_w in a ln–ln plot where the

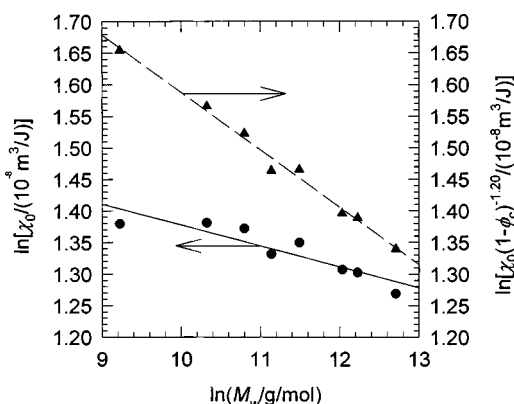


FIG. 3. The critical amplitude χ_0 for the eight samples as a function of molecular weight M_w on a ln–ln scale. The solid line represents the fit $\chi_0 = 5.48 \times M_w^{-0.03} (10^{-8} \text{ m}^3/\text{J})$ and the dashed line represents $\chi_0 = 12.07 \times (1 - \phi_c)^{-1.20} M_w^{-0.09} (10^{-8} \text{ m}^3/\text{J})$.

dashed line represents $\chi_0 = (12.07 \pm 0.58)(1 - \phi_c)^{-1.20} M_w^{-0.09 \pm 0.03} (10^{-8} \text{ m}^3/\text{J})$ with the standard deviation of $0.013(10^{-8} \text{ m}^3/\text{J})$. By comparing this with Eqs. (2b) and (2c), we obtain the exponent $n = 0.18$, and $g = -0.09$, which are in very good agreement with the theoretical results¹ of 0.18 and -0.06 . The standard deviations reported above for fitting Eq. (2) are smaller than that for fitting Eq. (1) (see also Figs. 2 and 3), which implies that Eq. (2) may be more suitable than Eq. (1) for describing the critical behavior of chain molecular solutions. With $b = 0.29$,¹ $n = 0.18 \pm 0.02$, and $g = -0.09 \pm 0.03$, the values of $(3n - 2b - g)$ was calculated to be 0.05 ± 0.06 , which satisfies the scaling law of $3n - 2b - g = 0$ derived by Sanchez.³

CONCLUSION

We have determined the correlation length ξ and the osmotic compressibility χ for critical solutions of polystyrene in methylcyclohexane (PS/MCH) via turbidity measurements. The experiments were performed for each of eight different molecular weights of PS. The average values of temperature exponents ($\gamma = 1.23$ and $\nu = 0.63$) were found to be in excellent agreement with their theoretical values according to the 3D Ising model ($\gamma = 1.23$ and $\nu = 0.63$). The average value of R that relates the amplitudes of correlation length, the osmotic compressibility and the order parameter of coexistence curve (ξ_0 , χ_0 , and B) is found to be 0.68 ± 0.03 , again in excellent agreement with its theoretical value of 0.67. The M_w exponents for the correlation length and the osmotic compressibility as defined by Eq. (1) are $n = 0.14 \pm 0.02$, and $g = -0.03 \pm 0.03$, which are quite different from those obtained by early light scattering experiments¹⁴ and critical adsorption measurements,⁵ but in agreements with the results we reported previously^{11,12,25} and also with theoretical predications.³ The values of n and g obtained from fitting ξ_0 and χ_0 to Eq. (2) are 0.18 ± 0.02 , -0.09 ± 0.03 , which are in excellent agreement with the theoretical values of 0.18 and -0.06 based on a Landau–Ginsburg–Wilson type model proposed by Shen *et al.*¹ and satisfy the scaling law of $3n - 2b - g = 0$ derived by Sanchez.³ The fitting precision using Eq. (2) is found to be better than those using Eq. (1), which, once again, supports that Eq. (2) is a better and more universal choice to describe the critical behavior of solutions of either short or long chain-molecules.

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