

# Universality in eight-arm star polystyrene and methylcyclohexane mixtures near the critical point

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Measurements of the coexistence curve and turbidity were made on different molecular mass samples of the branched polymer-solvent system eight-arm star polystyrene in methylcyclohexane near its critical point. We confirmed that these systems belong in the Ising universality class. The location of the critical temperature and composition as well as the correlation length, susceptibility, and coexistence curve amplitudes were found to depend on molecular mass and the degree of branching. The coexistence curve diameter had an asymmetry that followed a “complete scaling” approach. All the coexistence curve data could be scaled onto a common curve with one adjustable parameter. We found the coexistence curve amplitude to be about 12% larger for branched than linear polystyrenes of the same molecular mass in either solvent cyclohexane or methylcyclohexane. The two-scale-factor universality ratio  $R$  was found to be independent of molecular mass or degree of branching. © 2007 American Institute of Physics. [DOI: 10.1063/1.2771161]

## I. INTRODUCTION

A polymer in a solvent can have a critical solution point where the behavior of the system is dominated by the (critical) fluctuations and is successfully described by an Ising model. This critical solution point 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 specific polymer and solvent used. As the molecular mass of the polymer increases, the critical temperature increases and eventually approaches the  $\Theta$  temperature as the critical concentration approaches zero.<sup>1</sup> If one is using a sufficiently large molecular mass polymer in a solvent, then it is possible for the radius of gyration for the polymer coil to be comparable to the correlation length of the critical fluctuations, and the behavior of the system can crossover to mean field, as recently discussed by Anisimov and Sengers.<sup>2</sup>

A number of features associated with the critical points of polymer solutions have been described by universal equations. First, physical quantities for the system can be described by a power law, and hence “scale,” in reduced temperature ( $t = |(T_c - T)/T_c|$ ) with the same Ising exponents as apply for simple liquid-gas or liquid-liquid systems.<sup>3,4</sup> Also, the location of the critical point (critical temperature and composition) follows a specific path as the molecular mass of the polymer varies.<sup>1</sup> Finally, the critical amplitudes scale with molecular mass with universal exponents.<sup>1</sup> There are many layers of universality that appear to hold for linear polymers in solution, which make the study of such systems particularly intriguing. Large coiled molecules in a sea of small molecules seem to obey the same critical scaling as

small molecule liquid-liquid mixtures. Such observations are important as critical phenomena theory, with its associated scaling, is applied to ever more complicated systems. An additional complexity occurs when the polymers have a different topology, such as a star configuration. Star polymers are more compact and also typical of the topology of micelles.

Most experiments on polymer-solvent systems have been conducted using linear polymers, with only a few reporting results on star or randomly branched polymers in a solvent. Several careful experiments have been conducted on linear polystyrene (ps) in methylcyclohexane (mcy), which make this system ideal for comparison as a star topology replaces a linear one. Our paper continues to explore experimentally the applicability of universal relations in complex systems by investigating the location of the critical point, the shape of the coexistence curve, and the correlation length and susceptibility amplitudes for eight-arm star polystyrene of different molecular masses in methylcyclohexane. These are compared to other experimental and simulation results and to theoretical predictions.

Two recent numerical simulations have investigated the effect of polymer branching on the location of the critical point (the critical temperature and concentration). The first is a Monte Carlo (MC) simulation by Arya and Panagiotopoulos<sup>5</sup> who reported improved agreement with experimental coexistence curve data over either Flory-Huggins<sup>6</sup> or lattice cluster<sup>7</sup> theories which either ignore branching or use “a mean-field approximation which neglects the effects of fluctuations.”<sup>5</sup> Arya and Panagiotopoulos found that the critical temperature decreases as polymer branching increases. They also found that the Flory-

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Shultz relation describes their simulation results for the critical temperature  $T_c(N)$ , where  $N$  is the number of monomer units (degree of polymerization),

$$\frac{1}{T_c(N)} - \frac{1}{T_c(\infty)} \propto \frac{1}{\sqrt{N}} + \frac{1}{2N}, \quad (1)$$

with intercepts that depend on the degree of branching but slopes that are fairly constant. They make the usual association of  $T_c(\infty)$  with the  $\Theta$  temperature to find a minimal decrease in  $\Theta$  as the degree of branching increases. In addition, they find that the critical volume fraction of polymer  $\phi_c$  increases as the degree of branching increases (as others have found), but that  $\phi_c$  also scales with the molecular mass with “similar scaling exponents as those for their linear counterparts,”<sup>5</sup> where the exponent value is 0.37 independent of the degree of branching,

$$\phi_c \propto N^{0.37}. \quad (2)$$

They attribute the decrease in the critical temperature and the increase in the critical volume fraction to “the simultaneous contraction of the polymer with the degree of branching.”<sup>5</sup>

In another simulation, Yang *et al.*<sup>8</sup> reported the results of a generic molecular thermodynamic model for the location of the critical point as the degree of branching increased. Their results were comparable with the lattice cluster theory for large  $N$ , but found the same qualitative behavior as the MC simulation for  $T_c(N)$  and  $\phi_c$  when  $N$  was smaller: an increase in the branching causes an increased polymer miscibility that is seen as a decrease in the critical temperature and increase in critical volume fraction.

Interestingly, neither group investigated the shape of the coexistence curve as the degree of branching increased. When close to the critical temperature, all fluid systems<sup>3</sup> have been found to satisfy the scaling relationship  $\phi_1 - \phi_2 = Bt^\beta$ , where  $\phi_{1,2}$  are the volume fractions of polymer in each of the two phases,  $B$  is an amplitude that will depend on the system (and thus on the degree of branching), the reduced temperature  $t = |(T_c - T)/T_c|$ , and the universal Ising critical exponent<sup>9</sup>  $\beta = 0.326$ . Our results will show that for a particular number of monomers  $N$ , the value of  $B$  depends on the degree of branching.

Anisimov *et al.* have recently published several articles that indicate how coexistence curve (and other) data near a polymer-solvent critical point should be interpreted. The behavior of a system can be influenced by a mean-field theta domain when a “mesoscopic screening length”<sup>10</sup> (taken as the radius of gyration  $R_g$ ) is comparable to the characteristic size of the composition fluctuations, also called the correlation length  $\xi$ , ( $\xi = R_g/\sqrt{3}$ ).<sup>11</sup> Using measurements<sup>12</sup> of the radius of gyration for linear ps in mcx, there is a negligible contribution from the mean-field theta domain if we restrict our measurements to reduced temperatures  $t$  smaller than  $1.6 \times 10^{-2}$  for the range of molecular masses investigated.

The scaling relations for the coexistence curve, correlation length, and susceptibility  $\chi$ , when sufficiently close to the critical point to avoid correction to scaling terms<sup>3,4</sup> and in the limit of large  $N$ , are<sup>10</sup>

$$\phi_1 - \phi_2 = Bt^\beta, \quad B \propto N^{(\beta-1)/2} = N^{-0.337}, \quad (3a)$$

$$\xi = \xi_0 t^{-\nu}, \quad \xi_0 \propto N^{(1-\nu)/2} = N^{0.185}, \quad (3b)$$

$$\chi = \chi_0 t^{-\gamma}, \quad \chi_0 \propto N^{(1-\gamma)/2} = N^{-0.119}, \quad (3c)$$

where  $B$ ,  $\xi_0$ , and  $\chi_0$  are the leading amplitudes, and the critical exponents have the theoretical<sup>9</sup> (and well determined<sup>3</sup>) values  $\beta = 0.326$ ,  $\nu = 0.63$ ,  $\gamma = 1.237$ . The locations of the critical points ( $T_c$  and  $\phi_c$ ) have logarithmic corrections to mean-field behavior,<sup>10</sup> but the resulting deviations of  $T_c$  and  $\phi_c$  from Eqs. (1) and (2) were only observed for larger values of  $N$  than investigated in our experiment.

It was also shown that three (linear) polymer solutions all fell on the same scaled coexistence curve.<sup>2,13,14</sup> Two scaled variables were introduced:  $y = 2A(\phi - \phi_c)/(B\phi_c^\beta)$  and  $z = C|t|/\phi_c$ , where  $B$  is defined in Eq. (3a), and  $A$  and  $C$  are constants. A plot of  $y$  versus  $z$  superimposed all the coexistence data for all molecular masses in those three systems.<sup>2,14</sup> The combination  $K \equiv AC^{-\beta}$  was the same for all the polymer systems,<sup>2,14</sup> and a value of  $K = 0.98 \pm 0.08$  can be deduced using their published figure for the scaled coexistence curve data. The value of  $A$  is determined<sup>14</sup> by the slope of  $B\phi_c^\beta/2$  versus  $\phi_c$ , and  $C$  is then determined by  $K$ . We will test this universal coexistence curve for branched ps in mcx.

The coexistence curve is described both by its shape as well as by its asymmetry. The shape of the coexistence curve is described by the amplitude  $B$  in Eq. (3a), while the average of the volume fraction in each of the two phases is called the diameter of the coexistence curve and represents the asymmetry. Cerdeira *et al.*<sup>15</sup> have recently argued that any nonlinearity, or asymmetry, in the diameter comes from a “complete scaling” approach developed by Kim *et al.*<sup>16</sup> The diameter has the form<sup>15</sup>

$$(\phi_1 + \phi_2) = 2\phi_c(1 + D_1 t^{2\beta} + D_2 t^{(1-\alpha)} + D_3 t), \quad (4)$$

where the coefficients  $D_1 \propto B^2$  and  $D_2 \propto A_0^-$ , and  $A_0^-$  is the leading amplitude of the heat capacity in the two-phase region  $C_p \approx A_0^- t^{-\alpha}$ . While a diameter with a  $t^{2\beta}$  term was thought<sup>17</sup> to imply an incorrect choice for the order parameter, Cerdeira *et al.*<sup>15</sup> argued that such a term is actually expected from the complete scaling approach. In applying this approach to published coexistence curve data of nitrobenzene in a series of  $n$ -alkane mixtures, they found the  $t^{2\beta}$  term to dominate, while the  $t^{(1-\alpha)}$  and linear terms made negligible contributions to the diameter.

The experimental observations for linear and star polymers in solvents were recently discussed by Alessi *et al.*,<sup>18</sup> where they reported measurements on the location of the critical point for eight-arm star polystyrenes of different molecular masses in methylcyclohexane, as well as the full coexistence curve and the viscosity for one molecular mass. They found the critical temperature to be smaller in star than in linear polystyrene in methylcyclohexane for the same molecular mass, while the critical concentration was the same in the two systems. Their measured coexistence curve amplitude had a value larger for the star than for the linear polymer system. The diameter of the coexistence curve was adequately described by a straight line.<sup>18</sup>

As a fluid mixture approaches its critical point, it becomes cloudy, or turbid, because of the increase in the susceptibility of the mixture and in the correlation length  $\xi$  of the critical fluctuations. The turbidity  $\tau$  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, while  $I_0$  is the incident, light intensity. Assuming Ornstein-Zernike scattering,<sup>19</sup> an expression for the turbidity can be developed by integrating the light scattered out of the incident beam. A small asymmetry in the forward direction caused Fisher<sup>20</sup> to introduce a critical exponent  $\eta$  whose value<sup>9</sup> is small ( $\eta \sim 0.036$ ) and results in a negligible effect on the turbidity at the level of this experiment.<sup>21,22</sup> The turbidity is given by<sup>19</sup>

$$\tau = \tau_0(1+t)t^{-\gamma} \left[ \frac{2a^2 + 2a + 1}{a^3} \ell n(1+2a) - \frac{2(1+a)}{a^2} \right], \quad (5)$$

where

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

$a = 2k_0^2 \xi^2$ ,  $\xi = \xi_0 t^{-\nu}$ ,  $k_0 = 2\pi n/\lambda_0$ ,  $n$  is the refractive index of the mixture,  $\lambda_0$  is the vacuum wavelength of the light, the turbidity amplitude  $\tau_0$  is a quantity dependent on the system, and  $\nu$  and  $\gamma$  are universal critical exponents.  $\xi_0$  enters in a complicated fashion through  $a$ . The susceptibility amplitude  $\chi_0$  can be calculated from the value of  $\tau_0$  determined in this study and from our experimental measurements of  $n(\phi)$  that determine  $\partial n^2/\partial \phi$ .

The ratios of certain amplitudes are expected to be universal for all systems in a given universality class, which for polymer mixtures is expected to be Ising. One of those ratios connects the amplitudes  $\xi_0$ ,  $\chi_0$ , and  $B$  measured in this experiment using two-scale-factor universality,<sup>9,23</sup>

$$R = (Q_c)^{1/3} = \xi_0 \left( \frac{B^2}{k_B T_c \chi_0} \right)^{1/3} = 0.6931 \pm 0.0007. \quad (7)$$

The universality of this ratio for polymer solutions is particularly interesting since each of the amplitudes is also expected to have a universal dependence on  $N$ .

## II. EXPERIMENTAL METHODS

### A. Materials

Eight-arm star polystyrene, spanning the widest commercially available range in molecular mass, was purchased from Polymer Source who provided a characterization. Each arm had a polydispersity index less than 1.04 before being end capped with a small amount of butadiene, then linked to octafunctional silane. Size exclusion chromatography characterized the molecular masses and polydispersity  $M_w/M_n$  of the arms. Zimm and Berry plots from light scattering on the star polystyrenes in toluene determined  $M_w$ . Table I provides the parameters for each sample. The average number of branches for each sample was between 7.2 and 8.7, which is within their 10% experimental error of eight arms. Additional independent characterization<sup>18</sup> of the first three poly-

TABLE I. Polymer source sample number and characterization for each eight-arm star polystyrene used.

Sample	$M_w/M_n$	Branch $M_n$	Total $M_w$
P296-8S	1.04	9 800	74 000
P314-St8	1.03	25 300	228 000
P322-8S	1.02	34 600	282 000
P331-8S	1.03	45 500	391 000

mer samples confirmed the number of arms as eight and the average molecular mass to be within 6% of that stated by the manufacturer. The solvent methylcyclohexane was Aldrich's 99+% anhydrous, used without further purification.

Samples were prepared by mass either directly in the cell for the coexistence curve experiments or in a vial for the turbidity experiments. Each sample's volume fraction was calculated using the densities of ps and of mcy given in Alessi *et al.*<sup>18</sup> and neglected any volume loss on mixing. After preparing a mixture in a vial, the vial and a syringe were warmed above the critical temperature in order to transfer a homogeneous, one-phase sample into a turbidity cell using a 1.2  $\mu\text{m}$  solvent-resistant, disposable syringe filter. All samples were prepared close to the literature values<sup>18</sup> for the critical concentration and were transferred into cells on the bench where some water may be absorbed. We estimate the amount of water in any sample to be less than 0.05% by mass. We also directly measured the effect of water on the critical point, exponent, and amplitude for one of our samples.

### B. Coexistence curve procedure and data

Polystyrene in cyclohexane or mcy at atmospheric pressure, at which all our measurements occurred, has an upper critical consolute point identified by the system-dependent critical concentration and temperature. Below this point, the system is two phase and the coexistence curve can be mapped by determining the volume fraction of ps in each phase. For each of three molecular masses of eight-arm star ps in mcy, the volume fraction in each phase was determined as a function of temperature using measurements of the refractive index and a set of calibration measurements.

To measure the refractive index, we put the sample in a prism-shaped, stainless-steel cell with optical windows sealed with Kalrez o-rings and a Teflon washer on the fill-hole sealing screw. The volume of sample was approximately 6.5 ml with an air bubble of 0.5 ml to maintain a pressure of 1 atm. The cell was surrounded by two concentric cylinders that were temperature controlled using a LABVIEW program. The cell temperature was monitored with a calibrated Thermometrics thermistor combined with a Vishay standard resistor that was one arm of an AC Wheatstone bridge with the other arm an ESI seven-digit ratiotransformer. The balance voltage was detected by a Stanford Research Systems SR-850 lock-in amplifier. The precision in temperature was less than 0.1 mK with an accuracy of 20 mK. Since the cell was not actively temperature controlled, there was a long equilibration time (about 6 h after changing the temperature) before we mixed the system. A

small magnetic stirrer could be rotated into position and spin a stir flea on one of the cell's windows for a short period of time. The fluids were then left for at least another 2 h (when above the critical temperature) to 18 h (when below the critical temperature) to come to thermal equilibrium before measuring the refractive index in each phase.

The refractive index was determined by measuring the minimum deviated angle for He–Ne laser light passing through each phase. The laser beam was broken into two beams using polarizing beam splitters with one polarization beam passing through the upper phase and the other polarization through the lower phase, an offset of a few millimeters. Polarizers were used in front of the detectors to block light from the other phase. We used two methods to measure the minimum deviated angle: at select temperatures above the critical temperature, we used a Gaertner spectrometer with a precision of 20 arc sec to determine the actual deviated angle, but at all temperatures we used two position sensitive detectors (PSDs) (a Hamamatsu S1352) to measure relative angles with a precision of 5 and an accuracy of 45 arc sec. The PSD detectors convert a location to a voltage that was measured with a Keithley 2010 DMM; however, the PSDs lose resolution when the incident light intensity becomes too small, so a set of neutral density filters was used to optimize the intensity. The geometry of the beams and PSD detectors allowed the relative positions to be converted to appropriate angles. A LABVIEW program rotated the thermostat in  $0.25^\circ$  steps using a Newport motion controller ESP 300 and an SR50 rotational stage so that the minimum of the beam location on each PSD determined the minimum deviated angle. The resulting refractive indices (relative to air) had a resolution of 0.000 15.

Volume fraction  $\phi$  of ps in the mcy was determined from a set of calibration measurements. Using the Gaertner spectrometer, we measured the refractive index  $n$  as a function of temperature (290–330 K) in the one-phase region for four known concentrations of eight-arm star ps in mcy. As others have observed,<sup>24,25</sup> only the volume fraction of monomers in solution is important in determining the refractive index and not the total molecular mass. We found the following equation by performing a weighted fit to our calibration data:

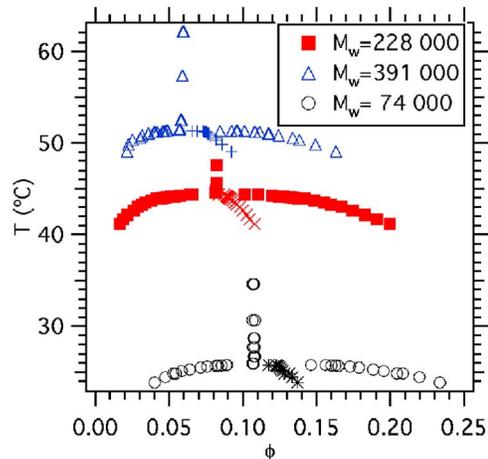


FIG. 1. (Color online) The measured coexistence curves for three molecular masses of eight-arm star ps in mcy are shown as a function of volume fraction of polystyrene in each phase. The diameter (average) in the two-phase region points to the critical point at the top of each curve. The error bars are smaller than the plotted symbols.

$$\phi = \frac{n - 1.4323 + 5.386 \times 10^{-4}T}{0.1713 + 5.59 \times 10^{-4}T}, \quad (8)$$

with  $T$  in  $^\circ\text{C}$ . This gives an equivalent volume fraction (to our error of  $\pm 0.001$ ) to the equation given by Zhou *et al.*<sup>24</sup> for linear ps in mcy. Thus, neither branching nor molecular mass is significant at this resolution; only the concentration of polymer and the type of solvent. Equation (8) gives  $\partial n / \partial \phi$ , which can be used when testing amplitude relations.

Coexistence curves were measured for three molecular mass samples. These data form a family of curves consistently seen in polymer-solvent systems with the critical temperature increasing and the critical concentration decreasing as the molecular mass increases. Our data are shown in Fig. 1 (we omit a few one-phase data for clarity). Data above the critical temperature reflect the composition measured when the system is one phase [volume fraction 0.108 for molecular mass 74 000 amu, 0.0825 for 228 000, and 0.059 for 391 000, where the uncertainty in the prepared composition was less than  $\pm 0.001$ ]. The average of the compositions of the polymer-rich lower phase and polymer-poor upper phase is referred to as the diameter, and extrapolating those data to

TABLE II. Parameter values for different molecular mass  $M_w$  eight-arm star polystyrene in methylcyclohexane. The uncertainties are one standard deviation estimates from the weighted fits, as described in the text.

$M_w$	$T_c$ (K) ( $\pm 0.5$ )	$\phi_c$ ( $\pm 0.001$ )	$B$ ( $\pm 0.002$ )	$n_c$ ( $\pm 0.0002$ )	$\xi_0$ (nm)	$\tau_0$ ( $\text{m}^{-1}$ )	$\chi_0$ ( $\times 10^{-8} \text{ m}^3/\text{J}$ )	$R$
74 000	299.0	0.122	0.978	1.4410	0.60 $\pm 0.01$	0.0112 $\pm 0.0002$	4.89 $\pm 0.05$	0.62 $\pm 0.01$
228 000	317.5	0.087 <sub>5</sub>	0.822	1.4255	0.75 $\pm 0.03$	0.0136 $\pm 0.0010$	5.1 $\pm 0.3$	0.68 $\pm 0.03$
282 000	...	...	...	(1.421)	0.82 $\pm 0.03$	0.0167 $\pm 0.0007$	6.1 $\pm 0.2$	...
391 000	324.6	0.071 <sub>5</sub>	0.715	1.4189	0.85 $\pm 0.04$	0.0817 $\pm 0.0008$	6.6 $\pm 0.3$	0.64 $\pm 0.03$

the critical temperature gives the critical concentration. Table II gives the values for the critical temperature and concentration, the values of the refractive index  $n_c$  at the critical temperature, as well as other parameters that will be discussed shortly.

Because some moisture could be present in our samples, we investigated the effect of water impurity on the location of the critical point as well as the shape of the curve for one molecular mass sample. After completing the coexistence curve measurements for the 228 000 molecular mass sample, we added 0.1% by mass water to the sample. This small amount of water is about twice as much as our estimated level of water in our samples yet does not change the refractive index of the mixture within our measurement error. It is, however, an impurity in the system that previous studies<sup>26</sup> in small molecule systems have found to make a significant change in the critical temperature, a small change in the critical composition, but no change in the amplitude  $B$  of the coexistence curve. By comparing the 228 000 molecular mass data with and without the water added, we found the critical temperature increased by 0.55 K, while the critical composition was unchanged. The difference in volume fraction between the lower and upper phases was within experimental error of the “nonwater” sample, and thus  $B$  and  $\beta$  were unchanged. The increase in the critical temperature was approximately the reported increase when preparing ps-mcy samples on the bench rather than in a dry box.<sup>18</sup> Since impurities cause linear changes in the critical temperature and composition, any water that is present in our samples would not change our results outside our experimental error.<sup>26</sup>

### C. Turbidity procedure and data

Our light scattering cells were commercial (Spectrocell) made of optical glass with a cylindrical design of 22 mm in diameter and a path length of 0.50 cm. Each had a fill tube which was flame heated and drawn closed to seal the sample. The temperature of the cell was controlled by immersion in a well-stirred, filtered water bath, as described previously.<sup>27,28</sup> The bath temperature, controlled with a Tronac PTC-41 to  $\pm 1.0$  mK over an hour, was monitored with a calibrated Thermometrics thermistor whose resistance was measured with a Keithley 2010 digital multimeter to an accuracy of  $\pm 10$  mK and a precision of  $\pm 0.1$  mK. One data run on a molecular mass sample of 282 000 was taken with our old optical equipment,<sup>27</sup> but it was verified with our new optical system before the rest of the turbidity data were taken.

The new optical system included an intensity stabilized He-Ne laser ( $\lambda_0=632.8$  nm, Melles Griot 05-STP-901) that provided an incident intensity that varied less than 0.2% long term. The beam passed through a beam expander/spatial filter creating a 1 cm beam, the center of which passed through a 2 mm aperture to eliminate all but one lasing mode and provide a uniform beam intensity to the cell. An optical chopper (New Focus 3501) broke the beam at a frequency of 390 Hz. The low power laser beam traveled through optical windows into a water bath where the cell was oriented with the laser beam along the cell’s cylindrical axis. The transmitted light intensity was detected by a photodiode with an ac-

ceptance angle of  $0.4^\circ$ . The intensity was measured with a Stanford Research Systems SR-830 lock-in amplifier synchronized with the optical chopper to detect the light intensity without any dc drift. The cell could be moved out of the beam path to determine the turbidity of the fluid sample. The measured turbidity is  $\tau=-(1/L)\ln(I_1/I_2)$ , where  $I_1$  and  $I_2$  are the transmitted intensities with and without the cell in the beam, respectively.

The procedure of taking intensity measurements with the cell in and out of the beam path corrects for reflected and absorbed lights from the bath, but not for reflected light from the cell windows nor scattering by the polymer coils when well above the critical temperature. The turbidity due to these sources contributes to a “background” turbidity  $\tau_b$ , which cannot be determined by the value of the turbidity well above the critical temperature, as is done for small molecule systems. Instead, the background turbidity is a fitting parameter.

After a new temperature was set with the Tronac, temperature equilibrium occurred within an hour, after which the sample was sloshed to assure uniformity (all turbidity measurements were made in the one-phase region). However, we waited an additional several hours to assure thermal equilibrium. These polymer-solvent systems took considerably longer to reach an equilibrium that was stable and reproducible than previously studied small molecule mixtures.<sup>27</sup>

Reproducible turbidity data were taken for each of four molecular masses in mcy when the system was in the one-phase region and within  $5^\circ$  of the critical point (reduced temperature  $t<0.016$ ). For two molecular mass samples (74 000 and 282 000), two different composition samples were measured and found to have the same turbidity within experimental error. Melnichenko *et al.*<sup>29</sup> have measured in linear ps and mcy the effect of noncritical compositions on the measured value of the correlation length amplitude and found that if the measured composition is within 25% of the critical composition, then the correlation length amplitude is larger, but within 10% of the value measured at the critical composition. The volume fractions of the samples we measured were 0.108 and 0.116 for 74 000, 0.066 for 228 000, 0.059 and 0.072 for 282 000 and 0.081 for 391 000, where the uncertainty in the prepared composition was less than  $\pm 0.005$ . These compositions are typically within 10% of our measured critical concentrations except for the 228 000 sample, which is about 25% below critical. We would expect the value of the correlation length for this molecular mass sample to be slightly high as a result, but within 10% of the true value.<sup>29</sup> The absolute turbidity data are shown in Figs. 2(a)–2(d).

## III. RESULTS AND DISCUSSION

### A. Coexistence curve

Our values for the critical compositions are larger than Alessi *et al.*<sup>18</sup> determined from less precise cloud point measurements on three different molecular masses of eight-arm star ps in mcy and from precise density measurements on one molecular mass (77 000). Figure 3 compares our values for the critical concentration for our star ps with those Alessi

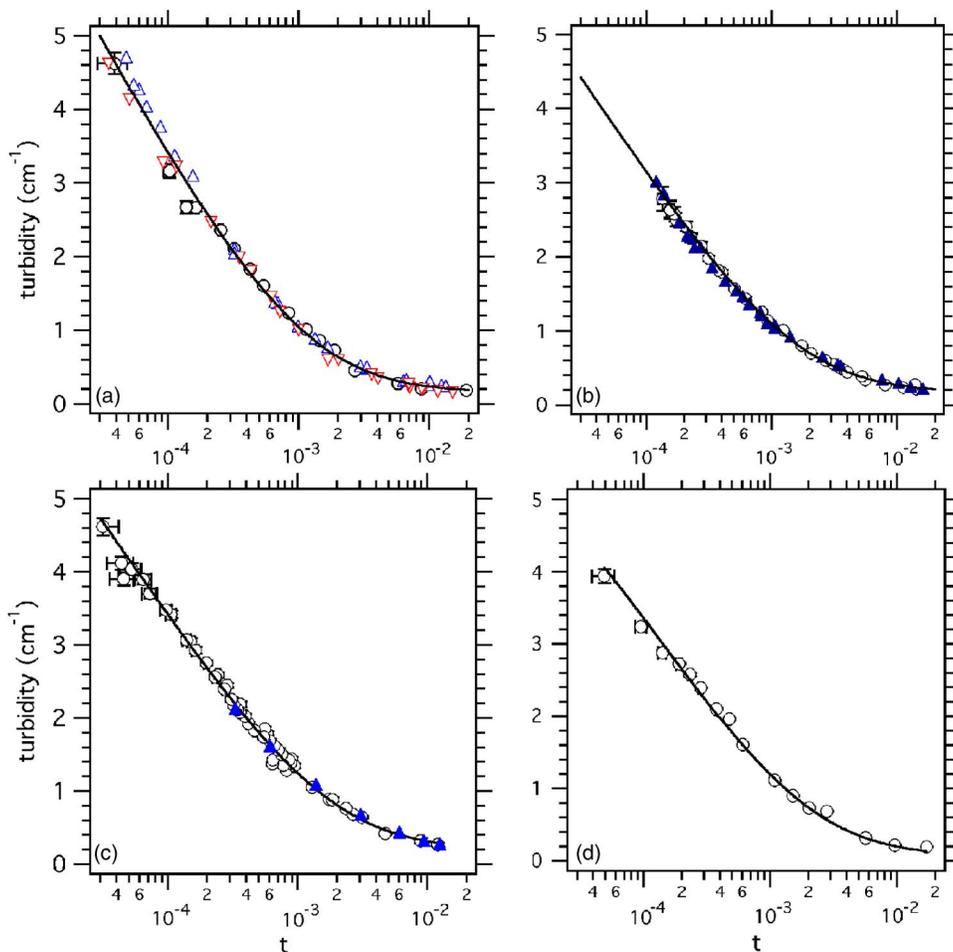


FIG. 2. (Color online) The measured turbidity plotted as a function of reduced temperature  $t$  for four molecular masses of eight-arm polystyrene in methycyclohexane. (a)  $M_w=74\,000$ , (b)  $M_w=228\,000$ , (c)  $M_w=282\,000$ , and (d)  $M_w=391\,000$ . The different symbols on each plot are for different runs of data and the error bars are shown on only one run for clarity.

*et al.*<sup>18</sup> measured on the same system. In addition, data for linear ps (Refs. 24, 30, and 31) and randomly branched ps (Ref. 32) in the same solvent are also shown. Our star ps and the randomly branched ps in mcy are shifted to larger values than has been found for linear ps of the same molecular mass in this solvent. This is consistent with Monte Carlo simulations<sup>5</sup> and a molecular thermodynamic model,<sup>8</sup> which found larger critical concentrations for branched versus linear polymers in a solvent. The MC simulation also found constant slopes (but different intercepts) for log-log plots of the critical volume fraction versus degree of polymerization  $N$  [see Eq. (2)], independent of the degree of branching. This is also consistent with our star data, but not for the data for randomly branched ps in mcy that has a smaller slope.<sup>32</sup>

However, the critical temperature does something quite distinct for star ps than linear ps in this mcy solvent. As Alessi *et al.*<sup>18</sup> observed in this same system, the critical temperatures are not only smaller in star than linear ps, but the dependence on molecular mass is quite different. Smaller values for the critical temperatures in branched versus linear polymer solvent systems are consistent with MC (Ref. 5) and the model of Yang *et al.*,<sup>8</sup> but the MC simulation finds a similar slope when plotting the reciprocal of the critical temperature versus the Flory-Shultz parameter  $1/\sqrt{N}+1/2N$  in Eq. (1), something Alessi *et al.*<sup>18</sup> pointed out for star and linear ps in another solvent, cyclohexane. However, our results on star ps, as well as those of Alessi *et al.*,<sup>18</sup> give a very different slope that is about twice the linear ps slope value, as

shown in Fig. 4. Another MC simulation showed that multi-generational dendrimers of a polymer in a solvent would result in a comparable increase in slope.<sup>33</sup> The intercept of the line through our data gives an estimate ( $347\pm 2$  K) for the  $\Theta$  temperature, where all stated uncertainties are one standard deviation error estimates. This result is consistent with values determined in either star<sup>18</sup> or linear<sup>13</sup> ps in mcy, which had the same value for the  $\Theta$  temperature of 345 K.

The shape of the coexistence curve is expected to follow a power law [Eq. (3a)] with a universal exponent  $\beta=0.326$  for systems in the Ising universality class. By calculating the difference in volume fraction  $\Delta\phi$  between the two phases as a function of the reduced temperature  $t$ , a log-log plot shows (Fig. 5) straight lines of slope of 0.326 for each molecular mass. This confirms that the Ising model describes this system, as others have reported on this and similar systems.<sup>18,30,31,34,35</sup> The lines are offset because the critical amplitude  $B$  in Eq. (3a) depends on the system and hence the molecular mass.

The values of  $B$  we obtain from a weighted fit of Eq. (3a) to our data when the exponent  $\beta$  is fixed at 0.326 are shown in Table II.  $B$  is expected to follow a power law in molecular mass with a universal exponent  $b=(\beta-1)/2=-0.337$  for large values of molecular mass.<sup>10</sup> Experimental values for this exponent are closer to  $-0.225$  as is shown in Fig. 6 for linear and star ps in cyclohexane<sup>34,35</sup> or mcy.<sup>18,31,36</sup> Our  $B$  values for small to moderate molecular masses are consistent with a power of  $-0.23$  and not with the

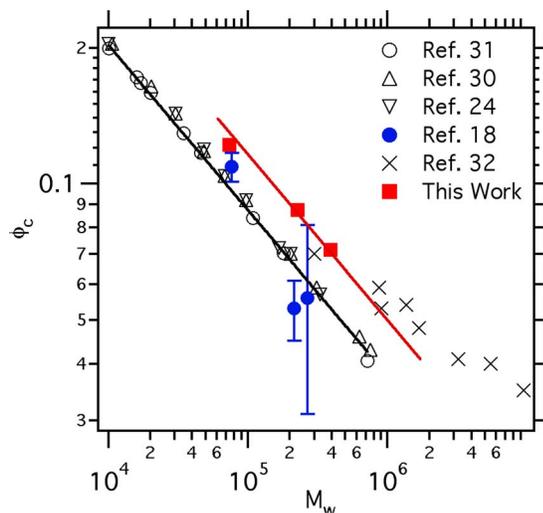


FIG. 3. (Color online) The critical volume fraction of ps for branched (solid symbols) or linear (open symbols) ps in mcy, where the ( $1\sigma$ ) error bars are smaller than the plot symbols except for the literature  $3\sigma$  errors for Ref. 18. Our eight-arm star results are larger than the eight-arm star results of Ref. 18 or linear ps systems of Refs. 24 and 30, or 31 at the same molecular mass  $M_w$ . Randomly branched ps (Ref. 32) also has a larger value as well as a different trend. The lines correspond to a power law with exponent (or slope) of  $-0.38$ .

asymptotic, theoretical slope of  $-0.337$ . The upward shift in the values of  $B$  for star versus linear ps is about the same (approximately 12%) for either solvent cyclohexane or methylcyclohexane, an observation we have not found in the literature previously. However, we can calculate from the data in a MC simulation,<sup>5,37</sup> which investigated the effect of branching on the coexistence curve for a small number of monomers, that branching causes an increase in  $B$  of approximately 6% at a fixed molecular mass (see Fig. 5).

Anisimov *et al.*<sup>2,14</sup> have proposed a scaling function that they found to apply universally for three (linear) polymer-solvent systems: ps in mcy, polymethylacrylate (PMMA) in 3-octanone, and ps in cyclohexane. Not only did all of the coexistence curve data for different molecular mass systems

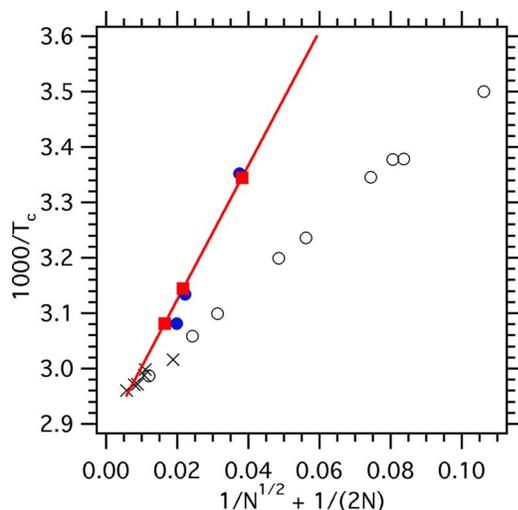


FIG. 4. (Color online) The inverse of the critical temperature measured in branched or linear ps in mcy is plotted against the Flory-Shultz parameter. The symbols are the same as in Fig. 3. The line is a guide to the eye for star ps data.

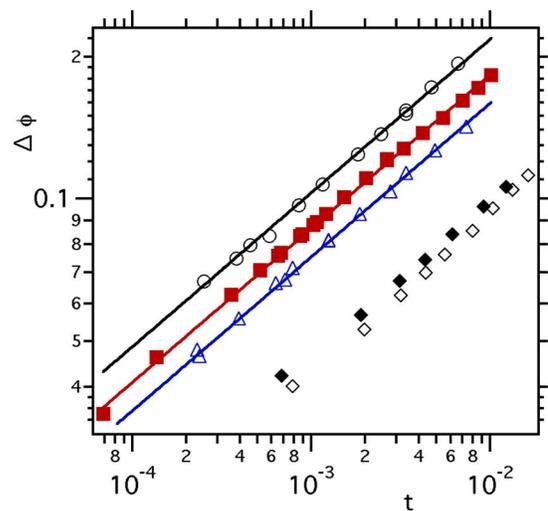


FIG. 5. (Color online) The top three lines and data points are the difference in volume fraction between the lower and upper phases as a function of reduced temperature  $t$  for the data shown in Fig. 1 using the same symbols. Each molecular mass falls on a straight line with the same slope (0.326) corresponding to the critical exponent  $\beta$ ; the different intercepts indicate a dependence of  $B$  on molecular mass. The data at the bottom right are from our calculations on MC simulation data (Refs. 5 and 37) at one molecular mass for linear (open diamonds) and branched “B4” (closed diamonds) and indicate a larger  $B$  for branched systems. (For convenience, the MC “density” difference has been divided by 5, while the corresponding reduced temperature has been divided by 10.)

collapse onto the same curve, but the two system-dependent parameters  $A$  and  $C$  were found to have a universal ratio  $K = AC^{-\beta} \approx 0.98 \pm 0.08$ . The value of  $A$  is  $2.07 \pm 0.03$  for our data, which gives  $C = 9.9 \pm 0.1$ . With only the experimentally determined parameter  $A$ , we can then calculate the scaled parameters  $y$  and  $z$  that neatly collapse all of our coexistence curve data onto one curve (see Fig. 7) that appears identical to the plot of Anisimov *et al.*<sup>2,14</sup> Thus, both star and linear polymer-solvent systems are described universally by the scaled function.

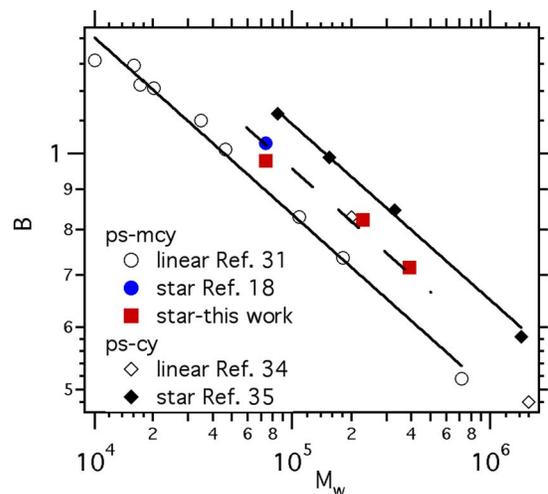


FIG. 6. (Color online) The amplitude of the coexistence curve  $B$  as a function of the molecular mass of ps in either cyclohexane (diamonds) or mcy (circles, squares) for linear (open symbols) or star (closed symbols) ps. The lines have slope of  $-0.225$  which is the result of fitting to the published linear ps data in mcy of Ref. 31 or the four-arm star data in cyclohexane of Ref. 35 when the critical exponent  $\beta = 0.326$ .

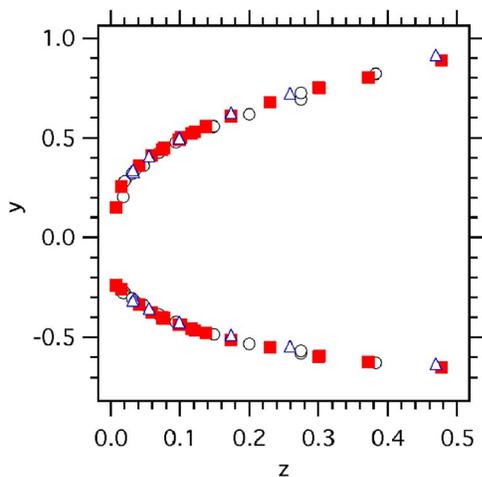


FIG. 7. (Color online) Scaled coexistence curve showing that all of our data fall on a common curve. The symbols are the same as in Fig. 1.

We can also look at the diameters of the coexistence curves to see if they are linear in temperature or if a critical anomaly is present. Alessi *et al.*<sup>18</sup> measured densities in one molecular mass (77 000) for star ps in mcy and found the diameter  $\bar{\rho}=(\rho_u+\rho_l)/2$  to be linear in temperature and not to have a significant  $t^{2\beta}$  or  $t^{(1-\alpha)}$  contribution. Cerdeirina *et al.*<sup>15</sup> have argued that the asymmetry (nonconstant diameter) in liquid-liquid systems would be described by Eq. (4) with a linear temperature dependence as well as contributions from  $t^{2\beta}$  and  $t^{(1-\alpha)}$ . The amplitude of the  $t^{(1-\alpha)}$  term is proportional to the amplitude  $A_0^-$  of the heat capacity anomaly,<sup>15</sup> which in polymer-solvent systems is extremely small because of the large correlation length amplitude and the two-scale-factor universality relation between them:  $X=(A_0^+\xi_0^3)/k_B=0.018\,80\pm 0.000\,08$  and  $A_0^+/A_0^-=0.530\pm 0.003$ .<sup>9</sup> Thus, the diameter for our systems should be described by linear and/or  $t^{2\beta}$  terms. Figure 8 shows the diameter of one molecular mass system along with a straight line and a line representing only  $t^{2\beta}$ ; the  $t^{2\beta}$  term describes the data better than the straight line, while a combination of a linear temperature dependence and a  $t^{2\beta}$  term improves the fit slightly. The

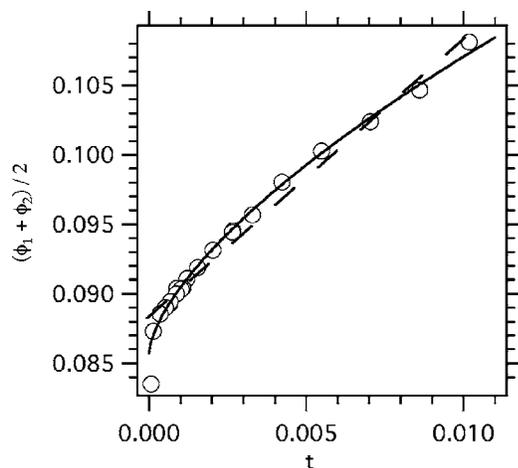


FIG. 8. The diameter of the  $M_w=228\,000$  star ps in mcy coexistence curve as a function of reduced temperature  $t$ . The solid line is a weighted fit to Eq. (4) given by  $(\phi_1+\phi_2)/2=(0.0857\pm 0.0003)+(0.437\pm 0.005)t^{2\beta}$ , while the dashed line is  $(\phi_1+\phi_2)/2=(0.0875\pm 0.0005)+(2.0\pm 0.1)t$ .

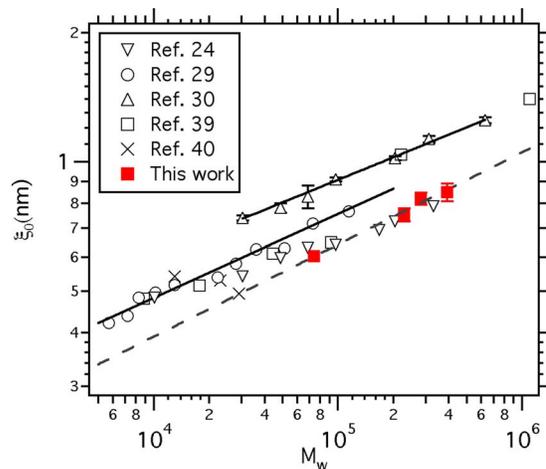


FIG. 9. (Color online) The correlation length amplitude plotted as a function of molecular mass for ps in mcy. Literature values for linear (open symbols) ps show significant differences among research groups even though a power law with exponent of 0.185 (solid lines) is typically consistent with each group's data. The dashed line also has slope of 0.185 and is a guide to the eye for our data.

equations for the lines are in the figure caption. The value for the critical concentration does not change significantly based on which equation is used to extrapolate to the critical temperature.

## B. Turbidity

The data from the four samples shown in Fig. 2 were analyzed using a properly weighted least-squares fit<sup>38</sup> by the function in Eq. (5), where the parameters  $\xi_0$ ,  $\tau_b$ , and  $\tau_0$  were free but the exponents  $\nu$  and  $\gamma$  were fixed at their theoretical (Ising) values of 0.63 and 1.237.<sup>9</sup> The critical temperature was constrained between the observed one- and two-phase temperatures. The resulting values of the parameters are given in Table II, along with the one standard deviation uncertainties.

The correlation length amplitude  $\xi_0$  is expected to follow a power law in molecular mass [see Eq. (3b)] with a power  $n=(1-\nu)/2=0.185$ . Unlike the molecular mass dependence of the order parameter  $B$ , the correlation length amplitude  $\xi_0$  is well described by this exponent for linear ps in mcy. Figure 9 illustrates the power law relationships for the reported data<sup>24,29,30,39,40</sup> for linear ps in mcy; however, the obviously different intercepts for the lines in Fig. 9 indicate a systematic error among the research groups that makes it difficult to determine a shift in intercept due to branching. Our fitted values of  $\xi_0$  for star ps are consistent with a power of 0.185 (a weighted fit gives  $n=0.21\pm 0.03$ ) and are roughly the same values for  $\xi_0$ , as found by An *et al.*,<sup>30</sup> who also used turbidity measurements on the linear ps in mcy. The more compact structure of a branched polymer would suggest a smaller correlation length amplitude, and our results are at the low end of the range of values reported for linear ps in this solvent.

Our turbidity data also allow us to determine the susceptibility amplitude  $\chi_0$  (see Table II) from Eq. (6) using the fitted value of  $\tau_0$  and our values of  $\partial n/\partial\phi$  from our measured refractive indices. For sufficiently large molecular masses,

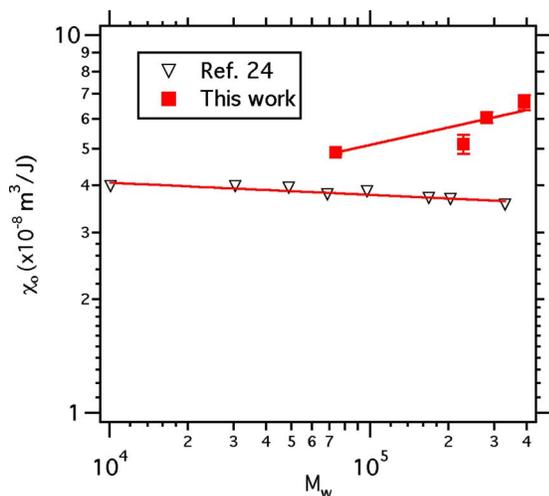


FIG. 10. (Color online) The susceptibility amplitude plotted as a function of molecular mass for ps in mcx. The data of Zhou *et al.* (Ref. 24) follow a power law with exponent of  $-0.03 \pm 0.02$ , while our data show a positive slope of  $0.15 \pm 0.07$ . The expected exponent is  $-0.12$ .

the amplitude  $\chi_0$  is expected<sup>10</sup> to be a simple power law in molecular mass with an exponent  $g = (1 - \gamma)/2 = -0.12$ . Shinozaki *et al.*<sup>39</sup> reported an exponent that was large and positive ( $+0.48 \pm 0.03$ ), while Zhou *et al.*<sup>24</sup> found it to be small and negative ( $-0.03 \pm 0.02$ ) when both measured linear ps and mcx. An *et al.*<sup>41</sup> determined a value of  $-0.05 \pm 0.03$  for PMMA and 3-octanone. Our values of  $\chi_0$ , shown in Fig. 10, result in a power of  $g = +0.15 \pm 0.07$ , which is remarkable because the sign of the power is positive. The large uncertainty in  $g$  results from the coupling of the free parameters used to fit the turbidity data, the restricted range of temperatures in the Ising regime, and the uncertainties in our calibration data for  $n(\phi)$  and its derivative.

### C. Amplitude ratio

We can also calculate the two-scale-factor universality ratio  $R$  to determine if it is universal for different molecular mass polymers and if it depends on branching. Theory predicts Eq. (7) with  $R = 0.6931 \pm 0.0007$  from a high-temperature series<sup>9</sup> and  $R = 0.6866 \pm 0.0004$  from an extended sine model,<sup>42</sup> where  $B$ ,  $\chi_0$ , and  $\xi_0$  are the leading critical amplitudes given in Table II for our star ps system. The resulting values of  $R$  are shown in Table II and compared in Fig. 11 with other literature values for several polymer-solvent systems.<sup>24,28,41</sup> Our  $R$  values, as most other determinations both in these systems and in small molecule liquid-liquid mixtures,<sup>27,43</sup> are smaller than the theoretical prediction. However, all values are within three standard deviations of theory and none show a systematic dependence on molecular size, structure, nor morphology.

## IV. CONCLUSION

By measuring the coexistence curve and the turbidity on eight-arm star polystyrene samples of different molecular masses in methylcyclohexane (the raw data are available electronically),<sup>44</sup> we could determine the locations of the critical points (temperature and composition), verify critical

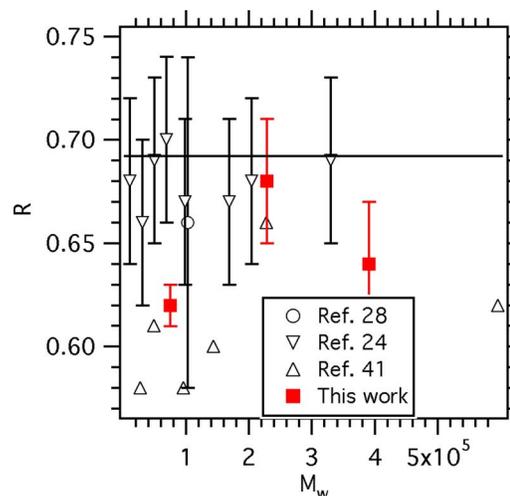


FIG. 11. (Color online) The two-scale-factor universality ratio  $R$  shows no dependence on molecular mass or branching in any of the polymer solutions. The solid line is the theoretical prediction of 0.69 from Refs. 9 and 42.

exponents, and determine the leading amplitudes. These were tested against what was predicted by current theory and against similar results for linear polymer systems and the few measurements in other branched polymer systems. Branching affects certain results, but many universal relationships were unchanged by the topology of the polymer.

We confirmed that this branched system near its critical point belonged in the Ising universality class and that the amplitudes scaled as a power law in molecular mass. Coexistence curve data and turbidity measurements were described by simple scaling relations in reduced temperature with Ising values for the exponents. We also confirmed the observation of Alessi *et al.*<sup>18</sup> that the critical temperature in these star polymer systems was much smaller than the same molecular mass linear system and that the trend in the reciprocal temperatures as a function of the Flory-Shultz parameter was much steeper than for a linear polymer in the same solvent. The amplitudes  $B$  and  $\xi_0$  were consistent with a power law in molecular mass with exponents similar to other polymer-solvent experimental results. While the amplitude  $\chi_0(M_w)$  was consistent with a power law, the exponent value was small and positive.

We also made observations that, while new, were not unexpected. The diameters of our coexistence curves were fitted better if a  $t^{2\beta}$  term was included, which is consistent with a recent prediction and observation.<sup>15</sup> All of our coexistence curve data collapse upon scaling with one adjustable parameter to a universal curve, confirming recently reported results for linear polymer systems.<sup>2,14</sup> We also found the critical concentration to vary as a power law with molecular mass with roughly the same exponent as a linear polymer system, but to be shifted to larger concentrations at any given molecular mass, which was expected from MC simulations and theory.<sup>5</sup>

Several observations had not been reported in the literature. There seems to be a consistent 12% increase in the amplitude  $B$  for a star versus linear polystyrene of the same molecular mass for both solvents, methylcyclohexane and cyclohexane. This trend upon branching was consistent with

data from a MC simulation. On the other hand, the amplitude  $\xi_0$  was not shifted substantially upon branching, although the values were at the low end of those reported for linear polystyrene in methylcyclohexane. However, the combination of amplitudes  $B$ ,  $\chi_0$ , and  $\xi_0$  did give a universal value of  $R$  that was slightly less than theory predicts, but independent of molecular mass or branching.

This system is intriguing because of the many layers of universality present: simple power laws with Ising exponents as the temperature is varied along the critical isochore, system-dependent amplitudes that follow simple scaling in molecular mass, a scaling function that collapses all the coexistence curve data onto a universal curve, the critical temperature and composition follow certain trends as the molecular mass changes or branching occurs, and a ratio of amplitudes that gives a universal constant  $R$ .

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<sup>44</sup>See EPAPS Document No. E-JCPSA6-127-016733 for the raw turbidity and coexistence curve data. This document can be reached through a direct link in the online article's HTML reference section or via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>).