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# Shear Viscosity of Liquid Sulfur near the Polymerization Temperature

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We present new measurements of the shear viscosity,  $\eta$ , of liquid sulfur from 392 K (118 °C) to 436 K (163 °C), near the polymerization temperature,  $T_p$  (432 K, 159 °C). The measurements have a precision of 0.1–0.6% and an accuracy of 2%. We find an extraordinary sensitivity near  $T_p$  to trace impurities. Our values of  $\eta$  above  $T_p$  are an order of magnitude greater than those in the literature. Our data can be described by a function constructed on the basis of current theories of polymer solutions and equilibrium polymerization.

## Introduction

The polymerization of liquid sulfur at 432 K (159 °C) is accompanied by a dramatic change in shear viscosity, from about 0.01 Pa·s below the polymerization temperature,  $T_p$ , to a peak of at least 100 Pa·s at about 453 K (180 °C). This global behavior of the viscosity of sulfur was studied in 1943 by Bacon and Fanelli<sup>1</sup> and in 1963 by Doi.<sup>2</sup> We report here new measurements of the viscosity in the temperature region very near to the polymerization transition of pure sulfur. We note that trace impurities can cause dramatic effects on the viscosity above  $T_p$ . We analyze the viscosity of liquid sulfur in the context of theories of polymer solutions and equilibrium polymerization.

Below the polymerization temperature,  $T_p$ , sulfur consists of mostly rings of eight sulfur atoms. Near  $T_p$ , some of the rings open and then concatenate to form mostly long diradical chains of a million or more atoms.<sup>3,4</sup> When the temperature is again lowered, the chains revert to mostly eight-membered rings. While eight-membered rings and polymeric chains predominate, other sulfur species are surely present in small amounts.<sup>5,6</sup> Wheeler, Kennedy, and Pfeuty<sup>7,8</sup> have suggested that an equilibrium polymerization like that in sulfur can be seen as a second-order phase transition for which the dimension of the order parameter,  $n$ , approaches zero, if the only important species are eight-membered rings and polymeric chains. From such a point of view, the properties of liquid sulfur can then be predicted from the known statistical mechanics of the  $n \rightarrow 0$  model. A number of equilibrium properties have been calculated and compared to experiments: the degree of polymerization,<sup>7</sup> the specific heat,<sup>7</sup> the density,<sup>9</sup> the dielectric constant,<sup>10</sup> and the phase diagram of sulfur in a solvent.<sup>11–13</sup> The  $n \rightarrow 0$  model and the various experiments are in every case in qualitative agreement, but also in every case are different in quantitative details. These discrepancies leave open intriguing questions as to the importance of species other than eight-membered rings and polymeric chains.<sup>14–16</sup>

We seek now to understand the behavior of a transport property, the shear viscosity,  $\eta$ , near  $T_p$ . One approach is to follow earlier workers<sup>17–19</sup> in devising a phenomenological function for the viscosity of liquid sulfur. By this line of reasoning, the temperature ( $T$ ) dependence of the shear viscosity of polymeric sulfur in a solvent of eight-membered ring sulfur will depend on the temperature dependence of the "solvent" of monomeric sulfur, on the weight fraction,  $c$ , of polymer as a function of the temperature, and on the average chain length,  $P$ , of the polymer as a function of temperature.<sup>17</sup> An Arrhenius equation,  $\eta_0 = b_1 \exp(b_2/T)$ , will adequately represent the background "solvent" viscosity,  $\eta_0$ , from the melting point at 393 K (120 °C) to 415 K (142 °C).<sup>17</sup> For low concentrations of polymer, the concentration dependence of the specific viscosity,  $\eta_{sp}$ , can be expressed as a Taylor's series in the weight fraction:<sup>20</sup>

$$\eta_{sp} = (\eta - \eta_0)/\eta_0 = [\eta]c + k_1[\eta]^2c^2 + k_2[\eta]^3c^3 + \dots \quad (1)$$

where  $[\eta]$  is the intrinsic viscosity, which is  $\eta_{sp}/c$  as  $c \rightarrow 0$ , and  $k_1$ , the Huggins coefficient,<sup>21</sup> is about 0.3 for a flexible polymeric coil in a good solvent.<sup>22</sup> The coefficient  $k_2$  has not been predicted.

The dependence of the viscosity on chain length enters through the dependence of  $[\eta]$  on molecular weight  $M$

$$[\eta] = KM^a = K'P^a \quad (2)$$

known as the Mark-Houwink equation,<sup>20</sup> where the constant,  $K$  (or  $K'$ ), and the exponent,  $a$ , depend on the particular polymer-solvent combination. Theoretical considerations indicate that  $0.5 < a < 0.8$  for flexible chains and that the higher value is favored for good solvents.<sup>20</sup> Combining eq 1 and 2, we expect the viscosity near  $T_p$  to behave as

$$(\eta - \eta_0)/\eta_0 = K'P^a(T)c(T) + k_1(K'P^a(T))^2c^2(T) + k_2(K'P^a(T))^3c^3(T) + \dots \quad (3)$$

Both  $c(T)$  and  $P(T)$  can be calculated from the  $n \rightarrow 0$  model of Wheeler et al.<sup>7,8</sup>

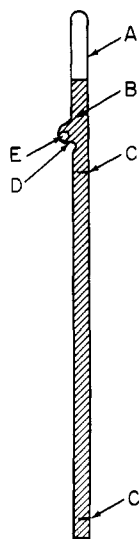
Another approach is that of Cates,<sup>23</sup> who has presented a model for the global behavior of sulfur which is based on the reptation of polymeric chains which can break and re-form. He gives an equation for  $\eta(T)$ :

$$\eta(T) = \lambda G_e(T)P^{1/2}(T)\tau_0^{1/2}(T)k^{-1/2}(T) \quad (4)$$

where  $\lambda$  is a free parameter,  $G_e$  is the plateau modulus,  $\tau_0$  is the

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**Figure 1.** The cell for determining the viscosity of liquid sulfur by measuring the fall time of a glass ball. The cell wall (A) is of Pyrex tubing (6-mm i.d., 8-mm o.d.). The 3-mm-o.d. ball (E) is of soft glass. The fiducial marks (C) for timing the fall of the ball are 11.5 cm apart. D is a bubble/indentation on the cell wall: the bubble serves as a storage place for the ball; the indentation serves as a ramp to center the falling ball. The sealed cell is about 18 cm long.

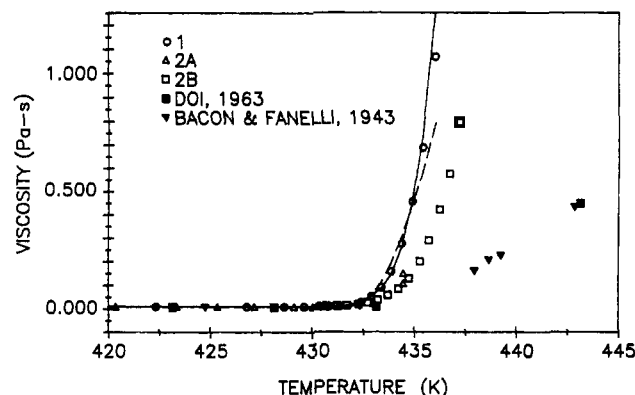
friction constant for Rouse motion of sections of the polymeric chain,  $P$  is the chain length, and  $k$  is the rate constant for the breakage of a bond between two sulfur atoms. Cates makes reasonable assumptions about the form of each of these parameters in order to obtain a function with two free parameters to fit the behavior of the viscosity of liquid sulfur. He can fit his function quite well to the data of Bacon and Fanelli<sup>1</sup> between 432 and 580 K, the range in which the sulfur is polymerized.

We will show that our data can be described rather well by eq 3 but that we have insufficient data above  $T_p$  to be able to define the parameters in eq 4.

### Experimental Methods

**General.** The experimental approach was to seal samples of very pure sulfur into glass tubes, each containing a glass ball and having two fiducial marks.<sup>24</sup> A cell was held in a temperature-controlled stirred fluid bath; a support allowed the rotation of the cell. The viscosity was determined at each temperature by measuring the fall time of the glass ball between the marks.

**Sample Preparation.** Sulfur with a purity of >99.999% was obtained from Fluka Chemical Co. (Ronkonkoma, NY). The sulfur was dried in an argon atmosphere of <1 ppm water or oxygen<sup>25</sup> overnight and then transferred to a Pyrex storage vessel. The storage vessel had an O-ring connector for attachment to a vacuum line and had the two Pyrex viscosity cells (see below) as appendages.<sup>26</sup> The O-rings were of fluorosilicon and were used without grease. That vessel was then connected to the vacuum line. The sulfur was degassed<sup>26</sup> by melting and pumping away the evolved gas; 14 melting cycles were required to remove all the gas. Sulfur was sublimed into the two viscosity cells, melted there, and poured back into the storage vessel; this "rinse" of the viscosity cells was done three times. The final samples of sulfur were then sublimed from the storage vessel into the viscosity cells, and the viscosity cells were sealed off under vacuum by melting the glass together. The sulfur remaining in the storage vessel was discolored and contained the dark specks thought to be characteristic of organic impurities.<sup>27</sup> The sulfur in the viscosity cells was a lovely yellow and stayed so, even after heating above  $T_p$  and cooling back again.



**Figure 2.** The viscosity of sulfur as a function of temperature. Samples 1 and 2 are from the present work. There were two heating runs, A and B, on sample 2. The literature data are those of Bacon and Fanelli (ref 1) and Doi (ref 2). The solid line is a fit to eq 5 in the text, with  $b_3$ ,  $b_4$ , and  $b_5$  free. The dashed line is a fit with  $b_4$  fixed at  $b_3^2/k_1$ , where  $k_1 = 0.3$ , and the cubic term omitted.

**Cell Design.** The cell design is shown in Figure 1.<sup>28</sup> Each cell had a bubble blown near its top, with an indentation just below the bubble. The bubble acted as a storage place for the glass ball. The indentation served as a ramp for centering the ball in the cell when the cell was tilted to drop the ball through the liquid. The cells were attached by glass-blowing to the sulfur storage vessel discussed above. The vessel and the cells were cleaned with chromic acid, followed by dilute hydrofluoric acid, and then rinsed several times with bidistilled water. They were attached to a vacuum line and dried by heating with a flame until the pressure reached  $10^{-5}$  mmHg.

**Temperature Measurement and Control.** The cells were studied in a well-stirred silicone oil bath, the temperature of which was controlled with an analog controller.<sup>29</sup> The temperature was measured with a platinum resistance thermometer.<sup>30</sup> The precision and accuracy of the temperature measurements were limited by the temperature control to 20 mK.

**Viscosity Measurement.** The viscosity was measured by timing the fall of a glass ball between the fiducial marks of the cell with a stopwatch. The resolution of the time of fall is limited by the observer response time. The fall times in sulfur ranged from 2 to 200 s in the temperature range which we studied. For each datum, the fall time was taken as the average of 3–10 measurements. The precision of the viscosity measurements was taken as the standard deviation of the mean of the set of measurements and varied from 0.1% to 0.6%. A plot of our data at their full resolution shows scatter at about the same level as the calculated precision.

The fall time,  $t$ , of the ball is related to the viscosity by  $\eta = k(\rho_B - \rho)t$ , where  $k$  is an instrument constant,  $\rho_B$  is the density of the ball, and  $\rho$  is the density of the sulfur.<sup>31</sup>  $\rho_B$  changes only about 0.02% over the temperature span of our data. The density of sulfur changes by about 1% over the temperature range of our data.<sup>32</sup> We have chosen to take  $(\rho_B - \rho)$  as a constant for our calibration. We have determined  $k(\rho_B - \rho)$  for each of our cells by measuring the time of fall in a fluid of known viscosity, namely, liquid sulfur near the melting point, where we have found our own measurements to be independent of sample history. We have taken as the calibration point the measurement of Bacon and Fanelli<sup>1</sup> at 391.95 K. In this temperature range, the data of Doi<sup>2</sup> agree with those of Bacon and Fanelli<sup>1</sup> within 1–2%. Thus, this calibration would give an accuracy of 1–2%, in the absence of other systematic errors. One possible source of systematic error is

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non-Newtonian behavior. The shear rate in our measurements<sup>31</sup> varied from 6 s<sup>-1</sup> at the highest temperature to 60 s<sup>-1</sup> at the lowest temperature, which is probably low enough to make shear effects unimportant.<sup>33</sup>

### Results and Data Analysis

**Light Effect.** We found<sup>28</sup> that the light source used to view the cell could affect the value of the fall time. The cell was kept in the covered, dark oil bath until a fall time measurement was to be made. Then the observation port was opened and a lamp directed on the cell in order to see the falling ball and the fiducial marks. We then made several determinations of the fall time. When the light source was a halogen lamp, we noticed that, at temperatures above  $T_p$ , the first fall times in the set of 10 were faster than were the later ones. Plots of the fall time versus real time showed 10% increases in the first minute, followed by a leveling off. This increase in viscosity upon illumination above  $T_p$  could be due to light-induced polymerization or due to local heating, which would also increase the extent of polymerization. When the light source was a fluorescent lamp, no such effect on the fall time was observed. The fluorescent lamp was used for illumination for all the data reported here.

**Impurity Effect.** In earlier work,<sup>28,34</sup> we noted dramatic relaxation times for the viscosity when the sulfur was brought to a new and higher temperature. Such effects were also reported by Doi.<sup>2</sup> Below  $T_p$ , for  $(T_p - T) < 2$  K, we observed that, on reaching a new temperature, the viscosity increased with time and then became steady. The relaxations required 2 or 3 days, and the increases were 2–10% of the viscosity. The relaxation curves could be described by exponential functions with time constants of 600–1100 min. The amplitude of this effect was larger as  $T_p$  was neared.

Above  $T_p$ , in the range of <4 K in which we made measurements, we observed that, on reaching a new temperature, the viscosity decreased with time over about a week, reaching a new steady-state value as much as 40% below the initial value. These relaxation curves were also exponential, with time constants of about 3000 min; the amplitude of the effect increased with  $T$ .

However, no such long relaxation times were observed on cooling (rather than heating), either above  $T_p$  or below  $T_p$ . Since any reversible chemical reaction gives the same relaxation time on heating or cooling, we suspected that an irreversible reaction, perhaps with an impurity, was the cause of the long relaxation times. Indeed, impurities are known to reduce the viscosity of polymeric sulfur.<sup>35</sup> Our studies of the viscosity near the ceiling temperature for the equilibrium polymerization of  $\alpha$ -methylstyrene show equilibration times of about an hour on heating or on cooling, during which the viscosity increases on polymerization and decreases on depolymerization.<sup>36</sup> By comparison, the relaxations in sulfur are in the wrong directions for the expected polymerization processes. In addition, we found that, on further temperature cycling of the sulfur samples, the relaxation times decreased and the viscosity values approached consistent values, as if the impurity were being used up.

We found that further purification of the sulfur by sublimation, and greater care in keeping the sulfur free of water and air, reduced the amplitude of the relaxation times and gave higher values of the viscosity. We believe that all the evidence is consistent with an hypothesis that trace impurities cause long relaxation times and lower the viscosity and that therefore the higher values of the viscosity are the better values.

**Viscosity Measurements.** Figure 1 shows the data taken on the two sulfur cells. For sample 1, we made a heating run as

TABLE I: Shear Viscosity,  $\eta$ , as a Function of Temperature,  $T$ , for Sample 1<sup>a</sup>

point no.	$T$ , K	$\eta$ , Pa·s	$\sigma_\eta$ , Pa·s
1	391.98	0.011 52	0.000 01
2	395.73	0.011 05	0.000 01
3	398.85	0.010 58	0.000 01
4	401.30	0.010 32	0.000 01
5	405.89	0.010 06	0.000 01
6	409.86	0.009 54	0.000 01
7	413.84	0.009 28	0.000 01
8	417.64	0.009 13	0.000 02
9	422.33	0.008 92	0.000 01
10	426.80	0.008 71	0.000 01
11	428.64	0.008 71	0.000 01
12	429.61	0.008 81	0.000 01
13	430.34	0.008 97	0.000 01
14	430.82	0.009 33	0.000 01
15	431.36	0.010 53	0.000 01
16	432.40	0.025 97	0.000 03
17	432.90	0.050 58	0.000 06
18	433.40	0.090 7	0.000 2
19	433.87	0.156 9	0.000 6
20	434.38	0.275 3	0.000 7
21	434.90	0.454 7	0.000 5
22	435.39	0.688	0.004
23	436.02	1.067	0.005

<sup>a</sup> The uncertainty in  $\eta$  is  $\sigma_\eta$ .

quickly as possible: 10–15 min was required for a temperature change, the measurements of  $\eta$  were made at a given  $T$  in 5–10 min, and all the data near  $T_p$  were collected within about 3 h. For each set of measurements at a  $T$  near  $T_p$ , there was still evidence of a decrease in  $\eta$  of about 0.5–1% during the data collection. We did not make measurements at still higher temperatures because the fall time was already 200 s at 436.02, making it impossible to take data quickly at higher temperatures. We consider that these data, listed in Table I, are the best we can obtain until even purer sulfur can be made and/or the viscosity measurements can be made even more quickly.

For sample 2, the data were taken on two heating runs, indicated as 2A and 2B. No effort was made to take the data quickly: the data near  $T_p$  were taken over about 3 days. Note that the viscosity is considerably lower than that for sample 1. We show also in Figure 1 the data of Bacon and Fanelli<sup>1</sup> and of Doi<sup>2</sup> which fall within the temperature range of our measurements. These viscosity data are even lower than those for our sample 2, but agree with one another. Our interpretation of the difference with our data is that impurities present in the samples of Bacon and Fanelli and of Doi affected their measurements, in spite of their careful attention to such impurities.

We have fitted<sup>37</sup> eq 3 in the following form to the data in Table I:

$$\eta = \eta_0 [1 + b_3 P^a(T) c(T) + b_4 (P^a(T) c(T))^2 + b_5 (P^a(T) c(T))^3] \quad (5)$$

where  $\eta_0 = b_1 \exp(b_2/T)$ . The  $b_i$  are free parameters. From data points 1–7, we determined  $b_1 = 2.00 \times 10^{-4} \pm 2 \times 10^{-6}$  Pa·s and  $b_2 = 1587 \pm 268$  K. We then fitted eq 5 to all 23 points. The quantities  $P(T)$  and  $c(T)$  were calculated from the model of Wheeler et al.;<sup>7</sup> the parametric equations for nonzero magnetic field were solved numerically by a method based on that suggested by Moldover.<sup>38</sup> The constants used were  $T_p = 432.15$  K, the (enthalpy of propagation)/ $R = 1360$  K, the (enthalpy of initiation)/ $R = 16507$  K, the (entropy of initiation)/ $R = 11.575$ , and the parametric variables  $am_0 = 1.74$  and  $b^2 = 2.006$ . The values taken for the critical exponents for  $n = 0$  were<sup>39</sup>  $\alpha = 0.235$ ,  $\beta = 0.3025$ ,  $\gamma = 1.16$ , and  $\delta = 4.83$ . We found that the fit to the data

(33) See, for example: Hanley, H. J. M. In *XVII Winter Meeting on Statistical Physics: Lectures on Thermodynamics and Statistical Mechanics*; Gonzalez, A. E., Vereas, C., Eds.; World Publishing Co.: Singapore, 1988.

(34) Greer, S. C. In *XVII Winter Meeting on Statistical Physics: Lectures on Thermodynamics and Statistical Mechanics*; Gonzalez, A. E., Vereas, C., Eds.; World Publishing Co.: Singapore, 1988. The viscosity values in Figure 2 of this paper should be divided by 1000.

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(38) Moldover, M. R. *J. Res. Natl. Bur. Stand.* **1978**, *83*, 329.

(39) Le Guillou, J. C.; Zinn-Justin, J. *J. Phys. Lett.* **1985**, *46*, L137.

was not very sensitive to any of these model variables. The exponent,  $a$ , was fixed at 0.8; the fit for eq 5 was not sensitive to the value of  $a$ . The uncertainty in the viscosity was taken as the experimental uncertainty given in Table I, since the propagated uncertainty from the temperature error was shown to be negligible.

When all parameters were left free, we obtained  $b_3 = 0.085 \pm 0.009$ ,  $b_4 = -0.00040 \pm 0.00004$ , and  $b_5 = 1.50 \times 10^{-6} \pm 5 \times 10^{-8}$ . This function is drawn as the solid line in Figure 1. Clearly, the function and the data for sample 1 begin to deviate at high temperatures, which was reflected in nonrandom residuals and a reduced  $\chi^2$  of 35. A fit to eq 5 with only the linear and quadratic terms was less successful than the fit including the cubic term. We note that the coefficients we found for eq 5 lead to a Huggins coefficient,  $k_1$ , of  $-0.047$ ; this coefficient is normally between  $+0.3$  and  $+0.5$ .<sup>20</sup>

If we fix  $k_1$  at 0.3, thus fixing  $b_4$  at  $k_1 b_3^2$ , the cubic term becomes undetermined. The fit with just the first two terms, and thus only one free parameter, is shown as the dashed line in Figure 1;  $b_3 = 0.0316 \pm 0.0006$  and the reduced  $\chi^2$  is 71. While the fit is not as good as with three free parameters, the qualitative agreement is satisfying.

We also attempted to fit eq 4, from the reptation model, to our data above  $T_p$ . We also tried putting the Arrhenius background viscosity into eq 4 as either a multiplicative factor or an additive

term. We were unable to get the nonlinear least-squares analysis to converge to any fit at all, perhaps because we have so little data in that temperature range.

## Conclusions

We believe that the extraordinary relaxations which we have observed in the viscosity of liquid sulfur are due to the reaction of the diradical polymeric sulfur with trace impurities. We have made new measurements near  $T_p$  on very pure sulfur which we believe to be closer to the true values than are any reported previously. However, even in our measurements the relaxation of the viscosity was not entirely eliminated. It is possible that the remaining problem is due to the reaction of the sulfur with the glass cell. Better measurements will require a careful choice of the cell material. A viscosity measurement technique which is fast and in which the shear rate can be varied is desirable.

Our measurements are consistent with current theories of polymer solutions and of equilibrium polymerization.

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## Critical Amplitude Scaling Laws for Polymer Solutions

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Critical properties of polymer solutions have amplitudes (scale factors) that depend on the degree of polymerization,  $N$ . The amplitudes vanish or diverge with characteristic exponents on  $N$ . The traditional critical exponents ( $\alpha$ ,  $\beta$ , etc.) characterize the divergence or vanishing of critical properties with respect to  $\epsilon \equiv |(T - T_c)/T_c|$ . For a polymer solution a pair of critical indices is required ( $a$ ,  $\alpha$ ), ( $b$ ,  $\beta$ ), etc., to characterize the behavior of the critical property. Scaling laws are derived for the  $N$  indices, and it is shown that a striking parallelism exists between the two sets of indices. For example, the scaling relationships,  $3\nu = 2\beta + \gamma = \mu + \nu$ , have a completely analogous form among the  $N$  indices:  $3n = 2b + g = m + n$ . Although the analogy is not complete, equations have been identified that transform one set of "sum rules" to the corresponding set of the other. In one approximation that is equivalent to assuming that the small correlation function index  $\eta$  equals 0, the  $N$  indices are shown to be related to the exponent  $r$  that characterizes the  $N$  dependence of the critical concentration ( $\phi_c \sim N^{-r}$ ). Heuristic arguments suggest that  $r$  is related to the Flory exponent that characterizes the size of the polymer chain at the critical point. The fundamental scaling variable for polymer solutions is identified as  $N^{m/\nu}\epsilon$  rather than the classical  $N^{1/2}\epsilon$ . This important identification allows for the experimental determination of the correlation length index  $n$  from existing coexistence curve data. Theoretical estimates of the  $N$  indices compare favorably with available experimental data with one exception. Data gaps and needed experiments are identified.

## Introduction

A growing body of experimental evidence<sup>1-15</sup> has convincingly shown that the critical point properties of a polymer solution under

going liquid-liquid phase separation are in the same universality class as the three-dimensional Ising model.<sup>16</sup> Critical exponents associated with the divergence or vanishing of various thermodynamic properties as the critical point is approached have been determined for polymer solutions; these include the  $\gamma$  and  $\nu$  exponents associated with the divergence of the susceptibility ( $\chi$ ) and the correlation length ( $\xi$ ),<sup>1-9</sup> respectively, and the  $\beta$  and  $\mu$  exponents associated with the vanishing of the concentration difference ( $\Delta\phi$ )<sup>10-13</sup> and interfacial tension ( $\sigma$ ),<sup>14,15</sup> respectively. In all cases the values of these critical exponents (or indices) agree well with values those assigned to the 3-D Ising model. As is well-known, binary mixtures of small molecules, liquid-vapor, and ferromagnetic critical phenomena also fall into this same universality class.<sup>16</sup>

Since the early light scattering work of Debye<sup>1</sup> to determine correlation lengths in polymer solutions, it has been known that the amplitudes of these various properties depend on polymer molecular weight. The amplitudes vanish or diverge with  $N$ , the

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