Living Poly(α-methylstyrene) near the Polymerization Line. 1. Mass Density and Polymerization Line for Solutions in Tetrahydrofuran

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ABSTRACT: We have measured the mass density, ρ, of solutions of living poly(α-methylstyrene) in tetrahydrofuran as a function of temperature, T, near the polymerization temperatures, T_p. We measure with a precision in density of 4×10^{-5}; the accuracy is limited by our knowledge of the composition to about 3%. We compare our $\rho(T)$ data to two models of equilibrium polymerization as a second-order phase transition: the $n \rightarrow 0$ magnet model (Kennedy, S. J.; Wheeler, J. *J. Chem. Phys.* **1983**, *78*, 1523) and the mean-field model (Tobolsky, A. V.; Eisenberg, A. *J. Colloid Sci.* **1962**, *17*, 49) as applied to a living polymer in a solvent. For both models we assume an ideal solution of the ionic polymer in the solvent and linear thermal expansions for the monomer, the polymer, and the solvent. The description of the data then requires the addition of constants ("background densities") for both models; the constants are probably related to the excess volumes of mixing. When such constants are included, both models provide good qualitative descriptions of $\rho(T)$ for living poly(α-methylstyrene) in tetrahydrofuran. The $n \rightarrow 0$ magnet model is capable of more accurate representations of the data. A model for a living polymer in a solvent which is more appropriate than the $n \rightarrow 0$ model is the dilute $n \rightarrow 0$ model (Kennedy and Wheeler, op. cit.), but the equation of state of the dilute $n \rightarrow 0$ model has not yet been developed. That the $n \rightarrow 0$ model describes so well the data for a system which includes a solvent suggests that the solvent does not affect strongly the percentage conversion of monomer to polymer at a given $T_p - T$). In the course of the measurements of the density and of other physical properties of this system in our laboratory, we have measured the polymerization line: the dependence of the polymerization temperature upon the initial mole fraction of monomer, x_m^*. Our measurements determine $T_p(x_m^*)$ from the changes in the slopes of physical properties (e.g., the density) and differ from determinations of the polymerization line which measure the monomer concentration at some value of T and then assume that to be the x_m^* when the polymerization line passes through that value of T.

I. Introduction

"Living" polymerization[1–3] requires the presence of an initiator species which activates the monomer. Then as the temperature is lowered, a "ceiling temperature", or polymerization temperature, T_p, is reached, at which the Gibbs free energy favors the propagation of the activated monomer into a polymer. The number of polymer molecules is determined by the concentration of initiator species. The equilibrium average molecular weight of the polymer is determined by the temperature (at constant pressure) and increases as the temperature is lowered. If termination reactions can be avoided, the polymer molecules will remain activated and can shrink or grow as the temperature is raised or lowered. The living polymer molecules can attain a state of dynamic chemical equilibrium with the monomer molecules. If the temperature is subsequently raised above the ceiling temperature, the Gibbs free energy again favors the monomer.

This reversible transition from monomer to polymer is rather like a phase transition and can be treated as such. The early work of Tobolsky and Eisenberg[4–6] was shown by Wheeler et al.[7] to be equivalent to a mean-field model of a magnetic phase transition. Mean-field models average over the fluctuations in the order parameter of the phase transition. For example, for a ferromagnetic, for which the order parameter is the magnetization, each molecular spin is treated as if it lies in a magnetic field which is the average of the magnetic fields of all the other molecules.[8] The treatment by Scott[9] of equilibrium polymerization in sulfur solutions using the Flory–Huggins theory of polymer solutions[10] has also been shown to be equivalent to a mean-field model.[11]

In 1980, Wheeler, Kennedy, and Pfeuty[7] recognized that the partition function for equilibrium polymerization modeled as the random walk of a polymer on a lattice is mathematically equivalent to the partition function for the n-vector model of magnetism, where n is the dimension of the order parameter. Unlike the mean-field models, the n-vector model allows for fluctuations in the order parameter. The dimension of the order parameter depends on the nature of the polymer system. For polymers which are linear chains, $n \rightarrow 0$. For polymers which are rings, $n = 1$.[12] For polymers with directional rings, $n = 2$.[13] When rings and chains are present, bicritical phenomena appear.[14] The addition of a solvent to a system of living linear polymers allows intersections between the polymerization transition and liquid–liquid phase transitions and the possibility of symmetric[15,16] and nonsymmetric[17] tricritical points. If the polymer is in a solvent and also can form both rings and chains, then even higher order critical points are possible.[18] The identification of the physical quantity which should be taken as the order parameter for these polymerizing systems remains unclear. However, the formal connection of equilibrium polymerization to the n-vector model allows the extensive theoretical framework developed for magnets to be put to use in making predictions about the behavior of polymerizing systems. Wheeler and his collaborators have produced such predictions for the thermodynamic properties of systems of organic living polymers[16] but have had little experimental data with which to compare the theory. The only data available have been a few measurements of the weight fraction of polymer as a function of temperature for polytetrahydrofuran.[19]

As a part of our program to produce data to test the mean-field and n-vector theories for equilibrium polym-

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erization, we present here new measurements of the mass density of living poly(α-methylstyrene) dissolved in tetrahydrofuran, using sodium naphthalide as the initiator.[20] The sodium naphthalide transfers an ion radical to the α-methylstyrene monomer to activate it, and then two activated monomers combine "head-to-head" to make an activated dimer. The polymer is formed by the successive "head-to-tail" addition of monomer to the activated dimer. Both ends of the polymer carry negative charges, precluding the joining of the ends to make polymeric rings: only polymeric chains will be present. The combination of two polymer chains is likewise precluded. Thus only polymeric chains will form, and the system is expected to be in the $n \to 0$ universality class. We note also that, in the temperature range of our experiments, 99.7% of the propagating species are ion pairs of the polymeric dianions and their counter cations, and only about 0.3% are dissociated into free ions.[2]

We are aware of no previously published data on the temperature dependence of the mass density of any *living* polymer, even though density measurements have been used to study the chemical kinetics of equilibrium polymerization.[21] We consider an equation for the mass density of the polymerizing solution which assumes ideality for the solution, which assumes linear thermal expansions for the monomer and for the polymer, and which assumes the density to be a function of the weight fraction of polymer, but not of the molecular weight of the polymer. The weight fraction of polymer can be predicted from either the mean field model or the $n \to 0$ model. We find that both models give good qualitative descriptions of the behavior of the mass density as a function of temperature when a constant "background" density, ρ_B, is included. The parameter ρ_B can be viewed as a correction for the excess volume of mixing, which is ignored when we assume an ideal solution. The presence of some terminated polymer could also contribute to ρ_B. The $n \to 0$ magnet model is, however, capable of more accurate descriptions of the data. Our results support the hypothesis that the equilibrium polymerization of α-methylstyrene falls in the $n \to 0$ universality class of the n-vector model of phase transitions.

Strictly speaking, the $n \to 0$ model is appropriate only for the equilibrium polymerization of a pure monomer, not for the polymerization of a monomer in a solvent. We did not study the pure monomer experimentally because we found that its polymerization produced a very viscous fluid. We did not apply the more appropriate *dilute* $n \to 0$ model[15,16] to our measurements because no equation of state has been developed for that model. That the $n \to 0$ model describes the data as well as it does indicates that the presence of the solvent does not affect the extent of the conversion of the monomer to polymer at a given $T_p - T$.

In the course of the measurements of the density and of other physical properties of this system in our laboratory, we have measured the polymerization line: the dependence of the polymerization temperature upon the initial mole fraction of monomer, x_m^*, at an essentially constant pressure (the vapor pressure of the solution). Our measurements determine $T_p(x_m^*)$ from the changes in the slopes of physical properties (e.g., the density) and are thus more direct than determinations of the polymerization line which measure the equilibrium monomer concentration at some value of T and then assume that to be the x_m^* when the polymerization line passes through that value T. We present our data on the polymerization line and fit to them the equation of Dainton and Ivin.[1,22]

II. Theory

We develop here an equation for the mass density as a function of temperature, $\rho(T)$, of a living polymer in solution by following the derivation by Kennedy and Wheeler[23] for the density at the analogous reversible polymerization in pure liquid sulfur.

(1) Assuming an ideal solution, we can write the total specific volume, v, at a given temperature as

$$v = v_m\Phi_m + v_p\Phi_p + v_s\Phi_s \qquad (1)$$

where v is the specific volume, Φ is the weight fraction in the solution, and subscripts m, p, and s refer to pure monomer, pure polymer, and pure solvent, respectively. If the initial mass of the monomer is m_0, that of the solvent is m_s, and the percentage conversion of monomer to polymer is ϕ_p, then

$$\Phi_p = \phi_p m_0/m_T, \quad \Phi_m = (1 - \phi_p)m_T, \quad \Phi_s = m_s/m_T \qquad (2)$$

where $m_T = m_0 + m_s$.

(2) To introduce the temperature dependence, we assume linear thermal expansions

$$\begin{aligned} v_m(T) &= v_m^\circ[1 + \alpha_m(T - T_p)] \\ v_p(T) &= v_p^\circ[1 + \alpha_p(T - T_p)] \qquad (3) \\ v_s(T) &= v_s^\circ[1 + \alpha_s(T - T_p)] \end{aligned}$$

where the α_m, etc., are the cubic thermal expansion coefficients, and the superscript ° refers to the quantity at T_p.

By combining eqs 1–3 and rearranging, we obtain

$$\begin{aligned} v(T) = {} & v_m^\circ[1 + \alpha_m(T - T_p)]m_0/m_T + \\ & v_s^\circ[1 + \alpha_s(T - T_p)]m_s/m_T + \\ & \Delta v^\circ[1 + \alpha(T - T_p)]\phi_p(T)\, m_0/m_T \qquad (4) \end{aligned}$$

where $\Delta v^\circ = (v_p^\circ - v_m^\circ)$ and $\alpha = (\alpha_p v_p^\circ - \alpha_m v_m^\circ)/\Delta v^\circ$. Then $\rho(T) = 1/v(T)$. Given all the thermodynamic parameters in eq 4, we can use the mean-field theory or the $n \to 0$ theory to calculate $\phi_p(T)$ and thus compute $\rho(T)$. What are the values of the thermodynamic parameters in eq 4? How do we calculate $\phi_p(T)$?

(1) Polymerization Temperature, T_p. The polymerization temperature for α-methylstyrene depends strongly on the initial concentration of monomer in the solution and only weakly on the nature of the solvent or the choice of initiator. T_p decreases as the initial concentration of monomer decreases and the concentration of solvent increases. It is convenient to choose concentrations such that T_p is below room temperature: then residual impurities will react with the initiator or with the initiated monomer rather than with the polymer, and also other side reactions are less likely at the lower temperatures. In addition, the pure liquid monomer forms a very viscous, even glassy, polymer, with very long equilibration times.[24] Thus the presence of solvent makes for more convenient handling and for shorter equilibration times for the samples.

T_p as a function of the weight fraction (Φ_m^*) or mole fraction (x_m^*) of initial monomer is the "polymerization line" for a given monomer. Dainton and Ivin[1,22] developed an equation for the polymerization line. The equilibrium constant for polymerization, K_p, for which a polymer molecule of k monomers combines with a monomer molecule to make a polymer molecule of $k + 1$ monomers, is $a_{k+1}/a_k a_m$, where a is the activity of each species. If $a_k \approx a_{k+1}$, then $K_p \approx 1/a_m$. If the solution is ideal and the

Table I
Samples of Living Poly(α-methylstyrene), Initiated by Sodium Naphthalide and Dissolved in Tetrahydrofuran, for Which Mass Density Measurements Are Reported[a]

sample/ dilatometer	x_m*	$I_0 \times 10^3$	$T_p{}^e$ (K)	$T_p{}^p$ (K)	ρ_B
1/A	0.37	1.8	295	291.7	0.0511
2/B	0.33	1.9	294	290.7	0.0402
4/C	0.26	1.8	291	290.0	0.0272

[a] The mole fraction of initial monomer is x_m* (with an uncertainty ± 0.01), the molar ratio of sodium naphthalide to initial monomer is I_0, and the experimental polymerization temperature is $T_p{}^e$ (with an uncertainty ±1 K). The value of T_p which gives the best theoretical description using the $n \rightarrow 0$ magnet model is $T_p{}^p$ (with an uncertainty ±0.5 K). The parameter ρ_B is the background density, as described in the text. Dilatometer A had a valve on it; dilatometers B and C had no valves and were thus completely sealed Pyrex.

standard state is the pure monomer, then $K_p \approx x_m{}^{-1} \approx \exp[(\Delta S_p{}^\circ/R) - (\Delta H_p{}^\circ/RT)]$, where x_m is the mole fraction of monomer at equilibrium, $\Delta H_p{}^\circ$ is the enthalpy of propagation in the standard state, and $\Delta S_p{}^\circ$ is the entropy of propagation in the standard state. Then $T = \Delta H_p{}^\circ/(\Delta S_p{}^\circ + R \ln x_m)$, for any T. At T_p, $x = x_m$*, so the polymerization line is

$$T_p = \Delta H_p{}^\circ/(\Delta S_p{}^\circ + R \ln x_m{}^*) \qquad (5)$$

In fact, if the solution is ideal, x_m depends only on T, so a measure of x_m at T is a measure of x_m* at T_p. Again, eq 5 assumes that solution is ideal and that $a_k \approx a_{k+1}$; the latter assumption may be problematic near T_p, where the polymer size is small and the addition of a monomer may have a significant effect on the activity.

For each of the samples studied here, we measured T_p as that temperature at which $\rho(T)$ began to deviate from its linear behavior at the higher temperatures. The three values of T_p determined in this way from our density measurements are listed in Table I and plotted in Figure 1. Figure 1 also shows data from the literature,[25-30] together with values derived from measurements made in our laboratory of the viscosity of living poly(α-methylstyrene) in tetrahydrofuran[24] and in methylcyclohexane[31] and of the small-angle scattering of neutrons from living poly(α-methylstyrene) in tetradeuterofuran.[32] We note that our measurements of the polymerization line, from different properties and by different workers, tend to lie lower than do those from the literature. We believe that this difference is due to the fact that in all our measurements, we took as T_p the temperature at which a physical property began to deviate from the background behavior for the unpolymerized sample, whereas most of the x_m*(T_p) measurements from the literature were determined by analyzing chemically the residual monomer concentration at a given temperature and then assuring that to be the concentration of monomer when the polymerization line passed through that temperature, regardless of the initial monomer concentration. We believe that this assumption, based upon the ideality of the solution, cannot be made for these ionic solutions. We have marked on Figure 1 those three measurements for which the monomer concentration was made at the ceiling temperature[25] or for which a correction for the nonideality was made;[28] one of the three measurements is consistent with our determinations, one is not, and one is ambiguous. We take as the polymerization line the measurements made in our own laboratory.

(2) Specific Volumes and Thermal Expansion Coefficients. For the first two terms of eq 4, we need values for the specific volume as a function of temperature and for the thermal expansion coefficient, for both the pure solvent and the pure monomer.

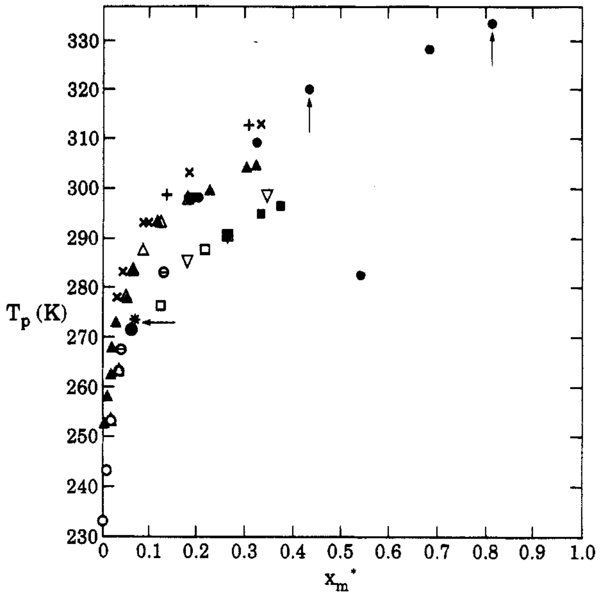

Figure 1. Polymerization line for living poly(α-methylstyrene) in tetrahydrofuran: ceiling temperature, T_p, as a function of mole fraction of initial monomer, x_m*. The literature data are from McCormick (ref 25, ●), Worsfold and Bywater (ref 26, ○), Cunningham (ref 27, ×), Tobolsky et al. (ref 28, *), Ivin and Leonard (ref 29, △), and Leonard and Malhorta (ref 30, +). Data from our laboratory are from measurements of the viscosity of living poly(α-methylstyrene) in methylcyclohexane (ref 31, ▽), of the viscosity in tetrahydrofuran (ref 24, □), of the density in tetrahydrofuran (this work, ■), and of the scattering of neutrons at small angles (ref 32, ⊖). The symbol ↑ marks two literature measurements which are direct measurements of x_m*(T_p); the symbol ← marks a literature measurement to which a correction was made for nonideality.

We made measurements with one of our dilatometers of the specific volume of neat tetrahydrofuran; our data are consistent with published values[33] within 0.1%. We fitted[34] the following power series to our data between 23 and 55 °C:

$$v_s\,(\mathrm{cm^3/g}) = a_1 + a_2 t + a_3 t^2 \qquad (6)$$

where t is the temperature in degrees Celsius, $a_1 = 1.0971 \pm 0.0006$, $a_2 = (1.239 \pm 0.004) \times 10^{-3}$, $a_3 = (3.41 \pm 0.02) \times 10^{-6}$, and uncertainties are at the 99% confidence interval. We then calculate v_s at T_p using eq 6 to get $v_s{}^\circ$ for each sample. From eq 6 we find $\alpha_s = 1.239 \times 10^{-3}$ K^{-1}.

For the specific volume of the neat monomeric α-methylstyrene, we fitted eq 6 to data from the literature[35] and obtained $a_1 = 1.077 \pm 0.007$, $a_2 = (9.6 \pm 2.1) \times 10^{-4}$, and $a_3 = (1.5 \pm 0.4) \times 10^{-6}$, where again t is in degrees Celsius and the uncertainty is at 99% confidence. We then calculate v_s at T_p using eq 6 to get $v_m{}^\circ$ for each sample. Since α_m is not well determined in eq 7, we use a value from the literature[36] of 9.774×10^{-4} K^{-1}.

(3) Change in the Specific Volume on Polymerization, Δv°. For the last term in eq 4, we need Δv°, the change in the specific volume on polymerization. We use the expression[23]

$$\Delta v^\circ \rightarrow \Delta H_p{}^\circ/[MT_p(\mathrm{d}P/\mathrm{d}T_p)] \qquad (7)$$

where → indicates the limit as T approaches T_p, M is the molecular weight of monomeric α-methylstyrene, and $\mathrm{d}P/\mathrm{d}T_p$ is the inverse of the pressure dependence of the polymerization temperature. Taking the experimentally measured values $\Delta H_p{}^\circ = 35.2$ kJ/mol[37] and $\mathrm{d}P/\mathrm{d}T_p = 57.8$ atm/K,[38] we get $\Delta v^\circ = -0.153$ cm^3/g if $T_p = 60$ °C for the pure monomer (the literature value[1]) or $\Delta v^\circ = -0.159$ cm^3/g if $T_p = 48$ °C for the pure monomer (the value from our polymerization line; see section IV.A); we use the latter value.

(4) Quantity $\alpha = (\alpha_p v_p^\circ - \alpha_m v_m^\circ)/\Delta v^\circ$. The difficulty in evaluating this quantity is that we have no measurements of α_p and v_p°. We will estimate α, show that it is small, and then omit it in eq 4.

We have no measurements of α_p and v_p° for living poly(α-methylstyrene) or for dead poly(α-methylstyrene). To estimate α, we use values for dead polystyrene ($\alpha_p \approx 2 \times 10^{-4}$ K^{-1} and $v_p^\circ \approx 1.06$ cm^3/g)[39] and the values given above for α_m and v_m°. We find $\alpha \approx 0.005$ K^{-1}. Then, in the third term of eq 4, $\alpha(T - T_p)$ will be 5% of Δv° when $T - T_p = 10$ K. We will therefore ignore $\alpha\,(T - T_p)$.

(5) Weight Fraction of Monomer Converted to Polymer, $\phi_p(T)$. We calculate $\phi_p(T)$ from both the "classical" mean-field model and from the "contemporary" $n \rightarrow 0$ magnet model; we follow Kennedy and Wheeler[16] for both calculations. Let $x_k(T)$ be the number of moles of species k present at T, divided by the sum of the number of moles of monomer initially present and the number of moles of solvent initially present. We assume that the initiation reaction goes to completion: that two initiator molecules generate one polymer molecule.

For the mean-field theory, the resulting equation of state is

$$x_m^* = x_m + x_i/2(1 - K_p x_m) \qquad (8)$$

where the subscript m refers to free monomer, the subscript i refers to the initiator, and the superscript asterisk denotes the quantity as initially introduced into the reaction vessel. The factor 2 enters for this particular system because two initiator molecules are required for each polymer molecule. Equation 8 is a quadratic equation for x_m, for the which the negative root is the physically meaningful one. Then the percentage conversion of monomer to polymer $\phi_p(T) = (x_m^* - x_m(T))(1 + n_s/n_m^*)$, where n_k is the number of moles of species k.

For the $n \rightarrow 0$ magnet model, the calculations have been described by Wheeler and Pfeuty[15] and by Kennedy and Wheeler,[16] to whom we refer the reader.

III. Experimental Methods

A. Sample Preparation. The activated polymers can be deactivated by reactions with impurities, especially with air and water.[2,40] In order to study reversible polymerization, we must avoid such irreversible deactivation. Extreme care must be taken to attain and maintain sample purity.

The materials were always handled in a high-vacuum manifold or in a glovebox with less than 4 ppm of oxygen or water.[41] Argon gas was used in the glovebox and for flushing the vacuum manifold, since nitrogen gas can have significant amounts of oxygen in it. No grease was used in the manifold valves. Even in the glovebox, transfers were made with gas-tight syringes.

All glassware was cleaned by soaking in chromic acid solution for 24 h, rinsing several times with bidistilled water, then rinsing with dilute hydrofluoric acid, and finally rinsing again several times with bidistilled water. The glassware was then dried by placing it in a vacuum oven at 373 K for several hours and by storing it in the glovebox for at least 24 h before use.

The sodium and potassium used as drying agents and in the preparation of the initiator were 99.95% pure, as obtained from Aldrich Chemical Co. They were stored and transferred in the drybox.

The monomeric α-methylstyrene as obtained from Aldrich Chemical Co. was 99% pure. It was first dried for 24 h over $CaCl_2$ and then degassed by four or five freeze–pump–thaw cycles on the vacuum manifold. Then it was distilled on the vacuum line to a flask containing a sodium mirror and dried further for several hours; usually the first sodium mirror was used up and a second was needed. The distillation removed the polymerization inhibitor (*p-tert*-butylcatechol) present in the commercial monomer. The α-methylstyrene was degassed after each mirror to remove any hydrogen produced by the reaction of water with sodium. α-Methylstyrene can be polymerized by pure sodium itself, which was indicated by the development of a light red color and by an increase in the viscosity. The beginning of such a polymerization indicates a high degree of dryness. The dry α-methylstyrene was then distilled to a storage flask on the vacuum manifold.

Just prior to the preparation of the polymer, the stored α-methylstyrene was distilled to a vessel with two connecting bulbs. One bulb contained a sodium mirror, onto which the α-methylstyrene was distilled. Then the clean α-methylstyrene was distilled to the second bulb, used to rinse that bulb, and poured back into the first bulb. The α-methylstyrene was then again distilled to the second bulb. It was then titrated with a concentrated initiator solution (injected through a septum) in the same way as was the THF (see below) to assure its absolute cleanliness.

Tetrahydrofuran (THF) as obtained from Aldrich Chemical Co. was 99.9% pure. It was degassed in the manner described above and then passed over several sodium mirrors, allowing several hours on each mirror and degassing after each mirror. The final drying stage was a distillation onto a pool of sodium–potassium alloy and a small amount of naphthalene. The naphthalene formed a small amount of the initiator sodium naphthalide, which is light green. The sodium naphthalide kept the THF clean by reacting with oxygen or water. (Over time the THF containing sodium naphthalide developed a red color, due to the formation of isomers of dihydronaphthalene[40] when the sodium naphthalide reacted with water.) The THF cleaned in this way was distilled again just before using it to make a sample.

Naphthalene as obtained from Baker Chemical Co. was >99% pure. It was dried in a desiccator with P_2O_5 for 24 h; its container was then evacuated and stored in the drybox. Then the naphthalene was weighed into a vacuum manifold flask containing a sodium mirror. Clean THF was then distilled from the sodium–potassium alloy into the flask with the naphthalene. The characteristic green of sodium naphthalide developed immediately. Since the initiator itself is decomposed by impurities, its rapid formation was an indication of the high purity of the materials. An excess of sodium over naphthalene was used in order to ensure that all the naphthalene was transformed into initiator.

The resulting initiator solution was too concentrated for the preparation of the polymer and had to be diluted by a factor of about 50. THF for the dilution, cleaned as described above, was distilled from the Na–K alloy to another flask. Since even this operation introduced impurities, the THF was further purified in the drybox by titrating out any remaining impurities by adding the concentrated initiator until a pale green color appeared and persisted.[28] This step was necessary because the more dilute initiator solution is even more sensitive to impurities. Then a known amount of the concentrated initiator solution was added to the clean THF to make the dilute initiator/THF solution. The dilute initiator solution was used within 24 h.

The dilatometer was first rinsed with a concentrated initiator solution to clean it. Then the required volume of a dilute initiator/THF solution was injected, after which the required volume of monomer was injected. The solution was then degassed several times by freezing with liquid nitrogen, pumping, and thawing. The dilatometer was closed by sealing the glass. The compositions of the three samples are given in Table I. The mole fraction of the initial monomer is denoted by x_m^* and the ratio of moles of initiator to moles of monomer is denoted by I_0. Two other samples (nos. 3 and 5) were prepared and studied[31] but are not reported here because failures in the dilatometers clearly caused significant termination of the polymer and thus compromised the data.

B. Density Measurement. We chose to use dilatometers because they allow high precision, permit the sample to remain totally sealed from the atmosphere, can be made entirely of chemically inert materials, and can be used for very viscous samples.

Our dilatometer design is shown in Figure 2. The material is Pyrex. The primary sample reservoir, A, has a volume of 12–14

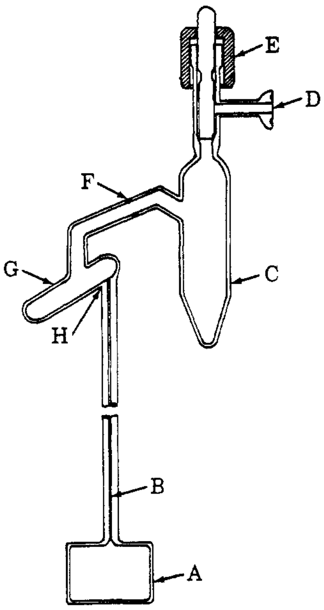

Figure 2. Dilatometer: A, primary sample reservoir; B, capillary tube (0.06-cm i.d., 200-mm length); C, degassing chamber; D, O-ring seal for connection to vacuum system; E, valve with Teflon seal; F, seal-off point; G, secondary sample reservoir; H, special joint (see text).

cm^3; the inner diameter of the capillary tube, B, is about 0.06 cm. The capillary tube, 20 cm in length, is graduated at 0.1-cm intervals and can be read with a magnifier to 0.01 cm. The primary sample reservoir contains a glass-enclosed magnetic stirring bar. The preparation chamber, C, is used as a place in which to mix the components and to degas the sample (via a connection to a vacuum line at D). The degassed sample can be temporarily sealed with the valve E until it is permanently sealed at F.

The secondary sample reservoir G allows for a large range of volume measurements. When the sample in A is heated, it rises in the capillary tube. When it reaches the top of the capillary tube, the measurements cannot proceed. Some experimenters have solved this problem by using a syringe to withdraw sample from the primary reservoir.[42] We did not want to use such a technique because the packing of the syringe is a source of leakage and contamination. We have chosen to use instead a secondary reservoir, G, in which fluid may be "stored" when the volume of the capillary tube is exceeded.[43] In order for excess fluid to flow smoothly from the capillary tube into the secondary reservoir, the reservoir must be at an angle, and the joint, H, must not allow any liquid to be trapped and flow back into the capillary tube. To make joint H, the capillary tube was cut at a 60° angle and the cut surface was polished; then the joint seal was made with a small torch flame, taking care not to damage the capillary tube.

A dilatometer was calibrated by filling with a weighed quantity of degassed distilled water and measuring the temperature at which the meniscus was at the first graduation of the capillary tube to get V_0, the volume of the primary reservoir, and measuring the height of the meniscus as a function of temperature to get the volume of the capillary tube at each graduation. We used in the values given by Kell[44] for $\rho(T)$ for water. The data listed in Table II have been corrected for the effect of the thermal expansion of V_0; the thermal expansions of the capillary tube and the stirring bar are negligible.[45] The radii of the capillary tubes varied along the length with a standard deviation ±0.0001 cm. The variation in the radii and the uncertainty in the measurement of the meniscus position set the *precision* of the dilatometers at about 4×10^{-5}. The *accuracy* of the measurements is limited by that of the compositions to about 3%.

The dilatometers were thoroughly cleaned with chromic acid solution, followed by tap water and distilled water, then dried in a vacuum oven for 24 h, and evacuated before being placed in the glovebox for filling (described above).

Table II
Mass Density, ρ, as a Function of Temperature, T, for Samples of Living α-Methylstyrene in Tetrahydrofuran, as Listed in Table I[a]

sample	point	T (K)	ρ (g/cm^3)	sample	point	T (K)	ρ (g/cm^3)
1	1	290.126	0.963 23	3	1	274.693	0.969 16
	2	290.291	0.962 67		2	275.380	0.967 77
	3	290.680	0.961 41		3	276.841	0.964 66
	4	291.072	0.960 16		4	278.125	0.961 90
	5	291.703	0.958 15		5	279.185	0.959 49
	6	292.553	0.955 37		6	281.056	0.955 04
	7	293.535	0.952 49		7	280.217	0.957 07
	8	294.490	0.950 72		8	282.126	0.952 41
	9	295.155	0.949 83		9	282.848	0.950 48
	10	296.515	0.948 33		10	283.634	0.948 43
	11	297.364	0.947 48		11	284.138	0.947 03
	12	299.570	0.945 29		12	284.500	0.946 04
	13	300.782	0.944 11		13	284.910	0.944 80
	14	303.746	0.941 25		14	285.362	0.943 46
	15	306.535	0.938 58		15	285.838	0.942 19
	16	309.916	0.935 43		16	286.361	0.940 63
	17	313.209	0.932 26		17	286.970	0.938 82
	18	316.038	0.929 55		18	287.453	0.937 28
2	1	282.577	0.969 71		19	287.835	0.936 12
	2	283.130	0.968 39		20	288.445	0.934 22
	3	284.058	0.966 05		21	288.961	0.932 62
	4	285.553	0.962 16		22	289.453	0.931 20
	5	286.403	0.959 82		23	289.950	0.929 91
	6	287.452	0.956 84		24	290.475	0.928 87
	7	288.591	0.953 48		25	290.976	0.928 03
	8	289.512	0.950 66		26	291.457	0.927 40
	9	290.612	0.947 20		27	292.017	0.926 67
	10	291.583	0.944 22		28	292.547	0.926 04
	11	291.112	0.945 64		29	293.340	0.925 18
	12	292.272	0.942 41		30	294.306	0.924 24
	13	293.137	0.940 76		31	295.427	0.923 03
	14	293.527	0.940 12		32	296.941	0.921 40
	15	294.208	0.939 18		33	298.537	0.919 79
	16	294.951	0.938 46		34	300.192	0.918 13
	17	296.011	0.937 33		35	301.888	0.916 39
	18	296.606	0.936 70		36	303.391	0.914 81
	19	298.142	0.935 19		37	305.024	0.913 09
	20	300.656	0.932 67		38	306.008	0.912 15
	21	302.426	0.930 89				
	22	304.114	0.929 24				
	23	306.220	0.927 17				
	24	308.138	0.925 31				

[a] The data are from the first heating run of each sample and are listed in the order in which the measurements were made.

The dilatometer design in Figure 2 was used for samples 2 and 4. For example 1, the design was different in that a Teflon valve was attached to the primary sample reservoir. The valve on sample 1 made it more susceptible to termination by impurities.

C. Temperature Control and Measurement. A dilatometer was held in a water/ethylene glycol bath, the temperature of which was controlled with an analog controller.[46,47] The temperature was measured with a digital platinum resistance thermometer.[48] The precision of the temperature measurements was limited by the temperature control to 0.002 K. The accuracy of the temperature measurements is 0.01 K.

D. Procedures. The filled and sealed dilatometer was placed in the bath at a temperature below T_p and the temperature increased. At each temperature, the sample was allowed to equilibrate until the meniscus height became constant. At temperatures below T_p, the equilibration times were 50–100 min; these relaxation curves contain information about the rate constant for depolymerization which we will report and analyze in more detail in a later paper.[31] At temperatures above T_p, apparent equilibration times were 5–10 min; however, we also saw hysteresis above T_p, which we will discuss below (section IV.B).

When during heating the sample meniscus reached the top of the capillary tube, the temperature was increased to force some of the sample into the secondary reservoir. Then the temperature was returned to its value just before the transfer of the sample to the secondary reservoir, and measurements were resumed.

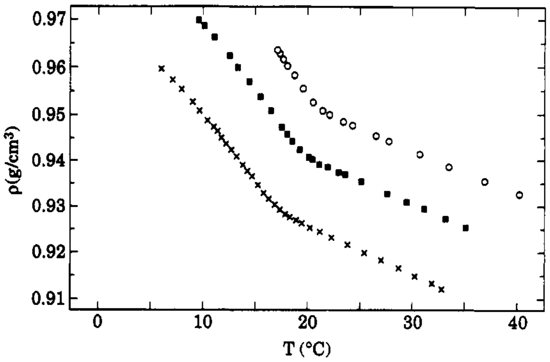

Figure 3. Mass density, ρ, as a function of temperature, T, for samples of living poly(α-methylstyrene) in tetrahydrofuran, as listed in Table I: sample 1 (○), sample 2 (■), sample 4 (×). Data shown are from the first heating run for each sample, as listed in Table II.

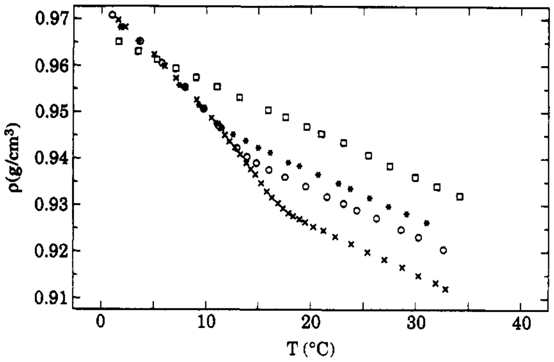

Figure 4. Mass density, ρ, as a function of temperature, T, for three consecutive runs on sample 4 (see Table I): run 1 (×), run 2 (○), run 3 (*). Also shown are data for the same sample after complete termination of the polymer (□).

The volume of the sample transferred was calculated from the change in the meniscus height and used to calculate the mass of sample remaining in the primary reservoir. The transfers introduced no discernible "jumps" in $\rho(T)$.

After a heating sequence, the bath was cooled and all the sample returned to the primary reservoir. Measurements were made on several heating sequences. Our design precluded making measurements during cooling.

IV. Results and Analysis

Our measurements of the mass densities, ρ, as functions of temperature, T, for the first heating runs of each of the three samples are plotted in Figures 3–5 and listed in Table II. Note that for each sample the density increases as the temperature decreases and then increases at a still greater slope after the onset of polymerization. Note also the dependence of the overall density range on x_m^*: the greater x_m^*, the greater the density.

A. Polymerization Line. As discussed in section II.1, in the course of our measurements of the mass density, we have measured three points on the polymerization line for living poly(α-methylstyrene) in THF. By examining Figure 3 (the measurements from the first heating runs for each sample), we estimated the values of T_p as the temperatures at which $\rho(T)$ changes slope from its linear behavior at higher temperatures.

These measurements of the ceiling temperature as a function of the initial monomer concentration, listed in Table I as T_p^e, are shown in Figure 1, along with other measurements from the literature[25–30] and along with measurements made in our own laboratory during the course of studies of the shear viscosity of living poly(α-methylstyrene) in THF using sodium naphthalide as the initiator[24] and in methylcyclohexane using n-butyllithium as the initiator[31] and during studies of the small-angle neutron scattering from living poly(α-methylstyrene) in tetradeuterofuran using the sodium naphthalide initiator.[32] The measurements made in our group, by different workers and during very different experiments, are consistent with one another. We note that our sets of data lie on the same line, within the scatter, independent of the solvent and of the initiator.

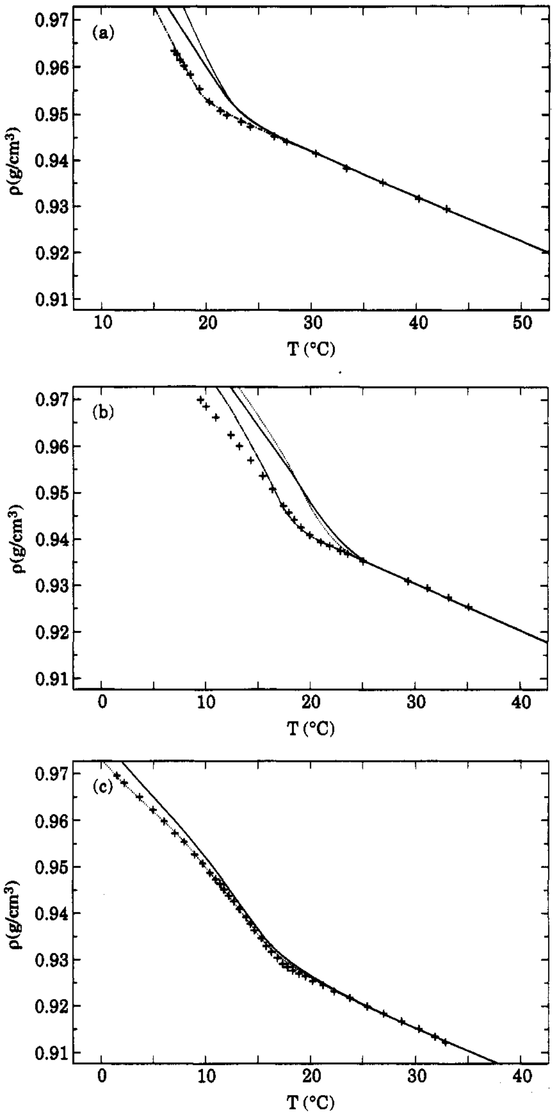

Figure 5. Mass density, ρ, as a function of temperature, T, for samples of living poly(α-methylstyrene) in tetrahydrofuran (see Table I), comparing the first heating run for each sample to the predictions of the $n \rightarrow 0$ magnet model and of the mean-field model. Figure 5a shows the data (+) for sample 1, Figure 5b shows those for sample 2, and Figure 5c for sample 4. In each case, the mean-field model prediction is shown as a solid line, the $n \rightarrow 0$ model using T_p^e is shown as a dotted line, and the $n \rightarrow 0$ model using T_p^p is shown as a dot-dash line.

However, as discussed in section II.1, our $T_p(x_m^*)$ data lie lower in temperature by about 10 K than do the data from the literature. We have noted above that we believe our measurements to be "truer" measurements of the polymerization in that we measure directly the changes in various physical properties due to the onset of polymerization.

Another possible cause of the difference between our measurements and those in the literature is that the physical properties which we study do not respond to the presence of polymer until there is a certain amount present, whereas the polymerization line should represent the very onset of polymerization. The fact that we get the same line regardless of the property we study (density, viscosity, neutron scattering) and regardless of whether the measurement is made by heating (density) or cooling (viscosity and neutron scattering) encourages us to believe that we are close to the true polymerization line.

We must also consider the possible effects of the presence of dead polymer on T_p. As we will show below, the presence of dead polymer raises the background density at temperatures above T_p, thus causing an apparent lowering of T_p. Dead polymer can only form from living polymer, so if a sample has never been cooled below T_p and thus has never contained living polymer, then it cannot contain dead polymer. For our studies of the density and the viscosity, the samples were frozen in the course of their preparation, in order to degas them. It is not likely that polymer formed during the fast freezing in liquid nitrogen, but it is possible that polymer formed during the subsequent warming of the samples. On the other hand, the samples used for neutron scattering had never been frozen, had never been cooled below T_p, and thus contained no dead polymer. We also note that, for the studies in the literature, those of Ivin and Leonard[29] and of Leonard and Malhorta[30] had been frozen, but the samples in all the other literature studies shown in Figure 1 had never been cooled below T_p. There seems to be no correlation, in our samples or in the literature, between the values of T_p and the freeze–thaw history of the sample. We therefore assume that there is no significant effect of dead polymer for the first heating runs, from which we determined T_p^e.

Our 12 data points do not suffice to determine both parameters in the Dainton and Ivin equation (eq 5), but if we fix $\Delta H_p°$ at the value measured calorimetrically of -35 kJ/mol of monomer (or -8.4 kcal/mol),[37] then we find[34] $\Delta S_p°$ to be -110 ± 1 J/(mol of monomer·K) (or -26.2 ± 0.2 cal/mol·K), where the uncertainty is given at the 99% confidence interval. This value for $\Delta S_p°$ is consistent with those in the literature.[1,2] Setting $x_m^* = 1$ in eq 5 and using these values of $\Delta H_p°$ and $\Delta S_p°$, we find $T_p = 48$ °C for pure α-methylstyrene. We used these values of $\Delta H_p°$ and $\Delta S_p°$ in all the data analysis.

B. Density Measurements. Let us first consider the hysteresis mentioned above. Figure 4 shows three heating runs for sample 4, together with data taken on the sample after the termination of all the polymer. Run 1 was made over a time period of 9 days, after which the sample was returned to the primary reservoir and run 2 was begun; run 2 took place over the next 7 days and run 3 over the next 10 days. The complete termination of the sample occurred 4 months after runs 1–3 and was caused by the accidental breaking of the glass casing of the stirrer bar.

We note that the density above T_p increased with each cycle for sample 4; such shifts were also observed for samples 1 and 2. We observed similar shifts with time and temperature in our measurements of the shear viscosity of this system.[24] We can think of two reasons for this upward shift of the density: (1) the termination of the polymer molecules, and (2) the metastable persistance of polymer molecules above T_p. As is shown by the measurements on the "dead" sample in Figure 4, polymer termination does lead to an increase in the background density. In spite of our care in sample preparation, impurities could have been present and could have caused polymer termination; the polymer molecules could have been terminated by reaction with the Pyrex cell walls; the polymer molecules could have been terminated by side reactions, such as the reaction of the sodium counterion with a hydride ion from the polymer.[2] Our subsequent studies of the small-angle neutron scattering from this system[32] have shown that, once formed, polymers can persist metastably unless the return to the region above T_p is achieved very slowly, with time for full equilibration at each step, or unless the sample is "annealed" by heating it to temperatures well above T_p. We believe that the shift in the density in the samples reported here was due to the termination of polymer molecules. We think this is more likely than a persistance of metastable polymers because these heating runs were done very slowly. We believe that the very first heating run is the most reliable data set. It is possible that some dead polymer was present even in this run, but we are encouraged by the absence of any discontinuities whenever the samples rested overnight during the data collections and by the consistency of the values of T_p from the first density runs with the values of T_p from our neutron scattering experiments,[32] for which the samples had never been cooled below T_p and thus could have no dead polymer (see section IV.A). Therefore, we report and analyze the density data from the first heating run for each sample.

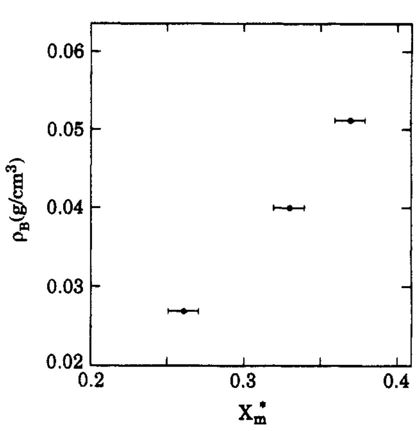

Figure 6. Background density parameter, ρ_B, as a function of the initial monomer concentration, x_m^*. The data are listed in Table I.

Figure 5 shows the data from the first run of each sample, together with predictions of the $n \to 0$ magnet model and of the mean-field model. The theoretical predictions were made with the parameter values given in scheme II: parameters were varied to test for sensitivity by visual examination of plots such as in Figure 5, but the parameters were not optimized by least-squares analysis.

In calculating the pedictions of the $n \to 0$ model, we used $\Delta v° = -0.159$; tests using -0.153 showed no significant effect. For the $n \to 0$ model parameter am_0 (which is related to the amplitude of the free energy[7]), we used 1.74, which is the value used by Kennedy and Wheeler for living polymers,[16] as opposed to the value 1.45, which they used for sulfur;[23] tests showed a change to 1.45 had no effect for sample 1, worsened the agreement for sample 2, and bettered the agreement for sample 4. Making I_0 smaller by a factor 2 had no effect for any sample.

Two parameters did emerge as important. First, it was necessary to add a background density to the theoretically predicted value:

$$\rho(T) = [v(T)]^{-1} + \rho_B \tag{9}$$

where $v(T)$ was calculated from eq 4 and ρ_B was determined by matching the experimental density to the calculated density at one point above T_p. These values of ρ_B are given in Table I and plotted in Figure 6. Second, the experimental values of T_p (determined as the temperatures at which $\rho(T)$ first deviated from the linear behavior at high temperatures) gave the best fit to the data only for sample 4, not for samples 1 and 2; Table I gives the experimental polymerization temperature (T_p^e) and the polymerization temperatures which give the best predictions from eq 9 (T_p^p).

In our analogous study of $\rho(T)$ near the polymerization temperature of liquid sulfur,[49] we found the agreement between the $n \rightarrow 0$ model and the data to be much improved if $\Delta v°$ were reduced to 60% of its expected value. Similar adjustments of $\Delta v°$ did not improve the agreement between the $n \rightarrow 0$ model and the data for living α-methylstyrene in THF.

The predictions of the mean-field model are also shown in Figure 5. The same values of ρ_B were used (eq 9, Table I) as for the $n \rightarrow 0$ magnet model. These predictions are not sensitive to the choice of T_p. Making I_0 smaller by a factor of 2 worsened the agreement with the data.

V. Discussion

We see from Figure 5 that the $n \rightarrow 0$ magnet model gives the correct *qualitative* behavior for $\rho(T)$ only after the addition of ρ_B to each data set. The need for ρ_B must be a reflection of the nonideality of the real solutions, whereas eq 4 assumes the solutions to be ideal. We note that we did not introduce a temperature dependence for ρ_B but merely used a temperature-independent constant. That ρ_B is positive means that the "excess volume" which it reflects is negative, which is to be expected for an ionic solution.[50] That ρ_B increases with x_m* (Figure 6) is reasonable, since the more concentrated the solution, the greater the nonideality.

The $n \rightarrow 0$ magnet model using for T_p the values T_p^e does not *accurately* represent the data below T_p for samples 1 and 2 but provides a beautiful representation for sample 4. One hypothesis is that this inaccuracy is also related to the nonideality of the solution: that the nonideality would be increasingly severe in the polymerizing region is not unreasonable; that the nonideality would be less severe in the most dilute solution is also not unreasonable. However, the dramatically better representation of sample 4 as compared to samples 1 and 2 is surprising. The fact that the description of the data for samples 1 and 2 can be made more satisfactory by adjusting T_p from T_p^e to T_p^p is also surprising, since it is hard to think of a reason why the "true" T_p would be *below* T_p^e. A "true" T_p *above* T_p^e could result if our indicator of the transition, the change of slope of $\rho(T)$, did not respond to the very onset of polymerization. It is likely that sample 4 was the best of the samples (i.e., contained less contamination from dead polymer) due to the improvement of our experimental technique with time and experience. Perhaps the presence of some dead polymer distorted $\rho(T)$ in such a way as to make $T_p^p < T_p^e$ for samples 1 and 2.

Figure 5 indicates that the mean-field model (with the addition of a background density) also gives good *qualitative* descriptions of the data. For samples 1 and 2, the mean-field theory gives predictions comparable to those of the $n \rightarrow 0$ magnet model when T_p is set at T_p^e, but its pedictions cannot be improved by changing T_p. For sample 4, for which $T_p^e = T_p^p$, the mean-field theory is not as successful as the $n \rightarrow 0$ magnet model.

VI. Conclusions

We present here measurements of the mass density as a function of temperature for solutions of living poly(α-methylstyrene) in tetrahydrofuran, initiated by sodium naphthalide. This work is a part of our program to study the thermodynamic and transport properties of systems undergoing equilibrium polymerization. We have published studies of the viscosity,[51] the mass density,[49] and phase equilibria with a solvent[52] near the equilibrium polymerization transition in liquid sulfur and a study of the liquid–liquid coexistence curve for living polystyrene in cyclohexane.[53] Such experiments are very difficult because it is so hard to prepare samples sufficiently free of impurities that they can be studied over a period of time without significant termination of the polymer. We believe the measurements reported in this paper to be the first density measurements to be published for a solution of a living polymer. The measurements are subject to the criticism that there may have been some termination of the polymer in the course of even the very first heating run. We respond that the three different samples are consistent with one another and that the work we present is the best that has been done or can presently be done.

Our previous study of the mass density of polymerizing sulfur[49] indicated that the $n \rightarrow 0$ magnet model does not give even a good qualitative description of $\rho(T)$ for sulfur and that the mean-field model gives only a qualitative description; it was proposed that liquid sulfur may belong in the $n = 1$ universality class because of its capability for forming ring polymers. The appropriate equation of state for an $n = 1$ model of equilibrium polymerization has not yet been developed, so no test of that model for sulfur could be made. We note that the data on $\rho(T)$ for liquid sulfur did not require the addition of a background density, which is understandable because the solution of polymeric sulfur in monomeric sulfur should be nearly ideal.

In the present study of the mass density of living poly(α-methylstyrene) in tetrahydrofuran (initiated by sodium naphthalide), we find that both the mean-field model and the $n \rightarrow 0$ model give good qualitative predictions of $\rho(T)$, once a background density, ρ_B, is added as a temperature-independent parameter. The need for ρ_B is understandable as an excess density of mixing, due to the nonideality of the solution which was ignored in both models. The accuracy of the $n \rightarrow 0$ model is better than that of the mean-field model for the two most concentrated samples, but only if T_p is adjusted downward by about 2 K from the value deduced from the deviation of $\rho(T)$ from its background behavior at the higher temperatures. For our best prepared and most dilute sample, the $n \rightarrow 0$ magnet model gives a beautifully accurate description of the data.

The more appropriate form of the n-vector magnet model would be the *dilute* $n \rightarrow 0$ model, for which the equation of state which we need to describe our data has not yet been developed. It is interesting that the $n \rightarrow 0$ model, strictly applicable for the polymerizing system in the absence of the solvent, works as well as it does in the presence of the solvent; this suggests that the presence of the solvent does not affect the extent of the conversion of monomer to polymer as a function of $T_p - T$, if T_p is taken as that of the monomer in the solvent.

We conclude that both models include the essential features of the polymerization transition in α-methylstyrene, except for the considerable nonideality of the solution. The $n \rightarrow 0$ model seems to be capable of more accurate predictions. We will test this conclusion further with other studies of this system and with studies of other living polymer solutions.

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References and Notes

(1) Sawada, H. *Thermodynamics of Polymerization*; Marcel Dekker, Inc.: New York, 1976.
(2) Szwarc, M. *Carbanions, Living Polymers, and Electron-Transfer Processes*; Interscience: New York, 1968.
(3) Webster, O. W. *Science* **1991**, *251*, 887.
(4) Tobolsky, A. V. *J. Polym. Sci.* **1957**, *25*, 220.
(5) Tobolsky, A. V.; Eisenberg, A. *J. Am. Chem. Soc.* **1960**, *82*, 289.
(6) Tobolsky, A. V.; Eisenberg, A. *J. Colloid Sci.* **1962**, *17*, 49.
(7) Wheeler, J. C.; Kennedy, S. J.; Pfeuty, P. *Phys. Rev. Lett.* **1980**, *45*, 1748. Wheeler, J. C.; Pfeuty, P. *Phys. Rev. A* **1981**, *24*, 1050.
(8) Stanley, H. E. *Introduction to Phase Transitions and Critical Phenomena*; Oxford University Press: New York, 1971.
(9) Scott, R. L. *J. Phys. Chem.* **1965**, *69*, 261.
(10) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(11) Wheeler, J. C.; Pfeuty, P. *Phys. Rev. Lett.* 1981, *46*, 1409; *J. Chem. Phys.* **1981**, *74*, 1050.
(12) Cordery, R. *Phys. Rev. Lett.* **1981**, *47*, 457.
(13) Helfrich, W.; Müller, W. In *Continuous Models of Discrete Systems*; University of Waterloo Press: Waterloo, Belgium, 1980.
(14) Wheeler, J. C.; Petschek, R. G.; Pfeuty, P. *Phys. Rev. Lett.* **1983**, *50*, 1633. Petschek, R. G.; Pfeuty, P.; Wheeler, J. C. *Phys. Rev. A* **1986**, *34*, 2391.
(15) Wheeler, J. C.; Pfeuty, P. *Phys. Rev. Lett.* **1981**, *46*, 1409; *J. Chem. Phys.* **1981**, *74*, 6415.
(16) Kennedy, S. J.; Wheeler, J. C. *J. Chem. Phys.* **1983**, *78*, 953.
(17) Wheeler, J. C. *Phys. Rev. Lett.* **1984**, *53*, 174; *J. Chem. Phys.* **1984**, *81*, 3635.
(18) Corrales, L. R.; Wheeler, J. C. *J. Chem. Phys.* **1989**, *90*, 5030.
(19) Dreyfuss, M. P.; Dreyfuss, P. *Polymer* **1965**, *6*, 93; *J. Polym. Sci., Polym. Chem. Ed.* **1966**, *4*, 2179; *Adv. Polym. Sci.* **1967**, *4*, 528.
(20) Szwarc, M.; Levy, M.; Milkovich, R. *J. Am. Chem. Soc.* **1956**, *78*, 2656.
(21) For example: Hui, K. M.; Ng, T. L. *J. Polym. Sci.* **1969**, *7*, 3101.
(22) Dainton, F. S.; Ivin, K. J. *Nature* **1957**, *162*, 705.
(23) Kennedy, S. J.; Wheeler, J. C. *J. Chem. Phys.* **1983**, *78*, 1523.
(24) Ruiz-Garcia, J. Ph.D. Dissertation, University of Maryland at College Park, College Park, MD, 1989.
(25) McCormick, H. W. *J. Polym. Sci.* **1957**, *25*, 488; **1959**, *49*, 327.
(26) Worsfold, D. J.; Bywater, S. *J. Polym. Sci.* **1957**, *26*, 299.
(27) Cunningham, R. E. *Nature* **1957**, *19*, 729.
(28) Tobolsky, A. V.; Rembaum, A.; Eisenberg, A. *J. Polym. Sci.* **1966**, *45*, 347.
(29) Ivin, K. J.; Leonard, J. *Eur. Polym. J.* **1970**, *6*, 331.
(30) Leonard, J.; Malhorta, S. L. *J. Polym. Sci.* **1983**, *9*, 1983.
(31) Zheng, K. M. Ph.D. Dissertation, University of Maryland at College Park, College Park, MD, 1991.
(32) Pfeuty, P.; Bellissent, R.; Boué, F.; Ploplis Andrews, A.; Zheng, K.; Andrews, K. P.; Greer, S. C., work in progress.
(33) Klages, F.; Möhler, K. *Chem. Ber.* **1948**, *81*, 411.
(34) Andrews, K. P.; Jacobs, D. T. *Physics Academic Software*, submitted. The program is a nonlinear least-squares routine which takes into account the correlations among parameters.
(35) Boundy, R. H., Boyer, R. F., Eds. *Styrene: Its Polymers, Copolymers, and Derivatives*; Reinhold: New York, 1952; p 698.
(36) Kroschwitz, J. I., Ed. *Encyclopedia of Polymer Science and Technology*; John Wiley: New York, 1989; Vol. 16, p 17.
(37) Roberts, D. E.; Jessup, R. S. *J. Res. Natl. Bur. Stand.* **1951**, *46*, 11.
(38) Kilroe, J. G.; Weale, K. E. *J. Chem. Soc.* **1960**, 3849.
(39) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; John Wiley: New York, 1989; p V-82.
(40) Fetters, L. J. *J. Res. Natl. Bur. Stand.* **1966**, *70A*, 421.
(41) Vacuum/Atmospheres Co., Hawthorne, CA 90250.
(42) Morrison, G.; Knobler, C. M. *J. Chem. Phys.* **1976**, *65*, 5507.
(43) Beysens, D.; Perrot, F. *Rev. Phys. Appl.* **1984**, *19*, 917.
(44) Kell, G. S. *J. Phys. Chem. Ref. Data* **1977**, *6*, 1109.
(45) The data in ref 31 have not been corrected for the thermal expansion of V_0.
(46) Greer, S. C. In *Building Scientific Apparatus*, 2nd ed.; Moore, J. H., Davis, C. C., Coplan, M. A., Eds.; Addison-Wesley: Reading, MA, 1989.
(47) Model PTC-41, Tronac, Inc., Orem, UT.
(48) Model 9540B, Guildline Instruments, Inc., Orlando, FL.
(49) Zheng, K. M.; Greer, S. C. *J. Chem. Phys.* **1992**, *96*, 2175.
(50) Gurney, R. W. *Ionic Processes in Solution*; Dover: New York, 1962; p 188.
(51) Ruiz-Garcia, J.; Anderson, E.; Greer, S. C. *J. Phys. Chem.* **1989**, *93*, 6980.
(52) Anderson, E. M.; Greer, S. C. *J. Chem. Phys.* **1988**, *88*, 2666.
(53) Ruiz-Garcia, J.; Greer, S. C. *Phys. Rev. Lett.* **1990**, *64*, 1983; **1990**, *64*, 3204.

Registry No. Poly(α-methylstyrene) anion, 37263-52-8.