Living poly(α-methylstyrene) near the polymerization line: VIII. Mass density, viscosity, and surface tension in tetrahydrofuran

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We consider the polymerization of α-methylstyrene, initiated by sodium naphthalide in the solvent tetrahydrofuran on time scales that permit full thermodynamic equilibrium between the monomer and the polymer. We present new measurements as a function of temperature of the mass density, the shear viscosity, and the liquid–vapor surface tension, and we compare the data to theoretical expectations when the polymerization is viewed as a phase transition. The mass density is well described by either mean field or nonmean field theories. The shear viscosity increases as the average degree of polymerization (DP) increases, but the exponent 3.4 is not reached, presumably because the DP is too small. The surface tension increases as the DP increases, indicating depletion of the polymer from the surface. © *2001 American Institute of Physics.*
[DOI: 10.1063/1.1346636]

I. INTRODUCTION

Equilibrium polymerization refers to the equilibrium, reversible formation of polymers from monomers. While the nature of the monomeric species (organic, inorganic, protein, amphiphilic), the nature of the bonds joining the monomers into polymers (covalent, ionic, hydrophobic), and the nature of the driving force for the polymerization or aggregation (enthalpic, entropic) vary, there are many common features to these systems. Such common features encourage us to learn more details about a particular system, in the hope that what we learn may be generalized to many other systems.

To this end, we have been studying the equilibrium polymerization of α-methylstyrene, initiated by sodium naphthalide in the solvent tetrahydrofuran to form a difunctional propagating/depropagating polymeric species.[1] We have previously studied various properties of this system near the ceiling temperature: the mass density,[2] the structure by small angle neutron scattering,[3] the extent of polymerization,[4] the shear viscosity,[5] the heat capacity,[6] the chemical kinetics,[7] and the development of the molecular weight distribution.[8] We have reviewed the issues in the physical chemistry of such systems.[9–11] We present here new measurements of the mass density, the liquid–vapor surface tension, and the shear viscosity for poly(α-methylstyrene) in tetrahydrofuran, made under conditions of equilibrium between the monomer and the polymer. The mass density and viscosity measurements are improvements over our previous efforts. The surface tension measurements, the first effort on such a system, are more qualitative than quantitative. We compare to the theoretical expectations for the behavior of these thermophysical properties.

A. Mechanism

Above the "ceiling temperature," T_p, α-methylstyrene initiated by sodium naphthalene reacts irreversibly and completely to form an active dimer:[1]

$$2l + 2M \rightarrow {}^-M_2^- , \tag{1}$$

but does not form a polymer. Below T_p, the active dimer propagates from both ends to form an active polymer:

$$^-M_2^- + M \rightleftharpoons {}^-M_3^- , \tag{2}$$

$$^-M_x^- + M \rightleftharpoons {}^-M_{x+1}^- . \tag{3}$$

Termination of the active polymers is avoided by careful attention to experimental procedure. At equilibrium, the polymers have a most probable distribution of molecular weights; the average molecular weight of that distribution gets larger as the temperature decreases below T_p.[8]

As the temperature is varied from above T_p to below T_p, to further below T_p, we expect the density, the viscos-

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ity, and the surface tension to reflect the change in the microscopic structure of the system, from monomers to polymers to larger polymers.

B. Theoretical background and prior experiments

1. General theory

Models for equilibrium polymerization have been at hand for 40 years, beginning with the work of Tobolsky and Eisenberg.[12] We focus here on recent work by Wheeler and co-workers,[13–20] and by Dudowicz et al.[21–23]

Dudowicz et al.[21–23] have recently developed a mean field lattice model of equilibrium polymerization that explicitly allows for a finite initiator concentration and for interaction between monomer and solvent. They have calculated a number of physical properties and find good qualitative agreement with observed behavior. The input parameters required for the implementation of this lattice theory are the enthalpy and entropy of propagation, and the initial concentrations of monomer and initiator.

For all mean field theories, the equation for the extent of polymerization, which is the fraction of initial monomer converted to polymer, is:[4]

$$\phi(T) = x_m^p(T)/x_m^0, \qquad (4)$$

with

$$x_m^p(T) = x_m^0 - x_m(T) \qquad (5)$$

and then

$$x_m(T) = x_m^0 - \{(x_i/2)[2 - K_p(T)x_m(T)]\}/$$
$$\{1 - K_p(T)x_m(T)\}, \qquad (6)$$

where x_m^0 is the initial mole fraction of monomer, $x_m^p(T)$ is the mole fraction of monomer incorporated into polymer, $x_m(T)$ is the mole fraction of monomer at equilibrium, x_i is the initial mole fraction of initiator, and $K_p(T)$ is the equilibrium constant for the polymerization step [Eqs. (2), (3)]. Equation (6) is a quadratic equation in $x_m(T)$. It follows that[12]

$$DP(T) = 2\phi(T)/r, \qquad (7)$$

where $r = N_i/N_m^0 = x_i/x_m^0$ and N represents the number of molecules of a given species. Then $x_i = r x_m^0$. The equilibrium constant, $K_p(T)$, can be obtained from $K_p(T) = \exp[(-\Delta H_p^0 + T\Delta S_p^0)/RT]$, where ΔH_p^0 and ΔS_p^0 are the enthalpy and entropy of polymerization in the standard state of pure monomer, and R is the gas constant. Values of ΔH_p^0 and ΔS_p^0 for α-methylstyrene are available from independent experiments, as will be discussed below.

Wheeler et al.[13–20] built on the work of de Gennes[24] and des Cloizeaux[25] to model equilibrium polymerization as a second order phase transition in the $n \to 0$ universality class. They predict a truly second order transition only at infinitely small concentrations of initiator: in the language of magnetic phase transitions, the initiator concentration is an "external field," and the transition is second order at zero external field. The model assumes that there is no energy of mixing between the monomer and the solvent, and that the system is close enough to the critical point for a parametric equation of state to be valid. The input parameters required for the implementation of this nonmean field theory are, as for the mean field model, the enthalpy and entropy of propagation in the standard state of pure monomer, and the initial concentrations of monomer and initiator. In its mean field limit, this theory is the same as the theory of Tobolsky and Eisenberg.[12] Comparisons of this model to experiments on poly(α-methylstyrene) have shown that the nonmean field theory gives a very good description of measurements, but that the mean field limit also does very well for many properties.[10,11]

For the nonmean field model of Wheeler et al. for equilibrium polymerization in a solvent, the extent of polymerization is obtained from:[20]

$$[K_p^{c0}(1+\zeta)/K_p(T)] - 1 = r(1 - b^2\theta^2), \qquad (8a)$$

$$x_b = \tfrac{1}{2} a\, m_0 \gamma r^{1-\alpha}\theta^2, \qquad (8b)$$

$$x_p = \tfrac{1}{2} a\, m_0 r^{2\cdot\alpha}\theta^2(1-\theta^2), \qquad (8c)$$

$$x_s = [\zeta/(1+\zeta)](1 - x_b - x_p), \qquad (8d)$$

which are Eqs. (5) and (12) in Ref. 20. The equilibrium constant K_p^{c0} refers to that for the pure monomer polymerizing at its T_p, which is calculated from ΔH_p^0 and ΔS_p^0 by putting $T = T_p^0$ for pure monomer. Indeed, $T_p^0 = \Delta H_p^0/\Delta S_p^0$. The parameter $\zeta(T)$ is the activity of the solvent relative to monomer, and is to be evaluated. Parameters $r(T)$ and $\theta(T)$ are parametric variables[20] indicating the proximity to the "critical point." The quantities $x_b(T)$, x_p, and x_s are the mole fractions of monomer-to-monomer bonds, polymer molecules, and solvent molecules, respectively. The constants α and γ are the critical exponents.[26] The constants a, m_0, and b are constants in the parametric representation.[13,19] Kennedy and Wheeler[19] have pointed out that for a case in which the dimer is the propagating species, there may be a distribution of locations of the initial dimer within the polymer molecules, and that this feature may affect the correspondence to the $n \to 0$ model. The model can be solved numerically at each temperature in order to calculate:

$$\phi(T) = (x_b(T) + x_p)/x_m^0. \qquad (9)$$

2. Mass density

The lattice-based theories of Kennedy and Wheeler[14] and of Dudowicz et al.[21] assume that all lattice sites occupy the same volumes and, therefore, do not immediately give a change in mass density on polymerization. Kennedy and Wheeler calculated the mass density as a function of temperature with two main assumptions:[2,14]

(1) Assuming no change of volume on mixing, they wrote the total specific volume, v, at a given temperature as:

$$v(T) = v_m(T)\phi_m(T) + v_p(T)\phi_p(T) + v_s(T)\phi_s, \qquad (10)$$

where v is the specific volume, ϕ with a subscript is the weight fraction in the solution, and subscripts m, p, and s refer to pure monomer, pure polymer, and pure solvent, respectively, and where the small amount of initiator is ig-

nored. 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, then

$$\phi_p(T) = \phi(T)(m_0/m_T),$$
$$\phi_m(T) = (1 - \phi(T))m_0/m_T, \quad \phi_s = m_s/m_T, \tag{11}$$

where $m_T = m_0 + m_s$, and ϕ_s is the only weight fraction which does not change with temperature.

(2) To introduce the temperature dependence, they assumed linear thermal expansions:

$$v_m(T) = v_m^0[1 + \alpha_m(T - T_p)],$$
$$v_p(T) = v_p^0[1 + \alpha_p(T - T_p)], \tag{12}$$
$$v_s(T) = v_s^0[1 + \alpha_s(T - T_p)],$$

where the α_m, etc., are the cubic thermal expansion coefficients, and the superscript ''0'' refers to the quantity at T_p. Combining Eqs. (10)–(12) and rearranging, Kennedy and Wheeler obtained:

$$v(T) = v_m^0[1 + \alpha_m(T - T_p)]m_0/m_T$$
$$+ v_s^0[1 + \alpha_s(T - T_p)]m_s/m_T$$
$$+ \Delta v^0[1 + \alpha(T - T_p)]\phi(T)m_0/m_T, \tag{13}$$

where $\Delta v^0 = (v_p^0 - v_m^0)$ is the change in volume on polymerization, and where $\alpha = (\alpha_p v_p^0 - \alpha_m v_m^0)/\Delta v^0$. Then $\rho(T) = 1/v(T)$. Given all the thermodynamic parameters in Eq. (13), we can use the mean field theory [Eqs. (4)–(6)] or the nonmean field theory [Eqs. (8)–(9)] to calculate $\phi(T)$ and thus $\rho(T)$.

Another approach is to consider the excess volume of the solution as a function of temperature. We can consider either the specific excess volume:

$$v_E(T) = v(T) - v_m(T)m_0/m_T - v_s(T)m_s/m_T, \tag{14}$$

or the molar excess volume:

$$V_E(T) = V(T) - x_m^0 V_m(T) - x_s V_s(T), \tag{15}$$

where V, V_m, and V_c are the molar volumes of the solution, the monomer, and the solvent, respectively (ignoring again the very small amount of initiator). Then we have from Eq. (13)

$$v_E(T) = \Delta v^0[1 + \alpha(T - T_p)]\phi(T)m_0/m_T, \tag{16}$$

or

$$V_E(T) = \Delta V^0[1 + \alpha(T - T_p)]\Phi(T)x_m^0, \tag{17}$$

where ΔV^0, the change of molar volume on polymerization, is $M\Delta v^0$, and M is the average molecular weight of the initial solution of monomer and solvent. By measuring $V_m(T)$ and $V_s(T)$, we can avoid assumption (2) [Eqs. (12)].

Prior experimental tests of Eq. (13) include measurements on polymerizing sulfur[27] and on poly(α-methylstyrene).[2] The earlier measurements on poly(α-methylstyrene) were made in a dilatometer with a resolution of 40 ppm, and required starting well below T_p and heating while measuring the density. This procedure can cause the production of metastable polymers.[3] Moreover, the dilato-

metric measurements showed considerable drift with time. The new measurements we present here, made in the magnetic suspension densimeter with a resolution of 20 ppm, show little change with time and were made on cooling from above T_p. We were also able to measure the densities of the monomer and the solvent in the same instrument and thus can calculate the excess volume for comparison to Eq. (17).

3. Shear viscosity

As the temperature of the solution of monomers and initiators in solvent passes through the ceiling temperature, polymers begin to form. While the number of polymer molecules is constant and is determined by the concentration of initiators, the average molecular weight and the volume fraction of the polymers both increase as the temperature decreases, and thus the viscosity of the solution increases as temperature decreases. Following Graessley,[28] we expect that the shear viscosity at zero shear rate, η_0, as a function of the concentration, c, for a concentrated polymer solution ($c \gtrsim 0.25$ g/cm^3) and as a function of the weight average molecular weight, M_w, to have the form:

$$\eta_0 \propto (cM_w)^b. \tag{18}$$

For nonentangled polymers (molecular weights $< 10^4$ g/mol, or degree of polymerization, DP, $< 10^2$), the exponent ''b'' is predicted[29] and measured[30] to be unity. For entangled polymers at high molecular weights, ''b'' is predicted to be 3.0,[31] but measured to be 3.4.[32] The crossover from $b=1$ to $b=3.0/3.4$ should occur at the molecular weight at which the polymer chains become entangled.

Our previous measurements of the shear viscosity of poly(α-methylstyrene) were made with a falling ball viscometer and had a resolution of 1%–4% with shear rates of 4 to 18 s^{-1}.[5] These new measurements made with the magnetic suspension rheometer have a resolution of about 4% and shear rates of 0.01–0.2 s^{-1}.

4. Surface tension

A solution of ''living'' poly(α-methylstyrene) is a solution of a polydisperse linear polymers, with both the ends negatively charged and carrying sodium counterions. Some of those ion pairs are solvent-separated,[33] leaving some of the polymers with net charges. Uncharged polymer chains in a good solvent can either adsorb onto the liquid–vapor interface and thus decrease the surface tension relative to that of the pure solvent, or the chains can deplete from the liquid–vapor interface and increase the surface tension relative to the pure solvent.[34] Charged species deplete from the surface and increase the surface tension.[35]

There are no prior reports of the surface tension of a solution of polymer in equilibrium with monomer. We report measurements with the magnetic suspension tensiometer of the surface tension of poly(α-methylstyrene) in tetrahydrofuran, precise to 6%. This precision does not permit a quantitative analysis, but confirms the depletion from the surface.

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II. EXPERIMENTAL METHODS

We have used a magnetic suspension instrument to measure the mass density, the shear viscosity, and the liquid–vapor surface tension, as functions of temperature, for a sample of poly(α-methylstyrene) initiated by sodium naphthalide in tetrahydrofuran.

A. Sample preparation

Samples in which equilibrium polymerization is to be studied must be prepared with great attention to the elimination of water and air, which terminate the "living" polymers. We have described our sample preparation in great detail previously, and refer the reader to those earlier papers.[8,36] We take particular care to keep the samples above T_p until we are ready to make measurements, so that the initiator can act as a scavenger to remove any residual air or water, and so that no "dead" polymers can form.

The sample used in this study was prepared from 3.528 g α-methylstyrene and 12.665 g tetrahydrofuran. Thus the initial mole fraction of monomer, x_m^0, was 0.1453 ± 0.0001. Initiator was added to reach a ratio of moles initiator to moles initial monomer, r, of $(2.5 \pm 0.1) \times 10^{-3}$. The sample was contained in a sealed borosilicate glass cell which fitted into the densimeter.[37]

B. Magnetic suspension densimeter/rheometer/tensiometer

Magnetic densimeters operate by suspending a magnetic buoy in the fluid of interest by means of the magnetic field of a solenoid.[38–40] In our instrument, the buoy is designed to float in the sample fluid, and the magnetic field is arranged to pull the buoy down into the fluid. The buoy position is sensed (e.g., by a differential transformer[41]) and that information is used in a feedback loop to control the current in the solenoid and thereby maintain the buoy in a fixed vertical position. The support current in the solenoid is a measure of the density of the fluid. If the cell containing the fluid is attached to a computer-controlled positioner, then the sample cell can be moved relative to the suspended buoy; the change in the support current due to the viscoelastic force on the buoy is a measure of the shear viscosity of the sample fluid.[42–45] If the positioner is used to move a liquid–vapor meniscus into contact with the buoy, then the change in the support current due to the force of the surface on the buoy is a measure of the surface tension of the sample fluid.

1. Density measurements

We have measured density in our laboratory with a magnetic densimeter for some years.[41,46,47] A balance of the forces on the buoy leads to the expression:[37,39]

$$\rho = A + BV^2, \tag{19}$$

where ρ is the mass density of the sample fluid in which the buoy is suspended, V is the voltage across a standard resistor in series with the solenoid, and A and B are calibration constants to be determined by suspending the buoy in fluids of known density. Figure 1(a) shows the calibration of this buoy in seven fluids,[36] which results in $A = 0.8540$

± 0.0004 g/cm^3 and $B = 0.117 \pm 0.002$ g/cm^3 V^2, where the uncertainty is one standard deviation. This calibration sets the *accuracy* of the density measurement at 0.1% for 99% confidence. The inherent *precision* of the density measurement is determined by the resolution, δV, of the voltage (± 0.0002) to be $2B\delta V$ V. At a typical V of 0.3 V, the precision is thus 20 ppm. The actual reproducibility is limited by sample conditions (see below).

2. Viscosity measurements

Our densimeter has been modified by the addition of a computer-controlled positioner for the sample cell, enabling the measurement of viscosity and surface tension in addition to density.[37] The essential features are a Newport Model 435 translation stage to provide precision vertical movement of the sample cell, under the control of a Newport Model 850A-2 linear actuator, which is in turn controlled by a Newport PMC-200P motion controller connected to a computer via a GPIB interface. The actuator has a position resolution of 0.1 μm and speeds of 40–500 μm/s. The buoy is brought into suspension and the density is measured as described above. Then the cell is moved at velocity, v, relative to the suspended buoy; the flow of the sample past the buoy exerts a viscoelastic force on the buoy, which changes the support current (voltage) required to maintain the suspension of the buoy. The balance of the forces on the buoy leads to the relation:[37,42,44]

$$\eta = C(\rho_v - \rho)/v, \tag{20}$$

where η is the viscosity of the fluid in which the buoy is suspended, C is a calibration constant, ρ_v is the apparent density when the cell is moving at velocity v, and ρ is the density measured when $v = 0$. Figure 2(a) shows the calibration of our buoy in four liquids of known viscosity; the behavior is, indeed, linear and has a zero intercept at $v = 0$. We find η(Pa s)$ = [913 \pm 13] \times 10^{-3}((\rho_v - \rho)/v)$, where ρ and ρ_v are in g/cm^3 and v is in mm/s and the uncertainty in C is given as one standard deviation. The viscosity measurements thus had a calibration accuracy of 4% at a 99% confidence level. The precision of the measurements for this sample was 2×10^{-4} Pa s or 4%. The maximum shear rates can be calculated[48] from $3v/2R$, where v is the velocity, and are very low, 0.01 to 0.2 s^{-1}. The data of Sakai *et al.*[49] on terminated poly(α-methylstyrene) in α-chloronaphthalene suggest[5] that the viscosity of the polymer solution we study will be independent of shear rate below 10–20 s^{-1}.

3. Liquid–vapor surface tension measurements

If the cell is moved downward until the liquid–vapor interface touches the suspended buoy, then the buoy is subjected to a force due to the surface tension, and the change in solenoid support current is a measure of that surface tension. A balance of the forces on the buoy[36] indicates that the surface tension, σ, is related to the change in the measured density from a value ρ when there is no surface force, to a value ρ_z when the buoy stretches the interface by a distance z:
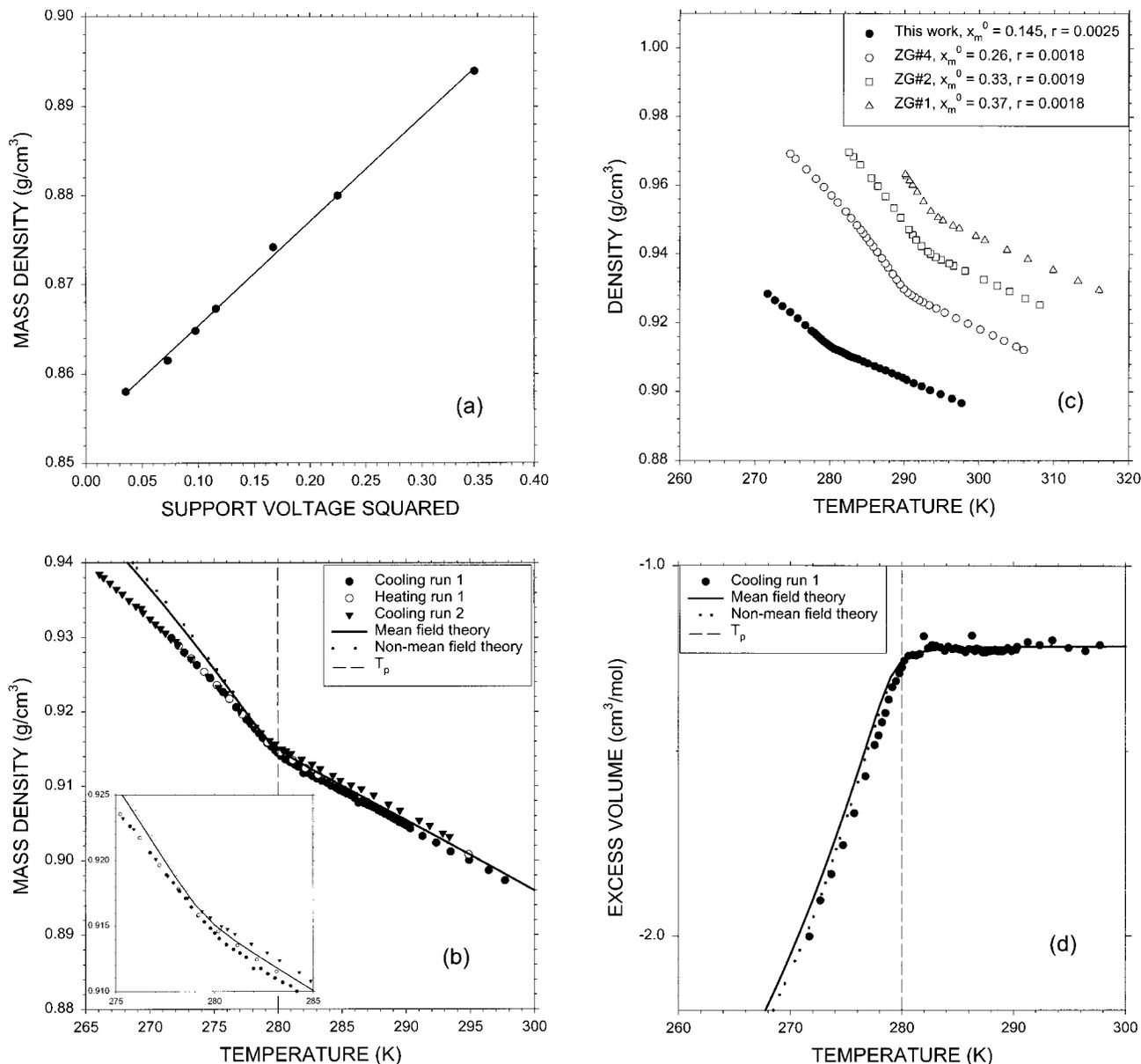
$$\sigma = D(\rho - \rho_z)/z, \tag{21}$$

FIG. 1. (a) Calibration of the magnetic suspension densimeter/rheometer for density measurements, with seven samples of known density, where the expected errors on the points are less than the size of the symbols and the scatter is caused by systematic differences among the standard fluids; (b) Mass density as a function of temperature for living poly(α-methylstyrene) in tetrahydrofuran, for an initial mole fraction of monomer of 0.1453 and a ratio of moles initiator to moles initial monomer of 0.0025, as measured by magnetic suspension densimeter on three runs and compared to the theoretical prediction (see text); (c) Comparison of new measurements to published measurements of Zheng and Greer (ZG) (Ref. 2); (d) Excess molar volume obtained from data in Fig. 1(a) (see text) and compared to theoretical calculation [Eq. (17)]. In (b) and (d), the dashed vertical lines indicate $T_p = (280 \pm 1)$ K.

where D is a calibration constant. The calibration of the buoy for surface tension with five fluids of known surface tension is shown in Fig. 3(a).[36] The y intercept of σ as a function of $(\rho - \rho_z)/z$ was expected to be zero but is not; we do not understand the source of this constant. The calibration gives σ (mN/m or dyne/cm) = $(7.5 \pm 1.7) + (596 \pm 42)(\rho - \rho_z)/z$, where ρ is in g/cm^3 and z is in mm and the uncertainties are given as one standard deviation. Thus the surface tension measurements are accurate to 20%. The scatter of the data (see below) is about 3%.

C. Temperature control and measurement

The temperature is controlled by pumping a mixture of water and ethylene glycol from a water bath, through insu-

lated lines and past the sample cell.[37] The temperature in the water bath[50] is controlled by an analog temperature controller (Tronac, Provo, UT, model PTC-41) to a precision of 1 mK.

The temperature at the sample cell is measured by a 5000 Ω thermistor (YSI, Yellow Springs, OH, model 46044) mounted near the sample cell. The thermistor is in series with a 50 KΩ standard resistor (Vishay Intertechnology, Malvern, PA) and a mercury battery.[50] The ratio of the voltage across the thermistor to that across the standard resistor is a measure of the temperature; it was calibrated against a calibrated platinum resistance thermometer and then the ''true'' temperature fitted to a power series in the ratio of voltages. As a result, the temperature is resolved to 0.2 mK
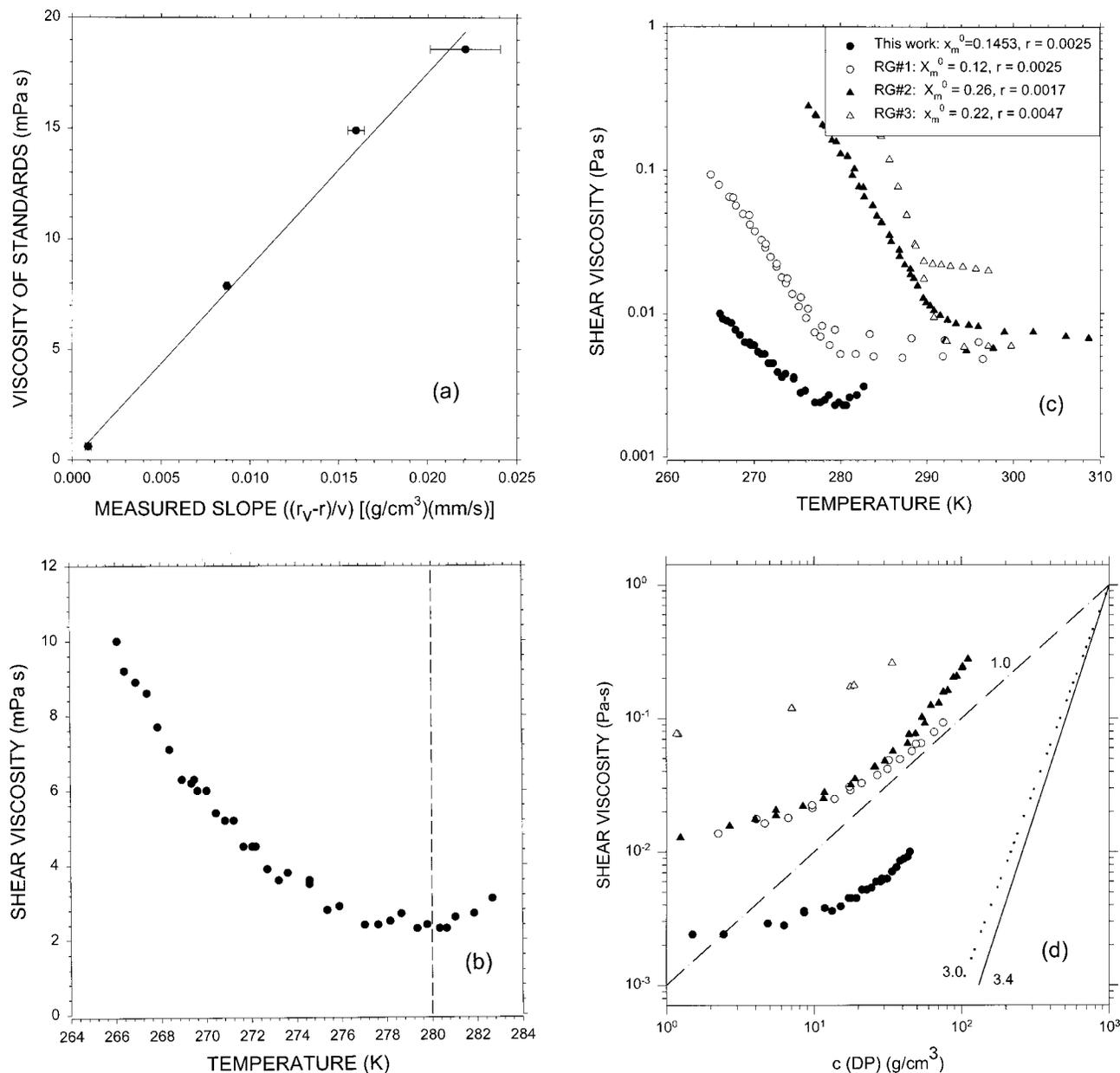
FIG. 2. (a) Calibration of the magnetic suspension densimeter/rheometer for viscosity measurements, with four samples of known viscosity (Ref. 36); (b) Shear viscosity as a function of temperature for living poly(α-methylstyrene) in tetrahydrofuran, for an initial mole fraction of monomer of 0.1453 and a ratio of moles initiator to moles initial monomer of 0.0025, as measured by magnetic suspension densimeter/rheometer on cooling run 2, with the dashed vertical line indicating $T_p = (280 \pm 1)$ K; (c) Comparison of new measurements to published measurements of Ruiz-Garcia and Greer (RGG) (Ref. 5); (d) Comparison of new data and RGG data [same symbols as in (c)] to theoretically expected exponential behavior at low molecular weight (slope=1) and high molecular weight (slope=3), and to experimental behavior usually observed (slope=3.4); the abscissa is the concentration (g/cm^3) times the degree of polymerization, DP (Ref. 32). In (b) and (d), the dashed vertical lines indicate $T_p = (280 \pm 1)$ K.

and is accurate to 10 mK. The long time (days) fluctuations in the temperature as measured by the thermistor were 2–3 mK.

D. General procedure

The sample was prepared in June of 1997, and the first cooling and heating density measurements were made in the month immediately thereafter. The subsequent density-viscosity-surface-tension measurements were made in the fall of 1997.

For a measurement run, the sample was thoroughly stirred at room temperature and then placed in the instrument. The temperature was decreased or increased stepwise.

After temperature control was achieved, the sample was allowed to equilibrate. On the first cooling and heating sequence, when only the density was measured, we allowed the sample to equilibrate until the support voltage became constant (about 15 min above T_p and about 60 min below T_p). On the later runs, the sample equilibrated for about 18 h before the measurements were made.[8]

III. RESULTS AND DISCUSSION

A. General

In the theoretical calculations for comparison with the experiments, we need values for the enthalpy and entropy of
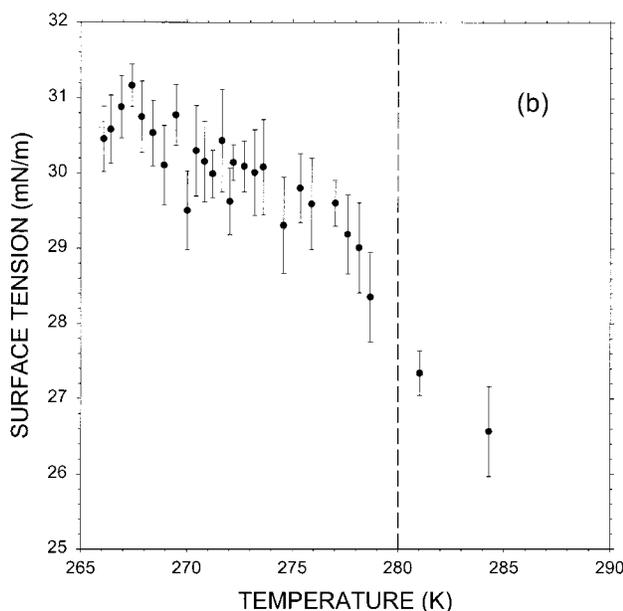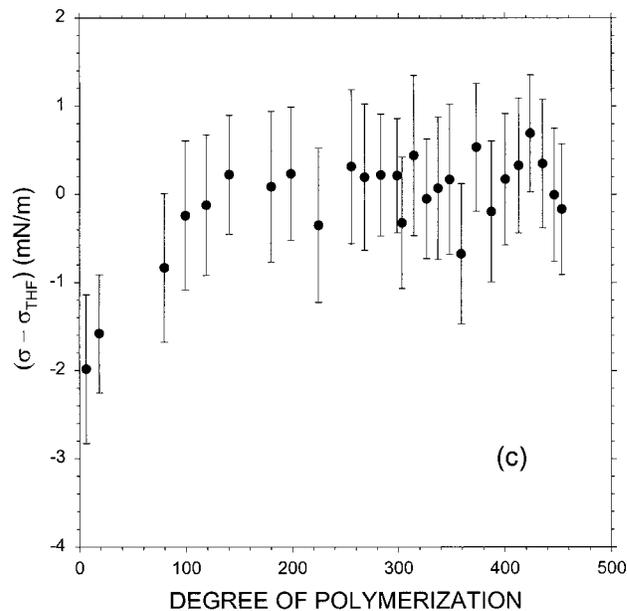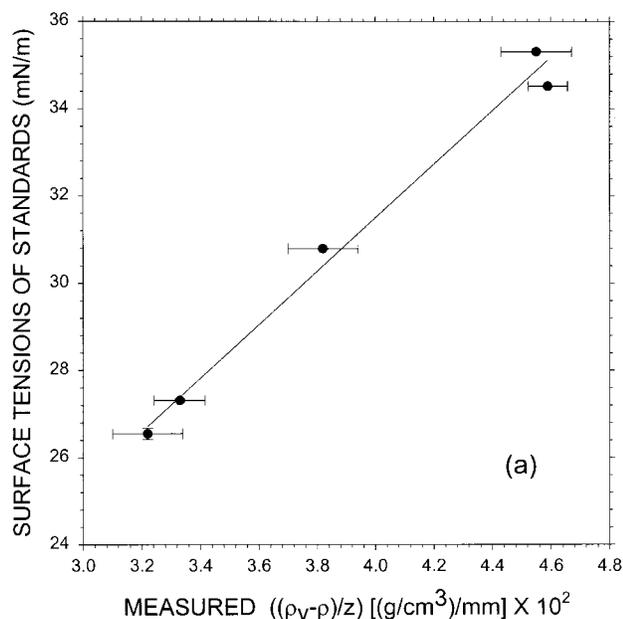
FIG. 3. (a) Calibration of the magnetic suspension densimeter/rheometer for surface tension measurements, with four samples of known viscosity (Ref. 36); (b) Surface tension as a function of temperature for living poly(α-methylstyrene) in tetrahydrofuran, for an initial mole fraction of monomer of 0.1453 and a ratio of moles initiator to moles initial monomer of 0.0025, as measured by the magnetic suspension densimeter/rheometer on cooling run 2, and with the dashed vertical line indicating $T_p = (280 \pm 1)$ K; (c) The difference between the surface tension of the solution and that of the pure solvent, as a function of the degree of polymerization as calculated from the mean field theory.

polymerization, ΔH_p^0 and ΔS_p^0. Roberts and Jessup[51] measured ΔH_p^0 for α-methylstyrene by combustion calorimetry and obtained (-35.2 ± 1.0) kJ/mol. ΔS_p^0 has been estimated to be -110 J/mol K by Van't Hoff or, equivalently, Dainton-Ivin,[52] analyses of the equilibrium monomer concentration.[53,54] Comparisons of experimental data with mean field theory for some properties have given best agreement for $\Delta S_p^0 = -105$ J/mol K.[3,4]

Figure 4 shows the extent of polymerization of poly(α-methylstyrene) as a function of temperature for the sample under study here, as calculated from the mean field theory [Eqs. (4)–(6)] and from the nonmean field theory [Eqs. (8)–(9)], for various values of ΔH_p^0 and ΔS_p^0. We have previously measured the extent of polymerization and established that this mean field theory describes the extent data.[4] It is clear from Fig. 4 that: (1) the calculations are more sensitive to ΔS_p^0 than to ΔH_p^0; (2) the values $\Delta H_p^0 = -35.2$ kJ and

$\Delta S_p^0 = -110$ J/mol K are choices that will give a T_p in the range seen experimentally for this sample; and (3) the mean field and nonmean field results are very similar. This choice of ΔS_p^0 of -110 J is different from that made $(-105$ J) by Das *et al.*,[4] for their most comparable data set, but the T_p for this sample was higher by 6 K for the Das data sets, and thus the difference could reflect the temperature dependence of ΔS_p^0.

B. Density measurements

Figure 1(b) shows the measurements of the density, ρ, on two cooling runs and one heating run; the data for the first cooling run are listed in Table I and remaining data are available.[36] We observe a change in slope of $\rho(T)$ at the polymerization temperature, T_p. We observe no jump or discontinuity in $\rho(T)$ at T_p, within our resolution of 20 ppm.

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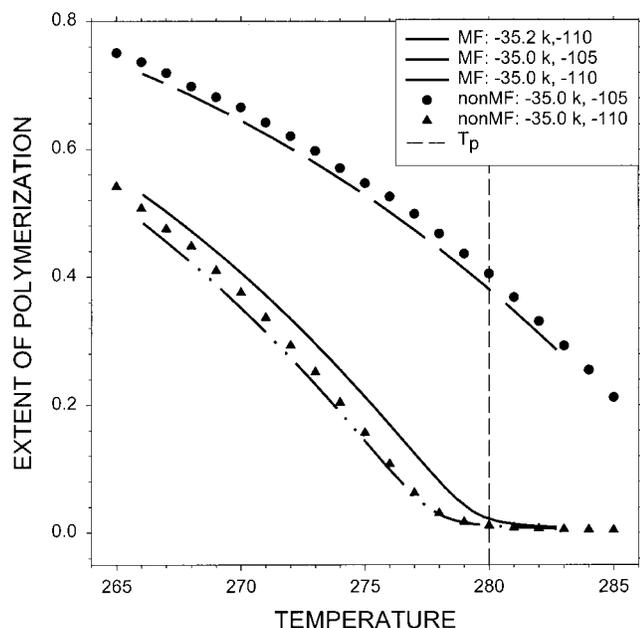
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FIG. 4. Predicted behavior of the extent of polymerization of poly(α-methylstyrene) for an initial mole fraction of monomer of 0.1453 and a ratio of moles initiator to moles initial monomer of 0.0025, as a function of temperature, as calculated from the mean-field theory [Eqs. (4)–(6)] and from the nonmean field theory [Eqs. (8)–(9)] with the legend indicating various values for the enthalpy and entropy of polymerization: ΔH_p^0 in kJ/mol and ΔS_p^0 in J/mol K. The dashed vertical line indicates a $T_p = (280 \pm 1)$ K, as indicated from the experiments.

We note a slight difference (about 0.01%) in the density above T_p from cooling run 1 to heating run 1, and a still larger difference (about 0.1%) for cooling run 2, made about three months after cooling run 1. This effect is similar to, but much smaller than, the shifts seen in the dilatometric measurements made on this system by Zheng and Greer.[2] Those dilatometer measurements had the disadvantage that, due to the instrument design, they could be made only on heating runs; thus the sample had to be cooled well below T_p before measurements began, and then heated during data collection. It has been our experience that once the living polymers form, they can persist metastably after heating above T_p. However, the shifts in $\rho(T)$ above T_p are rather small and do not alter the qualitative behavior of the system. The very good reproducibility of the $\rho(T)$ data below T_p indicates that the sample of living poly(α-methylstyrene) did not deteriorate significantly over the time period of the experiments.

Figure 1(c) compares the new data to the first runs of the earlier dilatometric measurements of Zheng and Greer.[2] The two sets of measurements are consistent with one another in terms of the overall dependence of ρ on x_m^0, and in terms of the dependence of the location of T_p on x_m^0.

We now compare the new data to the predictions of theory. The required parameters for Eqs. (13) and (17) are the masses of the components, T_p, $v_m(T)$, $v_s(T)$, $\alpha_m(T)$, $\alpha_s(T)$, $\alpha(T)$, and Δv^0. The initial masses of the components were given above. T_p is taken from the plot of $\rho(T)$ [see Fig. 1(b)] as the temperature at which the slope changes, which is 280 ± 1 K. To obtain $v_m(T)$ and $v_s(T)$, we measured the density as a function of temperature for pure

α-methylstyrene and for pure tetrahydrofuran in the magnetic densimeter, with the same buoy. For α-methylstyrene in the range 279–297 K, we find

$$\rho_m(T)(\text{g/cm}^3) = 1/v_m(T)$$
$$= (1.0645 \pm 0.0037) - (3.31 \pm 2.6)$$
$$\times 10^{-4} T - (7.3 \pm 4.5) \times 10^{-7} T^2, \quad (22)$$

where T is in K and the uncertainly is one standard deviation. For tetrahydrofuran in the range 279–297 K, we find

$$\rho_s(T)(\text{g/cm}^3) = 1/v_s(T)$$
$$= (1.088 \pm 0.036) - (4.29 \pm 2.5)$$
$$\times 10^{-4} T - (9.0 \pm 4.3) \times 10^{-7} T^2. \quad (23)$$

Then we use Eq. (22) to calculate $\alpha_m = -(1/\rho_m)(\partial \rho_m/\partial T)_p$, and likewise Eq. (23) to calculate α_s. We have shown previously that $\alpha = (\alpha_p v_p^0 - \alpha_m v_m^0)/\Delta v^0$ makes only a 5% contribution to the last term and can be ignored.[2] For Δv^0, we use[14] $\Delta v^0 = \Delta H_p^0/M T_p^0(dP/dT_p)$, with $\Delta H_p^0 = -35$ kJ/mol,[51] $M =$ molecular weight of monomer $= 118.18$, $T_p = 280$ K, and $(dP/dT_p) = +57.8$ atm/K[55] to obtain $\Delta v^0 = -0.18$ cm^3/g.

Figure 1(b) shows the predictions for the mass density as compared to the experimental data. As before,[2] we find it necessary to add a constant background density to match the theory to the data; this background value is 0.0133 g/cm^3. Both the mean field and nonmean field theories agree well with the data. The two theories are indistinguishable above T_p, and differ only slightly below T_p. Equation (13) for $\rho(T)$ assumes (a) no change of volume on mixing monomer and solvent, which is not so, and (b) linear thermal expansions for the monomer and the solvent, whereas the quadratic terms in Eqs. (22) and (23) are significant. The background ρ_B of 0.0133 g/cm^3 obtained in adjusting Eq. (12) to describe the data does not correspond to the V^E of -1.21 cm^3/mol discussed below, but is some convolution of corrections.

We get a more straightforward analysis by comparing Eq. (17) for the molar excess volume $V^E(T)$ to the experimentally determined $V^E(T)$ for cooling run 1, which we show in Fig. 1(d). The figure shows a constant ''volume change on mixing'' of about -1.21 cm^3/mol above T_p, then an increasingly negative ''effective V^E'' as the temperature decreases and polymerization progresses. We again ignore the term in α; we use the same thermodynamic parameters used above in the calculation of $\rho(T)$ for Fig. 1(b), and subtract the experimental volume of mixing of -1.21 cm^3/mol from the $V^E(T)$ obtained from Eq. (17). The mean field and nonmean predictions are nearly the same, and show a qualitative agreement with the data which is quite satisfying, given that there are no truly free parameters in the calculations.

C. Viscosity measurements

Figure 2(b) shows the measurements of the shear viscosity as a function of temperature, from cooling run 2. The viscosity is constant within error above about 279 K, then

TABLE I. Measured properties of living poly(α-methylstyrene) in tetrahydrofuran, initiated by sodium naphthalide, with an initial monomer mole fraction of 0.1453 ± 0.0001 and a ratio of moles initiator to moles monomer of $(2.5 \pm 0.1) \times 10^{-3}$. The density ($\rho$) measurements reported were made on the first cooling run. The viscosity (η) and surface tension (σ) measurements were made on the second cooling run. Uncertainties for T, ρ, and η are discussed in the text; the standard deviation for σ is listed.

T (K)	ρ (g/cm³)	T (K)	ρ (g/cm³)	T (K)	η (mPa s)	σ (mN/m)
297.705	0.89729	284.529	0.90975	284.303		26.6±0.6
296.423	0.89867	284.179	0.91001	282.671	3.1	
294.904	0.90003	283.864	0.91042	281.862	2.7	
293.470	0.90116	283.462	0.91069	281.031	2.6	27.3±0.3
292.355	0.90234	283.071	0.91102	280.654	2.3	
291.287	0.90327	282.697	0.91133	280.348	2.3	
290.332	0.90429	282.348	0.91174	279.785	2.4	
290.237	0.90446	281.983	0.91174	279.353	2.3	
290.004	0.90469	281.601	0.91260	278.700		28.4±0.6
289.816	0.90489	281.288	0.91293	278.646	2.7	
289.480	0.90512	280.968	0.91321	278.156	2.5	29.0±0.6
289.176	0.90548	280.596	0.91358	277.620	2.4	29.2±0.5
288.987	0.90568	280.237	0.91405	277.025	2.4	29.6±0.3
288.682	0.90596	280.008	0.91445	275.902	2.9	29.6±0.6
288.367	0.90622	279.791	0.91482	275.361	2.8	29.8±0.5
288.095	0.90649	279.482	0.91533	274.584	3.6	29.3±0.6
287.843	0.90674	279.157	0.91580	274.581	3.6	
287.505	0.90709	278.824	0.91647	274.578	3.5	
287.239	0.90732	278.528	0.91712	273.611	3.8	30.1±0.6
286.991	0.90748	278.223	0.91767	273.210	3.6	30.0±0.6
286.726	0.90770	277.919	0.91833	272.709	3.9	30.1±0.3
286.557	0.90793	277.560	0.91894	272.192	4.5	30.1±0.2
286.294	0.90774	276.732	0.92060	272.034	4.5	29.6±0.4
286.017	0.90837	275.719	0.92261	271.651	4.5	30.4±0.7
285.716	0.90874	274.714	0.92447	271.219	5.2	30.0±0.3
285.413	0.90896	273.673	0.92628	270.835	5.2	30.2±0.5
285.112	0.90922	272.681	0.92797	270.433	5.4	30.3±0.6
284.832	0.90945	271.698	0.92993	270.022	6.0	29.5±0.5
				269.615	6.0	
				269.476	6.3	30.8±0.4
				269.345	6.2	
				268.926	6.3	30.1±0.5
				268.391	7.1	30.5±0.4
				267.868	7.7	30.7±0.5
				267.404	8.6	31.2±0.3
				266.890	8.9	30.9±0.4
				266.406	9.2	30.6±0.5
				266.085		30.5±0.4
				266.065	10.0	

increases five-fold as the temperature decreases by 13 K. In Fig. 2(c), we compare these new data to the earlier falling ball measurements of Ruiz-Garcia and Greer (RG).[5] The present sample had a larger value of r, and thus lower degrees of polymerization and a less dramatic change in the viscosity, than did the RG samples.

In Fig. 2(c), we compare all the viscosity data to Eq. (18) by plotting the log of the shear viscosity versus the log of the product of the concentration, c, and the degree of polymerization, DP. The concentration is taken as the initial monomer concentration (0.20 g/cm³ for the present sample; see RG[5] for other values) multiplied by the extent of polymerization, $\Phi(T)$, as calculated by the mean field theory [Eqs. (4)–(7)]. The DP is used in place of M_w: DP is the number average molecular weight, M_n, divided by the monomer molecular weight and the ratio of M_w/M_n is a constant for an equilibrated Flory–Schulz molecular weight distribution.[8]

Figure 2(d) also includes three lines, to indicate the slopes [i.e., the exponent b in Eq. (18)] expected at low mo-

lecular weights ($b=1$), and at high molecular weights (entangled) both for theory (3.0) and from other experiments (3.4). This plot can be compared to Figs. 5.4–5.6 in Graessley,[28] where he plots ($c\,M_w$) and his abscissa is to be divided by 100 to compare to Fig. 2(d). At lowest (c DP), the data in Fig. 2(d) do not show the expected slopes of unity, which is probably because c is too low for the solution to be considered concentrated. The data sets do approach and pass slopes of 1, but none ever reaches a slope of 3.0/3.4, probably because the DP are too low.

D. Surface tension measurements

Figure 3(b) shows and Table I lists the surface tension measurements made on cooling run 2. The surface tension of the sample showed an overall increase of 19% as the temperature was lowered by 20 K. We also measured the surface tension of pure tetrahydrofuran as a function of temperature; those data showed a linear temperature dependence of σ_{THF}

$= (29.8 \pm 0.2) - (0.114 \pm 0.021)\, T$ (dyne/cm or mN/m),
where T is in °C and the uncertainties are one standard deviation. Then we can consider [Fig. 3(c)] the difference between the surface tension of the sample and that of the solvent, $(\sigma - \sigma_{THF})$, as a function of the average degree of polymerization as calculated (see Sec. III A) from mean field theory. We see that $(\sigma - \sigma_{THF})$ approaches the surface tension of the pure solvent as the polymer grows, from which we conclude that the polymer molecules are depleted at the surface.

IV. CONCLUSIONS

While we have previously reported mass density measurements for living poly(α-methylstyrene) in tetrahydrofuran, initiated by sodium naphthalide,[2] we are now able to prepare a better sample and to make the measurements in a magnetic suspension densimeter, avoiding cooling below T_p before the first data collection. We can use values $v_m(T)$ and $v_s(T)$ measured in the same instrument to calculate the ''excess volume'' of the polymerizing solution, for a more accurate comparison with theory. Both mean field and nonmean field theories give good agreement with the experimental density and excess volume measurements.

We have measured the shear viscosity of the equilibrated monomer+polymer in solvent as the temperature decreased and the average degree of polymerization increased. Consistent with earlier work, the data tend toward a 3.4 power law for the molecular weight dependence, but the polymers never reached a high enough molecular weight for that limiting behavior to be reached.

We measured the liquid–vapor surface tension of the equilibrated monomer+polymer in solvent as the temperature decreased and the average degree of polymerization increased. The measurements are not precise enough for a quantitative analysis, but do indicate that the polymers are depleted at the interface, which is to be expected for charged polymers. We are not aware of any prior use of a magnetic balance to measure surface tension, and we hope to develop this technique further.

ACKNOWLEDGMENT

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