FEATURE ARTICLE

Physical Chemistry of Equilibrium Polymerization

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Reversible polymerizations occur in inorganic, organic, and biological molecules. The thermodynamic states at which monomer-to-polymer reactions become favorable can be viewed as second-order phase transitions and can be profitably treated by the statistical mechanics of phase transitions. The nature and development of the microscopic structure of a solution of active polymers in equilibrium with the monomers pose interesting issues for the physical chemist.

I. Introduction

In 1956, Szwarc[1] wrote that "Polymeric molecules are born in an initiation process, they grow by a propagation process, and finally they 'die' in a termination process." In other words, the mechanisms of many polymerization reactions can be viewed as having three steps: (1) an initiation step, in which a monomer is activated to be reactive toward other monomers; (2) a propagation step, in which the activated monomer reacts with nonactivated monomers to form a polymer, which then remains active and able to gain or lose monomers; (3) a termination step, in which the active site of the polymer becomes inactive and the degree of polymerization of the polymer becomes fixed. Termination can be either "proper termination", in which the active site is deactivated, or "chain transfer," in which the active site is transferred to another molecule and induces the growth of another polymer.[2] The term "living polymer" was introduced by Szwarc[1,2] to refer to a polymerization of organic molecules in which termination is avoided, but in which true equilibrium is not necessarily reached.

Living polymerization is an important route for organic polymer synthesis for two reasons.[3,4] First, the presence of active sites on the living polymer allows for the manipulation of the polymer into interesting new polymer molecules. For example, a second type of monomer could be added to the living polymer solution and could react at the active site(s) to make copolymers, dendritic polymers, etc. Second, while both propagation and depropagation occur, the propagation reaction is usually much faster than the depropagation reaction. Thus, when polymerization commences, all initiated sites polymerize to equal extents, and all the polymer molecules are of nearly the same size. When depropagation later becomes significant, the molecular weights of the polymer molecules assume a distribution. Thus, if the living polymer molecules are terminated (the active sites deactivated by reaction with a terminating agent) before depropagation becomes important, then one can make polymers with very narrow molecular weight distributions.

When the termination step is avoided, then the active polymers can, in principle, come into chemical equilibrium with the constituent monomers. We will refer to this state as "reversible" or "equilibrium" polymerization. Considerations of living polymerizations have generally not allowed for full attainment of equilibrium but have assumed the termination of the growing polymers in an early and thermodynamically unstable state. The term "equilibrium polymerization" thus includes living polymers but is also more general in two respects: (1) It includes the approach to equilibrium, and (2) it includes reversible polymerizations other than those of organic monomers. For example, the polymerization of the protein actin[5] from a globular monomer to a filamentary polymer, which occurs by noncovalent interactions, can be treated as an equilibrium polymerization.

Let us focus on the propagation step of such a polymerization reaction.[2,6−8] For the systems of interest to us here, the entropy of propagation (ΔS_P) and the enthalpy of propagation (ΔH_P) have the same sign. There is a competition between entropic effects and enthalpic effects, and thus the sign of the Gibbs energy of propagation (ΔG_P) depends on the temperature. When ΔS_P and ΔH_P are both negative, then polymerization will occur only when the temperature is low enough for the enthalpic term in $\Delta G_P = \Delta H_P - T\Delta S_P$ to dominate; the temperature at which this occurs is called the "ceiling temperature". For example, the polymerizations of many organic molecules, including styrene and its derivatives, are exothermic and show a decrease in configurational entropy, because the monomers go from a state in which they are free in the solution to a state in which they are confined to the polymer chain. When ΔS_P and ΔH_P are both positive, then polymerization will occur only when the temperature is high enough for the entropic term to dominate; the temperature at which this occurs is called the "floor temperature". For example, the inorganic molecule sulfur has a propagation step which is endothermic and which shows an increase in configurational entropy, because the sulfur "monomers" are highly constrained rings of eight atoms, which polymerize into flexible linear chains.

For pure monomer at the polymerization temperature (ceiling or floor), $T_P = \Delta H_P/\Delta S_P$. The addition of solvent to a monomer/

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TABLE 1: Characteristics of Three Systems Showing Equilibrium Polymerization[i]

system	ΔH_P^0 (kJ/mol)	ΔS_P^0 (J/(mol K))	ΔV_p^0 (mL/mol)	T_p0 (K)	dT_p/dP (K/atm)	initiator
sulfur	13.3[a]	31[b]	−3.7[b]	432 ± 1[b]	−0.02 ± 0.01[c]	heat
α-methylstyrene	−35 ± 1[d]	−105 ± 1[e]	−18.8 ± 0.1[f]	321 ± 2[f]	0.0173 ± 0.001[g]	sodium naphthalide
actin	>0	>0	+79 ± 12[h]	NA	>0	KCl

[a] References 37, 40, and 121. [b] References 27 and 54. [c] Reference 16. [d] Reference 70. [e] Reference 79. [f] Reference 64. [g] Reference 11. [h] Reference 19. [i] ΔH_p^0 and ΔS_P^0 are the enthalpy and the entropy of propagation. T_p^0 is the polymerization temperature (ceiling or floor) for the pure monomer. ΔV_p^0 is the volume change on polymerization at T_p^0, per mole of monomer. Uncertainties are given as one standard deviation; when no uncertainty is given, none was given in the literature and is assumed that the uncertainty is equal to or greater than one in the least significant figure.

polymer system will increase the configurational entropy of the initial, monomeric state, relative to that of the final, polymeric state and therefore will lower ceiling temperatures and raise floor temperatures.[9] For the case of (1) an ideal solution and (2) no dependence of the activity of the polymeric species on chain length, then $T_p = \Delta H_P^0/[\Delta S_P^0 + R \ln(x_m^0)]$, where x_m^0 is the mole fraction of initial monomer, and ΔH_P^0 and ΔS_P^0 refer to the standard state of pure monomer; this equation is known as the Dainton–Ivin equation[6,7] and is equivalent to a Van't Hoff analysis.[10] The ceiling and floor temperatures also depend on pressure: An increase in pressure decreases the entropy of the initial monomeric solution and therefore raises ceiling temperatures[11−15] and usually lowers floor temperatures.[16] An exception is the case of actin, for which the floor temperature is raised by pressure,[17−19] because ΔS_P for actin has a different origin than that of covalent polymers (see below).

Thus, for a given monomer in a given solvent, in a phase diagram plotted in the variables pressure, temperature, and composition of initial monomer in solvent, there is a "polymerization surface". On one side of the surface, the system will consist of monomers (some of which are activated) in the solvent. On the other side of the surface, the system will consist of active polymers in equilibrium with the monomers, both in the solvent. As the system is moved further into the polymerizing region, the average chain length of the polymers will increase. Conversely, as the system is moved back toward the polymerization surface, the average chain length will decrease, until the polymerization line is crossed and the monomeric state is recovered. At constant pressure, the phase diagram may be viewed either as a "polymerization temperature" (ceiling or floor), T_p, as a function of solvent concentration, or as a "critical concentration" of monomer as a function of temperature. Furthermore, if the solvent is not a good one for the polymer, then the phase diagram is enriched by the appearance of a liquid–liquid coexistence curve, with its critical point.

If the polymerization transition can be viewed as a phase transition, then it can be treated by the statistical mechanics of phase transitions. Early workers compared polymerization transitions to discontinuous, first-order phase transitions, such as the melting/freezing transition.[5,15,20−23] In 1966, Semenchenko et al. suggested that the polymerization of sulfur might be a continuous phase transition.[24] In 1980, Wheeler et al.[25] predicted that the polymerization transition for linear polymers is a continuous, second-order transition, in the $n \to 0$ universality class, where "n" is the dimension of the order parameter.[26] Wheeler et al. applied their theory first to sulfur[25,27] and sulfur solutions[28−31] and later to organic living polymers and their solutions.[31−33] They showed that earlier "chemical equilibrium" theories of sulfur solutions,[34] of living polymers,[35−40] and of actin polymerization[5,20−23] are equivalent to the mean field limit of the $n \to 0$ model.

This non-mean field theory requires little input information: mainly ΔH_P^0 and ΔS_P^0. On the other hand, the theory assumes (1) that the solution of the monomer and the polymer in the solvent is ideal, (2) that the proximity to a critical point is such

that asymptotic critical behavior pertains, (3) that the parameters such as ΔH_P^0 do not depend on chain length, and (4) that the polymers are chains, not rings. The formation of rings alters the universality class to $n = 1$[41−44] and leads to a bicritical phenomenon,[45,46] which is the confluence of a (second order) polymerization to form chains, a (second order) polymerization to form rings, and a (first order) conversion between rings and chains.

When Wheeler and his collaborators published their theory of equilibrium polymerizations, there was little experimental work with which to test the theory. We set out to produce a body of thermophysical measurements appropriate to the task. As is always the way in research, that work led us to other interesting issues, such as the microscopic structure of a living polymer solution and the time development of that structure.

A fundamental quantity in the thermodynamic properties of a system undergoing equilibrium polymerization is the extent of polymerization, ϕ, which is the fraction of the monomer that has been converted to polymer, at equilibrium at a given temperature. Comparison of experimental values of ϕ to the mean field and to $n \to 0$ models is the most direct test of the models, since the fewest parameters are involved, but it is not necessarily the most sensitive test.

From ϕ, we can calculate the mass density,[27] ρ, and the heat capacity at constant pressure,[25] C_p, as functions of temperature. The mass density, a first derivative of the Gibbs energy, does not show a discontinuity at a second-order transition, while the heat capacity, a second derivative of the Gibbs energy, does show a discontinuity at a second-order transition.[47] We will consider the information available for these properties for each of three systems. We will also consider cases in which the solvent is a "poor" one for the polymer, and therefore there develops a liquid–liquid equilibrium, in addition to the polymer–monomer equilibrium.

We will also discuss the microscopic structure of these systems, including the transition from dilute polymer solutions near the polymerization line to semidilute[48] polymer solutions further into the polymerizing region, the nature of the molecular weight distributions, and the possibility of Coulombic associations in the organic living polymers.

II. Systems and Thermodynamics

We will consider here the equilibrium polymerizations of three different systems: sulfur, α-methylstyrene, and actin.

Table 1 lists various characteristics of these three systems. We note that sulfur and actin polymerize on heating and have floor temperatures, while α-methylstyrene polymerizes on cooling and has a ceiling temperature. Sulfur and actin polymers can break at any point on a chain (fragment); poly(α-methylstyrene) does not fragment. Chain transfer is not important for either the anionic polymerization of α-methylstyrene or the polymerization of actin; however, for sulfur, with its radical polymerization, chain transfer can occur. For α-methylstyrene, the number of polymers is determined by the essentially

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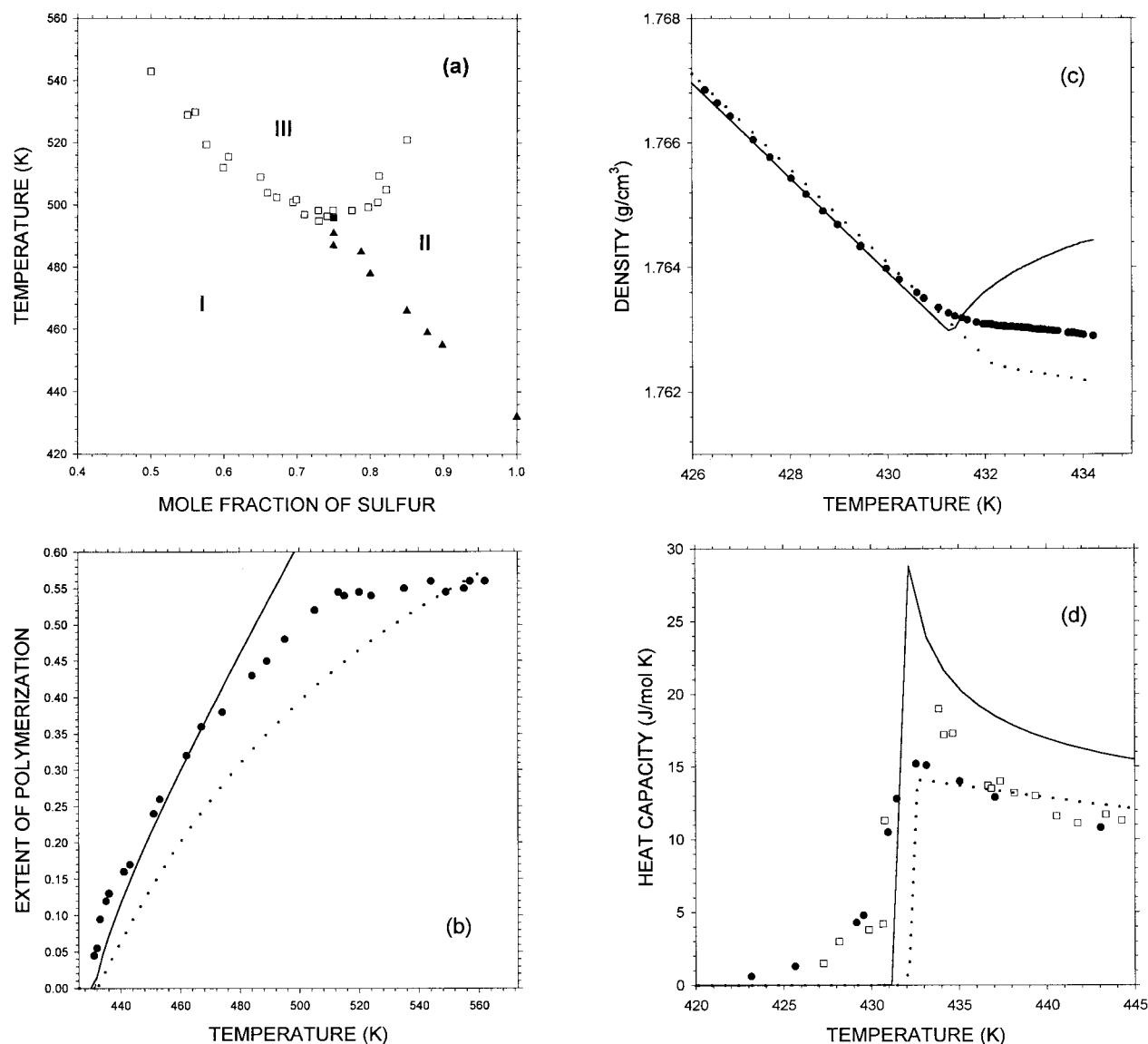
Figure 1. Equilibrium polymerization of sulfur: Comparison of experimental data with theoretical models for (a) the phase diagram in a solvent,[51,52] (b) the extent of polymerization,[53] (c) the mass density,[54] and (d) the heat capacity.[55,122] For (a), the solid triangles (▲) are points on the polymerization line; the open squares (□) are points on the coexistence curve; and the solid square (■) is the experimentally determined liquid−liquid critical point. Region I is a homogeneous mixture of monomeric sulfur in the solvent; region II is a homogeneous mixture of monomeric sulfur in chemical equilibrium with polymeric sulfur, both in the solvent; regions I and II meet at the polymerization line. Region III is a miscibility gap, with two coexisting phases. In (b)−(d), the symbols are the data, the dotted lines represent the mean field model, and the solid lines represent the non-mean field ($n \rightarrow 0$) model.

complete and irreversible initiation step and thus is permanently fixed by the number of initiator molecules. For actin and sulfur, the number of polymers formed is determined by an equilibrium constant for the initiation step. Sulfur and α-methylstyrene form fully flexible polymer chains, but polymeric actin is only semiflexible.

A. An Inorganic Monomer: Sulfur. The sulfur "monomer" is an eight-membered ring of sulfur atoms.[49] On heating to 432 K at 1 atm, the ring opens to form a diradical chain, and the chains concatenate to make long diradical chains of thousands of sulfur atoms. When the temperature is lowered below 432 K, the monomeric rings form again. Anisimov et al.[50] have reviewed the nature of the polymerization of sulfur.

Since the polymerization of sulfur is thermally initiated, the theories require the enthalpy and entropy of initiation as input information, as well as the enthalpy and entropy of polymerization.[37,40] As is clear from Table 1, these input parameters for sulfur are not well-known.

Figure 1a shows the *phase diagram* of sulfur in the solvent biphenyl, at the vapor pressure of the solution.[51,52] Region I is a homogeneous mixture of monomeric sulfur in the solvent. Region II is a homogeneous mixture of monomeric sulfur in chemical equilibrium with polymeric sulfur, both in the solvent. Regions I and II meet at the polymerization line of floor temperatures. Region III is a miscibility gap, with two coexisting phases (monomeric sulfur in the solvent on the left-hand branch and monomeric sulfur in chemical equilibrium with polymeric sulfur on the right-hand branch) and with a lower critical solution point. We will concentrate first on the case of pure sulfur, at a mole fraction of 1.0 on this diagram.

The *extent of polymerization*, φ, of pure sulfur as a function of temperature was measured by Koh and Klement[53] and first compared to the theories by Wheeler et al.[25] These measurements were difficult because they required the analysis of quenched sulfur samples. Figure 1b shows the data for φ(T), together with predictions from the mean field and the non-mean

field ($n \rightarrow 0$) models. Near T_p, the $n \rightarrow 0$ model is in reasonably good agreement with the data, but this model veers away from the data at higher temperatures and even becomes unphysical ($\phi > 1$); this is not surprising, since this theory is designed to work very near the transition. The mean field model gives a better global description of the data, even though it also is not accurate and does not level off as the data do. We cannot say whether these problems arise from the data, the input parameters, or the theories.

The *mass density*, ρ, of pure sulfur as a function of temperature was reviewed and remeasured by Zheng and Greer in 1992.[54] This was a more direct experiment than the measurement of the extent of polymerization but still was complicated by shifts in the data from run to run. This "hysteresis" has also been observed in poly(α-methylstyrene) and in actin and will be discussed below. Figure 1c shows the data from the first and most trustworthy run, compared to the predictions of the $n \rightarrow 0$ model and of the mean field model (using the parameters in Table 1).[27] First we note that no discontinuity is observed in $\rho(T)$, which is consistent with a second-order, continuous transition. However, we also see that neither theory gives a good description of $\rho(T)$. The $n \rightarrow 0$ model shows too sharp an upturn at the polymerization. The mean field model is offset in the polymerized region but gives the correct qualitative behavior. We can improve agreement by adjusting the input parameters, but the adjustments required do not seem reasonable.[54] Thus, the density, like the extent of polymerization, is consistent with a second-order phase transition but is described slightly better by the mean field model than by the $n \rightarrow 0$ model.

The *heat capacity at constant pressure*, C_p, of polymerizing pure sulfur was first compared to theory by Wheeler et al.[25] Figure 1d compares the mean field and $n \rightarrow 0$ models to the 1959 data of West[122] and to the 1971 data of Feher et al.[55] Since the theories predict only the heat capacity due to the polymerization process, the experimental data have been adjusted by subtracting a constant (35 J/(mol K) for the West data, 34 J/(mol K) for the Feher data) from each point. This introduces some error but is unavoidable since we do not have enough data to calculate the temperature dependence of the background C_p for sulfur. Once again, the mean field theory works better than the $n \rightarrow 0$ model.

Why does the $n \rightarrow 0$ model fail to describe the data for pure sulfur better than the mean field model? The pure sulfur system should be nearly an ideal solution of sulfur polymer in sulfur monomer and, in that respect, is consistent with the assumptions of the $n \rightarrow 0$ theory. The agreement is not better nearer to T_p, so the problem is not the closeness to the critical point. However, the $n \rightarrow 0$ model assumes that there are no polymeric rings, and polymeric rings are thought to be present in sulfur.[25,45,46,56–58] The equation of state needed to apply the $n = 1$ model to sulfur has not yet been developed.

Let us now return to the *phase diagram of sulfur in solution in biphenyl*, as shown in Figure 1a. For this system, the polymerization line does not meet the coexistence curve at the liquid−liquid critical point (mole fraction sulfur = 0.75, T_c = 496 K) but at a point on the sulfur-poor side (mole fraction sulfur = 0.73, T = 498 K). Except for the region between the liquid−liquid critical point and the intersection of the polymerization line, the coexisting phases are (1) a phase containing only monomeric sulfur and (2) a phase containing the polymer in equilibrium with the monomer. Katz et al.[51] found the sulfur + biphenyl diagram, as well as those of sulfur in nine other solvents, to be in qualitative agreement with the 1965 treatment

of Scott,[34] which we now know to classify as a mean field theory.[28] There has been no theoretical calculation of this phase diagram in the $n \rightarrow 0$ model, but the shape of the sulfur + biphenyl coexistence curve is consistent with proximity to a nonsymmetrical tricritical point.[28–31,52]

In summary, for sulfur, the extent of polymerization, the mass density, and the heat capacity are consistent with a second-order phase transition are described qualitatively by a mean field model and are not described well by the $n \rightarrow 0$ model. The presence of ring polymers could cause the $n \rightarrow 0$ model to be an inappropriate model. We await further development of the $n = 1$ model as a model for polymerizing sulfur.

B. An Organic Monomer: α-Methylstyrene. The monomer α-methylstyrene is convenient for study because it has a ceiling temperature which is above room temperature (321 K) for the pure monomer and which can be lowered by adding solvent.[59] The pure monomer forms a very viscous, even glassy, polymer, so we will consider living poly(α-methylstyrene) only in solution, in either a good solvent (tetrahydrofuran) or a poor solvent (methylcyclohexane). We consider the anionic polymerization of α-methylstyrene by two initiators: sodium naphthalide and *n*-butyllithium. Sodium naphthalide[60] reacts with α-methylstyrene to form a radical ion, which immediately forms a dimer with an active anionic site at each end; thereafter, monomers can be added or removed from either end. *N*-Butyllithium[61] reacts with α-methylstyrene to form an activated monomer with the alkyl part of the initiator on one side of the α carbon of the α-methylstyrene and with an active anionic site on the other side; thereafter, monomer is added or removed only at the one active site. The nature of the initiator will affect the chemical kinetics and the microscopic structure and will also affect the extent of reaction at a given temperature[62] and therefore the thermodynamic properties. The polymerization line for α-methylstyrene is the same, within experimental error, using the initiator sodium naphthalide in the solvent THF or using *n*-butyllithium in methylcyclohexane.[59] A given sample is defined by an initial mole fraction of monomer, x_m^0, and a ratio, r, of moles of initiator to moles of monomer.

Figure 2a shows the *phase diagram* of living poly(α-methylstyrene) in methylcyclohexane,[63] at a pressure of 1 atm. Region I is a homogeneous solution of monomeric α-methylstyrene in the solvent; a number of activated monomers (or dimers) will exist, determined by the number of initiator molecules. Region II is a homogeneous mixture of monomeric α-methylstyrene in chemical equilibrium with polymeric α-methylstyrene, both in the solvent. Regions I and II meet at the polymerization line of ceiling temperatures. Region III is a miscibility gap, with the two coexisting phases meeting at an upper critical solution point. The nature of the coexisting phases will depend on whether the temperature is above or below the intersection of the polymerization line with the coexistence curve.

For a good solvent such as tetrahydrofuran, the polymerization line remains, but there is no miscibility gap.[64] For this monomer (but not for all monomers), the polymerization line does not change very much as the solvent is changed from methylcyclohexane to tetrahydrofuran.[59] We will first focus on behavior near the polymerization line in tetrahydrofuran. We will compare the data to the mean field model and to the *dilute n* $\rightarrow$ 0 model, which is appropriate for equilibrium polymerization in a solvent.[33] The dilute $n \rightarrow 0$ model has the same assumptions and same input parameters as the $n \rightarrow 0$ model but has one additional parameter, which is the polymerization temperature of the pure monomer.

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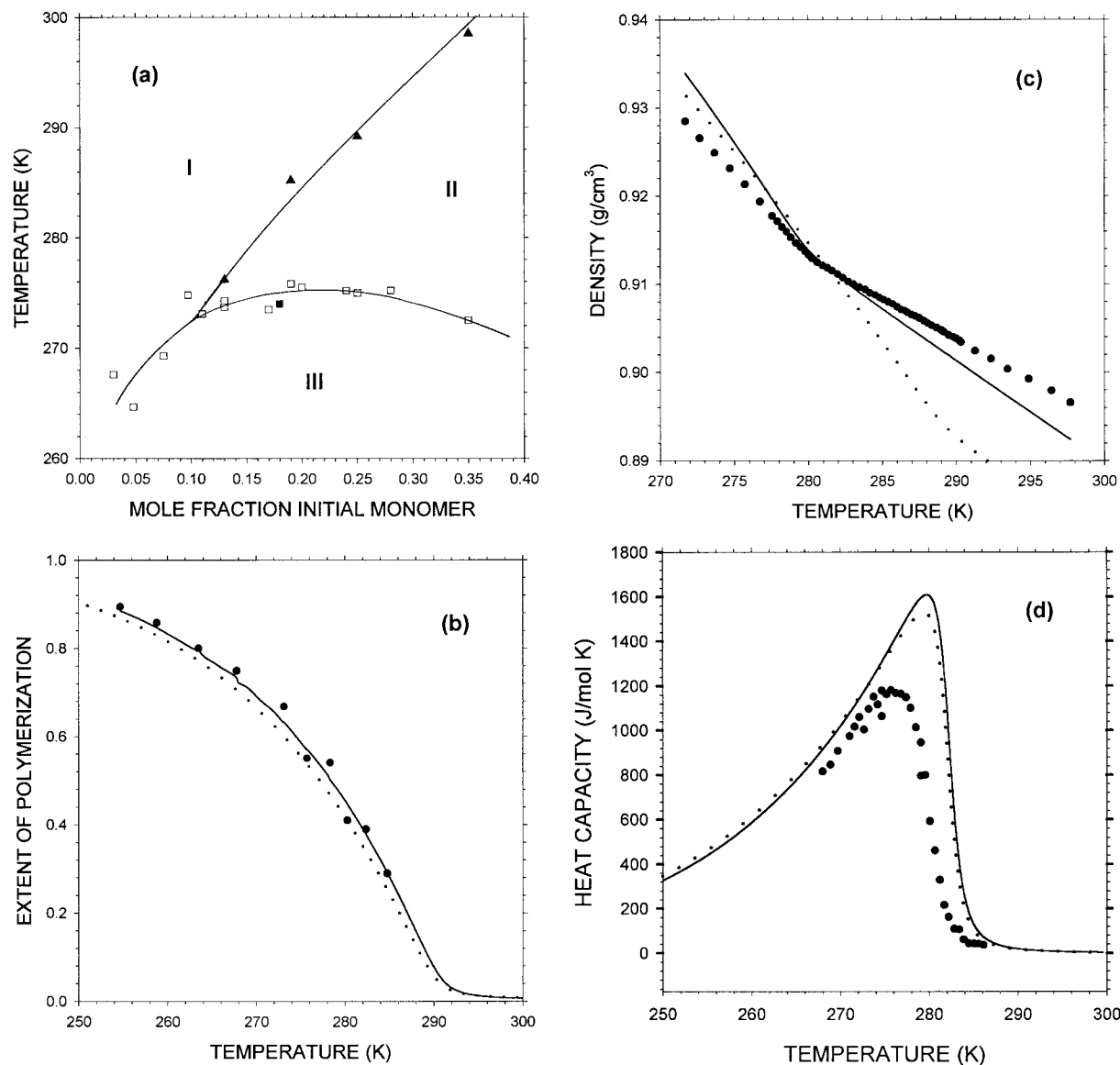
Figure 2. Equilibrium polymerization of α-methylstyrene: (a) the phase diagram in methylcyclohexane,[63] (b) the extent of polymerization,[62] (c) the mass density,[66] and (d) the heat capacity.[69] For (a), the solid triangles (▲) are points on the polymerization line; the open squares (□) are points on the coexistence curve; and the solid square (■) is the experimentally determined liquid−liquid critical point, and the lines are drawn to guide the eye. Region I is initiated monomer in solvent, region II is polymer in equilibrium with monomer, in solvent, and region III is a coexistence region of two phases. For (b)−(d), the symbols are the data, the dotted lines represent the mean field model, and the solid lines represent the non-mean field (dilute $n \rightarrow 0$) model.

Figure 2b shows the *extent of polymerization*[62] for a sample of α-methylstyrene in tetrahydrofuran, initiated by sodium naphthalide, for an initial mole fraction of monomer, x_m^0, of 0.15 and a ratio, r, of moles of initiator to moles of monomer of 4.4×10^{-3}. Both the mean-field model and the dilute $n \rightarrow 0$ model describe the measurements rather well. A statistical analysis gives a reduced goodness-of-fit (chi-squared) value[65] which is 4 times smaller for the dilute $n \rightarrow 0$ model than for the mean field model. Thus, the dilute $n \rightarrow 0$ model provides a better description of the extent of polymerization of α-methylstyrene than does the mean field model, but not dramatically better. We note that this plot for α-methylstyrene shows a "rounding" at T_p that is more noticeable than in the plot for sulfur (Figure 1b). The rounding is due to the fact that the transition is truly sharp only when the parameter analogous to the external field in the magnet model is zero; that parameter is r for α-methylstyrene[32] and is the equilibrium constant for

initiation, K_i, for sulfur.[25] Since $r > K_i$, the extent of polymerization shows more rounding for α-methylstyrene than for sulfur.

The *mass density* of polymerizing α-methylstyrene was studied by Zheng and Greer in 1992[64] and more recently by Gu and Greer.[66] Figure 2c shows the data of Gu for a sample of α-methylstyrene in tetrahydrofuran, initiated by sodium naphthalide, for $x_m^0 = 0.145$ and $r = 2.5 \times 10^{-3}$. These new measurements were made with a magnetic densimeter[67] on a cooling run. The previous measurements[64] were made in a dilatometer on heating from below T_p. We first note that, as for the density of polymerizing sulfur (Figure 1c), the density of polymerizing α-methylstyrene shows no discontinuity at the polymerization temperature and is consistent with the behavior expected at a second-order phase transition. We also note that, as for sulfur, the later runs showed evidence of incomplete depolymerization upon reheating, so we take the first cooling

run as the most reliable. While the calculation of the extent of polymerization from the theories is very direct, the calculation of the mass density from the theories requires[27] auxiliary information (the thermal expansions of the pure monomer and of the pure solvent[66] and the change in volume on polymerization[64]) and makes the assumption of an ideal solution and thus no excess volume of mixing. Figure 2c shows the calculations from the mean field and the dilute $n \rightarrow 0$ models. We have added a constant background density of 0.003 36 g/cm^3 for the mean field theory and 0.001 244 g/cm^3 for the dilute $n \rightarrow 0$ model, to account at least partly for the excess volume of mixing.[64] The agreement of the theories with these new, and presumably better, data is not as good as with the previously reported data.[64] However, the dilute $n \rightarrow 0$ model has the better overall behavior and might work very well if the temperature dependence of the excess volume were taken into account.

Figure 2d shows the *heat capacity*[68,69] at 1 atm pressure for a sample of α-methylstyrene in tetrahydrofuran, initiated by sodium naphthalide, with $x_m^0 = 0.102$ and $r = 4.8 \times 10^{-3}$. Like the heat capacity of polymerizing sulfur (Figure 1d), the heat capacity of polymerizing α-methylstyrene has a "lambda-like" anomaly, characteristic of a higher order phase transition. However, both theories give a peak in C_p that is sharper than the peak shown by the data. One possible explanation for this discrepancy is the fact that ΔH_P is assumed in the theories to be a constant, independent of degree of polymerization. In fact, calorimetric measurements of ΔH_P for poly(α-methylstyrene) show that it becomes about 15% more negative between a polymer of 50 monomers and one of 10 monomers.[70] This effect can be important for the studies of interest here, near the polymerization line where the polymers have a low degree of polymerization. Other contributions to the rounding of the heat capacity could come from the changing background heat capacity as the monomer converts to polymer,[71] from the nonideality of the solution, from the termination of one- end of the two-sited polymer molecules, and from uncertainties in the input parameters.[69] Thus, while the heat capacity data for polymerizing α-methylstyrene support the idea of a second-order phase transition, these data do not differentiate between the theoretical models.

Let us now return to the *phase diagram of polymerizing α-methylstyrene in a poor solvent, methylcyclohexane*,[63] shown in Figure 2a. We note that the initiator in this study was *n*-butyllithium ($r = 8 \times 10^{-3}$), which gives a polymer with just one active site. This diagram, like the phase diagram for polymerizing sulfur shown in Figure 1a, shows the presence of two kinds of second-order phase transitions: the polymerization transition and the liquid−liquid critical point. As the diagram shows, the polymerization line does not intersect the liquid−liquid critical point, but rather intersects the monomer-poor side of the coexistence curve. This phase diagram for a fixed initiator concentration can calculated in the mean field limit,[72] but not yet for the dilute $n \rightarrow 0$ model. The mean field model (not shown in the figure) agrees with the experimental phase diagram within its uncertainty.[63]

In summary, the equilibrium polymerization of α-methylstyrene is consistent with the model of the ceiling temperature as a second-order phase transition. The experimental data, especially the extent of polymerization as a function of temperature, are described slightly better by the dilute $n \rightarrow 0$ model than by the mean field model, but the mean field model has the virtue of simplicity.

C. A Biopolymer: Actin. Actin is a globular protein, present in all eukaryotic cells.[73,74] Its amino acid sequence changes very little from one species to another. Under particular conditions of temperature and salt concentrations, globular actin (G-actin) polymerizes into filamentary actin (F-actin). The mechanism for actin polymerization is not well understood, but one model is that the G-actin molecules first form a trimer in the presence of a salt (e.g., KCl) and that the trimer then propagates into helical, two-stranded F-actin. The bonding of the monomers to make the polymer is not covalent but is somehow hydrogen-bonded, electrostatic, and hydrophobic. This polymerization is reversible and should be akin to the polymerizations in sulfur and α-methylstyrene. On the other hand, there are interesting differences, as discussed in the beginning of section II.

Actin exhibits a floor temperature,[5] so both ΔH_P and ΔS_P must be positive. We are aware of no direct calorimetric measurements on polymerizing actin: ΔH_P and ΔS_P have been surmised from Van't Hoff plots[75,76] (see section I). The thermodynamics of actin polymerization will also depend on the particular conditions of the solution (ATP and salt concentrations, etc.) The result, as has recently been pointed out by Ivkov et al.,[77] is that there are no reliable values for ΔH_P and ΔS_P, even for the much-studied rabbit muscle actin. Thus, we cannot make theoretical calculations of the thermodynamic properties of actin for comparison with experiments.

There have not been precise, systematic experimental studies of either the polymerization line or the extent of polymerization for actin, but some data can be culled from the literature. Figure 3a shows data for the *polymerization line* for rabbit muscle actin for one set of conditions,[75,77] as an example of the general behavior. This graph is to be compared to Figure 1a for sulfur and to Figure 2a for α-methylstyrene. If we try to include data from other authors and at other conditions in this graph, we see a great deal of scatter.[77]

Figure 3b shows a few data for the *extent of polymerization* of rabbit muscle actin as a function of temperature, as derived from measurements of Asakura et al.[76] No measurements exist of the density or of the heat capacity of actin, as functions of temperature near the floor temperature.

Thus, the known thermodynamic properties of actin make it intriguing as a possible addition to the set of second-order phase transitions, but much experimental work remains to be done.

III. Structure

As a system capable of equilibrium polymerization passes from the monomeric side to the polymeric side of the polymerization line, the microscopic structure of the solution undergoes interesting changes. The activated monomers grow first as small, independent polymers, in a dilute solution. As the temperature is moved further and further into the polymerizing region, these growing polymers get larger and larger, until finally they begin to interpenetrate with one another and then form a semidilute solution.

Small-angle neutron scattering (SANS) is an excellent tool for studying this kind of structural change: Deuterium labeling allows for good contrast, and neutrons do not affect the samples in the way light often does. The *polymer growth and the dilute-to-semidilute transition* have been studied by SANS in sulfur,[78] in α-methylstyrene,[79] and in rabbit muscle actin.[77] The intensity as a function of wavenumber and temperature, $I(q,T)$, shows similar features for all three systems: a dramatic increase in scattering at small q as the polymerization progresses, which can be described qualitatively (for sulfur and for α-methylstyrene) by a mean field model or (for α-methylstyrene) by the dilute $n \rightarrow 0$ model. As mentioned above, the actin data cannot

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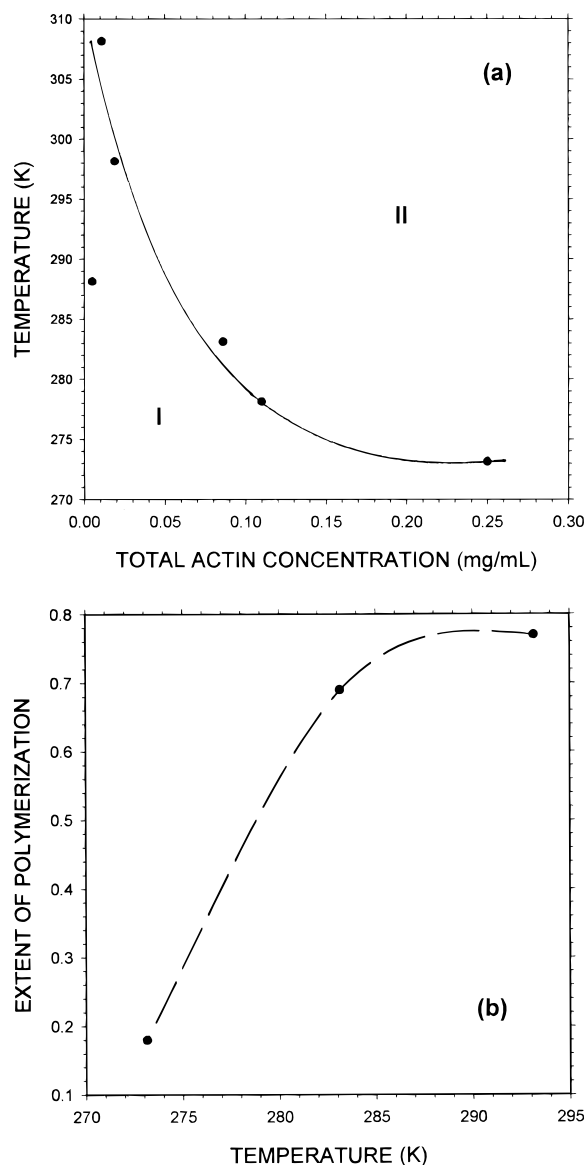
Figure 3. Equilibrium polymerization of actin: experimental data for (a) the phase diagram of rabbit muscle actin in a solvent and (b) the extent of polymerization. In graph (a),[75,77] region I is unpolymerized monomer (G-actin) in solvent (water), and region II is polymeric (F-actin) in equilibrium with G-actin in water, where the initiating salt is KCl (0.1 M) in the presence of 0.50 mM ATP and 0.10 mM CaCl$_2$; regions I and II are separated by a line of polymerization (floor) temperatures, through which a line is drawn to guide the eye. In graph (b),which is deduced from Figure 5 of Asakura et al.,[76,123] the total concentration of G-actin is 2.75 mg/mL, in the presence of 0.85 mM ATP and 1.20 mM MgCl$_2$.

be compared to theories because the thermodynamic input parameters are not known. For α-methylstyrene,[80] $I(0,T)$, which is related to the thermodynamic concentration susceptibility, shows a peak as a function of temperature below the polymerization temperature; this peak can be described by the dilute $n \rightarrow 0$ model, but not by the mean field model, and thus is evidence for the importance of fluctuations in such systems.[33]

Figure 4 shows the correlation length as derived from an Ornstein–Zernike analysis of $I(q,T)$ for (a) α-methylstyrene[80] and (b) rabbit muscle actin.[77] In both cases, the correlation length as a function of temperature, $\xi(T)$, begins to increase when the polymerization temperature is reached (on cooling for α-methylstyrene, on heating for actin). Since α-methylstyrene is a flexible polymer, the correlation length in the dilute regime
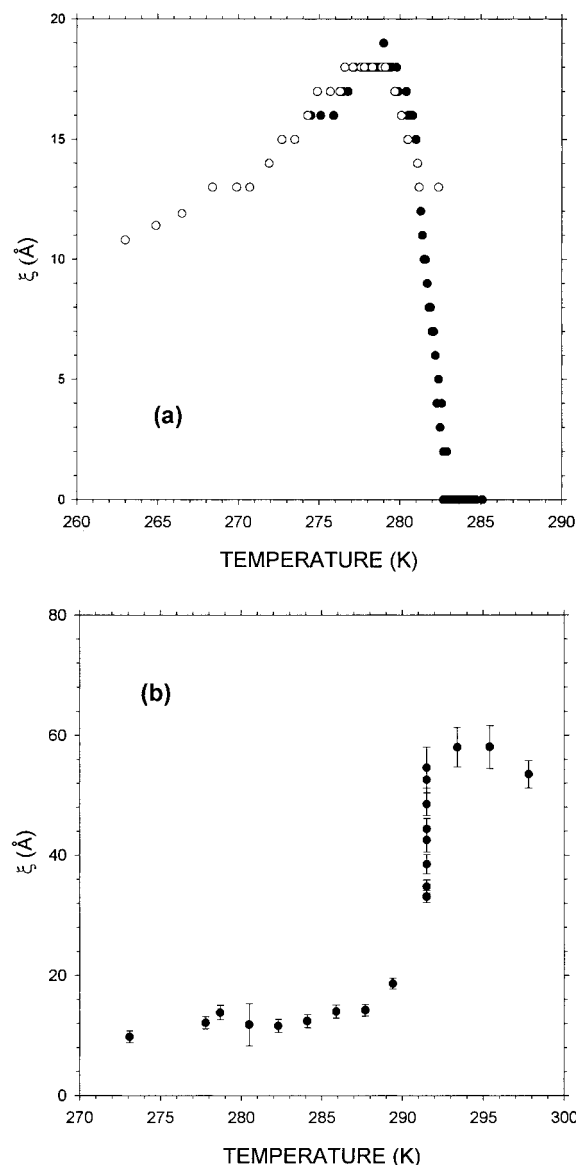
Figure 4. Correlation length, ξ, as a function of temperature near the polymerization temperature for (a) α-methylstyrene and (b) rabbit muscle actin. For (a),[79] the α-methylstyrene sample had a mole fraction of initial monomer of 0.12 and a ratio of moles of initiator (sodium naphthalide) to moles of monomer of 3.9×10^{-3}; the filled circles are data from the first cooling run on the sample, and the open circles are from the second cooling run. For (b),[77] the sample of rabbit muscle actin contained 3.00 mg/mL actin, 8.9 nM KCl, and 0.54 mM Ca^{2+}, and the data were collected on the initial heating run.

is proportional to the radius of gyration. Thus, the correlation length begins to increase as the temperature passes through the polymerization temperature and increases further as the polymers increase in average molecular weight. The transition from monomer to polymer at T_p gets sharper if the concentration of initiator is decreased. A peak in $\xi(T)$ is reached at about 18 Å and about 3 K below T_p; at still lower temperatures, the system is semidilute, and ξ is a measure of the mesh size of the interpenetrating polymer molecules. The behavior of $\xi(T)$ for α-methylstyrene can be described qualitatively by the dilute $n \rightarrow 0$ model or by the mean field model.[79]

For actin, a semiflexible polymer, the correlation length also increases on heating through T_p,[77] as shown in Figure 4b for a sample of rabbit muscle actin, at 3.00 mg/mL actin, 8.9 nM KCl, and 0.54 mM Ca^{2+}. The monomer-to-polymer transition gets sharper if the concentration of KCl is decreased. There is

some indication that a peak has been reached at about 58 Å. It is hard to interpret the dimensions for actin, since the monomer itself has dimensions of $37 \times 40 \times 67$ Å.[74] It is conceivable that the polymerizing actin solution reaches the semidilute regime at temperatures very near T_p and that the 58 Å dimension represents the mesh size. More experiments are clearly in order, but the general feature of a growing polymer on crossing T_p is clear.

For ionic systems such as poly(α-methylstyrene), *Coulombic associations* are another possible kind of structure.[2] Each active polymer molecule has at least one negative charge at one end of the polymer chain and has a positive counterion associated with that charge. The degree of association of the counterion with the anionic site will depend on the dielectric constant of the solvent and thus, for a given solvent, on the temperature. We can imagine rings, micelles, and "strings" or "threads" formed by Coulombic associations.[81] Fetters et al.[82] have used light and neutron scattering to study such structures in living poly(styrene) in benzene, initiated by *sec*-butyllithium and far below the polymerization temperature, and report the formation of cylindrical micelles by Coulombic association. Recent dynamic light scattering studies of the diffusion coefficient[83] of living poly(α-methylstyrene) in tetrahydrofuran, initiated by sodium naphthalide and near the polymerization line, show evidence even above T_p of an association of the initiated dimers into long "threads" and show evidence below T_p of polymeric micelles. More investigations of such structures is important, since the formation of rings can change the universality class for the polymerization transition, and the presence of such structures can affect the chemical kinetics and the molecular dynamics.

Another kind of structure in systems undergoing equilibrium polymerizations is the *molecular weight distribution (MWD)* of the polymer: both in the time development of the MWD and the nature of the final, equilibrium MWD. These issues were first considered by Brown and Szwarc in 1958[84] and later developed by Miyake and Stockymayer in 1965,[85] Oosawa in 1970,[86] Taganov in 1984,[87] and Milchev in 1997.[88] In general, the development of the MWD occurs in three stages. In the first step, if initiation is fast relative to propagation, then the initiated sites are all equally likely to propagate, propagation is favored over depropagation, and the polymers will have a narrow Poisson distribution. In this early, nonequilibrium stage, termination of the growing polymers will yield a narrow MWD. In the second stage, the equilibrium concentration of monomer is reached, and the equilibrium number-average molecular weight (M_n) is reached, but the MWD and the weight-average molecular weight (M_w) continue to develop. In the final stage, the full equilibrium MWD is achieved. That final MWD is expected to be a broad Flory−Schulz "most probable" distribution.[89−92] Schäfer[93] has studied the equilibrium MWD by renormalization group methods and predicts an exponential distribution that is probably indistinguishable from the Flory−Schulz distribution.

There are no experimental studies of either the *full* time development of the MWD or of the equilibrium MWD, for either sulfur or α-methylstyrene or for any other living polymerization of an organic monomer. The time development of the MWD has not been of interest to synthetic chemists, who mainly want to stop the polymerization in the first stage in order to produce a narrow MWD. The final, equilibrium MWD has not been studied because it is takes a long time to achieve: Miyake and Stockmayer[85] estimate 80 years for full equilibration for poly-(styrene)! The second stage of the polymerization process, the

achievement of the equilibrium degree of conversion of monomer to polymer, has been confirmed by Zhuang et al.[94] for α-methylstyrene in tetrahydrofuran with the sodium naphthalide initiator and requires only a few hours. Full equilibration of the α-methylstyrene system could be expected to take days.

For actin, there has been considerable study of the MWD because the F-actin molecules are large enough to be directly observed by fluorescence microscopy or electron microscopy and because the time scales are reasonable. The first stage takes less than an hour, and full equilibration takes days.[5,95] The transition from Poisson to exponential MWD's has actually been observed.[96,97] Indeed, exponential MWD's have frequently been observed in equilibrated actin.[98]

Finally, we note that the *tacticity* of the a living polymer such as poly(α-methylstyrene) is yet another aspect of structure.[9] Proton nuclear magnetic resonance was used by Brownstein et al. to study the polymerization of α-methylstyrene by various initiators and in various solvents.[99] Erusalimskii[100] has reviewed later work by J. Leonard, S. L. Malhotra and co-workers, and K.-F. Elgert and colleagues, and we refer the reader to Erusalimskii and to Kawamura[101] for details and extensive references. Further discussion of this interesting aspect of the structure is outside the scope of this review.

IV. Kinetics and Dynamics

In all three cases of equilibrium polymerization, we have observed a *"frozen-in polymer state"*: a tendency of the polymer, once formed, not to revert easily to monomer on retraversing the polymerization line. This was observed in the mass density measurements of sulfur,[66] in many of the studies of α-methylstyrene,[79,83,102] and also in the small-angle neutron scattering studies of actin.[77] For α-methylstyrene, this "frozen-in" polymer state was on one occasion observed to revert to the monomer after annealing at a temperature well above T_p.[79] The data in Figure 4a were taken on that sample, on the first cooling and on the second cooling after the annealing, and indicate that the behavior was reproducible despite the history of the sample. Other workers have discussed this phenom-enon.[103] We have no satisfactory explanation for this tendency of the polymer to "freeze-in".

The behavior of *transport properties* of these systems should reflect the changing microscopic structure: the changing MWD, Coulombic aggregations, etc. The only measurements of the diffusion coefficient near T_p in such a system were made by Ruiz-Garcia and Castillo[83] and are discussed above in section III. The only study of the shear viscosity near T_p is that of Ruiz-Garcia and Greer[102] on living poly(α-methylstyrene); this exploratory report raises interesting questions, including the question of the relationship between the dilute-to-semidilute transition and the state of polymer entanglement, but indicates that measurements in which shear rate can be varied and which are over a wider range of temperature (and thus a wider range of average molecular weight) are in order.

Last, knowledge of the *chemical kinetics* of systems undergo-ing equilibrium polymerization is important, particularly for understanding the time development of the MWD. At T_p, the rate constant for propagation, k_p, will equal the rate constant for depropagation, k_d. Below T_p, k_p must be greater than k_d. For ionic polymerizations, the rate constant for propagation, k_p, will depend on the nature of the counterion contact (free or ion pair).[2] Zhuang et al.[94] have recently reviewed the literature on the kinetics for α-methylstyrene, have shown that $k_p(T)$ has the expected behavior, and have made new measurements of k_p very near T_p.

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V. Issues and Outlook

A. Other Models. In science, we know that we must always be open to alternative models of natural phenomena. We have chosen here to view the phenomena observed in sulfur, α-methylstyrene, and actin as equilibrium polymerizations and as second-order phase transitions in the $n \rightarrow 0$ universality class. There may be other ways of thinking about these systems. In the case of sulfur, it has been suggested on the basis of measurement of the pair correlation function by neutron scattering[104−109] that the underlying transition may be a percolation phenomenon rather than a polymerization phenomenon; no predictive model has yet been developed for this point of view. Other studies of the pair correlation function support the standard picture of polymerization in sulfur.[110,111]

B. Outlook. Let us now review some issues of continuing interest in the physical chemistry of equilibrium polymerization.

There is a compelling need for experimental measurements on actin. We lack even the most fundamental thermodynamic quantities, the enthalpy and entropy of polymerization, and we lack careful studies of the density, the heat capacity, or the extent of polymerization for actin. Such studies could even be important in unraveling the detailed mechanism of actin polymerization, which in itself has profound physiological importance. We should also consider the polymerizing protein tubulin as an analogous system, differing in that tubulin forms very rigid polymeric rods.[112]

For the polymerizing organic monomers such as α-methylstyrene, there is much to be understood about the nature of the microscopic structure of the living polymer solution, how that structure changes as the temperature ranges across the polymerization line, and how that structure changes as the nature of the solvent is changed. The structural changes will include the transition from independent polymer chains, to interpenetrating chains, to entangled chains. Other structures in the solution will include the various kinds of Coulombic aggregations. Static and dynamic neutron and light scattering will be important tools for this study.

Understanding the nature of the microscopic structure of these systems may help us to understand the mystery of the "frozen-in" polymer state frequently seen, of polymeric molecules which persist into the nonpolymerizing region of the phase diagram. This state has been observed in all three systems discussed here and is not understood.

We have limited this discussion to three cases of the formation of linear polymers by equilibrium polymerization. Other systems that can be considered as equilibrium polymerizations include nonlinear aggregations such as micelles[113,114] and two- or three-dimensional networks.[115] An even broader definition of equilibrium polymerization would include other kinds of clustering processes and collective assemblies.[116] For example, the "stringlike cooperative motion" observed in computer simulations of glass-forming systems by Donati et al.[117] can be seen as analogous to the formation of linear polymers, even though the forces at work are very different. Donati et al. point out that such stringlike excitations were suggested in 1953 by Feynman to explain the superfluid transition in liquid helium.[118−120] Perhaps the exploration of equilibrium polymerization as presented here can lead to insights into these other varieties of equilibrium polymerization.

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