Lattice model of living polymerization. I. Basic thermodynamic properties

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A Flory-Huggins type lattice model of living polymerization is formulated, incorporating chain stiffness, variable initiator concentration r, and a polymer-solvent interaction χ. Basic equilibrium properties [average chain length L, average fraction of associated monomers Φ, specific heat C_P, entropy S, polymerization temperature T_p, and the chain length distribution $p(N)$] are calculated within mean-field theory. Our illustrative calculations are restricted to systems that polymerize upon cooling [e.g., poly(α-methylstyrene)], but the formalism also applies to polymerization upon heating (e.g., sulfur, actin). Emphasis is given to living polymer solutions having a *finite r* in order to compare theory with recent experiments by Greer and co-workers, whereas previous studies primarily focused on the $r \to 0^+$ limit where the polymerization transition has been described as a second order phase transition. We find *qualitative* changes in the properties of living polymer solutions for nonzero r: (1) L becomes independent of initial monomer composition ϕ_m^0 and temperature T at low temperatures [$L(T \ll T_p) \sim 2/r$], instead of growing without bound; (2) the exponent describing the dependence of L on ϕ_m^0 changes by a factor of 2 from the $r \to 0^+$ value at higher temperatures ($T \gtrsim T_p$); (3) the order parametertype variable Φ develops a long tail with an inflection point at T_p; (4) the specific heat maximum C_P^* at T_p becomes significantly diminished and the temperature range of the polymer transition becomes broad even for small r [$r \sim O(10^{-3})$]. Moreover, there are three characteristic temperatures for $r > 0$ rather than one for $r \to 0$: a ''crossover temperature'' T_x demarking the onset of polymerization, an r-dependent polymerization temperature T_p defined by the maximum in C_P (or equivalently, the inflection point of Φ), and a ''saturation temperature'' T_s at which the entropy S of the living polymer solution saturates to a low temperature value as in glass-forming liquids. A measure of the ''strength'' of the polymerization transition is introduced to quantify the ''rounding'' of the phase transition due to nonzero r. Many properties of living polymer solutions should be generally representative of associating polymer systems (thermally reversible gels, colloidal gels, micelles), and we compare our results to other systems that self-assemble at equilibrium. © *1999 American Institute of Physics.* [S0021-9606(99)50539-4]

I. INTRODUCTION

The tendency toward particle clustering is a ubiquitous phenomenon in condensed matter physics. The strength of the interparticle coupling in liquids typically ranges from weak van der Waals interactions to relatively strong ionic associations and covalent chemical bonds. The geometry of the molecular or colloidal clusters can be networklike, stringlike, or compact, globularlike structures (e.g., thermoreversible gels, linear ''living'' polymers, spherical micelles, respectively), depending on the geometrical form of the molecules, the symmetry and range of the interparticle interactions, and on the capacity of the clustering species to form multivalent contacts. Under equilibrium conditions, the extent of clustering varies with temperature, electrolyte concentration, or other control parameters that alter the strength and the nature of the interactions responsible for particle clustering.

The formation of ''stringlike'' structures is a common mode of clustering with special significance for materials science. Many natural materials (wool, silk, cotton, rubber, tendons, spider webbing, etc.) are condensation polymers formed by chains growing one monomer unit at a time to build long molecules whose properties are governed by growth conditions.[1] Synthetic polymer science is predicated on emulating these natural processes and on manipulating the conditions of formation to control the molecular architecture, mass, and molecular weight distribution for materials applications.[1] Moreover, stringlike structures also arise in connection with many phase transitions in condensed matter physics, so that the study of linear chain polymers formed at equilibrium has broad physical significance (see Sec. IV).

The present paper develops a fairly complete theoretical description for one of the simplest examples of clustering at equilibrium, the ''equilibrium polymerization'' of monomers to form stringlike structures. We specifically consider the situation in which the monomer is bifunctional and where the chain growth is initiated by a finite concentration of ''initiator.'' This type of system has been called a ''living poly-

mer'' system if the polymerization occurs reversibly at equilibrium.[2] A lattice model approach is taken in which all monomer and initiator molecules each occupy single lattice sites. The theory is formulated in terms of the system's total free energy, thereby enabling the computation of all thermodynamic properties of these associating systems. Our modeling incorporates the monomer-monomer (or, equivalently, the monomer-solvent) interparticle interactions governing fluid miscibility (the Flory χ parameter), so that the interplay between phase separation and particle clustering can also be investigated. The present paper focuses on providing a general understanding of the equilibrium thermodynamic properties of ''living polymers,'' including the average polymerization index L, entropy S, fraction of monomers converted to polymers Φ, and specific heat C_P. Our chain model also incorporates chain stiffness and variable initiator concentration since these variables are crucial to enable comparisons of the theory with recent extensive experiments by Greer and co-workers.[2,3] This minimal model of living polymerization can be generalized using the lattice cluster theory[4,5] to include monomer, initiator, and solvent molecular structures, specific interactions, fluid compressibility, and the capacity to form multifunctional associations of various kinds. Subsequent papers will emphasize the coupling that occurs between phase separation and polymerization and the resulting large shifts in the critical temperature and in the shape of the phase diagram of these polymerizing systems.

Previous studies have emphasized particular aspects of ''living polymerization.'' [6] Early works by Tobolsky and Eisenberg[7] and Scott[8] apply mean-field theory models to understand the tendency of heated sulfur to form a very viscous fluid at elevated temperatures. This type of modeling has been extended to metals, such as selenium.[9] Szwarc[10] summarizes early efforts at characterizing living polymers along with early theoretical models, while Greer provides an updated review on this topic.[2,3] The recent theoretical treatments of living polymerization by Wheeler et al.[11–18] and by Milchev et al.[19–23] utilize the machinery of spin models for phase transitions and of Monte Carlo simulation methods, respectively, and are representative of current theoretical efforts to describe living polymerization quantitatively. The scaling arguments of Cates[24] are also notable for the insights they provide into the role of excluded volume interactions on the properties of living polymers. All these recent theoretical treatments restrict attention to cases where the initiator concentration r is either very small or vanishing, but the present paper focuses instead on the case of $r>0$ since this situation arises in many physical applications of living polymerization. Greer and her co-workers[2] have pioneered the investigation of basic thermodynamic properties of living polymer solutions (specific heat, density, scattering intensity, correlation length, etc.) for finite r, as in our modeling, and we compare our theory to these measurements below.

The present investigation of living polymerization is also stimulated, in part, by recent observation of a phenomenon resembling living polymerization in molecular dynamics simulations of supercooled liquids.[25] The analysis of these simulations requires a knowledge of how the average degree of polymerization L varies with temperature in systems that

polymerize upon cooling, as well as a better understanding of how the transient clustering in living polymers influences the configurational entropy of the fluid as a whole. Lacking a clear exposition for these and other essential equilibrium properties of living polymers in the literature, we have undertaken the present theoretical treatment, in part, to provide this information in a readily accessible form.

Consultation with Greer[26] also indicated the need for incorporating chain stiffness into the modeling of living polymerization[27] since many natural living polymers (e.g., actin) are stiff to varying degrees.[28–31] The mathematical machinery has been designed so that increasing complexity in the molecular modeling can be incorporated as needed using the methods of the lattice cluster theory ($1/z$ and high temperature expansions).[4,5,31] This extended modeling would allow for the inclusion of short-range correlations along the growing chain arising from monomer shape, nonrandom mixing, compressibility, and more complicated interactions that must be considered in physically realistic modeling. At many points in our development, we make contact with particular findings obtained previously based on a variety of formalisms (spin models of phase transitions, kinetic models of chain clustering, etc.). The present free energy formulation of living polymerization enables the computation of thermodynamic quantities that have not been evaluated previously and that provide basic insights into the nature of particle clustering at equilibrium. A subsequent paper will describe the phase behavior of living polymer systems based on the lattice model presented in the next section.

II. LATTICE MODEL OF LIVING POLYMERIZATION

Consider a system composed of n_s solvent molecules, n_m^0 monomers of species M, and n_I molecules of the initiator I which activates the monomers and thereby enables them to propagate into polymers. In order to compare the theory with the recent extensive experiments of Greer and co-workers,[2,3,32,33] we assume that polymerization occurs under conditions of chemical equilibrium and that the smallest propagating species is a bifunctional dimer M_2I_2 which contains two molecules of the initiator I,

$$2M+2I\rightarrow M_2I_2, \tag{1}$$

$$M_iI_2+M\rightleftharpoons M_{i+1}I_2, \quad i=2,3,\dots,\infty. \tag{2}$$
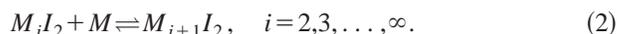
Since the reaction (1) is assumed to be irreversible, the equilibrium system may only contain unreacted monomers M, polymers M_iI_2 ($i=2,3,...,\infty$), and solvent molecules. The total numbers of the former species are designated by n_m and $\{n_i\}$, respectively. Conservation of mass requires that n_m and $\{n_i\}$ are related to the initial (i.e., before polymerization) number n_m^0 of monomers by

$$n_m^0=n_m+\sum_{i=2}^{\infty} in_i. \tag{3}$$

Because all the initiator is contained in the M_iI_2 ($i=2,3,\dots,\infty$) species, the total number n_I of initiator molecules and the total number of polymers $\{M_iI_2\}$ are related by

$$\frac{1}{2}n_I = \sum_{i=2}^{\infty} n_i. \qquad (4)$$

The system is described using a minimal incompressible Flory-Huggins (FH) lattice model[34] with a single site occupancy constraint for all monomers, solvent molecules, and initiator molecules. (See Scott[8] for a similar lattice model formulation for the polymerization of sulfur.) Thus, the total number N_l of lattice sites is written in terms of the numbers for the individual species as

$$N_l = n_s + n_m + \sum_{i=2}^{\infty} n_i(i+2) = n_s + n_m^0 + n_I, \qquad (5)$$

while the total Helmholtz free energy F for the system is given by

$$\frac{F}{N_l k_B T} = \phi_s \ln \phi_s + \phi_m \ln \phi_m + \sum_{i=2}^{\infty} \frac{\phi_i}{i+2} \ln \phi_i + \phi_s \phi_m \chi$$

$$+ \phi_s \chi \sum_{i=2}^{\infty} \phi_i + \sum_{i=2}^{\infty} \phi_i f_i, \qquad (6)$$

where $\phi_m = n_m/N_l$, $\phi_s = n_s/N_l$, and $\{\phi_i = n_i(i+2)/N_l\}$ denote the volume fractions for the residual (i.e., unpolymerized) monomers, the solvent, and polymers, respectively. χ is the monomer-solvent interaction parameter, f_i is the dimensionless specific free energy of an i-mer, which is composed of i monomers and two initiator molecules, and k_B is the Boltzmann constant. The specific free energy f_i is quoted below, while the quantities f_m and f_s are taken as vanishing identically since both solvent and monomer species are treated as entities occupying single lattice sites. The mass conservation constraints from Eqs. (3) and (4) can be conveniently reexpressed in terms of volume fractions as

$$\phi_m^0 = \phi_m + \sum_{i=2}^{\infty} i \frac{\phi_i}{i+2}, \qquad (7)$$

and

$$\frac{1}{2}\phi_I = \sum_{i=2}^{\infty} \frac{\phi_i}{i+2}, \qquad (8)$$

where $\phi_m^0 = n_m^0/N_l$ and $\phi_I = n_I/N_l$.

The condition of chemical equilibrium imposes the following relation between the chemical potentials $\{\mu_i\}$, μ_2, and μ_m, where the subscripts i, 2, and m represent, respectively, the i-mer $M_i I_2$, dimer $M_2 I_2$, and monomer species,

$$\mu_i = \mu_2 + (i-2)\mu_m, \quad i=3,4,...,\infty. \qquad (9)$$

On the other hand, the chemical potentials μ_α, $(\alpha \equiv 2,i,m)$ can be calculated directly from the free energy of Eq. (6) as,

$$\frac{1}{k_B T}(\mu_\alpha - c_\alpha \mu_s) = \frac{\partial(F/k_B T)}{\partial n_\alpha}\bigg|_{T,N_l,n_{\gamma \neq \alpha}}. \qquad (10)$$

The exchange chemical potential $\mu_\alpha^{ex} = \mu_\alpha - c_\alpha \mu_s$ [with μ_s the solvent chemical potential and with the coefficient $c_\alpha = 1, 4$, and $(i+2)$ for $\alpha \equiv m,2$, and i, respectively] emerges from Eq. (10) as a consequence of the assumed incompress-

ibility of the system. After simple algebra, the equilibrium condition in Eq. (9) takes the form in which the μ_s terms cancel identically,

$$\ln\left[\frac{\phi_i}{\phi_2 \phi_m^{i-2}}\right] = i - 2 - (i+2)f_i + 4f_2, \quad i=3,4,...,\infty. \qquad (11)$$

The specific free energy f_i $(i=2,3,...,\infty)$ is obtained from the Flory theory for semiflexible linear polymers as,[30]

$$f_i = \frac{1}{i+2}\ln\left[\frac{2}{z(i+2)}\right] + \frac{i+1}{i+2} - \frac{i}{i+2}\ln[1+(z-2)]$$

$$\times \exp(-\epsilon/k_B T)] + \frac{i-1}{i+2}\Delta f, \qquad (12)$$

where z is the lattice coordination number, ϵ denotes the "bending" energy (the energy difference between *gauche* and *trans* conformations), while Δf designates the free energy change due to the polymerization, a feature appended to the Flory specific free energy in order to describing the living polymer system. The chain stiffness factor $J \equiv 1 + (z-2)\exp(-\epsilon/k_B T)$ in Eq. (12) is the sole manifestation of chain semiflexibility in our modeling. In the completely flexible chain limit of vanishing bending energy $\epsilon \to 0$, we have $J \to z-1$, whereas the opposite limit $\epsilon \to \infty$ yields $J \to 1$, whereupon the polymers are modeled as stiff rods. Since the above free energy expressions are isotropic, we do not consider situations in which the semiflexible chains exhibit liquid crystalline ordering.[35,36]

Combining Eqs. (11) and (12) leads to the compact expression for the i-mer volume fraction ϕ_i,

$$\phi_i = (i+2)CA^{i-2}, \qquad (13)$$

with the quantity A given by

$$A \equiv \phi_m \exp(-\Delta f/k_B T)[1+(z-2)\exp(-\epsilon/k_B T)]$$

$$= \phi_m \exp(-\Delta f/k_B T)J, \qquad (14)$$

and with the prefactor C as

$$C \equiv (1/4)\phi_2. \qquad (15)$$

Substituting Eq. (13) into Eqs. (8) and (9) produces, after performing all the summations, the important relation between A and C,

$$C = (1/2)\phi_I(1-A), \qquad (16)$$

and between ϕ_m^0, ϕ_I, and ϕ_m,

$$\phi_m = \phi_m^0 - \frac{\phi_I}{2}\frac{(2-A)}{(1-A)}. \qquad (17)$$

The relation in Eq. (17) resembles the previously derived mean-field formula,[33,37]

$$x_m = x_m^0 - \frac{x_I}{2}\frac{2-x_m K_p(T)}{1-x_m K_p(T)}, \qquad (18)$$

where x_m is the mole fraction of unpolymerized monomers, x_m^o is the initial mole fraction of monomers before any polymerization or reaction with initiator, and $K_p(T) = \exp(-\Delta g/k_B T)$ is the equilibrium constant for the polymer-

ization reaction in Eq. (2). Equations (17) and (18) become identical upon the identification of the combination Δf $-k_B T \ln(J)$ with the specific single bond Gibbs free energy Δg of polymerization in the earlier models. Because $\ln J$ varies almost linearly with T^{-1} over the temperature ranges of interest, Δf is just obtained from Δg by removing the contributions to the enthalpy and entropy associated with chain semiflexibility since these contributions are treated separately in the free energy. More general descriptions, such as those provided by the lattice cluster theory, explicitly describe further aspects of the chain conformation statistics and thereby would provide somewhat different renormalizations of the free energy of polymerization. It will be interesting to determine whether these more molecular renormalizations affect the molecular weight distribution or other properties of the living polymer system. Within the present mean-field model, semiflexibility simply modifies the magnitudes of the enthalpy and entropy of polymerization, but does not change the values for the effective equilibrium constant $K_p(T)$. This observation justifies the use of the flexible chain theory to describe semiflexible living polymers,[27] whereupon the phenomenological free energy Δf contains contributions from conformational, packing, etc., influences.

Equation (17) can be solved analytically for ϕ_m,

$$\phi_m = \frac{B - \sqrt{B^2 - 4(\phi_m^0 - \phi_I)G}}{2G}, \tag{19}$$

with the parameters B and G defined by

$$B \equiv 1 + [\phi_m^0 - (1/2)\phi_I]G, \quad G \equiv \exp(-\Delta f/k_B T)J. \tag{20}$$

After inserting Eq. (13) and performing the summations in Eq. (6), the Helmholtz free energy F for the system reduces to the form,

$$\frac{F}{N_l k_B T} = (1 - \phi_m^0 - \phi_I)\ln(1 - \phi_m^0 - \phi_I) + \phi_m \ln \phi_m$$

$$+ \phi_m(1 - \phi_m^0 - \phi_I)\chi + \frac{\phi_I}{2(1-A)}$$

$$\times \left[(1-A)\ln \frac{\phi_I(1-A)}{z} + A \ln A - (2-A)\ln J \right.$$

$$\left. + \chi(1 - \phi_m^0 - \phi_I)(4 - 3A) + \frac{\Delta f}{k_B T} + 3 - 2A \right], \tag{21}$$

which uniquely specifies F for a given set of parameters T, ϕ_m^0, ϕ_I, χ, ϵ, and $\Delta f = \Delta g + k_B T \ln(J)$. The concentration $\phi_m(T, \phi_m^0, \phi_I)$ of unreacted monomers and the quantity $A(T, \phi_m^0, \phi_I)$ are given by Eqs. (19) and (14), respectively. The basic thermodynamic properties, such as internal energy E, specific heat C_V ($\approx C_P$ within the FH model), and entropy S of the system follow from Eq. (21) as standard derivatives of the free energy F.

Other basic properties of living polymer solutions are the extent of polymerization Φ, the average chain length L $\equiv \langle N \rangle$, and the molecular weight distribution $p(N)$. Φ is defined as the fraction of monomers converted into polymers,

$$\Phi \equiv \frac{\phi_m^0 - \phi_m}{\phi_m^0} = \frac{r}{2}\frac{(2-A)}{(1-A)}, \tag{22}$$

where $r \equiv \phi_I/\phi_m^0$ is the dimensionless initiator concentration. Equating $\Phi = 1 - \phi_m/\phi_m^0$ to zero and setting $\phi_I = 0$ in Eq. (19) for ϕ_m recovers the usual Dainton and Ivin equation[38] for the "polymerization temperature" $T_p^{(o)}$,

$$T_p^{(o)} = \frac{\Delta h}{\Delta s + k_B \ln \phi_m^0}, \tag{23}$$

appropriate to $r = 0$ or $r \to 0$, with Δh and Δs denoting, respectively, the enthalpy and the entropy of the polymerization reaction in Eq. (2). We term $T_p^{(o)}$ the "ideal polymerization temperature" since this transition corresponds to the idealized limit of $r \to 0$. When the initiator concentration r is nonzero, we *define* T_p more generally as the temperature at which the specific heat C_P has a maximum or, equivalently, at which there is an inflection point in the curve $\Phi(T)$ describing the extent of polymerization Φ as a function of temperature T (see next section). The average chain length L is determined from an average over *all* monomer containing species in the system,

$$L = \frac{\phi_m + \Sigma_{i=2}^{\infty} \phi_i \dfrac{i}{i+2}}{\phi_m + \Sigma_{i=2}^{\infty} \dfrac{\phi_i}{i+2}} = \frac{\phi_m^0(1-A)}{(1-A)\phi_m^0 - (1/2)\phi_I}. \tag{24}$$

Alternatively, we may introduce a definition $\hat{L}$ for the average chain length which excludes the unreacted monomers from the averaging process,

$$\hat{L} = \frac{\Sigma_{i=2}^{\infty} \phi_i \dfrac{i}{i+2}}{\Sigma_{i=2}^{\infty} \dfrac{\phi_i}{i+2}} = \frac{2-A}{1-A} = \frac{2}{r}\Phi. \tag{25}$$

Both of these definitions are considered below.

The probability distribution function $p(i)$ ($i = 1, 2, \ldots \infty$) for the chain molecular weight is represented as the fraction of polymers having i monomers of species M and can be simply evaluated to obtain

$$p(i) = \frac{n_i}{\Sigma_{i=1}^{\infty} n_i} = \frac{\delta(i,1)\phi_m + [1 - \delta(i,1)]D_p}{N}, \tag{26}$$

where $n_1 \equiv n_m$ and $\delta(k,l)$ is a Kronecker delta function such that $\delta(k,l) = 1$ if $k = l$ and equals zero otherwise. The polymeric contribution D_p to the $p(i)$ distribution is given by

$$D_p = D_A \exp(-i/\lambda), \quad D_A = (\phi_I/2)(1-A)/A^2,$$

$$\lambda = -1/\ln A, \tag{27}$$

while the norming constant N of $p(i)$ is a simple function of ϕ_m and ϕ_I,

$$N = \phi_m + (1/2)\phi_I. \tag{28}$$

The chain length L can be alternatively calculated as

$$L = \sum_{i=1}^{\infty} i p(i), \tag{29}$$

leading to the equivalence between Eqs. (24) and (29). Note that the decay length λ of the exponential part of the length distribution corresponds to *neither L nor $\hat{L}$.*

The properties of living polymer solutions defined by Eqs. (22)–(29) do not depend on the Flory–Huggins interaction parameter $\chi \sim 1/T$ in Eq. (7), but the phase behavior is strongly influenced by χ. (We expect that this situation may change within the lattice cluster theory since χ can acquire an entropic contribution, i.e., χ has an additional constant contribution beyond the $1/T$ dependence in simple Flory–Huggins theory. See Ref. 8.) Because our model assumes that all monomers in the fluid (i.e., free monomers, polymeric segments and solvent molecules) have the same size and that the fluid is incompressible, this idealization does not permit predicting the variation of the density with temperature near T_p without introducing unrealistic assumptions. A better theory, which distinguishes between different monomer structures and describes the presence of free volume, is necessary for such an estimation.

III. RESULTS

While the thermodynamic relations derived in Sec. II are rather general, the illustrative computations in this section are for cases in which both the enthalpy and the entropy of polymerization are negative. Under these conditions, chain growth occurs at temperatures below a ''ceiling temperature'' (also called the ''polymerization temperature'' T_p) and for initial monomer concentrations ϕ_m^0 greater than a temperature dependent ''critical polymerization concentration'' ϕ_m^*. Because we find almost complete insensitivity of all basic thermodynamic quantities considered in the present paper to polymer chain semiflexibility, the factor of J is dropped (i.e., set $J=1$ in the above formulas) and the values $\Delta h = -35$ kJ/mol and $\Delta s = -105$ J/(mol K) are chosen as determined from extensive experimental investigation of poly(α-methylstyrene) living polymerization by Greer *et al.*[2,3,32,33] in methylcyclohexane, where sodium naphthalide is the initiator species. The lattice coordination number z in all these illustrative calculations is taken as $z=6$, appropriate to a cubic lattice in three dimensions.

The average chain length is perhaps the most basic parameter describing a living polymer solution. Figure 1 depicts L as a function of temperature for several different initiator concentrations $\phi_I = r \phi_m^0$ and for an initial fixed monomer composition ϕ_m^0. We observe that L saturates at low temperatures to a constant plateau that depends strongly on the dimensionless initiator concentration $r = \phi_I/\phi_m^0$. Unlimited chain growth at low temperatures occurs in the absence of initiator. The inset to Fig. 1 shows that the low temperature value of the chain length L_p scales linearly with r^{-1} as,

$$L(T \ll T_p) \equiv L_p, \quad L_p \approx 2/r. \tag{30}$$

Flory previously introduced the approximation $L_p \approx 1/r$ for the living polymerization of ethylene oxide initiated with
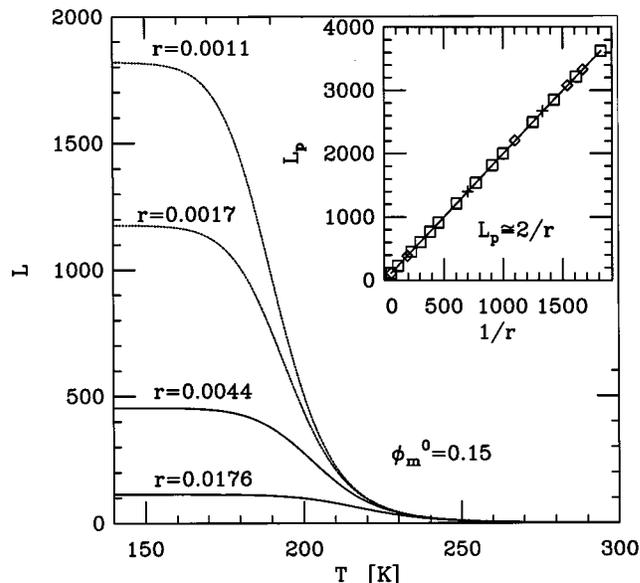
FIG. 1. Average chain length L of living polymers as a function of temperature T and initiator concentration r. We utilize the same values [Greer *et al.* (Refs. 3 and 33)] of $\Delta h = -35$ kJ/mol and $\Delta s = -105$ J/(mol K) in Figs. 1–13, unless otherwise specified. The initial monomer concentration ϕ_m^0 is fixed at 0.15. The inset shows that the low temperature ''plateau value,'' L_p of the chain length L, is inversely proportional to the initiator concentration, $L_p \approx 2/r$. Squares, diamonds, and pluses refer to $\phi_m^0 = 0.15$, 0.05, and 0.5, respectively. The chain length does not grow monotonically with temperature in living polymer solutions that polymerize upon heating (Ref. 8).

alkoxides.[1,34] The additional factor of two in Eq. (30) arises from the presence of two initiator molecules and, hence, the two active chain ends in the model. It may be shown[39] that this prefactor reduces to unity, as in Flory's treatment,[34] if only one chain end is active in the chain growth. Figure 1 also exhibits the conflicting influences of the initiator upon the polymerization process. The initiator is required to initiate chain growth, but its presence limits the average extent of chain growth because the initiator controls the maximum number of chains that may form.

Figure 2 depicts the temperature variation of the average chain length L with the initial monomer concentration ϕ_m^0 at a given dimensionless initiator concentration $r = \phi_I/\phi_m^0$. The main effect of changing ϕ_m^0 is to shift the polymerization transition temperature (see below). A higher ϕ_m^0 leads to an increased T_p, and the shift of T_p to elevated temperatures saturates to a limiting constant value as $\phi_m^0 \to 1$. The dependence of L on ϕ_m^0 at a constant T is found to be remarkably linear,

$$L(T) \approx 1 + \alpha(T) \phi_m^0, \tag{31}$$

over a large temperature range (i.e., T between 250 and 400 K; see Fig. 3). (The analytic origin of this approximation is discussed below.) At very low temperatures ($T \ll T_p$), L approaches a constant which is independent of both T and ϕ_m^0 (see Fig. 1). The lines in Fig. 3 extrapolate to $L \to 1$ at the concentration ϕ_m^*, which we term the ''critical polymerization concentration'' (cpc). This term is motivated by the observation that a minimal concentration ϕ_m^* is required for the polymers to begin growing. Analysis of Fig. 3 indicates that
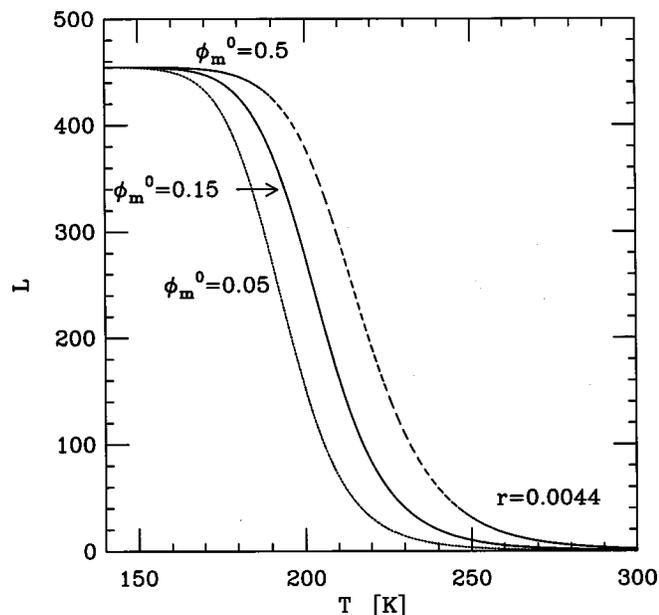
FIG. 2. Temperature dependence of average living polymer length L for a range of initial monomer concentrations ϕ_m^0 and for a fixed initiator concentration $r=0.0044$. Note that the main effect of ϕ_m^0 is to alter the location of the transition temperature.

FIG. 4. The concentration (ϕ_m^0) dependence of L is governed by the parameter α which denotes the slope of the curves in Fig. 3. The inset indicates that ϕ_m^* obey an Arrhenius temperature dependence to a good approximation.

ϕ_m^* and the slope $\alpha(T)$ governing the temperature dependence of the chain growth in Eq. (31) vary in near inverse proportionality,

$$\phi_m^*(T) \approx 1/\alpha(T), \tag{32}$$

FIG. 3. Dependence of the average living polymer length L on initial monomer concentration Φ_m^0 for a range of temperatures T and for a fixed initiator concentration $r=0.0044$. The variation with ϕ_m^0 at fixed temperature T is nearly linear above a critical value of ϕ_m^0 at which $L-1$ extrapolates to zero. We term this characteristic concentration the "critical polymerization concentration" (cpc) ϕ_m^* (see Fig. 4).

while Fig. 4 demonstrates that the slope $\alpha(T)$ decreases exponentially with temperature. The nearly Arrhenius temperature dependence of ϕ_m^*,

$$\phi_m^* \approx \exp(\Delta h/k_B T), \tag{33}$$

is apparent in the inset to Fig. 4 where $-\ln \phi_m^*$ is plotted versus $1/T$. The logarithm of the slope α (or $-\ln \phi_m^*$) vs $1/T$ yields the value $\Delta h = -34.9$ kJ/mol which nearly coincides with the enthalpy of polymerization ($\Delta h = -35.0$ kJ/mol) assumed in our calculations. The temperature dependence of ϕ_m^* in Eq. (33) is strikingly similar to that found in recent simulations of the critical micelle concentration by Floriano et al.[40] We mention this point because many aspects of associating polymers seem to be insensitive to the particular mode of association.[41] This view underlies the commonalities between living polymerization, thermoreversible gelation, and micelle formation (see Sec. IV).

The linear dependence of L in Fig. 3 conflicts with the commonly reported scaling[19–24] $L \sim (\phi_m^0)^{1/2}$ for the chain length from the mean-field theory of living polymers. Since these prior treatments take the initiator concentration to be extremely small or vanishing, we have performed calculations[39] for the living polymerization model without initiator ($r=0$) to analyze this discrepancy. The scaling $L \sim (\phi_m^0)^{1/2}$ is indeed recovered in the absence of initiator when the temperature is low ($T \ll T_p$). However, this computation indicates that the slope δ in a plot of $\ln(L-1)$ versus $\ln \phi_m^0$ approaches 1/2 very slowly (e.g., $\delta = 0.4736, 0.4897,$ and 0.4986 for $T=220, 200,$ and 170 K, respectively). The often cited $L \sim (\phi_m^0)^{1/2}$ scaling is thus restricted to a model for polymerization in the absence of initiator and in the limit of long chains. Thus, the presence of initiator *qualitatively* changes the character of living polymerization at both high and low temperatures. Recent measurements of nonionic mi-
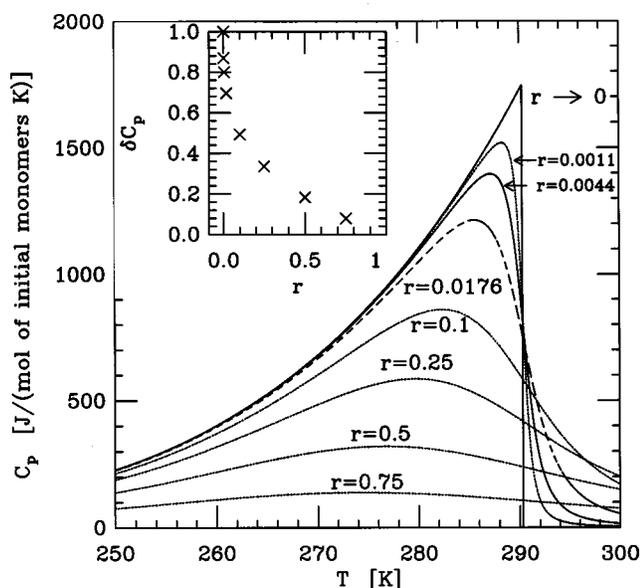
FIG. 5. Temperature dependence of the specific heat C_P for a living polymer solution over a range of initiator concentrations r and for a fixed initial monomer concentration $\phi_m^0 = 0.15$. The magnitude of the maximum C_P^* of C_P in the $r \to 0^+$ limit is independent of Δh. Observe the decrease of the ratio $\delta C_P \equiv C_P^*(r)/C_P^*(r \to 0^+)$ with increasing r.

FIG. 6. Temperature dependence of the specific heat C_P for living polymer solution over a range of initial monomer concentrations ϕ_m^0 and for a fixed initiator concentration $r = 0.0044$. The temperature (called the polymerization temperature T_p) corresponding to the maximum of C_P shifts to lower temperatures with decreasing ϕ_m^0, and the magnitude of the specific heat maximum is also affected. The inset compares the mean-field lattice model computations (Ref. 48) with experimental data of Greer *et al.* (Ref. 32) for the living polymer system with $\phi_m = 0.118$ and $r = 0.0032$.

celle forming liquids (for which living polymerization is thought to be an appropriate model) indicate a nearly linear dependence of L on the associating species (surfactant) concentration ϕ_m^0.[42–45]

The specific heat is another essential property of living polymer solutions which is useful for fixing the parameters of the living polymer model. Figure 5 presents calculations for the constant pressure heat capacity C_P as a function of temperature for a series of values for r. First, observe that $C_P(T)$ is greatly rounded for $r \neq 0$. A jump appears for $r \to 0^+$, which is typical for a second order phase transition in mean-field theory.[46] (Note that the limit $r \to 0^+$ in Fig. 5 does not correspond to the solution of the living polymerization model without initiator, but to the limit of a "very small" initiator concentration [e.g., $r \sim O(10^{-8})$].)

The polymerization "transition" is no longer a second order phase transition when r is finite, although this transition appears to bear some resemblance to one if r is sufficiently small. Several works[11–18] emphasize this relation of living polymerization to a second order phase transition, and it has been noted that r in the spin-model description[11] of living polymers plays the role of a magnetic field that inhibits the second order phase transition. The present paper emphasizes the commonly occurring experimental situation in which r is not "very small." Since critical fluctuations associated with equilibrium polymerization should be greatly suppressed for finite r, the mean-field theory should be an increasingly good approximation. The present work then complements previous studies[11–18] emphasizing the critical phenomena aspect of living polymerization. Our mean-field treatment appears to be adequate even for modest values of r, $r \gtrsim O(10^{-3})$ where there is no evidence for any kind of "critical phenomena" (i.e., measurable critical exponents, critical amplitudes, etc.).

The maximum C_P^* of each $C_P(T)$ curve in Fig. 5 defines a polymerization temperature T_p and a measure of the "strength" of the polymerization transition.[47] In particular, consider the ratio $\delta C_P \equiv C_P^*(r)/C_P^*(r \to 0)$, which ranges between 0 and 1 as exhibited in the inset to Fig. 5. Kennedy and Wheeler[18] have previously noted that $C_P^*(r \to 0)$ equals

$$C_P^*(r \to 0) \simeq k_B [\Delta h / k_B T_p^{(o)}]^2, \tag{34}$$

which is *independent* of Δh since the polymerization temperature $T_P^{(o)}$ is proportional to Δh [see Eq. (23)]. The specific heat maximum becomes very "diffuse" for high initiator concentration, and the ratio δC_P provides a useful means of estimating how much the polymerization transition is like a second order phase transition. The ratio δC_P also provides potentially important means of estimating the amount of initiator that is "active." The initiator can react with impurities in solution to modify the effective value of r.

Figure 6 displays the initial monomer dependence of the specific heat on composition ϕ_m^0. The initiator concentration $r = 0.0044$ is the same as in the measurements of Greer *et al.*[2,3,33] Both the polymerization temperature and the sharpness of the polymerization transition strongly depend on ϕ_m^0. When ϕ_m^0 grows, T_p is shifted to higher temperatures, while the sharpness of the polymerization transition (specified by the half width of the C_P peak) diminishes. T_p also coincides with the infection point in the $\Phi(T)$ curve (see below). The inset to Fig. 6 exhibits reasonable agreement of our calculations[48] with the experimental data of Greer *et al.*[32] for the system with $\phi_m^0 = 0.118$ and $r = 0.0032$.
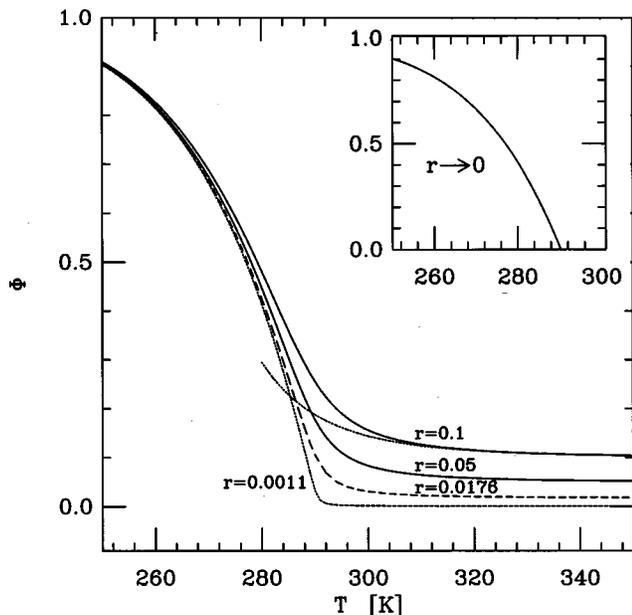
FIG. 7. Fraction Φ of monomers converted to polymers as a function of temperature T for the fixed initial monomer concentration $\phi_m^0 = 0.15$ and for a range of initiator concentrations r. Note the increasingly large tail which forms as r is increased. The dotted line for $r = 0.1$ shows Φ_{tail} as calculated from the high temperature expansion in Eq. (35). The inset considers Φ in the limit of an infinitesimal initiator concentration ($r \rightarrow 0^+$) where a nonanalytic temperature dependence is approached.

The extent of polymerization Φ, defined as the fraction of monomers converted into polymers, represents an order parameter type variable for living polymerization. As mentioned above, this language is loose since there is no true phase transition associated with the polymerization for $r \neq 0$. Figure 7 displays Φ as a function of temperature for several different values of r and for a fixed initial monomer concentration ϕ_m^0. The curves demonstrate that Φ develops a ''tail'' which becomes larger as r is increased. Starting from Eq. (22), the high temperature expansion of Φ is obtained as,

$$\Phi_{tail} = \Phi(T > T_p) = \Phi_\infty + \frac{r}{2}[A_\infty x + A_\infty^2 x^2 + \dots], \qquad (35)$$

where the high temperature expansion variable x is defined as

$$x \equiv \exp[-\Delta h / k_B T], \qquad (36)$$

and the coefficient A_∞ is the high temperature limit of the parameter A in Eq. (14),

$$A_\infty \equiv A(T \rightarrow \infty) = \phi_m(T \rightarrow \infty)\exp[\Delta s/k_B]$$
$$= (\phi_m^0 - \phi_I)\exp[\Delta s/k_B]. \qquad (37)$$

At very high temperatures, Φ simply reduces to the initiator concentration r,

$$\Phi_\infty \equiv \Phi(T \rightarrow \infty) = r. \qquad (38)$$

The high temperature expansion in Eq. (35) (dotted line) and the exact Φ are compared in Fig. 7 for $r = 0.1$.

The inflection point of Φ versus T also can be used to define the polymerization temperature T_p. Kennedy and

Wheeler[18] have shown that the specific heat C_P is approximately proportional to the derivative of the fraction of monomers converted into polymers Φ,

$$C_P \simeq \Delta h (d\Phi/dT), \qquad (39)$$

and we have verified that this approximation holds accurately (eight significant digit agreement) in our calculations. Equation (39) implies that the temperature at which the specific heat has a maximum (i.e., the ''polymerization temperature'' T_p) coincides with the T at which the $\Phi(T)$ curve exhibits an inflection point.

Figure 8(a) illustrates dependence of Φ on the monomer concentration. The main part of the figure presents Φ for representative ϕ_m^0 values and compares our calculations to the measurements of Greer $et\ al.$[3,33] for poly(α-methylstyrene) in methylcyclohexane. The measured values of Φ are denoted by squares, and ϕ_m^0 in the experimental sample equals 0.15. Increasing ϕ_m^0 produces an increase in Φ at a fixed T, as is found for the average polymer length L (see Fig. 2). The extent of polymerization is further considered in a different way in the inset to Fig. 8(a), where Φ is plotted as a function of ϕ_m^0 for a range of fixed temperatures. A critical polymerization concentration ϕ_m^* is estimated by extrapolating the linear portions of the $\Phi(\phi_m^0)$ curves to zero, analogous to the extrapolation of L to unity in Fig. 3. (Kumar and Panagiotopoulos[49] use the same method to determine the critical gelation concentration or gelation line in simulations of associating polymers with ''sticker'' groups.) The intercepts from the Φ-extrapolations are denoted by $\times$ in Fig. 9, and these estimates for the onset of polymerization nearly coincide with those obtained from the extrapolation of L to unity in Fig. 3 (the $\square$ symbols in Fig. 9). Notably, the extrapolated critical polymer concentrations from the $\Phi(\phi_m^0)$ and $L(\phi_m^0)$ curves lie very close to the ideal polymerization line in Fig. 9. The cpc curve and the ideal polymerization line $T_p^{(o)}$ seem to be identical. This finding is restricted to relatively small r, however, and for larger r, it becomes more difficult to extrapolate $\Phi(\phi_m^0)$ to zero to determine ϕ_m^* due to the nonlinearity of the $\Phi(\phi_m^0)$ function.

Kumar and Panagiotopoulos also suggest that the gelation transition in thermally reversible gels can be estimated effectively from a plot of the volume fraction of unassociated polymer versus the initial polymer concentration.[49] This criterion is based on a suggested analogy between thermally reversible gelation and micelle formation. Figure 8(b) considers the corresponding properties for a living polymer solution by plotting the monomer concentration ϕ_m versus the initial monomer concentration ϕ_m^0. The figure shows ϕ_m increasing linearly with ϕ_m^0 if ϕ_m^0 lies below the critical polymer concentration ϕ_m^*, and ϕ_m becoming nearly independent of ϕ_m^0 for $\phi_m^0 > \phi_m^*$. This phenomenon is strikingly similar to simulations of thermally reversible gels and observation and simulations of micelle formation (see Ref. 49).

It is apparent from the discussion above that distinct transition points emerge from the specific heat maximum (or equivalently the inflection point in the temperature dependence of Φ) and from extrapolating L to unity or Φ to zero. The specific heat maximum is identified as the true polymerization temperature T_p, since the maximum is a real rather

FIG. 9. Transition temperatures of living polymer solutions as a function of initial monomer concentration ϕ_m^0. The upper "crossover temperature" line denotes the loci where the fraction Φ of monomers converted into polymers is 5% greater than its high temperature limiting value $\Phi(T \to \infty) = r$. Solid line is the "ideal polymerization transition" line in the $r \to 0^+$ limit, and the squares and crosses represent estimates of the transition line from the "critical polymerization concentration" in Figs. 3 and 9, respectively. The ideal polymerization line thus coincides with the curve defining the critical polymerization concentration. The dot-dash and long-dash lines denote the polymerization transition temperatures at which specific heat has a maximum for $r = 0.0044$ and 0.1, respectively. The "saturation line" $T_s(\phi_m^0)$ corresponds to temperatures where the entropy of the living polymer solution approaches to within 5% of its limiting low temperature values S_o. We observe that the ratios of the crossover and saturation temperatures to the polymerization temperatures are nearly constant and equal to $T_x/T_p = 1.21 \pm 0.04$ and $T_p/T_s = 1.22 \pm 0.02$, respectively. r is varied in the range (0.0011, 0.0176) which is a factor of four larger and smaller than the reference value $r = 0.0044$.

FIG. 8. (a) Fraction of monomers converted to polymers as a function of temperature T for a fixed initiator concentration $r = 0.0044$ and a range of initial monomer concentrations ϕ_m^0. Squares denote the experimental data of Greer *et al.* (Ref. 33). Inset shows Φ versus ϕ_m^0 for fixed temperatures. The $\times$ in Fig. 9 denote the extrapolated values of ϕ_m^0 defining the onset of polymerization. (b) Volume fraction of unassociated monomers ϕ_m versus the initial volume fraction of monomers ϕ_m^0. Arrows in figure indicate critical polymerization concentration from Fig. 3. Parameter values of living polymerization model correspond to poly(α-methylstyrene) ($r = 0.0044$). The flattening of the $\phi_m(\phi_m^0)$ curve is characteristic of other associating systems (see Ref. 49).

than an extrapolated feature characteristic of the onset of polymerization. The polymerization lines $T_p(\phi_m^0)$ in Fig. 9 depend on the initiator concentration r, and the departures between $T_p(\phi_m^0)$ and the "ideal polymerization line" $T_p^{(o)}(\phi_m^0)$ of Dainton and Ivin increase with r. For the initiator concentrations considered by Greer *et al.* for poly(α-methylstyrene), the deviations between $T_p(\phi_m^0)$ and $T_p^{(o)}(\phi_m^0)$ should only be on the order of a few degrees and

thus difficult to resolve experimentally. However, more significant deviations can be expected for larger values of $|\Delta h|$ and r, leading to a greater separation between the critical polymerization concentration line $T(\phi_m^*)$ [or equivalently $T_p^{(o)}(\phi_m^0)$] and the true polymerization line $T_p(\phi_m^0)$. It will be interesting to examine this gap between the critical polymerization line $T_p^{(o)}(\phi_m^0)$ and the polymerization line $T_p(\phi_m^0)$ for other types of associating polymers.

The growth of initiated polymer chains above T_p should be reflected in changes of transport properties, such as viscosity, collective diffusion coefficient, etc., since these properties are generally sensitive to fluid heterogeneity. Previous measurements for sulfur and poly(α-methylstyrene) solutions identifiy the polymer transition temperature by a sharp increase in the viscosity as measured by a falling ball viscometer.[50,51] The initiation probability (the analog of initiator concentration) in sulfur solutions is extremely small[2,3] (yielding one of the few cases where the living polymerization transition has the appearance of a real second order phase transition). While the viscometric method provides a reasonable estimate for the polymerization temperature of sulfur solutions, we expect the polymerization to initiate at a

higher ''crossover'' temperature T_x when the initiator concentration is larger. The viscometric determination of the polymerization line must be performed very carefully.

The ''crossover temperature'' T_x is defined as the temperature at which the polymerization process first becomes detectable, and this definition, of course, depends somewhat on the method of measurement. Nevertheless, a good estimate for T_x may be obtained by considering the magnitude of uncertainty in the measurement process and by specifying the temperature where deviations emerge beyond this uncertainty. We therefore consider a criterion in which the fraction of polymerized monomer Φ is taken as 5% greater than its high temperature limit $\Phi(r, T \to \infty) = r$ as a reasonable order of magnitude detection limit for polymeric clustering. (This criterion is in the spirit of the Ginzburg criterion for the breakdown of homogeneity in a critical fluid mixture.[52]) The resulting ''crossover curve'' T_x is displayed in Fig. 9 as a function of ϕ_m^0 and surprisingly is nearly *independent* of the initiator concentration for r in the range $r \in (0.0011, 0.0176)$. Moreover, the concentration (ϕ_m^0) dependence of T_x is similar to that for T_p or $T_p^{(o)}$. The ratio $T_x/T_p = 1.21 \pm 0.04$ for $\phi_m^0 \in (0.01, 0.99)$ implies that a good estimate of T_x can be obtained from a knowledge of T_p. Thus, the crossover temperature T_x can occur well above T_p (see the example in Fig. 9), and therefore great caution must be exercised in deducing[51] T_p from viscometric or other transport measurements.

Living polymer solutions with initiator exhibit another characteristic temperature that does not exist for polymerizing systems without initiator. As discussed above, chain growth becomes limited at low temperatures, and the average chain length L ''saturates'' to $L_p = 2/r$ for $T \ll T_p$. The entropy S of the living polymer solution also drops precipitously upon cooling and likewise ''saturates'' at a temperature comparable to that where L ceases to vary with T. (The temperature dependence of S and its relation to L are described below.) Figure 9 presents the locus of saturation temperatures T_s at which S becomes 5% greater than its low temperature limit S_o. The saturation temperature T_s is almost independent of the initiator concentration for r in the range $r \in (0.0011, 0.0176)$, and its definition is similar in spirit to the definition of the Kauzmann temperature[53] in glass-forming liquids where the excess entropy is formally extrapolated to zero. Thus, living polymers systems with initiator have an onset temperature T_x (which can be well above T_p) where the polymers begin to grow, a ''transition'' temperature T_p where they grow rapidly and the system exhibits a specific heat maximum, and a ''saturation'' temperature T_s where they cease to grow and the entropy saturates, respectively. These three characteristic temperatures are essential to understanding the properties of living polymer systems.

In addition to the average chain length L and the order parameter Φ, the molecular weight distribution $p(N)$ is important for characterizing living polymers. Unfortunately, there have been few measurements[54] of $p(N)$. (There happen to be measurements of the molecular weight distribution for actin living polymers where the individual molecules can be directly observed by microscopy.[55]) The Flory-Huggins model produces purely exponential tails for this distribution
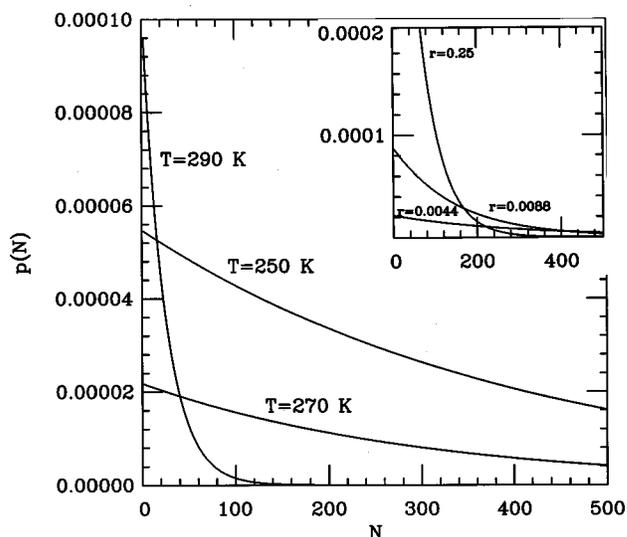
FIG. 10. Chain length N distribution $p(N)$ for living polymer solutions over a range of temperatures T and for fixed initial monomer $\phi_m^0 = 0.15$ and initiator concentrations $r = 0.0044$. The curves exhibit the increase in chain length upon cooling. The inset depicts the variation of $p(N)$ with r for fixed temperature $T = 270$ K and initial monomer concentration $\phi_m^0 = 0.15$. The values of $p(N=1)$ are not indicated in both figures since they lie off scale unless r is unreasonably large. The interaction parameter χ is taken as $\chi = 121/T$, so the polymerization occurs in the one-phase region.

of chain length N, as illustrated in Fig. 10 for a few temperatures but for constant $\phi_m^0 = 0.15$ and $r = 0.0044$. The inset to Fig. 10 shows how $p(N)$ changes with initiator content when $\phi_m^0 = 0.15$ and $T = 270$ K. The probability $p(N=1)$ for the monomers is not presented in both figures since it is off scale unless r is unreasonably large. For instance, $p(N=1, T = 270 \text{ K}) = 0.9935$, 0.9870, and 0.9635 for $r = 0.0044$, 0.0088, and 0.025, respectively. When the temperature is increased, the distribution becomes more steep, and the large N tail of $p(N)$ diminishes. A simple example illustrates this variation. The average chain length L, as estimated from Eq. (29) by taking a finite length i^* as the upper limit in the sum over i, converges slowly to the L of Eq. (24), especially at low temperatures. For $T = 250$ K, $\phi_m^0 = 0.15$, and $r = 0.0044$, we obtain $L = 7.46$, 9.74, 10.10, and 10.14 when $i^* = 1000$, 2000, 3000, and 4000, respectively. This example demonstrates that chains composed of a few thousand monomers are still statistically relevant even when L is fairly small. As already noted, the presence of initiator limits polymer growth, so the variation of $p(N)$ with initiator concentration is similar to that produced by a change in temperature. The examples of $p(N)$ are restricted to temperatures greater than the critical temperature for phase separation ($T > T_c$). Two molecular weight distributions exist for $T < T_c$, one for each coexisting phase.[39]

In order to ascertain the sensitivity of the molecular weight distribution $p(N)$ to the polymerization mechanism, additional calculations[39] have been performed for the model in which the propagating species $M_1 I_1$ has only *one* initiator molecule. The resulting distributions $p(N)$ for chains having one and two initiator molecules are found to be nearly identical numerically provided that the number of growing chains

is the same. The latter constraint implies that the initiator concentration r in the single initiator molecule per polymer system must be half of that for solutions with two initiator molecules per polymer.

The relation between the decay length λ of the molecular weight distribution $p(N)$,

$$p(N) \sim e^{-N/\lambda}, \quad N \to \infty, \tag{40}$$

in Eq. (26) and the equilibrium chain lengths L and $\hat{L}$ is not obvious at first glance from Eq. (26). Intuitively, λ should be more closely related to $\hat{L}$ since the tail of the $p(N)$ distribution refers exclusively to the distribution of the polymeric species. Inspection of Eqs. (26)–(28) implies that λ equals neither L nor $\hat{L}$. However, A may be expressed in terms of L through Eq. (24),

$$A = 1 - \frac{r}{2} \frac{L}{L-1}, \tag{41}$$

so that subsequent expansion of $\ln A$ as

$$\ln A = \ln\left[1 - \frac{r}{2} \frac{L}{L-1}\right] \approx \frac{r}{2} \frac{L}{L-1}, \tag{42}$$

leads to a representation of the decay length λ in the form,

$$\lambda = -1/\ln A \approx \frac{2}{r} \frac{L-1}{L} \approx L_p \frac{L-1}{L}, \tag{43}$$

where L_p is the saturation value of L at low temperatures, $L_p \approx 2/r$. Note that the approximation $\lambda \approx L_p(L-1)/L$ holds only for small r. To our surprise, $\hat{L}$ is also found to be well approximated by

$$\hat{L} \approx L_p(L-1)/L, \tag{44}$$

thereby indeed yielding the approximation $\hat{L} \approx \lambda$. Moreover, Eqs. (25) and (44) may be combined to produce the nontrivial relations,

$$\Phi \approx \frac{L-1}{L} \quad \text{or} \quad L \approx \frac{1}{1-\Phi}, \tag{45}$$

between the average chain length L and the extent of polymerization Φ. The exact relation between L and Φ is readily shown to be

$$L = \frac{1}{1-\Phi+r/2}, \tag{46}$$

which demonstrates that the applicability of Eq. (45) is restricted to small r. At high temperatures ($T > T_p$), the extent of polymerization is small, and inserting the high temperature expansion from Eq. (35) into Eq. (46) gives,

$$L \approx 1 + \frac{r}{2}[1 + A_\infty \exp(-\Delta h/k_B T)] + O(r^2), \tag{47}$$

where $A_\infty \sim \phi_m^0 \exp[\Delta s/k_B] + O(r^2)$. Equation (47) is also restricted to relatively high temperatures since Eq. (35) is a high temperature expansion. A similar scaling with temperature appears also in Eq. (31), which describes L for a broad range of temperatures in the vicinity of T_p and higher. Figure 11 compares $\hat{L}$ and λ for $r = 0.0044$ and demonstrates that
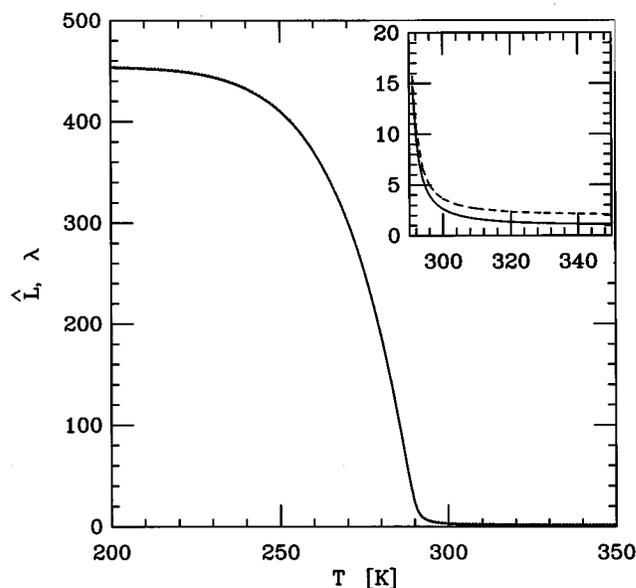
FIG. 11. Relation between the decay length λ of the molecular weight distribution $p(N)$ and the average polymer length $\hat{L}$ of a living polymer solution. The initial monomer concentration is $\phi_m^0 = 0.15$, while the initiator concentration is $r = 0.0044$. The monomers are not included in the averaging to calculate the chain length $\hat{L}$, and thus this average tends to be larger than L. $\hat{L}$ approaches L in the low temperature limit, however. The main figure shows that λ is very well approximated by $\hat{L}$, provided $T < T_p = 287.2$ K. On the other hand, the inset demonstrates that the deviation between $\hat{L}$ (dash curve) and L (solid curve) can be appreciable for $T > T_p$.

the approximation $\hat{L} = \lambda$ holds very well provided $T < T_p^{(o)}$. Equations (43)–(47) provide a method for estimating L (or Φ) from data for the molecular weight distribution of living polymers.

Excluded volume interactions within and between the polymers lead to deviations from the mean-field result in Eq. (26) for dilute polymer solutions. Scaling arguments[24,56] in this case predict that the exponential tail of the molecular weight distribution is multiplied by a factor $N^{\gamma-1}$, where γ is the "susceptibility" exponent of self-avoiding walks[56,57] $\gamma(d=3) = 1.16$. Simulations[19–23] for living polymerization (with $r = 0$) confirm these scaling arguments. Thus, an improved estimate of $p(N)$ can be obtained by incorporating these corrections to mean-field theory when excluded volume corrections are required.

One question posed by recent simulations of cooled liquids is how the existence of transient particle clustering affects the entropy of a liquid.[25] In particular, an inverse relation has been suggested between the dynamic cluster mass (which corresponds to L for living polymers) and the entropy of glasses.[58] Thus, we analyze the existence of a possible relation between L and the entropy S of a living polymer fluid. The entropy of the living polymer solution decreases sharply to a saturation value S_o at low temperatures, and the entropy also approaches a constant $S(T \to \infty)$ at high temperatures. This saturation value S_o is found to be proportional to the initial monomer concentration ϕ_m^0 and to the absolute value of the polymerization entropy $|\Delta s|$ for poly(α-methylstyrene) and $r = 0.0044$. We then define an ex-

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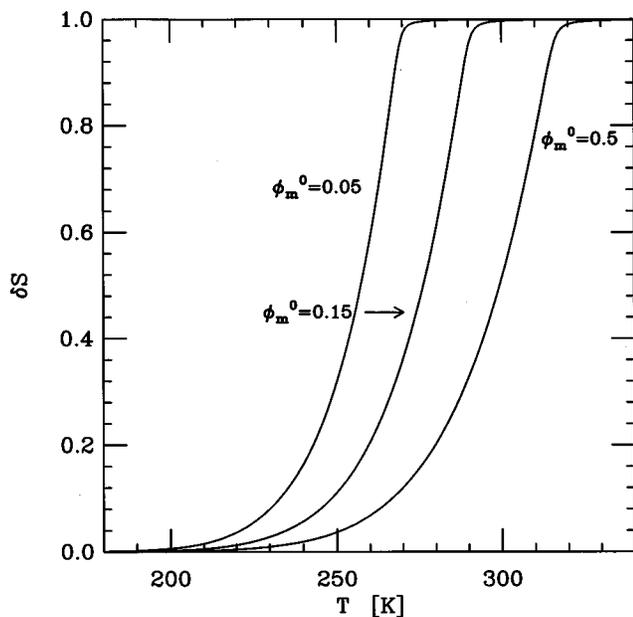
FIG. 12. Temperature dependence of the excess entropy $\delta S \equiv \Delta S / \Delta S(T \to \infty)$ of the living polymer solution for a range of initial monomer concentrations ϕ_m^0 at a fixed initiator concentration $r=0.0044$. The primary influence of varying ϕ_m^0 is to shift the transition temperature. The excess entropy δS is defined relative to the residual entropy ΔS of the polymer solution at low temperatures, and the excess entropy is normalized by its high temperature limit, so that $\delta S \equiv \Delta S / \Delta S(T \to \infty)$ is a dimensionless number ranging between 0 and 1.

FIG. 13. Relation between the excess entropy δS and the average chain length L of a living polymer solution for a range of initiator concentrations r and a fixed initial monomer concentration $\phi_m^0 = 0.15$. The excess entropy δS is defined as in Fig. 12. L is nearly proportional to $1/\delta S$ over almost the entire range of definition of L and δS. The inset shows that the inverse proportionality holds particularly well at more elevated temperatures closer to T_p.

cess entropy[59] ΔS relative to the low temperature ''residual entropy'' S_o, so that $\Delta S = S(T) - S_o$ becomes very small at low temperatures, and we further normalize the entropy by dividing ΔS by its high temperature value to obtain a ''normalized excess entropy'' $\delta S \equiv \Delta S / \Delta S(T \to \infty)$ which varies between 0 and 1. Figure 12 shows that δS decreases sharply with T where the transition temperature depends on ϕ_m^0. Figure 13 exhibits the cluster mass (L) as varying in inverse proportion to δS, and this relation is nearly independent of the initiator concentration r. This scaling arises because particle clustering has the general effect of reducing the entropy, an effect that has potential importance for understanding the significance of the general sharp drop in the entropy near the glass transition of cooled liquids.[25,47,53,58]

IV. DISCUSSION

Our lattice model, mean-field theory calculations for living polymer solutions indicate many important properties of these associating systems. Chain stiffness is found to have a marginal effect on these properties within the present mean-field theoretical framework. It is then quite justified to employ flexible chain models to semiflexible associating polymers.[27] In order to compare with recent experiments of Greer and co-workers,[2,3,32,33] emphasis is placed here on living polymer solutions with a *finite* initiator concentration r. This contrasts with previous studies[11–18] that primarily focus on the $r \to 0^+$ limit where the polymerization transition has previously been interpreted as a second order phase transition. When initiator is present ($r>0$), L is found to vary *linearly* with the initial monomer volume fraction ϕ_m^0, and

the slope α of this linear variation follows an Arrhenius relation over a wide temperature range. The intercept in plots of $L-1$ versus ϕ_m^0 defines a ''critical polymerization concentration'' $\phi_m^* \approx 1/\alpha$ at which polymerization initiates. In contrast, when initiator is absent and when the temperature is well below the polymerization temperature T_p, we find that L depends *nonanalytically* on initial monomer concentration as $L \sim \sqrt{\phi_m^0}$. The nonanalytic concentration dependence is commonly cited as a general property of living polymer solutions in mean-field theory, but this scaling is demonstrated here as actually having a restricted applicability. Thus, the presence of initiator induces a *qualitative change* in the properties of living polymer solutions. (Recent experiments[42–45] for micellar ''living polymers'' produce a near linear dependence on ϕ_m^0, suggesting that initiation or some effect like initiation is important for these systems as well.) The presence of initiator also enhances the chain growth at elevated T, but limits the growth at low T where L becomes *independent* of both ϕ_m^0 and T, $L(T \ll T_p) \approx 2/r$. The transient clustering of monomers into polymers upon cooling causes a precipitous drop in the entropy S of the living polymer solution, as found in glass-forming liquids. In particular, the excess entropy ΔS relative to its residual value S_o at low T varies inversely with the chain length $L \sim \Delta S(T \to \infty) / \Delta S$ to a very good approximation. The magnitude of the maximum C_P^* in C_P and the temperature (T_p) at which this maximum occurs are both dependent on r, the transition becoming more rounded with increasing r. This rounding is also apparent in the order parameterlike variable Φ. (Strictly speaking, no second order polymerization phase transition exists for $r>0$.) While a unique transition temperature $T_p^{(o)}$ may be

defined for living polymers without initiator, the presence of initiator leads to three *characteristic temperatures*: a ''cross-over temperature'' T_x where polymers first begin to form, a ''polymerization temperature'' T_p where the specific heat has a maximum, and a ''saturation temperature'' T_s where S nearly saturates to S_o and the polymers cease to grow. The analogy of this behavior of the entropy with that of super-cooled liquids has important ramifications for understanding the transport properties of both living polymers and super-cooled liquids.[25,47,53,58]

The molecular weight distribution $p(N)$ of living polymers also exhibits notable features. The distribution function in Eq. (26) consists of two parts—the monomer contribution plus an exponentially decaying contribution governing the polymerized species. The decay length λ of the exponential tail of $p(N)$ has no obvious mathematical relation to the average chain length, but we have obtained the useful approximation $\lambda \approx L_p(L-1)/L \approx L_p\Phi$, where $L_p \approx 2/r$ is the low temperature plateau value of L. This relation should allow the experimental determination of L or Φ from data for $p(N)$ of living polymers. We also find a near equivalence between $p(N)$ for chains with one or two growing ends if the distributions are compared for conditions with the same number of growing chains.

The rich behavior of living polymer solutions arises from a competition between the free energy of association of monomers and the entropy loss due to the formation of polymers. As the temperature is lowered, the energetic gain over-comes the entropic loss, thereby providing the physical origin of polymerization upon cooling. At very low temperatures, the association energy completely dominates the behavior of the system, and, consequently, the average polymer molecular weight depends only on the amount of initiator present. However, for high temperatures the entropic contribution exerts a larger effect, and a balance between the entropy loss and the energetic gain determines the exact nature of the molecular weight distribution. The competition between energetic gain upon ''clustering'' and the entropic loss upon reducing the number of particles in the system is common to many equilibrium aggregating systems, including amphiphilic micelle formation and the clustering observed in supercooled liquids.

The ubiquitous nature of equilibrium associations[41] implies that many of our findings for end-associating (''living'') polymers apply more generally to associating polymers and self-assembling particle clusters of other kinds. For example, the temperature dependence of the ''gelation'' line for thermoreversible gels formed by associating polymers appears to be very similar to the temperature dependence of the polymerization line for living polymers,[60] and this correspondence is also apparent in the calculations of Coniglio *et al.*[61,62] based on a mean-field model of polyfunctional chain association combined with solvent mediated polymer-polymer interactions. Recent lattice model simulations by Kumar and Pangiotopoulis[49] of polymer chains with associating ''sticker'' groups dispersed along the chain yield a gelation line that increases sharply with associating group concentration ϕ_m^0, a mass distribution $p(N)$ of clusters having an exponential tail,[63] a linear increase of cluster mass with

ϕ_m^0, and other features in common with living polymers (e.g., an upward shift of upper critical solution temperature associated with the sticking interactions). It would be interesting to determine the extent to which these phenomena *quantitatively* compare. The formation of spherical micelles from small amphiphile molecules also has features in common with living polymerization.[41] The ''critical micelle concentration'' exhibits an Arrhenius temperature dependence,[40] and ''polymerization'' (micelle formation) can occur either upon lowering or raising temperature, just as in ordinary living polymers. It is not clear yet whether the micelle mass increases linearly with the concentration of surfactant (monomer), but simulations do indicate a gradual mass increase with the surfactant concentration.[40] Aqueous living polymers commonly associate upon heating[27] (e.g., actin) or for concentrations above a critical micelle concentration,[64,65] and this situation also appears to occur in micelle forming systems,[40] suggesting a common tendency toward association with a positive entropy of association arising from ''hydrophobic'' polymer interactions in water.[65–67]

The phenomenon of ''living polymerization'' has a significance in condensed matter physics that transcends the synthesis of polymers with a broad molecular weight distribution. Stringlike structures occur at equilibrium in association with many condensed matter phase transitions[68–93] and in the stationary states of important nonequilibrium systems.[94–97] The study of living polymers also provides insights into these transitions. For example, the Feynman model[83–85,98] of the λ-transition in ^{4}He is a model with a living polymerization transition involving the proliferation of particle exchange loops in low temperatures in boson fluids.[83–87] The isotropic-nematic transition in certain liquid crystalline fluids[75–77] and the superconducting transition in type II superconductors[71,72] also involve polymerlike excitations, and indeed these transitions are largely driven by these ''defect'' structures.[74] Current cosmological models[79] and models of particle generation[68–70] in high energy physics both reduce to living polymerization models in a mean-field approximation, and much of the existing theoretical literature of living polymerization belongs to this context.

Recent molecular dynamics simulations[25] provide the first unambiguous evidence for the ''cooperative rearranging regions,'' hypothesized by Adam–Gibbs[58] to exist in supercooled liquids. These stringlike clusters of enhanced particle mobility (compare to Feynman's model of the λ-transition)[83–85] are observed to have a mass distribution with an exponential tail,[25] a characteristic feature of living polymerization. The present paper demonstrates that the average length (mass) of living polymers scales inversely with the excess entropy ΔS of the living polymer solution. This finding accords with the formal arguments presented by Adam and Gibbs[58] for glass-forming liquids. Donati *et al.*[25] argue that the barrier height for collective particle motion in glasses is proportional to the average string length of the mobile particle, which is consistent with the prior argument by Adam and Gibbs[58] that the barrier height for collective motion is governed by the mass of the ''cooperatively rearranging regions.'' The growth of polymer chains shown in Fig. 1 provides a natural mechanism for the large increases

in the apparent activation energies of polymer liquids, an increase which is also a conspicuous property of ''fragile'' glass-forming liquids. Note also that the tendency of L to saturate to a constant value at low temperatures corresponds to the general tendency for the relaxation in supercooled liquids to return to Arrhenius temperature dependence at low temperatures.[99] Further implications of this promising model of transport in glass-forming liquids will be discussed elsewhere.

ACKNOWLEDGMENTS

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