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Scaling Theory of Chemically Activated Living Polymerization in a Good Solvent

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ABSTRACT: We present a scaling theory of the living polymerization of material in a good solvent for the case where the total number of chains is fixed by an irreversible initiation reaction and conclude that excluded-volume interactions have only a very weak influence on the growth of the polymers. Our estimate for the crossover temperature to the semidilute regime is in good agreement with more elaborate calculations based on a mapping onto a magnetic problem and with experimental data. We find that the polymerization temperature and the crossover temperature to the semidilute regime merge in the limit of vanishing initiator concentration and discuss the implications this has for the nonclassical behavior of living polymers in the vicinity of this limit.

I. Introduction

Living polymers are macromolecular or supramolecular materials subject to a reversible (equilibrium) polymerization reaction. In solution, at least three classes of living polymer can be distinguished, which we, for later reference, denote as chemically activated living polymers, thermally activated living polymers, and equilibrium polymers. (These are equivalent to cases I, II, and III in the terminology of Tobolsky and Eisenberg.[1]) Of these three classes, perhaps the most diverse is that of the equilibrium polymers, in which all the monomers are in principle active, i.e., can bond with each other and polymerize.[2] The number of chains as well as their mean length is in that case not fixed but regulated by the external conditions such as the temperature and the concentration of dissolved material. Examples of equilibrium polymers include giant wormlike surfactant micelles,[3] certain microemulsions,[4] and supramolecular aggregates of discotic[5] and bifunctional molecules.[6]

In systems of chemically and thermally activated living polymers not all the monomeric material is active. In chemically activated systems usually a fixed number of monomers is activated through the reaction with initiator molecules. The activated monomers react with nonactivated monomers to form activated polymers, the total number of activated species remaining fixed. The living polymerization of poly(α-methylstyrene) conforms to this class of materials.[7] Thermally activated polymerization involves inactive monomers which themselves can become active through some equilibrium process that we need not discuss here. Again, the active monomers can bond with inactive ones to form activated polymers, although their combined number is now not fixed but determined by the equilibrium between active and inactive monomers. The polymerization of sulfur[1,8] and that of the protein g-actin into f-actin fibers[9] are sometimes seen as prototypes of this type of living polymerization.

It is well established that excluded-volume interactions qualitatively alter the equilibrium size distribution of equilibrium polymers. As a consequence, their mean degree of polymerization $\overline{N}$ has a different concentration dependence in dilute solution from that in semidilute solution. Scaling theory,[10] renormalization group calculations,[11,12] and Monte Carlo simulations[14] predict a growth law $\overline{N} \sim \phi^{\alpha}$ with the exponent α equal to $1/(\gamma + 1)$ in the dilute regime, crossing over to $(\nu d + \gamma - 2)/2(\nu d - 1)$ in the semidilute regime. Here, ϕ denotes the volume fraction of dissolved material, d the dimensionality of space, γ the critical exponent associated with the partition function of a self-avoiding chain, and ν that of the end-to-end distance.[13] For $d = 3$ we have $\gamma \simeq 1.157$ and $\nu \simeq 0.588$, so $\alpha \simeq 0.46$ in the dilute solution and $\alpha \simeq 0.60$ in the semidilute solution.[14] In the mean-field approximation, the growth exponent is one-half in both regimes. (Note that we have made the tacit assumption that ring closure does not take place, which seems to be true for most giant micelles.[2,10] We ignore rings for reasons of simplicity.[15])

Although one would imagine that excluded-volume interactions alter the behavior of chemically and thermally activated living polymers in a similar way as is the case for equilibrium polymers, the situation is not at all clear. It appears that many aspects of living polymerization can be as accurately described by mean-field theory as by approaches that go beyond the mean-field approximation. (See, e.g., the review paper by Greer[7] and work cited therein.) A plausible (but incomplete) explanation for this is that the limit where critical fluctuations associated with the polymerization transition become significant is often not reached in experiment. This is particularly true for chemically activated systems of which the polymerization transition becomes a true phase transition only in the limit of vanishing initiator concentration.[16] In actual experiment the initiator concentration is typically not exceedingly small.[17] Note, however, that away from the critical limit one still expects fluctuations arising from the polymeric nature of the assemblies to give rise to deviations from the predictions of mean-field theory. These fluctuations should be important if the solvent quality is good and the chains interact strongly.

Here, we show by means of a scaling theory that self-avoidance only very weakly influences the self-assembly of chemically activated living polymers, in part explaining the accuracy of the mean-field theory for this type of system. We find that the maximum in the isothermal osmotic compressibility observed close to the polymerization temperature is not caused by critical fluctuations, as was suggested elsewhere,[16] but by the crossing over from an essentially monomeric regime to a regime

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dominated by strongly fluctuating semidilute polymers. This causes the enhancement of the compressibility to persist even when the initiator concentration is not vanishingly small, and the polymerization transition is not a true phase transition. Our arguments carry over to thermally activated living polymers with a slight modification that we intend to address in future work.

The remainder of this paper is organized as follows. First, we discuss the free energy describing chemically activated living polymerization in section II and derive an expression for the equilibrium distribution of the chains. Our approach combines a non-mean-field (scaling theoretical) treatment of the individual chains, and a mean-field description of the living polymerization. In section III we show that in the dilute regime the self-interactions of the chains only weakly couple to the polymerization transition. We repeat the calculation for strongly overlapping chains in semidilute solution in section IV and find that in this regime the polymerization is not at all influenced by excluded-volume interactions. The conditions under which the crossover from dilute and semidilute solution behavior takes place is also evaluated in this section. Our predictions agree well with the numerical calculations of Pfeuty and Wheeler based on their "zero-component" magnetic theory[16] and with the experimental data of Greer and co-workers on the polymerization of poly(α-methylstyrene) in the solvent tetradeuteriumfuran.[18] We find that for vanishing initiator concentrations both transitions merge, a circumstance which in our view leads to the special nature of the polymerization transition in that limit.[16] In section V we discuss our results and give a simple scaling Ansatz for the compressibility of living polymer solutions that confirms our suggestion that the ("nonclassical") enhancement of the osmotic compressibility is linked with the crossing over from the dilute monomeric to the semidilute polymeric regime. The paper ends with a summary and some concluding remarks in section VI.

II. Free Energy

We consider a solution containing a variable number of inactive monomers in equilibrium with a fixed number of activated linear polymeric chains. The solvent quality is presumed to be good. Let ρ_a denote the (dimensionless) number density of all activated chains and ϕ_a their volume fraction. The former is proportional to the initiator concentration and a function of how many initiator molecules are needed to produce an active species, while the latter is not known a priori since it depends on the state of polymerization of the dissolved material. In the monomeric regime $\phi_a = \rho_a$, while in the polymerized regime $\phi_a > \rho_a$. To avoid having to specify the chemistry of the living polymerization, we keep ρ_a as a free system parameter.

For technical reasons, we assume that there are not only inactive monomers in the solution but also inactive chains that we suppress later on. The volume fraction of inactive chains is ϕ_i. The relevant free energy density $\mathscr{F}$ describing our system of living polymers can (within a saddle-point approximation) be written as

$$\beta\mathscr{F} = \sum_{n=i,a} \sum_{N=1}^{\infty} \rho_n(N)(\ln \rho_n(N) - 1 - \ln Z(N) + \beta F_n(N-1)) + \beta F_{\text{exc}} \quad (1)$$

in both dilute and semidilute solution, where $\beta \equiv 1/k_B T$ with k_B Boltzmann's constant and T the absolute temperature. The dimensionless number density of chains of type $n = i$ (inactive) and $n = a$ (active), and of degree of polymerization N, is given by $\rho_n(N)$, while $Z(N)$ is the single-chain partition function. $F_a \leqslant 0$ is the free energy change associated with the formation of a single bond on an active chain, and $F_i \geqslant 0$ is that of the formation of a bond on an inactive chain, where we note that a linear chain consisting of N monomers has $N - 1$ bonds. Below, we set $F_i \to \infty$ in order to suppress inactive dimers, trimers, and so on, but for now we assume that inactive chains do form. The excess free energy F_{exc} contains interaction terms that cannot be absorbed into $Z(N)$. Equation 1 generalizes an earlier Ansatz for equilibrium polymers, which may be obtained by putting $\phi_i = 0$.[19]

Before we minimize the free energy equation (1), we need to ensure the conservation of the number of active chains

$$\rho_a = \sum_{N=1}^{\infty} \rho_a(N) \quad (2)$$

as well as that of the overall mass dispersed in the solvent

$$\phi = \phi_i + \phi_a \quad (3)$$

where

$$\phi_n = \sum_{N=1}^{\infty} N \rho_n(N) \quad (4)$$

for $n = i$, a. It proves useful to introduce the Lagrange multipliers μ and λ, the former enforcing eq 4 and the latter eq 2. The equilibrium concentrations of active and inactive polymers then follow from the equality

$$\frac{\delta\mathscr{F}}{\delta\rho_n(N)} = -\mu N - \lambda\delta_{n,a} \quad (5)$$

with $\delta_{n,a}$ the usual Kronecker symbol, equal to unity if $n = a$ and equal to zero if $n = i$.

The functional derivative of eq 5 is readily performed because both $Z(N)$ and F_{exc} are (in principle) only functions of ϕ_n, making them invariants of the distribution functions (see also below). Note that of the inactive chains only the monomers survive when the limit $F_i \to \infty$ is taken and that for sufficiently long active polymers the inactive monomers are such small objects that for all practical purposes they may be viewed as part of the (effective) solvent. From eq 5 we thus find for our equilibrium distributions

$$\rho_n(N) = Z(N) \exp(-\mu N - \beta F_n(N-1) - \lambda\delta_{n,a}) \quad (6)$$

where the Lagrange parameters μ and λ can be eliminated with the help of eqs 2−4 provided we know $Z(N)$. The precise form of $Z(N)$ depends on whether the solution is dilute or semidilute. In the next section we first specify $Z(N)$ for conditions where the polymers, if present, are so dilute that they are widely separated from each other in the solution.

III. Polymerization in Dilute Solution

If the number density of active chains is sufficiently low and if these chains have not grown to the point where they start to interpenetrate, the chains are in the dilute regime. In that case interactions between the chains can be neglected, so we use the partition function of a self-avoiding walk[13,20]

$$Z(N) \sim N^{\gamma-1} z^N \tag{7}$$

valid in the long-chain limit $N \gg 1$, with γ the aforementioned critical exponent and z a nonuniversal constant of order unity. We arbitrarily set this constant equal to unity, as it merely renormalizes the binding (free) energy F_n. As we shall see below, the mean degree of polymerization $\overline{N}_a$ of the active material

$$\overline{N}_a = \frac{\phi_a}{\rho_a} \tag{8}$$

can be very large even before we reach the polymerization transition if $r \equiv \rho_a/\phi \ll 1$. (Note that this definition for the parameter r is slightly different from what is customary, allowing us to avoid specifying the stoichiometry of the initiation reaction.[7]) This implies that the asymptotic relation (7) can indeed be used to describe the polymerization transition, albeit only if the initiator concentration is sufficiently low.

If we introduce the shifted chemical potential $\tilde{\mu} \equiv \mu + \beta F_a$, insert eq 7 into eq 6, and eliminate λ, we find

$$\phi_i = \exp(-\tilde{\mu} + \beta F_a) \tag{9}$$

in the limit $F_i \to \infty$ where the mean degree of polymerization of inactive polymers becomes equal to unity, i.e., $\overline{N}_i = 1$, and

$$\phi_a = \gamma \rho_a \tilde{\mu}^{-1} \tag{10}$$

where the latter equality was obtained by replacing the summation in eq 4 by an integration, which is allowed provided $\overline{N}_a \gg 1$. Again, this is justified if $r \ll 1$, except very deeply into the monomeric regime. Equations 9 and 10 imply the following equation of state

$$A = rA\gamma\tilde{\mu}^{-1} + \exp(-\tilde{\mu}) \tag{11}$$

where $A \equiv \phi \exp(-\beta F_a)$. Focusing on small initiator concentrations equivalent to $r \ll 1$, we find that polymerization takes place only if $\tilde{\mu} \to 0$. It makes sense, then, to Taylor expand the exponential in eq 11 to first order in $\tilde{\mu}$, giving

$$A = 1 - \tilde{\mu} + rA\gamma\tilde{\mu}^{-1} \tag{12}$$

This quadratic equation in $\tilde{\mu}$ is readily solved to give

$$\tilde{\mu} = \frac{1}{2}(1 - A + \sqrt{(1 - A)^2 + 4\gamma r A}) \tag{13}$$

From eq 13 we find that, for $r = 0$, $\tilde{\mu} = 1 - A$ if $A \leqslant 1$ and $\tilde{\mu} = 0$ if $A \geqslant 1$. In other words, the chemical potential $\tilde{\mu}$ exhibits a discontinuity for the value $A = 1$ if $r = 0$, indicating that the polymerization transition becomes like a true phase transition at vanishing initiator concentration. For $r > 0$ the polymerization transition at $A = 1$ is not sharp but rounded.[17] This means that for $r > 0$ the polymerization transition no longer represents a true phase transition, as advertised in section I, although strong critical fluctuations may persist if r is small enough. Within our mean-field treatment of the polymerization transition we neglect the presence of these fluctuations. Had we in addition ignored excluded-volume interactions, we would have obtained eq 13 with a critical exponent $\gamma = 1$. We recall that γ attains a value somewhat larger than unity if the polymers are self-avoiding.[13] Consequently, for $r > 0$ excluded-volume interactions influence the polymerization transition by slightly enhancing its rounded nature.

With $\tilde{\mu}$ determined we find for the mean length of the polymers $\overline{N}_a = \gamma\tilde{\mu}^{-1} \sim \gamma$ for $A \ll 1$, $\overline{N}_a = \sqrt{\gamma/r}$ for $A = 1$, and $\overline{N}_a \sim 1/r$ for $A \gg 1$. The result for small A should of course read unity—the scaling theory is inaccurate in this limit because the chains are then not large enough for excluded-volume interactions to have an appreciable impact. Exactly at the polymerization transition $\overline{N}_a = \sqrt{\gamma/r} \gg 1$ if $r \ll 1$; i.e., around the transition the chains can indeed become sufficiently long to experience the effects of self-interactions, albeit only if the initiator concentration is low. For large binding energies $A \gg 1$ the chain length levels off. In this limit, all the available monomers are absorbed into the fixed number of chains.

For the fraction polymerized material we have $\eta = \phi_a/\phi = \gamma r \tilde{\mu}_a^{-1}$, so that $\eta \sim \gamma r$ for $A \ll 1$, $\eta = \sqrt{\gamma r}$ for $A = 1$, and $\eta \sim 1$ for $A \gg 1$. We note that at the transition, when $A = 1$, not a great amount of dissolved material is in the polymeric state, because $\eta = \sqrt{\gamma r} \ll 1$ if $r \ll 1$. This means that the degree of polymerization averaged over active and inactive species $\overline{N} \equiv \phi/(\phi_i + \rho_a) = 1/(1 - \eta + r)$ remains close to unity, except deeply into the polymerized regime.

IV. Polymerization in Semidilute Solution

If we venture too deeply into the polymerized regime, the chains may overlap and interpenetrate. From the scaling theory of polymers we estimate that this can only happen if $\phi \gg r^{\nu d - 1}$.[20] Only then the polymerization saturation does not occur until well after the chains have interpenetrated. Assuming this to be the case, we now evaluate how excluded-volume interactions influence the polymerization of the chains in the strongly overlapping regime.

In the semidilute regime not only self-interactions are important, but also interactions among different chains. It is not self-evident that the free energy of a strongly interacting, highly entangled polymeric solution can be expressed in the way as is done in eq 1. One has to realize, however, that according to the scaling theory of polymers, the chains behave ideally in the semidilute regime if viewed as chains of blobs.[20] As is well established, the size of a blob measures $\xi \approx l_K \phi_a^{-\nu/(\nu d - 1)}$ with l_K the Kuhn length of the chains. Noticing that the number of monomers inside a blob equals $(\xi/l_K)^{1/\nu}$, we find that eq 1 can be used if the partition function of a chain of degree of polymerization N is chosen such that

$$Z(N) \sim (\xi/l_K)^{(\gamma-1)/\nu} z^N \tag{14}$$

in the semidilute regime. Equation 14 crosses over, as it should, to eq 7 if the blob size becomes equal to the radius of gyration of the chains at the crossover temperature from the dilute to the semidilute regime. The scaling relation (14) accounts for the screening of self-interactions of a single chain beyond a blob length, leading to a renormalization of the chain-end enhancement factor. Our argument is slightly different from that of Cates for equilibrium polymers[10,14] but in fact is equivalent to it.

Repeating the calculations of the preceding section, we find that the intensive part of eq 14 can be absorbed in the Lagrange multiplier λ that fixes the number of chains in the solution. Consequently, the chemical potential is found to obey the mean-field result, i.e., eq 13 with γ set equal to unity. (Here, we tacitly assume that $\overline{N}_a \gg (\xi/l_K)^{1/\nu}$ and that only a relatively small mass fraction of the polymers is smaller than the blob size.) We conclude that in the semidilute regime *the growth* of the chains follows mean-field behavior, although that their statistical properties are still dominated by fluctuations that do not conform to a mean-field picture. Note further that the difference between dilute and semidilute behavior is very subtle and may be very difficult to observe experimentally.

An important question is how close the crossover temperature to the semidilute regime is to the polymerization temperature. This is easily calculated using standard arguments from the scaling theory of polymers.[20] The crossover to the semidilute regime occurs when the overall volume fraction of (active) polymers ϕ_a equals the internal concentration of segments of a single chain. For the latter we use the average degree of polymerization $\overline{N}_a$ divided by the volume of an average chain, which scales as $\overline{N}_a^{\nu d}$. Thus, the crossover occurs roughly when the equality $\phi_a = \overline{N}_a^{1-\nu d}$ holds, in which we insert the previously derived relations $\phi_a = \gamma\rho_a\tilde{\mu}^{-1}$ and $\overline{N}_a = \gamma\tilde{\mu}^{-1}$. This gives for the chemical potential of the monomers at the crossover to the semidilute regime $\tilde{\mu}^* = \gamma\rho_a^{1/\nu d} \to 0$ if $\rho_a \to 0$. In other words, this crossover moves arbitrarily close to the polymerization transition if we let the initiator concentration go to zero.

From eq 12 we find that the crossover value A^* of the control parameter A obeys

$$A^* = \frac{1 - \gamma\rho_a^{1/\nu d}}{1 - r\rho_a^{-1/\nu d}} \tag{15}$$

which in the limit $1 \gg \phi \gg r^{\nu d-1}$ simplifies to

$$A^* = 1 + \rho_a^{(\nu d-1)/\nu d}\phi^{-1} + ... \tag{16}$$

to leading order in a Taylor expansion. Hence, $A^* \to 1^+$ if $\rho_a \to 0$. To make the connection with experiment, let T_* denote the crossover temperature to the semidilute regime and T_p the polymerization temperature, where $A(T_*) = A^*$ and $A(T_\mathrm{p}) = 1$. We next Taylor expand the quantity $A(T) = \phi\exp(-\beta F_a(T))$ to linear order in $T - T_\mathrm{p}$, insert $T = T_*$, and combine the result with eq 16 to give

$$T_* - T_\mathrm{p} \simeq \frac{k_\mathrm{B}T_\mathrm{p}^{\ 2}}{\Delta h_a}\rho_a^{(\nu d-1)/\nu d}\phi^{-1} \tag{17}$$

where $\Delta h_a = -k_\mathrm{B}T^2\ \partial\beta F_a/\partial T|_{T_\mathrm{p}}$ is the enthalpy associated with formation of a bond at $T = T_\mathrm{p}$. In Table 1 we compare the prediction of eq 17 with the values deduced from the numerical evaluation of the magnetic theory of Pfeuty and Wheeler,[16] where we identify T_* with the temperature at which the correlation length given in Figure 4 of their paper exhibits a maximum.[21] The model parameters were chosen such as to be able to describe the polymerization of poly(α-methylstyrene) in the solvent tetrahydrofuran, which has an enthalpy of polymerization equivalent to about −35 kJ/mol.[7] The agreement with the predictions of Pfeuty and Wheeler is remarkably good, considering that in our scaling analysis we have dropped all unknown prefactors of order unity. It follows that under many practical conditions $T_* - T_\mathrm{p}$ is no more than a few Kelvin.

Table 1. Comparison of the Crossover Temperature Obtained from the Magnetic Theory of Pfeuty and Wheeler,[16] T_*^a, and That from Eq 17, T_*^b [a]

ϕ	$r \times 10^4$	T_p [K]	T_*^a [K]	T_*^b [K]
0.05	5.00	266	262	263
0.12	2.08	282	280	280
0.20	1.25	292	291	291
0.05	50.0	266	255	257
0.12	20.8	282	278	278
0.20	12.5	292	289	289

[a] T_p is the polymerization temperature, ϕ is the volume fraction of polymerizable material, and r is the ratio of the number of active chains and the number of monomers in the solution.

V. Discussion

Excluded-volume interactions influence the molecular weight distribution of chemically activated living polymers in a way similar to that of equilibrium polymers (if we suppress the formation of rings[15]). For $\overline{N}_a \gg 1$ the molecular weight distribution of both types of polymerization takes the form

$$\rho_a(N) = \frac{\rho_a}{N\Gamma(\gamma)}\left(\gamma\frac{N}{\overline{N}_a}\right)^{\gamma}\exp\left(-\gamma\frac{N}{\overline{N}_a}\right) \tag{18}$$

with Γ the usual gamma function. For chemically activated living polymers ρ_a is set by the initiator concentration, while for equilibrium polymers it is given by the equilibrium value $\rho_a = \phi_a/\overline{N}_a = \phi/\overline{N}_a$. Equation 18 holds in dilute and semidilute solution, provided we set $\gamma \simeq 1.157$ in dilute solution and $\gamma = 1$ in semidilute solution (at least for the majority of the mass polymerized into chains).

Despite the similarity of the shape of the distribution functions, the first moments of the size distributions of chemically activated living polymers and equilibrium polymers respond rather differently to the effects of excluded volume. As we have seen, the concentration and temperature dependence of the mean degree of polymerization $\overline{N}_a$ of living polymers is only very weakly influenced by interactions. This is not so for equilibrium polymers, for which $\overline{N}$ exhibits a qualitatively different growth behavior in dilute and semidilute solution.[14] (See section I.) That there should be such a difference in the response to interactions is perhaps not all that surprising, considering that equilibrium polymers can adjust both their mean length and their number, while chemically activated polymers can only adjust their mean length.

According to our scaling theory, the polymerization transition approaches the crossover to the semidilute regime with decreasing initiator concentrations. A similar trend may be deduced from the work of Pfeuty and Wheeler.[16] Our scaling estimate for T_*, eq 17, compares favorably with that work, as in fact it does with the experimental data of Greer and co-workers[18] on poly(α-methylstyrene) in tetradeuteriumfuran that

Table 2. Comparison of the Experimental Values of the Polymerization Temperature T_p^a and the Crossover Temperature to the Semidilute Regime T_*^a for Poly(α-methylstyrene) in the Solvent Tetradeuteriumfuran[18] and the Crossover Temperature T_*^b Obtained from Eq 17

c [g/cm^3]	$r \times 10^4$	T_p^a [K]	T_*^a [K]	T_*^b [K]
0.16	8.3	282	279	280
0.072	19	266	259	261
0.076	18	266	260	262

[a] As input, we used the experimental value for T_p and a polymerization enthalpy Δh_a equivalent to −35 kJ/mol. Results are shown for three concentrations of polymerizable material c in units of g/cm^3 and different values of r, the ratio of the number active chains and the total number of monomers in the solution.

we compiled in Table 2. Following the prescription of the previous section, we deduced the experimental T_* from the maximum in the measured correlation length shown in Figure 5 of ref 18. The volume fraction of dissolved material was estimated using the known molecular weights of the monomer and solvent involved and their specific volumes.[18] The table demonstrates once more that T_* can be quite close to T_p if the initiator concentration is sufficiently low.

We put forward that the special character of polymerization transition in the limit of vanishing initiator concentration $r \to 0$, as discussed by Pfeuty and Wheeler,[16] is caused by the simultaneous approach of a true (second order) phase transition and of a crossing over of the polymerized phase to the semidilute regime. In the semidilute regime, strong correlations between monomers persist on scales below the blob size. As we are going to make plausible next, the vicinity of a crossover to a semidilute regime at least partly accounts for the osmotic compressibility enhancement found both in the non-mean-field version of the magnetic theory and in experiment.[16,18]

To calculate the osmotic compressibility as probed in scattering experiments, we first estimate the osmotic pressure Π of the solution. In the monomeric regime, the contribution from the monomers clearly dominates the osmotic pressure, so for $A < 1$ the usual estimate for a dilute lattice gas $\Pi l_K^d \simeq k_B T(\phi_i + {}^1/_2\phi_i^2 + ...)$ should be applicable. On the other hand, if $A \gg 1$ and $r \to 0$, a significant amount of material is in the strongly overlapping polymeric state. From the scaling theory of polymers we know that for strongly overlapping polymers $\Pi \simeq k_B T \xi^{-d}$.[20] A natural interpolation formula forces itself upon us, namely

$$\Pi l_K{}^d / k_B T \simeq \phi_i + \frac{1}{2}\phi_i{}^2 + \phi_a{}^{\nu d/(\nu d - 1)} \qquad (19)$$

where we have again discarded a prefactor of order unity. This expression is sensible, because for $A < 1$ almost none of the material is in the polymeric state and $\phi_a \to 0$. For $A > 1$ an increasing fraction becomes part of the polymers, ultimately crossing over to the polymer dominated regime when $A \gg 1$ and $\phi_i \to 0$. Note that eq 19 is obtainable from eq 1 with an appropriate choice of F_{exc} (see also the discussion of ref 19).

Obtainable from eq 19 is the (scaled) osmotic compressibility defined as $\chi \equiv \phi k_B T\ \partial\phi/\partial\Pi l_K^d$. In Figure 1 we have plotted for $d = 3$ dimensions χ as a function of temperature for various values of $r \equiv \rho_a/\phi$. The volume fraction was set at $\phi = 0.05$, and for the dimensionless free energy parameter we chose, following the choice of ref 16, $\beta F_a = -34.8 \times 10^3 R^{-1} T^{-1} + 106 R^{-1}$ with R the molar gas constant. The curves shown in the figure very clearly exhibit a maximum slightly below $T_p \simeq 266$ K. The maximum in χ shifts to higher temperatures with decreasing values of r and becomes more pronounced. For $r = 0$, the variation of χ with T becomes singular at $T = T_p$. Our results are in qualitative accord with those of Pfeuty and Wheeler, making plausible our suggestion that the strong enhancement of the osmotic compressibility χ in the polymerized regime is not connected with critical fluctuations but rather with the properties of semidilute polymers.

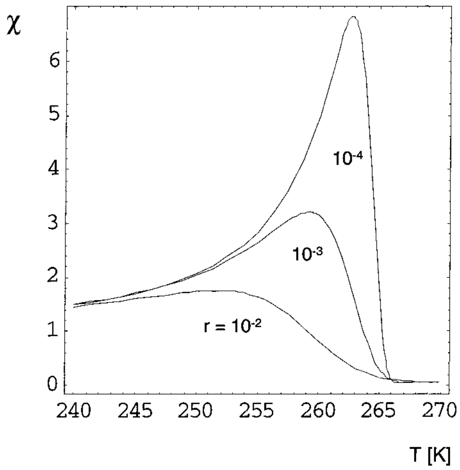

Figure 1. Osmotic compressibility $\chi \equiv \phi k_B T\ \partial\phi/\partial\Pi l_K{}^3$ as a function of temperature for the volume fraction $\phi = 0.05$. Indicated are results for three initiator concentrations, equivalent to $r = 10^{-2}$, 10^{-3}, and 10^{-4}. See the main text for details concerning our choice for the free energy of the formation of a bond.

It is in this context not difficult to explain why χ should indeed exhibit a maximum near the polymerization temperature T_p. We now understand that if the temperature is well below T_p, most of the material must be absorbed in strongly overlapping, semidilute polymers. Semidilute polymer solutions exhibit very strong concentration fluctuations, with a compressibility that is determined by the number density of blobs.[20] If the temperature goes up, the material depolymerizes, the blobs grow, and their number density goes down. The declining number of blobs in the solution gives rise to an increase of χ with temperature, as can indeed seen in Figure 1 for sufficiently low temperatures.

The compressibility keeps on rising with increasing temperature so long as this quantity is dominated by the presence of the polymers. At some point, however, the liberated monomers become so plentiful that these significantly contribute to the osmotic compressibility of the solution. Their release ultimately lowers χ with increasing temperature. The maximum in the compressibility occurs when the decrease in the number density of the blobs can no longer compensate for the released-monomer effect. This happens close to T_p, when the fraction polymerized material deminished rapidly with increasing temperature.

We finally note that a maximum in χ cannot be rationalized within a mean-field treatment of the interactions between the various species.[17]

VI. Concluding Remarks

The chemically activated living polymerization of material in a good solvent is characterized by two types of fluctuation that are, at least in principle, coupled. One type of fluctuation is associated with the conformational properties of the chains and the other with the polymerization transition. In a mean-field treatment of the problem one suppresses them both. The scaling theory presented in this paper ignores only the latter type of fluctuations through the use of an ideal entropy of mixing, but not the former since the effects of nonideal chain statistics are explicitly accounted for in the single-chain partition functions. Hence, the scaling theory should provide an accurate description of the state of affairs for conditions where the initiator concentration is not exceedingly small. The fluctuations of the distribution of material over the monomeric and polymeric state that occur around the polymerization transition are in that case relatively weak.

We find that excluded-volume interactions have only a very weak impact on the growth of chemically activated living polymers in dilute solution and that they have no impact at all in semidilute solution. This explains why a mean-field treatment of chemically activated living polymerization is often more accurate than expected.[7,17] (This contrasts with the behavior of flexible equilibrium polymers, for which a mean-field treatment is always inaccurate.[10−12,14]) Although the growth of chemically activated living polymers may be mean-field-like, the vicinity of the polymerization transition to the crossover to the semidilute regime does give rise to a nonclassical behavior of the osmotic compressibility. In qualitative agreement with the more elaborate calculations of Pfeuty and Wheeler[16] and with experiment,[18] we find that this quantity is strongly enhanced even when the initiator concentration is not very small.

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