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Scaling Theory of Interacting Thermally Activated Supramolecular Polymers

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ABSTRACT: By applying polymer scaling theory, we investigate the effects of steric interactions on the growth of a class of equilibrium polymers that require activation before polymerization can take place. The growth exponents that we obtain in dilute and semidilute solutions of such thermally activated supramolecular polymers are identical to those for isodesmic equilibrium polymers, but different from those of "living" supramolecular polymers that are chemically activated by reaction with an initiator. We also find that with increasing activation energy the crossover from the dilute to the semidilute regime shifts toward the polymerization transition and eventually merges with it, giving rise to nonclassical behavior in particular of the osmotic compressibility. It appears that steric interactions make the polymerization more co-operative in dilute solution, but less so in semidilute solution.

1. Introduction

Supramolecular polymers are linear assemblies subject to a *reversible* polymerization reaction. In contrast to conventional or "dead" polymers, the molecules that make up supramolecular polymers are in thermal equilibrium with each other, allowing them, at least in principle, to respond through their degree of assembly to changes in the ambient conditions such as the temperature, the type of solvent if present, the concentration, and so on. Supramolecular polymers are typically very polydisperse, they grow with increasing concentration and are self-healing, all of which are manifestations of the law of mass action.

In solution, at least three classes of supramolecular polymer have been identified, which we refer to as chemically activated equilibrium polymers, thermally activated equilibrium polymers, and equilibrium polymers.[1] (These correspond to cases I, II, and III in the terminology of Tobolsky and Eisenberg.[2]) Arguably, the chemically most diverse class is that of the equilibrium polymers, in which all the molecular building blocks are active, meaning that they can bond and polymerize.[3] Examples include giant wormlike surfactant micelles,[4] certain kinds of microemulsion,[5] and linear assemblies of discotic[6] and of bifunctionalized molecules.[7] Their mean molecular weight or size is not fixed but depends on the ambient conditions, as already advertised. Interestingly, orienting fields of electric, magnetic, or mechanical type couple to the polymerization,[1] as does confinement between repulsive walls.[8]

In systems of chemically and thermally activated equilibrium polymers, inactive (monomeric) material as well as active (polymeric) material is present.[9] In chemically activated systems, monomers are activated by chemical reaction with a fixed number of initiator molecules, which then each form an activated chain. Consequently, there is a fixed number of activated chains that can grow or shrink depending on the external conditions. The equilibrium polymerization of poly(α-methylstyrene) belongs to this class of material.[10]

Thermally activated polymers involve inactive monomers that can become active through some activation process, described by an activation constant that we denote by K.[1] The activated monomers can bond with inactive ones to form activated polymers, the total number of which is not fixed but regulated by two equilibria: activation and elongation. The polymerization of sulfur[2,11] and that of the protein g-actin into f-actin fibers[12] are sometimes seen as prototypes of this type of supramolecular polymerization. More recently, oligo(*p*-phenylenevinylene)s were found to behave as thermally activated equilibrium polymers in the solvent dodecane, and values of the activation constant were established as low as $K \approx 10^{-4}$, [13,14] implying a very high degree of co-operativity of the polymerization reaction.

If the supramolecular polymers are sufficiently flexible, their size-distribution should be affected by interactions within and among the polymeric chains. In a good solvent, these should be predominantly of the excluded-volume type. Indeed, excluded-volume interactions are known to have a subtle yet significant influence on the equilibrium size distribution of equilibrium polymers. Their mean degree of polymerization, $\bar{N}$, has a different concentration dependence in dilute (nonoverlapping) solution from that in semidilute (entangled) solution. Scaling theory,[15] renormalization group calculations,[16,17] and Monte Carlo simulations[18−21] agree upon a growth law $\bar{N} \sim \phi^{\lambda}$, with an exponent λ equal to $1/(\gamma + 1)$ in dilute solution crossing over to $(\nu d + \gamma - 2)/2(\nu d - 1)$ in the semidilute regime. Here, ϕ stands for the volume fraction of dissolved polymerizable 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.[22] The exponents γ and ν depend only on the dimensionality. For $d = 3$, we have $\gamma \simeq 1.157$ and $\nu \simeq 0.588$, so $\lambda \simeq 0.46$ in dilute and $\lambda \simeq 0.60$ in semidilute solution.[18] In the mean-field approximation, the growth exponent λ is one-half in both regimes.[23]

It turns out that excluded-volume interactions have an even subtler impact on the growth of chemically activated equilibrium polymers as that on equilibrium polymers:[24] their growth exponent remains mean-field-like both in dilute and in semidilute solution. This is possibly caused by the number of chains being fixed because chemically activated equilibrium polymers can only adjust their mean length, not their number. This is not to suggest that interactions do not affect the properties of

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solutions of chemically activated equilibrium polymers. Indeed, the crossover from the dilute to the semidilute regime approaches the polymerization transition with decreasing initiator concentration, giving rise to nonclassical behavior of thermodynamic properties such as the osmotic compressibility.[24] In the limit of vanishing initiator concentration, the polymerization transition in fact becomes a true phase transition.[25]

It should be noted that mean-field theory as well as approaches that go beyond the mean-field approximation both seem to describe many aspects of chemically activated equilibrium polymers quite well.[10] An explanation for this remarkable observation is that in experiments the initiator concentration is never vanishingly small, so in reality the polymerization transition never actually reaches the limit of a phase transition. Fluctuations in the degree of polymerization should therefore in practice be relatively weak, and the self-assembly is dominated by properties that are well represented by mean-field theories.

In a way, thermally activated equilibrium polymers are in between equilibrium polymers and chemically activated equilibrium polymers. They require an activation step, and one would therefore expect a similar kind of behavior as that of chemically activated equilibrium polymers in the corresponding limits of vanishing activation constant and vanishing initiator concentration. On the other hand, like equilibrium polymers thermally activated equilibrium polymers can adjust their number as well as their mean length, while chemically activated equilibrium polymers can only adjust their mean length. From this we would naively expect identical growth exponents λ in dilute and semidilute solution for thermally activated equilibrium polymers as for equilibrium polymers. However, the dilute polymerized regime should become vanishingly small in the limit $K \to 0$ for the same reasons as why this happens for chemically activated equilibrium polymers in the zero-initiator concentration limit: the chains grow exponentially and become entangled once they are formed. The crossover from the dilute to the semidilute regime should then also coincide with the polymerization transition, as happens to be the case for chemically activated equilibrium polymers.[24]

By applying similar scaling arguments as we did for chemically activated supramolecular polymers,[24] we show in this paper that self-avoidance influences the self-assembly of thermally activated equilibrium polymers in two ways. We confirm that the crossover to the semidilute regime approaches the polymerization point as we let $K \to 0$, causing the polymerization to be dominated by the strongly fluctuating semidilute polymers. This gives rise to a sharp peak in both the heat capacity and the osmotic compressibility. The growth laws we find are the same ones as that for equilibrium polymers, so, indeed, our expectation that thermally activated equilibrium polymers are in between equilibrium polymers and chemically activated equilibrium polymers is accurate.

The remainder of the paper is organized as follows. First, in section 2, we present a free energy that describes the equilibrium state of thermally activated equilibrium polymers. Our approach hinges on a non-mean-field treatment of the configurational statistics of the individual chains and a mean-field description of the equilibrium polymerization. Next, in section 3, we derive expressions for the mass distribution of activated chains both in dilute and semidilute solution. We approximately describe the behavior of thermally activated equilibrium polymers near the crossover from dilute to semidilute solution with the aid of an interpolation formula for the single chain partition function and obtain a concentration dependent growth exponent. We discuss the location of this crossover and that of the polymerization transition in section 4. By calculating the heat capacity and the osmotic compressibility, we show that the encroachment of the semidilute regime on the polymerization transition in the limit of $K \to 0$ strongly influences the thermodynamic properties of the polymers. We end this paper with a summary and some concluding remarks in section 5.

2. Free Energy

We consider the self-assembly of thermally activated equilibrium polymers in a good solvent, containing inactive monomers in equilibrium with active polymers. The concentration of inactive material is given by a (dimensionless) volume fraction ϕ_i, and that of the active material by ϕ_a. The overall mass dispersed in the solvent is constant, and is given by

$$\phi = \phi_i + \phi_a \tag{1}$$

where

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

with $\rho_a(N)$ the (dimensionless) number density of the activated polymers of degree of polymerization N. We can find the mean degree of polymerization of the active material through the equality

$$\bar{N}_a = \frac{\phi_a}{\rho_a} \tag{3}$$

where

$$\rho_a = \sum_{N=1}^{\infty} \rho_a(N) \tag{4}$$

denotes the (dimensionless) total number density of active chains. The equilibrium process that converts inactive monomers into active ones is subject to an activation constant K. Inactive monomers can react with active ones to produce active dimers and so on. We deduce that the volume fraction of the active species, ϕ_a, and the number density of active material, ρ_a, must be proportional to this constant.[1]

In both dilute and semidilute solution, we describe our system of linearly self-assembling polymers starting from a plausible ansatz for the grand potential, Ω^1. Our ansatz combines an ideal entropy of mixing favoring the monomeric state, and a free energy of the various individual species that drives the linear self-assembly, and is given by

$$\frac{\beta\Omega v}{V} = \phi_i[\ln \phi_i - 1 + \beta\mu] + \sum_{N=1}^{\infty} \rho_a(N)[\ln \rho_a(N) - 1 - \ln Z_a(\phi_a,N) + \beta\mu N] \tag{5}$$

where v is a microscopic volume that we need not specify, and $\beta \equiv 1/k_BT$ with k_B Boltzmann's constant and T the absolute temperature. The quantity V denotes the system volume, and μ the chemical potential of the monomers that enforces mass conservation. The dimensionless partition function $Z_a(\phi_a,N)$ counts all the configurational states of an active chain according to its Boltzmann weight in relation to that of an equal number of inactive monomers, and includes the free energy gain of association. As to be discussed below, the effects of excluded volume interactions inasmuch as they couple to the reversible polymerization are absorbed in this partition function, which is why it depends (at least in principle) on the overall concentration of active material ϕ_a.

Note that there are additional contributions to the grand potential that stem from interactions between the polymer segments. These we do not make explicit in eq 5 because they do not couple to the linear self-assembly. The reason is that these terms are proportional to powers of, e.g., ϕ_a, which after minimization with respect to the equilibrium distribution $\rho_a(N)$ gives rise to a contribution to the proportional to N. Hence, this term only renormalizes the chemical potential, μ, itself fixed by the overall concentration of material ϕ. We refer for a discussion of this point to a recent review paper.[1] Note further that in order to calculate the osmotic pressure from eq 5, one would have to include terms stemming from excluded-volume interactions dropped in eq 5. This we do implicitly in section 4.

In order to obtain the equilibrium distributions $\rho_a(N)$ and ϕ_i, we minimize the free energy by setting

$$\frac{\partial \Omega}{\partial \phi_i} = \frac{\partial \Omega}{\partial \rho_a(N)} = 0 \qquad (6)$$

and by demanding that $\partial^2\Omega/\partial\phi_i{}^2 > 0$ and $\partial^2\Omega/\partial\rho_a{}^2 > 0$. From eq 6, we find

$$\phi_i = \exp(-\beta G - \beta\tilde{\mu}) \qquad (7)$$

and

$$\rho_a(N) = \tilde{Z}_a(\phi_a,N)\exp(-\beta G - \beta\tilde{\mu}N) \qquad (8)$$

where for notational convenience we have absorbed all extensive terms into an effective chemical potential of an assembly, $\beta\tilde{\mu}N$, and all concentration independent intensive ones into an effective free energy *gain* of binding $\beta G > 0$.[26] The binding free energy, sometimes also referred to as the end-cap energy in the field of giant linear micelles, includes the free energy gain of association and depends also on the bending properties of the bonds.[1] This leaves a reduced partition function $\tilde{Z}_a(\phi_a,N)$ that describes the conformational states of the polymeric material, and depends on whether the solution is dilute or semidilute. It is important to stress that $\tilde{Z}_a(\phi_a,N)$ is *not* equal to $Z_a(\phi_a,N)$ since we put all intensive and extensive terms into the binding energy and the chemical potential, respectively. The first describes only the number of conformational states relative to that of a self-assembled ideal chain of equal length, while the latter still includes, e.g., the free energy gain of association.

In the next section we discuss the precise form of $\tilde{Z}_a(\phi_a,N)$ in dilute and semidilute solution, and introduce an interpolation formula that holds in both regimes.

3. Polymerization in Dilute and Semidilute Solution

The single-chain partition function $\tilde{Z}_a(\phi_a,N)$ plays an important role in the theory, because it regulates the equilibrium between the monomeric and polymeric states. If we neglect the excluded-volume effect, $\tilde{Z}_a$ is equal to the activation constant K and we find $\bar{N}_a \sim \phi_a{}^{1/2} \gg 1$ as one would within a mean-field approach,[1] at least deeply into the polymeric regime where $\phi\exp(\beta G) \gg 1$. Taking the excluded-volume effect into account, we first make a distinction between the dilute and semidilute regimes and apply established polymer scaling theory.[27] After that, we put forward an interpolation formula for the single-chain partition function and connect the two regimes.

In dilute solution the number of active chains is low and they do not interpenetrate. The mean distance between the chains is in that case larger than the mean coil size of the polymers. Given that this is so, it is justified to neglect the excluded-volume interactions between the chains and only account for the self-interaction of the chains. Note that the chains still interact through the chemical potential, which fixes the total number of monomers in the solution. It is also useful to point out that the mean degree of polymerization $\bar{N}_a$ averaged over all active monomers can be very large at the polymerization temperature, even though that the relative quantity of monomers absorbed in polymers is then still very small.[1]

Under these conditions, we can use the partition function of a self-avoiding walk that in our case reduces to[22,27]

$$\tilde{Z}_a(N) = KN^{\gamma-1} \qquad (9)$$

with γ the aforementioned critical exponent and $K < 1$ the "bare" activation constant between the inactive and active states. For an ideal chain $\gamma = 1$ and $\tilde{Z}_a$ becomes equal to the activation constant K.

The volume fraction of active chains, ϕ_a, can be determined from eq 2 by replacing the summation by an integration, which is allowed provided that $\bar{N}_a \gg 1$. This condition is obeyed even at the polymerization transition in the limit $K \rightarrow 0$ (see also below). To determine the chemical potential in terms of the mean degree of polymerization, we calculate the integrals in eqs 2 and 4 with eq 3 to find that $\beta\tilde{\mu} = \gamma/\bar{N}_a$. It turns out expedient to introduce the "mass action" variable $X \equiv \phi\exp(\beta G)$, the value of which dictates whether we are in the polymerized regime or not. (Recall that βG is a free energy gain, and positive by definition.)

Conservation of mass, (1), now gives

$$X = \exp\left(-\frac{\gamma}{\bar{N}_a}\right) + K\Gamma(\gamma+1)\left(\frac{\bar{N}_a}{\gamma}\right)^{\gamma+1} \qquad (10)$$

with Γ being the usual gamma function.[28] The first term counts the number of inactive monomers, the second the number of monomers in the activated (polymerized) state. It is easy to verify that $X \ll X_p \equiv 1$ in the monomer-dominated regime, $X \gg X_p$ in the polymerized regime and $X = X_p$ at the polymerization transition. See also Figure 1, showing that the smaller the value of K, the sharper the transition.

The ratio $X = \phi/\phi_p$ may be viewed as the ratio of the actual concentration ϕ and that at the polymerization point $\phi_p = \phi_p(T)$ at a given temperature T. At constant concentration ϕ, the temperature dependence of X follows from a Taylor expansion of βG to linear order around the polymerization temperature T_p, giving $X \approx \exp(-h_p(T - T_p)/k_BT_p{}^2)$ with $h_p = \partial\beta G/\partial\beta|_{T_p}$ being the enthalpy gain associated with the formation of a bond at $T = T_p$.[1] See also the discussion of section 4. For simplicity (and to keep the number of adjustable parameters as small as possible), we presume the activation step to be athermal, so in our analysis K is a constant of the temperature. This is not a serious restriction, since we mainly are interested in the polymerization at temperatures not too far removed from the polymerization temperature, and in fact seems to be borne out by available experimental data for supramolecular polymers of oligo(*p*-phenylenevinylene)s in dodecane.[13,14] Deeply into the polymerized regime, any temperature dependence of the activation constant merely renormalizes the enthalpy of bond formation, so our analysis remains accurate.[29]

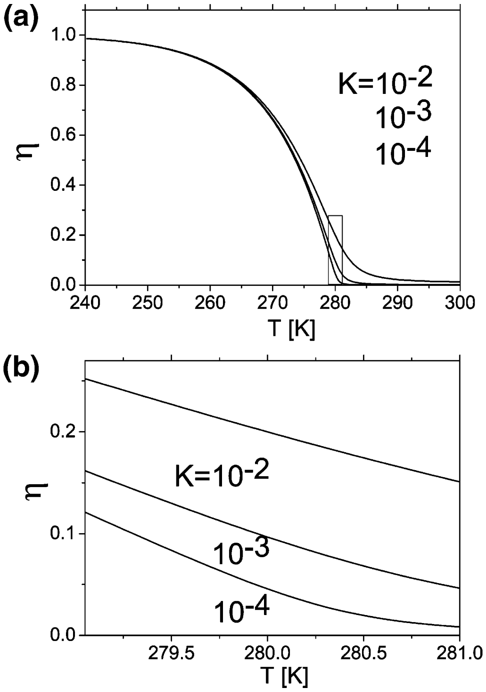


Figure 1. (a) Fraction of polymerized material, $\eta = \phi_a/\phi$, as a function of the temperature T, of a thermally activated polymerization taking place at a volume fraction of $\phi = 0.05$, given a polymerization temperature of $T_p = 280K$ and a bonding enthalpy of $h_p = 30\ k_BT_p$. Indicated are results for self-avoiding chains, for three different values of the activation constant $K = 10^{-2}$, 10^{-3}, and 10^{-4}. Part b is an enlargement of the box drawn in part a near the polymerization temperature. Increasing this constant K decreases the sharpness of the polymerization transition as shown in more detail in part b. See section 4 for a discussion of the choice values of the various parameters.

It is instructive to compare eq 10 with what one would have obtained for ideal polymers, for which $\gamma = 1$. It transpires that we can define an effective activation constant, $K_d \equiv K\Gamma(\gamma)/\gamma^\gamma \approx 0.9K$, which describes the sharpness of the polymerization transition for self-avoiding thermally activated equilibrium polymer chains in the dilute regime. Since $K_d < K$, we conclude that excluded volume interactions *increase* the sharpness of the transition, albeit only mildly so. This is opposite to what was found for chemically activated equilibrium polymers, for which interactions made the transition more "rounded", i.e., less sharp.[1] From eq 10, we furthermore deduce that deeply into the polymerized regime $1 \ll X \sim K_d\bar{N}_a^{\gamma+1}$, i.e., $\bar{N}_a \sim K_d^{-1/(\gamma+1)}X^{1/(\gamma+1)} \propto \phi^{1/(\gamma+1)}$. Hence we find the same growth exponent as that for equilibrium polymers.[15−18] The difference with equilibrium polymers is of course that the activation introduces a growth enhancement through the prefactor $K_d^{-1/(\gamma+1)} \gg 1$.

Sufficiently deeply into the polymerized regime, we expect the polymers to grow sufficiently long for them to overlap. When this happens, the polymeric solution becomes semidilute: the chains interpenetrate because the mean distance between the centers of mass of the chains is smaller than the mean coil size. This implies that there must be two types of chain: chains that are smaller than the entanglement length and chains that are larger than that.[15,16,18] The ones much smaller than the entanglement length are swollen due to self-exclusion. However, because the total number of monomers in these chains is relatively small, their contribution can be neglected: most of the polymerized material is in chains much larger than the entanglement length.[15,18]

Because intra- and interchain interactions are screened beyond the entanglement length or blob size, chains much larger than it behave (in a way) like ideal chains of blobs of size $\xi \approx l_K\phi_a^{-\nu/(\nu d-1)}$ with l_K the Kuhn length of the chains.[27] It is for this reason that the free energy of a strongly interacting and highly entangled polymeric solution can be expressed in a way as is done in eq 5. In fact, we can again use the partition function of a self-avoiding chain, except that we need to substitute the number of monomers in a chain, N, by the number of monomers in a blob, which is equal to $(\xi/l_K)^{1/\nu}$. So, for $N > (\xi/l_K)^{1/\nu}$, we put forward that in the semidilute regime

$$\tilde{Z}_a(\phi_a,N) \sim (\xi/l_K)^{(\gamma-1)/\nu}K \tag{11}$$

This scaling estimate crosses over smoothly to eq 9 for chains smaller than ξ, i.e., for $N < (\xi/l_K)^{1/\nu}$, as it should.[24] A slightly different but equivalent argument based on the configurational statistics of a free ends inside a blob, created by cutting a chain into two parts, was advanced by Cates for equilibrium polymers.[15]

Although one would expect corrections to scaling to be important, in particular near the crossover from dilute to semidilute solution, the scaling theory agrees with results of Monte Carlo simulations[18−21] and of renormalization group calculations [16,17] of the growth of equilibrium polymers, but also accurately describes experiments on linear micelles (see, e.g., ref 1 and references cited therein). A more recent application of it to chemically activated equilibrium polymers was shown to be consistent with renormalization group calculations and with experimental data on the polymerization of poly(α-methylstyrene) in tetradeuteriofuran.[24] In view of this, we put forward that for our purposes it is justified to ignore corrections to scaling for thermally activated polymers too.

Using our ansatz for $\tilde{Z}_a(\phi_a,N)$ for chains of degree of polymerization $N > (\xi/l_K)^{1/\nu}$, and ignoring the insignificant contribution from the chains with $N < (\xi/l_K)^{1/\nu}$, we again obtain an expression for the chemical potential from eq 3 in terms of the mean degree of polymerization, $\beta\tilde{\mu} = 1/\bar{N}_a$, and we can again express the mass action variable X as a function of $\bar{N}_a$, giving

$$X = \exp\left(-\frac{1}{\bar{N}_a}\right) + K^\alpha\bar{N}_a^{2\alpha}\left(\frac{X}{\phi}\right)^{1-\alpha} \tag{12}$$

with $\alpha \equiv (\nu d - 1)/(\nu d + \gamma - 2) \simeq 0.8$ in three spatial dimension. In the semidilute polymerized regime $1 \ll X \sim K^\alpha\bar{N}_a^\alpha X^{1-\alpha}\phi^\alpha - 1$, so $\bar{N}_a \sim \phi^{1/2\alpha}$. This means that we find the same growth exponent λ for thermally activated equilibrium polymers in the semidilute regime as was found for equilibrium polymers.[15] We can also define an effective activation constant valid in the semidilute regime, given by $K_{\rm sd} \equiv K^\alpha$. In contrast to the situation in the dilute regime, excluded-volume interactions in the semidilute regime *decrease* the sharpness of the polymerization transition relative to that of an ideal chain, because $K < K_{\rm sd} < 1$.

In summary, excluded-volume interactions make the polymerization more cooperative in dilute solution and less so in semidilute solution. As we show next, the latter effect will predominate in the limit $K \rightarrow 0$, for the crossover to the semidilute regime then approaches the polymerization transition.

In order to construct a unified theory of thermally activated supramolecular polymers in dilute and semidilute solution, we seek to construct an interpolation formula for $\tilde{Z}_a$. A way to do that is to realize that in the semidilute regime, the crossover from full to screened interactions occurs for chains of size $N \approx (\xi/l_K)^{1/\nu}$. This then suggests the following ansatz for the partition function of chains of all sizes in the semidilute regime

$$\tilde{Z}_a(\phi_a,N) \approx K\left(\frac{N(\xi/l_K)^{1/\nu}}{N+(\xi/l_K)^{1/\nu}}\right)^{\gamma-1} \approx K\left(\frac{N\phi_a^{-1/(\nu d-1)}}{N+\phi_a^{-1/(\nu d-1)}}\right)^{\gamma-1} \tag{13}$$

which happens to be approximately valid in the dilute limit too. The reason is that in dilute solution $\bar{N}_a \ll (\xi/l_K)^{1/\nu}$ with $\xi \approx l_K\phi_a^{-\nu/(\nu d-1)}$ the blob size *extrapolated* from the semidilute into the dilute regime. This extrapolated blob size is much larger than the actual blob size in the dilute regime, given by the average coil dimensions $\bar{N}_a^{\nu} l_K$. The mass fraction of monomers in chains larger than this extrapolated blob size is exponentially small and can be ignored, so eq 9 is retrieved for most of the mass assembled in chains. Finally we note that through the nontrivial concentration dependence of $\tilde{Z}_a(\phi_a,N)$ interactions between a chain and all the other chains are effectively included in the description of the self-assembly inasmuch as they couple to it, even in the dilute regime.

Repeating the above calculations for the interpolated partition function, eq 13, gives a self-consistent equation for the concentration of active material ϕ_a that we were not able to solve analytically. However, for the mean degree of polymerization we do find a useful relation with the chemical potential $\tilde{\mu}$

$$\bar{N}_a = \frac{\gamma_{\text{eff}}}{\beta\tilde{\mu}} \tag{14}$$

where γ_{eff} is an effective (concentration dependent) scaling exponent. This exponent can be expressed as a function of the group $\tau \equiv \beta\tilde{\mu}\phi_a^{-1/(\nu d-1)}$. It increases from a value of unity to that of γ with increasing values of τ.

The full expressions for γ_{eff} and ϕ_a can be found in the Appendix A. Eliminating $\tilde{\mu}$ in favor of eq 14 for $\bar{N}_a$ in our definition for τ, we get $\tau = \gamma_{\text{eff}}\phi_a^{-1/(\nu d-1)}/\bar{N}_a$. Because $\bar{N}_a \approx \phi_a^{-1/(\nu d-1)}$ at the crossover from the dilute to the semidilute regime we infer that at this crossover $\tau^* \approx \gamma_{\text{eff}}^*$, giving $\gamma_{\text{eff}}^* \approx 1.1$ in three spatial dimensions. In the dilute regime γ_{eff} approaches γ, and in the semidilute regime it approaches unity. The results are given in Figure 2, where we plotted γ_{eff} as a function of the number of blobs per chain $\bar{N}_a/g \simeq 1/\tau$, with $g = (\xi/l_K)^{1/\nu}$ again the number of monomers per blob. Our results for thermally activated equilibrium polymers show a similar concentration dependence of the effective critical exponent γ_{eff} as that found for equilibrium polymers,[18] suggesting that our interpolation formula, eq 13, is adequate.

Despite that we have not been able to analytically solve the self-consistent equation for ϕ_a, eq 24 in Appendix A, we can make headway by establishing a generalization of the eqs 10 and 12 and invoking a few approximations. First, we Taylor expand ϕ_i to the first order of $1/\bar{N}_a$, obtaining

$$\phi_i = \left(1 - \frac{\gamma_{\text{eff}}}{\bar{N}_a}\right)\exp(-\beta G) \tag{15}$$

which is allowed since even at the polymerization transition $\bar{N}_a \gg 1$ provided the activation constant K is sufficiently small. Next, we simplify eq 24 of Appendix A by using the estimate $U(\gamma,2,\tau) \approx \Gamma(\gamma_{\text{eff}})/\Gamma(\gamma)\tau^{-\gamma_{\text{eff}}}$, where U is the confluent hypergeometric function of the second kind.[28] It is based on the asymptotic relation of $U(a,b,z) \sim \Gamma(b-1)/\Gamma(a)z^{1-b}$ for small z, and that of $U(a,b,z) \sim z^{-a}$ for large values of z.[28] This way we have in the semidilute regime, where $\tau \ll 1$, $U(\gamma,2,\tau) \simeq 1/(\Gamma(\gamma)\tau)$, and in the dilute regime, where $\tau \gg 1$, $U(\gamma,2,\tau) \simeq 1/\tau^{\gamma}$. Combining these asymptotic relations leads to our estimate of $U(\gamma,2,\tau)$.

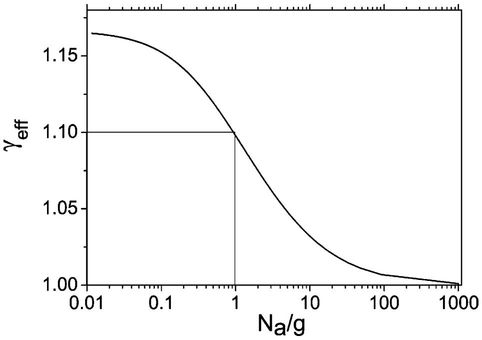


Figure 2. Scaling exponent γ_{eff} as a function of the number of blobs per chain, $\bar{N}_a/g$, according to our interpolation formula, eq 13. Note that at the crossover to the semidilute regime $g = \bar{N}_a$, so $\gamma_{\text{eff}}^* \approx 1.1$ in three spatial dimensions.

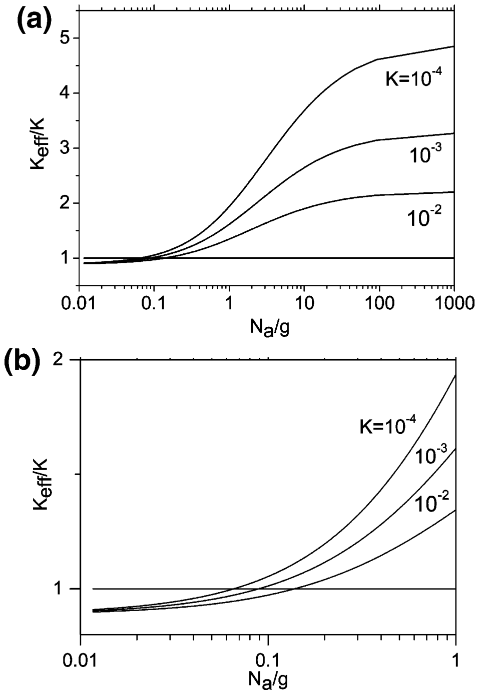


Figure 3. Effective activation constant, K_{eff}, relative to the bare activation constant, K, as a function of the number of blobs per chain, $\bar{N}_a/g$. Indicated in parts a and b are results for three different values of $K = 10^{-2}$, 10^{-3}, and 10^{-4}. Part b is an enlargement of the first part of part a and shows that only in the dilute regime the excluded-volume interactions reduce the effective activation constant and enhance the growth of the chains.

In this approximation, the law of mass action becomes

$$X = 1 - \frac{\gamma_{\text{eff}}}{\bar{N}_a} + \left(K\frac{\Gamma(\gamma_{\text{eff}})}{\gamma_{\text{eff}}^{\gamma_{\text{eff}}}}\right)^{1/(1+\zeta)} \bar{N}_a^{(\gamma_{\text{eff}}+1)/(1+\zeta)}\left(\frac{X}{\phi}\right)^{\zeta/(\zeta+1)} \tag{16}$$

where we defined $\zeta \equiv (\gamma - \gamma_{\text{eff}})/(\nu d - 1)$. Setting γ_{eff} to 1 respectively γ results in the expressions we found for the law of mass action for the semidilute and the dilute regime, eqs 10 and 12. The reader is reminded that the first two terms represent contributions from the inactive mononers, and the last one that of the active polymers. In the next section, we shall be applying eq 16 in order to evaluate the heat capacity and the osmotic compressibility, but only after discussing what exactly happens if we let $K \rightarrow 0$.

4. Discussion

As we have seen in the previous section, thermally activated equilibrium polymers exhibit identical growth exponents to those

Table 1. Ratio of the Crossover Temperature to the Semidilute Regime, T^*, and the Polymerization Temperature, T_p, as a Function of the Dimensionless Binding Enthalpy, h_p/k_BT, and Activation Constant, K, Where the Concentration of Dispersed Material Equals $\phi = 0.05$

K	(h_p/k_BT)	T^*/T_p
10^{-2}	30	0.92
10^{-3}	30	0.96
10^{-4}	30	0.98
10^{-2}	60	0.96
10^{-3}	60	0.98
10^{-4}	60	0.99
10^{-2}	90	0.97
10^{-3}	90	0.99
10^{-4}	90	0.99

of equilibrium polymers, albeit that their cooperative nature tends to enhance their mean molecular weight depending on the activation constant K. This activation constant is renormalized by excluded-volume interactions, and influences the location of the crossover from dilute to semidilute solution relative to the polymerization transition. Let us first discuss how this crossover is influenced by the activation constant.

It is instructive to introduce an effective activation constant

$$K_{\mathrm{eff}} \equiv \left(\frac{K\Gamma(\gamma_{\mathrm{eff}})}{\gamma_{\mathrm{eff}}^{\gamma_{\mathrm{eff}}}}\right)^{1/(1+\zeta)} \tag{17}$$

in eq 16. We can evaluate the contributions of the interactions in the dilute and semidilute regimes by setting γ_{eff} equal to γ and 1 respectively. If $K \approx 1$, the "dilute" prefactor $\Gamma(\gamma_{\mathrm{eff}})/\gamma_{\mathrm{eff}}^{\gamma_{\mathrm{eff}}}$ dominates and $K_{\mathrm{eff}} < K$. However, as K decreases, the exponent $1/(1 + \zeta)$ from the semidilute regime takes over, and $K_{\mathrm{eff}} > K$. We can determine the value of K when this happens, i.e., when the domination by the dilute-regime prefactor goes over to that of the semidilute regime, by setting $K_{\mathrm{eff}} = K$. With $\gamma_{\mathrm{eff}}^* \simeq 1.1$ we find $K = 0.12$. For lower values of K, the semidilute exponent dominates and $K_{\mathrm{eff}} > K$ at the crossover as is shown in Figure 3. So, contrary to an earlier analysis,[24] we find that in the limit $K \to 0$, interactions do not make the polymerization transition sharper, but in fact *less* sharp. It follows that calculations for the activation constant based on ideal chain statistics are inaccurate,[13,14] albeit that the error is not huge: the actual K relates to the measured one, K_{exp}, according to $K = K_{\mathrm{exp}}^{1/\alpha} \approx K_{\mathrm{exp}}^{1.2}$. Note further that if the thermally activated equilibrium polymers are sufficiently stiff, the impact of steric interactions should be small on account of the diminished volume exclusion.[16]

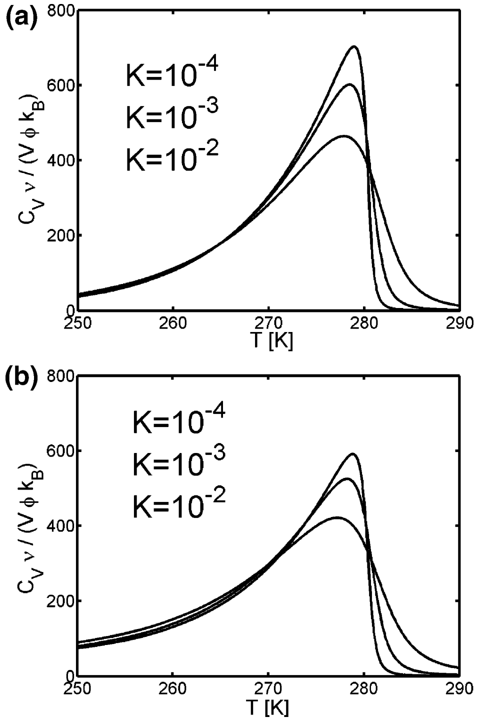


Figure 4. Dimensionless heat capacity, $C_V\nu/(V\phi k_B)$, of thermally activated equilibrium polymers as a function of the temperature T, at volume fraction $\phi = 0.05$, binding enthalpy $h_p/k_BT_p = 30$ and polymerization temperature $T_p = 280K$. Indicated in parts a and b are results for three different values of $K = 10^{-2}$, 10^{-3}, and 10^{-4}. Note that the peak of the heat capacity approaches T_p as $K \to 0$. See the main text for a discussion of the results obtained for ideal chains (a) and interacting chains (b).

The value of the effective activation constant determines the relative locations of the crossover to the semidilute regime and the polymerization transition, and it is of interest to investigate how precisely the semidilute regime encroaches upon the polymerization point as we let $K \to 0$. To describe the behavior of the polymers near the polymerization point, we focus on the mass action variable X. The distribution of material over active polymeric and inactive monomeric states is described by eq 16. To make connection with experiment, we first recall that the parameter $X \approx \exp(-\,h_p(T - T_p)/k_BT_p^2)$ can be expressed in terms of quantities that are observables, being the enthalpy associated with formation of a bond h_p and the polymerization temperature T_p. Next we note that for $K \to 0$, $\bar{N}_a \gg 1$ even in the dilute regime, allowing us to deduce from eq 16 that $\phi_a \sim (X - 1)\phi/X$ if we neglect the term $\gamma_{\mathrm{eff}}/\bar{N}_a \ll 1$ and realize that eq 16 may then be rewritten as $X \sim 1 - \phi_a \exp(\beta G)$. From this estimate we obtain for the fraction of polymerized material $\eta = \phi_a/\phi \simeq 1 - X^{-1}$, transforming the requirement $\phi_a \approx \bar{N}_a^{1-\nu d}$ at the crossover to the semidilute regime into

$$\left(\frac{\phi}{X^*}\right)^{\gamma+1}(X^* - 1)^{\nu d+\gamma} = K_{\mathrm{eff}}^{\nu d+\gamma-\gamma_{\mathrm{eff}}^*-1} \tag{18}$$

with $\gamma_{\mathrm{eff}}^* \simeq 1.1$ and X^* the value of X at the crossover from the dilute to the semidilute regime. We see that with decreasing value of K_{eff} the value of X^* approaches $X_p \equiv 1$, the polymerization point. Combining all this now gives the location of the crossover temperature T^* relative to the polymerization temperature T_p

$$-\left(\frac{h_p}{k_BT_p}\right)\left(\frac{T^* - T_p}{T_p}\right) \simeq K_{\mathrm{eff}}^{(\nu d+\gamma-\gamma_{\mathrm{eff}}^*-1)/(\nu d+\gamma)}\phi^{-(\gamma+1)/(\nu d+\gamma)} \tag{19}$$

which differs slightly from an earlier estimate.[1] This prediction is amenable to experimental verification in a way similar as was done for chemically activated equilibrium polymers.[24] We have listed our results of the crossover temperature T^* in Table 1. Evidently, $T^* \to T_p$ as $K \to 0$. We stress that the quantities h_p, T_p, T^*, and K are experimentally accessible, e.g., by means of heat capacity and osmotic compressibility measurements.

Let us now investigate how interactions modify thermodynamic properties such as the heat capacity and the osmotic compressibility. The heat capacity C_V is defined as $\partial\langle E\rangle/\partial T|_{N,V}$, where $\langle E\rangle$ denotes the ensemble average of the internal energy (or enthalpy) of the system. The latter quantity can be calculated from our free energy, by $\langle E\rangle = \partial\beta\Omega/\partial\beta|_{V,\beta\mu}$. We refer to Appendix B for details of the calculation. The final result is shown in Figure 4, where we indeed observe the sharpening of the transition with decreasing K. We chose the volume fraction

$\phi = 0.05$, the dimensionless enthalpy $h_p/k_BT_p = 30$ for activation constant values of $K = 10^{-2}$, 10^{-3}, and 10^{-4}. The enthalpy associated with the formation of a bond is typically large, so $h_p/k_BT_p \gg 1$.[13,24] The values of K we chose are inspired by experimental values obtained by Jonkheijm and co-workers.[13,14] The value of polymerization temperature was inspired by experimental work by Niranyan and co-workers on the polymerization of the protein g-actin.[25]

Thermally activated equilibrium polymers exhibit a strong enhancement in the heat capacity as is shown in Figure 4, parts a and b. The enhancement of the heat capacity is the result of the formation of polymeric chains at the polymerization transition and reflects the nearby phase transition that occurs for $K = 0$. Indeed, we find that with decreasing activation constant K, the fraction of polymerized material η near the polymerization temperature increases its sharpness, as can in fact also be observed in Figure 1. This causes the degree of polymerization averaged over active and inactive species, $\bar{N}_{\mathrm{n}}$, which determines the value of the heat capacity, eq 27 of Appendix B, to also increase dramatically when crossing the polymerization temperature. Note that for equilibrium polymers there is no sharp polymerization transition, so the heat capacity changes more gradually and does not have this strong enhancement.[18]

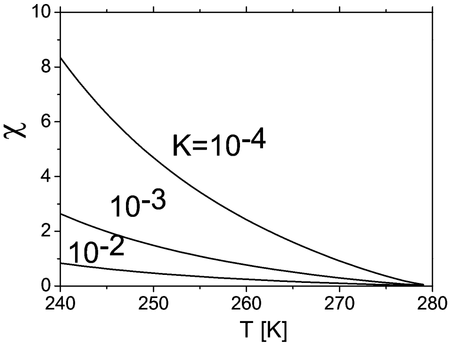
Comparing the three graphs from Figure 4, we conclude that the switching on of excluded-volume interactions decreases the sharpness of the polymerization transition as argued above albeit that the effect is fairly weak. We indeed found that $K_{\mathrm{eff}} > K$ for $K = 10^{-2}$, 10^{-3}, and 10^{-4} even deeply in the dilute regime as is shown in Figure 3. An increase of the effective activation constant causes a decrease of the cooperativity of the polymerization and, associated with that, a decrease of the growth enhancement.

We now turn to the osmotic compressibility that can be calculated from the osmotic pressure, Π. An estimate of the osmotic pressure of our solution containing inactive monomers and active chains can be obtained as follows. In the monomeric regime, the contribution from the monomers dominates the osmotic pressure, so for $X < 1$ the usual estimate for a dilute solution $\Pi l_K^d \approx k_BT(\phi_i + {}^1/_2\phi_i^2 + ...)$ should be applicable. On the other hand, for $X \gg 1$ the material is in the strongly overlapping polymeric state. From polymer scaling theory, we know that for strongly overlapping polymers, $\Pi \approx k_BT\xi^{-d}$.[27] This suggests an interpolation formula for the osmotic pressure[24]

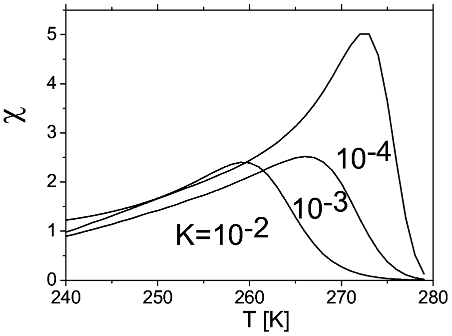
$$\frac{\Pi l_K^d}{k_BT} \approx \phi_i + \frac{1}{2}\phi_i^2 + \phi_a^{\nu d/(\nu d-1)} \tag{20}$$

where constants of proportionality of order unity have been dropped. From this expression we obtain the compressibility, defined as $\chi \equiv \phi k_BT\partial\phi/\partial\Pi l_K^d$. The results are plotted in Figure 5 b with the same parameter values as those for the heat capacity in Figure 4. Again, we find a peak that sharpens with decreasing values of K, except that the peak position moves in from below T_p to approach T_p for vanishing values of K. In contrast to the situation with the heat capacity, the osmotic compressibility exhibits its maximum at the crossover temperature to the semidilute regime, T^*, not at the polymerization temperature, T_p. See Figure 5b. For ideal chains, the enhancement of the osmotic compressibility shown in Figure 5a is very different.

We conclude that the osmotic compressibility is dominated by excluded-volume interactions, much more so than the heat capacity. The reason is as follows. If the material is in the monomeric state, we have a large number of particles, so the osmotic compressibility is low. As we approach the polymerization temperature, the material starts to polymerize and the monomers form coils of polymers. The number of these coils decreases and the osmotic compressibility goes up: the osmotic pressure is a colligative property. On the other hand, if the material is in the strongly entangled regime, the number of blobs is very high causing the osmotic compressibility to be small. As we increase the temperature the blobs grow larger and their number goes down, and as a result of that, the osmotic compressibility goes up. These two opposing processes result in a maximum of the osmotic compressibility at the crossover temperature.



(a) ideal, $h_p = 30k_BT_p$



(b) interacting $h_p = 30k_BT_p$

Figure 5. Isothermal osmotic compressibility χ of thermally activated equilibrium polymers as a function of the temperature T, given a volume a fraction $\phi = 0.05$, binding enthalpy $h_p/k_BT_p = 30$ and polymerization temperature $T_p = 280K$. Indicated are results for three different values of $K = 10^{-2}$, 10^{-3}, and 10^{-4} for ideal (a) and nonideal chains (b). Note that the peaks of the curves are at the positions given in table 1, i.e., at the crossover to the semidilute regime. See the main text for a discussion of the figures.

For ideal chains there are no dilute and semidilute regimes, and the osmotic pressure obeys the ideal Van't Hoff law $\Pi l_K{}^3/k_BT = \phi_i + \rho_a$. Hence, we find that the osmotic compressibility of the polymerized solution should decrease on the approach of the polymerization temperature, as shown in Figure 5a. The reason is that the material then depolymerizes, and as a result of that the total number density of particles increases on account of the liberated monomers. This increase in the number density of particles gives rise to a decrease of the osmotic compressibility of the solution.

Finally, we note that the larger the activation constant, the sharper the enhancement of the osmotic compressibility in the polymerized regime because more monomers are in that case absorbed in the chains under otherwise equal conditions.

5. Concluding Remarks

Thermally activated equilibrium polymerization involves "inactive" monomers that are in equilibrium with "activated" monomers and polymers. If the active state of a monomer is very much less favorable than the inactive state, the activated state can be stabilized by polymerization because this liberates a binding free energy. This binding free energy compensates for the higher free energy of the activated monomeric state. The thermally activated polymerization of material becomes sharper (more co-operative) the smaller the activation constant associated with the equilibrium between the active and inactive monomer states.

Our calculations show that excluded-volume interactions influence the shape of the equilibrium size distribution of thermally activated equilibrium polymers in a way similar to that of equilibrium polymers[18] and of chemically activated equilibrium polymers.[24] The growth laws that we find for thermally activated equilibrium polymers in dilute and semidilute solution are the same as those for equilibrium polymers, but different from those of chemically activated polymers.

In the limit of diverging activation energy, the dilute regime becomes vanishingly small and the growth of the polymers becomes dominated by the screened interactions characteristic of the semidilute regime. This makes the polymerization less cooperative than what would have been the case for ideal, noninteracting polymers. A similar situation is encountered in solutions of chemically activated equilibrium polymers in the limit of vanishing initiator concentration, except that for these the screened interactions have been predicted to have no impact whatsoever on the degree of cooperativity the polymerization reaction.[24]

It appears that thermally activated equilibrium polymers are in a sense in between equilibrium polymers and chemically activated equilibrium polymers. Indeed, they obey the same growth laws in dilute and semidilute solution as equilibrium polymers do, yet they require an activation step resulting in thermodynamic properties that are similar to those of chemically activated equilibrium polymers. In both chemically and thermally activated polymerization, the dilute regime disappears in favor of the semidilute regime with increasing cooperativity of the reaction process.

The scaling theory presented in this paper describes the thermal equilibrium between the supramolecular polymers at the level of a mean-field approximation, yet deals with the configurational statistics of the individual chains at a non-mean-field level. This implies that the theory does not properly describe the fluctuations in the distribution of material over the monomeric and the polymeric states near the polymerization transition. This, however, should not be a caveat since the activation constant is typically not exceedingly small, so the fluctuations arising from the polymerization transition may be modest. Nonetheless, we still find a strong enhancement of the heat capacity and of the osmotic compressibility near the polymerization transition. The former is caused by the vicinity of a true phase transition, the latter by the merging of the semidilute regime and the polymerization transition.

We conclude by remarking that thermally activated equilibrium polymers can be quite stiff and in some cases exhibit liquid crystalline states.[1,13] We intend to investigate the coupling between this kind of cooperative polymerization and liquid-crystalline phase transitions in the near future.

Appendix A

We obtain the integral for the mean degree of polymerization, $\bar{N}_a$, from eqs 2, 3, and 4, by replacing the summations by integrations and using the interpolated partition function $\tilde{Z}_a$ from eq 13. This way, we find

$$\phi_a^{1/(\nu d-1)}\bar{N}_a = \gamma(\gamma+1)\frac{U(\gamma,-1,\tau)}{\tau^2 U(\gamma,2,\tau)} + \gamma\frac{U(\gamma,0,\tau)}{\tau U(\gamma,2,\tau)} \quad (21)$$

where U is the confluent hypergeometric function of the second kind[28] and the parameter τ is defined as $\tau \equiv \beta\tilde{\mu}\phi_a^{-1/(\nu d-1)}$. In dilute regime we find $\bar{N}_a = \gamma/\beta\tilde{\mu}$, while in the semidilute regime $\bar{N}_a = 1/\beta\tilde{\mu}$ because there $\gamma = 1$. It is therefore prudent to introduce a concentration dependent scaling exponent, $\gamma_{\rm eff}$, by setting

$$\bar{N}_a = \frac{\gamma_{\rm eff}}{\beta\tilde{\mu}} \quad (22)$$

The self-consistent expression for $\gamma_{\rm eff}$ then becomes

$$\gamma_{\rm eff} = \gamma(\gamma+1)\frac{U(\gamma,-1,\tau)}{\tau U(\gamma,2,\tau)} + \gamma\frac{U(\gamma,0,\tau)}{U(\gamma,2,\tau)} \quad (23)$$

and we rewrite the parameter τ as $\tau = \gamma_{\rm eff}\, g/\bar{N}_a$, with $g = (\xi/l_K)^{1/\nu}$ the number of monomers in a blob.

Now that we have established a concentration dependent scaling exponent, we are in position to write the volume fraction of active material, ϕ_a, as a function of this scaling exponent and the mean degree of polymerization, by using eqs 3 and 4. The complete expression for ϕ_a using the interpolation formula for the single-chain partition function is given by

$$\phi_a^{(\nu d+\gamma)/(\nu d-1)} = K\,\Gamma(\gamma)\bar{N}_a\, U(\gamma,2,\tau)\exp(-\beta G) \quad (24)$$

We know that if $\tau \to 0$, $U(\gamma,2,\tau) \to 1/(\tau\Gamma(\gamma))$, and if $\tau \to \infty$, $U(\gamma,2,\tau) \to \tau^{-\gamma}$,[28] so we estimate $U(\gamma,2,\tau) \approx \Gamma(\gamma_{\rm eff})/\Gamma(\gamma)\tau^{-\gamma_{\rm eff}}$. This estimate, combined with eq 17, transforms ϕ_a into

$$\phi_a = K_{\rm eff}\bar{N}_a^{(\gamma_{\rm eff}+1)/(1+\zeta)}\left(\frac{X}{\phi}\right)^{(\zeta)/(\zeta+1)}\exp(-\beta G) \quad (25)$$

which is the expression used in eq 16.

Appendix B

We calculate the heat capacity from the definition $C_{\rm V} = \partial\langle E\rangle/\partial T|_{N,{\rm V}}$, where $\langle E\rangle$ denotes the ensemble average of the internal energy of the system. It can be calculated from $\langle E\rangle = \partial\beta\Omega/\partial\beta|_{{\rm V},\beta\mu}$ where we insert eq 5 to give

$$\langle E\rangle = \frac{V}{v}\left[-h(\phi_a-\rho_a)-\rho_a\frac{\partial \ln K}{\partial\beta}\right] \quad (26)$$

where V is the volume of the system, v is a reference volume, h=$h(T)$ is the enthalpy *gain* of a bond with $h_p \equiv h(T_p)$ at the polymerization temperature $T = T_p$. Ignoring the temperature dependence of the activation constant K, we obtain

$$C_V = \frac{V}{v}\phi\left\{-h\frac{\partial}{\partial T}\left[\eta - \frac{\eta}{N_a}\right] + c_b\eta\right\} \quad (27)$$

where $\eta = \phi_a / \phi$ is the fraction active material, $\bar{N}_a$ the degree of polymerization of the active species and $c_b \equiv -\partial h/\partial T$. (Note: the minus sign appears because of our definition of h as a free energy gain, implying that h is positive for exothermic processes and negative for endothermic ones.) The first term of the right-hand side of eq 27 can be calculated numerically with the given expressions we found for the mass action variable X, while the second one can be neglected. The reason is that c_b is the heat capacity associated with a single bond. If we model this bond as an harmonic oscillator, we find that its value increases from 0 to k_B upon crossing a certain Einstein temperature.[30] Since this term represents at most one thermal energy unit k_BT, it is negligible in comparison with the first term since typically $h_p \gg k_BT$.[1]

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