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Kinetic phase transition in polymerization

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We study the kinetics of a simple mean-field model of multifunctional polymerization. We are able to derive some exact results for the time dependence of some quantities of interest by making use of a transformed time variable. The gel fraction and the average of the reciprocal of the degree of polymerization are both evaluated in this model and exhibit nonanalytic behavior at the gelation point.

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Studies of the kinetics of the polymerization process and the approach to gelation pose a number of interesting problems in the physics of polymers [1–7]. The central quantity of interest is the distribution function $P(N,t)$, defined as the probability that at time t a randomly selected site, which must be occupied either by a solvent molecule or by a monomer, is in fact occupied by a monomer forming part of a polymer molecule of degree of polymerization N. The time at which $P(\infty,t)$ first becomes nonzero marks the gelation transition.

In this paper we present a procedure for calculating $P(N,t)$ in a simple kinetic model. Rather than adopt the combinatorial arguments of the early workers in this area [8–10], we use a generating-function technique to solve the differential equations for the various $P(N,t)$. In this model the $P(N,t)$ are analytic functions of time for all finite N, but $P(\infty,t)$ is nonanalytic at the gelation time t_{gel}.

We start by considering a mixture of monomers with nonpolymerizable solvent molecules in which the molecular fraction of monomers is p. In a polymerization process two molecules, of degree of polymerization m and n, respectively, combine to form a polymer of degree $m+n$. We denote by κ the reaction rate constant describing the probability per unit time that an available reaction site becomes bonded; in the mean-field approximation used here this rate does not depend on time or any other variable. The master equations for the distribution functions $P(N,t)$ with $N>1$ are derived in the Appendix and are of the form

$$\frac{d}{dt}P(N,t) = \frac{\kappa N}{2}\sum_{m+n=N} A(m)P(m,t)A(n)P(n,t)\Delta_{N_u}(m,n) - \kappa N A(N)P(N,t)\sum_{m=1}^{\infty} A(m)P(m,t)\Delta_{N_u}(m,N). \tag{1}$$

where Δ_{N_u} is a cutoff function to be described later and $A(N)$ is a function of N that depends on the functionality of the monomer. For example, for a fully multifunctional monomer we assume that $A(N)=1$ and is independent of N, since every site of a polymer remains capable of reaction with another polymer. For a bifunctional monomer, on the other hand, $A(N)=\frac{2}{N}$, since only the two end sites of a polymer chain are available for reaction. In the present work, we consider only the fully multifunctional case, and so put $A(N)=1$.

On intuitive grounds one expects the end result of Eq. (1) to be a single macromolecule of infinite size. There are, however, some mathematical subtleties involved in observing this phenomenon, as an approach that is too simpleminded risks violating the mass-conservation law, which demands that $\sum_{N=0}^{\infty} P(N,t)$ remain equal to p at all times. Accordingly we have artificially imposed an upper limit N_u to the size of molecules by including in Eq. (1) a cutoff function $\Delta_{N_u}(m,n)$ defined as

$$\Delta_{N_u}(m,n) = \begin{cases} 1 \text{ for } \min(m,n) \le N_u \\ 0 \text{ otherwise .} \end{cases} \tag{2}$$

The limit $N_u \to \infty$ is then taken after the completion of the formal calculations.

The first term in Eq. (1) represents the rate at which polymers of degree of polymerization m and n combine to produce one of degree of polymerization N $(= m+n)$. The second term represents removal of these N monomer units from the class contributing to $P(N,t)$ when a further reaction occurs. The kinetic equation for $P(1,t)$ can be obtained from Eq. (1) by imposing the boundary condition

$$P(0,t)=0 \ . \tag{3}$$

If at time $t=0$, only monomers and solvent are present, then

$$P(1,0) = p \ , \quad P(N,0) = 0 \ \text{ for } N>1 \ . \tag{4}$$

Introducing a normalized time $\tau \equiv \kappa p t$ and normalized distribution functions $Q(N,\tau) \equiv P(N,t)/p$, we find, for $N \le N_u$,

$$\frac{d}{d\tau}Q(N,\tau) = \frac{N}{2}\sum_{m+n=N} Q(m,\tau)Q(n,\tau) - NQ(N,\tau) \ , \tag{5}$$

where the conservation law has been used in obtaining the second term. The initial and boundary conditions are

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$$Q(1,0) = 1\,,\quad Q(N,0) = 0 \text{ for } N > 1 \tag{6}$$
$$Q(0,\tau) = 0.$$

The solution for Eqs. (5) is, for $N \leq N_u$,

$$Q(N,\tau) = q_N \tau^{N-1} e^{-N\tau}\,, \tag{7}$$

where the coefficient q_N is independent of τ and can be found recursively from the relations

$$q_N = \frac{N}{2(N-1)} \sum_{m+n=N} q_m q_n\,, \tag{8}$$

with $q_1 = 1$.

It is tempting to think that Eqs. (7) and (8) might provide the complete solution for all N, without the need for a cutoff. One is disabused of this idea, however, when one notes that for $\tau > 1$ every term in Eq. (7) decreases monotonically with time. (A few of these are illustrated in Fig. 1.) It is thus impossible to obey the mass conservation law without approaching the question of the infinite-mass component more circumspectly. The large-N limit of $\tau^{N-1}e^{-N\tau}$ resembles a δ function, and this suggests that a transition occurs at $\tau = 1$ to a state in which the infinite-mass component plays an important role.

While the general evaluation of $Q(N,\tau)$ for all time is somewhat difficult, we can obtain the two most useful physical quantities from the calculation fairly readily. These two quantities are the gel fraction $P(\infty,\tau)$ and the average inverse degree of polymerization $\langle 1/N \rangle$. This latter quantity is an important parameter in the evaluation of the Flory-Huggins free energy [11–15] used in some theories of phase separation [11].

In terms of the normalized distribution, the mass conservation law is

$$1 = \sum_{N=1}^{N_u} Q(N,\tau) + \bar{Q}(N_u,\tau)\,, \tag{9}$$

where $\bar{Q}(N_u,\tau) \equiv \sum_{N=N_u+1}^{\infty} Q(N,\tau)$ and is the "missing mass" accounting for contributions from all polymers with degree of polymerization larger than N_u. At large times this term is not necessarily equal to zero in the limit $N_u \to \infty$. Indeed, we will see that $\bar{Q}(\infty,\tau)$, the normalized probability of finding a polymer with infinite degree of polymerization at the normalized time τ, undergoes a transition from zero when τ is increased, reflecting the onset of gelation.

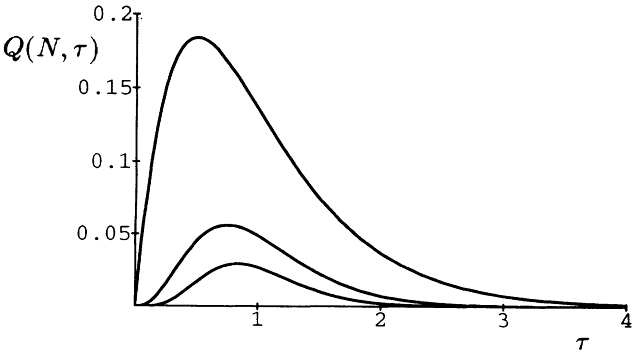

FIG. 1. The distribution functions $Q(N,\tau)$ as a function of τ at various values of N: from top to bottom, 2, 4, and 6.

Writing the conservation law at the limit $N_u \to \infty$, we have

$$1 = \frac{1}{\tau} \sum_{m=1}^{\infty} q_m \left(\frac{\tau}{e^\tau}\right)^m + \bar{Q}(\infty,\tau)\,. \tag{10}$$

As we have seen, the function $\tau e^{-\tau}$ has its maximum value at $\tau = 1$, and so we hazard the guess that $\bar{Q}(\infty,\tau) = 0$ for $\tau < 1$ and is nonzero for $\tau > 1$. To check the validity of this assumption we define the generating function

$$G(\tau) \equiv \sum_{m=1}^{\infty} q_m \left(\frac{\tau}{e^\tau}\right)^m\,. \tag{11}$$

Combining this with the recursion relation, Eq. (8), which tells us that

$$\sum_{m=1}^{\infty} m q_m \left(\frac{\tau}{e^\tau}\right)^m = \frac{G}{1-G}\,, \tag{12}$$

we find the nonlinear differential equation

$$\frac{1-G(\tau)}{G(\tau)} \frac{d}{d\tau} G(\tau) = \frac{1-\tau}{\tau}\,. \tag{13}$$

The solution of this equation that satisfies the initial condition $G(0) = 0$ has the remarkably simple form

$$G(\tau) = \tau\,. \tag{14}$$

Substitution of this result into Eq. (10) seems to suggest that $\bar{Q}(\infty,\tau)$ is zero at all time—a clearly incorrect result. So what has gone wrong?

We find the resolution to this difficulty if we try to use Eq. (11) to solve for the q_m by equating powers of τ. The expression is valid when $\tau < 1$, but fails to converge when $\tau > 1$. The trick to perform now is to note that although τ may be large, it is really only the combination τ/e^τ that enters the series. If we can find, for any large value of τ (> 1), a small time $\bar{\tau}$ (< 1) for which

$$\frac{\bar{\tau}}{e^{\bar{\tau}}} = \frac{\tau}{e^\tau}\,, \tag{15}$$

then we can replace τ by $\bar{\tau}$ in Eq. (14) to have a valid solution for $G(\tau)$. As illustrated in Fig. 2, it is always possible to find a value of $\bar{\tau} < 1$ for any $\tau > 1$. Equation (10) now gives us a more credible result for the normalized gel fraction as a function of time, namely,

$$\bar{Q}(\infty,\tau) = \begin{cases} 0 & \text{for } \tau \leq 1 \\ 1 - \frac{\bar{\tau}}{\tau} & \text{for } \tau > 1\,. \end{cases} \tag{16}$$

The form of this function is shown in Fig. 3. We see that the normalized gel fraction remains zero until $\tau = 1$, whereupon it initially rises linearly, varying as $2(\tau - 1)$, and then saturates at unity at large times, where it varies as $1 - e^{-\tau}$.

We now study the time behavior of the average of $\frac{1}{N}$, the inverse of the degree of polymerization, with respect

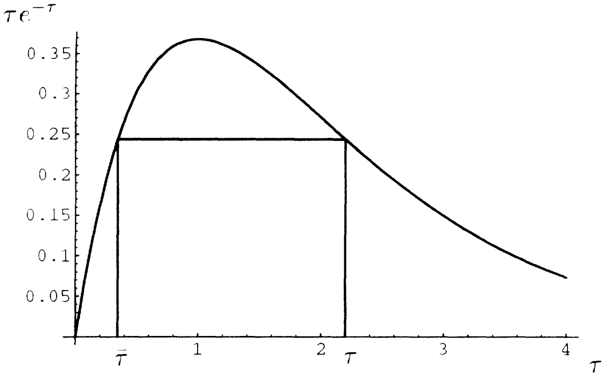

FIG. 2. This illustrates $\tau e^{-\tau}$ as a function of τ and the relation between $\bar{\tau}$ and τ for $\tau > 1$.

to the normalized distribution $Q(N,\tau)$. From the solution for the normalized distribution functions one can verify that

$$\begin{aligned}\left\langle \frac{1}{N} \right\rangle &= \sum_{N=1}^{\infty} \frac{1}{N} Q(N,\tau) \\ &= \frac{1}{\tau} \int_0^y \frac{dy'}{y'} \sum_{N=1}^{\infty} q_N {y'}^N \\ &= \frac{1}{\tau} \int_0^y \tau' \frac{dy'}{y'} \left[1 - \bar{Q}(\infty,\tau')\right] , \qquad (17)\end{aligned}$$

where $y = \tau e^{-\tau}$. When $\tau \leq 1$ the integral is trivially evaluated as $\tau - \frac{1}{2}\tau^2$. When $\tau > 1$ we again resort to our trick of replacing τ by $\bar{\tau}$ to find a result valid at large times and which takes into account the nonzero value of $\bar{Q}(\infty,\tau)$. The overall result is

$$\left\langle \frac{1}{N} \right\rangle = \begin{cases} 1 - \frac{1}{2}\tau & \text{for } \tau \leq 1 \\ \frac{1}{\tau}\left(\bar{\tau} - \frac{1}{2}\bar{\tau}^2\right) & \text{for } \tau > 1 \;. \end{cases} \qquad (18)$$

We thus see that $\langle 1/N \rangle$ is exactly 1/2 at the gelation transition. The time behavior of $\langle 1/N \rangle$ at these times is as $e^{-\tau}$ (see Fig. 4). This exact expression for $\langle 1/N \rangle$ in this model has been found useful in describing polymerization-induced phase separation in a polymer liquid-crystal mixture [11].

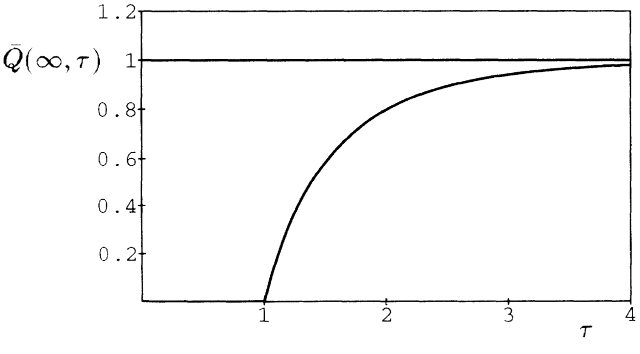

FIG. 3. The normalized probability $[\bar{Q}(\infty,\tau)]$ of finding any monomer to be part of a polymer with infinite degree of polymerization is shown as a function of normalized time τ. The horizontal line at 1 indicates the asymptotic value of $\bar{Q}(\infty,\tau)$ when $\tau \to \infty$.

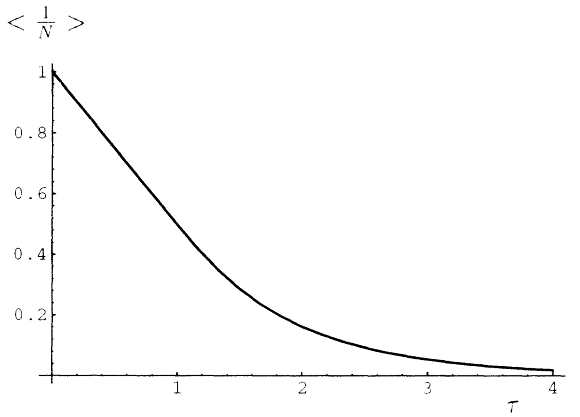

FIG. 4. This graph shows $\langle 1/N \rangle$, the average of the reciprocal of the degree of polymerization, as a function of τ.

In summary, we have found an interesting kinetic phase transition in a simple model of multifunctional polymerization. This transition has some similarity to the percolation transition [16]. By introducing a transformation in which the time variable τ is replaced by a reduced time $\bar{\tau}$ we were able to obtain an exact expression for the gel fraction and for the average of the reciprocal of the degree of polymerization as a function of time. Although the result is specific to the particular model considered, the qualitative nature of the results should be indicative of the behavior to be expected in some more realistic models.

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APPENDIX

The rate of change of the probability $P(N,t)$ that a given reaction site be occupied by a monomer forming part of a polymer of degree of polymerization N is due to two terms. The first of these is the result of two smaller molecules combining to form a larger one of degree N, while the second represents the loss of molecules of degree N caused by reaction with other molecules.

For the first term we must have a molecule of degree m combining with one of degree $N - m$. The probability that a reaction site is occupied by a molecule of degree m and is available for further reaction will be the product $A(m)P(m,t)$. Here $A(m)$ depends on the model chosen for functionality, being $\frac{2}{m}$ if only the end units of chains of bifunctional monomers can react, and being unity if, in the spirit of a mean-field model that mimics an infinite-dimensional space, each monomer can form an unlimited number of bonds. The probability that the other reaction site is available for formation of a polymer of degree N is then similarly $A(n)P(n,t)$ with $m + n = N$. Since formation of this bond recruits N monomers to form part of a polymer of degree of N, there is an additional factor of N. Finally, each bond has coupled two sites, and so we also have a factor of $\frac{1}{2}$ to normalize to a rate per reaction site. (This factor is present regardless of whether $m \neq n$ or $m = n$, as it does not arise from any correction of overcounting.) We then have

$$\left[\frac{d}{dt}P(N,t)\right]_1 = \frac{\kappa N}{2}\sum_{m+n=N} A(m)P(m,t)A(n)P(n,t)\ . \tag{A1}$$

The second term requires more careful treatment. When a polymer of degree N reacts with any other molecule, it reduces $P(N,t)$, and so we expect a factor of $NA(N)P(N,t)$ to occur, and a further factor of $\sum_{m=1}^{\infty} A(m)P(m,t)$ to allow for all possibilities of the other end of the bond. (No factor of $\frac{1}{2}$ occurs because now it is sufficient for either end of the bond to be of degree N. The special case of $m = N$ requires no correction factor since the double counting merely reflects the fact that two polymers of degree N are removed.) We then have

$$\left[\frac{d}{dt}P(N,t)\right]_2 = -\kappa NA(N)P(N,t)\sum_{m=1}^{\infty} A(m)P(m,t)\ . \tag{A2}$$

Before continuing with the expression for $\frac{d}{dt}P(N,t)$, we pause to note that reaction of the gel, for which N is infinite, with any other molecule does not reduce the number in the gel. We must thus make a distinction between finite and infinite N. We do this by choosing a large number N_u and classifying all molecules of degree larger than N_u as being part of the gel. Adding Eqs. (A1) and (A2) then gives us Eq. (1) of the text, as long as $N \leq N_u$. The sum of all terms with $N > N_u$ gives the result

$$\begin{aligned}\frac{d}{dt}P_{\rm gel}(t) = {} & \frac{\kappa}{2}\sum_{\substack{m+n>N\\ m,n\leq N_u}} (m+n)A(m)P(m,t)A(n)P(n,t)\\ & +\kappa\sum_{m\leq N_u} mA(m)P(m,t)A_{\rm gel}P_{\rm gel}(t)\ .\end{aligned} \tag{A3}$$

The first term on the right-hand side represents the union of two nongel molecules to make a component of the gel, while the second is the joining of one nongel molecule to the gel. The factor of $\frac{1}{2}$ is absent in the second term because either end of the bond could initially be in the gel.

This completes the derivation of Eq. (1). As a check, we note that the sum over all N of $\frac{d}{dt}P(N,t)$ vanishes, as long as the gel is included. To see this we note that Eqs. (A1) and (A3) contain terms that are symmetric in m and n, so that, for example,

$$\begin{aligned}&\sum_{m,n}(m+n)A(m)P(m,t)A(n)P(n,t)\\ &\qquad = 2\sum_{m,n} mA(m)P(m,t)A(n)P(n,t).\end{aligned} \tag{A4}$$

Then

$$\begin{aligned}\frac{1}{\kappa}\frac{d}{dt}\left[\sum_{N=1}^{N_u} P(N,t) + P_{\rm gel}(t)\right] = {} & \sum_{m+n\leq N_u} mA(m)P(m,t)A(n)P(n,t)\\ & -\sum_{N=1}^{N_u} NA(N)P(N,t)\left(\sum_{m=1}^{N_u} A(m)P(m,t) + A_{\rm gel}P_{\rm gel}(t)\right)\\ & +\sum_{\substack{m+n>N_u\\ m,n\leq N_u}} mA(m)P(m,t)A(n)P(n,t) + \sum_{m=1}^{N_u} mA(m)P(m,t)A_{\rm gel}P_{\rm gel}(t) = 0\ .\end{aligned} \tag{A5}$$

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