Kinetics of polymer gelation

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The kinetics of polymer growth and especially gelation are discussed for a system of reacting f-functional monomeric units. The gelation models of Flory and Stockmayer are examined, and their implications concerning sol–gel interaction after gelation has occurred are clarified. A new model, in which the gel does not cross link, is considered. A mathematical analysis shows that the onset of gelation is related to the formation of a shock-wave solution of the equation satisfied by the generation function.

I. INTRODUCTION

In the process of condensation polymerization, polymers are formed by the stepwise chemical bonding of pairs of free functional groups in the system. For the case where the basic monomeric units are assumed to contain f identical reactive groups, it is well known that gelation occurs during the polymerization process whenever f is greater than two. This is shown by the statistical theories of Flory[1] and Stockmayer.[2] It may be noted, however, that for times beyond the point of gelation, Flory and Stockmayer have each proposed different solutions with different rates of gel formation.[3] We shall show that these two solutions correspond to distinct assumptions concerning the gel's reactivity with the finite-size polymers (the sol), and the interreaction of groups on the gel itself. In Flory's model, the free groups in the sol can bond with those in the gel, and also the gel can cross link, meaning that bonds can form within the gel, while in Stockmayer's solution, we show that the gel and sol units never react.

Our analysis is based upon a kinetic approach, in which a kinetic equation which describes the actual non-linear dynamical process is constructed. This approach has the advantages over the statistical methods in that the time dependence appears explicitly, and in the case of gelation, the assumptions behind the different models become clearly manifest, as a different kinetic equation is needed in each case. The kinetic approach to polymerization was first considered by Dostal and Raff,[4] for the case $f = 2$, where however no gelation occurs. The general equation for $f > 2$ was considered by Stockmayer, but for times only up to the point of gelation. In a previous paper,[5] one of us used the kinetic equation to study the complete dynamics, including the dynamics of gelation, for the case $f = 3$. (For this value of f most of the results can be written explicitly.) Besides examining the gelation models of Flory and Stockmayer, we also considered a new model of gelation, in which we assume the sol and gel can interact, but that the gel cannot cross link. Thus, the gel is assumed to obey the same rules as the sol polymers, since in the usual Flory–Stockmayer theory, the sol polymers are assumed not to cross link.

In a recent work, Dusek[6] has solved the kinetic equation for the complete dynamics, for all $f > 2$, by a generating-function technique. His solution past the gelation point is equivalent to Flory's. In the present paper, we shall use a similar generating function technique to describe all three models of gelation mentioned above, for all $f > 2$. The mathematical details of these calculations will be relegated to three appendices; a comparative study of the results will be given first, in the following sections.

II. THE KINETIC EQUATION

The growth of polymers from f-functional units is described by the equation[7]

$$\frac{\partial \nu_k}{\partial t} = \frac{1}{2} \sum_{i+j=k} [(f-2)i+2]$$
$$\times [(f-2)j+2]\nu_i\nu_j - [(f-2)k+2]\nu_k X , \qquad (1)$$

where $\nu_k = \nu_k(t)$ is the concentration ($\equiv$ expected number per unit volume) of k-mers at time t. When no gel is present, X will be given by x_s, where we define

$$x_s \equiv \sum_{k=1}^{\infty} [(f-2)k+2]\nu_k . \qquad (2)$$

Equation (1) describes the process that i-mers and j-mers combine to form $(i+j)$-mers at a rate that is proportional to the product of the concentrations of free groups belonging to all i-mers and j-mers, or $[(f-2)i+2][(f-2)j+2]\nu_i\nu_j$, since a k-mer has $[(f-2)k+2]$ free groups. Note that the validity of this last fact depends upon the assumption that no rings or cycles are allowed to form, an assumption which is also crucial in the statistical theory. The first term in Eq. (1) represents all reactions which produce k-mers and therefore increase ν_k, and the second term represents all reactions of k-mers with other polymers, which decreases ν_k. The quantity $x_s = x_s(t)$ represents the total concentration of free groups on all polymers in the system. The symbol X is introduced into Eq. (1) to allow for future modifications when gelation will be discussed. Note that all quantities are taken to be nondimensional.

If the system is assumed to be monodisperse at $t = 0$, then the initial conditions are given by

$$\nu_k(0) = \begin{cases} 1, & k = 1, \\ 0, & k > 1. \end{cases} \tag{3}$$

The explicit solution to Eqs. (1)–(3) has been given by Stockmayer[2]:

$$\nu_k(t) = \frac{f[(f-1)k]!}{[(f-2)k+2]! \, k!} \frac{(ft)^{k-1}}{(1+ft)^{(f-1)k+1}}. \tag{4}$$

We give a derivation of this result in Appendix A. Equation (4) is equivalent to the distribution found in the statistical theory, if the time is replaced by the parameter $\alpha \equiv ft/(1+ft)$. The properties of Eq. (4) are as follows: The functions ν_k, for $k = 1, 2, 3, \ldots$, successively grow, peak, and decay, as larger polymers are always being formed. The time at which ν_k reaches its maximum is given by

$$t_{k,\text{max}} = \frac{1}{f(f-2)} \left[1 - \frac{f}{(f-2)k+2} \right]. \tag{5}$$

The moments of the distribution, defined by

$$M_n \equiv \sum_{k=1}^{\infty} k^n \nu_k, \tag{6}$$

are given by

$$M_0 = 1 - \frac{f}{2} \frac{ft}{1+ft}, \tag{7}$$

$$M_1 = 1, \tag{8}$$

$$M_2 = \frac{1 + 2ft}{1 - f(f-2)t}. \tag{9}$$

Note that M_1 gives the total concentration of units, which is a constant of the system. It follows directly from Eqs. (1) and (2) that the overall concentration of free groups satisfies a simple kinetic equation of self-reaction

$$\frac{dx_s}{dt} = -x_s^2 \tag{10}$$

and, indeed, from Eqs. (7) and (8) we find

$$x_s = (f-2)M_1 + 2M_0 = \frac{f}{1+ft}. \tag{11}$$

III. THE ONSET OF GELATION

As t approaches $t_c \equiv 1/f(f-2)$, M_2 given by Eq. (9) becomes infinite. By t_c, all $\nu_k(t)$ will have passed their peaks and will be decreasing, according to Eq. (5). This implies a loss of units to $k = \infty$, at a rate which is given by

$$\sum_{k=1}^{\infty} k \frac{d\nu_k}{dt} = -\frac{f^2(f-2)}{(f-1)}. \tag{12}$$

(For times less than t_c, this sum is zero.) At a small time δt past t_c, a gel, consisting of one or several infinite polymers and containing $(\delta t)f^2(f-2)/(f-1)$ units per unit volume, will exist. Thus, t_c marks the onset of gel growth.

This growth of gel is a result of a cascading of the growth process, in which the reaction rate goes faster and faster as the size of the polymers increases. At a

finite point in time, the gel begins to form—or, more precisely, the concentration of units which belong to the gel becomes finite. These units will not contribute to any of the M_n or to x_s. Thus, M_1 will represent the concentration of units belonging only to the finite size polymers, or the sol. The quantity $1 - M_1$ will give the concentration of units belonging to the gel. Likewise, x_s given by Eq. (2) will represent the concentration of free groups in just the sol. (It is for this reason that we used the subscript s.) We will use the quantity x_g to denote the concentration of free groups in the gel.

Next we shall consider the case $t > t_c$. Then it turns out that Eq. (4) no longer satisfies Eqs. (1) and (2) as they stand. We shall examine three models of gelation which correspond to different solutions or different expressions for X. Remember that X represents the total concentration of free groups with which a polymer may react. If, for example, we continue to set $X = x_s$ when a gel is present, we will be allowing the k-mers to react with the sol polymers only.

At $t = t_c$, $M_0 = (f-2)/2(f-1)$, $M_1 = 1$, $M_2 = \infty$, and $X = x_s = f(f-2)/(f-1)$. The solution past t_c must match Eq. (4) at $t = t_c$. Furthermore, since X must also be continuous, it follows from Eq. (1) that $d\nu_k/dt$ must also be continuous across t_c.

IV. THE FLORY MODEL

Flory's discussion of gelation is based upon the assumption that ν_k of Eq. (4) holds for $t > t_c$ as well as for $t < t_c$. When $t > t_c$, the moments, however, are no longer given by Eqs. (7)–(11), but by

$$M_0 = \frac{1}{2} \left[\frac{f}{1+ft} \zeta^{f-1} - (f-2)\zeta^f \right], \tag{13}$$

$$M_1 = \zeta^f, \tag{14}$$

$$M_2 = \frac{2(1+ft)\zeta^f - \zeta^{f-1}}{1 + ft - ft(f-1)\zeta^{f-2}}, \tag{15}$$

$$x_s = \frac{f}{1+ft} \zeta^{f-1}, \tag{16}$$

where $\zeta = \zeta(t)$ is the positive real root of

$$\zeta + \zeta^2 + \cdots + \zeta^{f-2} = \frac{1}{ft}. \tag{17}$$

These formulas are in somewhat different form than, but equivalent to, those of Flory (see Appendix B). When $f = 3$, $\zeta = 1/3t$ and when $f = 4$, ζ satisfies a quadratic equation, so for these two cases the moments can be written explicitly. Note that $\zeta(t_c) = 1$, and ζ decreases monotonically as t increases.

For Eq. (4) to satisfy Eq. (1), X must satisfy (see Appendix B)

$$\frac{dX}{dt} = -X^2 \tag{18}$$

or

$$X = \frac{f}{1+ft}. \tag{19}$$

This X is not equal to x_s, according to Eq. (16), and

therefore the ν_k satisfy a different kinetic equation when $t < t_c$ and $t > t_c$ in the sense that X is given by x_s of Eq. (2) when $t < t_c$, and by Eq. (19) when $t > t_c$. Inferring that the increase in X over x_s must come with the availability of the gel to react, we write $X = x_s + x_g$. Then, from Eqs. (16), (17), and (19), we find $x_g = X - x_s = (1 - \zeta)/t$.

It follows from Eq. (1) that x_s and x_g satisfy

$$\frac{dx_s}{dt} = -x_s^2 - x_g \sum [(f-2)k+2]^2 \nu_k , \tag{20}$$

$$\frac{dx_g}{dt} = -x_g^2 + x_g \sum (f-2)k[(f-2)k+2] \nu_k . \tag{21}$$

The nature of this model is clearly exhibited in these equations. The last term in Eqs. (20) and (21) represents the reaction of the sol and gel, because, when a k-mer bonds with the gel, the sol loses $[(f-2)k+2]$ free groups, while the gel gains only $(f-2)k$, as two free groups are reacted when a bond is made, and the rate of this reaction is given by the product of the concentrations of free groups, or $x_g[(f-2)k+2]\nu_k$. The first term on the rhs of Eq. (20) represents the usual reaction of sol groups with themselves. In the same way, the first term on the rhs of Eq. (20) represents the reaction of free groups in the gel with themselves. Thus, in this model the sol and gel interact, and also the gel can cross link. This agrees with the analyses of both Flory[1] and Stockmayer.[2] There is no term in Eqs. (20) and (21) which represents cascading. Such a term would not be proportional to either x_s or x_g, and in any case all the terms have already been accounted for. In this model, there is cascading only at the instant t_c; and after t_c, gel growth proceeds only by the interreaction of sol and gel.

V. THE STOCKMAYER MODEL

Consider a model in which the sol does not interact with the gel, so that $X = x_s$. The solution to Eq. (1) for $t > t_c$ which matches Eq. (4) at t_c is given by

$$\nu_k(t) = \nu_k(t_c) \frac{(f-1)t_c}{ft - t_c} , \tag{22}$$

and we have

$$M_0 = \frac{1}{2f(ft - t_c)} , \tag{23}$$

$$M_1 = \frac{(f-1)t_c}{ft - t_c} , \tag{24}$$

$$M_2 = \infty , \tag{25}$$

$$x_s = \frac{1}{ft - t_c} . \tag{26}$$

All concentrations and all of their moments that are finite decay as $1/t$ from their values at t_c. It turns out that this model of gelation is equivalent to the one proposed by Stockmayer, based upon the determination of the most probable distribution. He found that past the gelation point the sol distribution "sticks," in that the relative quantity of each polymer remains the same, but the overall amount of sol decreases, just as in Eq. (22) above. In Appendix C, we show that this sticking necessarily implies $X = x_s$ and the explicit solution (22).

Thus, we conclude that basic to Stockmayer's model is the assumption that sol and gel do not interact. This was neither explicitly assumed nor discussed by Stockmayer himself. The time dependence of his model has not been previously discussed.

In this model, we find that x_s satisfies

$$\frac{dx_s}{dt} = -fx_s^2 = -x_s^2 + \frac{f-1}{(ft - t_c)^2} . \tag{27}$$

The last term expresses the continuous cascading growth of sol into gel, which is the only way the gel is formed here. The expression for x_g depends upon the assumption concerning the self-reactivity of the gel, and has no effect on the properties of the sol, since the gel and sol do not interact. If, for example, the gel does not cross link, then x_g will be given by

$$x_g = (f-2)(1 - M_1) = \frac{f(f-2)(t - t_c)}{ft - t_c} \tag{28}$$

since the gel will contain on the average $(f-2)$ free groups for each unit in the gel, and

$$\frac{dx_g}{dt} = \frac{f-1}{(ft - t_c)^2} . \tag{29}$$

The term on the rhs matches the cascading term of Eq. (27). (Note that Stockmayer considered this case where the gel does not cross link.)

Thus, in this model, the kinetic equations (1) and (2) do not change when t passes t_c, but the solution changes and there is a discontinuity in $d^2\nu_k/dt^2$ at t_c. It is interesting to note that while M_1 appears to be a general constant of motion of Eqs. (1) and (2), the proof that $\sum k(\partial \nu_k / \partial t) = 0$ actually fails when M_2 is infinite. As this is the case in this model for all $t > t_c$, it is not inconsistent that M_1 depends upon time.

VI. A THIRD MODEL

We consider a third model of gelation in which the sol and gel can react, so that $X = x_s + x_g$, but, in contrast to the Flory model, the gel is assumed not to cross link.[5] When no cross links exist in the gel, the concentration of free groups belonging to it will be $(f-2)$ times its concentration of units:

$$x_g = (f-2)(1 - M_1) . \tag{30}$$

Thus,

$$X = x_s + x_g = (f-2) + 2 \sum \nu_k . \tag{31}$$

This differs from the expression $X = x_s$ of the Flory model when $t > t_c$, for then $M_1 < 1$.

It follows from Eqs. (1), (30), and (31) that x_s and x_g satisfy

$$\frac{dx_s}{dt} = -x_s^2 - x_g \sum [(f-2)k+2]^2 \nu_k , \tag{32}$$

$$\frac{dx_g}{dt} = x_g \sum (f-2)k[(f-2)k+2] \nu_k . \tag{33}$$

This explicitly displays the reaction of the sol with the gel, the absence of cross linking in the gel, and the absence of cascading in this model.

In Appendix C, we show that the $\nu_k(t)$ of Eqs. (1)–(31) is of the same form as Eq. (3), although we have not found the explicit time dependence. For $t \to \infty$, we have

$$\frac{d\nu_k}{dt} \approx -(f-2)[(f-2)k+2]\nu_k \tag{34}$$

so that

$$\nu_k \sim \exp\{-(f-2)[(f-2)k+2]t\} . \tag{35}$$

VII. CONCLUSION

The properties of the three models of gelation can be characterized by the behavior of M_1 as $t \to \infty$. For the Flory model, Stockmayer model, and our third model, we have, respectively,

$$M_1 \sim \begin{cases} (1/ft)^f , \\ \dfrac{f-1}{f}\dfrac{t_c}{t} , \\ e^{-t/t_c} . \end{cases} \tag{36}$$

In the third case, where no explicit expression for M_1 was found, the behavior of M_1 follows from Eq. (35), which shows, by the way, that the overwhelming contribution to all moments comes from ν_1. (The same is true in the Flory model.) The moment M_1 gives the concentration of units belonging to the sol, so Eq. (36) describes the relative rate at which the sol disappears in these three models. The slowest rate occurs in the Stockmayer model where the only way that gel can form is by cascading growth. Comparing the two models where sol–gel interaction is allowed, we see that the rate is slower in the Flory model, where the gel cross links, than in our model, where the gel does not, since the cross linking reduces the number of free ends available with which the sol polymers can interact. These are both faster than the Stockmayer model, showing the relative slowness of cascading growth. For each model, M_1 has a distinct asymptotic behavior. Thus, the nature of a gel should be easily determinable by a simple measurement of its rate of formation.

Another interesting comparison can be made by looking at the behavior of M_1 at t_c. In the limit $t \to t_c^+$, we have, for the derivative of M_1,

$$M_1'(t_c^+) = -f^2(f-2)/(f-1) \times \begin{cases} 2 , \\ 1 , \\ 2 , \end{cases} \tag{37}$$

for the three models, respectively. Thus, the slope of M_1 is always discontinuous at t_c, since $M_1'(t_c^-) = 0$. The two models of sol–gel interaction show a gelation rate that is twice that of the cascading (Stockmayer) model. Note that at $t = t_c$, the sum given by Eq. (12) has a value exactly half of $M_1'(t_c^+)$ and $M_1'(t_c^-)$ for the Flory model and our third model.

To make a direct comparison with the results that have been discussed in the literature, we can rewrite some of our expressions in the language of the statistical theory, suppressing time in favor of the quantity "extent of reaction" α defined as the fraction of groups which have reacted. When $t < t_c$, it is given by

$$\alpha = 1 - \frac{x_s}{f} \tag{38}$$

since the concentration of reacted units equals x_s and the total concentration of units (reacted and unreacted) equals f. Using Eq. (11) for x_s, we find $\alpha = ft/(1+ft)$, and eliminating t from Eq. (4), we find

$$\nu_k = \frac{(1-\alpha)^2}{\alpha} \frac{f[(f-1)k]!}{[(f-2)k+2]!k!}[\alpha(1-\alpha)^{f-2}]^k , \tag{39}$$

identical to the result of Flory and Stockmayer. Note that $t_c = 1/f(f-2)$ corresponds to $\alpha_c = 1/(f-1)$.

When $t > t_c$ (or $\alpha > \alpha_c$) we have

$$\alpha = 1 - \frac{x_s + x_g}{f} . \tag{40}$$

A useful quantity to describe the gel state is the fraction of units that belong to the gel, or the weight fraction of the gel, defined by

$$W_g = 1 - M_1 . \tag{41}$$

This quantity varies from 0 to 1 as t goes from t_c to infinity. Using the appropriate expressions for x_s, x_g, and M_1 in Eqs. (40) and (41), and eliminating t, we find that our results lead to the following expressions for W_g and ν_k as functions of α:

(a) For Flory's model we have

$$W_g = 1 - \zeta^f , \tag{42}$$

where $\zeta(\alpha)$ is determined by

$$\zeta + \zeta^2 + \cdots + \zeta^{f-2} = \frac{1-\alpha}{\alpha} . \tag{43}$$

In this model, ν_k are still given by Eq. (39), and α has the time dependence

$$\alpha = \frac{ft}{1+ft} . \tag{44}$$

In the limit $t \to \infty$, $\alpha \to 1$. For $f = 3$, we have explicitly

$$W_g = 1 - \left(\frac{1-\alpha}{\alpha}\right)^3 , \tag{45}$$

which agrees with Stockmayer's discussion [Ref. 2, Eq. (24)].

(b) For Stockmayer's model, under the restriction that the gel does not cross link, x_g is given by Eq. (28), and we find explicitly

$$W_g = \frac{f}{f-2}[(f-1)\alpha - 1] , \tag{46}$$

$$\nu_k = \frac{(f-1)}{(f-2)}(2 - \alpha f)\nu_k(\alpha_c) . \tag{47}$$

Here, α has the time dependence

$$\alpha = \frac{2}{f} - \frac{1}{f^2}\frac{1}{ft - t_c} \tag{48}$$

and in the limit $t \to \infty$, $\alpha \to 2/f$. The expression (46) agrees with Stockmayer's result [Ref. 2, Eq. (22)]. We note that the above expression for $\nu_k(\alpha)$ [Eq. (47)], although implicit in the work of Stockmayer, appears to be
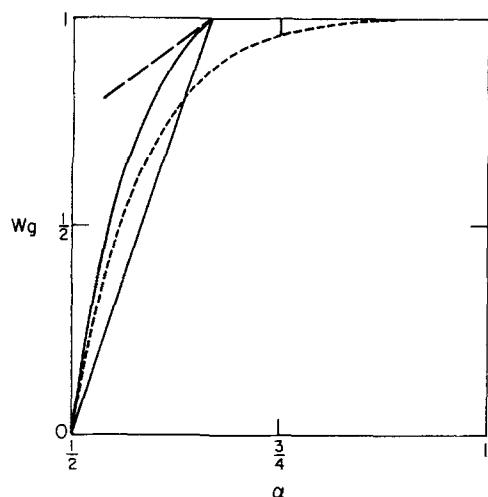
FIG. 1. Gel fraction as a function of extent of reaction, after Stockmayer, Ref. 2. Straight line, Eq. (46) (Stockmayer) (no intramolecular reactions permitted, sol and gel do not react); dotted curve, Eq. (45) (Flory) (intramolecular reactions in gel, sol and gel react); and curved full line, our model in which sol and gel react and no intramolecular reactions are permitted.

new. Stockmayer's discussion of gelation emphasized the behavior of $W_g(\alpha)$, as given by Eq. (46).

(c) For our model, we find

$$\alpha = \frac{2}{f}(1 - M_0) \qquad (49)$$

when $t \to \infty$, $\alpha \to 2/f$, since $M_0 \to 0$. To find $W_g(\alpha)$ explicitly, one must solve the equations for this model (see Appendix C), find M_0 and M_1 using Eqs. (C4) and (C5), and eliminate these from Eqs. (49) and (41). In the limit of $t \to \infty$, we have by virtue of the exponential decay in this model, as shown by Eq. (35), $M_0 \approx M_1 \approx \nu_1$. This implies

$$W_g \approx \frac{f\alpha}{2} \qquad (50)$$

for $t \to \infty$ or $\alpha \to 2/f$. Although α_{max} is the same for this model and Stockmayer's, the slope $dW_g/d\alpha$ as $\alpha \to \alpha_{max}$ is evidently different.

Stockmayer made a comparison of his and Flory's results by plotting W_g as a function of α, for the case $f = 3$, using equations identical to Eqs. (45) and (46) above (Ref. 2, Fig. 2). We have duplicated these curves in Fig. 1 in the present paper and have indicated schematically how $W_g(\alpha)$ appears for our model. From the above discussion, we know the upper intercept [using Eq. (49)] and slope [using Eq. (50)], and furthermore we know that on the lower end ($\alpha \approx \alpha_c$) the behavior of this model follows that of Flory's. Smoothly connecting these two ends together, we find the curve drawn in Fig. 1.

In a recent paper, Donoghue and Gibbs[10] have approached the problem of gelation by making numerical calculations of the distribution for a finite system of polymers. They used a statistical theory and evaluated the mean size distribution for fixed values of α. In Fig.

1 of Ref. 10, for example, they exhibit their calculated plots of $k\nu_k$ as a function of k, for a system of 100 trifunctional units, for various values of α. These curves show unambiguously the formation of the gel, as evidenced by the appearance of a second peak in the distribution at large k when α increases somewhat beyond α_c. The lower peak about $k = 0$ of course represents the sol, and for comparison they also plotted the "most probable distribution" to show the limiting sol distribution for large N. For this distribution the authors continue to use the Flory formula (39) when $\alpha > \alpha_c = \frac{1}{2}$, while it is the Stockmayer model which in fact represents the most probable distribution in the gelled state. Indeed, in their plot for $\alpha = 0.6$, the largest value considered in this figure, there is a noticeable discrepancy between their curve of $k\nu_k$ and that of Flory's distribution, at low values of k, which is not evident in the plots for smaller α. We have found that if the distribution reflecting Stockmayer's model—Eq. (47) above—is used in place of Eq. (39) for the limiting distribution, the discrepancy mentioned above disappears.

In Appendix A and Appendix B the generating function of the distribution is introduced. It is found to be a multivalued function of its parameter z with a point $z_0 > 1$ where the slope is infinite. The onset of gelation corresponds to this point's moving to $z = 1$. The evolution of the generating function is analogous to the evolution of the velocity field of a fluid during the formation of a shock wave, as the equations of fluid flow and the partial differential equation satisfied by the generating function are formally equivalent. This demonstrates in a precise and simple way—for the first time, to our knowledge—the fundamental correspondence between the mathematics describing the kinetics of a phase transition and that describing shock wave formation.

ACKNOWLEDGMENTS

APPENDIX A: DERIVATION OF $\nu_k(t)$, EQ. (4)

To solve Eq. (1), with X given by Eq. (2), we introduce the generating function

$$g \equiv \sum_{k=1}^{\infty} z^{(f-2)k+2}\nu_k , \qquad (A1)$$

where $g = g(z, t)$. This is equivalent to the generating function used by Dusek.[6] Then it follows that

$$\frac{\partial g}{\partial t} = \frac{1}{2}\left(\frac{\partial g}{\partial z}\right)^2 - z\left(\frac{\partial g}{\partial z}\right) \cdot x_s . \qquad (A2)$$

The equation for x_s, i.e., Eq. (10), follows by differentiating this with respect to z, and then setting $z = 1$. The function y, defined by

$$y = \frac{\partial g}{\partial z} - z x_s , \qquad (A3)$$

satisfies the simple equation

$$\frac{\partial y}{\partial t} = y \frac{\partial y}{\partial z} \qquad (A4)$$

whose solution is any function $u(\xi)$, where

$$\xi \equiv z + ty . \qquad (A5)$$

The function u may be determined by setting $t = 0$; then $\xi = z$, and $u(z) = y(z, 0) = f(z^{f-1} - z)$ according to the initial conditions (3). Thus, for all t, we have

$$y = f(\xi^{f-1} - \xi) . \qquad (A6)$$

The $\nu_k(t)$ follow by expanding y in powers of z, which may be done by writing

$$z = \xi(1 + ft) - ft\xi^{f-1} , \qquad (A7)$$

which follows from Eqs. (A5) and (A6), and using Lagrange's expansion[8] to find ξ as a power series in z. The coefficients of this series imply that ν_k is given by Eq. (4). The coefficient of z gives $1 - tx_s$, implying the expression (11) for x_s. Dusek solved Eq. (A2) directly to find

$$g = \frac{z}{2} f(1 - \alpha)\xi^{f-1} - \tfrac{1}{2}(f - 2)\xi^f , \qquad (A8)$$

which is equivalent to Eq. (A6).

APPENDIX B: FLORY'S MODEL OF GELATION

First of all, note that with a general function $X(t)$ in Eq. (1), the equation for the generating function g becomes

$$\frac{\partial g}{\partial t} = \frac{1}{2}\left(\frac{\partial g}{\partial z}\right)^2 - z\left(\frac{\partial g}{\partial z}\right)X . \qquad (B1)$$

For the ν_k to be given by Eq. (4), X must satisfy Eq. (18), for then Eqs. (B1) and (18) are formally identical to Eqs. (A2) and (10).

Even though the generating function equation is the same as in the pregelation case, the underlying rate equation is actually different, because x_s is not given by Eq. (11) and does not satisfy Eq. (10) when $t > t_c$. To calculate the moments and x_s, we may use the generating function g, differentiate with respect to z, and then set $z = 1$. In this way we find the expressions (13)–(16), where we write ζ for ξ at $z = 1$. The equation for ζ follows from Eq. (A7) and may be written

$$\zeta - 1 = ft(\zeta^{f-1} - \zeta) . \qquad (B2)$$

This equation has two positive real roots. The root $\zeta = 1$ corresponds to the pregelation case, and the results (7)–(11) follow from Eqs. (13)–(16) by setting $\zeta = 1$. The second root is determined by Eq. (17); this equation follows from Eq. (B2) by factoring out $(1 - \zeta)$. The second root applies when $t > t_c$. Note that $\zeta < 1$ and therefore $x_s < X$.

There remains the question why, when $t > t_c$, ζ should be given by Eq. (17) instead of by $\zeta = 1$. [Note that this problem does not arise when $t < t_c$, for then the root of

Eq. (17) gives an unphysical solution with $M_1 > 1$.] To answer this question, consider the function $y(z, t)$ given by (A5)–(A6). At $t = 0$, it has the form $y(z, 0) = fz(z^{f-2} - 1) \equiv u(z)$, and as time progresses, it "falls" back according to $y = u(z + ty)$. An illustration of this behavior is given in Fig. 2 for the case $f = 3$, where the initial function is simply a parabola. For all $t > 0$, y is a multivalued function of z. The proper value lies on the branch that intersects the origin, since according to its definition, $y(0, t) = 0$. At $z = 1$, y is single valued (and equal to zero) when $t < t_c$, and double valued when $t > t_c$, as shown in the example in Fig. 2. The value of y at this point is related to ζ by $y(1, t) = (\zeta - 1)/t$, and when $t > t_c$, the $y(1, t)$ on the proper branch [the $y(1, t) < 0$] gives the ζ of Eq. (17). Note that the height $|y(1, t)| = (1 - \zeta)/t$ equals the concentration of free groups in the gel x_g.

The evolution of the generating function described above is analogous to the phenomenon of shock wave formation in fluid dynamics. Indeed, the Euler equations for isentropic one-dimensional flow can be written[9]

$$\frac{\partial v}{\partial t} + v\frac{\partial v}{\partial x} = 0 , \qquad (B3)$$

where $v \equiv V - c$, V being the fluid velocity and c the velocity of sound. Except for a change of sign, this is identical to Eq. (A4). The main difference lies in the choice of the initial condition. The initial condition for $v(x)$ is usually taken to be a sinusoidal function, and as time progresses, the peaks lean over until at a certain point in time the slope at every other node is infinite. Beyond this, the solution is multivalued, and a vertical construction which corresponds to the shock wave must be made. In the gelation problem, the initial curve is parabola-like (for the monodisperse initial condition) and there is a multivaluedness and a point where y is vertical for all $t > 0$. The gelation corresponds to that point's moving to $z = 1$. Note that this vertical point
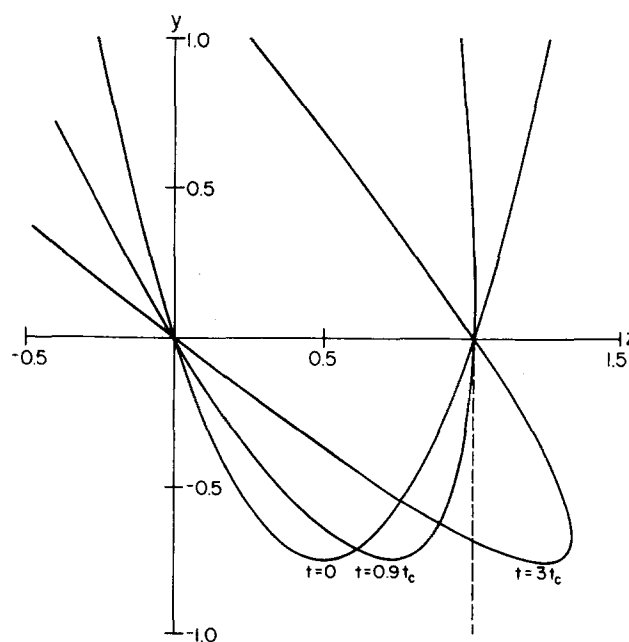

FIG. 2. The evolution of the generating function y as a function of z, for the case $f = 3$, where $t_c = 1/3$.

corresponds to a singularity in y on the complex z plane.

Note that Flory calculated the moments for $t > t_c$ from the known moments for $t < t_c$, by using the relation

$$\nu_k(t) = \frac{ft^*(1 + ft^*)}{ft(1 + ft)} \nu_k(t^*) , \qquad (B4)$$

where $t^* < t_c$ is a function of t and is determined by

$$\frac{ft^*}{(1 + ft^*)^{f-1}} = \frac{ft}{(1 + ft)^{f-1}} . \qquad (B5)$$

The correspondence to the results given here is made through the relations

$$\zeta = \frac{1 + ft^*}{1 + ft} , \quad \zeta^{f-1} = \frac{ft^*}{ft} . \qquad (B6)$$

APPENDIX C: GENERAL DISCUSSION OF GELATION

First note that the general solution of Eq. (B1) for any given $X(t)$, is given by a function of a similar form as Eq. (4):

$$\nu_k = a \frac{f[(f-1)k]!}{[(f-2)k+2]! k!} \frac{(f-\mu)^{k-1} \mu^{(f-2)k+2}}{f^{(f-1)k+1}} , \qquad (C1)$$

where a and μ are some functions of time. In the pregelation solution (4), we had $a = 1$ and $\mu = f/(1 + ft)$. For Eq. (C1) to match Eq. (4) at t_c, we must have

$$a_c = 1 , \quad \mu_c = f(f-2)/f-1) , \qquad (C2)$$

where the subscript c indicates the limit $t \to t_c^*$. Furthermore, since $d\nu_k/dt$ must be continuous at t_c, we find the restriction on the time derivatives a' and μ' at t_c:

$$\frac{a_c'}{f} + \frac{\mu_c'}{\mu_c} = -\mu_c . \qquad (C3)$$

The moments of Eq. (C1) are given by

$$M_0 = \frac{a}{2}[\mu \zeta^{f-1} - (f-2)\zeta^f] , \qquad (C4)$$

$$M_1 = a\zeta^f , \qquad (C5)$$

$$x_s = (f-2)M_1 + 2M_0 = a\mu \zeta^{f-1} , \qquad (C6)$$

with ζ determined by

$$\zeta + \zeta^2 + \cdots + \zeta^{f-2} = \frac{\mu}{f - \mu} . \qquad (C7)$$

To prove that Eq. (C1) satisfies Eq. (B1), observe that the generating function g of Eq. (C1) is given by

$$g = \frac{a}{2}[z\mu \zeta^{f-1} - (f-2)\zeta^f] , \qquad (C8)$$

where

$$\frac{\xi^{f-1} - \xi}{\xi - z} = \frac{\mu}{f - \mu} \qquad (C9)$$

determines ξ. [This is equivalent to Eq. (A7) with ft replaced by $(f - \mu)/\mu$.] Inserting this g into Eq. (B1), and requiring that terms of different powers of z (or ξ) vanish separately, we find the two equations

$$\frac{(f-2)(f-\mu)}{f\mu} \frac{a'}{a} + \frac{\mu'}{\mu} = -a\mu , \qquad (C10)$$

$$\frac{1}{f} \frac{a'}{a} + \frac{\mu'}{\mu} = -X \qquad (C11)$$

for a and μ, subject to the above boundary condition at t_c. Note that, as $t \to t_c^*$, Eqs. (C10) and (C11) both become identical to the single equation (C3), which is not sufficient to determine a_c' and μ_c' separately.

In the Flory model of gelation, where $X = f/(1 + ft)$, we have

$$a' = 0 , \quad \mu' = -\mu^2 . \qquad (C12)$$

Then Eq. (C1) agrees with the solution (4) in the text. We can also verify that Eq. (22) corresponds to Stockmayer's model of gelation. In his model, the relative amount of each polymer in the sol was found to be constant, so we take $\mu' = 0$ in the general solution (C1). Then from Eqs. (C10) and (C11)

$$a' = -f\mu_c a^2 , \qquad (C13)$$

which implies both that ν_k is given by Eq. (22) and $X = x_s$.

In our model of gelation, we have

$$X = (f-2) + a\mu \zeta^{f-1} - (f-2)a\zeta^f . \qquad (C14)$$

Although we cannot solve Eqs. (C10) and (C11) explicitly for all $t > t_c$, we can find a_c' and μ_c' as follows: Equations (C10) and (C11) imply that

$$\frac{a'}{fa\mu} = \frac{X - a\mu}{f(f-2) - \mu(f-1)} . \qquad (C15)$$

When $t \to t_c^*$, both the numerator and denominator of the rhs go to zero. Thus, we apply l'Hôpital's rule:

$$\frac{a_c'}{f\mu_c} = \lim_{t \to t_c} \frac{X' - a\mu' - \mu_c'}{-(f-1)\mu'} . \qquad (C16)$$

Using Eq. (C3), we find

$$X_c' = -f\mu_c^2 + (f-1)\left(\frac{\mu_c'}{\mu_c}\right)^2 . \qquad (C17)$$

From Eq. (C14) we find for this model

$$X_c' = -\mu_c^2 , \qquad (C18)$$

where we have used Eq. (C3) and also $\zeta_c' = 2\mu_c'/\mu_c$, which follows from Eq. (C7). Equating Eqs. (C17) and (C18), we find

$$\mu_c' = -\mu_c^2 , \quad a_c' = 0 . \qquad (C19)$$

(Note that there is another solution $\mu_c' = \mu_c^2$ which is unphysical.) Finally, we can use this to calculate M_1' for $t \to t_c^*$, for it follows from Eq. (C5) that

$$M_1'(t_c^*) = f(\mu_c'/\mu_c - \mu_c) \qquad (C20)$$

and using Eq. (C19) we find the value (39) given in the text.

[1]P. J. Flory, *Principles of Polymer Chemistry* (Cornell University, Ithaca, 1953), Chap. 9.
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[8]See, for example, Handbook of Mathematical Functions, edited by M. Abramowitz and I. A. Stegun (National Bureau of Standards, Washington, D.C., 1964), p. 14.

[9]See L. D. Landau and E. M. Lifshitz, Fluid Mechanics (Pergamon, London, 1959), p. 367.

[10]E. Donoghue and J. H. Gibbs, J. Chem. Phys. 70, 2346 (1979).