

## Critical Properties for Gelation: A Kinetic Approach

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The critical behavior of the gelation of polymers is studied as a kinetic process in which only surface interactions between polymers are assumed. It is found that gelation occurs when the exponent  $\omega$ , which characterizes the effective surface area, is greater than  $\frac{1}{2}$ , and that the exponent  $\tau$ , which characterizes the size distribution at the gel point, is related to  $\omega$  by  $\tau = \omega + \frac{3}{2}$ .

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In this Letter, we discuss the gelation transition in polymerization by considering polymerization as a time-dependent process represented by the kinetic equation<sup>1-5</sup>

$$\dot{c}_k = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{j=1}^{\infty} K_{kj} c_j \quad (1)$$

which describes the evolution in the concentration of  $k$ -mers, given by  $c_k(t)$ , due to random reactions between pairs of polymers. In (1) it is assumed that the rate that  $i$ -mers and  $j$ -mers react to form  $(i+j)$ -mers is given by  $K_{ij} c_i c_j$ , where  $K_{ij}$  is a transition matrix describing the collision process. There is no breakup processes, so that the reaction continues until gelation is complete (a single infinite polymer).

From the chemical-kinetic view that the probability that two chemical groups react is proportional to the product of their concentrations, it follows that  $K_{ij}$  is proportional to the number of ways an  $i$ -mer and a  $j$ -mer can combine. In the Flory-Stockmayer (FS) theory<sup>1,6</sup> of the step polymerization of  $f$  functional units,  $K_{ij}$  is given by  $[(f-2)i+2][(f-2)j+2]$ , for in this theory an  $i$ -mer always has  $[(f-2)i+2]$  free ends as a consequence of the assumptions that intramolecular reactions cannot occur, and that all free ends are equally reactive. With the above expression for  $K_{ij}$ , (1) can be solved explicitly [for certain initial conditions  $c_k(0)$ ] and it is found that at a certain time,  $t_c$ , there occurs a transition which manifests itself through a violation of the conservation of total mass,  $M_1 = \sum k c_k$ , of sol particles (finite-size clusters). The  $M_1(t)$  is constant before the gel point,  $t_c$ , and decreases past  $t_c$ , as the sol loses mass to the gel (infinite-size cluster).

While the properties of the gelation transition

are of interest as an example of critical-point behavior, the FS theory is not expected to be accurate about the gel point, because the underlying assumptions become unrealistic when the polymers are large.

An alternative to the chemical-kinetic theory of polymerization is the lattice-percolation model, where polymers are "grown" by randomly placing bonds between atoms on an appropriate lattice.<sup>7</sup> Since such a model allows intramolecular reaction and also takes steric hindrance into account, it is believed that the properties about the gel point are thus more accurately described than by the FS theory. The predictions of the critical behavior of these two theories are different; consider, for example, the exponent  $\tau$ , which describes the large- $k$  behavior of  $c_k$  precisely at the gel point such that

$$c_k(t_c) \sim \text{const} \times k^{-\tau} \quad (2)$$

asymptotically as  $k \rightarrow \infty$ . The FS theory gives  $\tau = \frac{5}{2}$ , independent of dimensionality  $d$ , while the percolation studies (using series expansions or computer simulations) give  $\tau = 2.06$  ( $d = 2$ ) and  $2.20$  ( $d = 3$ ).<sup>7</sup>

In this Letter, we discuss a kinetic theory of gelation which allows the gel-point behavior to be effectively modeled. We choose an expression for  $K_{ij}$  which goes beyond the restrictions of the FS theory, and for which we are able to determine some asymptotic properties of post-gel solutions, such as (2).

The dependence of  $K_{ij}$  on the cluster sizes  $i$  and  $j$  is of crucial importance for the  $k$  and  $t$  dependence of the size distribution.<sup>1,4,8</sup> For the model  $K_{ij} \sim 1$ ,  $c_k(t)$  decays exponentially for all  $t \geq 0$  (no gelation); for  $K_{ij} \sim i+j$ , the distribution  $c_k(t)$  approaches the form (2) (with  $\omega = \frac{3}{2}$ ) at  $in-$

finite time<sup>4,8</sup>; and for  $K_{ij} \sim ij$ , as in the FS theory, gelation occurs within a finite time. Here we consider models where gelation occurs in a finite time. We choose  $K_{ij} = s_i s_j$ , where  $s_i$  equals the number of *effectively* reactive sites on an  $i$ -mer. In the FS theory,  $s_i = (f - 2)i + 2$  is proportional to the volume of an  $i$ -mer (for large  $i$ ). To take into account the geometry of a polymer, and to allow for intramolecular reactions, we expect  $s_k$  to be proportional to the effective surface area of a cluster. Thus, assuming  $s_k$  to have an asymptotic behavior of the form

$$s_k \sim k^\omega \tag{3}$$

as  $k \rightarrow \infty$ , then we expect  $\omega$  to lie in the range

$$1 - 1/d < \omega < 1, \tag{4}$$

the lower limit reflecting the surface area of a compact solid in  $d$  dimensions, and the upper limit reflecting the FS limit of complete reactivity (equivalent to choosing a Bethe lattice in percolation studies).

For this model, existence and uniqueness of solutions to the initial value problem have been discussed by McLeod,<sup>9</sup> Leyvraz and Tschudi,<sup>5</sup> and White,<sup>10</sup> but no explicit solutions are known (other than for  $\omega = 0$  and 1). Here we consider a special solution of the form

$$c_k(t) = c_k(t_c) [1 + b(t - t_c)]^{-1} \quad (t \geq t_c) \tag{5}$$

in analogy with the case  $\omega = 1$ , where the post-gelation solution for monodisperse initial conditions is exactly of this form.<sup>3,5</sup> The question is then: Under what conditions are such solutions possible, and can one determine the  $k$  dependence of  $c_k$ ? To that end the *Ansatz* (5) is inserted into (1), yielding a recursion relation for  $c_k(t_c)$ , which has to be solved under the restrictions

$$\sum k c_k(t_c) = M_1(0) \equiv 1; \quad b = \sum k^\omega c_k(t_c). \tag{6}$$

For the generating functions

$$g(x) = \sum c_k(t_c) e^{kx}, \quad f(x) = \sum c_k(t_c) k^\omega e^{kx}, \tag{7}$$

where  $g(x) \simeq M_0(t_c) + x + o(x)$  for small  $x$ , we deduce from the recursion relation  $f(x) = b - [b^2 - 2bg(x)]^{1/2}$  and  $g(0) = M_0(t_c) = b/2$ , implying  $f(x) \simeq b - (-2bx)^{1/2}$  for small  $x$ . This branch-point singularity yields an asymptotic behavior

$$c_k(t_c) \sim (b/2\pi)^{1/2} k^{-3/2-\omega} \quad (k \rightarrow \infty). \tag{8}$$

The coefficient  $b$  varies between 0.27 and 1 for  $\omega$  between 0.5 and 1, as follows from numerically solving the recursion relation for the  $c_k(t_c)$ . The parameter  $t_c$  in (5), depending on  $\omega$  and on the

initial conditions at  $t = 0$ , cannot be determined within the present method.

For a general post-gelation solution, we have also determined the asymptotic behavior of  $c_k$ . Assuming only that  $M_1$  depends upon time, we obtain the result (8) with  $b$  replaced by  $\dot{M}_1(t_c)$ .<sup>11</sup>

Comparison of (8) and (2) yields

$$\tau = \omega + \frac{3}{2} \tag{9}$$

and with the help of (4) we have the inequalities

$$\frac{3}{2} - 1/d < \tau < \frac{5}{2}. \tag{10}$$

Thus, given the geometric exponent  $\omega$  characterizing the effective surface area of a large polymer, we have calculated the nonclassical values of the exponent  $\tau$ , its classical value being reached in the FS theory ( $\omega = 1$ ). Recent results on lattice percolation show that clusters are *compact* past the percolation point,<sup>12</sup> implying  $\omega = 1 - 1/d$ . Estimates for  $\tau$  obtained from (9) using this value are slightly below the lattice calculations for all  $d$ , as can be seen from Table I. We make the following comments:

(1) The solution (8) is only compatible with a finite  $M_1(t_c)$  for  $\omega > \frac{1}{2}$ . Therefore, the kinetic equation only allows solutions with a time-dependent mass (that is, with gelation) if  $\omega > \frac{1}{2}$ . This confirms a conjecture of Leyvraz and Tschudi that gelation cannot occur for  $\omega \leq \frac{1}{2}$ .<sup>5</sup> For  $\omega = \frac{1}{2}$  we expect gelation to occur at infinite time.

(2) The geometric exponent  $\omega$  is a coarse-grained measure for the outer surface of polymers, and represents the *number of reactive sites available for bonding between large clusters*. It should not be identified with the fine-grained external perimeter which penetrates the whole cluster<sup>12</sup> and is therefore proportional to the volume  $k$  of the cluster (implying  $\omega = 1$ )

(3) For general post-gelation solutions we can show the asymptotic behavior (8), but we cannot

TABLE I. Values of  $\tau$ .

$d$	FS	Lattice <sup>a</sup>	Eq. (9)
2	2.5	2.06	2
3	2.5	2.20	2.17
4	2.5	2.30	2.25
5	2.5	2.39	2.30
6	2.5	2.50	2.33
...	...	...	...
$\infty$	2.5	2.5	2.5

<sup>a</sup> Values deduced from Stauffer, Ref. 7.

determine  $\dot{M}_1(t_c)$  [which replaces  $b$  in (8)]. The special solution, (5), is of importance because it demonstrates that there exists at least one solution with a finite nonvanishing  $M_1(t_c)$ .

(4) The foregoing discussion concerned the  $k$  dependence of  $c_k(t_c)$ . Since at  $t=t_c$  no gel is yet present, this  $k$  dependence will not depend on the assumed interaction between sol and gel. However, that interaction strongly affects the time dependence of the post-gel solution. As in Stockmayer's classical theory of gelation<sup>1,3</sup> this interaction is absent here, because the gel is not present in the loss term of our kinetic equation, (1). One may modify the kinetic equation past the gel point by adding sol-gel interaction terms (as has been done in the classical theory to obtain different post-gel solutions, such as Flory's<sup>2,3</sup>). Such modifications may possibly change critical exponents concerned with the time dependence past the gel point.

(5) In our model, the post-gel behavior has the following properties: (a) The scaling postulate  $c_k(t) \sim c_k(t_c) \Phi(|t-t_c|k^\sigma)$  is not valid; (b) the exponent  $\beta$ , which determines the growth rate of the gel fraction close to the gel point, has the classical value 1; and (c) the exponents  $\gamma$  and  $\sigma$  are undefined. The exponent  $\beta$  is defined by the relation between gel growth,  $1-M_1(t)$ , and the extent of reaction,  $p(t)$ , such that  $1-M_1 \sim [p-p(t_c)]^\beta$ . In our model,  $1-p$  is proportional to the number of available reactive sites,  $\sum s_k c_k(t)$ , so that close to the gel point  $t-t_c \sim [p-p(t_c)]$ , since  $\dot{p}(t_c^+)$  is finite on account of (5) and (8). Then, since  $\dot{M}_1(t_c^+)$  is finite [on account of (5)],  $\beta$  has the value 1. The exponents  $\gamma$  and  $\sigma$  are related to the second and third moments of  $c_k(t)$ ,<sup>7</sup> which are infinite for all  $t \geq t_c$ . These post-gel results will most likely change if a sol-gel interaction is allowed. If such an interaction leads to scaling, there remains the question of whether the behavior belongs to the universality class of the classical theory, of the percolation models, or perhaps of an intermediate class as found by Herrman, Landau, and Stauffer for a kinetic simulation of polymerization on a lattice.<sup>13</sup>

(6) Equations (5) and (8) comprise new results for the coagulation equation (1), which has been extensively studied in the context of coagulation,<sup>14</sup> antibody-antigen interaction,<sup>4,15</sup> and galactic clustering,<sup>16</sup> as well as polymerization. In all the studies, solutions to (1) have been found only for  $K_{ij} = A + B(i+j) + Cij$ .<sup>14</sup> Perhaps the new solution given here will be useful in some of these

other problems concerning clustering.

After submission of this manuscript a paper by Leyvraz and Tschudi<sup>17</sup> appeared which confirms some of our conclusions.

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