

## Kinetics of Reversible Polymerization

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This paper extends the kinetic theory of irreversible polymerization (Smoluchowski's equation) by including fragmentation effects in such a way, that the most probable (equilibrium) size distribution from the classical polymerization theories is contained in our theory as the stationary distribution. The time-dependent cluster size distribution  $c_k(\alpha(t))$  in Flory's polymerization models  $RA_f$  and  $A_fRB_g$ , expressed in terms of the extent of reaction  $\alpha$ , has the same canonical form as in equilibrium, and the time dependence of  $\alpha(t)$  is determined from a macroscopic rate equation. We show that a gelation transition may or may not occur, depending on the value of the fragmentation strength, and, in case a phase transition takes place, we give Flory- and Stockmayer-type postgel distributions.

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**KEY WORDS:** Reversible polymerization; coagulation; fragmentation;  $RA_f$  and  $A_fRB_g$  models; gelation; clustering; aggregation.

### 1. INTRODUCTION

The available kinetic theory of polymerization does not contain the equilibrium theory of Flory<sup>(1)</sup> and Stockmayer<sup>(2)</sup> as a limiting case for large values of the time, due to absence of fragmentation effects. As clusters are growing in size, break-up processes become more important, and the irreversible coagulation reactions should be replaced by reversible coagulation-fragmentation reactions. In Smoluchowski's theory of (irreversible) coagulation<sup>(3,4)</sup> all clusters coalesce in the course of time into an infinite aggregate, and the limiting concentration for a given cluster size vanishes. Thus nontrivial stationary size distributions  $c_k$  at arbitrarily prescribed values of the extent of reaction  $\alpha$  are excluded, where  $\alpha$  represents the fraction of reacted groups. The present paper extends the kinetic theory of

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polymerization by including fragmentation in such a way, that the solutions of the Flory–Stockmayer (FS) theory appear as the stationary solutions of the theory.

The present theory of clustering describes reaction limited aggregation processes (RLA), and it is most instructive to quote Flory<sup>(5)</sup> on the limitations of the rate equation approach: “If the reaction is too fast or mobility too low to allow maintenance of the equilibrium concentration of pairs of reactants adjacent to one another in the liquid, then diffusion will become the rate-controlling step. Condensation polymerization generally proceeds by reactions of moderate rate such that no more than about one bimolecular collision in  $10^{13}$  between reactants is fruitful. Within the interval of time for this number of collisions, considerable diffusion of the molecule (...) may occur.”

In diffusion-limited aggregation (DLA) or ballistic models of aggregation, the amount of time required for the reactants to approach each other is much larger than the time required for the bonding reaction (high sticking probability). Here a cluster grows by addition of a single particle<sup>(6–9)</sup> or of another cluster,<sup>(10,11)</sup> which approach each other along diffusive or ballistic trajectories and have a high sticking probability between 1 and  $1/10$ .<sup>(12)</sup> The main results have been obtained by computer simulations.

In this paper we restrict ourselves to aggregation or polymerization processes that are limited by reaction rates and that are reversible.

Reversible polymerization is the combined process of formation and breakage of chemical bonds in a system of reacting polymers. These processes may be symbolized by the reversible reactions  $a_i + a_j \rightleftharpoons a_{i+j}$  ( $i, j = 1, 2, \dots$ ) where  $a_k$  denotes a cluster ( $k$ -mer), consisting of  $k$  monomeric units  $a_1$ . The forward rate constants  $K_{ij}$  describe the bimolecular coagulation process. The unimolecular fragmentation process is described by the backward rate constants  $F_{ij}$ . Other reactions, such as triple collisions and break-up into many particles are assumed to be absent.

In a statistical description of reversible polymerization one is interested in the concentrations of  $k$ -mers ( $k = 1, 2, \dots$ ), also referred to as the cluster size distribution  $c_k(t)$ . Its time evolution is given by the following infinite set of coupled nonlinear rate equations:

$$\dot{c}_k = \frac{1}{2} \sum_{i+j=k} (K_{ij}c_i c_j - F_{ij}c_{i+j}) - \sum_{j=1}^{\infty} (K_{kj}c_k c_j - F_{kj}c_{k+j}) \quad (1.1)$$

We are specially interested in the solution of (1.1) evolving from the monodisperse initial distribution

$$c_k(0) = M\delta_{k1} = \delta_{k1} \quad (1.2)$$

where  $M$  is the total concentration of monomers initially put into the system. For convenience the unit of volume will be chosen such that  $M = 1$ .

The rate constants in Eq. (1.1) depend on the polymerization model under consideration. In *Smoluchowski's coagulation equation* break-up processes are absent, so that  $F_{ij} = 0$ . In this paper we consider the kinetics of Flory's polymer models  $RA_f$  and  $A_fRB_g$ , where  $RA_f$  units carry  $f$   $A$  groups, forming  $A-A$  bonds, and  $A_fRB_g$  units carry  $f$   $A$  groups and  $g$   $B$  groups, forming  $A-B$  bonds. The formation of bonds between finite polymers is restricted by the same basic assumptions as used in the statistical theory of Flory and Stockmayer: (i) *polymers cannot form cross-links, so that cyclization does not take place* (ii) *identical chemical groups have a priori equal reactivity, independent of the size of the polymer to which they are attached*.

As a consequence of assumption (i) the polymers form *branched treelike structures*. An exception are the models  $RA_2$  and  $ARB$ , which form linear chains. As a consequence of assumption (ii), the bonding process in the FS theory may be thought of as a random process: i.e., an  $A$  group selected at random is bonded with a probability  $\alpha$  and bonding probabilities of any two  $A$  groups are independent. Here  $\alpha$  equals the extent of reaction, i.e., the total fraction of reacted  $A$  groups.

Using Stockmayer's method<sup>(2)</sup>  $c_k(\alpha)$  is found as the most probable solution consistent with a prescribed number of units and a prescribed number of clusters or, equivalently, a prescribed value of  $\alpha$ , i.e.,

$$M = 1 = \sum_k kc_k, \quad \mu = \sum_k c_k \quad (1.3)$$

Consequently it has the general form

$$c_k = Aw_k \xi^k / k! \equiv AN_k \xi^k \quad (1.4)$$

where the *amplitude*  $A$  and the *fugacity*  $\xi$  are Lagrange multipliers determined by the prescribed values of  $M$  and  $\mu$ . The combinatorial factor  $w_k$  represents the number of ways in which a cluster of size  $k$  can be constructed out of its constituent units. For later convenience the combination  $w_k/k!$  will be denoted by  $N_k$ .

For the  $RA_f$  model these numbers  $N_k$  have been calculated already by Stockmayer:

$$N_k = f^k [(f-1)k!] / [(f-2)k+2]! k! \quad (1.5)$$

For the  $A_fRB_g$  model these numbers can be found in Refs. 13, 14, and 15. The explicit form of  $A$  and  $\xi$  for the  $RA_f$  and  $A_fRB_g$  model can be found in

[14–17]. The *FS* theory is static by nature since its basic variable is not time, but the extent of reaction  $\alpha$ .

In a nonequilibrium state  $\alpha(t)$  is changing in time, and its time dependence is described by the macroscopic rate equation for the total concentration of reacted *A* groups. For the polymer models *ARB*, *ARB*<sub>2</sub>, *RA*<sub>3</sub>, Ziff has observed<sup>(4)</sup> the interesting property that the solutions  $c_k(t)$  of Smoluchowski's equation for monodisperse initial conditions keep the canonical form of the most probable *FS* solutions  $c_k(\alpha(t))$ .

The purpose of this paper is to extend Ziff's observation to coagulating systems that also allow break-up processes, and to present a kinetic theory of reversible polymerization. To carry out this program one needs to construct the appropriate expressions for  $K_{ij}$  and  $F_{ij}$ . Consider first the  $A_fRB_g$  model. Since the bonding process is considered to be a random process the coagulation coefficient  $K_{ij}$  is proportional to the number of possible *AB* reactions of free groups on an *i*-mer with those on a *j*-mer. The coefficient of proportionality is the rate constant for formation of a single *A–B* bond, which may be set equal to unity by choosing appropriate units of time. Thus<sup>(4,18)</sup>

$$K_{ij}(A_fRB_g) = s_i(f) s_j(g) + s_i(g) s_j(f) \quad (1.6)$$

with

$$s_k(f) = (f - 1)k + 1 \quad (1.7)$$

where  $s_k(f)$  and  $s_k(g)$  are, respectively, the number of unreacted *A* and *B* groups on a *k*-mer. By similar arguments one finds for the  $RA_f$  model

$$K_{ij}(RA_f) = \sigma_i(f) \sigma_j(f) \quad (1.8)$$

where  $\sigma_k(f)$  is the number of unreacted *A* groups on a *k*-mer:

$$\sigma_k(f) = (f - 2)k + 2 \quad (1.9)$$

The construction of the fragmentation coefficients  $F_{ij}$  for the above polymer models is one of the subjects of this paper, and will be dealt with in Section 2.

In general, little is known about the solution of the kinetic equation (1.1) containing the combined effects of coagulation and fragmentation. Existence and uniqueness of solutions for the continuous analog of equation (1.1) have been proved by Melzak<sup>(19)</sup> under the condition of uniformly bounded coagulation and fragmentation rates. Under less stringent conditions, allowing also for gelation to take place, an existence proof for solutions of the discrete equation (1.1) has recently been given by Spouge.<sup>(20)</sup> For the linear chain model *ARB*, where  $F_{ij}$  equals a constant,  $F_{ij} = \lambda$ , the kinetic equation (1.1) has been solved by Blatz and Tobolsky<sup>(21)</sup> for monodisperse initial conditions, and by Aizenman and Bak<sup>(22)</sup> and Ernst<sup>(23)</sup>

for general initial conditions. Smoluchowski's equation with  $F_{ij} = 0$  and  $K_{ij} = A + B(i + j) + Cij$  can be solved analytically (for a review, see Ref. 3). Barrow<sup>(24)</sup> has combined the above coagulation kernel  $K_{ij}$  with a constant fragmentation kernel  $F_{ij} = \lambda$ . He only solved the moment equation for the total number of clusters,  $\mu(t) = \sum c_k(t)$ , with an arbitrary initial condition, and showed that the kinetic equation (1.1) admits nontrivial stationary solutions only when  $B = C = 0$  and  $\lambda \neq 0$  (a case, already completely solved by Aizenman and Bak). Srivastava<sup>(25)</sup> considered coagulation processes  $a_i + a_j \rightarrow a_{i+j}$  with  $K_{ij} = A + B(i + j) + Cij$  and  $F_{ij} = 0$  in combination with the bimolecular fragmentation reaction  $a_i + a_j \rightarrow (i + j)a_1$ , and solved for the total number of clusters with an arbitrary initial condition.

Another approach to the kinetics of reversible aggregation has been followed by Perelson and collaborators.<sup>(26)</sup> These authors start from the most probable (FS) distribution  $c_k(\alpha)$  for a particular aggregation model, and construct the time-dependent cluster size distribution  $c_k(\alpha(t))$  by assuming that the time dependence of  $\alpha(t)$  is determined by the macroscopic rate equations with coagulation and fragmentation included. In this paper the relation between the above approach and the solution of the kinetic equation (1.1) with appropriate coagulation and fragmentation rates will be established.

The plan of this paper is as follows. Section 2 gives the construction of the fragmentation coefficients. The pregelation stage, the gelation transition and the postgelation stage of the  $RA_f$  model are presented, respectively, in Sections 3, 4, and 5. Section 6 is devoted to some comments. In Appendix A it is shown that the size distributions, constructed from probabilistic arguments, are indeed solutions of the kinetic equation. In Appendix B we summarize the corresponding results for the  $A_fRB_g$  model.

## 2. FRAGMENTATION COEFFICIENTS $F_{ij}$

In this section we describe the general procedure for constructing fragmentation coefficients  $F_{ij}$  for  $k$ -mer break-up into  $i$ -mers and  $j$ -mers with  $k = i + j$  for systems starting from the monodisperse initial distribution. In doing so we also determine the stationary size distribution  $c_k(\infty)$  for a given total mass per unit volume  $M$ .

Suppose that the coagulation kernel  $K_{ij}$  is given for the polymer model under consideration, then we impose the following two requirements on  $F_{ij}$ :

(i) *The normalization condition*: which requires that the total fragmentation rate of a  $k$ -mer be proportional to the number of bonds, i.e.,

$$\frac{1}{2} \sum_{i+j=k} F_{ij} = \lambda(k-1) \quad (2.1)$$

The *a priori* equal reactivity of the functional groups implies that all  $(k - 1)$  bonds in a  $k$ -mer are equivalent. In particular all bonds are equally breakable, and the total rate of  $k$ -mer break-up,  $\frac{1}{2} \sum F_{ij}$ , is proportional to the number of bonds. The constant of proportionality  $\lambda$  represents the fragmentation strength.

(ii) *The detailed balance condition*: which requires the existence of stationary solutions to Eq. (1.1). In a stationary state the number of  $k$ -mers lost to the  $i$ - and  $j$ -mers through fragmentation is exactly compensated by the number of  $k$ -mers formed out of  $i$ - and  $j$ -mers:

$$F_{ij}c_{i+j}(\infty) = K_{ij}c_i(\infty)c_j(\infty) \quad (2.2)$$

The detailed balance condition guarantees the existence of a stationary (as yet unknown) size distribution  $c_k(\infty)$ , and imposes a severe restriction on the form of  $F_{ij}$ , as will be seen below.

Once  $K_{ij}$  is given, the requirements (i) and (ii) uniquely determine both the equilibrium solutions  $c_k(\infty)$  and the fragmentation kernel  $F_{ij}$ . By combination of (2.1) and (2.2), the stationary solutions may be expressed in terms of the monomer concentration  $c_1(\infty)$  through the recursion relation

$$\lambda(k - 1)c_k(\infty) = \frac{1}{2} \sum_{i+j=k} K_{ij}c_i(\infty)c_j(\infty) \quad (2.3)$$

It can be put into the equivalent form

$$(k - 1)N_k = \frac{1}{2} \sum_{i+j=k} K_{ij}N_iN_j \quad (N_1 = 1) \quad (2.4)$$

after writing the stationary size distribution in the form

$$c_k(\infty) = \lambda \xi^k N_k = \lambda^{1-k} (c_1(\infty))^k N_k \quad (2.5)$$

Once the solution  $N_k$  of the recursion relation (2.4) is found, the equilibrium solution is known since the parameter  $\xi$  or, equivalently,  $c_1(\infty)$ , is fixed through the total mass per unit volume,<sup>2</sup> i.e.,  $M = 1 = \sum kc_k(\infty)$ .

The second equality in (2.5) also allows us, using the analysis of Cohen and Benedek,<sup>(27)</sup> to identify the fragmentation strength  $\lambda$  as  $\lambda = \exp(\varepsilon/k_B T)$ , where  $\varepsilon$  is the Gibbs free energy of a single chemical bond,  $T$  the absolute temperature and  $k_B$  is Boltzmann's constant. The kinetic theory of irreversible polymerization with  $F_{ij} = 0$  is recovered for  $\varepsilon \rightarrow -\infty$  so that  $\lambda \rightarrow 0$ , corresponding to infinitely strong bonds.

<sup>2</sup> Here it is assumed that all mass is contained in finite polymers (sol particles). Later we discuss the complications arising when a finite fraction of all mass is contained in one infinite cluster (gel).

Finally the fragmentation kernel follows from (2.5) and (2.2) as

$$F_{ij} = \lambda K_{ij} N_i N_j / N_{i+j} \quad (2.6)$$

Thus the kernel  $F_{ij}$  has been expressed in terms of the coagulation kernel  $K_{ij}$  and the factors  $N_k$ .

The quantities  $w_k$  defined by  $w_k$  defined by  $w_k = k! N_k$  have a simple combinatorial interpretation.  $w_k$  represents the number of distinct ways in which a  $k$ -mer can be constructed out of  $k$  monomeric units, assuming that units and functional groups are distinguishable. This can be seen as follows. In terms of  $w_k$  the recursion relation (2.4) takes the following form:

$$(k-1)w_k = \frac{1}{2} \sum_{i+j=k} \binom{k}{i} K_{ij} w_i w_j \quad (w_1 = 1) \quad (2.7)$$

According to the right-hand side of (2.7) one may choose  $i$  units out of  $k$  (distinguishable) units in  $\binom{k}{i}$  different ways in order to build  $i$ - and  $j$ -mers (which may be constructed in  $w_i w_j$  different ways). Since functional groups are distinguishable also, such  $i$ - and  $j$ -mers may be joined in  $K_{ij}$  ways. Finally every  $k$ -mer configuration is formed  $(k-1)$  times, since each of its  $(k-1)$  bonds joins some combination of an  $i$  and a  $j$  cluster and each of these  $(k-1)$  combinations has been counted as distinct. A similar interpretation of the recursion relation (2.7) has been given by Spouge.<sup>(28)</sup> The recursion relation (2.7) reflects the two basic assumptions of FS theory, since it is assumed that clusters are acyclic, and that every combination of two functional groups in the system is equally probable, requiring distinguishability of all functional groups in the system.

There is also a combinatorial interpretation of  $F_{ij}$  in Eq. (2.6). This equation states that the number of distinct ways for  $k$ -mers to break up into  $i$ - and  $j$ -mers ( $F_{ij} w_{i+j} / \lambda$ ) equals the number of bonds between an  $i$  and a  $j$  cluster in  $k$ -mer configurations ( $\binom{k}{i} K_{ij} w_i w_j$ ). Thus one finds that the combination of the normalization and detailed balance conditions (2.1–2.2) imposes on  $F_{ij}$  the requirement that all fragmentation processes  $a_k \rightarrow a_i + a_j$  occur at a rate proportional to the numbers of possible bonds. The constant of proportionality equals  $\lambda = \exp(\varepsilon/k_B T)$  in all cases.

The interpretation of  $F_{ij}$  also shows that the expression (2.6) for the fragmentation kernel is valid only when at every instant and for every polymer length the polymers are uniformly distributed over the various configurations. For systems starting from the monodisperse distribution this condition is satisfied since in this case the bonding process may be thought of as random. The complications arising for systems starting from more general initial conditions will be discussed in Section 6.

### 3. PREGELATION SOLUTIONS

In this section we construct the time-dependent size distribution before a possible gelation transition occurs and show that the solutions obtained in this way satisfy the kinetic equation (1.1) with the appropriate coagulation and fragmentation coefficients.

The method of finding time dependent size distributions is an extension of the probabilistic method used by Ziff for irreversible polymerization.<sup>(4)</sup>

We first consider Flory's  $RA_f$  model and construct the size distribution  $c_k(\alpha)$  for a given extent of reaction  $\alpha$ . Since  $\alpha$  represents the fraction of reacted  $A$  groups, it equals the probability that an  $A$  group, selected at random, has reacted. The size distribution is therefore given as

$$\begin{aligned} c_k(\alpha) &= N_k A(\alpha) (\xi(\alpha))^k \\ &= (w_k/k!) (\alpha/f)^{k-1} (1-\alpha)^{\sigma_k(f)} \end{aligned} \quad (3.1)$$

where  $\sigma_k$  is the number of unreacted  $A$  groups on a  $k$ -mer with  $\sigma_k(f)$  defined in (1.9). This may be seen as follows: The probability that a unit selected at random is contained in a  $k$ -mer equals  $kc_k(\alpha)$ , on account of our choice of the unit of volume (1.2–1.3). On the other hand it equals the probability for a specific  $k$ -mer configuration,  $(\alpha/f)^{k-1}(1-\alpha)^{\sigma_k}/k!$ , multiplied by  $kw_k$ , which is the number of distinct ways for choosing a unit in some specific configuration. Here  $(\alpha/f)^{k-1}$  gives the probability that  $(k-1)$   $A$  groups have reacted with a particular group out of the  $f$   $A$ 's on another unit, and  $(1-\alpha)^{\sigma_k}$  is the probability for  $\sigma_k$  unreacted  $A$  groups. Finally  $1/k!$  gives the probability that a configuration corresponds to a particular permutation of the  $k$  (distinguishable) units. The size distribution (3.1) is identical to the well-known Flory–Stockmayer (FS) distribution<sup>(1,2)</sup> for the  $RA_f$  model. The size distribution (3.1) has been constructed to satisfy the constraints (1.3).<sup>3</sup> The definition of  $\alpha$  implies

$$\alpha = \sum_k 2(k-1)c_k / \sum_k fkc_k = (2/f)(1-\mu) \quad (3.2)$$

Next we determine the time dependence of  $\alpha(t)$ , where  $\alpha(t)$  can be obtained from the macroscopic rate equation for the concentration of free  $A$  groups. As the total concentration of units equals unity ( $M=1$ ), we have for the total concentration of  $A$  groups,  $[A]=f$ , and for the concentration of reacted and free  $A$ 's respectively  $[A^R]=f\alpha$  and  $[A^F]=f(1-\alpha)$ . The

<sup>3</sup> The constraint  $\sum_k kc_k = M$  can only be satisfied as long as  $\alpha$  is smaller than some critical value, as we shall see below.



assumption of equal *a priori* reactivities of all  $A$  groups implies the rate equation

$$\frac{d}{dt} [A^R] = [A^F]^2 - \lambda [A^R] \quad (3.3)$$

where  $\lambda$  is the ratio of the rate constants of formation (coagulation) and breakage (fragmentation) of  $A-A$  bonds, which have concentration  $\frac{1}{2}[A^R]$ . We recall that the rate constant for formation of  $A-A$  bonds was set equal to unity by choosing appropriate units of time. By Arrhenius' law<sup>(29)</sup> the ratio  $\lambda$  of rate constants equals the Boltzmann factor  $\lambda = \exp(\varepsilon/k_B T)$ , where  $\varepsilon$  is the Gibb's free energy of a single  $A-A$  bond.

The rate equation (3.3) in terms of  $\alpha(t)$  reads

$$\dot{\alpha} = f(1 - \alpha)^2 - \lambda\alpha \quad (3.4)$$

to be solved subject to the initial condition  $\alpha(0) = 0$ . This corresponds to the monodisperse initial condition  $c_k(\alpha(0)) = \delta_{k1}$ , as can be verified from (3.1). Its solution reads

$$\alpha(t) = \alpha_0(1 - e^{-\Delta t}) / (1 - \alpha_0^2 e^{-\Delta t}) \quad (3.5)$$

where  $\alpha_0 = \alpha(\infty)$  is the stationary solution of (3.4):

$$\alpha_0 = [2f + \lambda - \Delta] / 2f \quad (3.6a)$$

with

$$\Delta = [\lambda^2 + 4f\lambda]^{1/2} \quad (3.6b)$$

In the absence of fragmentation ( $\lambda = 0$ )  $\alpha(t)$  in (3.5) reduces to  $\alpha(t) = ft / (1 + ft)$  with  $\alpha(\infty) = \alpha_0 = 1$ . Thus, only trivial equilibrium solutions  $c_k(\alpha(\infty))$  are found, in which the size distribution is vanishing for any finite  $k$  value. As soon as fragmentation occurs,  $\alpha_0 = \alpha(\infty)$  stays smaller than unity and the size distribution approaches  $c_k(\alpha_0)$ , which are the most probable FS solutions for the  $RA_f$  model at the prescribed extent of reaction  $\alpha_0$ .

After the construction of a time-dependent size distribution  $c_k(\alpha(t))$  with  $c_k(\alpha(0)) = \delta_{k1}$ , it remains to be shown that  $c_k(\alpha(t))$  is indeed a solution of the nonlinear kinetic equation (1.1) with the appropriate coagulation and fragmentation rate constants. This is done in Appendix A. It is of interest to note the proportionality between fragmentation and coagulation terms, i.e.,  $F_{ij}c_{i+j} = (\lambda/A)K_{ij}c_i c_j$ , which is a direct consequence of (2.6) and (3.1). It states that the rate of  $k$ -mer break-up into  $i$ - and  $j$ -mers ( $F_{ij}c_{i+j}$ ) is propor-

tional to the concentration  $b_{ij}$  of bonds between  $i$  and  $j$  clusters, which is given by

$$\begin{aligned} b_{ij} &= K_{ij} N_i N_j A(\alpha) (\xi(\alpha))^k \\ &= N_i (\xi(\alpha))^i \sigma_i(f) [A_j^F] \end{aligned} \quad (3.7)$$

Here we have introduced the concentration of free  $A$  groups on  $j$  mers, which is given by  $[A_j^F] = \sigma_j(f) c_j$ . The validity of (3.7) can be demonstrated easily, since  $\binom{k}{i} K_{ij} w_i w_j$  gives the number of distinct ways of forming a bond between an  $i$  and  $j$  cluster, and  $A(\alpha) (\xi(\alpha))^k / k!$  equals the probability for a specific  $k$ -mer configuration.

Before closing this section we derive the equation of motion for the zeroth moment  $\mu = \sum c_k$  in the  $RA_f$  model. By summing Eq. (1.1) over  $k$  and using (1.8) and (2.1) we obtain

$$\begin{aligned} \dot{\mu} &= -\frac{1}{2} \sum_{i,j} [K_{ij} c_i c_j - F_{ij} c_{i+j}] \\ &= -\frac{1}{2} (f - 2 + 2\mu)^2 + \lambda(1 - \mu) \end{aligned} \quad (3.8)$$

This moment equation is identical to the macroscopic rate equation (3.4) on account of (3.2). In a similar way one obtains the moment equation  $\dot{M} = 0$  for the total mass  $M = \sum k c_k$ . This conservation law is, however, only valid as long as no gelation occurs, as will be discussed in the next section. The equations of motion for the higher moments,  $\sum k^n c_k$ , in the presence of fragmentation processes cannot be expressed in terms of moments only.

#### 4. GELATION TRANSITION

We first investigate the time development of the size distribution in the  $RA_f$  model. An important point to note is that  $c_k(\alpha)$  in (3.1) reaches a maximum at  $\hat{\alpha}_k = (k - 1) / [(f - 1)k + 1]$ . The quantity  $\hat{\alpha}_k$  increases monotonically with  $k$  to the limiting value  $\alpha_c$  (critical extent of reaction):

$$\hat{\alpha}_\infty = 1 / (f - 1) = \alpha_c \quad (4.1)$$

as already shown by Flory.<sup>(1)</sup>

In the  $RA_2$  model  $\alpha_c = 1$ , in the  $RA_f$  model with  $f > 2$  the critical value  $\alpha_c < 1$ , and  $\alpha(t)$  may exceed  $\alpha_c$ . As soon as  $\alpha(t) > \alpha_c$ , all concentrations  $c_k(\alpha(t))$  have passed their maximum, and keep decreasing as time progresses, since  $\alpha(t)$  is an increasing function of time. The sol mass  $M(\alpha) = \sum k c_k$  can no longer be conserved, and must be decreasing. At the critical extent of

reaction  $\alpha_c$  a gelation transition occurs; or, equivalently, gelation occurs at the critical time  $t_c$ , determined by the relation  $\alpha(t_c) = \alpha_c$ . It can be calculated from (3.5) as

$$t_c = \Delta^{-1} \log[\alpha_0(1 - \alpha_0\alpha_c)/(\alpha_0 - \alpha_c)] \tag{4.2}$$

However,  $t_c$  does not necessarily exist, since the equation  $\alpha(t_c) = \alpha_c$  only has a real solution if  $\alpha_c < \alpha_0$ , as illustrated in Fig. 1. This condition yields the following restriction on the fragmentation strength for  $t_c$  to be real:

$$\lambda < \lambda_{\max} = f(f - 2)^2/(f - 1) \tag{4.3}$$

For strong bonds ( $\lambda$  small) gelation always occurs, as is the case in irreversible polymerization. However, if  $\lambda \geq \lambda_{\max}$ , i.e., if the Boltzmann factor  $\lambda = \exp(\epsilon/k_B T)$  becomes too large, the gelation transition is completely suppressed and  $M(\alpha)$  is conserved for all times. Only those  $c_k(\alpha)$  will pass through a maximum, for which  $\hat{\alpha}_k < \alpha_0$ . For larger  $k$  values the size distribution is monotonically increasing for all times. If  $\lambda$  becomes very large,  $\alpha_0$  becomes very small, and hardly any clustering occurs.

It is instructive to calculate the rate of change of the total mass,  $\dot{M} = \sum k \dot{c}_k = \dot{\alpha} \sum k dc_k/d\alpha$ . As long as  $t < t_c$  or  $\alpha < \alpha_c$ , the first constraint in (1.3) can always be satisfied and  $\dot{M} = 0$ . Thus  $M = \sum kc_k = 1$  is conserved for  $t < t_c$ . However, at  $\alpha_c = \hat{\alpha}_\infty$  the ratio  $(c_k^{-1} dc_k/d\alpha)_{\alpha_c}$  becomes independent

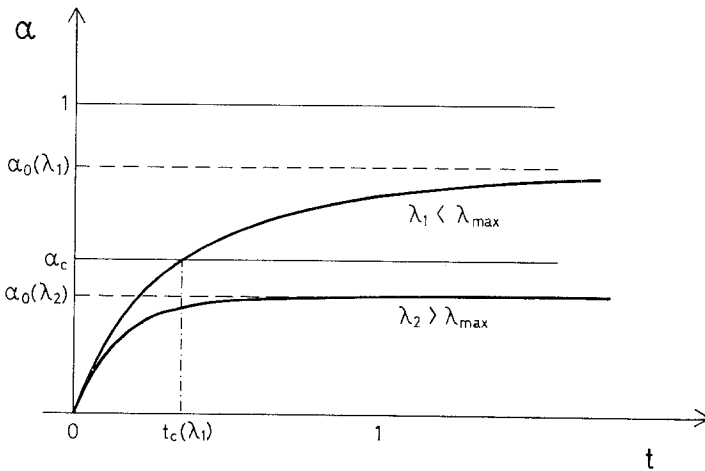


Fig. 1. The extent of reaction  $\alpha$  in the  $RA_f$  model (here we have chosen  $f = 3$ ) as a function of time for different values of the fragmentation strength  $\lambda$ . The asymptotic value  $\alpha_0(\lambda)$  may or may not exceed the critical extent of reaction  $\alpha_c = 1/(f - 1)$ , depending on the value of  $\lambda$ .

of  $k$ , since at the gel point  $(d\xi/d\alpha)_{\alpha_c} = 0$ . Thus, one finds a nonvanishing mass loss rate at  $\alpha_c$ :

$$\begin{aligned} \dot{M}(\alpha_c) &= \sum_k k \dot{c}_k(\alpha_c) \\ &= - \left[ \frac{(1+\alpha)\dot{\alpha}}{(1-\alpha)\alpha} \right]_{\alpha_c} = - \left[ \frac{f(f-1)}{f-2} \right] \dot{\alpha}(t_c) \end{aligned} \quad (4.4)$$

This result is interpreted as the formation of an infinite cluster (gel). At the gel point a cascading growth process occurs by which finite size clusters (sol particles) are being lost to the gel. This infinite cluster contains a finite fraction  $G(\alpha)$  of the total mass in the system, with

$$M(\alpha) + G(\alpha) = 1 \quad (4.5)$$

since, obviously, units must be contained either in the sol or in the gel.

The conservation of total mass or total number of units,  $M$ , for  $t < t_c$  follows immediately from the *kinetic equation* after multiplying (1.1) with  $k$ , summing over  $k$  and interchanging the order of summations. At  $t = t_c$ , however, this interchange is no longer allowed, since the sums do not converge uniformly. Consider, therefore, the flux  $\dot{M}^{(L)}(t)$  of smaller polymers with size  $k \leq L$  toward larger polymers with size  $k > L$ , where  $M^{(L)}(t) = \sum_{k=1}^L k c_k(t)$ . The kinetic equation (1.1) yields then

$$\dot{M}^{(L)}(t) = - \sum_{i=1}^L \sum_{j=L-i+1}^{\infty} i \{K_{ij} c_i c_j - F_{ij} c_{i+j}\} \quad (4.6)$$

Since the  $F$  term is proportional to the  $K$  term for monodisperse initial conditions i.e.,  $F_{ij} c_i c_j = (\lambda/A) K_{ij} c_i c_j$ , we shall restrict our discussion to the  $K$  term.

We are interested in the limit of  $\dot{M}^{(L)}(t_c)$  as  $L \rightarrow \infty$ , which is determined by the large- $k$  behavior of  $c_k$ . As long as  $t < t_c$ , or  $\xi(\alpha) < \xi(\alpha_c) = \xi_c$ , the size distribution is exponentially decreasing [see (3.1), with  $N_k$  given by (1.5)] and the limit vanishes, indicating conservation of total number of units contained in the sol. However, at  $t_c$  and in general: at the critical fugacity, the size distribution  $c_k(\alpha_c)$  decreases algebraically as  $k^{-5/2}$  ( $k \rightarrow \infty$ ),<sup>(27,30,31)</sup> and one easily verifies that  $\dot{M}^{(L)}(t_c)$  has a *nonvanishing* negative limit as  $L \rightarrow \infty$ , in agreement with the result derived in (4.4).

## 5. POSTGELATION SOLUTIONS

In classical gelation theory there exist various models of a gel. The two most prominent ones have been proposed by Flory and by Stockmayer. The

time dependence of the size distribution in the postgel stage will also differ with the model considered.

In Flory's interpretation all reactive groups, whether located on a sol particle or on the gel remain equally reactive. Since there is a finite fraction of all reactive groups on the gel, there is a finite probability for bonding of two such groups, leading to cyclic structures.

In the kinetic interpretation of Stockmayer's (equilibrium) model we assume that sol-gel interactions are completely absent. Consequently, the gel fraction is increased only by the cascading of sol particles to the gel, requiring (see Section 4) the validity of the relation  $\xi(t) = \xi_c$  for all  $t \geq t_c$ . This is the condition originally proposed by Stockmayer.

We first discuss the time dependence of the postgel solutions in Stockmayer's picture. Since the fugacity has the fixed value  $\xi_c$ , the relative size distribution above the gel point has the same value as at the point of gelation, i.e.,

$$c_k(t) = A(t) N_k \xi_c^k = M(t) c_k(t_c) \quad (5.1)$$

where  $M(t) = 1 - G(t) = \sum k c_k(t)$  is the fraction of monomers contained in the sol. The time dependence of  $M(t)$  in (5.1) remains to be determined. This can be done from the macroscopic rate equation for the concentration of clusters in the sol,  $\mu(t) = \sum c_k(t)$ . Since we assume total absence of sol-gel interactions  $\mu$  can only change through reactions in the sol. This yields for the rate of change in the concentration of clusters:

$$\dot{\mu} = -\frac{1}{2}[A_s^F]^2 + \frac{1}{2}\lambda[A_s^R] \quad (5.2)$$

The first term on the right-hand side accounts for coagulation processes, the second for fragmentation processes. The infinite clusters cascading from the sol to the gel have zero number concentration at all times, and do not contribute to  $\dot{\mu}$ .

All concentrations in (5.2) depend on time only through  $M(t)$  on account of (5.1), i.e.,

$$\begin{aligned} \mu &= \mu_c M \\ [A_s^F] &= f(1 - \alpha_c)M \\ [A_s^R] &= f\alpha_c M \end{aligned} \quad (5.3)$$

where  $\alpha_c = 1/(f-1)$  and  $\mu_c = 1 - \frac{1}{2}f\alpha_c$  are the values of the extent of reaction and concentration of clusters at the gel point. The resulting equation for the sol mass follows from (5.2) and (5.3) as

$$\dot{M} = a\lambda M - bM^2 \quad (5.4)$$

where

$$\begin{aligned} a &= f\alpha_c/2\mu_c = f/(f-2) \\ b &= f^2(1-\alpha_c)/2\mu_c = f^2(f-2)/(f-1) \end{aligned} \quad (5.5)$$

The solution of interest obeys the initial condition  $M(t_c) = 1$  and reads

$$M(t) = \left\{ \frac{b}{\lambda a} + \left( 1 - \frac{b}{\lambda a} \right) \exp[-\lambda a(t - t_c)] \right\}^{-1} \quad (5.6)$$

with  $t_c$  given in (4.2).

Equations (5.1) and (5.6) represent the time-dependent postgel size distribution  $c_k(t)$ , based on Stockmayer's picture of the postgel stage. One can verify by direct substitution that the size distribution  $c_k(t)$  in (5.1) is an exact solution of the kinetic equation (1.1) in the  $RA_f$  model with the appropriate rate constants of coagulation (1.8) and fragmentation (2.6). Furthermore the pregel distribution (3.1) with (3.4) and the postgel distribution (5.1) with (5.4) determine a function which is continuously differentiable at  $t_c$ . It is, therefore, the global solution of the kinetic equation corresponding to monodisperse initial conditions.

In case the chemical bonds are very strong ( $\lambda = 0$ ), the size distribution given by (5.1) and (5.6) reduces to the solution of the  $RA_f$  model for irreversible coagulation, as given in Ref. 15, i.e.,

$$c_k(t) = c_k(t_c)/[1 + b(t - t_c)] \quad (5.7)$$

where  $t_c = 1/[f(f-2)]$  on account of (4.2) and (3.6) for  $\lambda = 0$ .

Finally we remark that the model presented here is in essence, but not in detail, identical to the model originally proposed by Stockmayer. In the original equilibrium model it is assumed that the gel is acyclic and that the fugacity remains fixed at its critical value  $\xi_c$  beyond the gel point.

However, in the special case of absence of sol-gel interactions anything may be assumed concerning intramolecular reactions in the gel, and Stockmayer's additional requirement of an acyclic gel appears to be irrelevant in this case.

The last part of this section is devoted to *Flory's picture of the gel*, and the construction of the time dependent postgel size distribution and the corresponding kinetic equation.

In Flory's picture the bonding process is also random in the presence of a gel. Thus the extent of reaction  $\alpha$  retains the interpretation of the probability for an  $A$  group to be bonded. Therefore, the size distribution  $c_k(\alpha)$  of the finite size clusters is for  $\alpha > \alpha_c$  still given by the same expressions (3.1) and (3.5-3.6) as for  $\alpha \leq \alpha_c$ . The total fraction of units

contained in the sol,  $\sum kc_k(\alpha) = M(\alpha)$ , is smaller than unity. Since there is a finite fraction  $G(\alpha) = 1 - M(\alpha)$  of all units in the gel, there is also a finite probability for any free group in the gel to react with some other free group in the gel, thus giving rise to cyclic structures.

Thus we have constructed the time-dependent size distribution  $c_k(\alpha(t))$  in the postgel stage, based on Flory's interpretation of the gel. It differs from (5.1) with  $M(t)$  in (5.6), and is therefore not a solution of the kinetic equation (1.1). Does there exist a kinetic equation to which  $c_k(\alpha(t))$  in (3.1) is a solution? To answer this question we insert  $c_k(\alpha(t))$  in (1.1) and correct for the mismatch. For the  $RA_f$  model this leads to the following kinetic equation:

$$\dot{c}_k = \frac{1}{2} \sum_{i+j=k} [K_{ij}c_i c_j - F_{ij}c_{i+j}] - \sum_{j=1}^{\infty} [K_{kj}c_k c_j - F_{kj}c_{k+j}] - \sigma_k c_k [A_g^f] + \lambda \sigma_k N_k (\zeta(\alpha))^k [A_g^f] \quad (5.8)$$

The calculations are very similar to those given in Appendix A, and will not be repeated here. The additional terms on the second line of (5.8) represent, respectively, the loss of  $k$  clusters due to bonding with the gel and the gain of  $k$  clusters through break-up of the gel. The additional loss term has an obvious probabilistic interpretation in terms of rate equations. The additional gain term represents the concentration of bonds  $b_{k\infty}$  in the gel between an infinite cluster and a cluster of size  $k$ , as may be seen by comparison with (3.7), in which  $[A_f^f]$  is replaced by  $[A_g^f]$ . Therefore the fragmentation process in the gel takes place at a rate proportional to the corresponding concentration of bonds also.

## 6. DISCUSSION

In this paper we have constructed a kinetic theory of polymerization, which incorporates both bonding and break-up, to describe the time evolution of the cluster size distribution  $c_k$  in a polymerizing system, starting from monodisperse initial conditions,  $c_k(0) = \delta_{k1}$ . It can, therefore, describe a nontrivial equilibrium state. The resulting size distribution, obtained here, is the same as in the equilibrium theory of Flory and Stockmayer. Thus we have embedded the classical equilibrium theory of polymerization and gelation into a kinetic theory.

The  $RA_f$  model with  $f > 2$  and the  $A_f RB_g$  model with  $f > 1$  and  $g > 1$  (treated in Appendix B) may show a gelation transition depending on the magnitude of  $\lambda = \exp(\epsilon/k_b T)$ , where  $\lambda \equiv K_f/K_k$  is the ratio of the rate constants for a single fragmentation and coagulation reaction, and  $\epsilon$  represents the (Gibbs' free) energy of a single chemical bond. If  $\lambda$  is larger

than some  $\lambda_{\max}$ , calculated in (4.3), (weak bonds), gelation is suppressed. For  $\lambda < \lambda_{\max}$  (strong bonds) gelation occurs. For  $\lambda \rightarrow 0$  or  $\varepsilon \rightarrow -\infty$  one has the theory of irreversible polymerization, described by Smoluchowski's equation.<sup>(2,4)</sup>

We make some further comments. The solutions obtained here are valid for monodisperse initial conditions. In the case of more general initial conditions the fragmentation rate  $F_{ij}$  depends upon the distribution of  $k$ -mers over the various  $k$ -mer configurations ( $k = i + j$ ). As a consequence the kinetic equation (1.1) with the rate constants  $K_{ij}$  and  $F_{ij} = \lambda K_{ij} N_i N_j / N_{i+j}$  need not give an appropriate description of the process of reversible polymerization in general. Instead a microscopic rate equation should be constructed in terms of the concentrations  $c_{k\rho}$ , where  $\rho$  labels the various isomeric configurations of clusters of size  $k$ , involving rate constants  $K_{i\mu j\nu}^\rho$  and  $F_{i\mu j\nu}^\rho$  for the formation of a  $(k, \rho)$ -mer out of an  $(i, \mu)$ -mer and a  $(j, \nu)$ -mer, and the break-up of a  $(k, \rho)$ -mer, respectively. The average fragmentation rate is then given by

$$F_{ij}(t) = \left( \sum_{\mu, \nu, \rho} F_{i\mu j\nu}^\rho c_{k\rho} \right) / \sum_{\rho} c_{k\rho} \quad (6.1)$$

while the average coagulation rate  $K_{ij}$  retains its time-independent combinatoric value at all times. In the large-time limit detailed balance should hold:

$$F_{i\mu j\nu}^\rho c_{k\rho}(\infty) = K_{i\mu j\nu}^\rho c_{i\mu}(\infty) c_{j\nu}(\infty) \quad (6.2)$$

implying that eventually  $F_{ij}(t)$  assumes the equilibrium value  $\lambda K_{ij} N_i N_j / N_{i+j}$ .

As an example consider systems  $S_1$  and  $S_2$  initially consisting of only linear and only branched tetramers, respectively, as shown in Fig. 2. Both  $S_1$  and  $S_2$  cannot be reached from the monodisperse distribution and the *short-time behavior* of the rate of tetramer break-up into dimers in either systems,  $F_{22}(t) c_4(t)$ , is very different. Dimers may be produced directly from the linear tetramer chains, implying that the fragmentation rate  $F_{22}(t)$  in the system  $S_1$  remains finite as  $t \downarrow 0$ . On the other hand dimers are not among the fragmentation product of the branched tetramers, and the dominant processes of dimer production from tetramers in the system  $S_2$  for  $t \downarrow 0$  are symbolized in Fig. 2. It is readily verified that these processes yield a contribution to  $F_{22}(t)$  of the order of  $t^3$  as  $t \downarrow 0$ . In both systems  $F_{22}(t)$  will approach the value predicted by equilibrium theory in the limit of *large times*.

In our kinetic interpretation of the classical polymerization models of Flory and Stockmayer, we have paid special attention to the cluster size distribution in the post gelation stage, where the results of Flory differ from



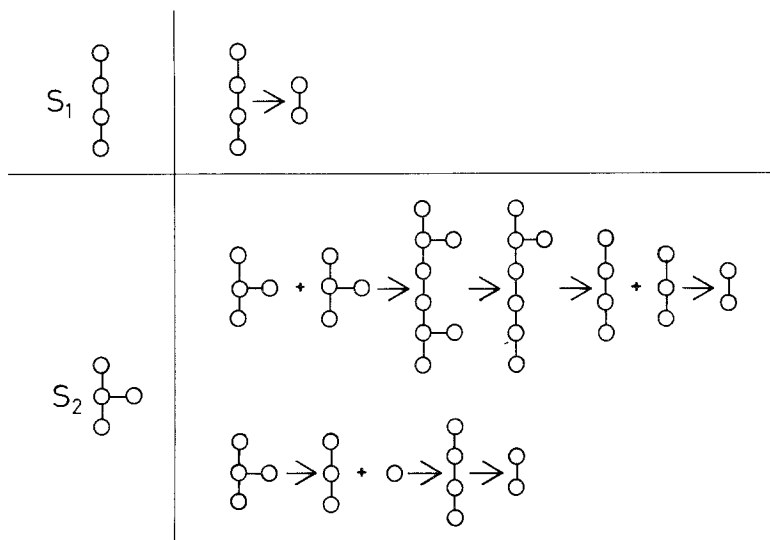


Fig. 2. The dominant processes of dimer production out of tetramers for short times ( $t \downarrow 0$ ) in the systems  $S_1$  (only linear tetramers initially) and  $S_2$  (only branched tetramers initially).

Stockmayer's.<sup>(2)</sup> Other postgel models, corresponding to different sol-gel or gel-gel interactions, may readily be constructed. Ziff<sup>(4)</sup> and Ziff and Stell<sup>(32)</sup> have suggested a model that allows sol-gel reactions, as does the Flory model, but where the gel may not cross-link. Other models are obtained by assuming weaker, or stronger, sol-gel interaction, or cross-links in the gel. A computer experiment in which the random bonding process of  $RA_f$  units is simulated has been carried out by Falk and Thomas.<sup>(33)</sup> In their "rings allowed" model all possible bonds are allowed and have equal probability of being formed. In their "rings forbidden" model all possible bonds are allowed save those, which lead to cross-links, so that all clusters are strictly acyclic. Falk and Thomas show that the "rings allowed" model and Flory's model for the pre and postgel stage are identical, as they should, since both models are based on the equireactivity principle. Similarly, the "rings forbidden" model should correspond to the model III of Ziff and Stell, since both models have the same basic assumptions. We have evidence, based on the exact solution for model III, that both models are indeed identical.

Various types of clustering processes involve two different types of bonds, with two different bond energies. For instance, the aggregation process of red blood cells, called rouleau formation<sup>(34-36)</sup> involves an elongation reaction with bond energy  $\epsilon_e$  and (less frequently) a branching reaction with bond energy  $\epsilon_b$  ( $\epsilon_e < \epsilon_b < 0$ ). We have also applied the present theory to such more complicated cases of reversible aggregation.<sup>(37)</sup>

Finally some comments on critical exponents, that describe the cluster size distribution in the vicinity of the gel point; i.e., in the scaling limit  $k \rightarrow \infty$  and  $t \rightarrow t_c$  with  $k^\sigma |t - t_c| = \text{const}$ , one may represent  $c_k(t)$  as

$$c_k(t) \sim k^{-\tau} \Phi(k |t - t_c|^{1/\sigma}) \quad (6.3)$$

In the classical Flory–Stockmayer theory, and therefore also in the present kinetic theory, the critical exponents  $\tau$  and  $\sigma$  have the typical mean field values  $\tau = 5/2$  and  $\sigma = 1/2$ .<sup>(30)</sup>

In recent years<sup>(38,39)</sup> Smoluchowski's coagulation equation has been modeled to account for surface interactions through the coagulation kernel  $K_{ij} \sim (ij)^\omega$  with  $\omega = 1 - 1/d$ , where  $d$  represents the space dimensionality of the system, and it was found that  $\tau = \omega + 3/2$  and  $\sigma = \omega - 1/2$ . It is of interest to know whether fragmentation affects this results. A fragmentation kernel modeling surface interactions may be constructed as follows. Assuming that only those bonds are breakable which are at the surface, we choose instead of (2.1) a normalization of  $F_{ij}$  proportional to  $(k^\omega - 1)$ . The detailed balance condition then leads to a fragmentation kernel of the form  $F_{ij} = \lambda (ij)^\omega N_i N_j / N_{i+j}$ , where now  $N_k$  is the solution of (2.4) with  $(k - 1)$  replaced by  $(k^\omega - 1)$ . We have repeated the calculations of<sup>(38,39)</sup> with fragmentation terms added to the kinetic equation, and we find that the same critical exponents apply for  $\lambda > 0$  as in the case of pure coagulation ( $\lambda = 0$ ). The scaling function  $\Phi(x)$ , however, becomes explicitly dependent on the fragmentation strength  $\lambda$ . Moreover we find that for sufficiently large values of the fragmentation strength gelation is suppressed. The detailed calculations leading to these results will be published elsewhere.

## APPENDIX A

In this appendix we show that the size distribution  $c_k(\alpha(t))$ , given in (3.1) and (3.2) for the  $RA_f$  and the  $A_fRB_g$  models, respectively, is indeed a solution of the kinetic equation (1.1) with the appropriate coagulation and fragmentation coefficients. We present arguments only for the  $RA_f$  model. In the case of the  $A_fRB_g$  model the discussion is very similar.

Consider first the left-hand side (LHS) of (1.1), which yields through (3.1)

$$\begin{aligned} \text{LHS (1.1)} &= \dot{\alpha}(dc_k/d\alpha) \\ &= \dot{\alpha}c_k \left( \frac{k-1}{\alpha} - \frac{\sigma_k(f)}{1-\alpha} \right) \end{aligned} \quad (\text{A1})$$

The rate constant  $K_{ij}$  and  $F_{ij}$  in the right-hand side (RHS) of (1.1) are given in (1.8) and (2.6). The fragmentation terms are proportional to the

coagulation terms on account of (2.6) and (3.1), i.e.,  $F_{ij}c_{i+j} = (\lambda/A)K_{ij}c_i c_j$ . Thus

$$\begin{aligned} \text{RHS (1.1)} &= [f(1-\alpha)^2/(\lambda\alpha) - 1] \frac{1}{2} \sum_{i+j=k} F_{ij}c_{i+j} \\ &\quad - \{1 - \lambda\alpha/[f(1-\alpha)^2]\} c_k \sum_{j=1}^{\infty} K_{kj}c_j \end{aligned} \quad (\text{A2})$$

The sum involving  $F_{ij}$  is given in (2.1); the factor in front of it equals  $\dot{\alpha}/(\lambda\alpha)$  on account of (3.4). The sum involving  $K_{kj}$  follows from (1.8) to be

$$\sum K_{kj}c_j = \sigma_k(f)[A^F] = f(1-\alpha)\sigma_k(f) \quad (\text{A3})$$

The factor in front of this sum in (A2) equals  $\dot{\alpha}/[f(1-\alpha)^2]$ . Inserting these results into (A2) demonstrates the equality of (A1) and (A2). Thus,  $c_k(\alpha(t))$  as given in (3.1) is the solution of the kinetic equation (1.1) for the  $RA_f$  model with monodisperse initial conditions. The complications arising when a gelation phase transition occurs are discussed in Section 5 for the  $RA_f$  model and at the end of Appendix B for Flory's model  $A_fRB_g$ .

## APPENDIX B

In this appendix we discuss the time-dependent behavior of the size distribution in Flory's polymerization model  $A_fRB_g$  before, at and beyond the gel point.

### The Pregel Stage

Let the extents of reaction of the  $A$  and the  $B$  groups be denoted by  $\alpha$  and  $\beta$ , respectively. In the  $A_fRB_g$  model units carry  $f$   $A$  groups and  $g$   $B$  groups, so that

$$f\alpha = g\beta = \sum_{k=1}^{\infty} (k-1)c_k = 1 - \mu \quad (\text{B1})$$

The size distribution takes the form

$$\begin{aligned} c_k(\alpha) &= N_k A(\alpha) \xi(\alpha)^k \\ &= N_k (\alpha/g)^{k-1} (1-\alpha)^{s_k(f)} (1-\beta)^{s_k(g)} \end{aligned} \quad (\text{B2})$$

where  $s_k(f)$  and  $s_k(g)$  represent the numbers of unreacted  $A$  and  $B$  groups, respectively, with  $s_k(f)$  given in (1.7). Here  $\alpha/g$  ( $=\beta/f$ ) is the probability

that an  $A$  group (or  $B$  group) is connected to a particular  $B$  group (or  $A$  group) out of a total of  $g$   $B$  groups (or  $f$   $A$  groups) on another unit. The interpretation of the remaining factors is analogous to that given below (3.1).

The time dependence of  $\alpha(t)$  is determined from the macroscopic rate equations. Let  $[A^R] = f\alpha = g\beta = [B^R]$  (which also gives the concentration of  $A$ - $B$  bonds), and  $[A^F] = f(1 - \alpha)$  and  $[B^F] = g(1 - \beta)$ , then one has

$$\frac{d}{dt} [A^R] = [A^F][B^F] - \lambda[A^R] \quad (\text{B3a})$$

and hence

$$\dot{\alpha} = g(1 - \beta)(1 - \alpha) - \lambda\alpha \quad (\text{B3b})$$

to be solved with  $\alpha(0) = \beta(0) = 0$ . This corresponds to monodisperse initial conditions, as can be seen from (B2). The Boltzmann factor  $\lambda = \exp(\varepsilon/k_B T)$  refers to the Gibbs' free energy  $\varepsilon$  of a single  $A$ - $B$  bond. The solution to Eq. (B3b) with  $\alpha(0) = 0$  reads

$$\alpha(t) = \alpha_0(1 - e^{-\Delta t}) / (1 - \alpha_0\beta_0 e^{-\Delta t}) \quad (\text{B4})$$

where  $\alpha_0$  and  $\beta_0$  with  $f\alpha_0 = g\beta_0$  are the stationary solutions of (B3b), i.e.,

$$\alpha_0 = (f + g + \lambda - \Delta) / 2f \quad (\text{B5a})$$

with

$$\Delta = [(f + g + \lambda)^2 - 4fg]^{1/2} \quad (\text{B5b})$$

Without fragmentation ( $\lambda = 0$ ), the quantity  $\Delta = |f - g|$ , so that for  $f > g$  it is found that  $\alpha_0 = g/f$  and  $\beta_0 = 1$ , indicating that all  $B$  groups have reacted. Analogous results are found for  $f < g$ . Absence of fragmentation leads again to a trivial stationary size distribution  $c_k(\alpha_0)$ , vanishing for any finite  $k$  value.

### The Gelation Transition

The behavior of the  $A_fRB_g$  model at the gel point is completely analogous to that found in the  $RA_f$  model. The size distribution  $c_k(\alpha)$  in (B2) reaches a maximum at  $\alpha = \hat{\alpha}_k$  where  $dc_k(\alpha)/d\alpha = 0$ . The limiting value  $\hat{\alpha}_\infty$  of the  $\hat{\alpha}_k$  determines again the critical extent of reaction  $\alpha_c$ :

$$\hat{\alpha}_\infty = g(f + g - 1)^{-1} \{1 - [(f - 1)(g - 1)/fg]^{1/2}\} = \alpha_c \quad (\text{B6})$$

with  $f\alpha_c = g\beta_c$ . If  $f = 1$  or  $g = 1$  then either  $\alpha_c = 1$  or  $\beta_c = 1$ , implying that the critical extent of reaction is only reached when all reactive groups of one

type have reacted. This only occurs at  $t = \infty$ , so that no gelation occurs within a finite time. However, if  $f, g > 1$ , then  $\alpha_c < 1$  and  $\beta_c < 1$ . As soon as  $\alpha(t) > \alpha_c$  the sol mass  $M(\alpha) < 1$  and gelation occurs. The critical time  $t_c$  is again determined by the solution of  $\alpha(t_c) = \alpha_c$ , and we obtain from (B4)

$$t_c = \Delta^{-1} \log[\alpha_0(1 - \beta_0\alpha_c)/(\alpha_0 - \alpha_c)] \quad (\text{B7})$$

The critical time  $t_c$  is only real if the stationary value  $\alpha(\infty) = \alpha_0$  in (B5) is larger than  $\alpha_c$ . This yields the following condition on the fragmentation strength for the occurrence of a gelation transition within a finite time:

$$\lambda < \lambda_{\max} = (f + g - 1)^{-1} \{ (f - 1)(g - 1)(f + g) + (f + g - 2)[f(f - 1)g(g - 1)]^{1/2} \} \quad (\text{B8})$$

Thus one sees that the fragmentation effects in the  $A_fRB_g$  model are completely analogous to those found in the  $RA_f$  model. The mass loss rate at the gel point  $t_c$  for the  $A_fRB_g$  model is given by

$$\begin{aligned} \dot{M}(\alpha_c) &= - \left[ \frac{(1 - \alpha\beta)\dot{\alpha}}{(1 - \alpha)(1 - \beta)\alpha} \right]_{\alpha_c} \\ &= -f \{ 1 + [fg/(f - 1)(g - 1)]^{1/2} \} \dot{\alpha}(t_c) \end{aligned} \quad (\text{B9})$$

showing that at  $t_c$  a macroscopic gel phase occurs in the system.

### Postgelation Stage

In Stockmayer's picture of the postgel stage, one finds again (5.1) for the size distribution in the  $A_fRB_g$  model. The concentration of clusters is determined by

$$\dot{\mu} = -[A_s^F][B_s^F] + \lambda[A_s^R] \quad (\text{B10})$$

where  $[B_s^F] = g(1 - \beta_c)M$ , and the remaining concentrations are given in (5.3). Here  $\mu_c = 1 - f\alpha_c$  and  $g\beta_c = f\alpha_c$  can be found in (B6). This leads again to an equation for  $M(t)$  of the form (5.4), where  $a$  and  $b$  are now given by

$$\begin{aligned} a &= f\alpha_c/\mu_c = [fg(f - 1)(g - 1)]^{-1/2} \\ b &= gf(1 - \alpha_c)(1 - \beta_c)/\mu_c \\ &= [fg(f + g - 2) + a^{-1}(f + g)]/(f + g - 1) \end{aligned} \quad (\text{B11})$$

Equations (5.1) and (5.6) represent again the time-dependent postgel size distribution  $c_k(t)$  for the  $A_fRB_g$  model in Stockmayer's picture. One can

again verify that the size distribution (5.1) is an exact solution of the kinetic equation with rate coefficients (1.6) and (2.6).

For irreversible coagulation ( $\lambda = 0$ ) the size distribution reduces again to (5.7) with  $b$  given in (B11), and the critical time  $t_c$  follows from (B7) and (B5–B6) by setting  $\lambda = 0$ , i.e.,

$$t_c = [2(g - f)]^{-1} \log[f(g - 1)/g(f - 1)] \quad (\text{B12})$$

In the special case  $g = f$ , Eq. (B12) reduces to  $t_c = [2f(f - 1)]^{-1}$ .

In Flory's picture of the postgel stage the extent of reaction  $\alpha$  (or  $\beta$ ) retains again the interpretation of the probability that an  $A$  group (or  $B$  group), selected at random, is bonded. As a consequence the size distribution  $c_k(\alpha)$  in Flory's picture has the form (2) in the postgel stage as well, where  $\alpha(t)$  is still given by (B3a,b). In these equations the concentration  $[B^F] = [B_s^F] + [B_g^F]$  represents now the unreacted  $B$  groups in the sol *and* in the gel, and similarly for  $[A^F]$  and  $[A^R]$ .

The derivation of the kinetic equation corresponding to Flory's gel picture for the  $A_fRB_g$  model proceeds along similar lines as that for the  $RA_f$  model. The result is

$$\begin{aligned} \dot{c}_k = & \frac{1}{2} \sum_{i+j=k} (K_{ij}c_i c_j - F_{ij}c_{i+j}) - \sum_{j=1}^{\infty} (K_{kj}c_k c_j - F_{kj}c_{k+j}) \\ & - c_k(s_k(f)[B_g^F] + s_k(g)[A_g^F]) + \lambda N_k(\xi(\alpha))^k (s_k(f)[B_g^F] + s_k(g)[A_g^F]) \end{aligned} \quad (\text{B13})$$

The additional terms on the second line of (B13) represent, respectively, the bonding of  $k$  clusters to the gel, and the formation of  $k$ -mers due to break-up processes in the gel. The additional gain term contains again as a factor the concentration of  $A$ - $B$  bonds between  $k$  clusters and the gel, where  $A$  groups and  $B$  groups on  $k$  clusters, bonded, respectively, to  $B$  and  $A$  groups in the gel, are treated separately. This shows that fragmentation processes in the gel take place at a rate proportional to the corresponding numbers of bonds for the  $A_fRB_g$  model also.

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## REFERENCES

1. P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1953).
2. W. H. Stockmayer, *J. Chem. Phys.* **11**:45 (1943).
3. R. L. Drake, *Topics in Current Aerosol Research*, Vol. 3, Hidy and Brock, eds. (Pergamon Press, New York, 1972), Part 2.
4. R. M. Ziff, *J. Stat. Phys.* **23**:241 (1980).
5. P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1953), Section III.2.
6. T. A. Witten and L. M. Sander, *Phys. Rev. Lett.* **47**:1400 (1981).
7. P. Meakin, *Phys. Rev. A* **27**:604 (1983).
8. M. Muthukumar, *Phys. Rev. Lett.* **50**:839 (1983).
9. L. M. Sander, in *Proceedings of the International Topical Conference on the Kinetics of Aggregation and Gelation, University of Georgia, 1984*, F. Family and D. P. Landau, eds. (North-Holland, Amsterdam, 1984).
10. P. Meakin, *Phys. Rev. Lett.* **51**:1119 (1983).
11. M. Kolb, R. Botet, and R. Jullien, *Phys. Rev. Lett.* **51**:1123 (1983); R. Botet, R. Jullien, and M. Kolb, *J. Phys. A: Math. Gen.* **17**:L75 (1984); R. Botet, R. Jullien, and M. Kolb, *J. Phys. Lett.* **45**:L211 (1984).
12. See many papers in *Proceedings of the International Topical Conference on the Kinetics of Aggregation and Gelation, University of Georgia, 1984*, F. Family and D. P. Landau, eds. (North-Holland, Amsterdam, 1984).
13. J. L. Spouge, *Macromolecules* **16**:5, 831 (1983).
14. P. G. J. van Dongen and M. H. Ernst, *J. Phys. A Math. Gen.* **17**:2281 (1984).
15. E. M. Hendriks and M. H. Ernst, *J. Coll. Interf. Sci.* **97**:176 (1984).
16. B. A. Trubnikov, *Dokl. Sov. Phys.* **16**:124 (1971).
17. P. G. J. van Dongen and M. H. Ernst, *J. Phys. A: Math. Gen.* **16**:L327 (1983).
18. J. L. Spouge, *Macromolecules* **16**:121 (1983).
19. Z. A. Melzak, *Trans. Am. Math. Soc.* **85**:547 (1957).
20. J. L. Spouge, *Math. Proc. Cambridge Philos. Soc.* **96**:351 (1984).
21. P. J. Blatz and A. V. Tobolsky, *J. Phys. Chem.* **49**:77 (1945).
22. M. Aizenmann and T. A. Bak, *Commun. Math. Phys.* **65**:203 (1979).
23. M. H. Ernst, *Studies in Statistical Mechanics*, Vol. X, Montroll and Lebowitz, Eds. (North-Holland, Amsterdam, 1983), Chap. 3.
24. J. D. Barrow, *J. Phys. A: Math. Gen.* **14**:729 (1981).
25. R. C. Srivastava, *J. Atmosph. Sci.* **39**:1317 (1982).
26. C. DeLisi and A. Perelson, *J. Theor. Biol.* **62**:159 (1976); A. Perelson and C. DeLisi, *Math. Biosciences* **48**:71 (1980).
27. R. J. Cohen and G. B. Benedek, *J. Phys. Chem.* **86**:3696 (1982).
28. J. Spouge, *J. Stat. Phys.* **31**:363 (1983).
29. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941), pp. 7 and 8.
30. D. Stauffer, A. Coniglio, and M. Adam, *Advances in Polymer Science*, Vol. 44, K. Dušek, ed. (Springer Verlag, Berlin, 1982).
31. R. M. Ziff, M. H. Ernst, and E. M. Hendriks, *J. Phys. A: Math. Gen.* **16**:2293 (1983).
32. R. M. Ziff and G. Stell, *J. Chem. Phys.* **73**:3492 (1980).
33. M. Falk and R. E. Thomas, *Can. J. Chem.* **52**:3285 (1974).
34. R. W. Samsel and A. S. Perelson, *Biophys. J.* **37**:493 (1982).
35. F. W. Wiegel and A. S. Perelson, *J. Stat. Phys.* **29**:813 (1982).

36. A. S. Perelson, in *Proceedings of the International Topical Conference on the Kinetics of Aggregation and Gelation, University of Georgia, 1984*, F. Family and D. P. Landau, Eds. (North-Holland, Amsterdam, 1984).
37. P. G. J. van Dongen and M. H. Ernst, in *Proceedings of the International Topical Conference on the Kinetics of Aggregation and Gelation, University of Georgia, 1984*, F. Family and D. P. Landau, eds. (North-Holland, Amsterdam, 1984).
38. R. M. Ziff, E. M. Hendriks, and M. H. Ernst, *Phys. Rev. Lett.* **49**:593 (1982); *J. Stat. Phys.* **31**:519 (1983).
39. F. Leyvraz and H. R. Tschudi, *J. Phys. A: Math. Gen.* **15**:1951 (1982).