Journal of Statistical Physics, Vol. 90, Nos. 1/2, 1998

Gelation and Cluster Growth with Cluster-Wall Interactions

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Received February 19, 1996; final August 20, 1997

Metallic cluster growth within a reactive polymer matrix is modeled by augmenting coagulation equations to include the influence of side reactions of metal atoms with the polymer matrix:

$$\begin{cases} \dot{c}_j = \frac{1}{2} \sum_{k=1}^{j-1} R_{j-k,k} c_k c_{j-k} - c_j \sum_{k=1}^{\infty} R_{jk} c_k - \delta_{1j} \lambda c_j p, & j = 1, 2,... \\ \dot{p} = -\lambda c_1 p \end{cases}$$

where $\lambda > 0$ and where c_k denotes the concentration of the kth cluster and p denotes the concentration of reactive sites available within the polymer matrix for reaction with metallic atoms. The initial conditions are required to be nonnegative and satisfy $\sum_{j=1}^{\infty} j c_j(0) = 1$ and $p(0) = p_0$. We assume that $R_{jk} = [dj^\alpha k^\alpha + (j+k)(j^\alpha + k^\alpha)]/(d+j+k)$ for $0 \leqslant \alpha \leqslant 1$, which encompasses both bond linking kernels $(R_{jk} = j^\alpha k^\alpha)$ and surface reaction kernels $(R_{jk} = j^\alpha + k^\alpha)$. Our analytical and numerical results indicate that the side reactions delay gelation in some cases and inhibit gelation in others. We provide numerical evidence that gelation occurs for the classical coagulation equations $(\lambda = 0)$ with the bond linking kernel $(d \to \infty)$ for $1/2 < \alpha \leqslant 1$. We examine the relative fraction of metal atoms, which coagulate compared to those which interact with the polymer matrix, and demonstrate in particular a linear dependence on λ^{-1} in the limiting case $R_{jk} = jk$, $p_0 = 1$.

KEY WORDS: Gelation; coagulation equations; cluster growth; infinite-dimensional dynamical systems; metallic clusters in a polymer matrix; Smoluchowski equations with side reactions.

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1. INTRODUCTION

Many processes in astrophysics, atmospheric physics, biology, colloidal chemistry, polymer science and the kinetics of phase transitions in binary alloys can be studied by means of cluster growth models.(1-8) In these models the system under consideration is viewed as consisting of a large number of clusters: $A_1, A_2, \ldots$, where A_k is assumed to consist of k particles A_1 which may be atoms, molecules, cells, etc., depending on the phenomenon which is to be described. Clusters can coagulate to form larger ones according to the reaction

$$A_j + A_k \rightarrow A_{j+k}$$

where R_{jk} is the reaction constant, also called the coefficient of coagulation or kernel, which satisfies $R_{jk} = R_{kj} \geqslant 0$. These reactions are assumed to be irreversible. We denote by $c_j(t) \geqslant 0$, $j = 1, 2, \ldots$, the expected number of clusters consisting of j particles per unit volume. The *coagulation equations* are:

$$\dot{c}_j = \frac{1}{2} \sum_{k=1}^{j-1} R_{j-k,k} c_{j-k} c_k - c_j \sum_{k=1}^{\infty} R_{jk} c_k, \qquad j = 1, 2, \ldots \tag{1}$$

where the first term represent the rate of change of the concentration of the j-clusters due to the coalescence of smaller clusters. The second term represent the change due to coalescence of the j-cluster with other clusters.

In this work we consider a certain physical and chemical process which occurs in the preparation of metal-polymer composites This process consists of the synthesis of metal-polymer composites in which microscopic metal or metal oxide particles are incorporated by the in-situ thermal or photolitic decomposition of solid solutions of organometallic complexes followed by phase separation in the polymer matrices. Examples for this type of process are the decomposition of iron carbonyls or the decomposition and oxidation of cobalt carbonyls complexes within a polymer matrix.(9, 10) The process considered in this work is the thermal decomposition of cobalt carbonyl complexes in a polystyrene matrix under inert atmosphere conditions (N_2), which, in the absence of oxygen, prevents the oxidation of the cobalt and affords the formation of zero-valent cobalt clusters homogeneously embedded in the polystyrene matrix. The zero-valent nature of these particles is associated with the "clean" chemistry of pristine metal atoms or metal surfaces, as opposed to the "dirty" chemistry which is the result of various other oxidation states of the metal, a situation which is avoided in our system by conducting the experiments under an inert atmosphere (N_2).

The overall chemical reaction is

$$n[Co_x(CO)_y] \xrightarrow[Polystyrene]{N_2,\ 90°C} Co_m^{(0)} + \text{Co-Polystyrene complexes} \qquad (2)$$

where $x = 2$, 4 or 6 and $y = 8$, 12 or 16. In the main reaction, the $Co_m^{(0)}$, $m \geqslant 2$ clusters are formed from smaller ones. The Co-Polystyrene complexes formed during this process **are not byproducts** of the main reaction, but rather a parallel reaction which competes with the main coagulation reaction. The extent of the secondary reaction depends on the reactivity of the cobalt precursor ($Co_x(CO)_y$) and the interaction parameter between the reactive cobalt species and the polystyrene molecules. These reactive, electron-deficient cobalt species are formed by the decomposition of the cobalt precursor due to the loss of one or more carbonyl ligands$^{(11)}$ (see pages 1054–1064 and pertinent references therein). Therefore, the rate of the main coagulation reaction will be dependent not only on the concentration of the cobalt precursor and rate coefficient of the coagulation reaction, but also on the concentration of the polystyrene in the system, or more specifically, the concentration of the reactive sites on the polymer capable of interacting with the cobalt precursor fragments, and the interaction parameter between the polymers and the metal species.

The reaction proceeds via several intermediates, however, the rate limiting step is the initial loss of a carbonyl group, which creates electron-deficient species, and therefore, the overall reaction may be approximated as a first order reaction. The electron-deficient species formed during the course of the decomposition are very reactive, and are capable of interacting very strongly with the polymeric matrix. Therefore, there are two major pathways for chemical reactions available for these metallic species:

(a) reactive electron-deficient species can aggregate to form clusters:

$$Co_j^{(0)} + Co_k^{(0)} \rightarrow Co_{j+k}^{(0)}$$

where $j, k = 1, 2, \ldots$ and $j+k$ is m in (2),

(b) reactive electron-deficient species can attach to the polystyrene matrix:

$$Co_j^{(0)} + \text{Polystyrene} \rightarrow \text{Co-Polystyrene}$$

where $j = 1, 2, \ldots$.

The stoichiometric details of the latter reaction are not yet elucidated. However, for the model considered in this paper we assumed that only single Co atoms ($j = 1$) react with the polystyrene and the attachment of these species to the polymeric matrix is considered as irreversible, and hence, each particle which is involved in this interaction will be excluded from further reaction with other particles. Moreover, the chemical bonding between these particles and the polymer reduces the reactive sites on the polymer and hence, limits the extent of the particle-polymer pathway. It is important to stress that the overall chemistry of the system is dependent on the relative importance and contribution of both pathways.

In order to translate the physical system into mathematical terms, we define c_j as the concentration of clusters of size j of *Co*. The actual realistic initial conditions (as implied by the physical situation), is some initial non-zero distribution of clusters of small sizes and not just the monodisperse case. However, for simplicity, it is useful to consider the monodisperse case.

In order to model this process we add an additional term to the first equation in the system (1), which describes the loss of single particles due to reaction with the polymer walls, and then couple the resultant system with an equation modeling the decrease of the number of reactive sites per unit volume, $p(t)$, in the polymer walls available for the reaction with the metal species. Denoting the coefficient of reaction between the metal species and the polymer by λ, the following system of nonlinear differential equations is obtained:

$$\begin{cases} \dot{c}_j = \dfrac{1}{2} \displaystyle\sum_{k=1}^{j-1} R_{j-k,k} c_k c_{j-k} - c_j \sum_{k=1}^{\infty} R_{jk} c_k - \delta_{1j} \lambda c_j p \\ \dot{p} = -\lambda c_1 p \end{cases}$$

for $t > 0$, $j = 1, 2, \ldots$, with initial conditions: $c_j(0) = \delta_{1j}$, $p(0) = p_0$, or more generally, for arbitrary non-negative initial conditions satisfying $\sum_{j=1}^{\infty} j c_j(0) = 1$ and $p(0) = p_0$.

In order to complete the mathematical description of the physical system under study we need to specify the form of the coefficients of coagulation R_{jk}. In the model describing the process of preparation of metal-polymer composites, the basic unit-clusters are atoms (metallic atoms). When two atoms react, they join together by means of an atom–atom bond. On the other hand when two large clusters join together, it is plausible to assume that they come into contact by a surface-reaction link instead of by a simple bond between two atoms of the cluster. As a consequence, we must take into account both behaviors in order to construct the appropriate reaction rate constants which describe the whole process. The simplest coagulation kernels related to our problem which occur in the literature are: $R_{jk} = j^{\alpha} k^{\alpha}$, $0 \leqslant \alpha \leqslant 1$,(4, 1, 12–16) and $R_{jk} = j^{\alpha} + k^{\alpha}$, $0 \leqslant \alpha \leqslant 1$.(4, 15) We note that for the additive kernel the rate of large–large and large–small interactions are of the same order of magnitude. This kernel describes processes in which the dominant mechanism is that of surface reaction. For the multiplicative kernel large–large interactions are of higher order of magnitude than large–small interactions. It applies to situations in which bond linking is the dominant mechanism. With this in mind, the form of the kernel which we propose to be appropriate to describe the coagulation process of metallic atoms is given by:

$$R_{jk}=\frac{dj^{\alpha}k^{\alpha}+(j+k)(j^{\alpha}+k^{\alpha})}{d+j+k} \tag{4}$$

where $0\leqslant\alpha\leqslant 1$, and where d is a parameter indicating the mean-cluster size at which there is a changeover in the mechanism of coagulation. Clearly, (4) reduces to $R_{jk}=j^{\alpha}k^{\alpha}$ when $d\rightarrow\infty$ and to $R_{jk}=j^{\alpha}+k^{\alpha}$ when $d=0$, however (4) is no longer a homogeneous function of j and k. For $0\leqslant\alpha<1$, the kernel (4) is a particular case of the more general kernel

$$R_{jk}=\frac{dr_jr_k+(j+k)(r_j+r_k)}{d+j+k} \tag{5}$$

where

$$\lim_{k\rightarrow\infty}\frac{r_k}{k}=0 \tag{6}$$

Assuming that $r\equiv\inf_{k\geqslant 1}r_k\neq 0$, it is easy to check that kernels of type (5) satisfy

$$(r_j+r_k)\leqslant R_{jk}\leqslant\left(\frac{d}{d+2}+\frac{2}{r}\right)r_jr_k \tag{7}$$

In our discussions only non-negative solutions will be considered. For kernels of type (5)–(6) and $\lambda\geqslant 0$, the existence of a continuously differentiable solution for arbitrary nonnegative initial conditions satisfying $\sum_{k=1}^{\infty}kc_k(0)=1$ was established by Rotstein,(17) extending the results of Tschudi and Leyvraz(13) for $\lambda=0$. The kernel $R_{jk}\leqslant j^{\alpha}k^{\alpha}$, $0\leqslant\alpha\leqslant\frac{1}{2}$, is included in this case. When $0\leqslant\alpha\leqslant\frac{1}{2}$ and $\lambda=0$, Ball and Carr(8) demonstrated that the solution is unique for all non-negative initial conditions. For $R_{jk}=jk$ and $\lambda=0$. McLeod(14) proved that the solution is unique for all $t\in[0,\tau]$, where $\tau<1$. For $R_{jk}\leqslant j^{\alpha}+k^{\alpha}$, $0\leqslant\alpha\leqslant 1$, and $\lambda=0$, White(18) showed that there exists at least one non-negative solution and that all the moments $M_n(t)=\sum_{k=1}^{\infty}k^nc_k(t)$ are bounded on bounded intervals. For kernels $R_{jk}\leqslant(j+k)$ and $\lambda=0$. Ball and Carr(8) established the existence of a solution for all t. They also proved that this solution is continuously differentiable.

Exact solutions for (3) with $\lambda = 0$ and monodisperse initial conditions are known for some very particular and simple kernels. For $R_{jk} = const$, which corresponds to $\alpha = 0$ and either $d = 0$ or $d \to \infty$ in (4), the solution was given by Smoluchowski.(1, 12, 5) For $R_{jk} = 1$ the solution is

$$c_k(t) = \left(\frac{t}{2}\right)^{k-1} \left(1 + \frac{t}{2}\right)^{-k-1}, \qquad \text{for} \quad k = 1, 2, \ldots \tag{8}$$

We will refer to this case as the Smoluchowski case. For $R_{jk} = jk$, which we will refer to as the prototype case and corresponds to $\alpha = 1$ and $d \to \infty$ in (4), the solution given by McLeod(14) for $t \leqslant 1$ and extended by Leyvraz and Tschudi(13) for all $t \geqslant 0$ is

$$c_k(t) = \begin{cases} \dfrac{k^{k-2}}{k!} t^{k-1} e^{-kt} & \text{if} \quad t \leqslant 1 \\[2ex] \dfrac{k^{k-2}}{k!} e^{-k} \dfrac{1}{t} & \text{if} \quad t \geqslant 1 \end{cases} \tag{9}$$

Calculating the total mass of the system from (9), yields

$$\sum_{j=1}^{\infty} j c_j(t) = \begin{cases} 1 & t \leqslant 1 \\ t^{-1} & t \geqslant 1 \end{cases} \tag{10}$$

The failure of mass-conservation at $t = 1$ is interpreted in terms of the formation of an infinite cluster or gel. More precisely, generalizing the analysis of White(18) and Hendriks *et al.*,(15) let us define for $w \geqslant 0$ and for $t \geqslant 0$ the momenta and the partial momenta or L-momenta:

$$M_w(t) := \sum_{k=1}^{\infty} k^w c_k(t), \qquad M_{w,L}(t) := \sum_{k=1}^{L} k^w c_k(t)$$

It can be seen from (3), multiplying the first equation by j^w, summing and rearranging terms, that $M_{w,L}(t)$ satisfy the differential equation:

$$\begin{aligned} M_{w,L} = {} & \frac{1}{2} \sum_{j=1}^{L-1} \sum_{k=1}^{L-j} c_j c_k R_{jk} [(j+k)^w - j^w - k^w] \\ & - \sum_{j=1}^{L} \sum_{k=L-j+1}^{\infty} c_j c_k R_{jk} j^w - \lambda c_1 p \end{aligned} \tag{11}$$

If

$$\lim_{L \to \infty} \sum_{k=1}^{L} c_k R_{jk} k^w < \infty \tag{12}$$

then

$$\lim_{L \to \infty} \sum_{j=1}^{L} \sum_{k=L-j+1}^{\infty} c_j c_k R_{jk} j^w = 0$$

and hence

$$\dot{M}_w = \frac{1}{2} \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} c_j c_k R_{jk}[(j+k)^w - j^w - k^w] - \lambda c_1 p = \lim_{L \to \infty} M_{w,L} \tag{13}$$

Let us now look at equation (13) with $w = 1$. For all t for which condition (12) is satisfied we have

$$\dot{M}_1(t) - \dot{p}(t) = 0 \qquad \text{or} \qquad M_1(t) - p(t) = 1 - p_0 \tag{14}$$

Otherwise, from (11)

$$\lim_{L \to \infty} [\dot{M}_{1,L}(t) - \dot{p}(t)] \leqslant 0$$

If there exists a time $0 \leqslant t_c < \infty$ such that $\dot{M}_1(t) - \dot{p}(t) = 0$ for all $t \leqslant t_c$, and $\dot{M}_1(t) - \dot{p}(t) < 0$ otherwise, we say that gelation has occurred and we call t_c the *gelation time*. It follows that $M_1(t) - p(t) = 1 - p_0$ for all $t \leqslant t_c$ and $M_1(t) - p(t) < 1 - p_0$ otherwise.

To gain intuition into the behavior predicted by these equations, we examine first what is known to happens in the absence of side reactions ($\lambda = 0$). From (10) note that for the prototype case and $\lambda = 0$, gelation occurs at $t_c = 1$. It is possible to arrive at a similar conclusion by looking at the second moment $M_2(t)$, which represents the mean cluster size of the system. Occurrence of gelation at $t = t_c$ implies failure of condition (12) for $w = 1$, which in turns implies, for $R_{jk} = jk$, that $\sum_{j=1}^{\infty} k^2 c_k$ diverges at $t = t_c$. Thus divergence of $M_2(t)$ gives an indication that gelation may have occurred, and convergence of $M_2(t)$ indicates that gelation has not occurred. Looking at (13) one sees that prior to gelation

$$\dot{M}_2 = M_2^2 \qquad \text{or} \qquad M_2(t) = \frac{1}{M_2^{-1}(0) - t} \tag{15}$$

hence $M_2(t)$ diverges when $t = M_2(0)^{-1}$.(15) In particular, for monodisperse initial conditions divergence occurs when $t = 1$ in accordance with (10). Another way to determine that gelation has occurred is given via consideration of $M_0(t)$.(15) For kernels satisfying (5)–(6) and $w = 0$, equation (13) is valid for all $t < \infty$, since condition (12) is valid for all $t < \infty$. This follows from (7) and the fact that $\lim_{L \to \infty} \sum_{k=1}^{L} kc_k = M_1(t) < \infty$ for all $t < \infty$. Looking at (13) with $R_{jk} = jk$, $w = 0$, and $\lambda = 0$, since prior to gelation $M_1(t) = 1$, one sees that up to gelation time,

$$\dot{M}_0 = -\tfrac{1}{2}M_1^2 = -\tfrac{1}{2} \qquad \text{or} \qquad M_0(t) = 1 - \tfrac{1}{2}t$$

which vanishes at $t_0 = 2$, indicating not that the total number of clusters vanishes within a finite time, but that the moment equation with $M_1(t) = 1$ is no longer valid for $t > t_c$, for some $t_c \leqslant 2$. Even though for this case the bound does not provide better information, it exemplifies a different way of determining occurrence of gelation; i.e., the vanishing of $M_0(t)$ within a finite time t_0 indicates that gelation has occurred prior to t_0.(4, 15) For more general kernels, the relation between the divergence of the second moment and occurrence of gelation has not been proved. However heuristic arguments in favour of the absence of singular points other than t_c for the model $R_{jk} = jk$ and $\lambda = 0$ lead to Hendriks *et al.*(15) to conjecture that for more general kernels, divergence of some moment at t_c indicates that gelation occurs at that point.

For $\lambda = 0$ and $R_{jk} = \psi(j, k)$, where ψ is a homogeneous function of degree of both variables, j and k; i.e., $\psi(sj, sk) = s^{\beta}\psi(j, k)$, Hendriks, Ernst and Ziff(15) addressed the question of occurrence of gelation and where appropriate, gave bounds on gelation time. Their results for $R_{jk} = j^{\alpha}k^{\alpha}$ yield gelation for $\alpha > 1$ and exclude gelation for $\alpha \leqslant \frac{1}{2}$, in concurrence with the results of Leyvraz and Tschudi.(16) For $\frac{1}{2} < \alpha \leqslant 1$ the criteria are inconclusive, although for $\alpha = 1$ the exact solution (9) exhibits gelation at $t_c = 1$. For the interval $\frac{1}{2} < \alpha < 1$, the question of occurrence of gelation is still open. However, there is evidence indicating that gelation occurs.(16) For $\lambda = 0$ and $R_{jk} \leqslant j^{\alpha} + k^{\alpha}$, $0 \leqslant \alpha \leqslant 1$, White(18) proved that if $\sum_{k=1}^{\infty} k^p c_k(0)$ is finite for some $p > \alpha$, then for any non-negative solution of the coagulation equations, $\sum_{k=1}^{\infty} k^p c_k(t)$ is bounded on bounded intervals.

An important issue which naturally arises regarding the system (3) with $\lambda > 0$ is to determine the effect of side reactions on the coagulation process, and in particular on the possible appearance of gelation. To our knowledge this question has not been addressed up to now. More specifically: are there situations in which the gelation phenomenon is inhibited as a consequence of side reactions? In Section 2 we show, that for $R_{jk} = jk$ the gelation time t_c is delayed as a consequence of side reactions and for kernels of type (5), or more generals kernels R_{jk} satisfying $\phi(j, k) \leqslant R_{jk} \leqslant \psi(j, k)$, where $\phi(j, k)$ and $\psi(j, k)$ are homogeneous functions of j and k the upper bounds on t_c are increased. We also study the influence of the parameter d in kernels of type (4) on the occurrence of gelation and on gelation time, finding, for monodisperse initial conditions that for the case $0 < d < \infty$, there is no gelation for $0 \leqslant \alpha \leqslant \frac{1}{2}$ and there is gelation for $\alpha > 1$. In Section 3, we develop a numerical test, which we call a *peaks test*, based on the convergence of the sequence of maxima, or peaks, of the numerical solutions for a sequence of finite systems which approach (3), to the peaks of the infinite system. With the aid of this test we can conjecture whether or not gelation occurs and, for the cases in which gelation indeed occurs, we obtain numerical upper bounds on gelation time. In particular we obtain numerical evidence of the occurrence of gelation for $R_{jk} = j^\alpha k^\alpha$, $\frac{1}{2} < \alpha < 1$, where the analytical tests were inconclusive. For more general kernels; i.e., kernels of type (4) with $d < \infty$ we obtain numerical evidence supporting the existence of a parameter α_d, $\frac{1}{2} \leqslant \alpha_d \leqslant 1$ which increases as d decreases such that for $\alpha \leqslant \alpha_d$ gelation does not occur and for $\alpha > \alpha_d$ gelation occurs. We also analyze the influence of side reactions on the occurrence of gelation finding that an increase in the value of λ can inhibit gelation for certain values of α.

With regard to the system (3), another important feature to clarify is to determine the fraction of the initial monomer concentration which eventually becomes incorporated into the metallic clusters as compared with the fraction which undergoes reaction with the polymer matrix. In Section 4, using numerical solutions, we present graphs illustrating the competition between the processes of coagulation and side-reaction for various values of λ and α, and for $p_0 = 1$ and $d \to \infty$. Furthermore we derive an analytical expression for the concentration of monomers that coagulate as a function of the concentration of monomers that attach to the polymer for the model $R_{jk} = jk$ which demonstrates linear dependence on λ^{-1} in the limiting case $p_0 = 1$.

2. ANALYSIS OF GELATION FOR THE MODEL WITH CLUSTER-WALL INTERACTIONS

In this section we study analytically the effect both of the side reactions and of the kernels satisfying (7) on the occurrence of gelation and gelation time by adapting the methods of ref. 15 (Section 5.1). We first address the influence of side reaction on gelation time and on the occurrence of gelation for the model $R_{jk} = \psi(j, k)$ where $\psi(j, k)$ is a homogeneous function of both j and k for the case $\lambda > 0$, next we study the particular case $R_{jk} = jk$, and finally we treat the question of whether or not gelation occurs for kernels satisfying (7). Such kernels need not be homogeneous functions either of j or of k. For models other than the prototype case it is difficult to solve the moment equations explicitly, but it is still possible to obtain bounds on the momenta which provide criteria for the occurrence of gelation and bounds on the gelation time. We construct upper and lower bounds for $M_2(t)$ and upper bounds for $M_0(t)$ analyzing them with the help of the following criteria which were discussed in the introduction:

1. the divergence of a lower bound for $M_2(t)$ at a finite time $t = t_2$ indicates that gelation may have occurred at some time $t_c \leqslant t_2$,
2. the divergence of an upper bound for $M_2(t)$ at $t = t_1$ shows that if gelation occurs at $t = t_c$, then $t_c \geqslant t_1$,
3. if an upper bound for $M_0(t)$ reaches zero at t_0 gelation has occurred at $t_c \leqslant t_0$.

Information on the influence of the side reactions on gelation time for homogeneous kernels is contained in the lemmas 2.1 and 2.2 below.

Lemma 2.1. If $R_{jk} = \psi(j, k)$ where $\psi(sj, sk) = s^{\beta}\psi(j, k)$, and $\beta > 0$,

(1) if $\psi(j, k)$ is convex and $\beta > 2$, then gelation occurs and

$$t_c < \frac{(M_2(0) - p_0)^{1-\beta}}{\psi(1, 1)(\beta - 1)}$$

(2) if $\psi(j, k)$ is concave and $\beta \leqslant 1$, then gelation does not occur.

Remark. Let us look at the monodisperse initial conditions case. For the kernel $R_{jk} = j^{\alpha}k^{\alpha}$, this lemma indicates that gelation occurs if $\alpha > 1$ with $t_c < (1 - p_0)^{1-2\alpha}/2\alpha - 1$, and that gelation does not occur if $\alpha \leqslant \frac{1}{2}$.

— For the kernel $R_{jk} = j^{\alpha}k^{\alpha}$ with $\frac{1}{2} < \alpha < 1$, the lemma is inconclusive, although for $\alpha = 1$ we will show in Lemma 2.2 that gelation indeed occurs.

— In the absence of side reactions, the lemma is correct with $p_0 = 0$ (see ref. 15).

— Note that the effect of side reactions is to increase the bounds on gelation time.

Proof. (1) Let us look at Eq. (13) with $w = 2$ and apply Jensen's inequality$^{(19)}$ to both variables of the convex function $\psi(j, k)$:

$$\dot{M}_2 - \dot{p} = \sum_{j,k=1}^{\infty} jkc_jc_k\psi(j, k) = M_1^2 \sum_{j,k=1}^{\infty} \frac{jkc_jc_k\psi(j, k)}{M_1^2}$$

$$> M_1^2\psi\left(\frac{M_2}{M_1}, \frac{M_2}{M_1}\right) = M_1^{2-\beta}\psi(1, 1)\, M_2^{\beta}$$

From (13) with $w=1$, $M_1(t)$ is a decreasing function of t. Since, by assumption $\beta>2$,

$$M_1^{2-\beta}(t) > M_1^{2-\beta}(0) = 1$$

and thus

$$\dot{M}_2 - \dot{p} > \psi(1, 1)\, M_2^\beta(t) \geqslant \psi(1, 1)(M_2(t) - p(t))^\beta$$

Solving this differential inequality:

$$M_2(t) > (M_2(0) - p_0)\left(1 - \frac{t}{t_1}\right)^{-1/(\beta-1)} + p(t), \qquad t_1 = \frac{(M_2(0) - p_0)(1-\beta)}{\psi(1, 1)(\beta - 1)}$$

At $t=t_1$ the lower bound for $M_2(t)$ diverges, thus according to criterion 1, $t_c < t_1$.

(2) From Eq. (13) with $w=2$,

$$\begin{aligned}\dot{M}_2 - \dot{p} &= \sum_{j,k=1}^{\infty} jkc_jc_k\psi(j,k)\\ &= M_1^2 \sum_{j,k=1}^{\infty} \frac{jkc_jc_k\psi(j,k)}{M_1^2}\\ &< M_1^2\psi\left(\frac{M_2}{M_1}, \frac{M_2}{M_1}\right) = M_1^{2-\beta}\psi(1, 1)\, M_2^\beta\end{aligned}$$

From (13) with $w=1$, $M_1(t)$ is a decreasing function of t. Since, by assumption, $\beta<1$,

$$M_1^{2-\beta}(t) < M_1^{2-\beta}(0) = 1$$

and since $p(t)$ is also a decreasing function of t we obtain

$$\dot{M}_2 - \dot{p} < \psi(1, 1)\, M_2^\beta(t) \leqslant \psi(1, 1)(M_2(t) - p(t) + p_0)^\beta$$

Solving this differential inequality and rearranging terms

$$M_2(t) < M_2(0)\left(1 + \frac{t}{t_2}\right)^{1/(1-\beta)}, \qquad \text{where } t_2 = \frac{M_2^{1-\beta}(0)}{\psi(1, 1)(1-\beta)}$$

This upper bound for $M_2(t)$ does not diverge for all $t \geqslant 0$, so $M_2(t)$ is always finite and gelation does not occur. This proves the second part of the lemma.

Remarks. By looking at equation (13) with $\psi(j, k)$ convex $\beta > 2$ and $w = 0$, and applying similar arguments to $M_0(t)$ we have

$$M_0(t) < M_0(0)\left(1 - \frac{(1-p_0)^{\beta}\, t}{t_0}\right)^{1/(\beta-1)} \qquad \text{where} \quad t_0 = \frac{2M_0^{\beta-1}(0)}{(\beta-1)\,\psi(1,1)}$$

At $t = t_0/(1-p_0)^{\beta}$ the upper bound for $M_0(t)$ vanishes, so according to criterion 3 gelation occurs and $t_c < t_0$. This bound is not better than the previous one, but corresponds to a more conclusive criterion.

— Examining Eq. (13) with $\psi(j, k)$ concave, $\beta \leqslant 1$ and $w = 0$ we conclude similarly that there exists a lower bound for $M_0(t)$ which does not vanish for all $t \geqslant 0$, in support of the conclusion of part 2 of the lemma.

Lemma 2.2. If $R_{jk} = jk$ and $\lambda > 0$, then gelation occurs, and

$$M_2(0)^{-1} < t_c < \frac{2M_0(0)}{(1-p_0)^2}$$

Remarks. For monodisperse initial conditions the above bounds may be written as

$$1 < t_c < \frac{2}{(1-p_0)^2}$$

— Comparing with the case $\lambda = 0$ where $t_c = M_2^{-1}(0)$ (15), treated in ref. 15, we see that as a consequence of the side reactions, t_c increases while remaining finite as a consequence of the side reactions.

Proof. It is easy to check from Eq. (13) with $w = 2$ and $r_k = k$ that,

$$\dot{M}_2 < M_2^2$$

Hence

$$M_2(t) < \frac{1}{M_2^{-1}(0) - t}$$

Thus by criterion 2, if gelation occurs then $t_c > M_2^{-1}(0)$.

Similarly from Eq. (13) with $w = 0$ and $r_k = k$,

$$\dot{M}_0 = -\tfrac{1}{2} M_1^2 - \lambda c_1 p \tag{16}$$

Prior to gelation $M_1(t) = 1 - p_0 + p(t)$, hence (16) becomes

$$\dot{M}_0(t) = -\tfrac{1}{2}[(1-p_0)^2 + 2(1-p_0)\,p(t) + p^2(t)] - \lambda c_1(t)\,p(t)$$

thus

$$\dot{M}_0(t) < -\tfrac{1}{2}(1-p_0)^2$$

Solving this differential inequality we obtain

$$M_0(t) < -\tfrac{1}{2}(1-p_0)^2 t + M_0(0)$$

Hence $M_0(t)$ vanishes by time t_0, where

$$t_0 = \frac{2M_0(0)}{(1-p_0)^2}$$

Thus, according to criterion 3,

$$t_c < \frac{2M_0(0)}{(1-p_0)^2}$$

In terms of the influence of the coefficients of coagulation on the gelation time, we have the following

Lemma 2.3. If $\lambda = 0$ and

$$\phi(j,k) \leqslant R_{jk} \leqslant \psi(j,k)$$

where $\phi(j,k)$ and $\psi(j,k)$ satisfy

$$\phi(sj, sk) = s^{\beta}\phi(j,k) \qquad \text{and} \qquad \psi(sj, sk) = s^{\gamma}\psi(j,k), \qquad \beta, \gamma > 0$$

(1) if $\phi(j,k)$ is convex and $\beta > 1$ then gelation occurs, and

$$t_c < \frac{M_2^{1-\beta}(0)}{\phi(1,1)(\beta-1)}$$

(2) if $\psi(j,k)$ is concave and $\gamma \leqslant 1$ then gelation does not occur.

Remark. For kernels satisfying (4) with $0 < d < \infty$ for $\alpha \leqslant \frac{1}{2}$ gelation does not occur and for $\alpha > 1$ gelation occurs with

$$t_c < \frac{M_2^{1-\alpha}(0)}{\alpha - 1}$$

just as it does for the kernel $R_{jk} = j^{\alpha}k^{\alpha}$ corresponding to $d \to \infty$.

The proof follows closely the arguments employed in Section 5.1 of ref. 15 replacing equality by inequality where appropriate (see ref. 17 for details). Similarly, it is possible to obtain

$$M_0(t) < M_0(0)\left(1 - \frac{t}{t_0}\right)^{1/(\beta - 1)} \qquad \text{where} \quad t_0 = \frac{M_0^{\beta - 1}(0)}{(\beta - 1)\,\phi(1, 1)}$$

At $t = t_0$ this upper bound for $M_0(t)$ vanishes, so according to criterion 3 gelation occurs and $t_c < t_0$. From Eq. (13) with $w = 0$, it is easy to conclude the existence of a lower bound for $M_0(t)$ which does not vanish for all $t \geqslant 0$.

3. PEAKS TEST FOR GELATION

In this section we present numerical results related to gelation which complement the analytical results presented in Section 2. The main difficulty facing numerical treatment of system (3) is that the system of differential equations is infinite. An associated finite system of coagulation equations with side reactions in which coagulation is allowed up to the N-cluster is

$$\begin{cases} \dot{c}_{j,N} = \dfrac{1}{2} \displaystyle\sum_{k=1}^{j-1} R_{k,\,j-k}\, c_{k,N}\, c_{j-k,N} - c_{j,N} \sum_{k-1}^{N-j} R_{jk}\, c_{k,N} - \delta_{1j} \lambda c_{j,N}\, p_N \\ \dot{p}_N = -\lambda c_{1,N}\, p_N \end{cases} \tag{17}$$

In Rotstein$^{(17)}$ it was shown that for kernels of type (5)–(6) the solutions of the sequence of finite systems approach the solution of the infinite system; i.e., there exist a subsequence $N_i \to \infty$ of natural numbers such that $\lim_{N_i \to \infty} c_{j,N_i}(t) = c_j(t)$ and $\lim_{N_i \to \infty} p_N(t) = p(t)$, uniformly on $[0, T]$, $0 \leqslant T < \infty$, for $j = 1, 2, \ldots$, where $\{\{c_j\}_{j=1}^{\infty}, p(t)\}$ is a solution of (3) and $\{\{c_{j,N}\}_{j=1}^{\infty}, p_N(t)\}$ are solutions of (17). Assuming the solution of (3) to be unique, implies that the subsequence $N_i \to \infty$ can be taken to be the set of natural numbers itself; i.e.,

$$\lim_{N \to \infty} c_{j,N}(t) = c_j(t) \qquad \text{for} \quad j = 1, 2, \ldots$$

The essential behavior of (17) is different from that of (3) because for (17) gelation does not occur since $\dot{M}_{1,N}(t) - \dot{p}_N(t) = 0$ for all $t < \infty$ and for all N. The material released as a consequence of the coagulation process is absorbed by the N-cluster since, by (17), $c_{N,N}(t)$ is an increasing function of time which in the limit $N \to \infty$ may be interpreted as corresponding to the gel concentration. However, the convergence of subsequences enables us to look at a sequence of solutions of problems of type (17) and infer from them possible behavior of the solutions of (3).

3.1. The Structure of the Solutions of the Infinite Systems, Existence of Peaks, and Relation Between Peaks and Gelation Time

Let us first consider the kernels $R_{jk}=1$ and $R_{jk}=jk$ for $\lambda=0$ with monodisperse initial conditions, for which exact results are known. For the case $R_{jk}=1$, from the solution given in (8), clearly for each k, $c_k(t)$ reach its maximum at $t_k=k-1$, and $t_k \to \infty$ as $k \to \infty$. For the prototype case, from (9) we observe that for each k, $c_k(t)$ reaches its maximum at $t_k=k-1/k$. We observe that the sequence $\{t_k\}_{k=1}^{\infty}$ is monotonically increasing and convergent: $\lim_{k\to\infty} t_k=1$. These remarks, together with numerical solutions for the kernels $R_{jk}=j^{\alpha}k^{\alpha}$, $0 \leqslant \alpha \leqslant 1$ and kernels of type (4) (see Fig. 1), lead us to the following.

Conjecture 3.1. Let $\{\{c_k(t)\}_{k=1}^{\infty}, p(t)\}$ be a solution of the infinite system (3) for monodisperse initial conditions. Then for each k there exist a $t_k \geqslant 0$ such that

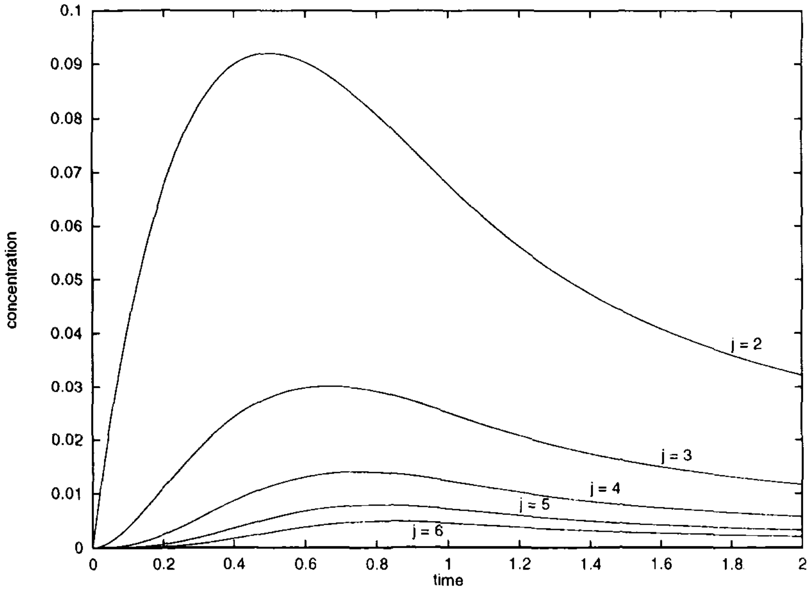

Fig. 1. Cluster solutions $c_j(t)$ for $j=2, 3, 4, 5$ and 6 for $R_{jk}=jk$, $\lambda=0$ and $N=100$.

$$\begin{cases} \dot{c}_k(t) > 0 & \text{if} \quad t < t_k \\ \dot{c}_k(t_k) = 0 & \\ \dot{c}_k(t) < 0 & \text{if} \quad t > t_k \end{cases}$$

Moreover, the sequence $\{t_k\}_{k=1}^{\infty}$ is monotonically increasing.

We call each of the elements t_k of this sequence a *peak* for the corresponding solution $c_k(t)$. The following lemma provides us a tool for finding numerical bounds on gelation time, given a sequence of peaks corresponding to solutions $\{\{c_j\}_{j=1}^{\infty}, p(t)\}$ of (3).

Lemma 3.1. Let us assume that conjecture 3.1 is true. If $t_0 = \lim_{k \to \infty} t_k$ exists, then $t_c \leqslant t_0$ where t_c is the gelation time.

Proof. By reductio ad absurdum let us assume that $t_c > t_0$. For all $t > t_0$, by Conjecture 3.1 and since $t > t_k$ for all k

$$\sum_{k=1}^{\infty} k\dot{c}_k(t) < 0 \tag{18}$$

On the other hand, for all $t \leqslant t_c$,

$$\sum_{k=1}^{\infty} kc_k(t) = 1 \tag{19}$$

From (18), for all $t > t_0$

$$\sum_{k=1}^{\infty} kc_k(t) < \sum_{k=1}^{\infty} kc_k(t_0)$$

In particular if $t_c > t_0$ one obtains $\sum_{k=1}^{\infty} kc_k(t_c) < 1$, in contradiction to (19). Therefore $t_c \leqslant t_0$.

3.2. Analysis of Gelation

We now employ the above remarks and results, restricting ourselves to values of $0 \leqslant \alpha \leqslant 1$ and monodisperse initial conditions. From the general existence theorem,$^{(17)}$ the uniqueness assumptions and Conjecture 3.1, it follows that for every k there exists a sequence $\{t_{k,N}\}_{k=1}^{\infty}$ of peaks, such that $\lim_{N \to \infty} t_{k,N} = t_k$, where t_k is the peak for the kth component of $c_k(t)$, the solutions of (3) for monodisperse initial conditions. We may now find an approximation on the bounds for the gelation time for infinite systems by looking at the peaks for numerical solutions for sequences of finite systems. This approach was carried out by using the Modified Euler Method with a step size $h = 0.01$ to calculate numerical solutions for systems of equations of type (17) with various kernels and values of λ and p_0, and for $N = 3, 5, 10, 50$ and 100. For each set of calculations the sequence of peaks was compiled in tables for various values of k and N, with entries $t_{k,3}, t_{k,5}, t_{k,10}, t_{k,50}$ and $t_{k,100}$. Looking at these tables we examine the convergence of $\{t_k\}_{k=1}^{\infty}$ and seek bounds on t_0. In Tables I–II we reproduce the results for the Smoluchowski and prototype cases respectively. In the case $N = 100$ only the first 50 peaks are given. The complete tables as well as the tables for other cases can be found in ref. 17. For the Smoluchowski case the sequence $\{t_{k,N}\}_{k=1}^{\infty}$ should satisfy $\lim_{N\to\infty} t_{k,N} = k-1$ and for the prototype case the sequence $\{t_{k,N}\}_{k=1}^{\infty}$ should satisfy $\lim_{N\to\infty} t_{k,N} = (k-1)/k$. Looking at Tables I–II we observe that for each k the values of $t_{k,N}$ decrease and appear to tend towards $k-1$ and $(k-1)/k$ respectively as N increases. This behaviour was corroborated for the prototype case making calculations for N up to 1000. As we know, $c_{N,N}(t)$ is an increasing function of time for each N, which in the limit $N \to \infty$ we interprete as corresponding to the gel concentration. For this reason we observe in Tables I–II that $t_{N,N} = 50.00$ for each N, the maximum time of calculation. The fact that $t_{k,N} = 50.00$ in Table I is to be interpreted as t_k occurring at a time t which is beyond the range of calculation. Looking at Tables I and II we can differentiate between two different behaviors of the peaks. For the Smoluchowski case the peaks tend to converge to an unbounded sequence. This behavior also appears in the numerical simulations for other kernels where gelation is not expected to occur and we consider it as characteristic for systems in which gelation does not occur. Moreover in ref. 17 we have observed that as α decreases the peaks are more spread out for a fixed value of N. For the prototype case we see that the sequence $\{t_{N-1,N}\}$, $N = 3, 5, 10, 50$ and 100, is given by

$$0.89, \quad 1.81, \quad 2.16, \quad 1.59, \quad 1.41$$

where the last value was taken from Table 7.3 in ref. 17, increases initially, then decreases. We shall refer to this sequence as the bounding sequence for the problem. We also made calculations for $N = 200$, 300, 400 and 500 obtaining $t_{199,200} = 1.29$, $t_{299,300} = 1.24$, $t_{399,400} = 1.20$ and $t_{499,500} = 1.18$. We assume that once the sequence starts to decrease it continues to decrease. Thus, for the prototype case the peaks are concentrated in a bounded interval of time implying that once the bounding sequence starts to decrease, each $t_{N-1,N}$ gives an upper bound on the gelation time. We consider this behaviour as being a positive indication of the occurrence of gelation. We

Table I. Peak Times for N-Dimensional Finite Systems for $R_{jk}=1$ Various Values of N and $\lambda=0$

k	$N=3$	$N=5$	$N=10$	$N=50$	$N=100$	$k-1$
1	0.00	0.00	0.00	0.00	0.00	0.00
2	1.51	1.03	1.00	1.00	1.00	1.00
3	50.00	2.64	2.01	2.00	2.00	2.00
4		13.07	3.12	3.00	3.00	3.00
5		50.00	4.53	4.00	4.00	4.00
6			6.80	5.00	5.00	5.00
7			11.91	6.00	6.00	6.00
8			50.00	7.00	7.00	7.00
9			50.00	8.00	8.00	8.00
10			50.00	9.00	9.00	9.00
11				10.01	10.00	10.00
12				11.01	11.00	11.00
13				12.03	12.00	12.00
14				13.06	13.00	13.00
15				14.10	14.00	14.00
16				15.16	15.00	15.00
17				16.26	16.00	16.00
18				17.39	17.00	17.00
19				18.57	18.00	18.00
20				19.80	19.00	19.00
21				21.11	20.01	20.00
22				22.50	21.01	21.00
23				24.00	22.02	22.00
24				25.63	23.03	23.00
25				27.42	24.04	24.00
26				29.41	25.06	25.00
27				31.63	26.09	26.00
28				34.16	27.12	27.00
29				37.07	28.16	28.00
30				40.48	29.20	29.00
31				44.54	30.26	30.00
32				49.52	31.34	31.00
33				50.00	32.43	32.00
34				50.00	33.53	33.00
35				50.00	34.66	34.00
36				50.00	35.80	35.00
37				50.00	36.97	36.00
38				50.00	38.17	37.00
39				50.00	39.39	38.00
40				50.00	40.65	39.00
41				50.00	41.95	40.00
42				50.00	43.28	41.00
43				50.00	44.66	42.00
44				50.00	46.09	43.00
45				50.00	47.57	44.00
46				50.00	49.12	45.00
47				50.00	50.00	46.00
48				50.00	50.00	47.00
49				50.00	50.00	48.00
50				50.00	50.00	49.00

Table II. Peak Times for N-Dimensional Finite Systems for $R_{jk}=jk$ Various Values of N and $\lambda=0$

k	$N=3$	$N=5$	$N=10$	$N=50$	$N=100$	$(k-1)/k$
1	0.00	0.00	0.00	0.00	0.00	0.00
2	0.89	0.57	0.51	0.50	0.50	0.50
3	50.00	1.02	0.72	0.67	0.67	0.67
4		1.81	0.88	0.75	0.75	0.75
5		50.00	1.04	0.81	0.80	0.80
6			1.22	0.84	0.84	0.83
7			1.43	0.88	0.86	0.86
8			1.71	0.90	0.88	0.88
9			2.16	0.92	0.90	0.89
10			50.00	0.94	0.91	0.90
11				0.98	0.93	0.91
12				0.98	0.93	0.92
13				0.99	0.94	0.92
14				1.01	0.95	0.93
15				1.02	0.96	0.93
16				1.04	0.97	0.94
17				1.05	0.98	0.94
18				1.07	0.98	0.94
19				1.08	0.99	0.95
20				1.10	1.00	0.95
21				1.11	1.00	0.95
22				1.12	1.01	0.95
23				1.14	1.01	0.96
24				1.15	1.02	0.96
25				1.17	1.03	0.96
26				1.18	1.03	0.96
27				1.19	1.04	0.96
28				1.21	1.04	0.96
29				1.22	1.05	0.97
30				1.24	1.05	0.97
31				1.25	1.06	0.97
32				1.26	1.07	0.97
33				1.28	1.07	0.97
34				1.29	1.07	0.97
35				1.31	1.08	0.97
36				1.32	1.08	0.97
37				1.33	1.09	0.97
38				1.35	1.09	0.97
39				1.36	1.10	0.97
40				1.38	1.10	0.98
41				1.39	1.11	0.98
42				1.41	1.11	0.98
43				1.43	1.12	0.98
44				1.44	1.12	0.98
45				1.48	1.13	0.98
46				1.48	1.13	0.98
47				1.50	1.13	0.98
48				1.53	1.14	0.98
49				1.59	1.14	0.98
50				50.00	1.15	0.98

find a third kind of behavior which is intermediate; i.e., the peaks do not increase beyond the calculation time (50.00), but the bounding sequence is still increasing even for $N = 150, 200$, and 250. In those cases we can not conclude anything about occurrence or non-occurrence of gelation. This considerations are employed to interprete numerical calculations which where made for some characteristic cases which we summarize next.

3.3. Influence of the Coefficients of Coagulation on Occurrence of Gelation

We analyze now the influence of kernels of type (1) on gelation time without side reactions. From the results of Hendriks *et al.*[15] and those of Section 2 we know that for kernels of type (1) with $d > 0$, gelation does not occur for $0 \leqslant \alpha \leqslant \frac{1}{2}$, for the limiting case $d \to \infty$ and $\alpha = 1$ we also know from (9) that gelation occurs and $t_c = 1$, and for the limiting case $d = 0$ we know that gelation does not occur for all $0 \leqslant \alpha \leqslant 1$. The question is still open regarding the cases $0 < d < \infty$, $\frac{1}{2} < \alpha \leqslant 1$ and $d \to \infty$, $\frac{1}{2} < \alpha < 1$. For the latter case it has been conjectured that gelation occurs in this interval of α.[16, 20] We expect the existence of a parameter α_d, $\frac{1}{2} \leqslant \alpha_d \leqslant 1$ which increases as d decreases such that for all $\alpha \leqslant \alpha_d$ gelation does not occur and for all $\alpha > \alpha_d$ gelation occurs.

The results for various values of d and α are displayed in Table III. We can see there that for all d considered and $\alpha \leqslant \frac{1}{2}$ there is no gelation, which

Table III. Analysis of Gelation for the Kernel $R_{jk} = [dj^{\alpha}k^{\alpha} + (j+k)(j^{\alpha}+k^{\alpha})]/(d+j+k)$ for Various Values of α and d and for $\lambda = 0$[a]

α	$d = \infty$	$d = 200$	$d = 100$	$d = 50$	$d = 20$	$d = 2$	$d = 0$
1.0	1.41	1.53	1.64	1.81	2.22	—	-
0.9				2.70	?		
0.8			3.75	?	?		
0.75	3.71		?	?			
0.7		5.83	?	?			
0.6	9.58	?	?	—			
0.55	14.43						
0.5	25.47	—	—	—	—	—	—
0.45	—						
0.0	—	—	—	—		—	—

[a] The numbers indicate the bounds on gelation time when gelation occurs, the dashes indicates that gelation does not occur and the question marks indicates that we can not decide about occurrence of gelation.

is in accordance with the analytical results with the exception of the results for the prototype case for $\alpha = \frac{1}{2}$, which are in contradiction to Lemma 2.1. This may be a result of the difference between the analytical method which is based on a conjecture regarding the second moment of the system, and the peaks-test; or it may be the result of a very small error in the numerical method. Since it has been conjectured to be in the borderline case between the occurrence and non-occurrence of gelation, our calculations may be very sensitive to very small numerical errors. For this reason we also made calculations for $\alpha = 0.45$ obtaining that there is no gelation. We also see that for $d = 0$ there is no gelation for all α tested in accordance with the analytical results. For the prototype case and $\frac{1}{2} \leqslant \alpha < 1$ we obtain numerical evidence of occurrence of gelation confirming what has been conjectured. For the remaining cases we see that as d decreases, the interval $(\alpha_d, 1)$ of occurrence of gelation becomes smaller, confirming our conjecture.

3.4. Influence of Side Reactions on Occurrence of Gelation

We analyze now the influence of the parameters λ and p_0 on occurrence of gelation for the case $R_{jk} = j^\alpha k^\alpha$. From the results of Section 2 we know that for $\lambda \geqslant 0$, gelation does not occur for $0 \leqslant \alpha \leqslant \frac{1}{2}$ and that gelation occurs for $\alpha = 1$. For this last value of α we know that when side reactions are not allowed, gelation occurs at $t_c = 1$ and it is delayed as a consequence of the side reactions. The question is still open regarding the cases $\frac{1}{2} < \alpha < 1$. For this interval and $\lambda = 0$ we showed in the former subsection that gelation indeed occurs. We expect, as in the case $\alpha = 1$, that the gelation time should be delayed as a consequence of side reactions. A natural question

Table IV. Numerical Bounds on the Gelation Time for $R_{jk} = j^\alpha k^\alpha$ for Various Values of α, λ, and p_0[a]

α	$\lambda = 0.1$, $p_0 = 0.1$	$\lambda = 0.1$, $p_0 = 0.5$	$\lambda = 0.5$, $p_0 = 0.5$	$\lambda = 1.0$, $p_0 = 1.0$	$\lambda = 10.1$, $p_0 = 1.0$	$\lambda = 20.0$, $p_0 = 1.0$	$\lambda = 100.0$, $p_0 = 1.0$
1.0	1.41	1.44	1.54				
0.9						?	—
0.8						?	—
0.7					?		—
0.6	10.30	?	?	?	—	—	—
0.5	—	—	—	—	—	—	—

[a] The numbers indicate the bounds on gelation time when gelation occurs, the dashes indicates that gelation does not occur and the question marks indicates that we can not decide about occurrence of gelation.

which arises is whether an increase in λ can inhibit gelation for certain values of α. The results for various values of λ, p_0 and α are displayed in Table IV. We can see numerical evidence supporting an affirmative answer to this question.

4. CLUSTER-POLYMER COMPETITION

A physically relevant issue regarding systems of type (3) is to evaluate the relative competition between the two processes: coagulation of metallic clusters and side-reaction of the metallic atoms with the polymer walls. To this end, we analyze graphs of $M_1(t) - c_1(t) = \sum_{j=2}^{\infty} jc_j(t)$, the mass of the non-monomer clusters, versus $p_0 - p(t)$, the concentration of reactive sites which are no longer available for reaction. We expect the slope of these graphs to increase as λ increases since the tendency of the monomers to react with the walls increases with increasing λ. We also expect the slope of these graphs to decrease with increasing α since the tendency of the monomers to coagulate increases with increasing α. To address this question we calculated $M_{1,N}(t) - c_{1,N}(t) = \sum_{j=2}^{N} jc_{j,N}(t)$ and $p_0 - p_N(t)$ using the Modified Euler Method with a step size $h = 0.001$ and for 1000 iterations, and put them in graphs of $M_{1,N} - c_{1,N}$ (concentration of atoms which coagulate) versus $p_0 - p_N$ (concentration of atoms which react with the polymer walls), for $N = 3$, 5, 10, 50 and 100, for kernels of type (4) with $d \to \infty (R_{jk} = j^{\alpha}k^{\alpha})$, for various values of α and λ and for $p_0 = 1$. In each graph (Figs. 2–3) there are three groups of solutions, which in order of decreasing slope correspond to $\lambda = 0.1$, $\lambda = 1$ and $\lambda = 10$. In each group there are five solutions (though we cannot distinguish between them fully in the graphs), which correspond to $N = 3$ to $N = 100$. Figure 2 correspond to the multiplicative kernel with $\alpha = 1$ and $p_0 = 1$ and Fig. 3, correspond to the multiplicative kernel with $\alpha = 0$ and $p_0 = 1$. Looking at the graphs, we can infer from the sequence of finite solutions, the expected limiting behavior of the infinite system. We observe that for $\alpha = 1$ the curves approaches a straight line with slope λ^{-1} as it is demonstrated below analytically. For $\alpha = 0$ we see that for early values of time the curves are similar to the corresponding ones for $\alpha = 1$. This can be explained as follows. At the beginning of the process the loss of metallic atoms by coagulation is mainly due to reaction between single atoms, and $R_{1,1} = 1$ for both cases. Later on in time the difference in slope can be seen as predicted. This gives us an experimental tool for estimating λ without complete information about the coagulation process.

As a comparative analytical example, we analyze the model (3) with $R_{jk} = jk$ and monodisperse initial conditions. Let us consider the first and

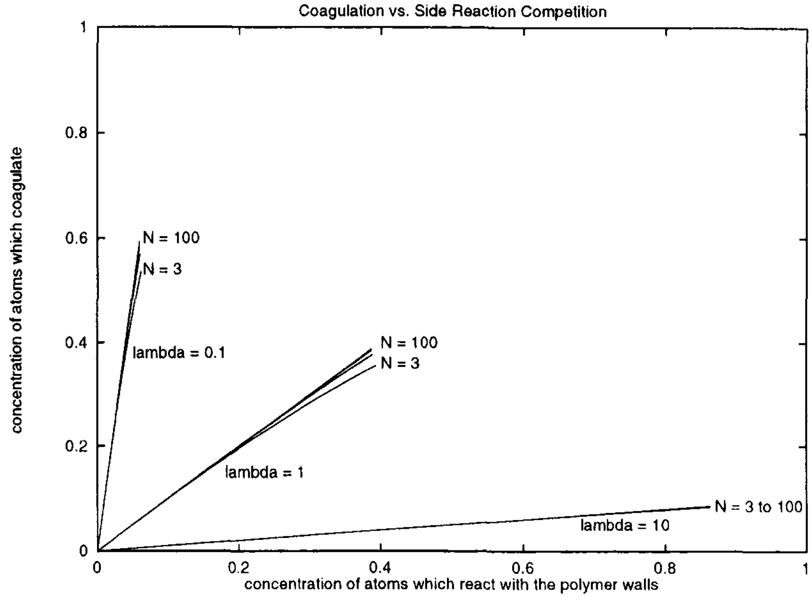

Fig. 2. Cluster coagulation vs. side-reaction competition for $R_{jk} = j^{\alpha}k^{\alpha}$, $\alpha = 1$, $p_0 = 1$, $\lambda = 0.1$, 1 and 10 respectively in order of decreasing slope.

last equations in (3) and Eq. (13) with $w = 1$. Prior to gelation we have the following system

$$\begin{cases} \dot{M}_1 = \lambda c_1 p, \\ \dot{c}_1 = -c_1 M_1 - \lambda c_1 p, \\ \dot{p} = -\lambda c_1 p \end{cases} \tag{20}$$

and from (14), $M_1 = p + 1 - p_0$. Substracting the second equation in (20) from the first one and solving the resulting system we obtain

$$M_1 - c_1 = \frac{p_0}{\lambda}\left(1 - \frac{p}{p_0}\right) - \frac{1}{\lambda}\ln\left(\frac{p}{p_0}\right)^{1-p_0} \tag{21}$$

This is an expression for the concentration of monomers which have coagulated as a function of the fraction of the concentration of the reactive sites at time t with respect to the initial concentration of reactive sites with λ as a parameter. Differentiating with respect to $p_0 - p$ we obtain

$$\frac{d(M_1 - c_1)}{d(p_0 - p)} = \frac{1}{\lambda}\left(1 + \frac{1 - p_0}{p}\right)$$

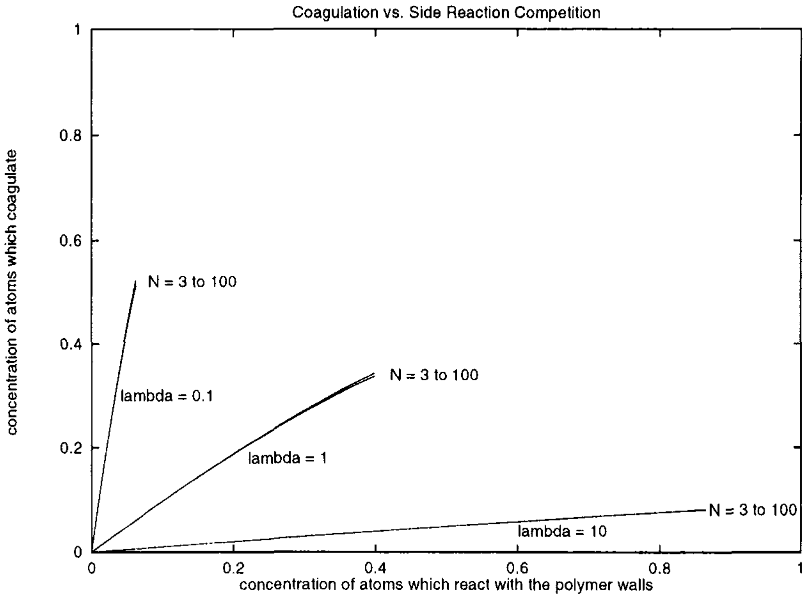

Fig. 3. Cluster coagulation vs. side-reaction competition for $R_{jk}=j^{\alpha}k^{\alpha}$, $\alpha=0$, $p_0=1$, $\lambda=0.1$, 1 and 10 respectively in order of decreasing slope.

which for the particular case in which $p_0=1$, reduces to

$$\frac{d(M_1-c_1)}{d(p_0-p)}=\frac{1}{\lambda}$$

We can see the linear dependence between M_1-c_1 and p_0-p with λ^{-1} as the proportionality constant. For kernels other than $R_{jk}=jk$, we cannot obtain such an analytical expression for the cluster-polymer competition but we expect similar influence of the parameter λ.

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