Generalized Smoluchovski equation with gelation

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We have considered coagulation processes containing n-polymer interactions and studied the sole processes of n-polymer coalescence by means of a generalized Smoluchovski equation, which is solved as an initial-value problem for the product kernel: $R(i_1,i_2,\ldots,i_n)=(i_1 i_2\cdots i_n)^{\omega}$ with $0<\omega<1$. A variety of novel critical behaviors and new critical exponents are found which are different from those obtained from the Smoluchovski equation. Our results can be regarded as higher-order approximations to the two-polymer collision processes and thus contribute towards our understanding of general coagulation processes.

I. INTRODUCTION

The critical behavior of irreversible coagulation processes have recently been studied extensively using the Smoluchovski equation.[1-14] This kinetic equation has been used to model the time evolution of the size distributions $c_m(t)$ in the coagulation processes, such as polymerization, clustering of colloidal particles, red blood cells, etc.,[14] in which the substance A_i's are assumed to react with each other according to the following scheme:

$$A_i + A_j \xrightarrow{R(i,j)} A_{i+j} , \tag{1.1}$$

where A_j denotes a j-mer, and $R(i,j)$ is the rate constant for the reaction of an i-mer and j-mer. This model can be described by the kinetic equation

$$\dot{c}_k(t)=\tfrac{1}{2}\sum_{i+j=k} R(i,j)c_i c_j - c_k \sum_{j=1}^{\infty} R(k,j)c_j . \tag{1.2}$$

In recent years it has been noticed that, for certain choices of the rate constants $R(i,j)$, the Smoluchovski equation (1.2) predicts the occurrence of a gelation transition at a finite time t_c (gel point), which is marked by a divergence of a mean cluster size and by the onset of mass flux from the finite size clusters (sol particles) towards the clusters of infinite size or gel. More recently, it is found that the kinetic equation (1.2) also predicts the instantaneous occurrence of a gelation transition for some special kernels.[14] To date, the system (1.2) has received considerable investigation, and many of its critical properties have been discussed. It is, however, quite clear that, apart from the binary collision, there must exist other possible kinds of reactions among the coagulating polymers such as tribasic, quadruple collisions or more generally n-tuple collision, in the real coagulation processes. Therefore, one must construct a kinetic equation, which is similar in form to the Smoluchovski equation, to describe the corresponding coagulation process which contains all possible reactions occurring in cluster growing process. To this end, it seems important to explore, first of all, the sole process of n-tuple coalescence, since the general coagulation process appears to be difficult to handle at present.

To go beyond the growth process (1.1) towards the most general coagulation processes,

$$\begin{aligned} &A_i + A_j \xrightarrow{R_2(i,j)} A_{i+j} , \\ &A_i + A_j + A_k \xrightarrow{R_3(i,j,k)} A_{i+j+k} , \\ &A_{i_1} + A_{i_2} + \cdots + A_{i_m} \xrightarrow{R_m(i_1,i_2,\ldots,i_m)} A_{i_1+i_2+\cdots+i_m} , \end{aligned} \tag{1.3}$$

one has, as a first step, to study the sole processes of n-polymer coalescence in which polymers react with one another in the manner

$$A_{i_1} + A_{i_2} + \cdots + A_{i_n} \xrightarrow{R(i_1,i_2,\ldots,i_n)} A_{i_1+i_2+\cdots i_n} \tag{1.4}$$

which are modeled on the following generalized Smoluchovski equation:

$$\begin{aligned} \dot{c}_m = &\frac{1}{n!}\sum_{i_1+i_2+\cdots+i_n=m} R(i_1,i_2,\ldots,i_n)c_{i_1}c_{i_2}\cdots c_{i_n} \\ &-\frac{c_m}{(n-1)!}\sum_{i_1,i_2,\cdots i_{n-1}=1}^{\infty} R(i_1,i_2,\ldots,i_{n+1},m) \\ &\times c_{i_1}c_{i_2}\cdots c_{i_{n-1}} . \end{aligned} \tag{1.5}$$

This kind of processes is of interest for the following reasons. First, it is a crucial step towards fully under-

standing the general coagulation processes, since such a sole process of n-tuple collision is relatively easy to deal with mathematically, and the resulting conclusions may provide insight into the essence of the real growth processes (1.3). Second, in some special circumstances the sole process of n-tuple coagulation itself may prove to be of great importance. For example, when breakup process is allowed it may be possible that the growth process prefers the tribasic coalescence to binary collision, since the structure formed in a three-polymer reaction process appears to be more stable than that generated by the binary collision process. It is an easy matter to note that the cluster generated by the sole process of n-tuple collision may generally exhibit a regular morphology. If this is the case, one should study the corresponding sole process of coagulation to obtain the relevant properties of the growing clusters. Nevertheless, there is not doubt that the probability of the occurrence of n-tuple collision is much smaller than that of binary interaction. This sole process is still interesting and deserves detailed investigation. We believe that a thorough study on the sole process of n-tuple coalescence will indeed contribute towards a better understanding of the general coagulation processes.

The main purpose of this paper is to study the kinetic equation (1.4) for the special product kernel

$$R(i_1,i_2,\ldots,i_n)=s_{i_1}s_{i_2}\cdots s_{i_n}\ , \tag{1.6a}$$

with

$$s_k=k^{\omega}\ , \tag{1.6b}$$

where ω is a geometric exponent characterizing the surface of a k-mer, and satisfies $0<\omega\leq 1$. Following the same lines of Ref. 8, we first discuss the exactly solvable model $\omega=1$, and then study the asymptotic behaviors of the size distribution for general ω. In Sec. II, we determine the generating function of the size distribution, and discuss the properties of the sole mass in the sol and gel phase. In Sec. III, we use the Lagrange expansion to derive an explicit solution of the size distribution for the monodisperse initial distribution. In Sec. IV, we discuss the structure of possible post-gel solution of (1.5) and derive the asymptotic results of the size distribution. Finally, in Sec. V we conclude our results and give some further remarks.

II. THE GENERATING FUNCTIONS AND THE SOL MASS

For the special case of $\omega=1$, the kinetic equation (1.5) turns into

$$\dot{c}_m(t)=\frac{1}{n!}\sum_{i_1+i_2+\cdots+i_n=m}(i_1i_2\cdots i_n)c_{i_1}c_{i_2}\cdots c_{i_n}$$
$$=\frac{mc_m}{(n-1)!}\sum_{i}^{\infty}(i_1i_2\cdots i_{n-1})c_{i_1}c_{i_2}\cdots c_{i_{n-1}}\ . \tag{2.1}$$

The time evolution of the size distribution $c_m(t)$ for a given initial distribution $c_m(0)$, subject to the normalization

$$M(0)=\sum_k kc_k(0)=1\ , \tag{2.2}$$

can be derived in terms of generating functions:

$$g(x,t)=\sum_{k=1}^{\infty}c_k(t)\exp(kx)\ , \tag{2.3a}$$

$$f(x,t)=g_x(x,t)=\sum_{k=1}^{\infty}kc_k(t)\exp(kx)\ , \tag{2.3b}$$

where the subscript x denotes a partial derivative with respect to x. The moments

$$M_n=\sum_{k=1}^{\infty}k^nc_k(t)\ , \tag{2.4}$$

if they exist, can be obtained from

$$g(x,t)=\sum_{n=0}^{\infty}(M_nx^n)/n!\ . \tag{2.5}$$

The initial values of these functions are given by

$$g(x,0)=\sum_{k=1}^{\infty}c_k(0)\exp(kx)=v(x)\ , \tag{2.6a}$$

$$f(x,0)=\sum_{k=1}^{\infty}kc_k(0)\exp(kx)=u(x)\ . \tag{2.6b}$$

Multiplying (2.1) with $m\exp(mx)$ and summing over m, we arrive at a partial differential equation for $f(x,t)$

$$f_t=\frac{1}{(n-1)!}f_x(f^{n-1}-M^{n-1})\ , \tag{2.7}$$

where $M=\sum_{k=1}^{\infty}kc_k(t)$. To solve Eq. (2.7) we introduce the inverse function $x=X(f,t)$. Using the identities $f_x=1/X_f$ and $f_t=-X_t/X_f$ we find a simple equation

$$X_t=-(f^{n-1}-M^{n-1})/(n-1)!\ . \tag{2.8}$$

Solving this equation for the initial condition $f(x,0)=u(x)$ we find a solution in the following two equivalent forms:

$$x=u^{-1}(f)-\left[tf^{n-1}-\int_0^t d\tau[M(\tau)]^{n-1}\right]\Big/(n-1)!\ , \tag{2.9}$$

$$f(x,t)=u\left[x+\left[tf^{n-1}-\int_0^t d\tau[M(\tau)]^{n-1}\right]\Big/(n-1)!\right]\ , \tag{2.10}$$

where $u^{-1}(f)=x$ is the inverse function of $f=u(x)$. For later purposes we write the solution in the following parametric form:

$$x=s-\{t[u(s)]^{n-1}-T\}/(n-1)!\ , \tag{2.11a}$$

$$f(x,t)=u(s)\ , \tag{2.11b}$$

where

$$T=\int d\tau[M(\tau)]^{n-1}\ . \tag{2.12}$$

These equations enable us to determine the sol mass

$M(t)=f(0,t)$ for a given initial distribution. Inserting $x=0$ into (2.11), we obtain a closed equation for $M(t)$:

$$M(t)=u[s(0,t)] , \tag{2.13a}$$

$$s(0,t)=\left[tf^{n-1}-\int_0^t d\tau[M(\tau)]^{n-1}\right]\Big/(n-1)!$$
$$=\left[\int_0^t \tau d\{[M(\tau)]^{n-1}\}\right]\Big/(n-1)! . \tag{2.13b}$$

Differentiating (2.13) with respect to t results in

$$M(t)=u'[s(0,t)]tMM^{n-1}/(n-2)! . \tag{2.14}$$

This equation combined with (2.13a) has two solutions for all t, provided $u'(s_0)=\infty$ with $s_0>0$. The first one is a constant solution

$$M_a(t)=M(0)=1 , \tag{2.15a}$$

corresponding to

$$s_a(t)=0 . \tag{2.15b}$$

The second one is

$$M_b(t)=u(s_b) , \tag{2.16a}$$

where $s_b(0,t)$ is determined from

$$1/t=\{u'(s_b)[u(s_b)]^{n-1}\}/(n-2)! . \tag{2.16b}$$

Following the same graphical analysis of the solution described in Ref. 8 one can easily prove that

$$M(t)=\min(1,M_b)=\begin{cases}1, & t\le t_c\\ M_b(t), & t\ge t_c ,\end{cases} \tag{2.17}$$

with the gel point t being given by

$$t_c=(n-2)!/M_2(0) . \tag{2.18}$$

Here we notice that as n increases the gel point t_c increases. This shows that the probability of n-tube collisions decreases with increasing n, and the gelation transition is unlikely to occur in systems with $n\to\infty$.

III. THE SIZE DISTRIBUTION

In this section we calculate the size distribution $c_m(t)$ for the monodisperse initial distribution, by means of the Lagrange expansion. It is clear that once the generating function $f(x,t)$ is known, the $c_m(t)$ can be found by expanding f in powers of $z=e^x$. For convenience we define

$$\bar f(z,t)=f(x,t)=\sum_{k=1}^{\infty} kz^k c_k(t) , \tag{3.1a}$$

$$\bar u(z)=u(x)=\sum_{k=1}^{\infty} kz^k c_k(0) . \tag{3.1b}$$

where $z=e^x$. In this notation the general solution (2.11) is given by

$$z=y\exp(-\{t[\bar u(y)^{n-1}-T]\}/(n-1!) , \tag{3.2a}$$

$$\bar f=\bar u(y) , \tag{3.2b}$$

where $y=e^s$. For any given (differentiable) $\bar f=\bar u(y)$ and $z(y)$, such that $z(y_0)=z_0$, the Lagrange expansion of f in powers of $(z-z_0)$ is

$$\bar f(z,t)=\bar u(y_0)+\sum_{k=1}^{\infty}\frac{(z-z_0)^k}{k!}\left[\left[\frac{d}{dy}\right]^{k-1}\bar u'(y)\left[\frac{y-y_0}{z(y)-z_0}\right]^k\right]_{y=y_0} . \tag{3.3}$$

To calculate $c_m(t)$ one must expand $f(z,t)$ about $z_0=0(x\to-\infty)$, where $y_0=u(y_0)=0$. Thus from the preceding equations we find

$$\bar f(z,t)=\sum_{k=1}^{\infty}\frac{z^k}{k!}\left[\left[\frac{d}{dy}\right]^{k-1}\bar u'(y)\exp\left[\frac{k}{N}[\bar u(y)^{n-1}-T]\right]\right]_{y=y_0} , \tag{3.4}$$

where $N=(n-1)!$. Comparing it with (3.1a), one obtains

$$c_k(t)=\left[\exp\left[-\frac{k}{N}T\right]\right]\Big/(kk!)\left[\left[\frac{d}{dy}\right]^{k-1}\bar u'(y)\exp\left[\frac{kt}{N}\bar u^{n-1}\right]\right]_{y=0} . \tag{3.5}$$

After some algebra, we arrive at

$$c_{q(n-1)+1}(t)=\left[\frac{[q(n-1)+1]t}{(n-2)!(n-2)!}\right]^q\exp\left[\frac{q(n-1)+1}{(n-1)!}T\right]\Big/\{[q(n-1)+1]^2q(n-1)\} ,$$
$$n=2,3,\ldots,\quad q=1,2,\ldots . \tag{3.6}$$

In deriving (3.6) we have made use of the monodisperse initial distribution $u(x)=e^x$. With this initial condition, one easily obtains from (2.16b)

$$s_b=\{\ln[(n-2)!/t]\}/(n-1) \tag{3.7}$$

and

$$M_b=u(s_b)=[(n-2)!/t] . \tag{3.8}$$

Thus from (2.12) and (2.17) it follows immediately that

$$T=\begin{cases} t, & t\le t_c \\ t_c+(n-2)!\ln(t/t_c), & t\ge t_c \end{cases} . \tag{3.9}$$

Substituting (3.9) into (3.6) we finally obtain

$$c_{q(n-1)+1}(t)=\left[\frac{[q(n-1)+1]t}{(n-2)!(n-2)!}\right]^q \exp\left[\frac{[q(n-1)+1]t}{(n-1)!}\right]\Big/[q(n-1)+1]^2 q(n-1), \quad t\le t_c \tag{3.10a}$$

$$c_{q(n-1)+1}(t)=\left[\frac{[q(n-1)+1]t_c}{(n-2)!(n-2)!}\right]^q \exp\left[\frac{[q(n-1)+1]t_c}{(n-1)!}\right](t/t_c)^{-1/(n-1)}/[q(n-1)+1]^2 q(n-1), \quad t\ge t_c \tag{3.10b}$$

$$c_m(t)=0, \quad m\neq q(n-1)+1 , \tag{3.11}$$

with $q=1,2,\ldots$, and $n=2,3,\ldots$. This solution reduces to the result derived of Ref. 8 for $n=2$. From (3.11) we find that the long-time behavior of $c(t)$ is given by

$$c_m(t)\sim b_m t^{-\alpha} , \tag{3.12}$$

with $\alpha=1/(n-1)$, which suggests that the possible exact post-gel solution will be of the form

$$c_m(t)=c_m(t_c)[1+\beta(t-t_c)]^{-1/(1-n)} , \tag{3.13}$$

where β is a constant, to be determined, and t_c is the gel point.

IV. THE EXACT POST-GEL SOLUTION AND THE ASYMPTOTIC BEHAVIOR OF $c_m(t)$

In this section we will discuss the exact post-gel solution (3.13), and use it to derive a recursion relation to study the long-time behavior of solutions of (1.4) for $0<\omega<1$. For simplicity, we restrict ourselves to the case $n=3$. The extension to the general n is straightforward.

When $n=3$, Eq. (1.4) can be written as

$$c_m(t)=\frac{1}{6}\sum_{i+j+k=m} R(i,j,k)c_i c_j c_k - \frac{c_m}{2}\sum_{i,j=1}^{\infty} R(i,j,m)c_i c_j . \tag{4.1}$$

Here we attempt to show that the size distribution in gelling systems approaches a special solution in the following sense

$$\lim_{t\to\infty} c_m(t)/c_1(t)=b_m , \tag{4.2}$$

where b_m $(m=1,2,\ldots)$ are bounded positive numbers with $b_1=1$.

First we consider a possible exact post-gel solution of (4.1) of the form

$$c_m(t)=c_m(t_c)[1+\beta(t-t_c)]^{-1/2} \quad (t\ge t_c) . \tag{4.3}$$

Writing $c_m(t)=b_m c_1(t)$, where $b_m=c_m(t_c)/c_1(t_c)$, and inserting the solution into (4.1) we obtain

$$-(\beta/2c_1^2)b_m=\frac{1}{6}\sum_{i+j+k=m} R(i,j,k)b_i b_j b_k - \frac{b_m}{2}\sum_{i,j=1}^{\infty} R(i,j,m)b_i b_j . \tag{4.4}$$

The unknown β may be eliminated by using (4.4) for $m=1$, and the following recursion relation results

$$\frac{1}{6}\sum_{i+j+k=m} R(i,j,k)b_i b_j b_k - \frac{b_m}{2}\sum_{i,j=1}^{\infty}[R(i,j,m)-R(i,j,1)]b_i b_j=0 . \tag{4.5}$$

The exact solution (4.3) has the remarkable property

$$M(t)=\sum_{k=1}^{\infty} kc_k(t)=M(t_c)/[1+\beta(t-t_c)]^{1/2} , \tag{4.6}$$

which indicates that the sol mass decreases in time for $t\ge t_c$.

Before proceeding we argue that the limiting ratio $b_m=\lim_{t\to\infty} c_m/c_1$ satisfies the recursion relation (4.5) provided that the b_m's satisfy the strict inequalities

$$2E_1^2<E_m<\infty, \quad m=2,3,\ldots , \tag{4.7}$$

where

$$E_m=\lim_{t\to\infty}\sum_{i,j=1}^{\infty} R(i,j,m)c_i c_j/[c_1(t)]^2 = \sum_{i,j=1}^{\infty} R(i,j,m)b_i b_j . \tag{4.8}$$

Here the infinite sums are assumed to be convergent.

In order to show that the coagulation equation (4.1) reduces to the recursion relation (4.5) as $t\to\infty$, we introduce

$$\sigma_m(t)=\frac{1}{2}\sum_{i,j=1}^{\infty} R(i,j,m)c_i c_j , \tag{4.9a}$$

$$S_m(t)=\int_0^t dt'\sigma_m(t') . \tag{4.9b}$$

The formal solution of (4.1) reads

$$c_m(t)=\exp[-S_m(t)]\left[c_m(0)+\int_0^t dt'\tfrac{1}{6}\sum_{i+j+k=m} R(i,j,k)c_i(t')c_j(t')c_k(t')\exp[S_m(t')]\right] . \tag{4.10}$$

The long-time behavior of $S_m(t)$ can be determined from $c_1(t)(t\to\infty)$, which in turn is given by (4.1) for $m=1$:

$$\dot{c}_1(t)=-c_1\sigma_1/2\simeq E_1c_1^2/2, \quad t\to\infty , \tag{4.11}$$

provided $E_1<\infty$. Therefore, one has in (4.9) as $t\to\infty$

$$\sigma_m(t)\simeq E_m c_1^2/2\simeq E_m/(2E_1^2t) , \tag{4.12}$$

$$S_m(t)\simeq(E_m/2E_1^2)\ln(t) , \tag{4.13}$$

provided $E_m<\infty$. On the basis of (4.12) and (4.13) the dominant long-time behavior of the t integral in (4.10) can be estimated as $t^{\nu(m)}$ with $\nu(m)=-1+E_m/(2E_1^2)$. This quantity diverges as $t\to\infty$ since $E_m>2E_1^2$. Thus, $c_m(0)$ may be neglected in (4.10), and the equation reduces to the long-time form

$$\int dt'\tfrac{1}{6}\sum_{i+j+k=m} R(i,j,k)c_i(t')c_j(t')c_k(t')\exp[S_m(t')]\simeq b_m c_1(t)\exp[S_m(t)] . \tag{4.14}$$

Differentiating (4.14) with respect to t yields

$$\tfrac{1}{6}\sum_{i+j+k=m} R(i,j,k)c_i(t)c_j(t)c_k(t)\simeq b_m(\sigma_m c_1+\dot{c}_1), \quad t\to\infty . \tag{4.15}$$

Using (4.2), (4.11), (4.12), and (4.13) we find

$$\tfrac{1}{6}\sum_{i+j+k=m} R(i,j,k)b_ib_jb_k=(E_m-E_1)b_m . \tag{4.16}$$

This is, in fact, the recursion relation (4.5). The cluster size distribution behaves as $c_m(t)\sim c_1(t)b_m\sim Cb_m/(t)^{1/2}$ $(m=1,2,\ldots,\ t\to\infty)$, where $Cb_m/(t)^{1/2}$ is the exact solution of the coagulation equation (4.1).

To determine the asymptotic solution of the recursion relation, we multiply (4.5) by m, and sum over m to obtain the following representation of the recursion relation:

$$\sum_{m=1}^{L} mb_m\sum_{i,j=1}^{\infty} R(i,j,1)b_ib_j=\sum_{i=1}^{L}\sum_{j=L-i+1}^{\infty}\sum_{k=L-i-j+1}^{\infty} kR(i,j,k)b_ib_jb_k . \tag{4.17}$$

If we assume that the solution b_m of the recursion relation at large m has algebraic m dependence, i.e.,

$$b_m\simeq Bm^{-\tau} \quad (m\to\infty) , \tag{4.18}$$

then, inserting the ansatz (4.18) into (4.17) leads to

$$E_1\sum_m mb_m=B^3(\lim L^{4+3\omega-3\tau})\int_0^1 dx\int_{1-x}^{\infty} dy\int_{1-x-y}^{\infty} dz\, xR(x,y,z)(xyz)^{-\tau} . \tag{4.19}$$

In nongelling systems one finds a consistent solution only if $\tau<2$. Thus, from (4.19) we find

$$\tau=1+3\omega/2 , \tag{4.20}$$

with

$$\omega<\tfrac{2}{3} \tag{4.21}$$

for nongelling systems, while

$$\tau=\tfrac{4}{3}+\omega \tag{4.22}$$

for gelling systems.

It should be emphasized that the asymptotic behaviors of $c_m(t)$ derived from (4.1) are obviously different than those from the Smoluchovski equation.[13] At fixed ω, the exponent τ, which characterizes the large m behavior of $c_m(t)$, is given by

$$\tau=\tfrac{3}{2}+\omega$$

for system (1.2), which is in contrast with (4.22). Comparing the exact post-gel solution of the Smoluchovski equation with (4.3), one may readily find that as $t\to\infty$, the $c_m(t)$, determined from (4.1), behaves as $c_m(t)\sim t^{-1/2}$, rather than $c_m(t)\sim t^{-1}$ deduced from the Smoluchovski equation.

For general n it is an easy matter to show that the possible exact post-gel solution

$$c_m(t)=c_m(t_c)/[1+\beta(t-t_c)]^{1/(n-1)} , \tag{4.23}$$

and the cluster size distribution approaches this exact solution as $t\to\infty$, or $c_m(t)/c_1(t)\to b_m$ for the gelling systems, with the critical exponent τ being given by

$$\tau=(n+1)/n+\omega \tag{4.24}$$

and

$$\omega>(n-1)/n \tag{4.25}$$

on account of the ansatz (4.18). From (4.23) and (4.24) one can recover the results of Ref. 12 by simply setting $n=2$. According to the previous discussion we find that for different n one has different asymptotic behaviors, and as $n \to \infty$ our results indicate that the gelation transition is impossible to take place for the sole process of n-tuple collisions with $n \to \infty$.

V. CONCLUSION

In the preceding sections we have discussed the sole processes of n-polymer coalescence by analyzing the corresponding generalized Smoluchovski equation. We have derived an explicit solution of the size distribution for the product kernel (1.5) for $\omega=1$, and obtained a general relation between ω and τ, viz.,

$$\tau=(n+1)/n+\omega$$

for $(n-1)/n<\omega\leq 1$. We have also derived a special post-gel solution, and discussed the long-time behavior of the size distribution. Our study shows that those sole n-polymer collision processes are indeed of great interest theoretically and practically since they do exhibit a variety of novel critical behaviors near gelation.

Now we would like to emphasize the following points to demonstrate what we have really achieved in the presentation.

(i) It seems that the existence of a unique solution of (1.4), as suggested by the explicit solution (3.10), (3.11), and the exact post-gel solution (4.23), can be proved following the same lines described in Ref. 2.

(ii) The gelation criteria can be derived from the moment equations for some characteristic kernels. As for the product kernel (1.5) we believe that gelation occurs for $\omega>(n-1)/n$, though as rigorous proof is lacking at present.

(iii) In the realistic coagulation processes, the many-polymer interactions should be taken into account as the masses of clusters grow large. Therefore one has to analyze the following kinetic equations:

$$\begin{aligned}\dot{c}_m(t)=&B_2\left[\sum_{i+j=m}R_2(i,j)c_ic_j/2-c_m\sum_{j=1}^{\infty}R_2(m,j)c_j\right]\\&+B_3\left[\sum_{i+j+k=m}R_3(i,j,k)c_ic_jc_k/6-c_m\sum_{i,j=1}^{\infty}R_3(m,i,j)c_ic_j/2\right]+\cdots\\&+B_n\left[\frac{1}{n!}\sum_{i_1+i_2+\cdots+i_n=m}R_n(i_1,i_2,\ldots,i_n)c_{i_1}c_{i_2}\cdots c_{i_n}\right.\\&\left.-\frac{c_m}{(n-1)!}\sum_{i_1,i_2,\cdots i_{n-1}=1}^{\infty}R_n(i_1,i_2,\ldots,i_{n-1}\ldots,m)c_{i_1}c_{i_2}\cdots c_{i_{n-1}}\right]\end{aligned}\tag{5.1}$$

instead of (1.2) or (1.4). Here B_i's are positive constants, satisfying $0\leq B_i\leq 1$. The kinetic system (5.1) is, in general, very difficult to deal with analytically. However, it can simplified for some specific cases. The simplest case is the so-called sole processes of the n-polymer interactions discussed in this paper, which correspond to $B_n \gg B_j$ for every $j\neq n$ in (5.1). When $B_2 \gg B_i$ $(i=3,4,\ldots)$, we see that (5.1) reduces to (1.2). In the case of $B_2\neq 0$, $B_3\neq 0$, and $B_i=0$ for $i=4,5,\ldots$, we have the following coagulation equations:

$$\begin{aligned}\dot{c}_m(t)=&B_2\left[\tfrac{1}{2}\sum_{i+j=m}R_2(i,j)c_ic_j-c_m\sum_{j=1}^{\infty}R_2(j,m)c\right]\\&+B_3\left[\tfrac{1}{6}\sum_{i+j+k=m}R_3(i,j,k)c_ic_jc_k\right.\\&\left.-\frac{c_m}{2}\sum_{i,j=1}^{\infty}R_3(i,j,m)c_ic_j\right].\end{aligned}\tag{5.2}$$

Since the sole processes of two- and three-polymer interactions have different critical exponents, it seems plausible to expect the following behavior for the system (5.2). For $B_3 \gg B_2$ there may exist a scaling time t_s such that

$$c_m(t)\sim A_m/t^{1/2}\tag{5.3}$$

for $t \ll t_s$, and

$$c_m(t)\sim A'_m/t\tag{5.4}$$

for $t \gg t_s$. This suggests that the long-time behavior of $c_m(t)$ may be dominated by the three-polymer interaction processes.

In addition, the complicated large-m behaviors of $c_m(t)$ are also expected for (5.2) as well as (5.1). The study in this present publication indeed provide an important step towards the solution of the general coagulation equation (5.1). We will deal with (5.1) in detail in a forthcoming work.

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