

Polymer growth through radical polymerization and termination

Shun-You Yang, Sheng-Qing Zhu, and Jianhong Ke*

College of Physics and Electronic Information Engineering, Wenzhou University, Wenzhou 325027, China

(Received 16 March 2009; revised manuscript received 8 July 2009; published 10 September 2009)

We propose a polymer growth model, in which propagating radicals can grow through propagation processes or annihilate through termination (disproportionation or combination) processes. Considering a simple case in which the propagation and termination rates of each polymer chain are both independent of its length, we then investigate analytically the kinetics of the model by means of the rate-equation approach. The propagating radicals will be exhausted eventually and only the inert polymers (the termination products of propagating radicals) can survive in the end. Moreover, the size distribution of propagating radicals can always take the form of the Poisson distribution at a given time, while that of inert polymers is dependent strongly on the details of the reaction-rate kernels. For the case in which the propagation rate constant J_1 is less than the termination rate constant J_2 , the size distribution of inert polymers can always take a power-law form $c_k(t) \sim k^{-2-J_1/(J_2-J_1)}$, in the region of $t \gg 1$ and $k \gg 1$. For the $J_1 > J_2$ case, the kinetic evolution of inert polymers is very complex and $c_k(t)$ can take one of the three forms: monotone decreasing, single peak (Poisson-like distribution), and double peak. For the special $J_1 = J_2$ case, $c_k(t)$ exhibits an exponential decay in size.

DOI: [10.1103/PhysRevE.80.031114](https://doi.org/10.1103/PhysRevE.80.031114)

PACS number(s): 05.70.Ln, 82.20.Nk, 82.30.Cf, 68.43.Jk

I. INTRODUCTION

The phenomenon of aggregation, in which small aggregates merge irreversibly to form large aggregates, has been investigated extensively in the last few decades [1–6]. The real-world examples include the process of crystal growth, the formation of cloud in atmosphere, and the growth of droplet. It is thus of theoretical and practical significance to understand the kinetics of aggregate growth. A lot of effort has been devoted to investigating the kinetic behavior of irreversible aggregation through the binary coalescence mechanism $A_i + A_j \rightarrow A_{i+j}$ [7–9]. Here, A_i denotes an aggregate consisting of i monomers, and two aggregates spontaneously combine into a larger aggregate A_{i+j} . With the help of the Smoluchowski rate equation [10], most of these investigations, which are related with aggregate growth, have been performed effectively. It is found that the size distribution of aggregates in irreversible aggregation processes may approach a scaling form at large times [11–13].

Recently, much attention has been paid to a great diversity of aggregate growth mechanisms. Leyvraz and Redner proposed an exchange-driven model for the evolution of city population [14]. Oshanin *et al.* investigated the equilibrium properties of a lattice-gas model with catalytic mechanism [15]. Laurenzi and Diamond studied the aggregation-fragmentation mechanism in a multiple component system [16], and so on [17–21]. Practically, there exist other growth mechanisms in chemical systems such as the free-radical polymerization. As we know, the free-radical polymerization has become an important polymerization method as far as its industrial utilization is concerned in the last century [22–25].

The free-radical polymerization in many actual industrial processes mainly consists of three stages: initiation, propagation, and termination. For example, the polymerization of ethylene can be well understood by a free-radical reaction

kinetics model illustrated in Table I (see also the kinetic scheme for methyl methacrylate polymerization in Refs. [26,27]). In the initiation stage, the initiator I is dissociated into two primary radicals R at the dissociation rate constant k_d and then the primary radical R is attached to a monomer M to form an initiated propagating radical P_1 at the association rate constant k_i . In the propagation process, an additional monomer M will be adsorbed to the propagating radical P_n at the rate constant k_p , namely, P_n becomes a larger propagating radical P_{n+1} (here, P_n denotes a propagating radical consisting of n repeating units). Such propagation processes can proceed continuously, while some termination processes take place. There are two different termination manners: disproportionation and combination. When two propagating radicals P_m and P_n meet, they can transform into two inert polymers, respectively, with m and n repeating units (i.e., D_m and D_n) due to disproportionation. Termination can also be caused by a combination reaction, in which two propagating radicals P_m and P_n meeting at their free-radical ends will produce one inert polymer D_{m+n} consisting of $m+n$ units.

With the development of the polymerization industry, more and more attention has been paid to the molecular weight distribution (MWD) of polymers [26–28] because the polymer's end-use properties are strongly dependent on its MWD. Crowley and Choi proposed a novel method for the

TABLE I. The scheme of free-radical polymerization.

Process	Scheme
Initiation	(i) $I \xrightarrow{k_d} 2R$
	(ii) $R + M \xrightarrow{k_i} P_1$
Propagation	(i) $P_n + M \xrightarrow{k_p} P_{n+1}$
Disproportionation	(i) $P_m + P_n \xrightarrow{k_{td}} D_m + D_n$
Combination	(i) $P_m + P_n \xrightarrow{k_{tc}} D_{m+n}$

*Corresponding author; kejianhong@yahoo.com.cn

calculation of the molecular weight distribution in free-radical polymerization of methyl methacrylate [27]. This method can compute the weight fraction of polymer in any molecular weight ranges but cannot deduce the explicit analytical expression of the MWD.

Motivated by these theoretical and experimental investigations on free-radical polymerization processes, we propose a simplified kinetics model for polymer growth through propagation and termination, which can be used to analytically investigate the properties of the MWD. Initially, the system consists of initiated propagating radical polymers (for instance, benzoyl peroxide initiation) and additional monomers (for instance, styrene monomers). A radical polymer with n repeating units is denoted as A_n , while an additional monomer is denoted as B_1 . The scheme of our model is defined as follows. When a propagating radical meets with B_1 , a propagation reaction takes place, i.e., the length of the propagating radical increases by one unit. The propagation

process can be described as the reaction $A_i + B_1 \xrightarrow{J_1(i)} A_{i+1}$, where the propagation rate kernel is denoted as $J_1(i)$ (equivalently, k_p in Table I). On the other hand, the termination process may also take place when two propagating radicals meet together. Let C_i denote the resulting inert polymer of a termination reaction that contains i units. The termination

process can then be described as $A_i + A_j \xrightarrow{J_2(i,j)} C_{i+j}$ (disproportionation) and $A_i + A_j \xrightarrow{J_3(i,j)} C_{i+j}$ (combination). Here, the disproportionation rate kernel is denoted as $J_2(i, j)$ (equivalently, k_{td} in Table I) and the combination rate kernel is denoted as $J_3(i, j)$ (equivalently, k_{tc} in Table I). As compared to the above general three-stage polymerization mechanism, our model neglects the initiation stage and is therefore applied only to such polymerization systems that the initiation rate is by far greater than the propagation (termination) rate.

We then investigate the size distribution (i.e., the MWD) of propagating radicals and that of inert polymers by means of the rate-equation approach. For the system with constant rate kernels, our results show that the size distribution of propagating radicals can always take the form of the Poisson distribution, while that of inert polymers can exhibit the monotone decreasing, single-peak, or double-peak structure in different cases. Intriguingly, these analytical results are in qualitative agreement with some experimental observations [29–31]. Thus, we believe that our model could provide some theoretical predictions for the size distribution of polymers in free-radical polymerization processes.

The rest of this paper is organized as follows. In Sec. II, we investigate the free-radical propagation-disproportionation model by using the rate-equation approach and then determine the analytical expressions of the polymer size distributions. In Sec. III, we discuss the kinetics of the free-radical propagation-combination model. In Sec. IV, we propose a general propagation model with both disproportionation and combination, and we then analyze the evolution behavior of the model at large times. A brief summary is given in Sec. V.

II. ANALYTICAL SOLUTION OF FREE-RADICAL PROPAGATION-DISPROPORTIONATION PROCESSES

In this work, we aim to analytically investigate the size distribution of radicals in free-radical polymerization systems. We shall study our model in the framework of the mean-field theory. The mean-field approximation neglects the spatial fluctuations in reactant concentrations and assumes that the polymerization reaction proceeds at a rate proportional to the concentration of each reactant. Assume that the free-radical polymerization system has spatial homogeneity. As a result, the polymers are considered to be distributed equably in the space throughout the whole process. Thus, we can analytically discuss the kinetics of the free-radical polymerization model with the help of the mean-field rate-equation approach. At time t , the concentration of the propagating radicals with k repeating units is defined as $a_k(t)$ and that of the inert polymers containing k units is denoted as $c_k(t)$, while the concentration of B_1 is denoted as $b_1(t)$. The governing rate equations for this model can then be written as

$$\frac{da_k}{dt} = J_1(k-1)b_1a_{k-1} - J_1(k)b_1a_k - a_k \sum_{i=1}^{\infty} J_2(k,i)a_i, \quad (1)$$

$$\frac{db_1}{dt} = -b_1 \sum_{i=1}^{\infty} J_1(i)a_i, \quad (2)$$

$$\frac{dc_k}{dt} = a_k \sum_{i=1}^{\infty} J_2(k,i)a_i. \quad (3)$$

In Eq. (1), the first two terms on the right-hand side account for the gain and loss in $a_k(t)$ due to the propagation reactions $A_{k-1} + B_1 \rightarrow A_k$ and $A_k + B_1 \rightarrow A_{k+1}$, respectively; while the third term represents the loss in $a_k(t)$ due to the disproportionation reactions $A_k + A_i \rightarrow C_k + C_i$ ($i=1, 2, 3, \dots$). Similarly, the term on the right-hand side of Eq. (2) accounts for the loss in $b_1(t)$ due to propagation reactions, while the term on the right-hand side of Eq. (3) represents the gain in $c_k(t)$ due to disproportionation reactions. On the other hand, it should be pointed out that the mean-field approximation can apply only to the system whose spatial dimension d is equal to or greater than an upper critical dimension d_c [9].

Here, we consider a special chain-shaped polymer system, in which the reaction abilities of a radical chain are independent of its length, namely, the rate kernels are time independent and size independent $J_1(i)=J_1$ and $J_2(i,j)=J_2$ for all i and j (J_1 and J_2 are two constants). It is sound because each propagating chain-shaped polymer has and only has two energetic and reactive ends, independent of its length. Meanwhile, constant rate kernels also imply that the polymers' diffusivities should follow the Stokesian dependence on their sizes (see, e.g., Ref. [32]). As Oshanin and Moreau pointed out, if the dependence of polymers' diffusivities on their sizes is non-Stokesian, the polymerization rate kernels at large times may be size dependent and the long-time kinetics of polymerization processes will be diffusion controlled [32]. As for branched polymers, their polymerization rate kernels

are also size dependent in most cases. However, since the above governing rate equations are coupled nonlinear differential equations, it is very difficult to deduce their explicit analytical solutions under general conditions. In this work, we focus only on the case with constant rate kernels.

Moreover, we assume that there only exist initiated propagating radicals and additional monomers at the beginning of the process and their initial concentrations are equal to A_0 and B_0 , respectively. So, the initial concentration condition can be described as $a_k(0)=A_0\delta_{k1}$, $b_1(0)=B_0$, and $c_k(0)=0$, $k=1,2,3,\dots$

Summing up Eq. (1) over all k , we obtain

$$\frac{dM_0^A}{dt} = -J_2(M_0^A)^2, \quad (4)$$

with the shorthand notation $M_v^A(t)=\sum_{j=1}^{\infty}j^v a_j(t)$. Obviously, $M_0^A(t)$ and $M_1^A(t)$ are the total number and the total mass of propagating radicals at time t , respectively. Under the monodisperse initial condition, we solve Eq. (4) to obtain

$$M_0^A(t) = A_0(J_2 A_0 t + 1)^{-1}. \quad (5)$$

Equation (5) indicates that the total number of propagating radical chains will decay as t^{-1} at large times. By using Eq. (4), we then obtain the concentration of B_1 ,

$$b_1(t) = B_0(J_2 A_0 t + 1)^{-J_1/J_2}. \quad (6)$$

So, the concentration of B_1 decreases as t^{-J_1/J_2} in the long-time limit.

Multiplying Eq. (1) with k and then summing up over all k , we can deduce the following differential equation:

$$\frac{dM_1^A}{dt} = J_1 b_1 M_0^A - J_2 M_0^A M_1^A. \quad (7)$$

Obviously, the solution of Eq. (7) is dependent on the relation between the rate constants J_1 and J_2 and, therefore, the kinetic behavior of the system has relation with the ratio of J_1 to J_2 . We then investigate the kinetic behavior of the system in three distinct cases of $J_1 > J_2$, $J_1 < J_2$, and $J_1 = J_2$.

A. $J_1 > J_2$ case

We first consider the $J_1 > J_2$ case, in which the propagation of polymers dominates over the corresponding disproportionation. In this case, Eq. (7) can be solved accurately to yield

$$M_1^A(\tau) = A_0 [C_1(1 - \tau^{1-J_1/J_2}) + 1] \tau^{-1}, \quad (8)$$

where $\tau = J_2 A_0 t + 1$ is the rescaled time variable and $C_1 = J_1 B_0 / [A_0(J_1 - J_2)]$. Equation (8) shows that the total mass of propagating radicals decreases with time and will decay to zero at $t \rightarrow \infty$ due to the continuing termination processes.

We then determine the size distribution $a_k(t)$ of propagating radicals. Substituting Eqs. (5) and (6) into Eq. (1), we can deduce the exact solution of $a_1(\tau)$ as follows:

$$a_1(\tau) = A_0 \tau^{-1} \exp[-C_1(1 - \tau^{1-J_1/J_2})]. \quad (9)$$

Again inserting Eqs. (5), (6), and (9) into Eq. (1), we can obtain the exact solution of $a_2(\tau)$. The rest can be deduced by

analogy. By employing this technique, one can obtain the exact expression

$$a_k(\tau) = \frac{A_0}{(k-1)!} \tau^{-1} [\lambda(\tau)]^{k-1} \exp[-\lambda(\tau)], \quad (10)$$

with the shorthand notation $\lambda(\tau) = C_1(1 - \tau^{1-J_1/J_2})$. Equation (10) shows that the size distribution of propagating radicals will decay to zero eventually. On the other hand, Eq. (10) also indicates that at a given time the radical size distribution can approach the famous Poisson distribution. Such an interesting phenomenon was also discovered by Lee and his co-workers [29], and their experimental result showed that the MWD of the polystyrenes approaches the Poisson distribution in the late stage of the anionic polymerization, and there are some similar results that the MWD may exhibit the Poisson distribution [30,31]. Thus, it might be reasonable that in some practical systems, free-radical propagation and disproportionation both proceed at constant rates. Moreover, Oshinin and Moreau investigated the effect of transport limitations on the homopolymerization kinetics and found that, in the early stage of polymerization, the MWD of the system with size-dependent rate kernels can also take the form of the Poisson distribution [32]. Thus, we could make a conjecture that the size distribution of propagating radicals in our model with size-dependent rate kernels might also approach the Poisson distribution in an early stage. We will defer the verification of this conjecture to a future work.

Since eventually all the free radicals will transform into inert polymers (the disproportionation products of free radicals), it is also of interest to investigate the evolution behavior of inert polymer chains. We first determine the total number and the total mass of inert polymer chains $M_0^C(t) = \sum_{j=1}^{\infty} c_j(t)$ and $M_1^C(t) = \sum_{j=1}^{\infty} j c_j(t)$. Summing up Eq. (3) over all k , we can obtain $\dot{M}_0^C(t) = J_2 [M_0^A(t)]^2$, with the exact solution $M_0^C(\tau) = A_0(1 - \tau^{-1})$. This indicates that $M_0^C(t)$ will remain at the value A_0 in the long-time limit. Similarly, multiplying Eq. (3) with k and then summing up over all k , the total mass of inert polymer chains can be obtained approximately as

$$M_1^C(\tau) \approx A_0(1 + C_1)(C_2 - \tau^{-1}), \quad (11)$$

where C_2 is an integration constant. Equation (11) indicates that the total mass of inert polymer chains will asymptotically remain at a certain quantity at large times.

By inserting Eqs. (5) and (10) into Eq. (3), we can straightforwardly determine the analytical solution of the size distribution $c_k(t)$ of inert polymer chains. It is found that the expression of $c_k(t)$ depends crucially on the relation between the rate constants J_1 and J_2 . We then deduce the analytical expression of $c_k(t)$ in three subcases of $J_2 < J_1 < 2J_2$, $J_1 = 2J_2$, and $J_1 > 2J_2$.

1. $J_2 < J_1 < 2J_2$ subcase

Substituting Eqs. (5) and (10) into Eq. (3), we can obtain the exact expression of the size distribution of inert polymer chains as follows:

$$c_k(\tau) = \frac{J_2 A_0}{C_1 (J_1 - J_2) k!} \tau^{J_1/J_2 - 2} [\lambda(\tau)]^k \exp[-\lambda(\tau)] + \frac{C_3}{k!} C_1^k k^{-J_2/(J_1 - J_2)} \int_{k\tau^{1-J_1/J_2}}^k dy \psi(y) y^{(2J_2 - J_1)/(J_1 - J_2)} + \frac{C_4}{k!} C_1^{k-1} k^{(J_1 - 2J_2)/(J_1 - J_2)} \int_{k\tau^{1-J_1/J_2}}^k dy \psi(y) y^{(3J_2 - 2J_1)/(J_1 - J_2)}, \quad (12)$$

where $C_3 = J_2 A_0 / (J_1 - J_2)$, $C_4 = C_3 (2J_2 - J_1) / (J_1 - J_2)$, and $\psi(y) = (1 - yk^{-1})^k \exp[-C_1(1 - yk^{-1})]$. It can be readily verified by numerical computations that $\int_0^k dy \psi(y) y^\eta$ will converge to a finite constant for $k \gg 1$ if $\eta > -1$. In the long-time limit, the size distribution of large inert polymers ($k \gg 1$) can be asymptotically expressed as

$$c_k(\tau) \approx \frac{C_4}{k!} C_1^{k-1} k^{(J_1 - 2J_2)/(J_1 - J_2)} \int_{k\tau^{1-J_1/J_2}}^k dy \psi(y) y^{(3J_2 - 2J_1)/(J_1 - J_2)}. \quad (13)$$

Thus, the size distribution of inert polymer chains can evolve to a steady-state form after a sufficiently long time. Moreover, for $1 \ll k \ll \tau^{J_1/J_2 - 1}$, Eq. (13) can be further rewritten as

$$c_k(\tau) \sim \frac{C_4^k}{k!} k^{(J_1 - 2J_2)/(J_1 - J_2)} \exp(-C_1). \quad (14)$$

Obviously, Eq. (14) takes the form of a Poisson-like distribution with power-law correction. Since $(J_1 - 2J_2) / (J_1 - J_2) < 0$ for this subcase, the peak position of this corrected distribution will shift to smaller k as compared to the standard Poisson distribution. Furthermore, based on the Stirling formula, $\Gamma(k+1) \sim \sqrt{2k\pi} k^k e^{-k}$, Eq. (14) can be reduced to $c_k(\tau) \sim \exp(-k \ln k + k + k \ln C_1)$. Thus, in the case of $J_1 B_0 \gg A_0 (J_1 - J_2)$, $c_k(\tau)$ asymptotically increases exponentially with k for relatively small k , then reaches a peak value at a certain size k_c , and finally decreases rapidly with k for $k > k_c$. In other words, $c_k(\tau)$ can approach a single-peak Poisson-like distribution. As for the case of $J_1 B_0 < A_0 (J_1 - J_2)$, $c_k(\tau)$ always decreases monotonically with increasing k .

2. $J_1 = 2J_2$ subcase

In this special subcase, from Eq. (3) we obtain the exact solution of the size distribution of inert polymers as follows:

$$c_k(\tau) = \frac{A_0}{C_1} \exp[-C_1(1 - \tau^{-1})] \sum_{j=k}^{\infty} \frac{[C_1(1 - \tau^{-1})]^j}{j!}. \quad (15)$$

Equation (15) shows that after a sufficiently long time, the size distribution of inert polymers can evolve to a nonzero steady-state distribution,

$$c_k(\tau) \approx \frac{A_0}{C_1} \exp(-C_1) \sum_{j=k}^{\infty} \frac{C_1^j}{j!}. \quad (16)$$

Moreover, $\sum_{j=k}^{\infty} C_1^j / j! \approx C_1^k / k!$ for $k \gg C_1$. Thus, the size distribution of large inert polymers can asymptotically exhibit the Poisson-like distribution at large times.

3. $J_1 > 2J_2$ subcase

In this subcase, the size distribution of inert polymer chains satisfies

$$c_k(\tau) = -\frac{A_0}{(k-1)!} \tau^{-1} [\lambda(\tau)]^{k-1} \exp[-\lambda(\tau)] + \frac{A_0}{(k-1)!} C_1^{k-1} k^{-J_2/(J_1 - J_2)} \int_{k\tau^{1-J_1/J_2}}^k dy \varphi(y) \left[1 - \frac{1 + C_1}{k} + \frac{C_1}{k^2} y \right] y^{J_2/(J_1 - J_2)}, \quad (17)$$

where $\varphi(y) = (1 - yk^{-1})^{k-2} \exp[-C_1(1 - yk^{-1})]$. In the region of $\tau \gg 1$ and $k \gg 1$, Eq. (17) can be asymptotically rewritten as

$$c_k(\tau) \approx \frac{A_0}{(k-1)!} C_1^{k-1} k^{-J_2/(J_1 - J_2)} \int_{k\tau^{1-J_1/J_2}}^k dy \varphi(y) y^{J_2/(J_1 - J_2)}. \quad (18)$$

Furthermore, Eq. (18) indicates that for $1 \ll k \ll \tau^{J_1/J_2 - 1}$ the size distribution of inert polymers also takes the form of Eq. (14), namely, the Poisson-like distribution with power-law correction. Similar to the above-discussed subcase of $J_2 < J_1 < 2J_2$, the large-time size distribution of inert polymers may abnormally increase along with k for a certain value range of k under the initial condition of $J_1 B_0 \gg A_0 (J_1 - J_2)$, while it decays consistently with k in the case of $J_1 B_0 < A_0 (J_1 - J_2)$. Moreover, since $(J_1 - 2J_2) / (J_1 - J_2) > 0$ for this subcase, the peak position of this corrected distribution will shift to larger k as compared to the standard Poisson distribution.

B. $J_1 < J_2$ case

We then investigate the system in which the disproportionation of polymers dominates over the corresponding propagation, namely, $J_1 < J_2$. Equation (10) is also valid for this case. In the long-time limit, Eq. (10) can be approximately reduced to

$$a_k(\tau) \approx \frac{A_0}{(k-1)!} \exp[-g(\tau)] g(\tau)^{k-1} \tau^{-1}, \quad (19)$$

where $g(\tau) = C_1 \tau^{1-J_1/J_2}$. Equation (19) also indicates that for the $J_1 < J_2$ case the radical size distribution can take the form of the Poisson distribution. This theoretical result is in qualitative agreement with the experimental results (see, e.g., Refs. [29–31]).

Then we deduce the analytical expression of the size distribution of inert polymers in the region of $\tau \gg 1$ and $k \gg 1$,

$$c_k(\tau) \approx \frac{J_2 A_0}{(J_2 - J_1)} (-C_1)^{J_2/(J_2 - J_1)} k^{-2 - J_1/(J_2 - J_1)} - f_1(\tau), \quad (20)$$

with the shorthand notation $f_1(\tau) \approx J_2 A_0 (-C_1)^{J_2/(J_2 - J_1)} [(J_2 - J_1)(k-1)!]^{-1} \exp[-g(\tau)] [g(\tau)]^{k-3 - J_1/(J_2 - J_1)}$. Obviously, $f_1(\tau)$ will tend to zero at $\tau \rightarrow \infty$. Thus, the size distribution of inert polymer chains can evolve to a nonzero steady-state form eventually; moreover, it can take the scale-free power-law form $c_k(\tau) \sim k^{-2 - J_1/(J_2 - J_1)}$ for large k .

For this case, the expression of the total number of inert polymer chains is the same as that in the $J_1 > J_2$ case, $M_0^C(\tau) = A_0(1 - \tau^{-1})$, and the total mass of inert polymer chains can be determined asymptotically at large times $M_1^C(\tau) \approx J_2 A_0 C_1 (C_5 - \tau^{-J_1/J_2}) / J_1$, where C_5 is an integration constant. This indicates that the total mass of inert polymers increases with time in the beginning of the process and then remains asymptotically at the value $J_2 A_0 C_1 C_5 / J_1$ in the long-time limit.

C. $J_1 = J_2$ case

Finally, we study the special case with the rate constant of radical disproportionation equal to the corresponding propagation rate constant. In this case, the expressions of $M_0^A(t)$ and $M_0^C(\tau)$ are both the same as those in the above $J_1 \neq J_2$ cases, and the concentration of B_1 is $b_1(t) = B_0(J_2 A_0 t + 1)^{-1}$, which decays as t^{-1} at large times. Substituting the above expression of $M_0^A(t)$ into Eq. (7), we can determine the total mass of propagating radicals,

$$M_1^A(\tau) = (B_0 \ln \tau + A_0) \tau^{-1}. \quad (21)$$

Equation (21) indicates that all the propagating radicals will die out at $t \rightarrow \infty$. Then we analyze the total mass of inert polymer chains. Multiplying Eq. (3) with k and then summing up over all k , we derive the expression $M_1^C(\tau) = A_0 + B_0 - [B_0(\ln \tau + 1) + A_0] \tau^{-1}$. Obviously, the total mass of inert polymer chains can remain at a finite quantity at large times $M_1^C(\tau) \approx A_0 + B_0$.

Introducing the generating function $G(z, t) = \sum_{k=1}^{\infty} z^k a_k(t)$, we recast Eq. (1) into

$$\frac{dG}{dt} = J_1 b_1 G(z-1) - J_2 G M_0^A. \quad (22)$$

Equation (22) can be solved exactly to yield $G(z, \tau) = A_0 z \tau^{B_0(z-1)/A_0-1}$. Expanding the expression of $G(z, \tau)$ in powers of z , one can obtain the exact expression of $a_k(\tau)$,

$$a_k(\tau) = \frac{A_0}{(k-1)!} \tau^{-\gamma-1} (\gamma \ln \tau)^{k-1}, \quad (23)$$

with the shorthand notation $\gamma = B_0/A_0$. Equation (23) shows that at a given time, the radical size distribution can also approach the Poisson distribution $a_k(\tau) \sim e^{-\gamma \ln \tau} (\gamma \ln \tau)^{k-1} / (k-1)!$.

Substituting Eq. (23) into Eq. (3), we can deduce the size distribution of inert polymer chains as follows:

$$c_k(\tau) \approx A_0 \gamma^{-1} (1 + \gamma^{-1})^{-k} - f_2(\tau), \quad (24)$$

with the shorthand notation $f_2(\tau) \approx A_0 [\gamma(k-1)!]^{-1} (1 + \gamma^{-1})^{-k} \exp[-(1 + \gamma) \ln \tau] [(1 + \gamma) \ln \tau]^{k-1}$. It is obvious that $f_2(\tau) \approx 0$ at $\tau \gg 1$. Equation (24) shows that the size distribution of inert polymers can evolve to a steady state after a sufficiently long time. Moreover, $c_k(\tau)$ decays exponentially with size k at large times $c_k(\tau) \sim \exp[-k \ln(1 + \gamma^{-1})]$. Thus, at large times, there hardly exist long inert polymer chains in the system.

To sum up, in radical propagation-disproportionation processes with constant rate kernels, the size distribution of radi-

cal chains always takes the form of the famous Poisson distribution, while that of inert polymers depends crucially on the ratio of the propagation rate constant J_1 to the disproportionation rate constant J_2 . We can conclude that (i) in the case of $J_1 > J_2$, the size distribution of inert polymers $c_k(\tau)$ can approach the Poisson-like distribution with power-law correction; (ii) in the case of $J_1 = J_2$, $c_k(\tau)$ has an exponential decay in size; and (iii) in the case of $J_1 < J_2$, $c_k(\tau)$ exhibits a power-law decay in size.

III. ANALYTICAL SOLUTION OF FREE-RADICAL PROPAGATION-COMBINATION PROCESSES

We now investigate the propagation-combination model, in which, once two propagating radicals touch each other, they will combine into one inert polymer chain. We also assume the propagation and combination abilities of a radical are independent of its chain length. For simplicity, we also set $J_1(i) = J_1$ and $J_3(i, j) = J_2$ for all i and j . The governing rate Eqs. (1) and (2) are also valid for this model, while the rate equation for inert polymer chains can be written as

$$\frac{dc_k}{dt} = \frac{J_2}{2} \sum_{i+j=k} a_i a_j. \quad (25)$$

The evolution behavior of propagating radicals in this model is the same as that in the above model with propagation and disproportionation. In this section, we only present the evolution properties of inert polymer chains.

Summing up Eq. (25), we can obtain the exact expression of the total number of inert polymer chains $M_0^C(\tau) = A_0(1 - \tau^{-1})/2$. This indicates that $M_0^C(\tau)$ will remain at the value of $A_0/2$ in the long-time limit.

Since the solution of Eq. (25) depends on the relation between the rate constants J_1 and J_2 , we then determine, respectively, the analytical expression of $c_k(t)$ in the following five cases.

A. $J_1 > 2J_2$ case

We first consider the $J_1 > 2J_2$ case, in which the propagation of polymers overwhelmingly dominates over the corresponding combination. Substituting Eq. (10) into Eq. (25), we can obtain the exact expression of $c_k(\tau)$,

$$\begin{aligned} c_k(\tau) = & -\frac{A_0}{(k-2)!} 2^{k-3} \tau^{-1} [\lambda(\tau)]^{k-2} \exp[-2\lambda(\tau)] \\ & + \frac{A_0 (2C_1)^{k-2}}{2(k-2)!} k^{-J_2/(J_1-J_2)} \int_{k\tau^{-1-J_1/J_2}}^k dy \xi(y) \\ & \times \left[1 - \frac{2(C_1+1)}{k} + \frac{2C_1}{k^2} y \right] y^{J_2/(J_1-J_2)}, \end{aligned} \quad (26)$$

where $\xi(y) = (1 - yk^{-1})^{k-3} \exp[-2C_1(1 - yk^{-1})]$. In the region of $\tau \gg 1$ and $k \gg 1$, the size distribution of inert polymer chains asymptotically approaches

$$c_k(\tau) \approx \frac{A_0}{2(k-2)!} (2C_1)^{k-2} k^{-J_2/(J_1-J_2)} \int_{k\tau^{1-J_1/J_2}}^k dy \xi(y) y^{J_2/(J_1-J_2)}. \quad (27)$$

For $1 \ll k \ll \tau^{J_1/J_2-1}$, the long-time size distribution of inert polymer chains follows the Poisson-like distribution with power-law correction,

$$c_k(\tau) \sim \frac{(2C_1)^k}{k!} k^{(2J_1-3J_2)/(J_1-J_2)} \exp(-2C_1). \quad (28)$$

Obviously, under the initial condition of $2J_1B_0 \gg A_0(J_1-J_2)$, $c_k(\tau)$ abnormally increases along with k for relatively small k , then reaches a peak value at a certain size k_c , and finally decreases consistently with k for $k > k_c$. While in the $2J_1B_0 < A_0(J_1-J_2)$ case, $c_k(\tau)$ is a monotone decreasing function of k .

B. $J_1=2J_2$ case

In this case, one can deduce the exact solution of the size distribution of inert polymer chains as follows:

$$c_k(\tau) = \frac{A_0}{4C_1} \exp[-2C_1(1-\tau^{-1})] \sum_{j=k-1}^{\infty} \frac{[2C_1(1-\tau^{-1})]^j}{j!}. \quad (29)$$

Thus, each $c_k(\tau)$ can remain at a nonzero value eventually. In the region of $\tau \gg 1$ and $k \gg 2C_1$, Eq. (29) can be rewritten as

$$c_k(\tau) \approx \frac{A_0}{4C_1(k-1)!} \exp(-2C_1)(2C_1)^{k-1}. \quad (30)$$

So, the size distribution of inert polymer chains in this case exhibits a steady-state Poisson-like distribution.

C. $J_2 < J_1 < 2J_2$ case

In this case, by substituting Eq. (10) into Eq. (25), we can obtain

$$\begin{aligned} c_k(\tau) &= \frac{A_0}{(k-1)!} C_1^{-1} 2^{k-3} (J_1/J_2 - 1)^{-1} \tau^{J_1/J_2-2} [\lambda(\tau)]^{k-1} \\ &\times \exp[-2\lambda(\tau)] + \frac{C_4}{2(k-1)!} (2C_1)^{k-2} k^{(J_1-2J_2)/(J_1-J_2)} \\ &\times \int_{k\tau^{1-J_1/J_2}}^k dy \phi(y) y^{(3J_2-2J_1)/(J_1-J_2)} \\ &+ \frac{C_3}{2(k-1)!} (2C_1)^{k-1} k^{-J_2/(J_1-J_2)} \\ &\times \int_{k\tau^{1-J_1/J_2}}^k dy \phi(y) y^{(2J_2-J_1)/(J_1-J_2)}, \quad (31) \end{aligned}$$

where $\phi(y) = (1-yk^{-1})^{k-1} \exp[-2C_1(1-yk^{-1})]$. Obviously, $(3J_2-2J_1)/(J_1-J_2) > -1$ in this case. Thus, in the region of $\tau \gg 1$ and $k \gg 1$, the size distribution of inert polymer chains can be expressed as

$$\begin{aligned} c_k(\tau) &\approx \frac{C_3}{2(k-1)!} (2C_1)^{k-2} k^{(J_1-2J_2)/(J_1-J_2)} \\ &\times \int_{k\tau^{1-J_1/J_2}}^k dy \phi(y) y^{(3J_2-2J_1)/(J_1-J_2)}. \quad (32) \end{aligned}$$

Furthermore, for $1 \ll k \ll \tau^{J_1/J_2-1}$, the size distribution of inert polymers also takes the form of Eq. (28). Thus, the evolution behavior of this case is mathematically similar to the above $J_1 > 2J_2$ case in this section.

D. $J_1=J_2$ case

Substituting Eq. (23) into Eq. (25), we can determine the size distribution of inert polymer chains for the special case of $J_1=J_2$,

$$c_k(\tau) \approx A_0 2^{k-3} \gamma^{-1} (2 + \gamma^{-1})^{1-k} - f_3(\tau), \quad (33)$$

with the shorthand notation $f_3(\tau) \approx A_0 2^{k-3} [\gamma(k-2)!]^{-1} (2 + 1/\gamma)^{1-k} \exp[-(2\gamma+1) \ln \tau] [(2\gamma+1) \ln \tau]^{k-2}$. Obviously, $f_3(\tau) \approx 0$ in the long-time limit. Thus, the size distribution of inert polymer chains will evolve to a steady state, finally. Moreover, $c_k(\tau)$ decreases exponentially with k in the region of $\tau \gg 1$ and $k \gg 1$, $c_k(\tau) \sim \exp\{-k \ln[1 + (2\gamma)^{-1}]\}$.

E. $J_1 < J_2$ case

In this case, substituting Eq. (19) into Eq. (25) yields

$$c_k(\tau) \approx \frac{J_2 A_0}{(J_2 - J_1)} (-C_1)^{J_2/(J_2-J_1)} 2^{J_1/(J_2-J_1)} k^{-2-J_1/(J_2-J_1)} - f_4(\tau), \quad (34)$$

with the shorthand notation

$$\begin{aligned} f_4(\tau) &\approx J_2 A_0 (-C_1)^{J_2/(J_2-J_1)} 2^{J_1/(J_2-J_1)} [(J_2 - J_1)(k-2)!]^{-1} \\ &\times \exp[-2g(\tau)] [2g(\tau)]^{k-4-J_1/(J_2-J_1)}. \end{aligned}$$

The value of $f_4(\tau)$ will decay to zero at $\tau \rightarrow \infty$. Equation (34) indicates that the size distribution of inert polymers can take the form of a steady-state power law at $\tau \gg 1$, $c_k(\tau) \sim k^{-2-J_1/(J_2-J_1)}$.

To sum up, in radical propagation-combination processes with constant rate kernels, the size distribution of radical chains always approaches the Poisson distribution at any time, while that of inert polymers exhibits three distinct regimes: the Poisson-like distribution with power-law correction in the $J_1 > J_2$ case, the exponential form in the $J_1 = J_2$ case, and the power-law form in the $J_1 < J_2$ case.

IV. ANALYTICAL SOLUTION OF FREE-RADICAL PROPAGATION PROCESSES WITH BOTH DISPROPORTIONATION AND COMBINATION

Finally, we study the propagation model with both disproportionation and combination, in which two propagating radical chains can form one inert polymer chain (i.e., combination) or two inert chains (i.e., disproportionation) when they come across. The kind of termination reaction depends mainly on the B -monomer's property and the reaction tem-

perature [24]. For simplicity, we assume that the rate constant of the disproportionation reaction is pJ_2 , while the rate constant of the combination reaction is $(1-p)J_2$, where $0 < p < 1$. It is obvious that this model will reduce to the propagation-disproportionation model if $p=1$ and the propagation-combination model if $p=0$. Similarly, the rate equation for the propagating radical chains is the same as Eq. (1). Thus, the evolution behavior of propagating radicals in this model is identical with that in the above-discussed models, and the rate equation for inert polymer chains can be written as

$$\frac{dc_k}{dt} = pJ_2a_k \sum_{i=1}^{\infty} a_i + \frac{(1-p)J_2}{2} \sum_{i+j=k} a_i a_j. \quad (35)$$

By using Eqs. (5) and (35), we determine the total number of inert polymer chains,

$$M_0^C(\tau) = \frac{A_0(1+p)}{2}(1-\tau^{-1}). \quad (36)$$

Equation (36) indicates that the total number of inert polymers increases with time in the beginning of the process and remains at a nonzero quantity after a sufficiently long time.

Obviously, the solution of Eq. (35) depends on the ratio of the rate constant J_1 to J_2 . We then determine, respectively, the analytical solution of $c_k(t)$ in the following five cases.

A. $J_1 > 2J_2$ case

Using Eqs. (10) and (35), we deduce the following exact solution of $c_k(\tau)$:

$$\begin{aligned} c_k(\tau) = & -\frac{A_0 p}{\tau(k-1)!} [\lambda(\tau)]^{k-1} \exp[-\lambda(\tau)] \\ & -\frac{A_0(1-p)}{\tau(k-2)!} 2^{k-3} [\lambda(\tau)]^{k-2} \exp[-2\lambda(\tau)] \\ & + \frac{A_0 p C_1^{k-1}}{k^{J_2/(J_1-J_2)}(k-1)!} \int_{k\tau^{-1/J_2}}^k dy \varphi(y) \left[1 - \frac{1+C_1}{k} \right. \\ & \left. + \frac{C_1}{k^2} y \right] y^{J_2/(J_1-J_2)} + \frac{A_0(1-p)(2C_1)^{k-2}}{2k^{J_2/(J_1-J_2)}(k-2)!} \int_{k\tau^{-1/J_2}}^k dy \xi(y) \\ & \times \left[1 - \frac{2(C_1+1)}{k} + \frac{2C_1}{k^2} y \right] y^{J_2/(J_1-J_2)}. \end{aligned} \quad (37)$$

In the long-time limit, the first two terms in the right-hand side of Eq. (37) can be ignored as compared to the other two terms. So, the size distribution of inert polymers will evolve to a steady-state distribution after a sufficiently long time. It follows from Eq. (37) that $c_k(\tau) \approx 0$ for $k \gg \tau^{1/J_2-1}$.

We then analyze the properties of the size distribution of relatively small inert polymers, which may be of more interest. For $1 \ll k \ll \tau^{1/J_2-1}$, we have $c_k(\tau) \sim k^{(J_1-2J_2)/(J_1-J_2)} \times [pC_6 C_1^k \exp(-C_1) + k(1-p)(2C_1)^k \exp(-2C_2)]/k!$ (C_6 is a constant). Thus, we can conclude that (i) under the condition of $2J_1 B_0 \leq A_0(J_1 - J_2)$, the steady-state size distribution $c_k(\infty)$ decays rapidly with k ; (ii) under the condition of $2J_1 B_0 > A_0(J_1 - J_2) \geq J_1 B_0$, the evolution of inert polymers is as-

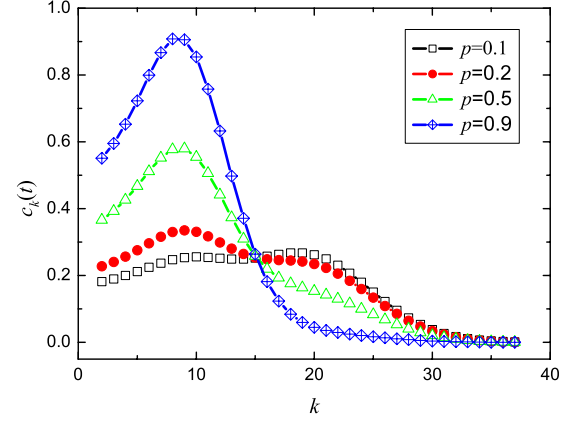


FIG. 1. (Color online) Plots of the size distribution of inert polymers $c_k(t)$ vs size k . At large times, $c_k(t)$ can take a single-peak or double-peak form for a different value of p . Here, all numerical computations have the same initial condition: $A_0=100$, $B_0=700$, and $J_1/J_2=3.0$.

ymptotically dominated by the combination of propagating radicals and $c_k(\infty)$ also decays consistently with k ; and (iii) under the condition of $A_0(J_1 - J_2) < J_1 B_0$, the disproportionation and combination of propagating radicals both play important roles and $c_k(\infty)$ exhibits a fairly complex and interesting distribution. Obviously, if $J_1 B_0 \gg A_0(J_1 - J_2)$, both the third term and the fourth term in the right-hand side of Eq. (37) increase with k for relatively small k and then, respectively, reach a peak value nonsynchronously, and, thus, the steady-state size distribution of inert polymers may approach a double-peak form. Of course, in some cases (e.g., $p \rightarrow 0$), the fourth term in the right-hand side of Eq. (37) may dominate over the third term and, hence, $c_k(\tau)$ will exhibit a single-peak structure. These arguments can be verified by numerical computations, which are illustrated in Fig. 1. As shown in Fig. 1, the size distribution of inert polymer chains can approach the interesting double-peak distribution in some cases. Moreover, we find that the size distribution of inert polymers also depends crucially on the value of p (see also Fig. 1).

B. $J_1 = 2J_2$ case

In this case, we can obtain the exact solution of the size distribution of inert polymers as follows:

$$\begin{aligned} c_k(\tau) = & \frac{A_0 p}{C_1} \exp[-C_1(1-\tau^{-1})] \sum_{j=k}^{\infty} \frac{[C_1(1-\tau^{-1})]^j}{j!} \\ & + \frac{A_0(1-p)}{4C_1} \exp[-2C_1(1-\tau^{-1})] \sum_{j=k-1}^{\infty} \frac{[2C_1(1-\tau^{-1})]^j}{j!}. \end{aligned} \quad (38)$$

In the region of $\tau \gg 1$ and $k \gg 2C_1$, Eq. (38) can be rewritten as the superposition form of two Poisson distributions,

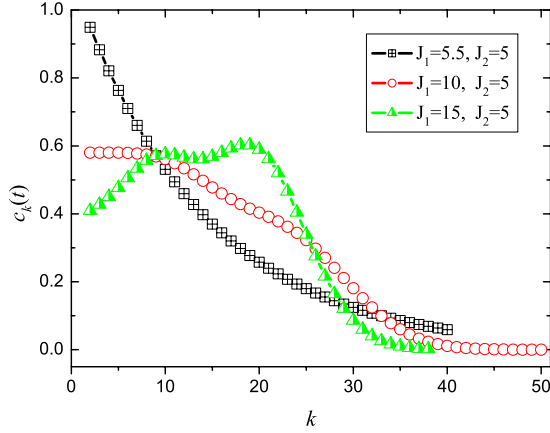


FIG. 2. (Color online) Plots of the size distribution of inert polymers $c_k(t)$ vs size k . For different ratio of J_1 to J_2 , $c_k(t)$ can take one of the three forms: monotone decreasing, single peak, and double peak. Here, all numerical computations have the same initial condition: $A_0=100$, $B_0=700$, and $p=0.1$.

$$c_k(\tau) \approx \frac{A_0 p}{k!} \exp(-C_1) C_1^k + \frac{A_0(1-p)}{4C_1(k-1)!} \exp(-2C_1) (2C_1)^{k-1}. \quad (39)$$

Thus, the evolution of inert polymers mainly depends on the details of the initial condition such as the values of p , A_0 , and B_0 .

C. $J_2 < J_1 < 2J_2$ case

In this case, the long-time size distribution of inert polymer chains is

$$c_k(\tau) \approx \frac{C_4 p}{k!} C_1^{k-1} k^{(J_1-2J_2)/(J_1-J_2)} \int_{k\tau^{-1/J_2}}^k dy \psi(y) y^{(3J_2-2J_1)/(J_1-J_2)} + \frac{C_4(1-p)}{2(k-1)!} (2C_1)^{k-2} k^{(J_1-2J_2)/(J_1-J_2)} \times \int_{k\tau^{-1/J_2}}^k dy \phi(y) y^{(3J_2-2J_1)/(J_1-J_2)}. \quad (40)$$

For $1 \ll k \ll \tau^{J_1/J_2-1}$, Eq. (40) can be rewritten asymptotically as $c_k(\tau) \sim k^{(J_1-2J_2)/(J_1-J_2)} [p C_1^k \exp(-C_1) + k(1-p) C_7 (2C_1)^k \times \exp(-2C_1)] / k!$ (C_7 is a constant). Thus, the evolution behavior of this case is mathematically the same as the above $J_1 > 2J_2$ case in this section. Of course, provided that all the other parameters (except for the two rate constants J_1 and J_2) are the same, the ratio of J_1 to J_2 will play an important role in the evolution behavior of $c_k(\tau)$ (see Fig. 2).

D. $J_1 = J_2$ case

We then investigate the $J_1 = J_2$ case. Substituting Eq. (23) into Eq. (35), we can obtain the analytical expression of $c_k(\tau)$ as follows:

$$c_k(\tau) \approx A_0 p \gamma^{-1} (1 + \gamma^{-1})^{-k} + A_0 (1-p) 2^{k-3} \gamma^{-1} (2 + \gamma^{-1})^{1-k} - f_5(\tau), \quad (41)$$

with the shorthand notation

$$f_5(\tau) \approx A_0 p [\gamma(k-1)!]^{-1} (1 + \gamma^{-1})^{-k} \exp[-(1 + \gamma) \ln \tau] \times [(1 + \gamma) \ln \tau]^{k-1} + A_0 (1-p) 2^{k-3} [\gamma(k-2)!]^{-1} \times (2 + \gamma^{-1})^{1-k} \exp[-(2\gamma + 1) \ln \tau] [(2\gamma + 1) \ln \tau]^{k-2}.$$

The value of $f_5(\tau)$ is asymptotically equal to zero at $\tau \gg 1$. Thus, the size distribution of inert polymers $c_k(\tau)$ will evolve to a steady state after a sufficiently long time. Moreover, $c_k(\tau)$ decreases exponentially with size at large times

$$c_k(\tau) \sim p \exp[-k \ln(1 + \gamma^{-1})] + (1-p)(2 + \gamma^{-1}) \times \exp[-k \ln[1 + (2\gamma)^{-1}]] / 8.$$

E. $J_1 < J_2$ case

In this case, we can obtain the size distribution of inert polymer chains by substituting Eqs. (5) and (19) into Eq. (35),

$$c_k(\tau) \approx \frac{J_2 A_0 (-C_1)^{J_2/(J_2-J_1)}}{(J_2 - J_1)} k^{-2-J_1/(J_2-J_1)} [(1-p) 2^{J_1/(J_2-J_1)} + p - f_6(\tau)], \quad (42)$$

with the shorthand notation

$$f_6(\tau) \approx 2^{J_1/(J_2-J_1)} [(1-p)/(k-2)!] \exp[-2g(\tau)] \times [2g(\tau)]^{k-4-J_1/(J_2-J_1)} + [p/(k-1)!] \times \exp[-g(\tau)] [g(\tau)]^{k-3-J_1/(J_2-J_1)}.$$

Obviously, $f_6(\tau) \approx 0$ at $\tau \gg 1$, and the size distribution of inert polymers has a steady-state power-law decay at large times $c_k(\tau) \sim k^{-2-J_1/(J_2-J_1)}$.

To sum up, in racial propagation processes with both disproportionation and combination, the size distribution of radical chains always exhibits the Poisson distribution, while that of inert polymers depends strongly on the relation between the rate constants J_1 and J_2 as well as initial condition (the values of p , A_0 , and B_0). If $J_1 < J_2$, the size distribution of inert polymers $c_k(\tau)$ always takes the power-law form. If $J_1 = J_2$, $c_k(\tau)$ decays exponentially with size. If $J_1 > J_2$, $c_k(\tau)$ can approach one of the three distinct forms: monotone decreasing, single peak (Poisson-like distribution), and double peak, which depends on the details of initial condition.

V. SUMMARY

We have proposed a simple kinetics model for free-radical polymerization processes, in which propagating radicals can grow via propagation and can also be annihilated by termination (disproportionation or combination). Considering the case in which each polymer's propagation and termination abilities are independent of its length, we then studied the kinetic behavior of the model on the basis of the mean-field rate equations. The results showed that the size distribution of propagating radicals and that of inert polymer chains are dependent strongly on the details of the reaction-rate kernels.

For the model with propagation and disproportionation, the size distribution of propagating radicals approaches the Poisson distribution, while that of inert polymers $c_k(t)$ can

evolve to a steady state after a sufficiently long time. At large times, $c_k(t)$ has the form of a power law in the $J_1 < J_2$ case, while it decreases exponentially with size in the $J_1 = J_2$ case. Most intriguingly, in the $J_1 > J_2$ case, $c_k(t)$ can take the form of a single-peak Poisson-like distribution or has a monotonic rapid decay in size, which depends crucially on the details of the initial condition including initial concentrations and reaction rates. For the propagation and combination model, we have found similar results for propagating radicals and inert polymers.

Finally, we have also studied the propagation-termination model, in which two different termination reactions can simultaneously occur. The results for propagating radicals are the same as those in the model only with disproportionation

or combination, while inert polymers have more complex evolution behaviors. The size distribution of inert polymers can take a power-law form in the $J_1 < J_2$ case and can approach an exponential decay in the $J_1 = J_2$ case, while it can also exhibit a double-peak structure or a single-peak Poisson-like distribution in the $J_1 > J_2$ case (see Figs. 1 and 2).

ACKNOWLEDGMENTS

This project was supported by the National Natural Science Foundation of China under Grants No. 10775104 and No. 10305009.

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