

# GELATION OF A REVERSIBLE MARKOV PROCESS OF POLYMERIZATION

**Dong Han**

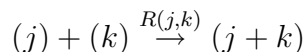
Department of Mathematics, Shanghai Jiao Tong University  
Shanghai 200030, P. R. China  
donghan@mail.sjtu.edu.cn

## **Abstract**

A reversible Markov process as a chemical polymerization model which permits the coagulation and fragmentation reactions is considered. We present a necessary and sufficient condition for the occurrence of a gelation in the process. We show that a gelation transition may or may not occur, depending on the value of the fragmentation strength, and, in case the gelation takes place, a critical value for the occurrence of the gelation and the mass of the gel can be determined by close forms.

## **1 Introduction**

For systems of interacting polymers evolving through the irreversible aggregation reaction



whereby polymers of lengths  $j$  and  $k$  link themselves together to form a polymer of length  $j+k$  (the number  $R(j,k)$  denotes the corresponding reaction rate), the standard approach is through Smoluchlovski's coagulation equations to describe the coupled evolution of the densities  $c_j(t)$  of polymers made up of  $j$  units ( $j = 1, 2, 3, \dots$ ) in an infinite-volume homogeneous system (Ziff, Ernst and Hendriks 1983 and Ball, Carr and Penrose 1986). An alternative approach allowing a more detailed description has been pioneered by Marcus (1968) and studied in detail by Lushnikov (1978), which is the

stochastic counterpart of Smoluchlovski's coagulation equations, namely the Marcus-Lushnikov coagulation model or process. The connection between the two models is as follows: let  $N_1(t), N_2(t), \dots, N_N(t)$  be the random variables denoting the numbers of monomers, dimers, ...,  $N$ -mers at time  $t$  in Marcus-Lushnikov process, then the expected values  $(1/V)E[N_j(t)]$  should coincide in the thermodynamic limit  $N \rightarrow \infty, V \rightarrow \infty$  and  $N/V = \rho$  with the densities  $c_j(t)$  of Smoluchlovski's model (see Hendriks, E. M., Spouge, J. L., Eibl, M and Schreckenber, M. 1985). Various aspects of the two models have been extensively studied by many authors (see refs.[3], [5], [8], [12], [15], [19], [21], [25], [27], [29-30] and [42-46]). Recently, rigorous mathematics was brought to bear on the two models making the cooperation between mathematics and physics more fruitful. For readers who are interested in the mathematical aspects of the models, we recommend the survey paper of Aldous (1999).

Perhaps what makes the two models both interesting and difficult is the possible occurrence of a gelation, the density dropping phenomenon, within a finite time. In the Smoluchlovski's model this manifests by an apparent lack of conservation of the density of units:

$$\sum_{j=1}^{\infty} j c_j(t) < \sum_{j=1}^{\infty} j c_j(0) \quad (1)$$

for  $t > t_c$ , where  $t_c$  is a critical time of gelation transition. This density dropping phenomenon seems to contradict the fact that particles are neither created nor destroyed, but the contradiction is resolved once one realizes that the left-hand side of (1) represents only the contribution of all polymers of finite length to the total density of units. This is also interpreted as an indication of the formation of gel, or an infinite size cluster (see refs.[7], [9], [20], [24], [26], [34], [39] and [47-49]). Gelation in the case  $R(j, k) = jk$  is known to be equivalent to the emergence of a giant component in the random graph theory, a result which was initiated by Erdős-Rényi (1960) and extensively studied by many authors ([2], [6], [22] and [31-32]).

For Smoluchlovski's model the kinetic theory of polymerization does not contain the equilibrium theory of Flory (1953) and Stockmayer (1943) as a limiting case for large values of the time, due to the absence of fragmentation effects. In fact, as clusters are growing in size, break-up processes become more important, and the irreversible coagulation reaction should be replaced by coagulation-fragmentation reaction. Van Dongen and Ernst (1983, 1984) and Spouge (1984) are the first ones to extend Smoluchlovski's coagulation equations by including fragmentation reaction. Since then, many studies about the kinetic equations and its stochastic counterpart containing

the combined effects of coagulation and fragmentation have been done (see refs.[4], [10-11], [16-18], [23], [36], [40-41] and [44] ).

Although there are many studies devoted to the deterministic and stochastic models based on the coagulation-fragmentation reaction of polymerization, the kinetic model of reversible polymerization proposed by Van Dongen and Ernst (1984) and its stochastic counterpart have received minimal attention. It is worthwhile to study the kinetic model of reversible polymerization in order to predict the occurrence of a gelation transition, depending on the value of the fragmentation strength, in the equilibrium theory of Flory and Stockmayer.

This paper investigates the gelation problem in a stochastic counterpart of the kinetic model of reversible polymerization. The main objective of this paper is to present a necessary and sufficient condition for the occurrence of a gelation. Section 2 gives the description of a reversible Markov process of polymerization considered in the paper. A necessary and sufficient condition for the occurrence of a gelation is proved in Section 3. Some applications, including two examples and a proposition, are contained in Section 4. The paper concludes in Section 5, with some discussions on the gelation.

## 2 A Reversible Markov Process of Polymerization

As in [8] and [41], we restrict our discussion on homogeneous systems of polymers where diffusion effects are ignored. We also assume that intramolecular reactions do not occur, and therefore only branched-chain (non-cyclic) polymers are formed and all un-reacted functional groups are equally reactive. A state of a finite homogeneous system of polymers of lengths 1, 2, 3, ...,  $N$  in the volume  $V$  is described by a vector  $\underline{n} = (n_1, n_2, \dots, n_k, \dots, n_N)$ , the  $k$ th component of which is the number of  $k$ -mers. Now define, as in [17], a Markov process of polymerization as follows: the process, denoted by  $\{M_N(t), t \geq 0\}$ , is a continuous-time Markov process on the state space

$$\Omega_N = \{ \underline{n} \in \{0, 1, 2, \dots, N\}^N : \sum_{k=1}^N kn_k = N \} \quad (2)$$

with transition rates

$$Q_{\underline{n} \underline{n}'} = \begin{cases} \frac{R(k,l)}{N^2} n_k n_l, & \underline{n}' = n_{kl}^+, \quad k \neq l \\ \frac{R(k,l)}{N^2} n_k (n_k - 1), & \underline{n}' = n_{kl}^+, \quad k = l \\ \frac{F(k,l)}{N} n_{k+l}, & \underline{n}' = n_{kl}^- \\ 0 & \text{otherwise} \end{cases} \quad (3)$$

where

$$\begin{aligned} n_{kl}^+ &= \{n_1, \dots, n_k - 1, \dots, n_l - 1, \dots, n_{k+l} + 1, \dots, n_N\} \\ &\quad \text{if } k \neq l, \\ n_{kl}^+ &= \{n_1, \dots, n_k - 2, \dots, n_{2k} + 1, \dots, n_N\} \\ &\quad \text{if } k = l, \\ n_{kl}^- &= \{n_1, \dots, n_k + 1, \dots, n_l + 1, \dots, n_{k+l} - 1, \dots, n_N\} \\ &\quad \text{if } k \neq l, \\ n_{kl}^- &= \{n_1, \dots, n_k + 2, \dots, n_{2k} - 1, \dots, n_N\} \\ &\quad \text{if } k = l. \end{aligned}$$

In (3),  $R(k, l)$  represents the coagulations rate which describe the congelation process linking  $k$ -mers and  $l$ -mers to form  $(k + l)$ -mers,  $F(k, l)$  represents the fragmentation rate which describe the fragmentation process from  $(k + l)$ -mers to  $k$ -mers and  $l$ -mers, and  $R(k, l)$  and  $F(k, l)$  satisfy the following detailed balance condition (see Van Dongen and Ernst 1984):

$$R(k, l) f(k) f(l) = \lambda F(k, l) f(k + l) \quad (4)$$

where  $\frac{1}{\lambda}$  ( $\lambda > 0$ ) represents the fragmentation strength and  $k! f(k)$  denotes the number of distinct ways of forming a  $k$ -mers from  $k$  distinguishable units. The equation (4) states that the number of distinct ways for  $(k + l)$ -mers to break up into  $k$ -mer and  $l$ -mers ( $\lambda F(k, l) f(k + l)$ ) equals the number of bonds between  $(k)$  and  $(l)$  clusters in  $(k + l)$ -mer configurations ( $R(k, l) f(k) f(l)$ ). The choice of  $Q_{\underline{n} \underline{n}'}$  reflects the fact that in the homogeneous system (ignoring diffusion effects), reaction occurs with a probability proportional to the number of reactants and inversely proportional to the volume; here the density is taken to be equal to one, so that the volume coincides with the total number of units  $N$ .

As has been shown in [17] that the Markov process  $\{M_N(t), t \geq 0\}$  is a reversible Markov chain and has a unique stationary distribution:

$$P_N(\underline{n}) = \frac{1}{\pi_N} \prod_{k \geq 1} \frac{[\frac{N}{\lambda} f(k)]^{n_k}}{n_k!}, \quad \underline{n} \in \Omega_N, \quad (5)$$

where

$$\pi_N = \pi_N\left(\frac{N}{\lambda}\right) = \sum_{\underline{n} \in \Omega_N} \prod_{k \geq 1} \frac{\left[\frac{N}{\lambda} f(k)\right]^{n_k}}{n_k!}. \quad (6)$$

$\pi(N)$  is usually called the partition function of the process. It has an integral formula

$$\pi_N = \pi_N\left(\frac{N}{\lambda}\right) = \frac{1}{2\pi i} \int_{\Gamma} \exp\left\{\frac{N}{\lambda} F(x) - N \log x\right\} x^{-1} dx \quad (7)$$

where  $\Gamma$  denotes a contours surrounding the origin  $x = 0$  and the series  $F(x)$

$$F(x) = \sum_{k=1}^{\infty} f(k) x^k \quad (8)$$

has a positive radius,  $r$ , of convergence, that is  $F(x) < \infty$  for  $0 \leq x < r$ .

### 3 A Necessary and Sufficient Condition for Gelation

In this section we first give a definition of a gelation in the reversible Markov process of polymerization.

**Definition 1.** *Let  $N_k$  be a random number of  $k$ -mers and  $E(\cdot)$  denotes the expectation corresponding to the stationary probability distribution  $P_N(\cdot)$  in (5). We say that there is a gelation in the reversible polymerization process, or the reversible polymerization process has a gelation, if and only if there is a critical value  $\lambda_c > 0$  such that*

$$\lim_{N \rightarrow \infty} \frac{1}{N} \sum_{k=1}^N k E(N_k) = 1 \quad (9)$$

for  $\lambda \leq \lambda_c$  and

$$\lim_{N \rightarrow \infty} \frac{1}{N} \sum_{k=1}^N k E(N_k) < 1 \quad (10)$$

for  $\lambda > \lambda_c$ .

Note that the definition above is the same as usually used in physical literature. Other definitions of gelation can be found in refs. [1], [7] and [23]. If we denote the mass of the sol and gel by  $S(\lambda)$  and  $G(\lambda)$  respectively, then

$$S(\lambda) + G(\lambda) = 1$$

and

$$G(\lambda) = 1 - M(\lambda) = 1 - \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{k=1}^N kE(N_k). \quad (11)$$

Thus,  $G(\infty) = \lim_{\lambda \rightarrow \infty} G(\lambda)$  can be defined as the maximum mass of the gel.

**Theorem 1** *If there exists a gelation in the reversible polymerization process, then*

$$F'(r) < \infty, \quad F''(r) = \infty \quad (12)$$

and the critical value  $\lambda_c$  satisfies

$$\lambda_c \geq rF'(r) \quad (13)$$

We now mention our main results in the following theorem.

**Theorem 2** *Let  $f(k) = c_k r^{-k} k^{-\beta}$ , where  $c_k > 0$  and  $c_k \rightarrow c > 0$  as  $k \rightarrow \infty$ . Then a necessary and sufficient condition for the occurrence of a gelation in the process is that the number  $\beta$  satisfies*

$$2 < \beta < 3. \quad (14)$$

Moreover, the critical value  $\lambda_c$ , of gelation satisfies  $\lambda_c = rF'(r)$  and

$$S(\lambda) = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{k=1}^N kE(N_k) = 1$$

for  $\lambda \leq \lambda_c$  and

$$S(\lambda) = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{k=1}^N kE(N_k) = \frac{\lambda_c}{\lambda} + [1 - \frac{\lambda_c}{\lambda}](3 - \beta)\Gamma(3 - \beta) < 1 \quad (15)$$

for  $\lambda > \lambda_c$ .

**Remark 1.** For  $\lambda > \lambda_c$ , we have

$$\begin{aligned} G(\lambda) &= 1 - M(\lambda) = 1 - \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{k=1}^N kE(N_k) \\ &= [1 - \frac{rF'(r)}{\lambda}][1 - (3 - \beta)\Gamma(3 - \beta)]. \end{aligned}$$

Moreover, the function  $M(\lambda)$  is continuous on  $[0, \infty)$  and  $M'(\lambda)$  is discontinuous at  $\lambda = \lambda_c$ . In particular,  $G(\infty) = \lim_{\lambda \rightarrow \infty} G(\lambda) = 1 - (3 - \beta)\Gamma(3 - \beta)$ , which being the maximum mass of the gel and only depending on  $\beta$ .

**Remark 2.** With no rigorous argument we can see from (17) that there is no gelation when  $\beta = 2$  or  $\beta = 3$  since  $\Gamma(1) = 1$  and  $\lim_{\beta \rightarrow 3} (3 - \beta)\Gamma(3 - \beta) = 1$ .

## 4 Applications

In this section we show two examples and a proposition.

**Example 1.**  $RA_a$  model ( $a \geq 3$ ).

The numbers  $f(k)$  for  $RA_a$  model have been calculated already by Stockmayer:

$$f(k) = \frac{a^k[(a-1)k!]}{k![(a-2)k+2]}.$$

Since the coagulation coefficients

$$R(i, j) = [(a-2)i+2][(a-2)j+2],$$

the fragmentation coefficients  $F(i, j)$  can be taken as in Van Dongen and Ernst (1984):

$$\sum_{i+j=k} F(i, j) = \frac{2}{\lambda}(k-1).$$

Hence

$$2(k-1)f(k) = \sum_{i+j=k} R(i, j)f(i)f(j).$$

We can calculate (see ref. [17]) that  $\beta = 5/2$ ,  $c_k \rightarrow \sqrt{(a-1)/[2\pi(a-2)^5]}$ ,

$$r = \lim_{k \rightarrow \infty} \frac{f(k)}{f(k+1)} = \frac{(a-2)^{(a-2)}}{a(a-1)^{(a-1)}}$$

and  $\lambda_c = rF'(r) = (a-1)/[a(a-2)^2]$ . Thus the mass of gelation for  $\lambda > \lambda_c$  is

$$G(\lambda) = \left[1 - \frac{(a-1)}{\lambda a(a-2)^2}\right] \left[1 - \frac{\sqrt{\pi}}{2}\right]$$

and the maximum mass of gelation  $G(\infty) = 1 - \frac{\sqrt{\pi}}{2}$ .

**Example 2.**  $RA_\infty$  model.

For  $RA_\infty$  model we have  $f(k) = k^{k-2}/k!$  and  $R_{ij} = ij$ . It can be checked (see ref. [17]) that  $\beta = 5/2$ ,  $r = e^{-1}$ ,  $c_k \rightarrow 1/\sqrt{2\pi}$  and  $\lambda_c = rF'(r) = 1$ . Thus

$$G(\lambda) = \left[1 - \frac{1}{\lambda}\right] \left[1 - \frac{\sqrt{\pi}}{2}\right]$$

for  $\lambda > \lambda_c$  and  $G(\infty) = 1 - \frac{\sqrt{\pi}}{2}$ .

To model surface interactions, the coagulation and fragmentation coefficients can be taken as

$$R(i, j) = i^\sigma j^\sigma$$

and

$$\sum_{i+j=k} F(i, j) = \frac{2}{\lambda}(k-1)^\sigma, \quad (16)$$

where  $\sigma \geq 0$ . Note that  $k^\sigma - 1$  proposed by van Dongen and Ernst (1984) has been replaced by  $(k-1)^\sigma$ . When  $\sigma = 1$ , the model has been well studied by van Dongen and Ernst (1984).

Assume that the positive numbers  $f(k)$  satisfies (4), and therefore

$$2(k-1)^\sigma f(k) = \sum_{i+j=k} i^\sigma j^\sigma f(i) f(j). \quad (17)$$

We now present a proposition in the following.

**Proposition 1.** *If the numbers  $f(k)$  satisfies (21) and its convergence radius  $r$  is positive, then a necessary and sufficient condition for the occurrence of a gelation is*

$$\frac{1}{2} < \sigma < \frac{3}{2} \quad (18)$$

and

$$\sum_{k=1}^{\infty} k^{1+\sigma} f(k) r^k = \infty. \quad (19)$$

Moreover, the critical value of the gelation satisfies  $\lambda_c = rF'(r)$  and

$$G(\lambda) = \left[1 - \frac{\lambda_c}{\lambda}\right] \left[1 - \left(\frac{3}{2} - \sigma\right) \Gamma\left(\frac{3}{2} - \sigma\right)\right] \quad (20)$$

for  $\lambda > \lambda_c$  and  $\frac{1}{2} < \sigma < \frac{3}{2}$ .

## 5 Summary and Discussion

As can be seen that the necessary and sufficient condition for gelation in the paper is mainly based on the assumption that  $f(k)$  is of the form  $c_k r^{-k} k^{-\beta}$

or  $r^k f(k) = O(1/k^\beta)$ . It is known that many polymer models such as  $RA_a$ ,  $RA_\infty$  and  $A_aRB_b$  are of the form. When  $2 < \beta < 3$ ,  $r^k f(k) = O(1/k^{\alpha+1})$  is corresponding to Lévy stable densities  $p_\alpha(x)$ , where  $\alpha = \beta - 1$ , since Lévy stable densities are asymptotically of the form  $1/x^{\alpha+1}$ . If one extends the condition, for example  $\beta \geq 3$ , then the definition of a gelation in (9) and (10) must be modified.

For the coagulation rate kernels  $R(j, k) = j^\sigma k^\sigma$ , there exist a gelation when  $1/2 < \sigma \leq 1$  and instantaneous gelation when  $\sigma > 1$  in irreversible polymer model (Jeon 1999). Comparing this with Proposition 1 we see that the property of gelation in irreversible polymer model is different from that one in the reversible polymer model especially when  $1 < \sigma < 1 + 1/2$ .

By the results of this paper we can draw a conclusion that the reversible Markov process of polymerization is more complete than the deterministic counterpart (the kinetic model of reversible polymerization proposed by Van Dongen and Ernst 1984), in the sense that it allows the investigation of finite-size effects and fluctuations.

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