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Kinetics of copolymerisation and gelation

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Abstract. The kinetic equation for a copolymerisation system is established following Flory's two assumptions. We solve the kinetic equation for the $A_f + A_2$ system with arbitrary initial conditions. The exact solution for a copolymerisation system with constant deposition is also obtained. The post-gel solutions corresponding to Stockmayer's and Flory's models are investigated. The pre-gel solution to the kinetic equation for the $A_f + A_g$ system with arbitrary initial conditions is given.

1. Introduction

The statistical theory of condensation polymerisation was established many years ago. For some simple models, Flory (1936) obtained the size distribution using a probability argument. Later a more elaborate statistical method was used by Stockmayer (1943) and the size distribution, as well as the gelation condition, were obtained for a general f -functionality system, the system with $A_f + A_2$ basic units and the system with $A_f + A_2 + B_2$ basic units. Stockmayer (1944, 1952) also established a theory of condensation polymerisation systems with arbitrary functionalities.

In the appendix of the paper by Stockmayer (1943), the author mentioned that the size distribution for an f -functionality system can be derived from the kinetic equation written by him. The kinetic equation written by Stockmayer is a special case of the general coagulation equation

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_j K_{kj} c_j \quad (1)$$

where $c_k(t)$ is the concentration of k -mer at time t . The two terms on the right-hand side of the equation are the usual gain and loss terms.

Equation (1) was first established by Smoluchowski (1916), and has been investigated by many authors since. Because of the applications of the coagulation equation in aerosol physics, the continuous version of equation (1) has been studied extensively (Drake 1972). For the development connected with the exact solution of the discrete equation, for some special kernels and the exact solution for arbitrary initial conditions see McLeod (1962), van Dongen and Ernst (1983, 1984), Ziff *et al* (1983), Bak and Lu (1987) and Lu (1987).

Obviously, the Smoluchowski equation discussed above can only describe the coagulation process in a system, where the particles are composed of only one kind

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of basic units. The coagulation equation for multicomponent systems has been investigated by some authors. Gelbard and Seinfeld (1978) investigated the multicomponent aerosol balance equation including coagulation and growth, and the kinetic equation with a constant coagulation coefficient and linear growth laws was solved. The coagulation equation for the two-component system was investigated by Lushnikov (1976). Lushnikov considered the case when the collision frequency is independent of the particle composition, but remains dependent on the total masses of the coagulation particles. The multicomponent coagulation equation is generally difficult to solve, but it is useful in establishing kinetic theories concerned with various interesting phenomena.

In this paper, we study the kinetics of copolymerisation, i.e. coagulation in a system with two kinds of basic units. After the work of Stockmayer, the $A_f + A_2$ and $A_f + A_g$ systems for antibody-antigen reactions were also investigated by Goldberg (1952a, b). Macken and Perelson (1985) reviewed and extended the results for multicomponent mixtures by using branching theory, combined with a rate-equation approach, which gives an explicit expression for the extension of a reaction as a function of time.

The essence of the branching theory, as pointed out by Whittle (1965), is a disguised treatment of certain combinatorial problems. The question is, firstly, to see if we can obtain the explicit size distribution directly from the kinetic equation and, secondly, to see if the kinetic theory can give some results which may not be easy to obtain by using statistical methods and branching theory. Following Flory's assumption of equal reactivities, the detailed forms of the coagulation equations corresponding to the system containing particles composed of A_f and A_g basic units, and the system containing particles composed of A_f and B_g basic units, are ascertained. Then we define the moments and derive a general equation for the moments before 'gelation'. We solve the equation with polydisperse initial conditions and give the general solution in terms of a configuration number determined by a recursive relation. For a special kind of polydisperse initial conditions, for which all the initial particles are of only two kinds, one containing only f -functionality units with a size distribution $c_{k0}(0)$, and the other containing only bifunctional units with size distribution $c_{01}(0)$, we obtain the explicit form of the size distribution. In addition, we also consider a case with deposition and an explicit solution is obtained. We also obtain the post-gel solution corresponding to the Flory and the Stockmayer models respectively. Finally, the kinetic equation for the system $A_f + A_g$ is solved and the pre-gel solution is given. Before ending this introduction, we want to mention the shortcomings of the kinetic description of polycondensation based on Flory's two assumptions. It neglects the excluded-volume effects between growing molecules and the change in local viscosity due to polymerisation.

2. Kinetic equation and moments

The general form of the kinetic equation for a copolymerisation system can be written as

$$\frac{dc_{kl}}{dt} = \frac{1}{2} \sum_{\substack{i+j=k \\ p+q=l}} K_{ip,jq} c_{ip} c_{jq} - c_{kl} \sum_{i,p} K_{kl,ip} c_{ip} \quad (2)$$

where $c_{kl}(t)$ is the concentration of the particles for which the number of one kind of

basic units is k , and the number of another kind of basic units is l . $K_{ip,jq}$ is a rate constant for the irreversible reaction between molecules ip and molecules jq .

The detailed form of the rate constant $K_{ip,jq}$ depends on the model we consider. The simplest model is the one in which the basic units all have the same kind of functionalities. Considering this simple model, we have two kinds of systems: the $A_f + A_g$ system and the $A_f + B_g$ system. Following the assumption of equal reactivity, i.e. that reactivities of the identical functionalities are independent of the size of the polymer, we have

$$K_{ip,jq} = \sigma_{ip}\sigma_{jq} \quad (3)$$

$$K_{ip,jq} = \sigma_{ip}(A)\sigma_{jq}(B) + \sigma_{ip}(B)\sigma_{jq}(A) \quad (4)$$

corresponding to the $A_f + A_g$ and the $A_f + B_g$ models, respectively. In (3) σ_{ip} is the number of free functionalities of ip molecules and we obtain easily that

$$\sigma_{ip} = (f-2)i + (g-2)p + 2. \quad (5)$$

In (4), $\sigma_{ip}(A)$ is the number of free functionalities of type A in ip molecules, and $\sigma_{ip}(B)$ is the number of free functionalities of type B in the ip molecules. We have

$$\sigma_{ip}(A) = (f-1)i - p + 1 \quad (6)$$

$$\sigma_{ip}(B) = (g-1)i - p + 1. \quad (7)$$

The special model which Stockmayer investigated is the system $A_f + A_2$; in this case we have

$$\sigma_{kl} = (f-2)k + 2 = \sigma_k \quad (8)$$

and the corresponding kinetic equation can be written as

$$\frac{dc_{kl}}{dt} = \frac{1}{2} \sum_{\substack{i+j=k \\ p+q=l}} [(f-2)i+2][(f-2)j+2]c_{ip}c_{jq} - [(f-2)k+2]c_{kl} \sum_{i,p} [(f-2)i+2]c_{ip}. \quad (9)$$

Obviously, in writing equations (2) and (9), Flory's second assumption, i.e. the neglect of ring formation, has been used.

In this paper, we concentrate on solving the kinetic equation (9) and the kinetic equation

$$\begin{aligned} \frac{dc_{kl}}{dt} = \frac{1}{2} \sum_{\substack{i+j=k \\ p+q=l}} [(f-2)i+(g-2)p+2][(f-2)j+(g-2)q+2]c_{ip}c_{jq} \\ - c_{kl} \sum_{i,p} [(f-2)k+2+(g-2)l+2][(f-2)i+(g-2)p+2]c_{ip}. \end{aligned} \quad (10)$$

The kinetic equation for the $A_f + B_g$ system can then be solved in the same way.

To investigate the fundamental behaviour of the copolymerisation system, the evolution of the moments is useful. We define the moments as

$$M_{mn} = \sum_{k,l} k^m l^n c_{kl}(t). \quad (11)$$

We have $M_{00} = \sum_{k,l} c_{kl}(t)$, which is obviously the total number of molecules at time t , and $M_{01} + M_{10}$ which is the total number of basic units in the system. Multiplying (2) by $k^m l^n$ summing over all possible k, l and rearranging the terms, we have the moment equation

$$\frac{dM_{mn}}{dt} = \frac{1}{2} \sum_{i,j,p,q} [(i+j)^m (p+q)^n - i^m p^n - j^m q^n] K_{ip,iq} c_{ip} c_{jq}. \quad (12)$$

This equation is only valid up to a 'gel point', at which the conservation of mass will be violated.

3. The size distribution for the $A_f + A_2$ system with polydisperse initial conditions

We consider the kinetic equation (9) with initial conditions

$$c_{kl}(t=0) = c_{kl}(0). \quad (13)$$

Introducing the following transformations:

$$c_{kl} = x_{kl} \exp\left(-\sigma_{kl} \int_0^t \mu(t') dt'\right) \quad (14)$$

$$\tau = \int_0^t \exp\left(-2 \int_0^{t'} \mu(t'') dt''\right) dt' \quad (15)$$

where $\mu(t) = \sum_{k,l} c_{kl} \sigma_{kl}$ is the total number of free functionalities, we then have

$$\frac{dx_{kl}}{d\tau} = \frac{1}{2} \sum_{\substack{i+j=k \\ p+q=l}} [(f-2)i+2][(f-2)j+2] x_{ip} x_{jq} \quad (16)$$

which has the following solution:

$$x_{kl} = \sum_{h=1}^{k+l} N_{klh} \tau^{h-1}. \quad (17)$$

Substituting (17) into (16) and comparing the coefficients of the same power of τ , we have the recursive relation

$$(h-1)N_{klh} = \frac{1}{2} \sum_{\substack{i+j=k \\ p+q=l \\ e+g=h}} [(f-2)i+2][(f-2)j+2] N_{ipe} N_{jqg} \quad (18)$$

with $N_{kl1} = c_{kl}(0)$.

Before gelation, we have

$$d\mu/dt = -\mu^2 \quad (19)$$

$$\mu = \mu_0 / (1 + \mu_0 t). \quad (20)$$

Hence we have

$$c_{kl} = \sum_{h=1}^{k+l} N_{klh} \left(\frac{t}{1 + \mu_0 t}\right)^{h-1} (1 + \mu_0 t)^{-[(f-2)k+2]} \quad (21)$$

where $\mu_0 = \sum_{k,l} c_{kl}(0) \sigma_{kl}$ is determined by the initial conditions. N_{klh} and the recursive relation (18) have a physical explanation. N_{klh} is the configuration number of aggregates composed of k f -functionality units and l bifunctional units, and h initial particles. Because the aggregate is composed of h initial particles, it has $(h-1)$ new bonds. It can be separated in $(h-1)$ places into two particles. One is composed of i f -functionality units, p 2-functionality units and e initial particles, and the other is composed of j f -functionality units, q 2-functionality units and g initial particles, with $i+j=k$, $p+q=1$, $e+g=h$. The right-hand side of (18) is the total number of ways we can separate the molecule, which is equal to $(h-1)$ times the number of ways the reverse process to build up the kl molecule out of h initial particles can be performed.

One of the special kinds of polydisperse initial conditions is that for which in the initial state there are only two special kinds of particles, one containing f -functionality units only with the size distribution $c_{k0}(0)$ and the other containing bifunctional units only with the size distribution $c_{01}(0)$. For these special initial conditions, we can obtain an explicit solution written in a compact form:

$$c_{kl} = \sum_{\{n_j\}, \{r_j\}} \frac{[(f-2)k+m+n]!}{[(f-2)k+2] \prod_j n_j! \prod_j r_j!} \prod_j \{[(f-2)j+2]c_{j0}(0)\}^{n_j} \prod_j (2c_{0j}(0))^{r_j} \times \left(\frac{t}{1+\mu_0 t}\right)^{n+m-1} \left(\frac{1}{1+\mu_0 t}\right)^{(f-2)k+2} \tag{22}$$

where the summation goes over all possible $\{n_j\}, \{r_j\}$, which satisfy $\sum_j jn_j = k, \sum_j jr_j = l$ and $m = \sum_j n_j, n = \sum_j r_j$. The mathematics required to obtain (20) is given in the appendix.

It is interesting to look at some special cases of (22). When $c_{k0}(0) = N\delta_{k1}$ and $c_{01} = L\delta_{11}$, the result becomes

$$c_{kl} = \frac{[(f-1)k+l]!}{[(f-2)k+2]! k! l!} f(fN)^k (2L)^l \left(\frac{t}{1+(fN+2L)t}\right)^{k+l-1} \times \left(\frac{1}{1+(fN+2L)t}\right)^{(f-2)k+2} \tag{23}$$

which agrees with the result obtained by using a statistical method and branching theory. The other special case is $c_{k0}(t=0) = c_{k0}(0)$ and $c_{01}(t=0) = 0$. This is the case of a single-parameter coagulation equation with polydisperse initial conditions. From the appendix, it is not difficult to obtain the result

$$c_k(t) = \frac{1}{[(f-2)k+2]!} \sum_{\{n_j\}} \frac{[(f-2)k+m]!}{\prod_j n_j!} \left(\frac{1}{1+\mu_0 t}\right)^{(f-2)k+m+1} t^{m-1} \prod_j [\sigma_j c_j(0)]^{n_j} \tag{24}$$

Since we have published this result in a previous paper (Bak and Lu 1987) we shall not discuss this result here in detail.

4. Copolymerisation with a constant deposition

In this section, we give a slight extension of the $A_f + A_2$ copolymerisation system by including a constant deposition. To our knowledge the explicit size distribution is not easy to get using branching theory, while the kinetic method gives the exact result without any difficulty.

The kinetic equation in this case is

$$\frac{dc_{kl}}{dt} = \frac{1}{2} \sum_{\substack{i+j=k \\ p+q=l}} \sigma_{ip} \sigma_{jq} c_{ip} c_{jq} - c_{kl} \sum_{iq} \sigma_{ki} \sigma_{jq} c_{iq} - sc_{kl} \tag{25}$$

We consider monodisperse initial conditions, with

$$c_{kl}(t=0) = N\delta_{k1} \delta_{l0} + L\delta_{l1} \delta_{k0} \tag{26}$$

Introducing the transformations

$$c_{kl} = x_{kl} \exp\left(-\int_0^t [(f-2)k+2]\mu(t') dt' - \int_0^t s dt'\right) \tag{27}$$

$$\tau = \int_0^t \exp\left(-2\int_0^{t'} \mu(t'') dt'' - \int_0^{t'} s dt''\right) dt' \tag{28}$$

we have the same kinetic equation as (16). The solution is

$$x_{kl} = \frac{[(f-1)k+l]!}{[(f-2)k+2]!k!l!} (fN)^k (2L)^l \tau^{k+l-1}. \tag{29}$$

Before gelation we have

$$\tau = \frac{1 - \exp(-st)}{s + (fN + 2L)[1 - \exp(-st)]} \tag{30}$$

$$\exp\left(-\int_0^t [(f-2)k+2]\mu(t) dt' + \int_0^t s dt\right) = e^{-st} \left(\frac{s}{s + (fN + 2L)(1 - e^{-st})}\right)^{(f-2)k+2} \tag{31}$$

We then have the explicit size distribution

$$c_{kl} = \frac{[(f-1)k+2]!}{[(f-2)k+2]!k!l!} \exp(-st)(fN)^k (2L)^l e^{-st} \left(\frac{s}{s + (fN + 2L)(1 - e^{-st})}\right)^{(f-2)k+2} \times \left(\frac{1 - \exp(-st)}{s + (fN + 2L)(1 - e^{-st})}\right)^{k+l-1}. \tag{32}$$

When $f \rightarrow \infty$, the analytical form of t_c is simple:

$$t_c = \frac{1}{s} \ln \frac{M_{20}(0)}{M_{20}(0) - s}. \tag{33}$$

The post-gel solution can be obtained easily following the method illustrated in the next section.

5. Post-gel solutions

After gelation, there are two models for condensation polymerisation. One is the Stockmayer model, the other is the Flory model. As Ziff and Stell (1980) showed, kinetically Stockmayer’s model means keeping the original form of the kinetic equation unchanged, i.e. sol can only react with sol. Flory’s model, on the other hand, means keeping the functional form of the total number of the free functionalities in the system unchanged, i.e. free functionalities can react as before irrespective of whether they are in the sol and in the gel.

We illustrate our method with the $A_f + A_2$ system and monodisperse initial conditions. First we consider Stockmayer’s model, which means solving the kinetic equation (9) after $t > t_c$, where t_c is given by

$$t_c = [f(f-2)N]^{-1}. \tag{34}$$

After transformations (14) and (15), for equation (16) with monodisperse initial conditions we have the solution

$$y = fN(z_1 + y\tau)^{f-1} + 2L(z_1 + y\tau)z_2 \tag{35}$$

with

$$y = \partial G / \partial z_1 \quad G = \sum_{kl} x_{kl} z_1^k z_2^l \tag{36}$$

Unfortunately, there is no simple form for the solution of equation (9) after gelation. To obtain the solution we need to construct an equation for $\mu(t)$. An easy way to get the equation is to replace

$$z_1 = \exp\left(-\int_0^t \mu(t') dt'\right) \quad z_2 = 1 \tag{37}$$

in equation (33).

Noting that in this case we have

$$y = \sum_{k,l} [(f-2)k+2] x_{kl} z_1^{(f-2)k+1} z_2 = \mu(t) \exp\left(\int_0^t \mu(t') dt'\right) \tag{38}$$

(35) gives the relation which μ satisfies:

$$\begin{aligned} \mu(t) \exp \phi(t) = fN \left(\exp[-\phi(t)] + \mu(t) \exp \phi(t) \int_0^t \exp[-2\phi(t')] dt' \right)^{f-1} \\ + 2L \left(\exp[-\phi(t)] + \mu(t) \exp \phi(t) \int_0^t \exp[-2\phi(t')] dt' \right) \end{aligned} \tag{39}$$

where $\phi(t) = \int_0^t \mu(t') dt'$.

The existence of the post-gel solution for a single-parameter coagulation equation was shown by Leyvraz and Tschudi (1981). For the two-parameter coagulation equation (9), we have a similar situation. Introducing

$$\psi = \exp \phi(t) \tag{40}$$

we have $\dot{\psi}(t) = \psi(t)\mu(t)$ and (39) can be written as

$$\dot{\psi}(t) = fN \left(\psi^{-1}(t) + \dot{\psi}(t) \int_0^t \psi^{-2}(t') dt' \right)^{f-1} + 2L \left(\psi^{-1}(t) + \dot{\psi}(t) \int_0^t \psi^{-2}(t') dt' \right). \tag{41}$$

Differentiating (41), we have

$$\ddot{\psi}(t) = \left[f(f-1)N \left(\psi^{-1}(t) + \dot{\psi}(t) \int_0^t \psi^{-2}(t') dt' \right)^{f-2} + 2L \right] \ddot{\psi}(t) \int_0^t \psi^{-2}(t') dt'. \tag{42}$$

Obviously $\ddot{\psi}(t) = 0$ is a solution and this leads to equation (19), and the result (20), corresponding to the solution before gelation. It is not easy to get another solution from (42) and our analytical method can only give the relation (39).

For Flory's model after gelation, the size distribution will keep the original form as (23). An important feature is that we can obtain the mass in the sol and in the gel, which is useful in polymer chemistry. For Flory's model, we have the following kinetic equation:

$$\frac{dc_{kl}}{dt} = \frac{1}{2} \sum_{\substack{i+j=k \\ p+q=l}} [(f-2)i+2][(f-2)j+2] c_{ip} c_{iq} - c_{kl} [(f-2)k+2] \frac{\mu_0}{1+\mu_0 t} \tag{43}$$

where $\mu_0 = fN + 2L$. This equation can be solved in the same way as equation (9) and gives a relationship which determines the time-dependent sol and gel masses. Ziff and

Stell (1980) used a time-dependent function $\zeta(t)$ and gave the expression for the sol and the gel masses as a function of $\zeta(t)$. We think the formulation expressed in this paper is somewhat clearer.

To solve equation (43), we introduce

$$G = \sum_{k,l} c_{kl} z_1^{(f-2)k+2} z_2^l \tag{44}$$

and

$$y = \frac{\partial G}{\partial z_1} - z_1 \frac{\mu_0}{1 + \mu_0 t}. \tag{45}$$

We then have a partial differential equation from (43):

$$\partial y / \partial t = y \partial y / \partial z_1. \tag{46}$$

For monodisperse initial conditions (24), we have the solution

$$y = Nf(z_1 + ty)^{f-1} + 2L(z_1 + ty)z_2 - (z_1 + ty)(fN + 2L). \tag{47}$$

Set

$$\zeta = z_1 + ty. \tag{48}$$

We have

$$y = Nf\zeta^{f-1} + 2L\zeta z_2 - \zeta(fN + 2L) \tag{49}$$

and

$$z_1 = \zeta - t[Nf\zeta^{f-1} + 2L\zeta z_2 - \zeta(fN + 2L)]. \tag{50}$$

We further set $z_1 = z_2 = 1$ and equation (50) becomes

$$1 = \zeta - tNf[\zeta^{f-1} - \zeta]. \tag{51}$$

Obviously, $\zeta = 1$ is a solution, which corresponds to the pre-gel solution. The other positive real solution can be obtained from

$$\zeta + \zeta^2 + \dots + \zeta^{f-2} = 1/fNt \tag{52}$$

corresponding to the post-gel solution.

We calculate the total number of free functionalities of the gel first.

From (44) we have

$$\sum_{k,l} c_{kl} [(f-2)k + 2] = \left(\frac{\partial G}{\partial z_1} \right)_{\substack{z_1=1 \\ z_2=1}}. \tag{53}$$

In (53), $\partial G / \partial z_1$ can be obtained from (45), with y given in (47). After some algebra, we get the following fairly simple form for ζ :

$$\sum_{k,l} c_{kl} [(f-2)k + 2] = \frac{1}{1 + (fN + 2L)t} (Nf\zeta^{f-1} + 2L\zeta). \tag{54}$$

It is not difficult, but tedious, to get M_{00} from (49). In doing this, we only need to perform an integration in terms of the parameter ζ . The result is

$$M_{00} = \frac{fN}{2(1 + \mu_0 t)} \zeta^{f-1} + \frac{L}{1 + \mu_0 t} \zeta - \frac{1}{2} N(f-2)\zeta^f. \tag{55}$$

It is then easy to get

$$M_{10} = \frac{1}{(f-2)(1+\mu_0 t)} \left(\frac{1}{2} N f \zeta^{f-1} + L \zeta \right) + \frac{1}{2} N \zeta^f \tag{56}$$

and

$$M_{01} = \frac{L}{1+(fN+2L)t} \zeta. \tag{57}$$

6. The $A_f + A_g$ system

In this section we briefly discuss the solution of the kinetic equation for the $A_f + A_g$ system. The kinetic equation is written as (10). To solve this equation, we introduce

$$c_{kl} = x_{kl} \exp\left(-[(f-2)k + (g-2)l + 2] \int_0^t \mu(t') dt'\right) \tag{58}$$

where

$$\mu = \sum_{k,l} \sigma_{kl} c_{kl} \tag{59}$$

with

$$\sigma_{kl} = (f-2)k + (g-2)l + 2 \tag{60}$$

and

$$\tau = \int_0^t \exp\left(-2 \int_0^{t'} \mu(t'') dt''\right) dt'. \tag{61}$$

From equation (10) we have

$$\frac{dx_{kl}}{dt} = \frac{1}{2} \sum_{\substack{i+j=k \\ p+q=l}} \sigma_{ip} \sigma_{jq} x_{ip} x_{jq}. \tag{62}$$

Equation (62) has the solution

$$x_{kl} = \sum_{h=1}^{k+l} N_{klh} \tau^{h-1} \tag{63}$$

where N_{klh} satisfies the following recursion relation:

$$(h-1)N_{klh} = \frac{1}{2} \sum_{\substack{i+j=k \\ p+q=l \\ e+g=h}} \sigma_{ip} \sigma_{jq} N_{ipe} N_{jqg}. \tag{64}$$

N_{klh} and the recursion relation (64) have a physical explanation, which is just the same as the one we have given for the $A_f + A_2$ system.

Before gelation μ satisfies (19) and the solution is given by (20). We have

$$\tau = t(1 + \mu_0 t)^{-1} \tag{65}$$

where

$$\mu_0 = \sum_{k,l} \sigma_{kl} c_{kl}(0) \tag{66}$$

and

$$c_{kl} = x_{kl}(1 + \mu_0 t)^{-[(f-2)k+2+(g-2)l]} \tag{67}$$

The solution before gelation can be written as

$$c_{kl} = \sum_{h=1}^{k+l} N_{klh} \left(\frac{t}{1 + \mu_0 t} \right)^{h-1} (1 + \mu_0 t)^{-[(f-2)k+(g-2)l+2]} \tag{68}$$

The post-gel solution can be obtained in the same way as for the $A_f + A_2$ system and we hope to discuss this in a future publication.

7. Conclusions and discussion

The kinetic equation for copolymerisation can be established following Flory’s two assumptions. We solved the kinetic equation for the $A_f + A_2$ and $A_f + A_g$ systems with arbitrary initial conditions. The kinetic method has been generalised to the copolymerisation system with deposition. Then it would be interesting to know if the statistical method and branching theory can be used to obtain the exact result. The continuous version of the coagulation equation can be solved by using a Laplace transformation, but it is difficult to get the explicit expressions for arbitrary initial conditions.

Appendix. Derivation of the result (22)

Introducing the transformations (14) and (15), we only need to solve equation (16). By using the generating function

$$G = \sum_{kl} x_{kl} z_1^k z_2^l \tag{A1}$$

we have the partial differential equation

$$\partial G / \partial \tau = \frac{1}{2} (\partial G / \partial z_1)^2 \tag{A2}$$

The solution of (A2) is

$$y = \sum_k c_{k0}(0) [(f-2)k+2] (z_1 + y\tau)^{(f-2)k+1} + 2 \sum_l c_{0l}(0) (z_1 + y\tau) z_2^l \tag{A3}$$

satisfying the initial condition

$$G(\tau = 0) = \sum_k c_{k0}(0) z_1^k + \sum_l c_{0l} z_2^l \tag{A4}$$

where $y = \partial G / \partial z_1$.

The Lagrange expansion gives

$$x_{kl} = \sum_{\{n_j\}, \{r_j\}} \frac{[(f-2)k+m+n]! \tau^{m+n-1}}{[(f-2)k+2]! \Pi_j n_j! \Pi_j r_j!} \prod_j \{[(f-2)j+2] c_{j0}(0)\}^{n_j} \prod_j [2c_{0j}(0)]^{r_j} \tag{A5}$$

Hence we have (22) after calculating $\mu(t)$ and related functions.

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