Pre- and post-gel size distributions in (ir)reversible polymerisation

## LETTER TO THE EDITOR

# Pre- and post-gel size distributions in (ir)reversible polymerisation

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**Abstract.** A class of irreversible coagulation processes can be modelled by Smoluchowski's coagulation equation with rate constants $K_{ij} = A + B(i+j) + Cij$ (non-negative $A$, $B$ and $C$). For $C \neq 0$ a gelation transition occurs. We obtain explicit solutions for the size distribution $c_k(t)$ with $c_k(0) = \delta_{k1}$. Next, we construct and solve the equations for reversible polymerisation by incorporating break-up processes in the kinetic equation with a unimolecular fragmentation rate $F_{ij} = \lambda N_i N_j K_{ij}/N_{i+j}$. The degeneracy factors $N_k$ obey $(k-1)N_k = \frac{1}{2} \sum K_{ij} N_i N_j$ with $i + j = k$ and $N_1 = 1$, and the strength parameter $\lambda = \exp(g/k_B T)$, where the binding energy $g \to -\infty$ for irreversible coagulation. Here explicit results are only given for Flory's polymerisation models $RA_f$ and $BRA_{f-1}$. In the vicinity of the gel point we verify the scaling hypothesis and calculate critical exponents.

Smoluchowski's equation for rapid coagulation models the time evolution of the size distribution $c_k(t)$ in coagulation processes, such as polymerisation, clustering of colloidal particles, aerosols, red blood cells etc (Drake 1972), in the following form:

$$\dot{c}_k = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{j=1}^{\infty} K_{kj} c_j \tag{1}$$

to be solved subject to the monodisperse initial condition $c_k(0) = \delta_{k1}$. The purpose of the present letter is first to determine the global solution of (1) for the general bilinear kernel $K_{ij} = A + B(i+j) + Cij$ with $A$, $B$, $C$ non-negative, and next, to extend these results by including break-up or fragmentation effects.

The terms in the kinetic equation (1) represent the gain and loss of $k$-clusters. The rate at which $i$- and $j$-clusters combine is given by $K_{ij} c_i c_j$. Several polymerisation models of Flory and Stockmayer correspond to special cases of the bilinear kernel: the $RA_f$ model ($A-A$ bonds, no cycles, monomers with $f$ equireactive $A$-groups ($f = 2$, $3, 4, \ldots$), and $K_{ij} = \sigma_i \sigma_j$ with $\sigma_k = (f-2)k + 2$) and the $B_g RA_f$ model ($A-B$ bonds, no cycles, monomers with $f$ equireactive $A$-groups ($f = 1, 2, \ldots$) and $g$ equireactive $B$-groups ($g = 1, 2, \ldots$), and $K_{ij} = s_i(A)s_j(B) + s_i(B)s_j(A)$ with $s_k(A) = (f-1)k + 1$ and $s_k(B) = (g-1)k + 1$. In these models the coagulation kernels are proportional to the number of possibilities to form an $(i+j)$-mer out of an $i$-mer and a $j$-mer.

An important property of (1) is the conservation of total mass of sol particles (finite size clusters): $M_1(t) = 0$, which applies as long as $\sum_{i,j} i K_{ij} c_i c_j < \infty$. The instant $t_c$ (gel point), at which $\sum_{i,j} i K_{ij} c_i c_j$ diverges, marks the onset of gelation, characterised by $M_1(t) < 0$. This property is interpreted as the formation of a superparticle (gel),

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whose mass is comparable to that of the entire system. Such a gelation transition occurs at a finite time $t_c$ for coagulation kernels with $C \neq 0$, as we shall see below.

For later use we introduce the $n$th moment of the size distribution $M_n(t) = \sum_{k=1}^{\infty} k^n c_k(t)$, where $M_0$ and $M_1$ denote respectively the total number and total mass of sol particles.

*Pre-gelation solutions* to (1) of the general form $c_k(t) = \mathcal{A}(t)N_k(\xi(t))^k$ with $c_k(0) = \delta_{k1}$ are well known for the models $RA_f$ and $BRA_{f-1}$ (Ziff and Stell 1980, Cohen and Benedek 1982). Drake (1972) was able to write down a formal series for the pre-gelation solution with arbitrary $A$, $B$ and $C$ and with $c_k(0) = \delta_{k1}$. Spouge (1983a, b) showed that the general bilinear kernel allows solutions of the above form, without giving the explicit time dependence of $\mathcal{A}(t)$ and $\xi(t)$. *Post-gelation solutions* to (1) have only recently been found by Ziff (1980) and Ziff and Stell for the $RA_f$ model and by Leyvraz and Tschudi (1981) for the $RA_\infty$ model. In addition, Leyvraz and Tschudi were able to prove the existence of global solutions (valid for all $t$) for general initial conditions.

In order to determine pre-gelation solutions, we introduce

$$\beta_k(t) = \sum_j K_{kj} c_j(t) = Ck + B + (Bk + A)M_0(t)$$

$$c_k(t) = a_k(\theta) \exp\left(-\int_0^t \beta_k(t')dt'\right) \qquad \theta(t) = \int_0^t dt' \exp\left(-\int_0^{t'} \beta_0(t'')dt''\right) \qquad (2)$$

and transform (1) into $da_k/d\theta = \frac{1}{2}\sum_{i+j=k} K_{ij}a_i a_j$. Its solution with $a_k(0) = \delta_{k1}$ reads $a_k(\theta) = N_k\theta^{k-1}$, where the coefficients $N_k$ satisfy the recursion relation

$$(k-1)N_k = \frac{1}{2} \sum_{i+j=k} K_{ij}N_i N_j \qquad (N_1 = 1). \qquad (3)$$

Hence the pre-gelation solution $(t < t_c)$ can be written as $c_k(t) = \mathcal{A}N_k\xi^k$ with

$$\mathcal{A}(t) = \theta^{-1} \exp\left(-\int_0^t [B + AM_0(t')]\,dt'\right) = \frac{\dot{\theta}}{\theta}$$

$$\xi(t) = \theta \exp\left(-\int_0^t [C + BM_0(t')]\,dt'\right). \qquad (4)$$

The so-called degeneracy factors $N_k$ for the models $RA_f$ and $BRA_{f-1}$ have been recently reviewed by Cohen and Benedek, and new results for the model $B_g RA_f$ have been found by Spouge (1983c). For our purpose only the large-$k$ behaviour of $N_k$ is of interest, which shall be determined below.

To obtain explicit expressions for $\mathcal{A}$ and $\xi$ in (4) we derive the following moment equations from (1):

$$\dot{M}_0 = -\frac{1}{2}(AM_0^2 + 2BM_0 M_1 + CM_1^2) \text{ (all } t) \qquad \dot{M}_2 = A + 2BM_2 + CM_2^2 \ (t < t_c). \qquad (5)$$

If $C = 0$, this equation shows that $M_2(t) < \infty$ and consequently $\sum_{i,j} iK_{ij}c_i c_j < \infty$ for all $t < \infty$. Hence $M_1(t) = 1$ for all finite $t$, and no gelation occurs. If $C \neq 0$, the solution $M_2(t)$ of (5) diverges at a finite time $t_c$ (gel point), and $M_1(t) = 1$ only for $t < t_c$. The value of the time $t_c$ (where $M_2(t_c) = \infty$) has already been obtained by Drake, who suggested (apparently unaware of the phase transition at $t = t_c$) that the kinetic equation (1) was physically meaningless for $t > t_c$, and implied that the bilinear kernel with $C \neq 0$ is not a physically valid coagulation kernel. Similar conclusions are implied in other publications (e.g. McLeod 1964, Klett 1975).

In order to solve (5) we distinguish between three cases: $B^2 > AC$, $B^2 = AC$ and $B^2 < AC$, and define

$$m_0(\tau) = M_0(t) + B/A \qquad m_2(\tau) = M_2(t) + B/C \qquad \mu_0^2 = B^2/A^2 - C/A$$

$$\tau = \tfrac{1}{2}At.$$

For $B^2 > AC$ and $\tau < \tau_c = \tfrac{1}{2}At_c$, we find the pre-gelation solutions (Drake 1972)

$$m_0(\tau) = \mu_0 \coth \mu_0(\tau_0 + \tau) \qquad m_2(\tau) = (A\mu_0/C) \coth 2\mu_0(\tau_c - \tau)$$

$$\tau_0 = (1/\mu_0)\tanh^{-1}[A\mu_0/(B+A)] \qquad \tau_c = (1/2\mu_0)\tanh^{-1}[A\mu_0/(B+C)]. \tag{6}$$

The case $B^2 < AC$ can be obtained by everywhere replacing $\mu_0$ by $i|\mu_0|$ (where $i = \sqrt{-1}$), leading to goniometric rather than hyperbolic functions. Taking the limit $\mu_0 \to 0$ will yield the corresponding results for $B^2 = AC$. We shall restrict ourselves to $B^2 > AC$. The result (6) is combined with (2) to yield

$$\int_0^t \beta_0(t')\,dt' = 2\log[(\sinh \mu_0(\tau + \tau_0))/(\sinh \mu_0\tau_0)]$$

$$\theta(t) = (2/\mu_0 A)(\sinh \mu_0\tau)(\sinh \mu_0\tau_0)/(\sinh \mu_0(\tau + \tau_0)), \tag{7}$$

from which the coefficients (4) in the pre-gelation solution can be deduced:

$$\mathscr{A}(t) = \tfrac{1}{2}\mu_0 A(\sinh \mu_0\tau_0)/[(\sinh \mu_0\tau)(\sinh \mu_0(\tau + \tau_0))]$$

$$\xi(t) = (2/\mu_0 A)(\sinh \mu_0\tau)[(\sinh \mu_0\tau_0)/(\sinh \mu_0(\tau + \tau_0))]^{1+2B/A} \exp(2\mu_0^2\tau). \tag{8}$$

This result constitutes the solution $c_k(t) = \mathscr{A}N_k\xi^k$ of (1) for $t < t_c$ with monodisperse initial conditions and arbitrary $A$, $B$ and $C$. According to Spouge (1983a) such solutions are only possible when the kernel is bilinear. In the *special case* $C = 0$ the solution $c_k(t) = \mathscr{A}N_k\xi^k$ is valid for all $t$.

Next, we consider *post-gelation solutions*. Smoluchowski's equation also allows a solution of the form

$$c_k(t) = c_k(t_c)/[1 + b(t - t_c)] \tag{9}$$

provided $c_k(t_c)$ satisfies the relation

$$\tfrac{1}{2} \sum_{i+j=k} K_{ij} c_i(t_c) c_j(t_c) = (\beta_k(t_c) - b)c_k(t_c) = (C + BM_0(t_c))(k-1)c_k(t_c). \tag{10}$$

The second equality follows from the solubility requirement: $b = \beta_1(t_c)$. The solution reads $c_k(t_c) = (C + BM_0(t_c))N_k R^k$ on account of (3), where $R$ is some (as yet) undetermined constant. The solutions (9) are post-gelation solutions, since the sol mass $M_1(t) = [1 + b(t - t_c)]^{-1}$ is no longer constant. The following argument shows that the pre- and post-gelation solutions can be matched, i.e. $c_k(t_c^+) = c_k(t_c^-)$, such that $c_k(t)$ is continuously differentiable at $t = t_c$. The $c_k(t)$ are continuous (and as solutions to (1) continuously differentiable at $t_c$), provided we choose $R = \xi_c \equiv \xi(t_c)$ (a subscript 'c' will denote values at $t = t_c$) and provided the following relation is valid:

$$\mathscr{A}_c = \tfrac{1}{2}A\mu_0 \coth\mu_0\tau_c - \tfrac{1}{2}A\mu_0 \coth\mu_0(\tau_c + \tau_0) \stackrel{?}{=} C + BM_0(t_c)$$

$$= -A\mu_0^2 + B\mu_0 \coth\mu_0(\tau_c + \tau_0). \tag{11}$$

On the first line the relation $\mathscr{A}_c = \dot{\theta}_c/\theta_c$ has been used in combination with (7); on the second line the expression for $m_0(\tau_c)$ has been inserted. With the help of (6) we find

after a straightforward but lengthy calculation

$$\text{RHS}(11) = \text{LHS}(11) = C + B/(1 + (K_{11}/C)^{1/2}),$$

proving the matching condition (11). This calculation also yields

$$M_0(t_c) = [1 + (K_{11}/C)^{1/2}]^{-1} \qquad b = \beta_1(t_c) = (K_{11}C)^{1/2} + B/[1 + (C/K_{11})^{1/2}]. \qquad (12)$$

In summary: for arbitrary non-negative $A$, $B$ and $C$ (with $C \neq 0$) the post-gel solution (9) will be reached for monodisperse initial conditions.

In the following part we show that $c_k(t_c) \simeq q_0 k^{-\tau}$ ($k \to \infty$) and discuss the properties of $c_k(t)$ near the gel point. The large-$k$ behaviour of $c_k(t_c) \equiv [C + BM_0(t_c)]n_k$ can be determined from the small-$x$ behaviour of the generating functions; for $x \uparrow 0$ we have

$$G(x) \equiv \sum_{k=1}^{\infty} n_k e^{kx} \simeq P_0 + P_1 x + \dots \qquad F(x) \equiv \sum_{k=1}^{\infty} k n_k e^{kx} \simeq P_1 + \dots$$

where the quantities

$$P_0 \equiv \sum_{k=1}^{\infty} n_k = M_0(t_c)[C + BM_0(t_c)]^{-1} \qquad P_1 \equiv \sum_{k=1}^{\infty} k n_k = [C + BM_0(t_c)]^{-1}$$

are given through (12). We first observe that the $n_k$ satisfy the recursion relations (3) on account of (10), implying

$$F = C^{-1}\{1 - BG - [(1 - BG)^2 - ACG^2 - 2CG]^{1/2}\}.$$

The dominant small-$x$ singularity in $F(x)$ is a branch point, since the argument of the square root on the RHS of this equation vanishes for the given value of $G(0) = P_0$, and we find

$$F(x)/P_1 \simeq 1 - [-2bx/C]^{1/2} \qquad (x \uparrow 0).$$

The above branch point singularity implies, according to Hendriks *et al* (1983), an algebraic tail in $c_k(t_c)$ of the form $c_k(t_c) \simeq (b/2\pi C)^{1/2} k^{-5/2}$ ($k \to \infty$). The critical properties of $c_k(t)$ can be obtained most easily by considering $c_k(t)/c_k(t_c) \simeq Q^k$ ($t \uparrow t_c$) in (2) and expanding $\log Q$ in powers of $(t - t_c)$, where

$$\log Q = \log\left(\frac{\theta}{\theta_c}\right) - \int_{t_c}^{t} [C + BM_0(t')]dt' \simeq -\tfrac{1}{2}Cb(t - t_c)^2 \qquad (t \uparrow t_c). \qquad (13)$$

The coefficient of $(t - t_c)$ in (13) vanishes on account of the matching condition (11), and the coefficient of $(t - t_c)^2$ has been simplified by using the relation $\dot{M}_0(t_c) = -bM_0(t_c)$. The resulting scaling form for the size distribution in the scaling limit $t \uparrow t_c$, $k \to \infty$ with $k(t_c - t)^{1/\sigma}$ fixed, becomes

$$c_k(t) \simeq (b/2\pi C)^{1/2} k^{-\tau} \exp[-\tfrac{1}{2}Cbk(t_c - t)^{1/\sigma}]$$

where the critical exponents $\tau = \tfrac{5}{2}$ and $\sigma = \tfrac{1}{2}$ are universal within the class of models with $K_{ij} = Cij + B(i + j) + A$ and arbitrary non-negative $A$, $B$ and $C$ with $C \neq 0$. The method of Ernst *et al* (1982) can be applied to calculate the remaining critical exponents and critical amplitudes, and one finds that the model with a general bilinear kernel belongs to the same universality class as the simple $RA_\infty$ model with $K_{ij} = ij$. Inclusion of fragmentation effects, to be discussed below, will introduce a fourth model parameter $\lambda$ (measuring the fragmentation strength), but does not change the universality class.

The previous kinetic theories of coagulation (including the polymerisation models $B_gRA_f$, and $RA_f$) describe irreversible polymerisation and only allow for trivial stationary solutions $c_k(\infty) = 0$. The most probable solutions in the Flory–Stockmayer (FS) theory of polymerisation, with an arbitrarily prescribed value of the extent of reaction $\alpha$, can only appear as stationary solutions in models for reversible polymerisation. In the remaining part of this letter we include fragmentation in such a way that the FS solutions appear as the stationary solutions of (14). Let $F_{ij}$ be the rate coefficient for the unimolecular fragmentation process of a $k$-mer into an $i$-mer and a $j$-mer; then we have the kinetic equation for reversible polymerisation in the form

$$\dot{c}_k = \tfrac{1}{2} \sum_{i+j=k} (K_{ij}c_ic_j - F_{ij}c_k) - \sum_{j=1}^{\infty} (K_{kj}c_kc_j - F_{kj}c_{k+j}) \tag{14}$$

to be solved subject to the initial condition $c_k(0) = \delta_{k1}$. Since all bonds within a $k$-mer are equivalent, we impose that the total *fragmentation rate* of a $k$-mer is *proportional to the number of bonds*, i.e. $\tfrac{1}{2}\sum_{i+j=k} F_{ij} = \lambda(k-1)$. By Arrhenius's law, $\lambda$ is proportional to the Boltzmann factor $\exp(g/k_BT)$, where $g$ is the free energy of a single bond, $k_B$ is Boltzmann's constant and $T$ the temperature.

Furthermore the existence of stationary solutions $c_k(\infty)$ imposes the following *detailed balance condition* on the fragmentation coefficient: $F_{ij}c_{i+j}(\infty) = K_{ij}c_i(\infty)c_j(\infty)$. Combining both conditions yields a recursion relation for $c_k(\infty)$, related to (3), whose solution is $c_k(\infty) = \lambda(c_1(\infty)/\lambda)^k N_k$, where $N_k$ is defined in (3). Hence, detailed balance has enabled us to construct for a given coagulation kernel $K_{ij}$ the fragmentation kernel in the form

$$F_{ij} = \lambda K_{ij}N_iN_j/N_{i+j}. \tag{15}$$

The solution (pre-gel solution) of the kinetic equation (14) for reversible polymerisation ($\lambda \neq 0$) in the absence (presence) of gelation is given by the solution $c_k(t)$ to (1) for irreversible polymerisation ($\lambda = 0$), provided $t$ is replaced by the solution $t^*(t)$ of the equation $dt^*/dt = 1 - \lambda/\mathcal{A}(t^*)$ with $t^*(0)-0$, where $\mathcal{A}(t)$ is given by (8). This equation can be solved explicitly for the general bilinear kernel and the result shows that for bilinear kernels with $C \neq 0$ the gelation transition is suppressed for $\lambda \geq \lambda_0$, where $\lambda_0$ is some critical fragmentation strength. The gel point $t_c(\lambda)$ for $\lambda < \lambda_0$ can be calculated from the equation $t^*(t_c) = t_c^*$, where $t_c^*$ is the gel point for irreversible coagulation, calculated in (6). In the post-gel state ($t > t_c$) the equation for $t^*(t)$ reads $dt^*/dt = 1 - \lambda[1 + b(t^* - t_c^*)]/\mathcal{A}_c$, with initial value $t^*(t_c) = t_c^*$.

As a illustration of the results for reversible polymerisation we give the solutions for the polymerisation models $RA_f$ (pre-gelation) and $BRA_{f-1}$. The solution of (14) can be constructed along the same lines, as followed by Ziff. The first step is to find the most probable solutions for the $RA_f$ and $BRA_{f-1}$ models respectively (see Cohen and Benedek 1982)

$$c_k = (\alpha/f)^{k-1}(1-\alpha)^{(f-2)k+2}N_k \qquad c_k = \alpha^{k-1}(1-\alpha)^{(f-1)k+1}[1-(f-1)\alpha]N_k \tag{16}$$

where the $N_k$ are the solutions of (3) for the corresponding coagulation kernels $K_{ij}$, and $\alpha$ is the extent of reaction or fraction of reacted $A$-groups. The next step is to replace $\alpha$ in (16) by the time dependent solution $\alpha(t)$ of the macroscopic rate equations, which read for these models respectively

$$\dot{\alpha} = f(1-\alpha)^2 - \lambda\alpha \qquad \dot{\alpha} = (1-\alpha)[1-(f-1)\alpha] - \lambda\alpha \tag{17}$$

with initial condition $\alpha(0) = 0$. The solutions are standard. In the $RA_f$ model gelation

occurs at $\alpha_c = (f-1)^{-1}$. For sufficiently large values of $\lambda$, $\alpha$ approaches a stationary value smaller than $\alpha_c$, so that the phase transition is suppressed. This happens for $\lambda > \lambda_0 = f(f-2)^2/(f-1)$. Post-gel solutions (existing for $\lambda < \lambda_0$) can be constructed from (9) in a similar way. A detailed discussion of the kinetic theory of reversible polymerisation will be published elsewhere.

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