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A Method To Determine the Most Suitable Model of Coagulation Regarded as a Gelation Process

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In this note, a method to investigate the characteristics of a geling system is presented. It is well-known that gelation time is prolonged from the value predicted by the Flory–Stockmayer model because of intraparticle cross-linking. I believe another effect should be taken into consideration. If hard particles are formed in the course of the reactions, the functional groups buried in the inner part of the particles may find it difficult to participate in the interparticle cross-linking. There is no method to investigate this effect now.

The coagulation kinetics (eq 1) makes it possible to consider this problem.

$$\frac{dc(j,t)}{dt} = \frac{1}{2}\sum_{k+l=j} r(k,l)c(k,t)c(l,t) - c(j,t)\sum_{i=1}^{\infty} r(i,j)c(i,t) \tag{1}$$

where $c(j,t)$ is the concentration of j-mer at time t, $c(1,0) = 1$, and $c(j \neq 1,0) = 0$.

The interparticle cross-linking rate constant $r(i,j)$, expressed by the form $\kappa i^\alpha j^\alpha$, is essentially important in this study. The constants that are proportional to the volume (or mass $\alpha = 1$: Flory–Stockmayer model) or the surface area ($\alpha = {}^2/_3$) of particles are included in this category.

Equation 1 without intraparticle cross-linking has been the subject of considerations by many authors.[1-10] When the explicit solutions are known, it is easy to determine the exponent α. Unfortunately, solutions have been obtained only when α is zero or unity.[1]

In a previous paper[11] I have derived the approximate solution of the Flory–Stockmayer model accompanied with intraparticle cross-linking. The same treatment is possible for the present problem.

Let us imagine a cross-linking reaction that proceeds under the following conditions: (1) The number of functional groups in a primary polymer at time $t = 0$ is f ($\gg 1$). (2) These groups are consumed mainly by intraparticle cross-linking (the conversion being $1 - \xi(t)$, where $\xi(t)$ does not depend on the particle size). The consumption of these groups by interparticle cross-linking is negligibly small. (3) $r(i,j)$ is proportional to [the number of the functions in a particle]$^\alpha$. (4) The exponent α does not change throughout the reaction.

Under these conditions, $r(i,j)$ to form an $(i + j)$-mer from an i-mer and j-mer becomes

$$r(i,j) = \kappa(if\xi(t))^\alpha(jf\xi(t))^\alpha \tag{2}$$

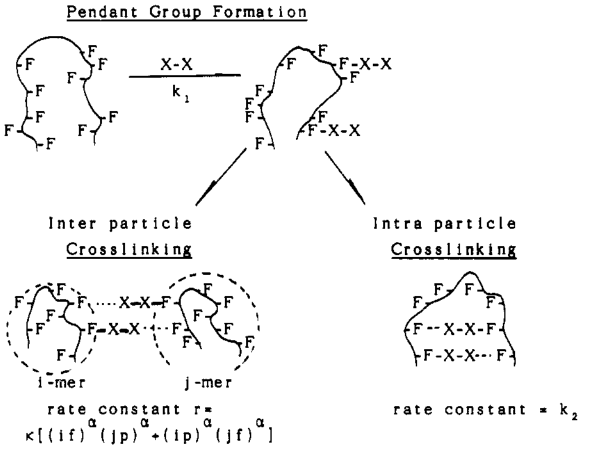
Then the ratio of $r(i,j)$ and $r(k,l)$ becomes

$$\text{ratio} = (ij/kl)^\alpha \tag{3}$$

This ratio does not depend on $f\xi(t)$. Consequently, the particle size distribution functions with different f and $\xi(t)$ agree with one another only by the transformation of time. Here we make size distribution functions $c(j,t)$ and $c(j,(\tau(t))$ correspond to the rate constants $r(i,j) = \kappa i^\alpha j^\alpha$ and to $r(i,j,f,\xi(t)) = \kappa(ij)^\alpha(f\xi(t))^{2\alpha}$, respectively. Then it follows

$$dc(j,\tau)/dt = (f\xi(t))^\alpha(f\xi(t))^\alpha\kappa\left[\frac{1}{2}\sum_{k+l=j}(kl)^\alpha c(k,\tau)c(l,\tau) - \sum_{i=1}^{\infty}(ij)^\alpha c(i,\tau)c(j,\tau)\right] \tag{4}$$

Scheme I



From eq 4, the time t and $\tau(t)$ are related by the following simple equation:

$$d\tau(t)/dt = (f\xi(t))^\alpha(f\xi(t))^\alpha = (f\xi(t))^{2\alpha} \tag{5}$$

If the macrogelation occurs at time C in the system with the rate constant $r(i,j)$, the gelation should be observed at such t_g as expressed by eq 6 in the system with $r(i,j,f,\xi(t))$. That is to say, if t_g's are observed as a function of f and

$$\int_0^{t_g}(f\xi(t))^\alpha(f\xi(t))^\alpha\, dt = C \text{ (constant)} \tag{6}$$

$\xi(t)$, the exponent α can be determined. The procedure shall be shown in the following example.

We consider the following two-step reactions that go well with the actual cases. Here, f (the number of functional F groups in a primary polymer) is fixed, while x_0 (the initial number of cross-linking agents X–X) is varied. We assume that the reaction takes place only between the F and X groups (Scheme I). If f is much greater than x_0, the concentration of pendant group polymer–F–X–X is expressed by eq 9:

$$dx(t)/dt = -2k_1 f x(t) \tag{7}$$

$$dp(t)/dt = 2k_1 f x(t) - k_2 f p(t) \tag{8}$$

where $x(t)$ is the concentration of X–X at time t. Then

$$p(t) = x_0\frac{2k_1}{2k_1 - k_2}[e^{-k_2 f t} - e^{-2k_1 f t}] = x_0\xi(t) \tag{9}$$

The cross-linking occurs between polymer–Y–X–X (p) and polymer–F (f) in two particles. Then, from eq 6

$$2\int_0^{t_g} f^\alpha p(t)^\alpha\, dt = 2\int_0^{t_g}[f x_0 \xi(t)]^\alpha\, dt = C \tag{10}$$

or

$$2\int_0^{t_g} f^\alpha \xi(t)^\alpha\, dt = C(x_0)^{-\alpha} \tag{11}$$

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By differentiating eq 11 with respect to t_g, we find

$$2[fp(t_g)]^\alpha = \alpha C\left[-\frac{d(\ln x_0)}{d(t_g)}\right] \tag{12}$$

When t_g and $\xi(t_g)$ are observed as a function of f and x_0, the exponent α can be determined from the slope of the line ln $[fp(t_g)]$ versus ln $[d(\ln x_0)/d(t_g)]$.

When an asymmetric cross-linking agent (X′–X) with very large k_1 and small k_2 is used, $p(t)$ becomes approximately $x_0 \exp(-k_2ft)$. Then

$$-C\frac{dx}{d(t_g)}x_0^{-\alpha-1} = fe^{-k_2\alpha f t_g} \tag{13}$$

$$\ln C + \ln\left[-\frac{dx_0}{d(t_g)}\right] - (\alpha + 1)(\ln x_0) = -k_2\alpha f t_g \tag{14}$$

The above relation allows us to determine α from the experimental values of t_g, x_0, and y.

Experiments to verify the usefulness of this method are being performed by using a functional microgel with an almost monodisperse size distribution and various cross-linking densities. The results will be reported in the near future.

References and Notes

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