Crosslinking Reaction Regarded as Coagulation I. Gelling Time of Expanded Flory–Stockmayer Model Determined Numerically

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ABSTRACT: Gelling time τ_g of the crosslinking in which the rate constants of inter cluster reactions between i -mer and j -mer is proportional to $(ij)^\alpha$ ($1/2 < \alpha \leq 1$) are determined by numerical calculation. Linear relation between $M_\rho^{1/\delta(\rho,\alpha)}$ (M_ρ is the ρ -th moment of cluster size) and time τ , derived by theoretical considerations is adopted. It becomes clear that the linear relation between $M_\rho^{1/\delta(\rho,\alpha)}$ and τ holds approximately not only for τ near τ_g but a rather wide range of τ .

KEY WORDS Crosslinking Reaction / Gelling Time / Coagulation / Cluster Size Distribution / Numerical Calculation / Asymptotic Solution /

Crosslinking of polyfunctional compounds is very complicated. To form bonding of two clusters, diffusion, mutual contact and penetration, and chemical reactions of functional groups must occur. The reaction system would change drastically by many factors influencing these individual processes. To take these factors into the considerations, kinetic expression seems most suitable. In this study, relation between two characteristic values in crosslinking is considered.

One of the most important characteristic values in crosslinking reactions is the gelling time. When two clusters (i -mer and j -mer) are going to react, a part of functional groups have been consumed already by inter and intra clusters crosslinking. And perfect mutual penetration would be impossible for two clusters because of a network structure. If the rate determining process is a chemical reaction, rate constant of crosslinking becomes proportional to the number of functions which are able to participate to inter clusters bonding.

These factors are introduced into the rate constant $r(i,j)$ as follows¹:

$$r(i,j) = \kappa [fi\xi(t)]^\alpha [fj\xi(t)]^\alpha \quad (1)$$

$(f \gg 1)$

where κ is constant, f is the number of functional groups in a primary polymer, and $\xi(t)$ is the fraction of remaining functional groups at time t . α is the parameter concerning mutual penetration of two clusters, larger than zero and smaller than unity (Flory–Stockmayer model or transparent model).

Equation 1 is important because the effects of shape and structure of a cluster at the moment of reaction are introduced spontaneously by parameter α . If all functions can react with the same rate constant (transparent cluster), α is equal to unity. When a clusters is spherical and the density of functions is proportional to l^{-D} (l is the distance from the center of a cluster), and only the functions on the surface can react, α decreases to $(2-D)/(3-D)$.

The purposes of this study are determination of gelling time as a function of α by numerical calculation and

presentation of an experimental method for the determination of α .

The relation between α and gelling time can also be determined by simulation according to several cluster-cluster aggregation models.^{2,3} α itself would be affected by many factors, such as rotation and deformation of a cluster after the combination of two clusters. The latter factor would be affected by the flexibility of conjugated chains. If α can be determined experimentally by a kinetic method, the phenomenological value would be useful for considerations of mechanism of crosslinking.

Gelling time is defined mathematically as the time interval necessary for ρ -th moment M_ρ ($\rho > 1$, $\sum j^\rho n_j$, n_j : number of j -mer) of cluster size to diverge to infinity. M_ρ can be determined easily if cluster size distribution is known.

The evolution of cluster size distribution is described as follows:

$$\frac{dn_j}{dt} = \frac{1}{2} \sum_{k=1}^{j-1} r(k,j-k)n_k n_{j-k} - \sum_{i=1}^{\infty} r(i,j)n_i n_j \quad (2)$$

$n_j(t)$ is the concentration of j -mer at time t . At the present, $n_1(0)$ and $n_j(0)$ ($j \neq 1$) are taken as unity and zero respectively. Equation 2 with the rate constant containing time t can be simplified as eq 4 by simple transformation of time t by eq 3:

$$\tau = \int_0^t \kappa n_0 [f\xi(t)]^{2\alpha} dt \quad (3)$$

$$\frac{dC_j}{d\tau} = \frac{1}{2} \sum_{k=1}^{j-1} k^\alpha (j-k)^\alpha C_k C_{j-k} - \sum_{i=1}^{\infty} i^\alpha j^\alpha C_i C_j \quad (4)$$

$$\frac{1}{2} \leq \alpha \leq 1, \quad C_i = n_i/n_0 \quad \left(\sum_{i=1}^{\infty} j C_i = 1 \right)$$

Then the problem is the determination of τ_g by using C_j .

The properties of this equation have been investigated extensively.^{4–14} Gelation does occur for α larger than $1/2$.^{6,9} But an explicit C_j and gelling time are not obtained for general α , except only for α equal to 1.

Of course it is possible to determine C_j for any α , and for finite time interval by numerical calculation.

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However the difficulty in this method is as follows. For the determination of gelling time, it is necessary to extrapolate M_ρ to infinity but not to a finite value. To solve this problem, we make use of an asymptotic solution near τ_g , derived by theoretical considerations.

C_j and M_ρ

Leyvraz and Tschudi⁶ proved that the following asymptotic relation holds for large j ($j \rightarrow \infty$), and for τ near gelling time τ_g :

$$C_j = j^{-3/2-\alpha} \exp[-j^\alpha(\tau_g - \tau)^{2\alpha/(2\alpha-1)}] \quad (5)$$

From eq 5, M_ρ ($\rho > 1$) was derived:

$$M_\rho \sim (\tau_g - \tau)^{\delta(\rho, \alpha)} \quad (6)$$

$$\delta(\rho, \alpha) = -[2(\rho - \alpha) - 1]/(2\alpha - 1)$$

Or

$$M_\rho^{1/\delta(\rho, \alpha)} \sim (\tau_g - \tau) \quad (6')$$

Equation 6' indicates a linear relation between $M_\rho^{1/\delta}$ and t . This relation facilitate the determination of gelling time. For extrapolation, we took into consideration the following two points. First, M_ρ values sufficiently larger than unity (the contribution of large clusters to M_ρ was predominate) were used. Secondly, M_ρ values in the time interval where M_1 remained unity were adopted.

Calculation of Size Distribution C_j , ρ -th Moment M_ρ and $1/M$

Calculation of C_j is carried out by the Runge-Kutta-Gill method with decimal place of accuracy -9 . Maximum j and subdivision of time were fixed at 2000 (or 4000), and the values between 0.1 and 0.05, respectively. The values of ρ were 2, 3, and 4. The accuracy of the results was confirmed.

RESULTS AND DISCUSSION

As a typical example, $1/M_2$ for α equal to 0.55 is plotted against τ in Figure 1. There is no difference between two values for $j_{\max}$ equal to 2000 and 4000 in the time interval where M_1 remains unity.

In Figure 2, variation in $1/M_2$ for α 0.95 with time is shown. We could not recognize appreciate differences in the results obtained for two different values of subdivision (0.05 and 0.1). The value of subdivision 0.1 is sufficiently small to obtain accurate C_j . The values of subdivision and $j_{\max}$ were fixed at 0.1 and 2000, respec-

Figure 1. Values of $1/M_2$ by varying maximum j for α equal to 0.55.

tively for calculation of M_2 .

In Figure 3, $1/M_2 \sim \tau$ relations for various α are summarized. It is easy to understand that the extrapolation of $1/M_2$ to zero is very difficult, especially for small α values. $M_2^{1/\delta(2, \alpha)}$ is plotted against τ in Figure 4. Almost linear relations appeared in wide intervals of time and this facilitated extrapolation. In time intervals where M_1 is unity, we have chosen eight time points in larger side. The least squares approximation was adopted to determine first order equations. The determined lines are traced in the same Figure 4. $M_3^{1/\delta(3, \alpha)}$ and $M_4^{1/\delta(4, \alpha)}$ are also plotted against τ in Figures 5 and 6, respectively. Linearity of these lines is good except at time zero in all cases.

The intersections of the lines on τ axis (τ_g) are summarized in Table I. The values of τ_g thus determined for ρ equal to 2 are plotted against α in Figure 7. τ_g can be expressed approximately by eq 7:

Figure 2. Values of $1/M_2$ calculated by varying time of subdivision for α equal to 0.95.

Figure 3. Decrease of $1/M_2$ with reaction time τ for various α .

Figure 4. Variation of $M_2^{(2\alpha-1)/(3-2\alpha)}$ with reaction time τ and determination of τ_g .

Figure 5. Variation of $M_3^{(2\alpha-1)/(2\alpha-5)}$ with reaction time τ and determination of τ_g .

Figure 6. Variation of $M_4^{(2\alpha-1)/(2\alpha-7)}$ with reaction time τ and determination of τ_g .

Table I. τ_g s determined by using different M_ρ s ($\rho=2, 3, 4$)^a

α	$\tau_g(2)$	$\tau_g(3)$	$\tau_g(4)$
0.55	23.4	23.2	22.7
0.60	9.74	9.76	9.68
0.65	5.65	5.67	5.67
0.70	3.81	3.83	3.83
0.75	2.79	2.78	2.73
0.80	2.16	2.16	2.16
0.85	1.72	1.73	1.72
0.90	1.41	1.42	1.40
0.95	1.18	1.18	1.18
1.00	1.00	1.00	1.00

^a $\tau_g(\rho)$: gelling time τ_g determined from ρ -th moment M_ρ .

$$\tau_g = \frac{1}{8.902 \times 10^{-2} - 1.3034\alpha + 2.2144\alpha^2} \quad (7)$$

It is thus possible to determine τ_g of expanded Flory–Stockmayer model exactly by numerical calculation. If we combine eq 7 and time transformation (eq 3), we obtain eq 8.

$$\frac{1}{8.902 \times 10^{-2} - 1.3034\alpha + 2.2144\alpha^2} = \int_0^{\tau_g} \kappa N_0 [f \xi(t)]^{2\alpha} dt \quad (8)$$

κ can be determined at time zero. $\xi(t)$ is observable. Then all values on the right side of eq 8 can be determined by experiment or calculation. Then we can predict τ_g for fixed α . Inversely, if κ , t_g and $\xi(t)$ can be determined experimentally, it is possible to determine α .

Figure 7. τ_g determined by extrapolation of $M_3^{(2\alpha-1)/(3-2\alpha)}$ to zero.

An almost linear relation holds between $M_2^{1/(2,\alpha)}$ and τ , that is, eq 9 holds, even at the first stage of the reaction.

$$\frac{2\alpha-1}{3-2\alpha} M_2^{2/(2\alpha-3)} \frac{dM_2}{dt} \sim \frac{d\tau}{dt} = \kappa N_0 [f \xi(t)]^{2\alpha} \quad (9)$$

If variation in $\xi(t)$ for a sufficiently short time interval is smaller than that of M_2 , the linear relation holds between $\log[dM_2/dt]$ and $\log M_2$ with a slope $2/(2\alpha-3)$:

$$\frac{2}{2\alpha-3} \log M_2 + \log \left[\frac{dM_2}{dt} \right] \sim 2\alpha \log [\xi(t)] + \text{const.} \quad (9')$$

M_2 is the same as $P_w \times M_1$ (P_w : weight average degree of polymerization) and M_1 is unity. Then α at any instant can be determined by measurement of P_w during reaction. The change of α is considered to reflect the mechanism of crosslinking reactions.

The reason why this linear relation holds approximately for so wide time intervals, is not clear. This problem will be discussed in the next article.

The results obtained in this study are applicable to a crosslinking system with small f (equal to 3, 4, 5...) by simple modification of eq 1 and using observed values of M_0 (number of molecules). This modification and determination of experimental values of α will be reported in another article.

REFERENCES

1. T. Fukutomi, *Macromolecules*, **24**, 616 (1991).
2. J.-M. Debierre and L. Turban, *J. Phys., A, Math. Gen.*, **20**, L239 (1987).
3. V. Tamas, "Fractal Growth Phenomena II. Cluster Growth Model." World Scientific, Singapore, New Jersey·London·Hong Kong, 1989, and references cited in this book.
4. A. Lushnikov, *J. Colloid Interface Sci.*, **45**, 549 (1973).
5. F. Leyvraz and H. R. Tschudi, *J. Phys., A, Math. Gen.*, **14**, 389 (1981).
6. F. Leyvraz and R. Tschudi, *J. Phys., A, Math. Gen.*, **15**, 1951 (1982).
7. F. Leyvraz, *Phys. Rev. A*, **29**, 854 (1984).
8. R. M. Ziff and G. Stell, *J. Chem. Phys.*, **73**, 3492 (1980).
9. R. M. Ziff, E. M. Hendriks, and M. H. Ernst, *Phys. Rev. Lett.*, **49**, 593 (1982).
10. R. M. Ziff and M. H. Ernst, *Phys. Rev. Lett.*, **49**, 593 (1982).
11. M. H. Ernst, E. M. Hendriks, and R. M. Ziff, *J. Phys., A, Math. Gen.*, **15**, 1743 (1982).
12. E. M. Hendriks, M. H. Ernst, and R. M. Ziff, *J. Stat. Phys.*, **31**, 519 (1983).
13. R. Botet and R. Jullien, *J. Phys., A, Math. Gen.*, **17**, 2517 (1984).
14. H. Hayakawa, *J. Phys., A, Math. Gen.*, **20**, L801 (1987).