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# CURING THEORY AND SCALING STUDY: CROSSLINKING REACTION OF THE $A_a$ TYPE

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## ABSTRACT

The process of the $A_a$-crosslinking reaction is considered as a whole to approach the threshold of the sol-gel transition. By a rational way, without Stirling's approximation, the asymptopic form of the Flory-Stockmayer distribution near the gel point is obtained to reach a generalized scaling law.

## INTRODUCTION

For the $A_a$-crosslinking reaction, the behavior of polymer moments below and above the gel point, which is regarded as the threshold of the sol-gel transition, is discussed in detail. From the Flory-Stockmayer distribution [1, 2] a reasonable approach to the threshold of sol-gel transition [1-10] is proposed without Stirling's approximation [8, 10] to reach the asymptotic form of the equilibrium number fraction distribution of $n$-mer as

$$\tilde{P}_n = a\left[\frac{1}{2\pi(a-1)(a-2)}\right]^{1/2} n^{-5/2} \exp\left[-\left(k-\frac{3}{2}\right)\frac{n}{n_\xi(k)}\right]. \tag{1}$$

This expression involves the integer $k$ which takes the values 2, 3, 4, . . . , and the generalized typical size $n_\xi(k)$ which takes the form

$$n_\xi(k) = \frac{(2k - 3)(a - 2)}{(a - 1)^3} |p - p_c|^{-2}, \tag{2}$$

with the gel point given by

$$p_c = \frac{1}{a - 1}. \tag{3}$$

As a direct consequence, it is easy to find that as a generalization of the scaling law [8, 9], the relations

$$\begin{aligned} &\tau - 2 = \sigma\beta \\ &k + 1 - \tau = \sigma\gamma_k, \quad k = 2, 3, \ldots, \end{aligned} \tag{4}$$

hold true.



## POLYMER MOMENTS OF $A_a$ CROSSLINKING REACTION

Let us consider a crosslinking system in which each monomer $A_a$ keeps $a$-functionality. Let $p$, $p'$, and $p''$ be the total, sol, and gel equilibrium fractional conversions, respectively, and $S$ the sol fraction. Under the assumptions of equireactivity and of no intramolecular reaction between A-groups in the sol, we have, by means of polymer statistics [3, 4, 7],

$$S = \left(1 - p + S\frac{1 - p'}{1 - p}p\right)^a, \tag{5}$$

$$S(1 - p') = (1 - p)\left(1 - p + S\frac{1 - p'}{1 - p}p\right)^{a-1}, \tag{6}$$

and

$$S\frac{1 - p'}{1 - p} = S^{(a-1)/a}. \tag{7}$$

Now let us express $p$, $p'$, and $p''$ in terms of the sol fraction $S$. Substituting Eq. (7) into Eq. (6) gives

$$p = \frac{1 - S^{1/a}}{1 - S^{(a-1)/a}} \tag{8}$$

By combining Eqs. (8) and (7), we have

$$p' = \frac{S^{(a-2)/a} - S^{(a-1)/a}}{1 - S^{(a-1)/a}} . \tag{9}$$

From the relation

$$1 - p = S(1 - p') + (1 - S)(1 - p'')$$

together with Eqs. (8) and (9), we obtain

$$p'' = \frac{(1 - S^{1/a})(1 + S^{(a-1)/a})}{1 - S} . \tag{10}$$

The expressions of $p$, $p'$, and $p''$ indicate that the three kinds of equilibrium fractional conversions are connected by the sol fraction $S$, which is an observable quantity.

When $S = 1$, the expressions of $p$, $p'$, and $p''$ become indeterminate, i.e., 0/0, and then, application of the L'Hospital's rule leads us directly to the results

$$p_c = \frac{1}{a-1}, \quad p_c' = \frac{1}{a-1}, \quad \text{and} \quad p_c'' = \frac{2}{a}, \tag{11}$$

where $p_c, p_c'$, and $p_c''$ are the gel points with respect to the total, sol, and gel equilibrium fractional conversions, respectively.

It is obvious that with any one of the equilibrium fractional conversions $p$, $p'$, and $p''$, the discussion of curing theory will be straightforward. But, in order to make the scaling study of this paper easier, we shall choose the total equilibrium fractional conversion $p$ to proceed.

For a random $a$-functional crosslinking system, the Flory-Stockmayer distribution [1, 2] $p_n$ takes the form

$$P_n = C_n p^{n-1}(1 - p)^{an-2n+2}, \tag{12}$$

with

$$C_n = \frac{a(an - n)!}{n!(an - 2n + 2)!}, \tag{13}$$

where $P_n$ is the equilibrium number fraction distribution of $n$-mer.

It is known that the first moment $M_1$ can be evaluated [3] by means of $P_n$ in Eq. (12) as follows:

$$M_1 = \sum_n nP_n = \begin{cases} 1, & \text{for } p \leqslant p_c \\ S, & \text{for } p \geqslant p_c. \end{cases} \tag{14}$$

Note that the gel point $p_c$ can be regarded as the threshold of the sol-gel transition and, then, when $p \geqslant p_c$, the sol fraction $S$, which is closely related to $p$ as given in Eq. (8), varies from 1 to 0.

Let us deal with the second moment $M_2$. Taking $p$ as a variable to differentiate the right- and left-hand sides of Eq. (14) yields

$$M_2 = \frac{1 + p}{1 - (a - 1)p} M_1 + \frac{p(1 - p)}{1 - (a - 1)p} \frac{d}{dp} M_1. \tag{15}$$

To obtain the second moment $M_2$

$$M_2 = \sum_n n^2 P_n = \begin{cases} \dfrac{F_2(p)}{p_c - p}, & \text{for } p \leqslant p_c \\ \dfrac{T_2(p)}{p - p_c}, & \text{for } p \geqslant p_c \end{cases} \tag{16}$$

where

$$F_2(p) = \frac{1 + p}{a - 1}, \tag{17}$$

$$T_2(p) = -\frac{S(1 + p) + p(1 - p)\, dS/dp}{a - 1}, \tag{18}$$

and

$$\frac{dS}{dp} = -\frac{a(1 - S^{(a-1)/a})^2 S^{(a-1)/a}}{(a - 1)S^{(a-2)/a} - (a - 2)S^{(a-1)/a} - 1}, \tag{19}$$

$dS/dp$ being derived from Eq. (8).

For the $k$th moment $M_k$, the analogous differentiation procedure done consecutively from $M_2$ yields

$$M_k = \sum_n n^k P_n = \begin{cases} \dfrac{F_k(p)}{(p_c - p)^{2k-3}}, & \text{for } p \leqslant p_c \\[2ex] \dfrac{T_k(p)}{(p - p_c)^{2k-3}}, & \text{for } p \geqslant p_c \end{cases} \qquad k = 3, 4, \ldots, \tag{20}$$

with the recursion formula

$$M_k = \frac{1 + p}{1 - (a - 1)p} M_{k-1} + \frac{p(1 - p)}{1 - (a - 1)p} \cdot \frac{d}{dp} M_{k-1}, \qquad k = 3, 4, \ldots. \tag{21}$$

This formula can lead us directly to the recursion formula

$$R_k(p) = [(1 + p)(p_c - p) + (2k - 5)p(1 - p)] \frac{R_{k-1}(p)}{a - 1} + \frac{(p_c - p)p(1 - p)}{a - 1} \frac{d}{dp} R_{k-1}(p), \qquad k = 3, 4, \ldots, \tag{22}$$

with

$$R_k(p) = \begin{cases} F_k(p), & \text{for } p \leqslant p_c \\ T_k(p), & \text{for } p \geqslant p_c. \end{cases} \tag{23}$$

Thus, $F_k(p)$ and $T_k(p)$ can be evaluated, respectively, by taking $F_2(p)$ and $T_2(p)$ in Eqs. (17) and (18) as starting points.

It is clear that by making use of Eqs. (9) and (10), the $k$th moment for

$p \geqslant p_c$ as given in Eqs. (16) and (20) can be reformulated in terms of $p'$ or $p''$. For brevity, we shall not discuss it further.

## SCALING STUDY OF THE SOL-GEL TRANSITION

Let us consider the moments near the gel point $p_c$ ($|p - p_c| \ll 1$) [8-10]. For $p = p_c$ it is easy to evaluate the quantities $dp/dS$, $F_2(p)$, and $T_2(p)$ in Eqs. (19), (17), and (18) to give

$$A_1 = -\left(\frac{dS}{dp}\right)_{p_c} = \frac{2a(a-1)}{a-2} \tag{24}$$

and

$$A_2 = F_2(p_c) = T_2(p_c) = \frac{a}{(a-1)^2}. \tag{25}$$

Furthermore, when $p = p_c$, the recursion formula in Eq. (22) turns into the form

$$A_k = \frac{(2k-5)(a-2)}{(a-1)^3} A_{k-1}, \qquad k = 3, 4, \ldots, \tag{26}$$

with

$$A_k = F_k(p_c) = T_k(p_c)$$

to give

$$A_k = \frac{(2k-5)!!\,a(a-2)^{k-2}}{(a-1)^{3k-4}}, \qquad k = 3, 4, \ldots, \tag{27}$$

where we have made use of $A_2$ as the starting point for the recursion.

Consequently, when $|p - p_c| \ll 1$, the sol fraction $S$ in Eq. (5) takes the form, by use of $A_1$ in Eq. (24),

$$S = 1 - A_1(p - p_c), \qquad \text{for } p \geqslant p_c. \tag{28}$$

It is known that the relation

$$S + G = 1 \tag{29}$$

between the sol fraction $S$ and the gel fraction $G$ holds true. Thus we have, from Eq. (28),

$$G = A_1(p - p_c), \qquad \text{for } p \geqslant p_c. \tag{30}$$

From Eqs. (16) and (20) we immediately obtain the $k$th moment $M_k$ for $k \geqslant 2$ by means of $A_k$ in Eqs. (25) and (27):

$$M_k = \int_0^\infty n^k \tilde{P}_n \, dn = \frac{A_k}{|p - p_c|^{2k-3}}, \qquad k = 2, 3, \ldots, \tag{31}$$

for $|p - p_c| \ll 1$. Note that $\tilde{P}_n$ acts as the asymptopic form of the Flory-Stockmayer distribution near the gel point.

Now let us deal with the asymptopic form of the Flory-Stockmayer distribution. From Eq. (31) we introduce

$$X_k = \frac{\int_0^\infty n^k \tilde{P}_n \, dn}{\int_0^\infty n^{k+1} \tilde{P}_n \, dn} = \frac{A_k}{A_{k+1}} |p - p_c|^2, \qquad k = 2, 3, \ldots, \tag{32}$$

to recast the $k$th moment as well as the $(k + 1)$th one into the forms

$$\int_0^\infty n^k \tilde{P}_n \, dn = \frac{(A_k)^{k-1/2}}{(A_{k+1})^{k-3/2}} X_k{}^{3/2-k} \tag{33}$$

and

$$\int_0^\infty n^{k+1} \tilde{P}_n \, dn = \frac{(A_k)^{k-1/2}}{(A_{k+1})^{k-3/2}} X_k{}^{1/2-k}. \tag{34}$$

Differentiating both sides of Eq. (33) with respect to $X_k$ and then taking into consideration Eq. (34) yields

$$\int_0^\infty n^k \left[\frac{d\tilde{P}_n}{dX_k} + \left(k - \frac{3}{2}\right) n\tilde{P}_n\right] dn = 0, \qquad k = 2, 3, \ldots, \tag{35}$$

to give

$$\frac{d\widetilde{P}_n}{dX_k} + \left(k - \frac{3}{2}\right) n\widetilde{P}_n = 0. \tag{36}$$

It is easy to solve this equation to obtain

$$\widetilde{P}_n = C(n,k) \exp \left[-\left(k - \frac{3}{2}\right) nX_k\right], \quad k = 2, 3, \ldots. \tag{37}$$

Hence the integration constant $C(n,k)$ can be determined by Eq. (33) such that

$$\int_0^\infty Y^k C(YX_k^{-1},k) \exp \left[-\left(k - \frac{3}{2}\right)Y\right] dY = \frac{(A_k)^{k-1/2}}{(A_{k+1})^{k-3/2}} X_k^{5/2}. \tag{38}$$

Note that we have made use of the substitution

$$nX_k = Y. \tag{39}$$

As a direct result, a partial differential equation can be deduced from Eq. (38):

$$\frac{\partial C(YX_k^{-1},k)}{\partial X_k} = \frac{5}{2} \frac{C(YX_k^{-1},k)}{X_k}, \tag{40}$$

with the solution

$$C(YX_k^{-1},k) = g(Y,k)X_k^{5/2}. \tag{41}$$

This form can be rewritten, by means of the substitution given in Eq. (39), in the form

$$C(n,k) = g(nX_k,k)X_k^{5/2} \tag{42}$$

As $n$ and $X_k$ in $g(nX_k,k)$ take the form of $nX_k$, and $C(n,k)$ is independent of $X_k$, $g(nX_k,k)$ has to take the form

$$g(nX_k,k) = B_k(nX_k)^{-5/2} \tag{43}$$

to give

$$C(n,k) = B_k n^{-5/2}. \tag{44}$$

The constant $B_k$ can be determined by using Eq. (38), and then we have, with the aid of the expressions for $A_k$ in Eqs. (25) and (27),

$$B = B_k = a\left[\frac{1}{2\pi(a-1)(a-2)}\right]^{1/2}, \tag{45}$$

where $B$ means that the constant $B_k$ is independent of $k$. Thus, the asymptopic form of the Flory-Stockmayer distribution in Eq. (37) can be written explicitly as

$$\widetilde{P}_n = Bn^{-5/2} \exp\left[-\left(k - \frac{3}{2}\right) nX_k\right], \qquad k = 2, 3, \ldots, \tag{46}$$



where we have not made use of Stirling's approximation to obtain the exponent 5/2 [8, 10].

Let us further introduce a generalized typical size $n_\xi(k)$, which is a generalization of the typical size with $k = 2$ [10], as

$$n_\xi(k) = X_k^{-1} = \frac{(2k-3)(a-2)}{(a-1)^3} |p - p_c|^{-1/\sigma}, \qquad k = 2, 3, \ldots, \tag{47}$$

with

$$\sigma = 1/2 \tag{48}$$

to reformulate $\widetilde{P}_n$ in the form

$$\widetilde{P}_n = Bn^{-\tau} \exp\left[-\left(k - \frac{3}{2}\right)\frac{n}{n_\xi(k)}\right], \qquad k = 2, 3, \ldots, \tag{49}$$

with

$$\tau = 5/2. \tag{50}$$

Since $\widetilde{P}_n$ is characterized by the generalized typical size $n_\xi(k)$, we can take $\widetilde{P}_n$ with a definite $k'$ to evaluate the $k$th moment $M_k$ with a definite $k$ such that

$$
\begin{aligned}
M_k &= \int_0^\infty B n^{k-\tau} \exp\left[-\left(k' - \frac{3}{2}\right)\frac{n}{n_\xi(k')}\right] dn \\
&= B\lambda^{-(k-3/2)} \int_0^\infty t^{(k-3/2)-1} e^{-t} dt \\
&= B\lambda^{-(k-3/2)}\, \Gamma\left(k - \frac{3}{2}\right),
\end{aligned}
\tag{51}
$$

with

$$\lambda = \left(k' - \frac{3}{2}\right)\frac{1}{n_\xi(k')}$$

where $\Gamma\left(k - \frac{3}{2}\right)$ is the conventional Gamma function.

For $k \geqslant 2$, we have, from Eq. (51),

$$
\begin{aligned}
M_k &= \int_0^\infty B n^{k-\tau} \exp\left[-\left(k' - \frac{3}{2}\right)\frac{n}{n_\xi(k')}\right] dn \\
&= A_k |p - p_c|^{-\gamma_k}, \qquad k, k' = 2, 3, \ldots,
\end{aligned}
\tag{52}
$$

with

$$\gamma_k = 2k - 3. \tag{53}$$

Though the left-hand side of Eq. (52) involves $k$ and $k'$, the right-hand side, which is in accordance with the right-hand side of Eq. (31), is independent of $k'$.

When $k = 1$, we have, from Eq. (51),

$$
\begin{aligned}
M_1 &= B\lambda^{1/2} \int_0^\infty t^{-3/2} e^{-t} dt \\
&= B\lambda^{1/2}\, \Gamma\left(-\frac{1}{2}\right)
\end{aligned}
$$

$$= a\left[\frac{\lambda}{2(a-1)(a-2)}\right]^{1/2}\frac{\Gamma(-1/2)}{\Gamma(1/2)}. \tag{54}$$

Note that the integrand $t^{-3/2}\,e^{-t}$ is divergent at $t = 0$. In order to overcome this difficulty, we extend the expression of $M_k$ given in Eq. (51) to the complex form

$$M(Z) = B\lambda^{-Z}\int_0^\infty t^{Z-1}e^{-t}\,dt$$
$$= B\lambda^{-Z}\,\Gamma(Z), \tag{55}$$

where $Z$ is a complex parameter and the gamma function $\Gamma(Z)$ satisfies

$$\Gamma(1-Z) = -Z\Gamma(-Z). \tag{56}$$

Consequently, we have

$$M_k = M(ReZ) \tag{57}$$

and

$$\Gamma(1-ReZ) = -ReZ\,\Gamma(-ReZ), \tag{58}$$

with

$$ReZ = k - \frac{3}{2}.$$

For $k = 2$ and $ReZ = 1/2$, Eqs. (57) and (58) become

$$M_2 = B\lambda^{-1/2}\int_0^\infty t^{-1/2}e^{-t}\,dt$$
$$= a\left[\frac{1}{2(a-1)(a-2)\lambda}\right]^{1/2} \tag{59}$$

and

$$\frac{\Gamma(1/2)}{\Gamma(-1/2)} = -\frac{1}{2}, \tag{60}$$

respectively. The relation in Eq. (60) is not useful for evaluating the second moment $M_2$ in Eq. (59), but it is useful for treating the divergent behavior of the first moment $M_1$ in Eq. (54). When Eq. (60) is substituted in Eq. (54) and the divergent behavior of $M_1$ is removed, we obtain

$$B\lambda^{1/2} \int_0^\infty t^{-3/2} e^{-t}\, dt = \frac{1}{2} A_1 (p - p_c), \qquad \text{for } p \geqslant p_c, \tag{61}$$

where we have made use of $|p - p_c| = \pm(p - p_c)$ and then chosen the one with the negative sign.

Comparing Eq. (61) with Eq. (30), we obtain

$$\begin{aligned} G &= 2 \int_0^\infty B n^{1-\tau} \exp\left[-\left(k' - \frac{3}{2}\right) \frac{n}{n_\xi(k')}\right] dn \\ &= A_1 (p - p_c)^\beta, \qquad \text{for } p \geqslant p_c, \end{aligned} \tag{62}$$

with

$$\beta = 1. \tag{63}$$

Alternatively, we can further approach the sol fraction $S$ with the expression given in Eq. (49).

Since the distribution $\tilde{P}_n$ given in Eq. (49) has been obtained only by use of Eq. (31) without involving the expression for the sol fraction $S$ in Eq. (28), it is reasonable to introduce a constant $D$ of the form

$$D = \frac{2}{A_1 (p - p_c)} - 2 \tag{64}$$

to give, from Eq. (61),

$$\begin{aligned} S &= D \int_0^\infty n \tilde{P}_n\, dn \\ &= D B \lambda^{1/2} \int_0^\infty t^{-3/2} e^{-t}\, dt \\ &= 1 - A_1 (p - p_c), \qquad \text{for } p \geqslant p_c \end{aligned} \tag{65}$$

and

$$G = 2\int_0^\infty n\widetilde{P}_n\,dn = A_1(p - p_c). \tag{66}$$

This expression is in accordance with that given in Eq. (52).

## THE SCALING LAW

We present a brief discussion of the generalized scaling law.

By introducing the generalized typical size $n_\xi(k)$ into the right-hand sides of Eqs. (52) and (62), we have

$$\int_0^\infty Bn^{k-\tau}\exp\left[-\left(k' - \frac{3}{2}\right)\frac{n}{n_\xi(k')}\right]dn = A_k\left(\frac{A_k}{A_{k+1}}\right)^{\sigma\gamma_k} n_\xi(k)^{\sigma\gamma_k},$$

$$k = 2, 3, \ldots, \tag{67}$$

and

$$\int_0^\infty Bn^{1-\tau}\exp\left[-\left(k' - \frac{3}{2}\right)\frac{n}{n_\xi(k')}\right]dn = \frac{A_1}{2}\left(\frac{A_{k+1}}{A_k}\right)^{\sigma\beta} n_\xi(k)^{-\sigma\beta},$$

$$\text{for } p \geqslant p_c. \tag{68}$$

Application of the scaling transformation $T$,

$$Tn_\xi = Ln_\xi \quad (L \text{ being a positive real number}), \tag{69}$$

$$Tn = Ln, \tag{70}$$

to Eqs. (67) and (68) gives immediately

$$\tau - 2 = \sigma\beta \tag{71}$$

$$k + 1 - \tau = \sigma\gamma_k, \quad k = 2, 3, \ldots. \tag{72}$$

These relations, arising in essence from the generalized typical size, are the generalization of the scaling law which is associated with the typical size characterized by $k = 2$ [9, 10].

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