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CROSSLINKING REACTION OF TYPE A_a INVOLVING INTRAMOLECULAR CYCLIZATION

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ABSTRACT

An alternative way is proposed to approach crosslinking reactions of Type A_a by taking into consideration intramolecular cyclization. The sol fraction for postgelation is investigated to deduce the equilibrium number distribution of n-mer, with the Flory-Stockmayer distribution as a criterion. Furthermore, scaling study leads directly to a generalized scaling law.

1. INTRODUCTION

As is well-known, the crosslinking theory for polymers was initiated by Flory and Stockmayer [1-3]. For a system involving intramolecular cyclization, the reaction was investigated by Harris, Kilb, Gordon, Abmad, and Stepto [4-8]. Miller and Macosko [9, 10] proposed a recursion method for dealing with the problem of postgelation properties of network polymers. In this paper an alternative way is proposed to approach the crosslinking reaction of Type A_a with intramolecular cyclization. For postgelation [9-14] the sol fraction is studied in detail by taking the Flory-Stockmayer gel point as a criterion. Accordingly, an equilibrium number fraction distribution of n-mer is deduced and its reliability is examined by means of the Flory-Stockmayer distribution [1, 2].

In the theory of branching processes, a probability generating function together with a differentiation technique as proposed by Gordon [15, 16] can be used for evaluation of the moments of the distribution. Alternatively, based on the distribution proposed in this paper, a direct differentiation technique is used to obtain a recursion formula that is suitable for both pregelation and postgelation states in evaluating the moments of the distribution explicitly.

In the same way as in our previous paper [14], a scaling study [17, 18] can be used without difficulty to reach a generalized scaling law, which holds good no matter whether intramolecular cyclization is considered or not.

2. SOL FRACTION FOR POSTGELATION

In this section the sol fraction for postgelation [9-14], in which intramolecular cyclization is involved, is investigated by taking the Flory-Stockmayer gel point as a criterion.

Let us consider a crosslinking system with N monomers in which each monomer A_a keeps its a-functionality, i.e., carries a functional groups. Let p_t, p_t', and p_t'' be the total, sol, and gel equilibrium fractional conversions, respectively. Furthermore, each of the conversions can be separated into two parts, such that

$$p_t = f + p, \tag{1}$$

$$p_t' = f' + p', \tag{2}$$

$$p_t'' = f'' + p'', \tag{3}$$

where p = fraction of functional groups that have reacted intermolecularly
p' = fraction of functional groups that have reacted intermolecularly in the sol
p'' = fraction of functional groups that have reacted intermolecularly in the gel
f = fraction of functional groups that have reacted intramolecularly
f' = fraction of functional groups that have reacted intramolecularly in the sol
f'' = fraction of functional groups that have reacted intramolecularly in the gel.

The relation in Eq. (1) was proposed by Gordon [7] in treating ring-chain competition kinetics in linear polymers. For simplicity, p, p', and p'' are referred to as the total, sol, and gel crosslinking conversions, and f, f', and f'' are the total, sol, and gel intramolecular cyclization conversions.

Furthermore, let us introduce a quantity q, referred to as the total crosslinking probability, which is defined by

$$q = \frac{aNp}{aN - aNf} = \frac{p}{1 - f}, \tag{4}$$

where q takes values in the range from zero to unity. This expression shows that q is, in essence, closely related to the total intramolecular cyclization conversion f, which is expressible in terms of both sol and gel intramolecular cyclization conversions f' and f'' (see Eq. 12).

Equation (4) can be rewritten as

$$p = (1 - f)q. \tag{5}$$

Similarly, two quantities q' and q'' are introduced:

$$p' = (1 - f')q', \tag{6}$$

$$p'' = (1 - f'')q''. \tag{7}$$

Now let us begin to deal with the sol fraction S for postgelation. According to the meaning of f' and p', as defined in Eq. (2), $aN'f'$ means the number of functional groups having reacted intramolecularly in the sol and $aN'p'$ means the number of functional groups having reacted intermolecularly in the sol, where N' is the total number of monomers in the sol. Then, $aN' - aN'f' - aN'p'$ is the number of remaining functional groups in the sol, and these groups have the possibility to take a further part in crosslinking. Alternatively, according to the meaning of f and p, as defined in Eq. (1), the total number of remaining functional groups in the system is equal to $aN - aNf - aNp$, and these groups also have the possibility to take further part in crosslinking. Furthermore, from the meaning of q introduced in Eq. (4), the probability of finding a functional group in the system which joins crosslinks with a certain n-mer in the sol is

$$q\,\frac{aN' - aN'f' - aN'p'}{aN - aNf - aNp} = qS\,\frac{(1 - f')(1 - q')}{(1 - f)(1 - q)}, \tag{8}$$

where we have made use of Eqs. (5) and (6). Note that in Eq. (8) the term

$$\frac{aN' - aN'f' - aN'p'}{aN - aNf - aNp} = S\frac{(1 - f')(1 - q')}{(1 - f)(1 - q)}$$

is the conditional probability of finding a functional group in the sol which links with a certain *n*-mer.

The probability of finding a functional group in the system that is not involved in crosslinking is $(1 - q)$. Thus, the probability of finding a functional group in the sol is

$$1 - q + qS\frac{(1 - f')(1 - q')}{(1 - f)(1 - q)}.$$

If free monomer is removed from the sol, it will have, on the average, $a(1 - f')$ functionality for crosslinking. Under the assumption of equal reactivity, the probability of finding a monomer in the sol is

$$\left(1 - q + qS\frac{(1 - f')(1 - q')}{(1 - f)(1 - q)}\right)^{a(1-f')}.$$

It should be noted that the exponent $a(1 - f')$ does not arise from an exact probability consideration, but rather represents an average approximation.

Since the sol fraction S $(= N'/N)$ which varies from 1 to 0 is, in essence, the probability of finding a monomer in the sol, we have

$$S = \left(1 - q + qS\frac{(1 - f')(1 - q')}{(1 - f)(1 - q)}\right)^{a(1-f')}, \tag{9}$$

which applies under the assumption of equal reactivity and the mean average approximation ($a(1 - f')$ functionality).

Let us deal with an alternative expression involving the sol fraction S. The quantity $S(1 - q')$ is the probability of finding a functional group in the sol which does not participate in crosslinking. This quantity can be evaluated in an alternative way. The probability of finding a functional group in the system which does not take part in crosslinking is $(1 - q)$. If this functional group is in the sol, the conditional probability

$$\left(1 - q + qS\frac{(1-f')(1-q')}{(1-f)(1-q)}\right)^{a(1-f')-1}$$

should be considered. Thus, we have

$$S(1-q') = (1-q)\left(1 - q + qS\frac{(1-f')(1-q')}{(1-f)(1-q)}\right)^{a(1-f')-1} \tag{10}$$

Equation (10) holds under the assumption of equal reactivity and the mean average approximation ($a(1-f')$ functionality).

Furthermore, solving Eqs. (9) and (10) leads to

$$S = \left(\frac{1-q}{1-q'}\right)^{a(1-f')}. \tag{11}$$

Since the aNf functional groups that have reacted intramolecularly are given by the sum of $aNSf'$ and $aN(1-S)f''$ functional groups and these have reacted intramolecularly in the sol and in the gel, respectively, we have

$$f = Sf' + (1-S)f''. \tag{12}$$

Similarly, we have

$$(1-f)q = S(1-f')q' + (1-S)(1-f'')q''. \tag{13}$$

When S approaches unity, the above two relations give

$$f_c = f_c', \qquad \text{for } S = 1 \tag{14}$$

and

$$q_c = q_c', \qquad \text{for } S = 1, \tag{15}$$

respectively, where the symbol c signifies the critical point of the sol-gel transition.

Now let us express q, q', and q'' in terms of the sol fraction S.

Combining Eqs. (9) and (11) gives

$$q = \frac{1 - S^{1/a*}}{1 - \dfrac{1 - f'}{1 - f} S^{(a*-1)/a*}} \tag{16}$$

and

$$q' = 1 - (1 - q)S^{-1/a*} \tag{17}$$

with

$$a* = a(1 - f'). \tag{18}$$

When the two expressions of q and q' are substituted in Eq. (13), q'' is obtained:

$$q'' = \frac{1 - f}{(1 - f'')(1 - S)\left(1 - \dfrac{1 - f'}{1 - f} S^{(a*-1)/a*}\right)} \Bigg[1 - S^{1/a*} + \left(\frac{1 - f'}{1 - f}\right)^2 \left(S^{(2a*-1)/a*} - S^{2(a*-1)/a*}\right)\Bigg]. \tag{19}$$

When the sol fraction S tends to unity together with $f_c' - f_c$, the expressions for q, q', and q'' become indeterminate. As both f and f' are continuous in the neighborhood of $S = 1$, they can be taken as parameters without involving differentiation. Thus, application of the L'Hospital's rule by taking only the sol fraction S as variable leads us directly to the results

$$q_c = q_c' = \frac{1}{a(1 - f_c) - 1}, \tag{20}$$

$$q_c'' = \frac{2}{a(1 - f_c'')}. \tag{21}$$

Substituting q_c, q_c', and q_c'' in Eqs. (5), (6), and (7), and then further substituting the results in Eqs. (1), (2), and (3), we find that

$$p_{tc} = p_{tc}' = (1 - f_c)q_c + f_c = \frac{af_c(1 - f_c) + 1 - 2f_c}{a(1 - f_c) - 1}, \tag{22}$$

$$p_{tc}'' = (1 - f_c'')q_c'' + f_c'' = \frac{2 + af_c''}{a}, \tag{23}$$

where p_{tc}, p_{tc}', and p_{tc}'' are the gel points with respect to the total, sol, and gel equilibrium fractional conversions, and the three different forms characterize the same gel point of the sol-gel transition in an equivalent manner.

If the intramolecular cyclization conversion in the sol is not considered, the expression for p_{tc} in Eq. (22), by putting $f_c = 0$, can be reduced to the form

$$p_{tc}(f_c = 0) = \frac{1}{a - 1}. \tag{24}$$

By comparison of Eqs. (22) and (24), we find that the inequality

$$p_{tc} > p_{tc}(f_c = 0) = \frac{1}{a - 1} \tag{25}$$

holds true. This inequality agrees with the experimental fact that the observed p_{tc} is larger than $1/(a - 1)$.

As the inequality in Eq. (25) is deduced in this paper from the two expressions for the sol fraction S for postgelation in Eqs. (9) and (10), it leads us to believe that these two expressions involving the intramolecular cyclization are reasonable.

Furthermore, the total equilibrium fractional conversion $p_t = f + p$ in Eq. (1) can be rewritten in the form

$$p = p_t \left(1 - \frac{f}{p_t}\right), \tag{26}$$

where the quantity f/p_t is the total probability of intramolecular reaction defined by Ahmad and Stepto [8], i.e.,

$$\lambda = f/p_t. \tag{27}$$

We can recast the expression of the gel point in Eq. (22) in the form

$$p_{tc} = \frac{1 - \lambda_c p_{tc}}{(1 - \lambda_c)(a(1 - \lambda_c p_{tc}) - 1)} \tag{28}$$

with

$$\lambda_c = f_c / p_{tc}. \tag{29}$$

Note that at the gel point we have $\lambda_c p_{tc} = f_c \ll 1$. When terms in $\lambda_c p_{tc}$ are neglected, the expression for p_{tc} becomes the result of Ahmad and Stepto [8],

$$p_{tc}(\lambda_c p_{tc} = 0) = \frac{1}{(1 - \lambda_c)(a - 1)}. \tag{30}$$

It is evident that the order

$$p_{tc} > p_{tc}(\lambda_c p_{tc} = 0) > p_{tc}(f_c = 0) \tag{31}$$

holds true.

In this section we previously introduced 13 quantities (p_t, p_t', p_t'', f, f', f'', p, p', p'', q, q', q'', S) subject to the 10 relations given in Eqs. (1), (2), (3), (5), (6), (7), (9), (10), (12), and (13), and thus only three of the 13 quantities are independent. When the three independent quantities taken as observables are suitably chosen, such as p_t, p_t', and S, the remaining 10 can be evaluated without difficulty.

3. EQUILIBRIUM NUMBER FRACTION DISTRIBUTION OF *n*-MER AND THE MOMENTS OF THE DISTRIBUTION

In this section an equilibrium number fraction distribution of n-mer is proposed, and its reliability is examined by means of Flory-Stockmayer distribution [1, 2]. Furthermore, based on the distribution, a direct differentiation technique is used to obtain a recursion formula which is suitable for both pregelation and postgelation in evaluating the distribution moments explicitly.

If the equilibrium number fraction distribution of n-mer P_n is given, its kth moment M_k can be evaluated by

$$M_k = \sum_n n^k P_n, \qquad k = 0, 1, 2, \ldots. \tag{32}$$

In this paper NP_n gives the number of n-mers in the sol, where N is the total number of monomers in the system. It follows that $NM_0 = \sum_n NP_n$ is the total number of n-mers with $n = 1, 2, \ldots,$ in the sol. Now let us discuss the quantity $aN'p'$, which is the number of functional groups having participated in crosslinking in the sol. It is obvious that $aN'p'/2$ is the number of pairing functional groups in the sol which have reacted in crosslinking. Thus, $N' - aN'p'/2$ is the total number of n-mers in the sol to give

$$NM_0 = \sum_n NP_n = N' - \frac{aN'p'}{2}. \tag{33}$$

This expression can be further reformulated in terms of q' and a^*, with the aid of Eqs. (6) and (18), in the form

$$M_0 = \sum_n P_n = S\left(1 - \frac{a^*q'}{2}\right), \tag{34}$$

where we have made use of the expression for the sol fraction, $S = N'/N$.

Now let us turn our attention to the expression for the first moment M_1. By considering the meaning of NP_n mentioned above, nNP_n is seen to be equal to the number of monomers involved in the n-mer in the sol. Then $\sum_n nNP_n$ is just the total number of monomers in the sol, N', i.e., $NM_1 = N'$, to give

$$M_1 = \sum_n nP_n = S, \tag{35}$$

where $S = N'/N$ has been used as above.

We shall see that the equilibrium number fraction distribution P_n can be deduced from the zeroth moment by means of Eq. (34), and can also be used to evaluate the first moment M_1 to give a result in agreement with Eq. (35) obtained by intuitive reasoning.

Now let us begin to deduce the number distribution P_n from the zeroth moment M_0 in Eq. (34) by means of a Lagrange expansion.

With the aid of the sol fraction expression in Eq. (11), the zeroth moment in Eq. (34) can be rewritten as

$$M_0 = \sum_n P_n = \left(\frac{1-q}{1-q'}\right)^{a^*}\left(1 - \frac{a^*q'}{2}\right) \tag{36}$$

to give

$$M_0 = (1 - q)^{a^*}\left[Z^{a^*}\left(1 - \frac{a^*}{2}\right) + \frac{a^* Z^{a^*-1}}{2}\right], \tag{37}$$

where we have made use of the substitution

$$Z = \frac{1}{1 - q'}. \tag{38}$$

Let us rewrite the sol fraction in Eq. (9) in the form

$$S^{1/a^*} = 1 - q + qS\frac{(1 - f')(1 - q')}{(1 - f)(1 - q)}. \tag{39}$$

When the sol fraction S on both sides of this equation takes the form used in Eq. (11), we have

$$\frac{1 - q}{1 - q'} = 1 - q + q\frac{1 - f'}{1 - f}\left(\frac{1 - q}{1 - q'}\right)^{a^*-1}. \tag{40}$$

On substituting the quantity Z in Eq. (38) into this equation, we find, after dividing by the factor $(1 - q)$,

$$Z = 1 + t\phi(Z) \tag{41}$$

with

$$t = \frac{1 - f'}{1 - f}\, q(1 - q)^{a^*-2}, \tag{42}$$

$$\phi(Z) = Z^{a^*-1}. \tag{43}$$

Furthermore, the expression for the zeroth moment M_0 in Eq. (37) can be regarded as a function of Z,

$$f(Z) = M_0 = (1 - q)^{a^*}\left(Z^{a^*}\left(1 - \frac{a^*}{2}\right) + \frac{a^* Z^{a^*-1}}{2}\right) \tag{44}$$

and with $Z = 1$ it takes the form

$$f(1) = (1 - q)^{a^*}. \tag{45}$$

By means of Lagrange's expansion theorem [19], $f(Z)$ in Eq. (44) can be expanded as a power series in t by the formula

$$f(Z) = f(1) + \sum_{n=2} \frac{t^{n-1}}{(n-1)!} \left\{ \frac{d^{n-2}}{dZ^{n-2}} \left[\frac{df(Z)}{dZ} \left(\phi(Z) \right)^{n-1} \right] \right\}_{Z=1}, \tag{46}$$

in which t from Eq. (42) and $\phi(Z)$ from Eq. (43) are involved. This expansion formula is subject to the restriction condition given by Eq. (41).

Through a straightforward calculation, we get, by use of $\phi(Z)$ in Eq. (43),

$$\left\{ \frac{d^{n-2}}{dZ^{n-2}} \left[\frac{df(Z)}{dZ} \left(\phi(Z) \right)^{n-1} \right] \right\}_{Z=1} = \frac{a^*(1 - q)^{a^*} \Gamma(a^*n - n + 1)}{n\Gamma(a^*n - 2n + 3)} \tag{47}$$

where Γ stands for the Gamma function.

Substituting t as given by Eq. (42), $f(1)$ given by Eq. (45), and the differentiation form given by Eq. (47) into the Lagrange expansion (46) gives

$$M_0 = \sum_n P_n, \tag{48}$$

where

$$P_n = C_n(f') \left(\frac{1 - f'}{1 - f} \right)^{n-1} q^{n-1} (1 - q)^{a^*n-2n+2} \tag{49}$$

with

$$C_n(f') = \frac{a^*\Gamma(a^*n - n + 1)}{n!\Gamma(a^*n - 2n + 3)}. \tag{50}$$

It should be noted that P_n is the equilibrium number fraction distribution of n-mer, which involves the total intramolecular cyclization conversion f and the intramolecular cyclization conversion in the sol f'.

Now let us examine the reliability of the number distribution P_n by means of Flory-Stockmayer distribution [1, 2].

When the expressions for f and p in Eqs. (12) and (5) are introduced in $p_t = f + p$ in Eq. (1), we obtain

$$p_t = f'S + (1 - S)f'' + (1 - f)q. \tag{51}$$

For a crosslinking reaction, if intramolecular cyclization in the sol is not considered, i.e., $f' = 0$, the total equilibrium fractional conversion p_t becomes

$$p_t = q + \Delta, \qquad \text{for } f' = 0 \tag{52}$$

with

$$\Delta = (1 - S)(1 - q)f''. \tag{53}$$

This p_t for $f' = 0$ is, in essence, the equilibrium fractional conversion of Flory and Stockmayer [1, 2].

For pregelation as the intramolecular cyclization conversion in the gel, f'', vanishes, we have

$$\Delta = 0 \tag{54}$$

to give, from Eq. (52),

$$p_t = q, \qquad \text{for } f' = f'' = 0. \tag{55}$$

This relation can help us to reduce the distribution P_n in Eq. (49) directly to the result

$$P_n = C_n(p_t)^{n-1}(1 - p_t)^{an-2n+2} \tag{56}$$

with

$$C_n = \frac{a(an - n)!}{n!(an - 2n + 2)!} \tag{57}$$

This form is the well-known Flory-Stockmayer distribution [1, 2].

For postgelation as the sol fraction S changes from unity to zero and q changes from q_c to unity, we have

$$(1 - S)(1 - q) \ll 1. \tag{58}$$

At the starting and end points for postgelation, i.e., $S = 1$ and $S = 0$, the small quantity $(1 - S)(1 - q)$ takes the value of zero.

Since the intramolecular cyclization conversion in the gel f'' is always less than unity, the inequality

$$\Delta = (1 - S)(1 - q)f'' < (1 - S)(1 - q) << 1 \tag{59}$$

holds true.

Finally, we see from $p_t = q + \Delta$ for $f' = 0$ in Eq. (52) that we have

$$p_t - q = \Delta < (1 - S)(1 - q) << 1, \qquad \text{for } f' = 0. \tag{60}$$

It follows that, as a good approximation, we have

$$p_t \approx q, \qquad \text{for } f' = 0. \tag{61}$$

In order to simplify our discussion, we rewrite the distribution P_n in Eq. (49) in the form

$$P_n = C_n(f')(1 - f')^{n-1}(q)^{n-1}(1 - q)^{a^*n-n+1}[(1 - f)(1 - q)]^{1-n}, \tag{62}$$

in which the quantity $(1 - f)(1 - q)$ can be further expressed in terms of the total fractional conversion p_t in Eq. (1), in view of Eq. (5),

$$(1 - f)(1 - q) = 1 - p_t. \tag{63}$$

On substituting this, the distribution in Eq. (62) takes the form

$$P_n = C_n(f')(1 - f')^{n-1}(q)^{n-1}(1 - q)^{a^*n-n+1}(1 - p_t)^{1-n}. \tag{64}$$

When the intramolecular cyclization conversion in the sol, f', is not considered, the distribution in Eq. (64) becomes

$$P_n = C_n q^{n-1}(1 - q)^{an-n+1}(1 - p_t)^{1-n}, \qquad \text{for } f' = 0, \tag{65}$$

where p_t for $f' = 0$ is, in essence, the total fractional conversion of Flory and Stockmayer, and C_n is as given in Eq. (57).

For postgelation with the good approximation $p_t \approx q$ for $f' = 0$ in Eq. (61), the terms q^{n-1} and $(1 - q)^{an-n+1}$ in Eq. (65) can be replaced by $(p_t)^{n-1}$ and

$(1 - p_t)^{an-n+1}$, respectively. Thus, the distribution P_n of Eq. (65) reduces immediately to the Flory-Stockmayer distribution.

We now turn to the recursion formula for polymer moments.

By making use of the number distribution P_n in Eq. (49), the kth moment M_k can be expressed as

$$M_k = \sum_n C_n(f')\left(\frac{1-f'}{1-f}\right)^{n-1} n^k q^{n-1}(1-q)^{a^*n-2n+2}, \quad \text{for } k = 0, 1, 2, \ldots. \tag{66}$$

Differentiation of this equation with respect to q gives

$$M_{k+1} = \frac{1}{1-(a^*-1)q}\left(q(1-q)\frac{\partial M_k}{\partial q} + (1-q)M_k\right), \quad \text{for } k = 0, 1, 2, \ldots. \tag{67}$$

This is the recursion formula for the distribution moments.

On substituting the zeroth moment M_0 of Eq. (34) into the recursion formula, this gives, through straightforward calculations, the first moment M_1 in the form

$$M_1 = \sum_n nP_n = S, \tag{68}$$

in accordance with Eq. (35) which had been obtained by intuitive reasoning.

The expression of the zeroth moment M_0 for postgelation in Eq. (34) can be extended to pregelation. For pregelation ($q \leqslant q_c$), $S = 1$ and $f'' = 0$. Then from Eqs. (12) and (13) we have $f' = f$ and $q' = q$. By substituting $S = 1$, $f' = f$, and $q' = q$ in Eq. (34), we obtain directly $M_0 = 1 - a(1-f)q/2$ for pregelation. Thus, the zeroth moment M_0 for both pre- and postgelation can be written as

$$M_0 = \sum_n P_n = \begin{cases} 1 - \dfrac{a(1-f)q}{2}, & \text{for } q \leqslant q_c \\[2ex] S\left(1 - \dfrac{a(1-f')q'}{2}\right), & \text{for } q \geqslant q_c. \end{cases} \tag{69}$$

Obviously, the first moment M_1 for both pre- and postgelation takes the forms (by means of Eq. 35)

$$M_1 = \sum_n nP_n = \begin{cases} 1, & \text{for } q \leqslant q_c \\ S, & \text{for } q \geqslant q_c. \end{cases} \tag{70}$$

Furthermore, application of the recursion formula (67) to the first moment M_1 in Eq. (70) gives the expression for the second moment M_2 explicitly:

$$M_2 = \sum_n n^2 P_n = \begin{cases} \dfrac{V_2(q)}{1 - (a^* - 1)q}, & \text{for } q \leqslant q_c \\[2ex] \dfrac{T_2(q)}{(a^* - 1)q - 1}, & \text{for } q \geqslant q_c \end{cases} \tag{71}$$

with

$$V_2(q) = 1 + q, \tag{72}$$

$$T_2(q) = -\left(q(1 - q)\frac{\partial S}{\partial q} + (1 + q)S\right), \tag{73}$$

$$\frac{\partial S}{\partial q} = \frac{a^*\left(1 - \dfrac{1 - f'}{1 - f} S^{(a^*-1)/a^*}\right) S^{(a^*-1)/a^*}}{(a^* - 1)q \dfrac{1 - f'}{1 - f} S^{(a^*-2)/a^*} - 1}. \tag{74}$$

Note that the symbol $a^* = a(1 - f')$ has been defined in Eq. (18). The second moment M_2 becomes infinity at $q = q_c$, where q_c is as given in Eq. (20). This singularity property shows that the sol-gel transition happens.

By successive recursion, we obtain the third moment explicitly,

$$M_3 = \sum_n n^3 P_n = \begin{cases} \dfrac{V_3(q)}{[1 - (a^* - 1)q]^3}, & \text{for } q \leqslant q_c \\[2ex] \dfrac{T_3(q)}{[(a^* - 1)q - 1]^3}, & \text{for } q \geqslant q_c, \end{cases} \tag{75}$$

with

$$V_3(q) = (a^* - 1)q(1 - q)(1 + q) + [1 - (a^* - 1)q](1 + 3q), \tag{76}$$

$$T_3(q) = -[(a^* - 1)q(1 - q) + (1 - (a^* - 1)q)(1 + q)]\left[q(1 - q)\frac{\partial S}{\partial q} + (1 + q)S\right] - (1 - (a^* - 1)q)q(1 - q)\left((2 - q)\frac{\partial S}{\partial q} + S + q(1 - q)\frac{\partial^2 S}{\partial q^2}\right), \tag{77}$$

where

$$\frac{\partial^2 S}{\partial q^2} = \frac{1}{(a^* - 1)q\dfrac{1 - f'}{1 - f}S^{(a^*-2)/a^*} - 1}\left[(a^* - 1)\left(S^{-1/a^*} - 3\frac{1 - f'}{1 - f}S^{(a^*-2)/a^*}\right) \times \frac{\partial S}{\partial q} - q\frac{(a^* - 1)(a^* - 2)(1 - f')}{a^*(1 - f)}S^{-2/a^*}\left(\frac{\partial S}{\partial q}\right)^2\right]. \tag{78}$$

Note that $\partial S/\partial q$ is given explicitly in Eq. (74).

Taking the expression for M_3 in Eq. (75) as the starting point for the recursion, one can find, by repeated application of the recursion formula (67), that a general expression of the kth moment for $k \geqslant 3$ can be expressed as

$$M_k = \sum_n n^k P_n = \begin{cases} \dfrac{V_k(q)}{[1 - (a^* - 1)q]^{2k-3}}, & \text{for } q \leqslant q_c \\[2ex] \dfrac{T_k(q)}{[(a^* - 1)q - 1]^{2k-3}}, & \text{for } q \geqslant q_c, \end{cases} \tag{79}$$

where $V_k(q)$ and $T_k(q)$ are subject to the same recursion formula

$$H_k(q) = (2k - 5)(a^* - 1)q(1 - q)H_{k-1} + (1 - (a^* - 1)q)\left((1 + q)H_{k-1} + q(1 - q)\frac{\partial H_{k-1}}{\partial q}\right), \quad k = 3, 4, 5, \ldots, \tag{80}$$

with

$$H_k = \begin{cases} V_k(q), & \text{for } q \leqslant q_c \\ T_k(q), & \text{for } q \geqslant q_c. \end{cases} \tag{81}$$

This recursion formula can be used repeatedly in evaluating the explicit form of the M_k moments.

4. SCALING STUDY OF SOL-GEL TRANSITION

In this section, as we have done in a previous paper [14], a scaling study [17, 18] can proceed without difficulty.

Let us consider the polymer moments near the gel point, i.e., $|q - q_c| \ll 1$. As in the neighborhood of q_c, the total intramolecular cyclization conversion f and the intramolecular cyclization conversion in the sol f' vary steadily, and so they can be taken as parameters not subject to differentiation. Thus, $(dS/dq)_{q_c}$ can be evaluated by Eq. (74) to give

$$A_1 = -\left(\frac{dS}{dq}\right)_{q_c} = \frac{2a(1-f_c)[a(1-f_c)-1]}{a(1-f_c)-2}, \tag{82}$$

where we have made use of L'Hospital's rule.

It is easy to find $V_2(q)$ and $T_2(q)$ in Eqs. (72) and (73) at the gel point by writing

$$A_2 = \frac{V_2(q_c)}{a(1-f_c)-1} = \frac{T_2(q_c)}{a(1-f_c)-1} = \frac{a(1-f_c)}{[a(1-f_c)-1]^2}. \tag{83}$$

By taking $V_2(q_c)$ and $T_2(q_c)$ as starting points, repeated application of the recursion formula in Eq. (80) can lead us to the result

$$\begin{aligned} A_k &= V_k(q_c)[a(1-f_c)-1]^{3-2k} = T_k(q_c)[a(1-f_c)-1]^{3-2k} \\ &= \frac{(2k-5)!!a(1-f_c)[a(1-f_c)-2]^{k-2}}{[a(1-f_c)-1]^{3k-4}}, \quad k = 3, 4, \ldots . \end{aligned} \tag{84}$$

Consequently, when $|q - q_c| \ll 1$, the sol fraction S in Eq. (11) takes the form, by use of A_1 in Eq. (82),

$$S = 1 - A_1(q - q_c), \quad \text{for } q \geqslant q_c. \tag{85}$$

Since

$$S + G = 1, \tag{86}$$

we have, from Eq. (85),

$$G = A_1(q - q_c), \qquad \text{for } q \geqslant q_c. \tag{87}$$

From Eqs. (71) and (79) we obtain immediately M_k for $k \geqslant 2$ by use of A_k in Eqs. (83) and (84):

$$M_k = \int_0^\infty n^k \tilde{P}_n dn = \frac{A_k}{|q - q_c|^{2k-3}}, \qquad k = 2, 3, \ldots, \tag{88}$$

where $\tilde{P}_n$ is defined as the asymptopic form near the gel point of the number distribution P_n in Eq. (49).

Now let us deal with the asymptopic form of the number distribution P_n in Eq. (49). From Eq. (88) we introduce X_k, defined as

$$X_k = \frac{\int_0^\infty n^k \tilde{P}_n dn}{\int_0^\infty n^{k+1} \tilde{P}_n dn} = \frac{A_k}{A_{k+1}} |q - q_c|^2, \qquad k = 2, 3, \ldots, \tag{89}$$

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

$$\int_0^\infty n^k \tilde{P}_n dn = \frac{(A_k)^{k-(1/2)}}{(A_{k+1})^{k-(3/2)}} X_k^{(3/2)-k} \tag{90}$$

and

$$\int_0^\infty n^{k+1} \tilde{P}_n dn = \frac{(A_k)^{k-(1/2)}}{(A_{k+1})^{k-(3/2)}} X_k^{(1/2)-k}. \tag{91}$$

Differentiating both sides of Eq. (90) with respect to X_k and then taking into consideration Eq. (91) yields

$$\int_0^\infty n^k \left[\frac{d\tilde{P}_n}{dX_k} + \left(k - \frac{3}{2} \right) n\tilde{P}_n \right] dn = 0, \qquad k = 2, 3, \ldots, \tag{92}$$

to give

$$\frac{d\tilde{P}_n}{dX_k} + \left(k - \frac{3}{2}\right)n\tilde{P}_n = 0, \qquad k = 2, 3, \ldots, \tag{93}$$

with the solution

$$\tilde{P}_n = C(n,k) \exp\left[-\left(k - \frac{3}{2}\right)nX_k\right]. \tag{94}$$

We shall see that the asymptopic form $\tilde{P}_n$ is, in essence, independent of k.

By the procedure we used in a previous paper [14], the integration constant $C(n,k)$ in Eq. (94) can be determined by

$$C(n,k) = B_k n^{-5/2} \tag{95}$$

with

$$B_k = B = a(1 - f_c)[2\pi(a(1 - f_c) - 1)(a(1 - f_c) - 2)]^{-1/2} \tag{96}$$

As B_k is independent of k, the symbol k is deleted, i.e., $B_k = B$, and the asymptopic form $\tilde{P}_n$ can be rewritten as

$$\tilde{P}_n = Bn^{-\tau} \exp\left[-\left(k - \frac{3}{2}\right)\frac{n}{n_\xi(k)}\right], \qquad k = 2, 3, \ldots, \tag{97}$$

where

$$\tau = 5/2 \tag{98}$$

and

$$n_\xi(k) = X_k^{-1} = \frac{(2k - 3)(a(1 - f_c) - 2)}{(a(1 - f_c) - 1)^3} \,|q - q_c|^{-1/\sigma}, \tag{99}$$

with

$$\sigma = 1/2. \tag{100}$$

The quantity $n_\xi(k)$ is a generalization of the typical size with $k = 2$ defined by Stauffer [18].

It is clear that the factor $(k - 3/2)$ in $\tilde{P}_n$ in Eq. (97) can be canceled by the same factor in $n_\xi(k)$, and thus the asymptopic form $\tilde{P}_n$ though formally dependent on k, is, in essence, independent of k. We also find, from $n_\xi(k)$ and B, that the intramolecular cyclization conversion f_c is involved in the asymptopic form $\tilde{P}_n$ in Eq. (97).

By the same method as in a previous paper [14], the scaling study can be done without difficulty. For brevity, we only state the final results without proof (for details, see Ref. 14).

Near the gel point, the kth moment M_k in Eq. (89) can be expressed as

$$\begin{aligned} M_k &= \int_0^\infty Bn^{k-\tau} \exp\left[-\left(k' - \frac{3}{2}\right)\frac{n}{n_\xi(k')}\right] dn \\ &= A_k\,|q - q_c|^{-\gamma_k}, \qquad k, k' = 2, 3, \ldots, \end{aligned} \tag{101}$$

with

$$\gamma_k = 2k - 3, \tag{102}$$

and the gel fraction G in Eq. (87) can be written as

$$\begin{aligned} G &= 2B\int_0^\infty n^{1-\tau} \exp\left[-\left(k' - \frac{3}{2}\right)\frac{n}{n_\xi(k')}\right] dn \\ &= A_1(q - q_c)^\beta, \qquad \text{for } q \geqslant q_c, \end{aligned} \tag{103}$$

with

$$\beta = 1. \tag{104}$$

For the sol fraction S in Eq. (85), we have

$$\begin{aligned} S &= DB\int_0^\infty n^{1-\tau} \exp\left[-\left(k' - \frac{3}{2}\right)\frac{n}{n_\xi(k')}\right] dn \\ &= 1 - A_1(q - q_c), \qquad \text{for } q \geqslant q_c, \end{aligned} \tag{105}$$

with

$$D = \frac{2}{A_1(q - q_c)} - 2, \tag{106}$$

where the critical exponents τ, σ, β, and γ_k for $k \geqslant 2$ satisfy the relations

$$\tau - 2 = \sigma\beta \tag{107}$$

$$k + 1 - \tau = \sigma\gamma_k, \qquad k = 2, 3, \ldots . \tag{108}$$

These relations are generalizations of the scaling law, with $k = 2$, due to Stauffer [18].

As the generalized scaling law given in Eqs. (107) and (108) agrees with the law in a previous paper [14] that did not involve intramolecular cyclization, the generalized scaling law holds for the A_a crosslinking reaction, no matter whether intramolecular cyclization is involved or not.

5. CONCLUSIONS

This paper deals with the problem of pre- and postgelation properties of network polymers of the A_a type involving intramolecular cyclization in the sol. With the assumption of equireactivity and the mean approximation of intramolecular cyclization in the functional groups, expressions for the sol fraction are used to deduce an equilibrium number-fraction distribution of n-mers in which intramolecular cyclization in the sol is involved. Based on the distribution, a direct differentiation technique is utilized to obtain a recursion formula that is suitable for both pre- and postgelation in evaluating the distribution moments explicitly.

In the same way as in a previous paper [14], a scaling study can, without difficulty, reach a generalized scaling law which holds no matter whether intramolecular cyclization is considered or not.

REFERENCES

[1] P. J. Flory, *J. Am. Chem. Soc.*, *63*, 3083, 3091, 3096 (1941).
[2] W. H. Stockmayer, *J. Chem. Phys.*, *11*, 45 (1943).
[3] W. H. Stockmayer, *J. Polym. Sci.*, *9*, 69 (1952); *11*, 424 (1953).

[4] F. E. Harris, *J. Chem. Phys.*, *23*, 1518 (1955).

[5] R. W. Kilb, *J. Phys. Chem.*, *62*, 969 (1958).

[6] M. Gordon and G. R. Scantlebury, *J. Polym. Sci., Part C*, *16*, 3933 (1968).

[7] M. Gordon and W. B. Temple, *Makromol. Chem.*, *152*, 277 (1972).

[8] Z. Ahmad and R. F. T. Stepto, *Colloid Polym. Sci.*, *258*, 663 (1980).

[9] C. W. Macosko and D. R. Miller, *Macromolecules*, *9*, 199 (1976).

[10] D. R. Miller and C. W. Macosko, *Ibid.*, *9*, 206 (1976).

[11] G. R. Dobson and M. Gordon, *J. Chem. Phys.*, *43*, 705 (1965).

[12] M. Gordon and G. Scantlebury, *J. Chem. Soc.*, p. 1 (1967).

[13] A.-C. Tang, *The Statistical Theory of Polymeric Reactions*, Science Press, Beijing, China, 1981 (in Chinese).

[14] A.-C. Tang, Z.-S. Li, C.-C. Sun, and X.-Y. Tang, *J. Macromol. Sci.-Chem.*, *A25*(1), 41 (1988).

[15] M. Gordon, *Proc. R. Soc. London*, *A268*, 240 (1962).

[16] K. Dusek, M. Ilavsky, and S. Lunak, *J. Polym. Sci., Polym. Symp.*, *52*, 29 (1975).

[17] P. G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, London, 1979.

[18] D. Stauffer, A. Coniglio, and M. Adam, *Adv. Polym. Sci.*, *44*, 103 (1982).

[19] E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis*, Reprinted, Cambridge University Press, Cambridge, 1952.

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