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# ON THE INTRAMOLECULAR CYCLIZATION OF $A_a$ TYPE CROSSLINKING REACTION

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## ABSTRACT

By taking into consideration of intramolecular cyclization, the $A_a$ type crosslinking reaction is investigated to give the sol fraction for postgelation from which the equilibrium number fraction distribution is deduced. Furthermore, by means of differentiation technique, a recursion formula for evaluating the kth polymer moment is obtained.

## INTRODUCTION

As is well known, the crosslinking theory for polymers was initiated by Flory-Stockmayer[1-3]. For a system involving intramolecular cyclization, the reaction was investigated by Harris, Kilb, Gordon, Ahmad, and Stepto[4-8]. In this paper, an alternative way is proposed to approach the $A_a$ type crosslinking reaction in which the intramolecular cyclization is involved. The sol fraction for a post-gel is studied in detail to deduce the eqilibrium number fraction distribution with Flory-Stockmayer distribution as a criterion. In the theory of branching processes, a probability generating function method has been proposed by Gordon[9,10] for the evaluation of polymer moments. In this paper, by means of the number distribution characterized by intramolecular cyclization, a direct differentiation technique is used to obtain a recursion formula that holds true for both pregelation and postgelation states in evaluating the kth polymer moment explicitly.

## 1. SOL FRACTION FOR POSTGELATION

Let us consider a crosslinking system associated with monomer $A_a$ having a-functionality. Let p and p' be the total and sol equilibrium fraction conversions, respectively. Furthermore, each of the conversions can be separated into two parts in the forms

$$p = q + f \tag{1}$$
$$p' = q' + f' \tag{2}$$

where

q = fraction of functional groups that have reacted intermolecularly

$q'$ = fraction of functional groups that have reacted intermolecularly in the sol

$f$ = fraction of functional groups that have reacted intramolecularly

$f'$ = fraction of functional groups that have reacted intramolecularly in the sol.

Note that the relation in Eq.(1) was proposed by Gordon[7] in treating ring-chain competition kinetics in linear polymers.

From probability consideration, each of the functional group of monomer $A_a$ may have three kinds of probabilities in the sol for postgelation such that

1. The probability of finding a functional group in the system that is not involved in crosslinking is $1-q-f$.
2. The probability of finding a functional group in the system which joins crosslinks with a certain n-mer in the sol is $qS(1-f'-q')/(1-f-q)$, where S represents the sol fraction which varies from 1 to 0 for postgelation.
3. The probability of finding a functional group in the system which participates in intramolecular cyclization in the sol is $f'S^{1/a}$.

Since the sol fraction S can be interpreted as the probability of finding a monomer in the sol, it is not difficult to find that the sol fraction S can be expressed in terms of the three kinds of probabilities mentioned above in the form

$$S = \left(1 - f - q + qS\frac{1 - f' - q'}{1 - f - q} + f'S^{1/a}\right)^a \tag{3}$$

For brevity, we only state without argument that from probability consideration, an alternative expression of S can be obtained

$$S = \left(\frac{1 - f - q}{1 - f' - q'}\right)^a \tag{4}$$

It should be noted that the two expressions of S given by Eqs.(3) and (4) are independent.

In the above discussion, we have introduced 7 quantities($q,q',f,f',p,p',S$) subject to the 4 relations given in Eqs.(1), (2), (3) and (4), and thus only three of the 7 quantities are independent. When the three independent quantities taken as observables are suitably chosen, such as $p$, $p'$ and $S$, the remaining 4 can be evaluated without difficulty.

Now let us discuss the gel point of $A_a$ type crosslinking reaction involving intramolecular cyclization. Applying Eq.(4) to the term $(1-f'-q')/(1-f-q)$ appearing in the right hand side of Eq.(3) gives

$$S = (1 - f - q + qS^{(a-1)/a} + f'S^{1/a})^a. \tag{5}$$

By differentiating the both sides of Eq.(5) with respect to S, and then, by considering the critical condition $S \longrightarrow 1$ with $f=f'=f_c$, we obtain

$$q_c = (1 - f_c)/(a - 1) \tag{6}$$

where the symbol c signifies the critical point of the sol-gel transition. Thus, the gel point $p_c$ involving intramolecular cyclization can be easily written as, by means of Eqs.(1) and (6)

$$p_c = f_c + q_c = f_c + (1 - f_c)/(a - 1) \; . \tag{7}$$

If the intramolecular cyclization conversion in the sol is not considered, the gel point $p_c$ in Eq.(7), by putting $f_c$=0, can be reduced to the form

$$p_c(f_c=0) = 1/(a - 1) \; . \tag{8}$$

This form is the well known gel point without cyclization obtained by Flory-Stockmayer[1,2]. It is clear that the inequality

$$p_c > p_c(f_c=0) \tag{9}$$

holds good. This inequality agrees with the experimental fact that the observed $p_c$ is larger than 1/(a-1). When a=2, both gel points $p_c$ and $p_c(f_c=0)$ given by Eqs.(7) and (8) take the same value of unity. This means that no gelation occurs for the case of a=2, no matter whether intramolecular cyclization is considered or not.

## 2. EQUILIBRIUM NUMBER FRACTION DISTRIBUTION

Let us rewrite the sol fraction S in Eq.(4) in the form

$$S = F(z) = (1 - f - q)^a z^a \tag{10}$$

with

$$z = 1/(1 - f' - q') \; . \tag{11}$$

By combining the two independent expressions of sol fraction given by Eqs.(3) and (4), an alternative expression of z can be obtained

$$z = \frac{1}{1 - f'} + t\phi(z) \tag{12}$$

with

$$t = \frac{q(1 - f - q)^{a-1}}{(1 - f')(1 - f - q)} \; , \qquad \phi(z) = z^{a-1} . \tag{13}$$

By means of Lagrange's expansion theorem[11], the sol fraction S=F(z) in Eq.(10) can be expanded as a power series in t by the formula

$$S=F(z)=F\left(\frac{1}{1-f'}\right) + \sum_{n=2} \frac{t^{n-1}}{(n-1)!} \left\{ \frac{d^{n-2}}{dz^{n-2}} \left[ \frac{dF(z)}{dz} (\phi(z))^{n-1} \right] \right\}_{z=\frac{1}{1-f'}} \tag{14}$$

This expansion formula is subject to the restriction condition given by Eq.(12). A straightforward calculation leads us to the result, from Eq.(14)

$$S = \sum_{n=1} nP_n \tag{15}$$

where $P_n$, which is the equilibrium number fraction distribution of n-mer, takes the form

$$P_n = \frac{a(an-n)!}{n!(an-2n+2)!}\left(\frac{q}{1-f'}\right)^{n-1}\left(\frac{1-f-q}{1-f'}\right)^{an-2n+2} . \tag{16}$$

Under the assumption that no intramolecular cyclization occurs in the sol(f'=0), the distribution $P_n$ can be reduced, for pregelation, to

$$P_n = \frac{a(an-n)!}{n!(an-2n+2)!} q^{n-1}(1-q)^{an-2n+2} . \tag{17}$$

This form is the well known Flory-Stockmayer equilibrium number fraction distribution. In obtaining the distribution in Eq.(17), we have made use of f=f'=0. For the case of postgelation, the distribution $P_n$ in Eq.(16) can be reduced approximately to the one given by Eq.(17). For brevity, the detail is omitted here.

## 3. RECURSION FORMULA FOR THE KTH MOMENT

The kth moment $M_k$ is defined as

$$M_k = \sum_{n=1} n^k P_n , \quad k = 0, 1, 2, \ldots \tag{18}$$

where $P_n$ is given by Eq.(16), in which the intramolecular cyclization is involved. By differentiating the both sides of Eq.(18) with respect to q, a recursion formula of polymer moments involving $M_k$ and $M_{k+1}$ can be deduced

$$M_{k+1} = \frac{1}{1-f-(a-1)q}\left[q(1-f-q)\frac{\partial M_k}{\partial q} + (1+q-f)M_k\right], \quad k=0,1,\ldots \tag{19}$$

This recursion formula is suitable for both pre-gel and post-gel in evaluating the polymer moments explicitly.

From the probability meaning of the distribution $P_n$, it is not difficult to find that the zeroth moment $M_0$ is the number of n-mer with n=1, 2, 3,... in the sol per total number of monomers in the crosslinking system, i.e.

$$M_0 = \sum_{n=1} P_n = \begin{cases} 1 - \dfrac{aq}{2(1-f)} , & \text{for pre-gel} \\[2ex] S\left[1 - \dfrac{aq'}{2(1-f')}\right], & \text{for post-gel} \end{cases} \tag{20}$$

From this expression, we can easily obtain, via the recursion formula (19), the first moment $M_1$

$$M_1 = \sum_{n=1} nP_n = \begin{cases} 1, & \text{for pre-gel} \\ S, & \text{for post-gel} \end{cases} \tag{21}$$

This expression is in agreement with that given by Eq.(15) which has been obtained by means of Lagrange expansion method. Taking $M_1$ as starting point, we can obtain $M_2$, with consecutive recursion

$$M_2 = \sum_{n=1} n^2 P_n = \begin{cases} \dfrac{V_2}{1 - f - (a - 1)q}, & \text{for pre-gel} \\[2ex] \dfrac{T_2}{f + (a - 1)q - 1}, & \text{for post-gel} \end{cases} \tag{22}$$

with

$$V_2 = 1 + q - f \tag{23}$$

$$T_2 = - [q(1 - q - f)\frac{\partial S}{\partial q} + (1 + q - f)S] \tag{24}$$

$$\frac{\partial S}{\partial q} = \frac{a(1 - S^{(a-1)/a})S^{(a-1)/a}}{(a - 1)qS^{(a-2)/a} - (1 - f')} . \tag{25}$$

From the expression of $M_2$ which is taken as starting point, one can approach, by repeated application of the recursion formula (19), a general expression of the kth moment $M_k$ for $k \geqslant 2$

$$M_k = \sum_{n=1} n^k P_n = \begin{cases} \dfrac{V_k}{[1 - f - (a - 1)q]^{2k-3}}, & \text{for pre-gel} \\[2ex] \dfrac{T_k}{[f + (a - 1)q - 1]^{2k-3}}, & \text{for post-gel} \end{cases} \tag{26}$$

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

$$H_k = (2k-5)(a-1)q(1-q-f)H_{k-1} + (1-f-(a-1)q)[q(1-f-q)\frac{\partial H_{k-1}}{\partial q} + (1+q-f)H_{k-1}]. \tag{27}$$

Note that $H_k$ is used to denote either $V_k$ for pre-gel or $T_k$ for post-gel.

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