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## CURING THEORY INVOLVING CYCLIZATION

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### ABSTRACT

By means of a probabilistic approach, the Stockmayer type polycondensation in which cyclization is involved is investigated to give the sol fraction post-gel explicitly. This theoretical sol fraction is tested by the  $A_2, A_3-B_1, B_2$  type reaction of 1.4-butanediol, 1.1.1-trimethylol propane, adipic acid and caproic acid to give reasonable result.

### INTRODUCTION

As is well known, the curing theory of polycondensation was initiated by Flory and Stockmayer[1,2]. Miller and Macosko[3,4] proposed a recursion method for dealing with the problem of post-gel properties of network polymers. Systems involving intramolecular cyclization were investigated by Harris, Kilb, Gordon, Dusek, Ahmad and Stepto[5-10]. In the earlier publication[11], some of the present authors have treated  $A_3-B_2$  type polymerisation reaction of adipic acid and trimethylol propane in which the intramolecular cyclization has been considered. In this paper, an attempt is made to extend the Stockmayer  $A_{a_1}, \dots, A_{a_s}-B_{b_1}, \dots, B_{b_t}$  type theory to the case where the intramolecular cyclization is involved. By means of a probabilistic approach, the Stockmayer type sol fraction for post-gel is proposed. Furthermore, by using parameter-fitting process, the  $A_2, A_3-B_1, B_2$  type sol fraction is tested by the reaction of 1.4-butanediol, 1.1.1-trimethylol propane, adipic acid and caproic acid. It is shown that the sol fraction involving cyclization proposed in this paper is applicable.

### 1. THE SOL FRACTION POST-GEL INVOLVING CYCLIZATION

Let us consider a Stockmayer type[2] polycondensation system which contains two species of monomers  $A_{a_1}, \dots, A_{a_s}$  and  $B_{b_1}, \dots, B_{b_t}$  with  $a_i$  ( $i=1, 2, \dots, s$ ) and  $B_j$  ( $j=1, 2, \dots, t$ ) functionalities, respectively. Let  $S_{a_i}$  and  $S_{b_j}$  be the sol fraction with respect to the

monomers  $A_{a_i}$  and  $B_{b_j}$ . Let us use  $p_a, p'_a$  and  $p_b, p'_b$  to which the A and B species correspond to denote the total and the sol fractional conversions, respectively. As extension of the relations proposed by Gordon[7] in treating ring-chain competition kinetics in linear polymers, each of the conversions for network polymers can be separated in the form

$$p_a = q_a + f_a, \quad p'_a = q'_a + f'_a \tag{1}$$

$$p_b = q_b + f_b, \quad p'_b = q'_b + f'_b \tag{2}$$

where

- $q_a(q_b)$  = fraction of functional groups that have reacted intermolecularly for species A(B),
- $q'_a(q'_b)$  = fraction of functional groups that have reacted intermolecularly in the sol for species A(B),
- $f_a(f_b)$  = fraction of functional groups that have reacted intramolecularly for species A(B),
- $f'_a(f'_b)$  = fraction of functional groups that have reacted intramolecularly in the sol for species A(B).

In order to make our discussion easier, two quantities are introduced

$$X_i = a_i N_{a_i} / (\sum_i a_i N_{a_i}), \quad i = 1, 2, \dots, s$$

$$Y_j = b_j N_{b_j} / (\sum_j b_j N_{b_j}), \quad j = 1, 2, \dots, t \tag{3}$$

where  $N_{a_i} (N_{b_j})$  is the number of monomers  $A_{a_i} (B_{b_j})$ .

From  $q_a(q_b)$  and  $f_a(f_b)$  as well as  $q'_a(q'_b)$  and  $f'_a(f'_b)$ , one can get from a number balance of groups the corresponding values for the gel  $q''_a(q''_b)$  and  $f''_a(f''_b)$  as follows

$$q_a = \sum_i X_i S_{a_i} q'_a + (1 - \sum_i X_i S_{a_i}) q''_a \tag{4}$$

$$q_b = \sum_j Y_j S_{b_j} q'_b + (1 - \sum_j Y_j S_{b_j}) q''_b \tag{5}$$

$$f_a = \sum_i X_i S_{a_i} f'_a + (1 - \sum_i X_i S_{a_i}) f''_a \tag{6}$$

$$f_b = \sum_j Y_j S_{b_j} f'_b + (1 - \sum_j Y_j S_{b_j}) f''_b \tag{7}$$

where  $S_{a_i} (S_{b_j})$  represents the sol fraction of monomer  $A_{a_i} (B_{b_j})$  for

species A(B) which varies from 1 to 0 post-gel. It should be noted that if cyclization already occurs before the gel point, some of the cycles in the gel can be considered elastically inactive. The sum of intramolecular bonds in sol and those corresponding to elastically inactive cycles would be related to  $f$ . Furthermore, we emphasize that a cyclic threaded through by another chain could be elastically effective.

Now let us concentrate our attention on a functional group A of monomer  $A_{a_i}$  in the species  $A_{a_1}, \dots, A_{a_s}$ . From probability considerations, a functional group A of monomer  $A_{a_i}$  may have three kinds of probabilities in the sol post-gel such that

1. The probability of finding a functional group A of monomer  $A_{a_i}$  that is unreacted is
 
$$1 - q_a - f_a \tag{8}$$

2. The probability of finding a functional group A of monomer  $A_{a_i}$  which reacts intermolecularly with that of B in monomer  $B_{b_j}$  ( $j=1,2,\dots,t$ ) which is connected to a certain n-mer in the sol is

$$q_a \sum_{j=1}^t Y_j S_{b_j}^{(b_j-1)/b_j} \tag{9}$$

Note that the factor  $\sum_j Y_j S_{b_j}^{(b_j-1)/b_j}$  means (the number of unreacted functional group B in the sol)/(the total number of unreacted functional group B).

3. The probability of finding a functional group A of monomer  $A_{a_i}$  which participates in intramolecular cyclization in the sol is

$$f_a' S_{a_i}^{1/a_i} \tag{10}$$

Note that the term  $S_{a_i}^{1/a_i}$  represents the probability of finding a functional group A of monomer  $A_{a_i}$  in the sol and the cyclization conversion for species A in the sol,  $f_a'$ , just defined above can be interpreted as (the number of functional groups for species A in the series  $A_{a_1}, \dots, A_{a_s}$

that have reacted intramolecularly with the functional group for species B in monomer  $B_{b_j}$  ( $j=1,2,\dots,t$ ) in the

sol)/(the total number of functional groups for species A in the series  $A_{a_1}, \dots, A_{a_s}$  in the sol).

It should be pointed out that the probabilities (9) and (10) in which intermolecular reaction and intramolecular cyclization are respectively involved are regarded mutually independent. This is not the case of competition between intermolecular reaction and intramolecular cyclization treated by Gordon and Scantlebury[7], or Dusek and Vojta[8] or Ahmad and Stepto[10], using the theory of branching processes[TBP]. It seems that the mutually independent case of the probabilities (9) and (10) may be improved, we shall see in the next section, by using parameter-fitting process to treat the experimental results.

Since the sol fraction  $S_{a_i}$  can be interpreted as the probability of finding a monomer  $A_{a_i}$  of series  $A_{a_1}, \dots, A_{a_s}$  in the sol, it is not difficult to find that the sol fraction  $S_{a_i}$  can be expressed in terms of the three kinds of probabilities in the expressions (8), (9) and (10) in the form

$$S_{a_i} = (1 - q_a - f_a + q_a \sum_{j=1}^t Y_j S_{b_j}^{(b_j-1)/b_j} + f'_a S_{a_i}^{1/a_i})^{a_i} \quad (11)$$

$i=1,2,\dots,s$

Under the assumption that no competition occurs between intermolecular reaction and intramolecular cyclization, it seems that a similar expression of  $S_{a_i}$  in Eq.(11) can be deduced by the zeroth generating function of the theory of branching processes[7,8,9], and the terms corresponding to  $q_a \sum_{j=1}^t Y_j S_{b_j}^{(b_j-1)/b_j}$  and  $f'_a S_{a_i}^{1/a_i}$  can be expressed in terms of dummy parameters of TBP. Furthermore, under the assumption that no intramolecular cyclization occurs in the sol ( $F'_a=0$ ), the expression of  $S_{a_i}$  in Eq.(11) can be reduced to the form by writing

$$S_{a_i} = (1 - p_a + q_a \sum_{j=1}^t Y_j S_{b_j}^{(b_j-1)/b_j})^{a_i} \quad (12)$$

where  $p_a$  is the total conversion for species A without cyclization in the sol. When  $q_a$  in  $q_a \sum_{j=1}^t Y_j S_{b_j}^{(b_j-1)/b_j}$  in Eq.(12) is replaced by

$p_a$ , we can obtain the result of the earlier publication[13]

$$S_{a_i} = (1 - p_a + p_a \sum_{j=1}^t Y_j S_{b_j}^{(b_j-1)/b_j})^{a_i} \tag{13}$$

It is easy from the zeroth generating function to derive this expression by the theory of branching processes to give the result

in which the term corresponding to  $\sum_j Y_j S_{b_j}^{(b_j-1)/b_j}$  is expressible

in term of dummy parameters of TBP. In a previous paper[12], the expression of sol fraction  $S_a$  for  $A-B$  type polycondensation was quite different from that of sol fraction  $S_{a_i}$  in Eq.(11). The main

difference is that in the previous paper, the term of probability

of cyclization  $f'_a S_a^{1/a}$  was not considered and the exponent a of

$(\dots)^a$  was replaced by the term  $a(1-f'_a)$ . From probability consideration, it enables us to believe that the expression of  $S_{a_i}$  given

by Eq.(11) is a reasonable one in contrast with that of  $S_a$  presented in the previous paper[12].

An alternative expression involving  $S_{a_i}$  can be obtained by means of probability theory by writing

$$S_{a_i} (1-q'_a - f'_a) = (1-q'_a - f'_a) (1-q'_a - f'_a + q'_a \sum_{j=1}^t Y_j S_{b_j}^{(b_j-1)/b_j} + f'_a S_{a_i}^{1/a_i})^{a_i-1} \tag{14}$$

where the term  $S_{a_i} (1-q'_a - f'_a)$  represents the probability of finding a functional group A in monomer  $A_{a_i}$  which is unreacted in the

sol. It is not difficult to find via probability analysis that the probability meaning of the expression on the right hand side of Eq.(14) has the same meaning as the term on the left hand side of Eq.(14). Note that the expression in Eq.(14) is closely related to the first generating function of TBP.

Combining Eqs.(11) and (14) yields

$$S_{a_i} = [(1 - q'_a - f'_a)/(1 - q'_a - f'_a)]^{a_i}, \quad i=1,2,\dots,s \tag{15}$$

Similarly, as we have just done for  $S_{a_i}$ , the sol fraction  $S_{b_j}$  for species B takes two different forms by writing

$$S_{b_j} = (1 - q_b - f_b + q_b \sum_{i=1}^s X_i S_{a_i}^{(a_i-1)/a_i} + f_b' S_{b_j}^{1/b_j})^{b_j} \quad (16)$$

$j=1,2,\dots,t$

and

$$S_{b_j} = [(1 - q_b - f_b)/(1 - q_b' - f_b')]^{b_j}, \quad j=1,2,\dots,t \quad (17)$$

Combining Eqs.(11) and (15) yields

$$1/a_i = S_{a_1}^{1/a_1}, \quad i=2,3,\dots,s \quad (18)$$

Similarly, we have, from Eqs.(16) and (17)

$$1/b_j = S_{b_1}^{1/b_1}, \quad j=2,3,\dots,t \quad (19)$$

Furthermore, let us define the total sol fraction  $S$  in the following form

$$S = S_a + S_b \quad (20)$$

where  $S_a$  and  $S_b$  are used to denote the total sol fractions with respect to species A and B, i.e.

$$S_a = \sum_{i=1}^s X_{a_i} S_{a_i}, \quad S_b = \sum_{j=1}^t X_{b_j} S_{b_j} \quad (21)$$

with

$$X_{a_i} = N_{a_i} / (\sum_{i=1}^s N_{a_i} + \sum_{j=1}^t N_{b_j}), \quad X_{b_j} = N_{b_j} / (\sum_{i=1}^s N_{a_i} + \sum_{j=1}^t N_{b_j}) \quad (22)$$

By considering  $s+t-2$  relations in Eqs.(18) and (19), it is not difficult to find that in the  $2s+2t$  relations in Eqs.(11), (15), (16) and (17), only  $s+t+2$  are independent. In this section, we have introduced  $s+t+15$  quantities ( $S, S_a, S_b, S_{a_i}, S_{b_j}, p_a, p_b, p_a', p_b', q_a, q_b, q_a', q_b', f_a, f_b, f_a', f_b'$ ) and these quantities are subject to  $s+t+12$  independent relations, i.e.  $s+t+9$  arise from Eqs.(1), (2), (11), (15)-(21), and the remaining three are given by

$$q_a = r_b q_b, \quad f_a = r_b f_b, \quad \sum_i X_i S_{a_i} f_a' = r_b \sum_j Y_j S_{b_j} f_b' \quad (23)$$

where the stoichiometric ratio  $r_b$  is defined as

$$r_b = \left( \sum_j b_j N_{b_j} \right) / \left( \sum_i a_i N_{a_i} \right). \tag{24}$$

Thus we conclude that only three of the  $s+t+15$  quantities are independent. It seems that a complete characterization of  $A_{a_1}, \dots,$

$A_{a_i}-B_{b_1}, \dots, B_{b_t}$  type polycondensation involving cyclization may require three independent quantities.

By making use of Eqs.(11), (15)-(19) via conventional algebraic techniques, and then by taking into consideration of the critical conditions  $S_{a_i} \rightarrow 1, S_{b_j} \rightarrow 1, f'_a = f_a = f_a^C$  and  $f'_b = f_b = f_b^C$ , we can

obtain the gelation condition in the following form

$$(1 - f_a^C)(1 - f_b^C) - (a_w - 1)(b_w - 1)q_a^C q_b^C = 0 \tag{25}$$

with

$$a_w = \left( \sum_i a_i^2 N_{a_i} \right) / \left( \sum_i a_i N_{a_i} \right), \quad b_w = \left( \sum_j b_j^2 N_{b_j} \right) / \left( \sum_j b_j N_{b_j} \right) \tag{26}$$

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

If intramolecular cyclization conversion in the sol is not considered, the gelation condition in Eq.(25) turns into the form

$$1 - (a_w - 1)(b_w - 1)q_a^C q_b^C = 0. \tag{27}$$

This is the well known gelation condition without cyclization obtained by Stockmayer[2].

## 2. THE $A_2, A_3-B_1, B_2$ TYPE POLYCONDENSATION REACTION

In this section, the sol fractions involving intramolecular cyclization given by Eqs.(11), (14), (16), (17), (20) and (21) are tested by the  $A_2, A_3-B_1, B_2$  type polycondensation reaction of 1,4-butanediol, 1,1,1-trimethylol propane, adipic acid and caproic acid. This reaction has been studied by one of the present authors Zheng with  $r_b=1$ [14]. In his experiment, the  $A_2, A_3-B_1, B_2$  type polycondensation reaction just mentioned above with para-toluenesulfonic acid as catalyst was carried out separately in thirty-five vessels under the temperature of 114 °C. Each vessel was used for the purpose of measurement of polymer quantities with respect to different reaction time. In the experiment, the total sol fraction,  $S$ , and the sol equilibrium fractional conversion for species B,  $p'_b$ , were measured. For the measurement of the quantity  $p'_b$ , the saponification method was used with respect to each vessel. In order to fit Zheng's experimental results of  $S$  and  $p'_b$ , we choose the three



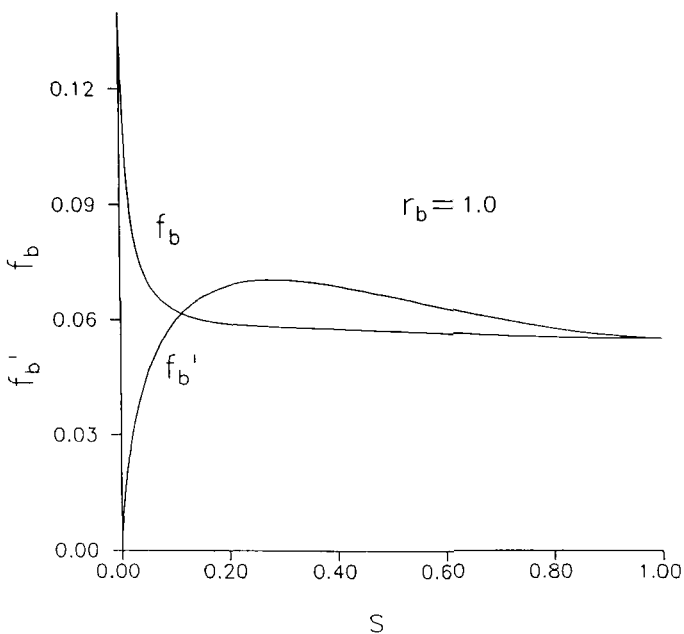


Fig. 1: The assigned values of  $f_b$  and  $f'_b$  against the assigned values of  $S$ .

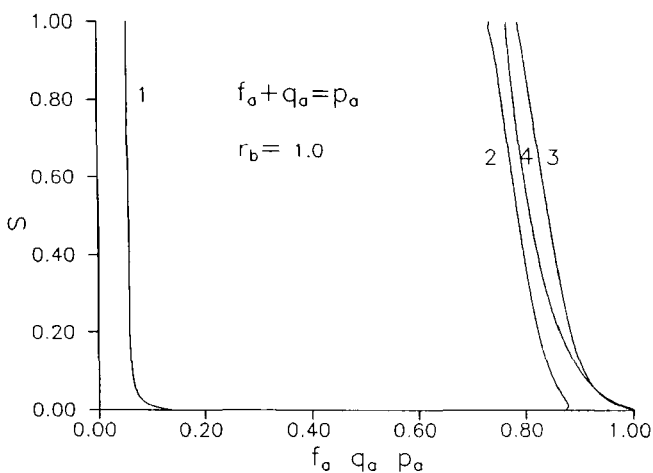


Fig. 2: the calculated values of  $p_a$ ,  $q_a$  and  $f_a$  against the assigned values of  $S$ . Curves 1, 2<sup>a</sup> and 3 are the calculated values of  $f_a$ ,  $q_a$  and  $p_a$  against the assigned values  $S$ , respectively. Curve 4 is the theoretical values of  $p_a$  against  $S$  without cyclization.

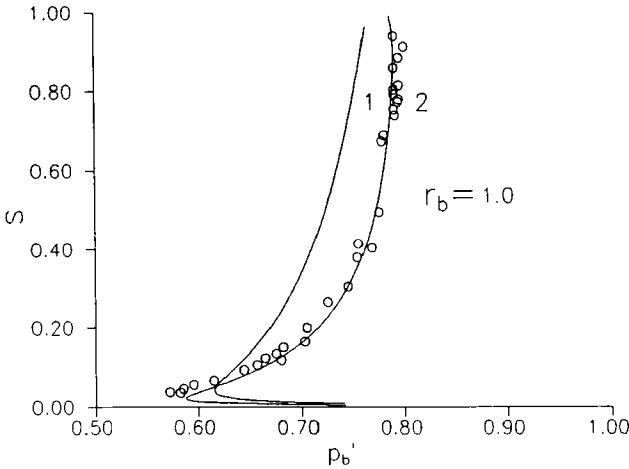


Fig. 3: The sol fraction conversion for species B,  $p_b'$ , against the total sol fraction S. curve 1: the theoretical curve without cyclization in the sol; Curve 2: the theoretical curve involving cyclization in the sol; the symbols are the experimental results of Zheng[14].

quantities S,  $f_b$  and  $f_b'$  as parameters in the 19 quantities discussed in the proceeding section, and their values are suitably assigned as shown in Fig.1. Thus the values of the remaining 16 quantities ( $S_a, S_b, S_{a_2}, S_{a_3}, S_{b_1}, S_{b_2}, P_a, P_a', P_b, P_b', q_a, q_a', q_b, q_b', f_a, f_a', f_b, f_b'$ ) can be solved without difficulty by means of the 16 independent equations given by Eqs.(1), (2), (11), (14),(16), (17), (20) and (23). In order to elucidate the relation  $p_a = q_a + f_a$  in Eq.(1), the calculated values of  $f_a, q_a$  and  $p_a$  are plotted against the assigned values of S with respect to curve 1, curve 2 and curve 3 as shown in Fig. 2, where the theoretical curve of  $p_a$  against S without cyclization is plotted as curve 4 for comparison. Furthermore, the calculated results show that the theoretical values of S and  $p_b'$  are in accordance with those of Zheng's experimental results[14]. For brevity, only the total sol fraction S against the sol equilibrium fractional conversion for species B,  $p_b'$ , is shown in Fig. 3. For comparison, the theoretical result of  $A_2, A_3-B_1, B_2$  type without cyclization in the sol is shown in Fig.3.

By means of the sol fraction in Eqs.(11), (15)-(17) the  $A_{a_1}, \dots, A_{a_s} - B_{b_1}, \dots, B_{b_t}$  type equilibrium number fraction distribu-

tion in which the cyclization is involved can be obtained with the aid of Lagrange's expansion technique. As extension, we can obtain a recursion formula that holds true for both pre-gel and post-gel in evaluating the  $k$ th polymer moment explicitly. For brevity, all these are omitted here.

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