

On the polycondensation reaction of $A_a-B_bC_c$ type

Tang Au-Chin, Li Ze-Sheng, Sun Chia-Chung*, and Tang Xin-Yi

Institute of Theoretical Chemistry and Department of Chemistry, Jilin University, Changchun, Jilin 130021, People's Republic of China

Summary

The curing theory for polycondensation reaction of $A_a-B_bC_c$ type is investigated in detail to give gelation condition explicitly. Furthermore, a recursion formula for evaluating the polymer moments is obtained. This formula is suitable for both pre-gel and post-gel.

1. Introduction

As is well known, the curing theory for polycondensation reactions has been initiated by Flory-Stockmayer(1,2). Miller and Macosko(3,4) have proposed a recursion method in dealing with the problem of post-gel properties of network polymers. It is known that in the theory of branching processes, the probability generating function with differentiation technique proposed by Gordon(5,6) can be used for evaluation of polymer moments. In the previous papers(7,8), a reasonable way to approach A_a and $A_a \dots A_{as} - B_b \dots B_{bt}$ polycondensation reactions has been proposed by the present authors. In this paper, the polycondensation reaction of $A_a - B_b C_c$ type is investigated involving monomer A_a with a- functionalities in reacting with monomer $B_b C_c$ with b- and c- functionalities. The sol fraction for post-gel is discussed in detail to approach gelation condition by taking Stockmayer's $A_a - B_b$ result as a criterion(2). By means of Lagrange expansion of sol fraction, the equilibrium number fraction distribution is deduced. Furthermore, by applying a direct differentiation technique to the equilibrium distribution, a recursion formula for polymer moments is obtained. This formula is suitable for both pre-gel and post-gel in evaluating the polymer moments explicitly.

2. Sol Fraction, Gelation Condition and Distribution

In this section, we shall make use of the explicit form of sol fraction to approach both gelation condition and equilibrium number fraction distribution.

Let us consider a system involving monomer A_a with a- functionalities and monomer $B_b C_c$ which contains two species B and C associated with b- functionalities and c- functionalities, respectively. The system characterized by $A_a - B_b C_c$ means that the chemical reaction takes place only between A and B, or A and C. In order to make our discussion easier, some notations are prior introduced such that, p_a : the total equilibrium fractional conversion of species A; $p_b(p_c)$: the total equilibrium fractional conversion of species B(C) associated with $B_b C_c$; p'_a : the sol equilibrium fractional conversion of species A; $p'_b(p'_c)$: the sol equilibrium fractional conversion of species B(C) associated with $B_b C_c$; S_a : the sol fraction of A_a ; S_{bc} : the sol fraction of $B_b C_c$.

During the course of polycondensation, the number of reacted functional groups of type A must be equal to the sum of the number of reacted functional groups of type B and type C to give

*To whom offprint requests should be sent

$$p_a = (b/a)rp_b + (c/a)rp_c, \quad r = N_{bc}/N_a \quad (1)$$

where N_a and N_{bc} are the number of monomers with respect to A_a and B_bC_c .

Under the assumptions of equireactivity and no intramolecular reaction occurred in the sol, it is not difficult to find, from probability considerations, that the nine quantities p_a , p'_a , p_b , p'_b , p_c , p'_c , S_a , S_{bc} , and r are subject to the five independent relations by writing

$$S_a = \left(1-p_a + \frac{b}{a}rp_b S_{bc} \frac{1-p'_b}{1-p_b} + \frac{c}{a}rp_c S_{bc} \frac{1-p'_c}{1-p_c} \right)^a \quad (2)$$

$$S_a \frac{1-p'_a}{1-p_a} = \left(1-p_a + \frac{b}{a}rp_b S_{bc} \frac{1-p'_b}{1-p_b} + \frac{c}{a}rp_c S_{bc} \frac{1-p'_c}{1-p_c} \right)^{a-1} \quad (3)$$

$$S_{bc} = \left(1-p_b + p_b S_a \frac{1-p'_a}{1-p_a} \right)^b \left(1-p_c + p_c S_a \frac{1-p'_a}{1-p_a} \right)^c \quad (4)$$

$$S_{bc} \frac{1-p'_b}{1-p_b} = \left(1-p_b + p_b S_a \frac{1-p'_a}{1-p_a} \right)^{b-1} \left(1-p_c + p_c S_a \frac{1-p'_a}{1-p_a} \right)^c \quad (5)$$

$$S_{bc} \frac{1-p'_c}{1-p_c} = \left(1-p_b + p_b S_a \frac{1-p'_a}{1-p_a} \right)^b \left(1-p_c + p_c S_a \frac{1-p'_a}{1-p_a} \right)^{c-1} \quad (6)$$

Relations (1)-(6) signify that only three of the nine quantities mentioned above are independent.

Now let us turn our attention to the gelation condition. With the aid of Eqs.(2) and (3), the sol fraction S_a can be expressed as

$$S_a = \left(\frac{1-p_a}{1-p'_a} \right)^a \quad (7)$$

Applying Eqs.(3)-(7) to Eq.(2) together with Eq.(1) yields

$$p_a = \left[1 - S_a^{1/a} + \frac{c}{a}rp_c \left((1-p_b + p_b S_a^{(a-1)/a})^b (1-p_c + p_c S_a^{(a-1)/a})^{c-1} - (1-p_b + p_b S_a^{(a-1)/a})^{b-1} (1-p_c + p_c S_a^{(a-1)/a})^c \right) \right] \left[1 - (1-p_b + p_b S_a^{(a-1)/a})^{b-1} (1-p_c + p_c S_a^{(a-1)/a})^c \right]^{-1} \quad (8)$$

When $S_a=1$, p_a in Eq.(8) becomes indeterminate, i.e. 0/0, and then, application of the L'Hospital's rule leads us directly to the result

$$[(a-1)/a][b(b-1)rp_b^2 + c(c-1)rp_c^2 + 2bcrp_b p_c] = 1 \quad (9)$$

This relation is the gelation condition of polycondensation for type $A_a-B_bC_c$. If the monomer of type B_bC_c reduced to the monomer of type B_b , i.e. $c=0$, the gelation condition in Eq.(9) turns into the form

$$(a-1)(b-1)p_a p_b = 1 \quad .$$

This is the well known gelation condition, due to Stockmayer(2), of the polycondensation reaction of type A_a-B_b .

By making use of Lagrange expansion(9) of sol fraction S

$$S = \sum_{m,l,i,i'} \sum_{i+i'=m+l-1} (m+1)P_{ml}(i,i') \quad (10)$$

with

$$S = X_a S_a + X_{bc} S_{bc}, \quad X_a = N_a/(N_a + N_{bc}), \quad X_{bc} = N_{bc}/(N_a + N_{bc}) \quad (11)$$

we can find, with the aid of S_a and S_{bc} in Eqs.(2)-(6), that the equilibrium number fraction distribution $P_{ml}(i, i')$ takes the form

$$P_{ml}(i, i') = X_a C_{ml}(i, i') r^1 p_b^i p_c^{i'} (1-p_b)^{bl-i} (1-p_c)^{cl-i'} (1-p_a)^{am-i-i'} \quad (12)$$

with

$$C_{ml}(i, i') = \left(\frac{c}{a}\right)^1 \frac{a(am-m)!(m-1)!}{m!(am-m-1+1)!(bl-i)!(cl-i')!} \cdot \sum_j \frac{(bl-j)!(cl-1+j)!}{j!(1-j)!i-j!(i'-1+j)!} \left(\frac{b}{c}\right)^j \quad (13)$$

Note that the expansion formula of sol fraction S in Eq.(10) is just the first moment M_1 , i.e. $S=M_1$. It is worth while to point out, due to Stockmayer(2), that the distribution $P_{ml}(i, i')$ in Eq.(12) is defined into the post-gel region, where it becomes an improper distribution with total mass equal to S , the sol fraction. This implies that the later expressions for the k th moment M_k expressed in terms of $P_{ml}(i, i')$ hold only for sol. For brevity, we only state without proof that when the monomer of type $B_b C_c$ reduces to the monomer of type B_b , i.e. $c=0$, the distribution in Eq.(12) can reduce to the well known Stockmayer distribution of the polycondensation reaction of type $A_a-B_b(2)$.

3. The Polymer Moments

In this section, we shall deal with the recursion formula of polymer moments by means of a direct differentiation technique. This formula is suitable for both pre-gel and post-gel in evaluating the polymer moments explicitly.

By use of the equilibrium number fraction distribution $P_{ml}(i, i')$ in Eq.(12), the k th polymer moments M_k are defined as

$$M_k = \sum_{m,l} \sum_{i,i'} (m+1)^k P_{ml}(i, i'), \quad k = 0, 1, 2, \dots \quad (14)$$

$i+i'=m+1-1$

In section 2, we have mentioned that in the nine quantities $p_a, p_a', p_b, p_b', p_c, p_c', S_a, S_b$ and r , only three quantities are independent. Let us choose p_b, p_c , and r as independent partial differentiation variables to differentiate the both sides of Eq.(14). As a direct result, three algebraic equations can be obtained. By solving the algebraic equations, a recursion formula of polymer moments involving M_k and M_{k+1} can be deduced

$$M_{k+1} = \frac{1}{D^\circ - D} \left(E M_k + F [p_b(1-p_b) \frac{\partial M_k}{\partial p_b} + p_c(1-p_c) \frac{\partial M_k}{\partial p_c}] + I r \frac{\partial M_k}{\partial r} \right) \quad (15)$$

$$k = 0, 1, 2, \dots$$

where

$$D^\circ = 1 \quad (16)$$

$$D = [(a-1)/a][b(b-1)rp_b^2 + c(c-1)rp_c^2 + 2bcrp_b p_c] \quad (17)$$

$$E = (1/a)X_a [a + b(b-1)rp_b^2 + c(c-1)rp_c^2 + 2ap_a + 2bcrp_b p_c] + (1/a)X_{bc} [a + (a-1)brp_b^2 + (a-1)crp_c^2] \quad (18)$$

$$F = 1 + (a-1)p_a \quad (19)$$

$$I = (1-p_a)(bp_b + cp_c) + brp_b^2 + crp_c^2 - ap_a \quad (20)$$

The recursion formula in Eq.(15) is suitable for both pre-gel and post-gel in evaluating the polymer moments explicitly. When the zeroth moment M_0

$$M_0 = \begin{cases} X_a(1-ap_a) + X_{bc} & , \text{ for pre-gel}(D \leq D^\circ) \\ X_a S_a(1-ap_a') + X_{bc} S_{bc} & , \text{ for post-gel}(D \geq D^\circ) \end{cases} \quad (21)$$

is taken as the starting point for recursion, one can find that the right hand side of recursion formula produces a factor $D^\circ - D$ in the numerator, it cancels the same factor $D^\circ - D$ in the denominator to eliminate the divergence of M_1 for $D = D^\circ$ to give

$$M_1 = \begin{cases} 1, & \text{for pre-gel}(D \leq D^\circ) \\ S, & \text{for post-gel}(D \geq D^\circ) \end{cases} \quad (22)$$

Furthermore, from the first moment M_1 , we can obtain M_2 , by means of consecutive recursion

$$M_2 = \begin{cases} W_2 / (D^\circ - D), & \text{for pre-gel}(D \leq D^\circ) \\ U_2 / (D - D^\circ), & \text{for post-gel}(D \geq D^\circ) \end{cases} \quad (23)$$

where

$$W_2 = E \quad (24)$$

$$U_2 = - \left[ES + IX_a X_{bc} (S_{bc} - S_a) + F \left(p_b (1 - p_b) \left(X_a \frac{\partial S_a}{\partial p_b} + X_{bc} \frac{\partial S_{bc}}{\partial p_b} \right) + p_c (1 - p_c) \left(X_a \frac{\partial S_a}{\partial p_c} + X_{bc} \frac{\partial S_{bc}}{\partial p_c} \right) \right) + Ir \left(X_a \frac{\partial S_a}{\partial r} + X_{bc} \frac{\partial S_{bc}}{\partial r} \right) \right] \quad (25)$$

For brevity, the explicit expressions of partial differentiations $\partial S_a / \partial z$, $\partial S_{bc} / \partial z$, $z = p_b, p_c, r$ in Eq.(25) are omitted here.

From the expression of M_2 in Eq.(23) which is taken as the starting point, one can approach, by repeated application of the recursion formula (15), a general expression of the k th moment M_k for $k \geq 2$

$$M_k = \begin{cases} W_k / (D^\circ - D)^{2k-3}, & \text{for pre-gel}(D \leq D^\circ) \\ U_k / (D - D^\circ)^{2k-3}, & \text{for post-gel}(D \geq D^\circ) \end{cases} \quad (26)$$

where W_k and U_k are subject to the same recursion formula

$$L_k = (2k-5)JL_k + (D^\circ - D) \left(EL_{k-1} + F[p_b(1-p_b) \frac{\partial L_{k-1}}{\partial p_b} + p_c(1-p_c) \frac{\partial L_{k-1}}{\partial p_c}] + Ir \frac{\partial L_{k-1}}{\partial r} \right) \quad (27)$$

with

$$J = [(a-1)/a] \left(Fp_b(1-p_b)[2rb(b-1)p_b + 2rbcp_c] + Fp_c(1-p_c)[2rc(c-1)p_c + 2rbcp_b] + Ir[b(b-1)p_b^2 + c(c-1)p_c^2 + 2bc p_b p_c] \right) \quad (28)$$

Note that L_k is used to denote either W_k for pre-gel or U_k for post-gel. It is obvious that the expression for M_k in Eq.(26) diverges for $k \geq 2$ when $D = D^\circ$, and the gelation condition is deduced immediately

$$D - D^\circ = 0. \quad (29)$$

This expression is in accordance with the form in Eq.(9) deduced from sol fraction in section 2.

By the same way as we have done in the previous papers in treating the polycondensation reactions(7,8), the scaling study(10,11) can proceed without difficulty to reach the same generalized scaling law.

References

1. Flory P-J(1941) J. Am. Chem. Soc. 63: 3083, 3091, 3096.
2. Stockmayer W-H(1943) J. Chem. Phys. 11: 45.
3. Macosko C-W, Miller D-R(1976) Macromol. 9: 199.
4. Miller D-R, Macosko C-W(1976) Macromol. 9: 206.
5. Dobson G-R, Gordon M(1965) J. Chem. Phys. 43: 705.
6. Gordon M, Scantlebury G(1967) J. Chem. Soc. Pl.

7. Tang A-C, Li Z-S, Sun C-C, Tang X-Y(1988) J. Macromol. Sci.-Chem. A25(1): 41.
8. Tang A-C, Li Z-S, Sun C-C, Tang X-Y(1988) Macromol. 21: 797.
9. Whittaker E-T, Watson G-N(1952) A Course of Modern Analysis, Cambridge University(Reprinted), Cambridge.
10. de Gennes P-G(1979) Scaling Concepts in Polymer Physics, Cornell University Press, London.
11. Stauffer D, Coniglio A, Adam M(1982) Adv. Polym. Sci. 44: 103.

Accepted September 11, 1990 C