of PS as depicted in Figure 5c, when the helix axis is regarded as the KP chain contour. This structure gives the value 14.0 Å for d_b, which is too large compared to the above estimate 11.1 Å for d_b from the experimental $[\eta]$ data. It is therefore hard to accept the structure shown in Figure 5c for the characteristic helix (straight line) of the a-PS chain. Furthermore, it should be emphasized that the KP chain cannot explain the anisotropic light scattering phenomena at all, since in this model, any property that depends on the local structure must be cylindrically symmetric around the chain contour. The above two reasons may suffice to reject the KP chain model in representing the a-PS chain in solution.

In this paper, we have determined the HW model parameters for the a-PS chain and therefrom visualized its local and global conformations in solution. The extension of the study to $\langle S^2 \rangle$ for the same a-PS samples is in progress to confirm the present conclusion.

Registry No. PS, 9003-53-6.

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Polycondensation Reaction of $RA_a + RB_b$ Type Involving Intramolecular Cyclization

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ABSTRACT: An attempt is made to approach the polycondensation reaction of $RA_a + RB_b$ type, involving intramolecular cyclization, by use of an alternative procedure. The sol fraction for a postgel is investigated to deduce an equilibrium number fraction distribution of the $RA_a + RB_b$ type reaction, with the Stockmayer distribution as a criterion. Furthermore, the zero, the first, and the second polymer moments are evaluated explicitly to reach a gelation condition.

Introduction

As is well-known, the curing theory for polycondensation reactions of $RA_a + RB_b$ and $RA_{a1} \ldots A_{as} + RB_{b1} \ldots B_{bt}$ type has been initiated by Stockmayer.[1,2] Harris, Kilb, Gordon and co-workers, and Ahmad and Stepto[3-7] have studied the polymer system in which intrmolecular cyclization is involved. Miller and Macosko[8,9] have proposed a recursion method in dealing with the problem of postgel properties of network polymers. In this paper, an alternative way to approach the polycondensation reaction of $RA_a + RB_b$ type is proposed, by taking into consideration intramolecular cyclization. The sol fraction for a postgel[8-13] is investigated in detail to deduce an equilibrium number fraction distribution of $(m + l)$-mers. The reliability of this distribution is further examined by the Stockmayer distribution.[2]

It is known that in the theory of branching processes, the probability generating function from differentiation technique proposed by Gordon[14,15] can be used for evaluation of polymer moments. Alternatively, on the basis of the distribution proposed in this paper, a direct differentiation technique is taken to obtain the recursion formula that is suitable for both the pregel and the postgel in evaluating the polymer moments explicitly. As a direct result, the gelation condition is obtained and examined with the Stockmayer gelation condition as a criterion.

Sol Fraction and Equilibrium Number Fraction Distribution

Let us consider a polycondensation system which contains two species of monomers A and B with a and b functionalities, respectively. Let S_a and S_b be the sol fractions with respect to A and B species. Let us use p_{ta}, p'_{ta}, p''_{ta} and p_{tb}, p'_{tb}, p''_{tb}, to which the A and B species correspond, to denote the total, sol, and gel equilibrium fractional conversions. Furthermore, each of the conversions p_{ta}, p'_{ta}, p''_{ta} and p_{tb}, p'_{tb}, p''_{tb} can be separated into two parts such that

$$p_{ta} = f_a + p_a \qquad p'_{ta} = f'_a + p'_a \qquad p''_{ta} = f''_a + p''_a \tag{1}$$

$$p_{tb} = f_b + p_b \qquad p'_{tb} = f'_b + p'_b \qquad p''_{tb} = f''_b + p''_b \tag{2}$$

where p_a (p_b) is the fraction of A (B) functionalities that have reacted intermolecularly and f_a (f_b) the fraction of A (B) functionalities that have reacted intramolecularly. It should be noted that as p'_a (p'_b), p''_a (p''_b), f'_a (f'_b), and f''_a (f''_b) are extents of reaction normalized to total number of groups in sol or gel, thus p'_a (p'_b) is defined as the fraction of A (B) functionalities in the sol that have reacted intermolecularly, p''_a (p''_b) as the fraction of A (B) functionalities in the gel that have reacted intermolecularly,

f'_a (f'_b) as the fraction of A (B) functionalities in the sol that have reacted intramolecularly, and f''_a (f''_b) as the fraction of A (B) functionalities in the gel that have reacted intramolecularly. The relations $p_{ta} = f_a + p_a$ in eq 1 and $p_{tb} = f_b + p_b$ in eq 2 are a generalization of Gordon's formula[6] in treating ring–chain competition kinetics in linear polymers. For simplicity, p_a (p_b), p'_a (p'_b), and p''_a (p''_b) are referred to as the total, sol, and gel polycondensation conversions for species A (B) and f_a (f_b), f'_a (f'_b), and f''_a (f''_b) the total, sol, and gel intramolecular cyclization conversions for species A (B).

Furthermore, let us introduce two quantities q_a and q_b referred to as probabilities associated with intermolecular reactions by writing

$$q_a = \frac{aN_a p_a}{aN_a - aN_a f_a} = \frac{p_a}{1 - f_a}$$

$$q_b = \frac{bN_b p_b}{bN_b - bN_b f_b} = \frac{p_b}{1 - f_b} \tag{3}$$

where both q_a and q_b take the values in the range from zero to unity and where N_a and N_b are used to denote the total number of monomers for species A and B, respectively.

Similarly, four quantities q'_a, q'_b, q''_a, and q''_b are introduced as follows

$$\begin{aligned} p'_a &= (1 - f'_a)q'_a & p'_b &= (1 - f'_b)q'_b \\ p''_a &= (1 - f''_a)q''_a & p''_b &= (1 - f''_b)q''_b \end{aligned} \tag{4}$$

For the polycondensation system of $RA_a + RB_b$ type, the number of functional groups that have reacted intermolecularly for A species equals $aN_a(1 - f_a)q_a$, and the number of functional groups that have reacted intermolecularly for B species equals $bN_b(1 - f_b)q_b$. It is clear that we have $aN_a(1 - f_a)q_a = bN_b(1 - f_b)q_b$ to give

$$(1 - f_a)q_a = r_b(1 - f_b)q_b \tag{5}$$

where the stoichiometric ratio r_b is defined as bN_b/aN_a.

Similarly, we have

$$f_a = r_b f_b, \quad s_a f'_a = r_b s_b f'_b \tag{6}$$

$$s_a(1 - f'_a)q'_a = r_b s_b(1 - f'_b)q'_b \tag{7}$$

where s_a and s_b are the sol fractions with respect to species A and B.

As, for species A (B), the total number of functional groups $aN_a f_a$ ($bN_b f_b$) having reacted intramolecularly is a sum of the functional groups $aN_a S_a f'_a$ ($bN_b S_b f'_b$) in the sol and $aN_a(1 - S_a)f''_a$ ($bN_b(1 - S_b)f''_b$) in the gel having reacted intramolecularly, the relations

$$f_a = S_a f'_a + (1 - S_a)f''_a, \quad f_b = S_b f'_b + (1 - S_b)f''_b \tag{8}$$

hold true. Similarly, we have

$$(1 - f_a)q_a = S_a(1 - f'_a)q'_a + (1 - S_a)(1 - f''_a)q''_a \tag{9}$$

$$(1 - f_b)q_b = S_b(1 - f'_b)q'_b + (1 - S_b)(1 - f''_b)q''_b \tag{10}$$

Now let us deal with the sol fractions S_a and S_b for the postgel. Under the assumption of equireactivity, the sol fraction S_a for species A can be expressed by means of probability consideration as

$$S_a = \left(1 - q_a + q_a S_b \frac{(1 - f'_b)(1 - q'_b)}{(1 - f_b)(1 - q_b)}\right)^{a^*} \tag{11}$$

$$S_a = \left(\frac{1 - q_a}{1 - q'_a}\right)^{a^*} \tag{12}$$

where $(1 - q_a)$ is the probability of finding an unreacted A group on the basis of all A groups that have not participated in intramolecular reaction, $q_a S_b(1 - f'_b)(1 - q'_b)/[(1 - f_b)(1 - q_b)]$ is the probability of finding in the system a functional group of A species that undergoes intermolecular reaction and links with a certain $(m + l)$-mer in the sol, and $a^* = a(1 - f'_a)$ is the functionalities (a) effectively reduced due to intramolecular reaction. It should be noted that the expression for a^* does not arise from an exact probability consideration but rather from a mean average approximation. In parallel with the expressions of S_a in eq 11 and 12, the sol fraction S_b for species B can be written as

$$S_b = \left(1 - q_b + q_b S_a \frac{(1 - f'_a)(1 - q'_a)}{(1 - f_a)(1 - q_a)}\right)^{b^*} \tag{13}$$

$$S_b = \left(\frac{1 - q_b}{1 - q'_b}\right)^{b^*} \tag{14}$$

with $b^* = b(1 - f'_b)$. Note that the four expressions involving the sol fractions S_a and S_b in eqs 11–14 are independent, i.e. any one of the four expressions cannot be deduced from the remaining other three.

By means of the Lagrange expansion method together with the sol fraction expressions in eq 11–14, it is not difficult to prove that for the first moment M_1, the identity

$$M_1 = \sum_{\substack{m=0\, l=0 \\ m+l \geq 1}}^{\infty} \sum^{\infty} (m + l)P_{ml} = S \tag{15}$$

holds true, where

$$S = X_a S_a + S_b S_b, \quad X_a = \frac{N_a}{N_a + N_b}, \quad X_b = \frac{N_b}{N_a + N_b} \tag{16}$$

and where the equilibrium number fraction distribution, P_{ml}, takes the form

$$P_{ml} = X_a C_{ml}(f'_a,f'_b)\left(\frac{1 - f'_a}{1 - f_a}\right)^{m-1}\left(\frac{1 - f'_b}{1 - f_b}\right)^{l}(q_a)^l(q_b)^{m-1}(1 - q_a)^{a^*m-m-l+1}(1 - q_b)^{b^*l-l-m+1} \tag{17}$$

with

$$C_{ml}(f'_a,f'_b) = \frac{a^*\Gamma(a^*m - m + 1)\Gamma(b^*l - l + 1)}{m!l!\Gamma(a^*m - m - l + 2)\Gamma(b^*l - l - m + 2)} \tag{18}$$

Note that Γ denotes the gamma function. The method to obtain P_{ml} by means of a Lagrange expansion is described in the Appendix. It is worth while to point out, from the work of Stockmayer,[2] that the distribution P_{ml} in eq 17 is defined into the postgel region, where it becomes an improper distribution with total mass equal to S, the sol fraction. This implies that the later expressions for the kth moment M_k expressed in terms of P_{ml} hold only for sol.

Now let us examine the reliability of the number distribution P_{ml} by mens of the Stockmayer distribution.[2]

When the expressions of p_a (p_b) and f_a (f_b) in eq 3 and 8 are introduced in $p_{ta} = f_a + p_a$ ($p_{tb} = f_b + p_b$) in eq 1 (eq 2), the results are

$$p_{ta} = S_a f'_a + (1 - S_a)f''_a + (1 - f_a)q_a \tag{19}$$

$$p_{tb} = S_b f'_b + (1 - S_b)f''_b + (1 - f_b)q_b \tag{20}$$

For a polycondensation reaction, if the intramolecular cyclization conversion in the sol is not considered, i.e., $f'_a = 0$ ($f'_b = 0$), the total equilibrium fractional conversion p_{ta} (p_{tb}) becomes

$$p_{ta} = q_a + \Delta_a, \qquad \text{for} \quad f'_a = 0 \tag{21}$$

$$p_{tb} = q_b + \Delta_b, \qquad \text{for} \quad f'_b = 0 \tag{22}$$

with

$$\Delta_a = (1 - S_a)(1 - q_a)f''_a \tag{23}$$

$$\Delta_b = (1 - S_b)(1 - q_b)f''_b \tag{24}$$

Note that p_{ta} (p_{tb}) for $f'_a = 0$ ($f'_b = 0$) in eq 21 (eq 22) is in essence the equilibrium fractional conversion of Stockmayer.[2]

For a pregel, as the intramolecular cyclization conversion in the gel f''_a (f''_b) vanishes, i.e., $f''_a = 0$ ($f''_b = 0$), we have $\Delta_a = 0$ and $\Delta_b = 0$ to give, from eq 21 (eq 22)

$$p_{ta} = q_a, \qquad \text{for} \quad f'_a = f''_a = 0$$

$$p_{tb} = q_b, \qquad \text{for} \quad f'_b = f''_b = 0 \tag{25}$$

These two relations can help us to reduce the distribution P_{ml} in eq 17 directly to the result

$$P_{ml} = X_a C_{ml}(p_{ta})^l (p_{tb})^{m-1}(1 - p_{ta})^{am-m-l+1}(1 - p_{tb})^{bl-l-m+1} \tag{26}$$

with

$$C_{ml} = \frac{a(am - m)!(bl - l)!}{m!l!(am - m - l + 1)!(bl - l - m + 1)!} \tag{27}$$

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

For a postgel, as the sol fraction S_a (S_b) changes from unity to zero and q_a (q_b) changes from the critical value $(q_a)_c$ ($(q_b)_c$) to unity, we have $(1 - S_a)(1 - q_a) \ll 1$ and $(1 - S_b)(1 - q_b) \ll 1$. It is obvious that at the starting and end points for a postgel, i.e., $S_a = 1$ ($S_b = 1$) and $S_a = 0$ ($S_b = 0$), the value of the small quantity $(1 - S_a)(1 - q_a)$ ($(1 - S_b)(1 - q_b)$) becomes zero to give

$$\Delta_a = (1 - S_a)(1 - q_a)f''_a < (1 - S_a)(1 - q_a) \ll 1 \tag{28}$$

$$\Delta_b = (1 - S_b)(1 - q_b)f''_b < (1 - S_b)(1 - q_b) \ll 1 \tag{29}$$

where we have made use of the intramolecular cyclization conversions in the gel f''_a and f''_b, always less than unity. We see from eq 21 with $p_{ta} = q_a + \Delta_a$ for $f'_a = 0$ and from eq 22 with $p_{tb} = q_b + \Delta_b$ for $f'_b = 0$ that we have, with the aid of eq 28 and 29

$$p_{ta} - q_a = \Delta_a < (1 - S_a)(1 - q_a) \ll 1, \quad \text{for } f'_a = 0 \tag{30}$$

$$p_{tb} - q_b = \Delta_b < (1 - S_b)(1 - q_b) \ll 1, \quad \text{for } f'_b = 0 \tag{31}$$

It follows that as a good approximation, we have

$$p_{ta} \sim q_a, \qquad \text{for} \quad f'_a = 0$$

$$p_{tb} \sim q_b, \qquad \text{for} \quad f'_b = 0 \tag{32}$$

For a postgel, under this good approximation, the distribution P_{ml} in eq 17 can be reduced to the Stockmayer distribution in eq 26.

In this section, we have already introduced 26 quantities p_x, p'_x, p'_x, f_x, f'_x, f''_x, q_x, q'_x, q''_x, S_x, p_{tx}, p'_{tx}, and p''_{tx} with x = a, b, and these quantities are subject to 23 relations, (1)–(14). Thus, only three of the 26 quantities are independent. When the three independent quantities which are taken as observables are suitably chosen, such as p'_{ta} and S_a, the rest of the series of quantities can be evaluated without difficulty.

Polymer Moments and Gelation Condition

Based on the distribution given in eq 17, a direct differentiation technique proposed in a previous paper[13] can be used to obtain a recursion formula for polymer moments. For brevity, we only state the result without proof. For the kth polymer moment

$$M_k = \sum_{\substack{m=0 \, l=0 \\ m+l \geq 1}}^{\infty} \sum^{\infty} (m + l)^k P_{ml} \tag{33}$$

the corresponding recursion formula can be written as

$$M_{k+1} = \frac{1}{D}\left(EM_k + q_a F(1 - q_a)\frac{\partial M_k}{\partial q_a} + q_b I(1 - q_b)\frac{\partial M_k}{\partial q_b} \right) \qquad k = 0, 1, 2, \ldots \tag{34}$$

with

$$D = 1 - (a^* - 1)(b^* - 1)q_a q_b \tag{35}$$

$$F = 1 + (b^* - 1)q_b \qquad I = 1 + (a^* - 1)q_a \tag{36}$$

$$E = (X_b + X_a q_a)F + (X_a + X_b q_b)I \tag{37}$$

This recursion formula is suitable for both the pregel and the postgel. Since for M_0 (see eq 39) the right-hand side of the recursion formula will produce a factor D in the numerator, it will cancel the same factor D in the denominator to eliminate the divergence of M_1 for $D = 0$. Thus, the expression for M_{k+1} in eq 34 diverges for $k \geq 1$ when $D = 0$.

Let us consider the zeroth moment M_0. By means of the relations

$$\frac{N'_a}{N_a + N_b} = X_a S_a, \quad \frac{N'_b}{N_a + N_b} = X_b S_b \tag{38}$$

with N'_a (N'_b) being the number of monomers for species A (B) in the sol, the zeroth moment M_0 can be evaluated explicitly by writing

$$\begin{aligned} M_0 = \sum_{m,l} P_{ml} &= X_b + [1 - a(1 - f_a)q_a]X_a, \quad \text{for pregel} \\ &= X_b S_b + [1 - a(1 - f'_a)q'_a]X_a S_a, \quad \text{for postgel} \end{aligned} \tag{39}$$

Taking this expression as the starting point for recursion, one can reach, by repeated application of the recursion formula (34), the kth moment explicitly. For brevity, only the first moment M_1 and the second moment M_2 are given as follows

$$\begin{aligned} M_1 = \sum_{m,l} (m + l)P_{ml} &= 1, \quad \text{for pregel} \\ &= S, \quad \text{for postgel} \end{aligned} \tag{40}$$

$$\begin{aligned} M_2 = \sum_{m,l} (m + l)^2 P_{ml} &= \frac{V_2(q_a,q_b)}{D}, \quad \text{for pregel} \\ &= \frac{T_2(q_a,q_b)}{-D}, \quad \text{for postgel} \end{aligned} \tag{41}$$

where

$$V_2(q_a,q_b) = E \tag{42}$$

$$T_2(q_a,q_b) = -\left(ES + q_a F(1 - q_a)\frac{\partial S}{\partial q_a} + q_b I(1 - q_b)\frac{\partial S}{\partial q_b} \right) \tag{43}$$

with

$$\frac{\partial S}{\partial q_a} = -\frac{X_a X_b}{q_a} S_a + \frac{X_a X_b}{q_a} S_b + X_a \frac{\partial S_a}{\partial q_a} + X_b \frac{\partial S_b}{\partial q_a} \tag{44}$$

$$\frac{\partial S}{\partial q_b} = \frac{X_a X_b}{q_b} S_a - \frac{X_a X_b}{q_b} S_b + X_a \frac{\partial S_a}{\partial q_b} + X_b \frac{\partial S_b}{\partial q_b} \tag{45}$$

in which

$$\partial S_a/\partial q_a = \left[a^*\left(1 - \frac{1-f'_b}{1-f_b}S_b{}^{(b^*-1)/b^*}\right)S_a{}^{(a^*-1)/a^*}\right] \Bigg/ \left[(a^*-1)(b^*-1)q_aq_b\left(\frac{1-f'_a}{1-f_a}\right)\left(\frac{1-f'_b}{1-f_b}\right) \times S_b{}^{(b^*-2)/b^*}S_a{}^{(a^*-2)/a^*} - 1\right] \quad (46)$$

$$\partial S_a/\partial q_b = \left[a^*(b^*-1)q_a\left(\frac{1-f'_b}{1-f_b}\right)S_b{}^{(b^*-2)/b^*}S_a{}^{(a^*-1)/a^*} \times \left(1 - \frac{1-f'_a}{1-f_a}S_a{}^{(a^*-1)/a^*}\right)\right] \Bigg/ \left[(a^*-1)(b^*-1) \times q_aq_b\left(\frac{1-f'_a}{1-f_a}\right)\left(\frac{1-f'_b}{1-f_b}\right)S_b{}^{(b^*-2)/b^*}S_a{}^{(a^*-2)/a^*} - 1\right] \quad (47)$$

$$\partial S_b/\partial q_a = \left[b^*(a^*-1)q_b\left(\frac{1-f'_a}{1-f_a}\right)S_a{}^{(a^*-2)/a^*}S_b{}^{(b^*-1)/b^*} \times \left(1 - \frac{1-f'_b}{1-f_b}S_b{}^{(b^*-1)/b^*}\right)\right] \Bigg/ \left[(a^*-1)(b^*-1) \times q_aq_b\left(\frac{1-f'_a}{1-f_a}\right)\left(\frac{1-f'_b}{1-f_b}\right)S_a{}^{(a^*-2)/a^*}S_b{}^{(b^*-2)/b^*} - 1\right] \quad (48)$$

$$\partial S_b/\partial q_b = \left[b^*\left(1 - \frac{1-f'_a}{1-f_a}S_a{}^{(a^*-1)/a^*}\right)S_b{}^{(b^*-1)/b^*}\right] \Bigg/ \left[(a^*-1)(b^*-1)q_aq_b\left(\frac{1-f'_a}{1-f_a}\right)\left(\frac{1-f'_b}{1-f_b}\right) \times S_a{}^{(a^*-2)/a^*}S_b{}^{(b^*-2)/b^*} - 1\right] \quad (49)$$

It is known that the zeroth and first moments do not diverge at the gel point and the second moment is divergent at the gel point. The singularity property of the second moment M_2 can deduce a gelation condition immediately

$$D = 1 - [a(1-(f_a)_c) - 1][b(1-(f_c)_c) - 1](q_a)_c(q_b)_c = 0 \quad (50)$$

where we have made use of the expression for D in eq 35.

Now let us examine the gelation condition with the Stockmayer gelation condition as a criterion.

Substitution of $p_a = (1-f_a)q_a$ ($p_b = (1-f_b)q_b$) given in eq 3 into the relation $p_{ta} = f_a + p_a$ ($p_{tb} = f_b + p_b$) in eq 1 (in Eq 2) yields

$$q_a = \frac{p_{ta} - f_a}{1 - f_a}, \qquad q_b = \frac{p_{tb} - f_b}{1 - f_b} \quad (51)$$

to give, from gelation condition (50)

$$[a(1-(f_a)_c) - 1] \times [b(1-(f_b)_c) - 1]\frac{[(p_{ta})_c - (f_a)_c][(p_{tb})_c - (f_b)_c]}{(1-(f_a)_c)(1-(\mathrm{f}_b)_c)} = 1 \quad (52)$$

Furthermore, the total probability of intramolecular reaction λ defined by Ahmad and Stepto[7] is expressible in terms of f_a (f_b) and p_{ta} (p_{tb})

$$\lambda = f_a/p_{ta} = f_b/p_{tb} \quad (53)$$

where we have made use of $f_a = r_bf_b$ and $p_{ta} = r_bp_{tb}$. Thus, the gelation condition (50) can be expressed in terms of λ, by writing

$$\left(a - \frac{1}{1-\lambda_c(p_{ta})_c}\right)\left(b - \frac{1}{1-\lambda_c(p_{tb})_c}\right) \times (p_{ta})_c(p_{tb})_c(1-\lambda_c)^2 = 1 \quad (54)$$

with

$$\lambda_c = \frac{(f_a)_c}{(p_{ta})_c} = \frac{(f_b)_c}{(p_{tb})_c} \quad (55)$$

Note that at the gel point, we have $\lambda_c(p_{ta})_c = (f_a)_c \ll 1$ and $\lambda_c(p_{tb})_c = (f_b)_c \ll 1$. When no terms of $\lambda_c(p_{ta})_c$ and $\lambda_c(p_{tb})_c$ are retained, eq 54 becomes the result of Ahmad and Stepto[7]

$$(a-1)(b-1)(p_{ta})_c(p_{tb})_c(1-\lambda_c)^2 = 1 \quad (56)$$

When no terms of λ_c in eq 56 are retained as $\lambda_c \ll 1$, we get the well-known Stockmayer gelation condition[2]

$$(a-1)(b-1)(p_{ta})_c(p_{tb})_c = 1 \quad (57)$$

As a direct result of gelation conditions in eq 50, 56, and 57, it is not difficult to obtain the ordering of gel points

$$(p_{ta})_c(\text{this paper}) > (p_{ta})_c(\text{Ahmad–Stepto}) > (p_{ta})_c(\text{Stockmayer}) \quad (58)$$

$$(\mathrm{p}_{\mathrm{tb}})_c(\text{this paper}) > (p_{tb})_c(\text{Ahmad–Stepto}) > (p_{tb})_c(\text{Stockmayer}) \quad (59)$$

where

$$(p_{ta})_c(\text{this paper}) = (f_a)_c + \left[\frac{r_b[1-(f_a)_c][1-(f_b)_c]}{[a(1-(f_a)_c) - 1][b(1-(f_b)_c) - 1]}\right]^{1/2} \quad (60)$$

$$(p_{tb})_c(\text{this paper}) = (f_b)_c + \left[\frac{[1-(f_a)_c][1-(f_b)_c]}{r_b[a(1-(f_a)_c) - 1][b(1-(f_b)_c) - 1]}\right]^{1/2} \quad (61)$$

$$(p_{ta})_c(\text{Ahmad–Stepto}) = \frac{1}{1-\lambda_c}\left(\frac{r_b}{(a-1)(b-1)}\right)^{1/2} \quad (62)$$

$$(p_{tb})_c(\text{Ahmad–Stepto}) = \frac{1}{1-\lambda_c}\left(\frac{1}{r_b(a-1)(b-1)}\right)^{1/2} \quad (63)$$

$$(p_{ta})_c(\text{Stockmayer}) = \left(\frac{r_b}{(a-1)(b-1)}\right)^{1/2} \quad (64)$$

$$(p_{tb})_c(\text{Stockmayer}) = \left(\frac{1}{r_b(a-1)(b-1)}\right)^{1/2} \quad (65)$$

By the same procedure we have used in a previous paper in treating the polycondensation reaction,[13] the scaling study[16,17] can proceed without difficulty to reach a generalized scaling law and it holds true no matter whether the intrmolecular cyclization is considered or not.

Appendix. The Application of the Lagrange Expansion Method

The first moment M_1 is defined as

$$M_1 = \sum_{\substack{m,l \\ m+l\geq 1}}^{\infty} (m+l)P_{ml} = S \quad (\mathrm{A1})$$

with

$$S = X_aS_a + X_bS_b \quad (\mathrm{A2})$$

Since m and l mean m monomers of type A_a and l monomers of type B_b involved in the $(m + l)$-mer, we have, from eq A1 and A2

$$\sum_{\substack{m,l\\ m+l\geq 1}}^{\infty} mP_{ml} = X_aS_a \tag{A3}$$

$$\sum_{\substack{m,l\\ m+l\geq 1}}^{\infty} lP_{ml} = X_bS_b \tag{A4}$$

Let us rewrite the expression of sol fraction S_a in eq 11 in the form

$$S_a^{1/a^*} = 1 - q_a + q_aS_b\frac{(1 - f'_b)(1 - q'_b)}{(1 - f_b)(1 - q_b)} \tag{A5}$$

Substituting the expression of sol fraction S_a in eq 12 in the left-hand side of eq A5 yields

$$\frac{1 - q_a}{1 - q'_a} = 1 - q_a + q_aS_b\frac{(1 - f'_b)(1 - q'_b)}{(1 - f_b)(1 - q_b)} \tag{A6}$$

Furthermore, applying the expression of sol fraction S_b in eq 14 gives

$$\frac{1 - q_a}{1 - q'_a} = 1 - q_a + q_a\frac{1 - f'_b}{1 - f_b}S_b^{(b^*-1)/b^*} \tag{A7}$$

With the aid of the expression of sol fraction S_b in eq 13, we have, from eq A7

$$\frac{1 - q_a}{1 - q'_a} = 1 - q_a + q_a\frac{1 - f'_b}{1 - f_b}\left(1 - q_b + q_bS_a\frac{(1 - f'_a)(1 - q'_a)}{(1 - f_a)(1 - q_a)}\right)^{b^*-1} \tag{A8}$$

to give

$$\frac{1 - q_a}{1 - q'_a} = 1 - q_a + q_a\frac{1 - f'_b}{1 - f_b}\left[1 - q_b + q_b\left(\frac{1 - f'_a}{1 - f_a}\right)\left(\frac{1 - q_a}{1 - q'_a}\right)^{a^*-1}\right]^{b^*-1} \tag{A9}$$

In order to make the discussion of Lagrange expansion easier, we define Z_a, t_a, and $\phi(Z_a)$ in the forms

$$Z_a = \frac{1}{1 - q'_a} \tag{A10}$$

$$t_a = \frac{q_a(1 - f'_b)}{(1 - q_a)(1 - f_b)} \tag{A11}$$

$$\phi(Z_a) = \left(1 - q_b + q_b\frac{1 - f'_a}{1 - f_a}(1 - q_a)^{a^*-1}Z_a^{a^*-1}\right)^{b^*-1} \tag{A12}$$

Then eq A9 is expressible in terms of Z_a, t_a, and $\phi(Z_a)$

$$Z_a = 1 + t_a\phi(Z_a) \tag{A13}$$

Furthermore, the expression of sol fraction S_a in eq 12 can be expressed as

$$S_a = (1 - q_a)^{a^*}(Z_a)^{a^*} \tag{A14}$$

Thus X_aS_a can be regarded as a function of Z_a:

$$f(Z_a) = X_aS_a = X_a(1 - q_a)^{a^*}(Z_a)^{a^*} \tag{A15}$$

By means of Lagrange expansion theorem,[18] $f(Z_a)$ in eq A15 can be expanded as a power series in t_a by the formula

$$f(Z_a) = f(1) + \sum_{l=1}^{\infty}\frac{(t_a)^l}{l!}\left\{\frac{d^{l-1}}{dZ_a^{\,l-1}}\left[\frac{df(Z_a)}{dZ_a}(\phi(Z_a))^l\right]\right\}_{Z_a=1} \tag{A16}$$

with

$$f(1) = X_a(1 - q_a)^{a^*} \tag{A17}$$

in which t_a in eq A11 and $\phi(Z_a)$ in eq A12 are involved. This expansion formula is, in essence, subject to the restriction condition given in eq A13. Through a straightforward calculation, we have, from eq A16

$$\sum_{\substack{m,l\\ m+l\geq 1}}^{\infty} mP_{ml} = X_aS_a \tag{A18}$$

with

$$P_{ml} = X_aC_{ml}(f'_a,f'_b)\left(\frac{1 - f'_a}{1 - f_a}\right)^{m-1}\left(\frac{1 - f'_b}{1 - f_b}\right)^{l}(q_a)^l(q_b)^{m-1}(1 - q_a)^{a^*m-m-l+1}(1 - q_b)^{b^*l-l-m+1} \tag{A19}$$

$$C_{ml}(f'_a,f'_b) = \frac{a^*\Gamma(a^*m - m + 1)\Gamma(b^*l - l + 1)}{m!l!\Gamma(a^*m - m - l + 2)\Gamma(b^*l - l - m + 2)} \tag{A20}$$

Since the expression of X_aS_a in eq A18 is in accordance with that of X_aS_a in eq A3, P_{ml} in eq A19 is just the equilibrium number fraction distribution of the $(m + l)$-mer.

Similarly, as we have just done, we can obtain the expansion formula of $X_bS_b = \sum_{m,l}lP_{ml}$ in eq A4 to deduce the same distribution as given in eq A19.

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