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A_a–B_b-Type Stockmayer Distribution and Scaling Study

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ABSTRACT: For the polycondensation reaction system described by the A_a–B_b-type Stockmayer distribution, a recursion formula is proposed for the evaluation of the kth radius that holds true for both pregel and postgel. By taking advantage of the recursion formula near the gel point, a scaling law, characterized by the kth radius as well as the critical exponent of the mean square radius of gyration proposed by Zimm and Stockmayer, is obtained.

Introduction

With the equilibrium fraction distribution P_{ml} for the A_a–B_b-type polycondensation reaction proposed by Stockmayer,[1] the kth radius, which can be regarded as a generalization of the A_a-type radius proposed by Dobson and Gordon,[2] is investigated to give a recursion formula that holds true for both pregel and postgel. By means of the recursion formula, which is closely related to the known recursion method of Spouge,[3,4] the scaling behavior of the kth radius near the gel point is revealed to reach a scaling law that is characterized by the kth radius as well as the critical exponent of mean square radius of gyration proposed by Zimm and Stockmayer.[5]

A_a–B_b-Type Stockmayer Distribution and Mean Square Radius of Gyration

In order to study the mean square radius of gyration, we shall discuss first the combinatorial coefficient in the A_a–B_b-type Stockmayer distribution,[1] where A_a–B_b denotes the polycondensation reaction system; monomer A_a, having a functionalities, may react with monomer B_b, having b functionalities.

As is well-known, the A_a–B_b-type Stockmayer distribution takes the form[1]

$$P_{ml} = \frac{X_a}{m_a} a C_{ml} (p_a)^l (p_b)^{m-1} (1-p_a)^{am-m-l+1} (1-p_b)^{bl-l-m+1} \tag{1}$$

with

$$X_a = \frac{m_a N_a}{m_a N_a + m_b N_b} \tag{2}$$

$$C_{ml} = \frac{(am-m)!(bl-l)!}{m!l!(am-m-l+1)!(bl-l-m+1)!} \tag{3}$$

where the distribution is associated with the $(m+l)$-mer, m_a (m_b) is the molecular weight of monomer A_a (B_b), N_a (N_b) is the total number of monomers of A_a (B_b), p_a (p_b) is the equilibrium fractional conversion for species A (B), and C_{ml} is the combinatorial coefficient.

By means of polymer chemical kinetics and statistics, the combinatorial coefficient C_{ml} in eq 3 can be expressed as

$$C_{ml} = \frac{1}{m+l-1} \sum_{i,j} N(m,l,i,j) \tag{4}$$

with

$$N(m,l,i,j) = \frac{1}{2}\{(ai-i-j+1)[b(l-j)-(m-i)-(l-j)+1] + (bj-i-j+1)[a(m-i)-(m-i)-(l-j)+1]\} C_{ij} C_{m-i,l-j} \tag{5}$$

Furthermore, eq 4 can be rewritten as

$$\sum_{i,j} \frac{N(m,l,i,j)}{C_{ml}} = m+l-1 \tag{6}$$

Since the term $m+l-1$ on the right-hand side of eq 6 is the number of bonds in the $(m+l)$-mer, the term $N(m,l,i,j)/C_{ml}$ on the left-hand side of eq 6 should be the number of bonds associated with an imagined split of the $(m+l)$-mer. From the expression of $N(m,l,i,j)$ in eq 5, it is not difficult to find that the term $N(m,l,i,j)/C_{ml}$ is the number of bonds in the $(m+l)$-mer whose splitting produces two moieties of $(i+j)$ and $(m-i)+(l-j)$ units, respectively.

The A_a–B_b-type square radius of gyration is defined as

$$R_{m+l}{}^2 = \sum_{k=1}^{m+l} \frac{m_k r_k{}^2}{m m_a + l m_b} \tag{7}$$

where r_k is the distance of the kth mass point from the center of gravity of the molecule, and m_k is m_a or m_b depending on the running index $k = 1, 2, ..., m+l$. A simple argument leads to the transformation, proposed by Zimm and Stockmayer[5]

$$R_{m+l}{}^2 = \frac{1}{2(m m_a + l m_b)^2} \sum_{k,s} m_k m_s r_{ks}{}^2 \tag{8}$$

where r_{ks} is the distance in space from the kth to the sth mass point. With cyclic molecules being excluded, the mean square radius $\langle R_{m+l}{}^2 \rangle$, which averages the fluctuations in time of $R_{m+l}{}^2$ due to Brownian motion, can be evaluated by means of Gordon's method[2] to give

$$\langle R_{m+l}{}^2 \rangle = \frac{b_0{}^2}{(m m_a + l m_b)^2} \sum_{h}^{m+l-1} [(m-m_h)m_a + (l-l_h)m_b](m_h m_a + l_h m_b) \tag{9}$$

where the index h in the summation is used to denote the hth bond in the $(m+l)$-mer, and b_0 is the average bond length. In eq 9, $m_a m_h + m_b l_h$ and $m_a(m-m_h) + m_b(l-l_h)$ are the weights associated with the two moieties $m_h + l_h$ and $(m-m_h) + (l-l_h)$ produced by cutting the hth bond of the $(m+l)$-mer into $m+l-1$ bonds. It should be noted

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that $\langle R_{m+l}^2\rangle$ in eq 9 can be regarded as a generalization of the A_a-type mean square radius of gyration proposed by Dobson and Gordon.[2]

In the case where the system is described by the A_a–B_b-type Stockmayer distribution in eq 1, $\langle R_{m+l}^2\rangle$ in eq 9 can be expressed as

$$\langle R_{m+l}^2\rangle = \frac{b_o^2}{(m_a m + m_b l)^2}\sum_{i,j}\frac{N(m,l,i,j)}{C_{ml}}[(n-i)m_a + (l-j)m_b](m_a i + m_b j) \quad (10)$$

In obtaining this expression, we have considered the meaning of $N(m,l,i,j)/C_{ml}$ in the relation given by eq 6. The summation in eq 10 with respect to i and j means that splitting the $(m+l)$-mer produces two moieties of $i+j$ and $(m-i)+(l-j)$ units, respectively.

In the Scaling Study section, we shall prove that the asymptotic form of the mean square radius of gyration $\langle R_{m+l}^2\rangle$ near the gel point is expressed as

$$\langle \tilde{R}_{m+l}^2\rangle = \frac{2B_2}{p_b^c E(p_b=p_b^c)}\left(\frac{\pi}{2H(p_b=p_b^c)}\right)^{1/2}(m_a m + m_b l)^{1/2} \quad (11)$$

The expressions of B_2, $H(p_b=p_b^c)$ and $E(p_b=p_b^c)$, will be given by eqs 35, 38, and 52. When the functionalities a and b are equal together with $m_a = m_b$, $n = m + l$, and $p_a = p_b$, the asymptotic form in eq 11 becomes

$$\langle \tilde{R}_n^2\rangle = \frac{b_o^2}{4}\left(\frac{2\pi(a-1)}{a-2}\right)^{1/2} n^{1/2} \quad (12)$$

This is the well-known asymptotic form of the A_a-type mean square radius of gyration proposed by Zimm and Stockmayer.[5]

Recursion Formula of the *k*th Radius

By using the A_a–B_b-type Stockmayer distribution in eq 1, the kth radius is defined as

$$\langle R^2\rangle_k = \sum_{m,l}(m_a m + m_b l)^k\langle R_{m+l}^2\rangle P_{ml}, \quad k = 0, 1, 2, \ldots \quad (13)$$

Since the mean square radius of gyration $\langle R_{m+l}^2\rangle$ in eq 10 is independent of equilibrium fractional conversions p_a and p_b, we can choose p_a and p_b as variables to differentiate both the right- and left-hand sides of eq 13 without difficulty to give

$$\langle R^2\rangle_{k+1} = \frac{1}{D}\left(E\langle R^2\rangle_k + F\frac{\partial\langle R^2\rangle_k}{\partial p_a} + I\frac{\partial\langle R^2\rangle_k}{\partial p_b}\right), \quad k = 0, 1, 2, \ldots \quad (14)$$

with

$$D = 1 - (a-1)(b-1)p_a p_b \quad (15)$$

$$E = m_a[X_a + b p_b X_b + (b-1)X_a p_a p_b] + m_b[X_b + a p_a X_a + (a-1)X_b p_a p_b] \quad (16)$$

$$F = [m_a(b-1)p_a p_b + m_b p_a](1-p_a) \quad (17)$$

$$I = [m_b(a-1)p_a p_b + m_a p_b](1-p_b) \quad (18)$$

$$X_b = 1 - X_a = m_b N_b/(m_a N_a + m_b N_b) \quad (19)$$

It is obvious that when the kth radius $\langle R^2\rangle_k$ is given, the $(k+1)$th radius can be evaluated by using the recursion formula in eq 14. This recursion formula holds true for both pregel and postgel. Since $\langle R^2\rangle_0$ and $\langle R^2\rangle_1$ are not involved in the scaling study, we shall discuss first, in this section, the second radius $\langle R^2\rangle_2$.

From the definition of the kth radius in eq 13, we have

$$\langle R^2\rangle_2 = \sum_{m,l}(m_a m + m_b l)^2\langle R_{m+l}^2\rangle P_{ml} \quad (20)$$

Substituting the mean square radius $\langle R_{m+l}^2\rangle$ given by eq 10 and the equilibrium number fraction distribution given by eq 1 in eq 20 yields

$$\langle R^2\rangle_2 = \frac{b_o^2 m_a p_b}{a X_a(1-p_a)(1-p_b)} \times \left[\frac{a-1}{m_a}T_1 - \frac{1}{m_b}V_1 + M_1\right]\left[\frac{b-1}{m_b}V_1 - \frac{1}{m_a}T_1 + M_1\right] \quad (21)$$

where M_1 is the first moment

$$M_1 = \sum_{m,l}(m_a m + m_b l)P_{ml} \quad (22)$$

and T_1 and V_1 are associated with the second moment in the following manner

$$M_2 = T_1 + V_1 \quad (23)$$

with

$$T_1 = \sum_{m,l} m_a m(m_a m + m_b l)P_{ml} \quad (24)$$

$$V_1 = \sum_{m,l} m_b l(m_a m + m_b l)P_{ml} \quad (25)$$

Furthermore, M_1, T_1, and V_1 can be evaluated by the differentiation method proposed by some of the present authors[6] to give the second radius $\langle R^2\rangle_2$ explicitly as follows

$$\langle R^2\rangle_2 = \begin{cases} \dfrac{W_2}{(p_b^c - p_b)^2} & \text{for pregel} \\ \dfrac{Q_2}{(p_b - p_b^c)^2} & \text{for postgel} \end{cases} \quad (26)$$

with

$$W_2 = \frac{b_o^2 m_a p_b}{a X_a(1-p_a)(1-p_b)}\left(\frac{1}{p_b^c + p_b}\right)^2 \times (p_b^c)^4[b(a-1)p_b X_b + (a-1)X_a[1 + (b-1)p_a p_b] - a p_a X_a - X_b[1 + (a-1)p_a p_b] + D][\text{interchanging } a \text{ and } b \text{ in the preceding square bracket}] \quad (27)$$

$$Q_2 = \frac{b_o^2 m_a p_b}{a X_a(1-p_a)(1-p_b)}\left(\frac{1}{p_b^c + p_b}\right)^2 \times (p_b^c)^4\left\{\frac{a-1}{m_a}\left[E X_a S_a + \left(\frac{I}{p_b} - \frac{F}{p_a}\right)X_a X_b S_a + X_a F\frac{\partial S_a}{\partial p_a} + X_a I\frac{\partial S_a}{\partial p_b}\right] - \frac{1}{m_b}[\text{interchanging } a \text{ and } b \text{ and } F \text{ and } I \text{ in the preceding square bracket}] + DS\right\}\{\text{interchanging } a \text{ and } b \text{ and } F \text{ and } I \text{ in the preceding brace}\} \quad (28)$$

$$p_b^c = [r_b(a-1)(b-1)]^{-1/2} \quad (29)$$

$$r_b = \frac{bN_b}{aN_a} \quad (30)$$

where p_b^c is the well-known gel point proposed by Stockmayer[1] and r_b is the stoichiometric ratio. In eq 28, S_a and S_b, which are sol fractions with respect to species A_a and B_b, have been discussed in detail in the paper (see ref 6).

By choosing $\langle R^2\rangle_2$ as the starting point for successive recursions, we obtain, by using the recursion formula in eq 14, the kth radius $\langle R^2\rangle_k$ as follows

$$\langle R^2\rangle_k = \begin{cases} \dfrac{W_k}{(p_b{}^c - p_b)^{2k-2}} & \text{for pregel} \\ \dfrac{Q_k}{(p_b - p_b{}^c)^{2k-2}} & \text{for postgel} \end{cases} \tag{31}$$

where W_k and Q_k satisfy the same recursion formula

$$U_{k+1} = (2k-2)HU_k + \frac{(p_b{}^c)^2}{p_b{}^c + p_b}(p_b{}^c - p_b)\left(EU_k + F\frac{\partial U_k}{\partial p_a} + I\frac{\partial U_k}{\partial p_b}\right) \tag{32}$$

with

$$H = \frac{(p_b{}^c)^2}{p_b{}^c + p_b}\left(\frac{p_b{}^c F}{2p_a} + \left(1 - \frac{p_b{}^c}{2p_b}\right)I\right) \tag{33}$$

$$U_k = \begin{cases} W_k & \text{for pregel} \\ Q_k & \text{for postgel} \end{cases} \tag{34}$$

Scaling Study

Let us first study the behavior of the second radius $\langle R^2\rangle_2$ near the gel point. In the expression of the second radius $\langle R^2\rangle_2$ in eq 26, there are two quantities, W_2 and Q_2, involved. By means of the expressions of W_2 and Q_2 given by eqs 27 and 28, it is not difficult to find, near the gel point, that W_2 and Q_2 take the same form

$$B_2 = W_2(p_b{=}p_b{}^c) = Q_2(p_b{=}p_b{}^c) = \frac{b_0{}^2 m_a (p_b{}^c)^3}{4aX_a(1 - r_b p_b{}^c)(1 - p_b{}^c)}\left[(a-1)bp_b{}^c X_b + aX_a(1 - r_b p_b{}^c) - \frac{bX_b}{b-1}\right]\left[(b-1)ar_b p_b{}^c X_a + bX_b(1 - p_b{}^c) - \frac{aX_a}{a-1}\right] \tag{35}$$

Thus, the second radius near the gel point can be expressed as, from eq 26,

$$\langle \tilde{R}^2\rangle_2 = \frac{B_2}{|p_b - p_b{}^c|^2} \tag{36}$$

Furthermore, by taking B_2 as the starting point for successive recursions, we obtain, from the recursion formula in eq 32,

$$B_k = W_k(p_b{=}p_b{}^c) = Q_k(p_b{=}p_b{}^c) = (2k-4)!!H(p_b{=}p_b{}^c)^{k-2}B_2 \tag{37}$$

with

$$H(p_b{=}p_b{}^c) = \frac{p_b{}^c}{4}\left[\frac{1}{r_b}(1 - r_b p_b{}^c)\left(\frac{m_a}{a-1} + m_b r_b p_b{}^c\right) + (1 - p_b{}^c)\left(\frac{m_b}{b-1} + m_a p_b{}^c\right)\right] \tag{38}$$

where we have made use of the expression of H in eq 33. Thus, the kth radius near the gel point takes the form, by using eq 31,

$$\langle \tilde{R}^2\rangle_k = \frac{B_k}{|p_b - p_b{}^c|^{2k-2}}, \quad k = 2, 3, \ldots \tag{39}$$

With the aid of eq 13, $\langle \tilde{R}^2\rangle_k$ can be rewritten as

$$\langle \tilde{R}^2\rangle_k = \int_0^\infty\int_0^\infty (m_a m + m_b l)^k \langle \tilde{R}_{m+l}{}^2\rangle \tilde{P}_{ml}\, dm\, dl = \frac{B_k}{|p_b - p_b{}^c|^{2k-2}}, \quad k = 2, 3, \ldots \tag{40}$$

where $\langle \tilde{R}_{m+l}{}^2\rangle$ and $\tilde{P}_{ml}$ are asymptotic forms with respect to $\langle R_{m+l}{}^2\rangle$ and P_{ml}. In a previous paper,[6] the asymptotic form $\tilde{P}_{ml}$

$$\tilde{P}_{ml} = A(m_a m + m_b l)^{-\tau-1}\exp\left[-\left(k - \frac{3}{2}\right)\frac{m_a m + m_b l}{n_\xi(k)}\right] \tag{41}$$

has been obtained with

$$A = \frac{p_b{}^c m_a m_b E(p_b{=}p_b{}^c)}{2[2\pi H(p_b{=}p_b{}^c)]^{1/2}} \tag{42}$$

$$n_\xi(k) = (2k-3)H(p_b{=}p_b{}^c)|p_b - p_b{}^c|^{-1/\sigma} \tag{43}$$

$$\tau = \frac{5}{2} \tag{44}$$

$$\sigma = \frac{1}{2} \tag{45}$$

Note that the asymptotic form $\tilde{P}_{ml}$ is characterized by the critical exponents τ and σ and the generalized typical size $n_\xi(k)$, which is a generalization of the typical size proposed by Stauffer et al.[7] The scaling experiments of τ and σ in eqs 44 and 45 are exactly the same as for the A_a-type system. In the integral equation given by eq 40, only the asymptotic form of the mean square radius of gyration $\langle \tilde{R}_{m+l}{}^2\rangle$ is unknown. Let us solve for $\langle \tilde{R}_{m+l}{}^2\rangle$ by means of the Laplace transformation. It is reasonable to predict that $\langle \tilde{R}_{m+l}{}^2\rangle$ is a function of $m_a m + m_b l$; then with the substitution $n = m_a m + m_b l$, the integral equation given by eq 40 can be transformed into the following form

$$\int_0^\infty F(n)e^{-nt}\, dn = f(t) \tag{46}$$

with

$$F(n) = An^{k-5/2}\langle \tilde{R}_{m+l}{}^2\rangle(n) \tag{47}$$

$$f(t) = \frac{m_a m_b (k-2)! B_2}{H(p_b{=}p_b{}^c)}t^{1-k} \tag{48}$$

$$t = \frac{|p_b - p_b{}^c|^2}{2H(p_b{=}p_b{}^c)} \tag{49}$$

In eq 47, A has been given by eq 42 and $\langle \tilde{R}_{m+l}{}^2\rangle(n)$ means that $\langle \tilde{R}_{m+l}{}^2\rangle$ is a function of n. Equation 46 shows a Laplace transformation of $F(n)$ to $f(t)$. By means of the inverse Laplace transformation technique, we have, from eq 46,

$$\langle \tilde{R}_{m+l}{}^2\rangle = \frac{2B_2}{p_b{}^c E(p_b{=}p_b{}^c)}\left(\frac{\pi}{2H(p_b{=}p_b{}^c)}\right)^{1/2}(m_a m + m_b l)^\rho \tag{50}$$

with

$$\rho = \frac{1}{2} \quad (51)$$

$$E(p_b{=}p_b^c) = m_a\left(X_a + bp_b^cX_b + \frac{X_a}{a-1}\right) + m_b\left(X_b + ar_bp_b^cX_a + \frac{X_b}{b-1}\right) \quad (52)$$

where B_2 and $H(p_b{=}p_b^c)$ have been given by eqs 35 and 38 and the scaling experiment of ρ in eq 51 is exactly the same as for the A_a-type system. When the functionalities a and b are equal together with $m_a = m_b$, $n = m + l$, and $p_a = p_b$, the asymptotic form $\langle \tilde{R}_{m+l}^2 \rangle$ in eq 50 can be reduced to the well-known A_a-type mean square radius of gyration given by eq 12. It should be noted that the asymptotic form of gyration $\langle \tilde{R}_{m+l}^2 \rangle$ is characterized by the same critical exponent $\rho = {}^1/_2$ obtained by Zimm and Stockmayer[5] for the A_a-type polycondensation.

Substituting the asymptotic form $\langle \tilde{R}_{m+l}^2 \rangle$ given by eq 50 in eq 40 yields

$$\frac{B_2}{2H(p_b{=}p_b^c)} \int_0^\infty n^{k-\tau+\rho} \exp\left[-\left(k - \frac{3}{2}\right)\frac{n}{n_\xi(k)}\right] dn = B_k\left(\frac{(2k-3)B_k}{(2k-2)B_{k+1}}\right)^{\sigma\delta_k} n_\xi(k)^{\sigma\delta_k} \quad (53)$$

with

$$\delta_k = 2k - 2, \qquad k = 2, 3, \ldots \quad (54)$$

Application of the scaling transformation T

$$Tn_\xi(k) = Ln_\xi(k) \quad (L \text{ being a positive real number}) \quad (55)$$

$$Tn = Ln \quad (56)$$

to eq 53 gives immediately

$$k - \tau + \rho + 1 = \sigma\delta_k, \quad k = 2, 3, \ldots \quad (57)$$

These relations, arising from the kth radius, are referred to as the scaling law, which is associated with the critical exponent ρ of mean square radius of gyration given by eq 51, proposed by Zimm and Stockmayer.[5]

References and Notes

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