The *k*th Radius of Gyration of A_{a1}, A_{a2}–B_bC_c Type Polymerization#

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By means of polymer chemical kinetics and statistics, the combinatorial coefficient of the A_{a1}, A_{a2}–B_bC_c type distribution is factorized to approach the explicit expression of the mean square radius of gyration. Furthermore, a recursion formula for the evaluation of the *k*th radius of gyration is obtained.

It is known that the radius of gyration for the A_a type polymerization has been investigated by Gordon.[1)] In this paper, the *k*th radius of gyration for the A_{a1}, A_{a2}–B_bC_c type polymerization due to Miller and Macosko[2)] is discussed by means of an alternative way involving the factorization of the combinatorial coefficient of the number distribution. By taking advantage of a differential technique, a recursion formula which holds true for both pre-gel and post-gel is obtained for the evaluation of the *k*th radius of gyration.

1. The A_{a1}, A_{a2}–B_bC_c Type Distribution and Mean Square Radius of Gyration

In order to study the mean square radius of gyration, we shall discuss first the combinatorial coefficient of the number distribution for the A_{a1}, A_{a2}–B_bC_c type polymerization due to Miller and Macosko.[2)] Let us consider a system of polymerization having three kind of monomers A_{a1}, A_{a2}, and B_bC_c, where A_{a1} has a_1-functionality, A_{a2} has a_2-functionality, and B_bC_c has two different kind of functionalities with respect to b and c. The symbol A_{a1}, A_{a2}–B_bC_c means that the monomer A_{a1} (A_{a2}) may react with the species B_b or C_c in monomer B_bC_c, but A_{a1} does not react with A_{a2} and the species B_b does not react with the species C_c.

By means of polymer statistics, the A_{a1}, A_{a2}–B_bC_c type distribution $P_{n_1n_2l}(k_1, k_2)$ can be obtained by writing

$$P_{n_1n_2l}(k_1,k_2) = N_A^0 C_{n_1n_2l}(k_1,k_2)x_1^{n_1}x_2^{n_2}r_c^l P_b^{k_1}P_c^{k_2} \cdot(1-P_b)^{bl-k_1}(1-P_c)^{cl-k_2}(1-P_a)^{\sum_{j=1}^{2}(a_j-1)n_j-l+1} \tag{1}$$

with

$$N_A^0 = \sum_{k=1}^{2} a_k N_{ak} \tag{2}$$

$$r_c = \frac{cN_{bc}}{N_A^0} \tag{3}$$

$$x_i = \frac{a_iN_{a_i}}{N_A^0}, \quad i=1,2 \tag{4}$$

$$P_a = r_bP_b + r_cP_c \tag{5}$$

$$r_b = \frac{bN_{bc}}{N_A^0} \tag{6}$$

$$C_{n_1n_2l}(k_1,k_2) = \frac{\left[\sum_{j=1}^{2}(a_j-1)n_j\right]!(n_1+n_2-1)!}{n_1!n_2!\left[\sum_{j=1}^{2}(a_j-1)n_j-l+1\right]!(bl-k_1)!(cl-k_2)!} \cdot\sum_{\alpha}\frac{(bl-\alpha)!(cl-l+\alpha)!}{\alpha!(l-\alpha)!(k_1-\alpha)!(k_2-l+\alpha)!}\left(\frac{b}{c}\right)^{\alpha} \tag{7}$$

where $P_{n_1n_2l}(k_1,\ k_2)$ represents the number of the (n_1+n_2+l)-mer consisting of n_1 numbers of A_{a1}, n_2 numbers of A_{a2}, and l numbers of B_bC_c, and N_{a1}, N_{a2}, and N_{bc} are used to denote the total number of monomers A_{a1}, A_{a2}, and B_bC_c, respectively. Note that k_1 is the number of chemical bounding formed from A_{a1} and species B_b or A_{a2} and species B_b, and k_2 is the number of chemical bounding formed from A_{a1} and C_c or A_{a2} and species C_c. It is obvious that $k_1+k_2=n_1+n_2+l-1$. In the expression of Eq. 1, P_a, P_b, and P_c are the extent of reactions for A, B, and C groups, respectively. $C_{n_1n_2l}(k_1,\ k_2)$ in Eq. 1 is referred to as the combinatorial coefficient of the distribution $P_{n_1n_2l}(k_1,\ k_2)$. Furthermore, by means of chemical kinetics and statistics,[3)] the combinatorial coefficient $C_{n_1n_2l}(k_1,\ k_2)$ in Eq. 7 can be factorized into a summation form. For brevity, we only give the result without proof that

$$C_{n_1n_2l}(k_1,k_2) = \frac{1}{n_1+n_2+l-1}\sum_{i_1,i_2,j,\nu,\nu'}[N_b(n_1,n_2,l,k_1,k_2,i_1,i_2,j,\nu,\nu') + N_c(n_1,n_2,l,k_1,k_2,i_1,i_2,j,\nu,\nu')] \tag{8}$$

with

$$N_b(n_1,n_2,l,k_1,k_2,i_1,i_2,j,\nu,\nu') = \frac{1}{2}\left\{(bj-\nu)\left[\sum_{k=1}^{2}(a_k-1)(n_k-i_k)-(l-j)+1\right] + [b(l-j)-(k_1-\nu-1)]\left[\sum_{k=1}^{2}(a_k-1)i_k-j+1\right]\right\} C_{i_1i_2j}(\nu,\nu')C_{n_1-i_1,n_2-i_2,l-j}(k_1-\nu-1,k_2-\nu') \tag{9}$$

$$N_c(n_1,n_2,l,k_1,k_2,i_1,i_2,j,\nu,\nu') = \frac{1}{2}\left\{(cj-\nu')\left[\sum_{k=1}^{2}(a_k-1)(n_k-i_k)-(l-j)+1\right] + [c(l-j)-(k_2-\nu'-1)]\left[\sum_{k=1}^{2}(a_k-1)i_k-j+1\right]\right\} \cdot C_{i_1i_2j}(\nu,\nu')C_{n_1-i_1,n_2-i_2,l-j}(k_1-\nu,k_2-\nu'-1). \tag{10}$$

#This paper is written in memory of our intimate friend Professor Hiroshi Kato.

It is not difficult to find that Eq. 8 can be rewritten as

$$\frac{1}{C_{n_1n_2l}(k_1,k_2)}\sum_{i_1i_2j\nu,\nu'}[N_b(n_1,n_2,l,k_1,k_2,i_1,i_2,j,\nu,\nu') +N_c(n_1,n_2,l,k_1,k_2,i_1,i_2,j,\nu,\nu')]=n_1+n_2+l-1. \qquad (11)$$

Since the term n_1+n_2+l-1 on the right hand side in Eq. 11 is the number of bonds in the (n_1+n_2+l)-mer, the term $\sum_{\nu\nu'}[N_b(\cdots)+N_c(\cdots)]/C_{n_1n_2l}(k_1,k_2)$ on the left hand side of Eq. 11 should have the meaning of number of bonds associated with an imagined split of (n_1+n_2+l)-mer. From the expressions of $N_b(\cdots)$ and $N_c(\cdots)$ in Eqs. 9 and 10, it is not difficult to find that the term $\sum_{\nu\nu'}[N_b(\cdots)+N_c(\cdots)]/C_{n_1n_2l}(k_1,k_2)$ is the number of bonds in (n_1+n_2+l)-mer whose splitting produces two moieties of (i_1+i_2+j) and $(n_1-i_1)+(n_2-i_2)+(l-j)$ units, respectively.

The square radius of gyration for A_{a1}, A_{a2}–B_bC_c type is defined as

$$R^2_{n_1+n_2+l}(k_1,k_2)=\sum_{k=1}^{n_1+n_2+l}\frac{m_kr_k^2}{n_1m_{a1}+n_2m_{a2}+lm_{bc}} \qquad (12)$$

where r_k is the distance of the kth mass point from the center of gravity of the molecule, and m_k which depends on the running index $k=1,2,\cdots,\ n_1+n_2+l$ is equal to m_{a1}, m_{a2}, or m_{bc} which are the molecular weight of monomers A_{a1}, A_{a2}, and B_bC_c, respectively. A simple argument leads to the transformation, due to Zimm and Stockmayer[3)]

$$R^2_{n_1+n_2+l}(k_1,k_2)=\frac{1}{2}\left(\sum_{k=1}^{2}n_km_{ak}+lm_{bc}\right)^{-2}\sum_{i,j}m_im_jr_{ij}^2 \qquad (13)$$

where r_{ij} is the distance in space from the ith to the jth mass point. With no intramolecular reactions occurring in finite species, the mean square radius of gyration $\langle R^2_{n_1+n_2+l}(k_1,k_2)\rangle$, which averages the fluctuations in time of $R^2_{n_1+n_2+l}(k_1,k_2)$ due to Brownian motion, can be evaluated by means of Gordon's method to give

$$\langle R^2_{n_1+n_2+l}(k_1,k_2)\rangle=b_0^2\left(\sum_{k=1}^{2}n_km_{ak}+lm_{bc}\right)^{-2}\sum_{h}^{n_1+n_2+l}\left[\sum_{k=1}^{2}(n_k-n_{kh})m_{ak}+(l-l_h)m_{bc}\right]\cdot\left(\sum_{k=1}^{2}n_{kh}m_{ak}+l_hm_{bc}\right) \qquad (14)$$

where the index h in the summation is used to denote the hth bond in the (n_1+n_2+l)-mer, and b_0 is the average bond length. In Eq. 14, $\sum_{k=1}^{2}n_{kh}m_{ak}+l_hm_{bc}$ and $\sum_{k=1}^{2}(n_k-n_{kh})m_{ak}+(l-l_h)m_{bc}$ are the weights associated with the two moieties $(n_{1h}+n_{2h}+l_h)$-mer and $[(n_1-n_{1h})+(n_2-n_{2h})+(l-l_h)]$-mer produced by cutting the hth bond of the (n_1+n_2+l)-mer.

Considering the meaning of $\sum_{\nu\nu'}[N_b(\cdots)+N_c(\cdots)]/C_{n_1n_2l}(k_1,k_2)$ in the relation given by Eq. 11, we can obtain the transformation of Eq. 14

$$\langle R^2_{n_1+n_2+l}(k_1,k_2)\rangle=\frac{b_0^2}{C_{n_1n_2l}(k_1,k_2)}\left(\sum_{k=1}^{2}n_km_{ak}+lm_b\right)^{-2}\sum_{i_1i_2j\nu\nu'}\left(\sum_{k=1}^{2}i_km_{ak}+jm_{bc}\right)\cdot\left[\sum_{k=1}^{2}(n_k-i_k)m_{ak}+(l-j)m_{bc}\right][N_b(n_1,n_2,l,k_1,k_2,i_1,i_2,j,\nu,\nu')+N_c(n_1,n_2,l,k_1,k_2,i_1,i_2,j,\nu,\nu')]. \qquad (15)$$

2. Recursion Formula of the kth Radius of Gyration and the Calculation of the Mean Square Radius of Gyration

By using the A_{a1}, A_{a2}–B_bC_c type distribution $P_{n_1n_2l}(k_1,k_2)$ in Eq. 1, the kth radius of gyration is defined as

$$\langle R^2\rangle_k=\sum_{n_1n_2lk_1k_2}\left(\sum_{k=1}^{2}m_{ak}n_k+m_{bc}l\right)^k\langle R^2_{n_1+n_2+l}(k_1,k_2)\rangle P_{n_1n_2l}(k_1,k_2) \qquad k=0,1,2,\cdots. \qquad (16)$$

Since the mean square radius of gyration $\langle R^2_{n_1+n_2+l}(k_1,k_2)\rangle$ in Eq. 15 is independent of the quantities P_a, P_b, P_c, x_1, x_2, r_b, and r_c, we can choose P_b, P_c, x_1, and r_c as variables to differentiate both right and left hand sides of Eq. 16 to give

$$\langle R^2\rangle_{k+1}=\frac{1}{D}\left\{E+Fr_c\frac{\partial}{\partial r_c}+I\left[P_b(1-P_b)\frac{\partial}{\partial P_b}+P_c(1-P_c)\frac{\partial}{\partial P_c}\right]+Jx_1\frac{\partial}{\partial x_1}\right\}\langle R^2\rangle_k \qquad (17)$$

with

$$D=1-(\bar{a}-1)(\alpha+\beta P_a) \qquad (18)$$

$$E=\bar{m}_a(\alpha+\beta P_a+1)+m_{bc}\bar{a}P_a \qquad (19)$$

$$F=(1-P_a)(\bar{m}_a\beta+m_{bc})-[\bar{m}_a+m_{bc}(\bar{a}-1)]\alpha \qquad (20)$$

$$I=\bar{m}_a+m_{bc}(\bar{a}-1)P_a \qquad (21)$$

$$J=[\bar{m}_a+m_{bc}(\bar{a}-1)P_a][(a_1-1)(\alpha+\beta P_a)-1]-[m_{a1}+m_{bc}(a_1-1)P_a][(\bar{a}-1)(\alpha+\beta P_a)-1] \qquad (22)$$

$$\alpha=r_bP_b(1-P_b)+r_cP_c(1-P_c) \qquad (23)$$

$$\beta=bP_b+cP_c-1 \qquad (24)$$

$$\bar{a}=\sum_{i=1}^{2}a_ix_i \qquad (25)$$

$$\bar{m}_a=\sum_{i=1}^{2}m_{ai}x_i. \qquad (26)$$

It is obvious that when the kth radius of gyration $\langle R^2\rangle_k$ is given, the $(k+1)$th radius of gyration $\langle R^2\rangle_{k+1}$ can be calculated by using the formula in Eq. 17. This formula holds true for both pre-gel and post-gel.

From the definition of the kth radius of gyration in Eq. 16, we have

$$\langle R^2\rangle_2 = \sum_{i_1 i_2 j\nu\nu'} \left(\sum_{k=1}^{2} m_{ak} n_k + m_{bc} l\right)^2 \langle R^2_{n_1+n_2+l}(k_1,k_2)\rangle P_{n_1 n_2 l}(k_1,k_2). \quad (27)$$

Substituting the mean square radius of gyration $\langle R^2_{n_1+n_2+l}(k_1,k_2)\rangle$ given by Eq. 15 and the number distribution $P_{n_1 n_2 l}(k_1,k_2)$ given by Eq. 1 in Eq. 27 yields

$$\langle R^2\rangle_2 = \frac{b_0^2}{N_A^0(1-P_a)}\left[\frac{P_b}{1-P_b}(bV_1 - S_1) + \frac{P_c}{1-P_c}(CV_1 - S_2)\right] \cdot \left[\sum_{k=1}^{2}(a_k - 1)T_k - V_1 + M_1\right] \quad (28)$$

with

$$M_1 = \sum_{n_1 n_2 l k_1 k_2} \left(\sum_{k=1}^{2} n_k m_{ak} + l m_{bc}\right) P_{n_1 n_2 l}(k_1,k_2) \quad (29)$$

$$T_1 = \sum_{n_1 n_2 l k_1 k_2} n_1 \left(\sum_{k=1}^{2} n_k m_{ak} + l m_{bc}\right) P_{n_1 n_2 l}(k_1,k_2) \quad (30)$$

$$T_2 = \sum_{n_1 n_2 l k_1 k_2} n_2 \left(\sum_{k=1}^{2} n_k m_{ak} + l m_{bc}\right) P_{n_1 n_2 l}(k_1,k_2) \quad (31)$$

$$V_1 = \sum_{n_1 n_2 l k_1 k_2} l \left(\sum_{k=1}^{2} n_k m_{ak} + l m_{bc}\right) P_{n_1 n_2 l}(k_1,k_2) \quad (32)$$

$$S_1 = \sum_{n_1 n_2 l k_1 k_2} k_1 \left(\sum_{k=1}^{2} n_k m_{ak} + l m_{bc}\right) P_{n_1 n_2 l}(k_1,k_2) \quad (33)$$

$$S_2 = \sum_{n_1 n_2 l k_1 k_2} k_2 \left(\sum_{k=1}^{2} n_k m_{ak} + l m_{bc}\right) P_{n_1 n_2 l}(k_1,k_2) \quad (34)$$

Furthermore, M_1, T_1, T_2, V_1, S_1, and S_2 can be evaluated by the differentiation method proposed by some of the present authors[4] to give the second radius of gyration $\langle R^2\rangle_2$ explicitly as follows

$$\langle R^2\rangle_2 = \begin{cases} b_0^2 N_A^0 KL/\mathrm{D}^2, & \text{for pre-gel} \\ b_0^2 N_A^{0\prime} K'L'/\mathrm{D}^{2\prime}, & \text{for post-gel} \end{cases} \quad (35)$$

with

$$K = (a_2 - a_1)x_1 x_2\left(\frac{m_{a2}}{a_2} - \frac{m_{a1}}{a_1}\right) + [(\bar{a} - 1)\beta + 1]\frac{m_{bc}}{c}r_c + \bar{a}\left(\sum_{i=1}^{2}\frac{m_{ai}}{a_i}x_i + \frac{m_{bc}}{c}r_c\right) \quad (36)$$

$$L = (a_2 - a_1)(\alpha + \beta P_a)x_1 x_2\left(\frac{m_{a2}}{a_2} - \frac{m_{a1}}{a_1}\right) + [\beta - \bar{a}(\alpha + \beta P_a) + 1]\frac{m_{bc}}{c}r_c + \bar{a}(\alpha + \beta P_a)\left(\sum_{i=1}^{2}\frac{m_{ai}}{a_i}x_i + \frac{m_{bc}}{c}r_c\right) \quad (37)$$

$$K' = (a_2 - a_1)x_1' x_2'\left(\frac{m_{a2}}{a_2} - \frac{m_{a1}}{a_1}\right) + [(\bar{a}' - 1)\beta' + 1]\frac{m_{bc}}{c}r_c' + \bar{a}'\left(\sum_{i=1}^{2}\frac{m_{ai}}{a_i}x_i' + \frac{m_{bc}}{c}r_c'\right) \quad (38)$$

$$L' = (a_2 - a_1)(\alpha' + \beta' P_a')x_1' x_2'\left(\frac{m_{a2}}{a_2} - \frac{m_{a1}}{a_1}\right) + [\beta' - \bar{a}'(\alpha' + \beta' P_a') + 1]\frac{m_{bc}}{c}r_c' + \bar{a}'(\alpha' + \beta' P_a')\left(\sum_{i=1}^{2}\frac{m_{ai}}{a_i}x_i' + \frac{m_{bc}}{c}r_c'\right) \quad (39)$$

$$D' = 1 - (\bar{a}' - 1)(\alpha' + \beta' P_a'). \quad (40)$$

The parameters $N_A^{0\prime}$, r_b', r_c', x_i', $\bar{a}'$, α', and β' in Eqs. 38, 39, and 40 are defined as

$$N_A^{0\prime} = \sum_{i=1}^{2} a_i N_{ai}' \quad (41)$$

$$r_b' = bN_{bc}'/N_A^{0\prime} \quad (42)$$

$$r_c' = cN_{bc}'/N_A^{0\prime} \quad (43)$$

$$x_i' = a_i N_{ai}'/N_A^{0\prime}, \quad i = 1,2 \quad (44)$$

$$\bar{a}' = \sum_{i=1}^{2} a_i x_i' \quad (45)$$

$$\alpha' = r_b' P_b'(1 - P_b') + r_c' P_c'(1 - P_c') \quad (46)$$

$$\beta' = bP_b' + cP_c' - 1 \quad (47)$$

where $N_{ai}'(i=1,2)$ and N_{bc}' are the total number of monomers of $A_{ai}(i=1,2)$ and B_bC_c in sol, respectively, and P_a', P_b', and P_c' are the extent of reactions of A, B, and C groups in sol, respectively.

By choosing $\langle R^2\rangle_2$ as starting point for successive recursions, we obtain, by using the recursion formula in Eq. 16, the kth radius of gyration $\langle R^2\rangle_k$ with $k>2$ as follows

$$\langle R^2\rangle_k = \begin{cases} W_k/D^{2k-2}, & \text{for pre-gel} \\ Q_k/D^{2k-2}, & \text{for post-gel} \end{cases} \quad (48)$$

where W_k and Q_k satisfy the same recursion formula

$$U_{k+1} = HU_k + D\left\{E + Fr_c\frac{\partial}{\partial r_c} + I\left[P_b(1-P_b)\frac{\partial}{\partial P_b} + P_c(1-P_c)\frac{\partial}{\partial P_c}\right] + Jx_1\frac{\partial}{\partial x_i}\right\}U_k \quad (49)$$

with

$$H = (2k-2)\{(\bar{a}-1)(\alpha + \beta P_a)F + 2I(\bar{a}-1)[P_b(1-P_b)(bP_a - r_bP_b) + P_c(1-P_c)(cP_a - r_cP_c)] + (a_1 - a_2)x_1[(b-1)r_bP_b^2 + (c-1)r_cP_c^2 + 2br_cP_bP_c]J\} \quad (50)$$

$$U_k = \begin{cases} W_k, & \text{for pre-gel} \\ Q_k, & \text{for post-gel.} \end{cases} \quad (51)$$

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