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Notes

Conversion Dependence of the Average Mean-Square Radii of Gyration for Hyperbranched Polymers Formed by AB$_g$ Type Monomers

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Introduction

Hyperbranched polymers are typically prepared by polymerization of AB$_g$ type monomers, where A and B are two different functional groups capable of reacting with each other and g is the number of B groups. When g is 2 or greater, polymerization of such monomers gives highly branched polymers, in which the formation of infinite large network structure was avoided.[2]

The mean-square radius of gyration is the important statistical parameter in conformational statistics of polymer chains. The quantity may be averaged over the polymer molecular weight distribution to give the average mean-square radius of gyration, which is experimentally accessible. For example, the z-average mean-square radius of gyration is generally determined from light scattering experiments,[1] and therefore understanding this quantity varying with the conversion or reaction time may help to improve the present knowledge about the architecture of the elementary structure and formation kinetics.

In the note, a decomposition formula of the combinatorial coefficient, which counts for the isomeric structures formed by the same number of AB$_g$ type monomers, is first determined. The statistical interpretation of this formula, which is similar to the argument proposed by Dobson and Gordon[5,6] and some of the authors[9] for the branched polymers, is proposed to give the mean-square radius of gyration without excluded-volume effect. Then the theoretical calculations for the average mean-square radii are carried out to give the explicit expressions of the weight- and z-average mean-square radii of gyration depending on the conversion of B groups, in which the contribution of the unreacted monomers in hyperbranched polymer systems is included and excluded, respectively.

Number of Isomeric Structures and Mean-Square Radius of Gyration

The molecular weight distribution P_n for AB$_g$ type hyperbranched polymer system can be expressed as[2]

$$P_n = W_0 C_n (1 - gx) x^{n-1} (1 - x)^{gn-n+1} \tag{1}$$

with

$$C_n = \frac{(gn)!}{(gn - n + 1)!n!} \tag{2}$$

where x is the conversion of B groups and C_n is the combinatorial coefficient which stands for the number of isomeric structures formed by n AB$_g$ monomers. In obtaining the above equations, the assumption of ideal network polymerization was retained; i.e., all functional groups of the same type are equally reactive, all groups react independently, and no intramolecular reactions occur in finite species. The combinatorial coefficient C_n satisfies the decomposition formula

$$C_n = \frac{1}{2(n-1)} \sum_i C_i C_{n-i} (gn - n + 2) \tag{3}$$

To interpret eq 3 more clearly, let us rewrite it in a symmetric form

$$(n-1)C_n = \sum_{i<n} E(n,i) \tag{4}$$

with

$$E(n,i) = \frac{1}{2}\{(gi - i + 1)C_i C_{n-i} + [g(n-i) - (n-i) + 1]C_{n-i} C_i\} \tag{5}$$

For an arbitrary n-mer in the ensemble of molecules, there exist in general $(n - 1)$ bonds formed during the polymerization process without intramolecular reaction. Considering an arbitrary bond in a hyperbranched polymer chain formed by n monomers, where the monomers are defined as mass points for the sake of simplicity, there must be two moieties of the molecule if this bond is split, in which the number of mass points found in these two moieties of the molecule is i and $(n - i)$, respectively. Note that the term $(n - 1)C_n$ on the left-hand side of eq 4 is the number of bonds in the n-mers including all isomeric structures formed by n AB$_g$ monomers. Therefore, the term $(gi - i + 1)C_iC_{n-i}$ on the right-hand side of eq 5 is the number of bonds formed by B groups in the i-mers reacting with A groups in the $(n - i)$-mers. The term $[g(n - i) - (n - i) + 1]C_{n-i}C_i$ is the number of bonds formed by A groups in the i-mers reacting with B groups in the $(n - i)$-mers. The summation in eq 5 with respect to i gives the total number of bonds formed during polymerization in the n-mers including all isomeric structures. Obviously, the term $E(n,i)/C_n$ should be the number of bonds in the n-mer, whose splitting produces two moieties of i and $n - i$ mass points, respectively.

The mean-square radius of gyration $\langle R_n^2 \rangle$, which averages the fluctuations in time of R_n^2 due to Brownian motion proposed by Dobson and Gordon,[5,6] is expressed

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as

$$\langle R_n{}^2\rangle = \frac{b^2}{n^2}\sum_{h=1}^{n-1}(n - n_h)n_h \tag{6}$$

where b is the effective bond length. The index h in the summation of eq 6 is used to denote the hth bond in the n-mer. The term n_h and $n - n_h$ on the right-hand side of eq 6 are the number of mass points associated with the two moieties produced by imaginary cutting the hth bond in the n-mer. As mentioned above, $E(n,i)/C_n$ is the number of bonds whose splitting produced moieties of i and $n - i$ mass points, respectively. Then the mean-square radius of gyration in eq 6 can be expressed as

$$\begin{aligned}\langle R_n{}^2\rangle &= \frac{b^2}{n^2}\sum_{i<n}(n - i)i\frac{E(n,i)}{C_n} \\ &= \frac{b^2}{2C_n n^2}\sum_{i<n} i(n - i)\{(gi - i + 1)C_nC_{n-i} + \\ &\qquad [g(n - i) - (n - i) + 1]C_{n-i}C_i\}\end{aligned} \tag{7}$$

The summation in eq 7 with respect to i means that splitting the n-mer produces two moieties of i and $n - i$ units. Since the number of units in those two moieties varies from 1 to $n - 1$, the summation in eq 7 contains all the moieties with a different number of mass points. When the functionalities A and B are equal, the form in eq 7 can be reduced to the form of A_{g+1} type mean-square radius of gyration proposed by Zimm and Stockmayer.[3,4]

Average Mean-Square Radii of Gyration

The number-, weight-, and z-distribution of hyperbranched polymers can be defined as

$$N(n) = \frac{P_n}{M_0}, \quad W(n) = \frac{M_0}{M_1}nN(n), \quad Z(n) = \frac{M_0}{M_2}n^2N(n) \tag{8}$$

where M_i ($i = 0, 1, 2$) are the polymer moments and can be calculated analytically. The number-, weight-, and z-average mean-square radii of gyration can be defined as

$$\langle R^2\rangle_n = \sum_n \langle R^2\rangle_n N(n) = \langle R^2\rangle_0 \tag{9}$$

$$\langle R^2\rangle_w = \sum_n \langle R_n{}^2\rangle W(n) = \frac{M_0}{M_1}\sum_n \langle R^2\rangle nN(n) = \frac{M_0}{M_1}\langle R^2\rangle_1 \tag{10}$$

$$\langle R^2\rangle_z = \sum_n \langle R_n{}^2\rangle Z(n) = \frac{M_0}{M_2}\sum_n \langle R^2\rangle n^2N(n) = \frac{M_0}{M_2}\langle R^2\rangle_2 \tag{11}$$

where $\langle R^2\rangle_k$ ($k = 0, 1, 2$) is the kth polymer radius

$$\langle R^2\rangle_k = \sum_n \langle R_n{}^2\rangle n^kN(n) \quad k = 0, 1, 2 \tag{12}$$

Substituting the mean-square radius of gyration $\langle R_n{}^2\rangle$ in eq 7 and the number distribution $N(n)$ in eq 8 into eq 12, the second polymer radius can be obtained through direct summation

$$\langle R^2\rangle_2 = b^2\frac{gx(1 - x)}{(1 - gx)^4} \tag{13}$$

Unfortunately, the zeroth polymer radius $\langle R^2\rangle_0$ and the first polymer radius $\langle R^2\rangle_1$ cannot be calculated analytically in this way. Since the mean-square radius of gyration $\langle R_n{}^2\rangle$ in eq 7 is independent of the conversion of B groups x, it can be chosen as a variable to differentiate both sides of eq 12. Letting $k = 1$ yields

$$x(1 - x)\frac{\mathrm{d}\langle R^2\rangle_1}{\mathrm{d}x} + \langle R^2\rangle_1 - \frac{b^2gx(1 - x)}{(1 - gx)^3} = 0 \tag{14}$$

The boundary condition in eq 14 is $\langle R^2\rangle_1 = 0$ for $x = 0$; therefore, the first polymer radius can be solved

$$\langle R^2\rangle_1 = b^2\left[\frac{g(1 - x)}{(1 - g)^3x}\ln\frac{1 - gx}{1 - x} + \frac{g(1 - x)(gx + g^2x - 2)}{2(1 - g)^2(1 - gx)^2}\right] \tag{15}$$

Consecutively, the zeroth polymer radius $\langle R^2\rangle_0$ may be calculated as

$$\langle R^2\rangle_0 = \frac{1 - x}{x}\left[\int\frac{1 - gx}{(1 - x)^2}\langle R^2\rangle_1\,\mathrm{d}x + C\right] \tag{16}$$

where C is a constant determined by boundary condition $\langle R^2\rangle_0 = 0$ for $x = 0$. However, the $\langle R^2\rangle_1$ is so complex, it is too difficult to give an explicit expression of the zeroth polymer radius. The zeroth polymer radius can be calculated numerically, and the detailed numerical calculation is omitted. Substituting eqs 13 and 15 into eqs 10 and 11 yields the explicit expressions of the weight- and z-average mean-square radii of gyration depending on the conversion of B groups

$$\langle R^2\rangle_w = b^2\left[\frac{g(1 - x)(1 - gx)}{(1 - g)^3x}\ln\frac{1 - gx}{1 - x} + \frac{g(1 - x)(gx + g^2x - 2)}{2(1 - g)^2(1 - gx)}\right] \tag{17}$$

$$\langle R^2\rangle_z = b^2\frac{gx(1 - x)}{(1 - gx)(1 - gx^2)} \tag{18}$$

In the experimental procedure, the low molecular weight materials, such as residual monomer, etc., are usually separated from the polymer systems by precipitation. Here we only give the z-average mean-square radii of gyration excluding the unreacted monomers without detail calculation.

$$\langle R^2\rangle'_z = b^2\frac{gx(1 - x)[1 - (1 - x)^g]}{[(1 - gx^2) - (1 - gx)^3(1 - x)^g](1 - gx)}$$

Summary and Conclusions

In accordance with the expressions given above, we can predict the variation of the average mean-square radii of gyration during polymerization. The results obtained in the note are expressed as the function of the conversion of B groups. As the conversion of B groups can be written in terms of the branching density or reaction time,[7,8] the average mean-square radius of gyration can be rewritten as a function of branching density or reaction time. In the experimental procedure, a small fraction of sample is extracted from the reaction bath at various times during the polymerization reaction and examined through light scattering. Experimental measurement of the structure functions at small momentum transfer can yield information on the *z*-average mean-square radius of gyration varying with the conversion of B groups or reaction time or branching density. The conversion of B groups, as well as reaction time and branching density, can be measured by means of NMR and FTIR and other techniques. Our results are convenient to compare with experimental data since all quantities in the formulas are experimentally accessible. To our knowledge there has not yet been any experiment performed to study the conversion dependence of the mean size for the hyperbranched polymers. One can imagine that the experiments such as light scattering techniques can be carried out to give more information about the mean size varying with the conversion during polymerization, the growth picture and the elementary structure of hyperbranched polymers, and so on.

As the result of an ideal statistically polycondensation, which is the basic model used to describe the polymerization process, the effect of no equal rate constants, no sterical hindrance, and no cyclization are assumed in most theoretical considerations,[2,7] which may not be fulfilled in reality, and therefore certain deviations are to be expected when comparing with experimental results. Unfortunately, the molecular parameters cannot be calculated analytically whenever these imperfect factors are taken into account. In this case, computer simulation techniques should be the powerful tools to investigate the molecular parameters[10,11] and are not further discussed in the paper. It should be noted that the excluded-volume effect is not taken into consideration in obtaining the mean-square radius of gyration, so the results are only suitable for the θ state of polymer solution. This problem will be treated in a later publication.

Finally, we want to stress that the method proposed in this paper is applicable not only to the ploycondensation of AB_g type monomers but also self-condensation vinyl polymerization, as well as other polymerization processes, such as the polycondensation of AB_g type monomers including multifunctional core moieties, which is added to control the molecular weight distribution. Although the ideal statistical polymerization whose kinetics is described by Smoluchowski-like coagulation equation is assumed, here we state that, as a basic model of the polymerization process, the analytic results presented in this paper still provide an effective way of understanding the physical properties of hyperbranched polymers during their formation.

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