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Conversion Dependence of the *z*-Average Mean Square Radii of Gyration for Hyperbranched Polymers with Excluded Volume Effect

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ABSTRACT: The concept of subchain for hyperbranched polymer systems is investigated. Taking AB_f type polycondensation reaction as an example, the subchain number distribution is obtained explicitly. As a direct application of the subchain number distribution, the mean square radius of gyration is given, where the excluded volume effect is taken into consideration. Furthermore, the *z*-average mean square radius of gyration is evaluated as the function of the conversion of functional groups, in which the contribution of unreacted monomers in hyperbranched polymer systems is included and excluded, respectively.

Introduction

Hyperbranched polymers have received considerable attention in recent years, partly because they do show properties very similar to dendrimers, which are of particular interest for utilization in catalysis, supermolecular chemistry, and biochemistry,[1] and partly because their syntheses are accomplished by simple one-pot polycondensations of multifunctional monomers.[2−4] However, only after Kim and Webster published the synthesis of pure hyperbranched polyarylenes from AB_2 monomer in 1988[2] did this class of polymers become a topic of intensive research of many groups. Hyperbranched polymers are typically prepared by polymerization of AB_f type monomers, where A and B are two different functional groups capable of reacting with each other, and f is the number of B groups. When f is 2 or greater, polymerization of such monomers gives highly branched polymers, in which the formation of infinite large network structure was avoided. A multitude of hyperbranched polymers synthesized via polycondensation of AB_2 and AB_f ($f > 2$) monomers have been reported, and reviews were published recently.[3]

The physical properties of polymer materials depend crucially on the molecular parameters, such as the molecular number distribution, the average molecular weight, the mean square end-to-end distance and the mean square radius of gyration and so on. The theoretical description of polycondensations leading to branched polymers was first proposed by Flory[5] and Stockmayer[6] and further theoretical approach was investigated by Gordon,[8,9] Burchard,[10] and others.[11−13] In these works, the molecular weight distribution and the average molecular weight and the average mean square radius of gyration without excluded volume effect were given explicitly. Recent development on this subject came from Moller and co-workers, who derived the distribution of branching units over the molecules and obtained the conversion dependence of the branching density.[14]

The mean square end-to-end distance and the mean square radius of gyration are both the most important statistical parameters in conformational statistics of polymer chains. For dendritic or hyperbranched polymer systems, only the mean square radius of gyration is meaningful. From the architecture of a hyperbranched polymer, one can see that the mean square radius of gyration is smaller than that of a linear polymer chain of the same molecular weight due to the branching effect. For the dendrimer systems, in which the branching density has the value 1.0, Boris and Rubinstein calculated the dependence of the radius of gyration on its generation to give a maximum attainable generation according to the excluded volume effect.[20] Although the topological structures of the hyperbranched polymer and dendrimer are similar, but the branching density of the hyperbranched polymer is smaller than that of the dendrimer, so a number of linear units exist inside the hyperbranched polymer skeleton. This means that the molecular weights, as well as the mean square radii of gyration, of the hyperbranched polymers increase as the conversion of function group increase without limitation. The mean square radius of gyration may be averaged over the polymer molecular weight distribution to give the average mean square radius of gyration, which increases with the conversion of functional groups or reaction time, and is experimental accessible. For example, the *z*-average mean square radius of gyration is generally determined from light-scattering experiments.[10] Experimental measurement of the structure functions at small momentum transfer can yield the *z*-average mean square radius of gyration varying with the conversion of groups or reaction time, and therefore, understanding the *z*-average mean square radius of gyration varying with the conversion or reaction time may help to improve present knowledge about the architecture of the elementary structure and formation kinetic.

From the theoretical point of view, there are two methods being used to calculate the average mean square radius of gyration. One is the computer simulation based on the formation kinetic, which is not discussed in detail in this paper.[17−19] Another is by an analytical technique, such as the statistical method,[5−7] stochastic theory of branching processes,[9] the kinetic approach method,[16] and so on. It should be pointed out, to our knowledge, that no analytical technique has been proposed to calculate the average mean square radius of gyration for the hyperbranched polymer systems in which the excluded volume effect was taken into consideration. As far as most real polymeric systems are concerned, the influences of excluded volume effect on many static and dynamic properties of polymers chains

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are evident and thus should be taken into consideration. A polymer chain takes a randomly coiled form in a good solvent, and therefore the swelling of the polymer chains occurring during dissolution of the sample in good solvent can increase the radius of gyration due to the excluded volume effect.

This work gives a theoretical approach to calculate the average mean square radius of gyration for hyperbranched polymer systems with excluded volume effect. The results should be treated as just the first approximation of real values. First, we proposed a concept of subchain for the hyperbranched polymer systems. By taking AB_f type polycondensation reaction as an example, the explicit subchain number distribution in the n-mers is investigated. Second, the mean square radius of gyration of hyperbranched polymer of n-mer in good solvent is investigated by the way of the subchain number distribution, where the excluded volume effect is taken into consideration. Finally, the z-average mean square radius of gyration is given as the function of the conversion of B groups x, in which the contribution of the unreacted monomers in hyperbranched polymer systems is included and excluded, respectively.

The Subchain Number Distribution

Let us begin with the definition of the subchain in the n-mer. For an arbitrary n-mer in the ensemble of molecules, there should have in general $(n - 1)$ bonds linked by n monomers, in which the intramolecular reaction was being neglected. Consider the ith unit and the jth unit in an arbitrary n-mer, there is only one path leading from the ith to the jth unit, and the number of bonds on a path connecting unit i with unit j is denoted as l which can be varied from 1 to $n - 1$. The path consisting of l bonds, in which possess $l + 1$ units, constitutes one of the subchains in an arbitrary n-mer. The subchain number distribution constituted by l bonds in the n-mer is denoted as $N(n, l)$, which is the decreasing function of l and has different values according to the topological structure governed by polymerization kinetics. With an increase of the number of the shorter subchains in the n-mer, the number of branching units in the n-mer also increases. Thus, the topological structure of randomly branched polymer chains can be characterized in terms of the subchains number distribution. Obviously, the total number of subchains $\sum_l N(n, l)$ in an arbitrary n-mer is $n(n - 1)/2$. For the linear polymer chains, the subchain number distribution is $N(n,l) = n - l$, but for hyperbranched polymer chains the subchain number distribution takes different values controlled by the polymerization kinetics. Subsequently, we take the AB_f type polycondensation reaction as an example to give the subchain number distribution. In the polymerization reaction occurring in a continuously stirred tank reactor, in which the slow diffusion process is eliminated by stirring and the polymerization process is limited by reaction of functional groups, the hyperbranched polymers can be formed through AB bonds with assumption of no cycles, where A and B are unreacted functional groups on different polymers. From the architecture of a hyperbranched polymer formed by the AB_f type polycondensation, the number of unreacted A and B groups in an n-mer can be counted. There is only one free A group per molecule, and there are $(gn - n + 1)$ free B groups in an n-mer. The basic kinetic model described above polymerization process is a Smoluchowski-like coagulation equation,[6,15] where coagulation kernel is proportional to the number of unreacted functional groups on both polymers. Flory derived for a given degree of conversion of the B groups, x, that the molecular weight distribution is given by the following expressions[5]

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

with

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

where C_n is the combinatorial coefficient which stands for the number of isomeric structures formed by n AB_f monomers, and W_0 is the total number of AB_f type monomers in the system. For the hyperbranched polymer systems, where the molecular weight distribution is given by eq 1, the average mean square radius of gyration in the Θ state can be worked out by means of the stochastic theory of branching processes[9] or the kinetic equation approach and a decomposition formula of the combinatorial coefficient proposed by some authors.[16] Here, we only give the explicit expression of the mean square radius of gyration without further discussion.

$$\langle R_n^{\,2}\rangle_\Theta = \frac{b^2}{2C_n n^2} \sum_{i<n} i(n - i)\{(fi - i + 1)C_n C_{n-i} + [f(n - i) - (n - i) + 1]C_{n-i} C_i\} \tag{3}$$

On the other way, the square radius of gyration for a hyperbranched polymer chain consisting of n mass points with fixed conformation is defined as

$$R_n^{\,2} = \sum_{i=1}^{n} \frac{r_i^{\,2}}{n} \tag{4}$$

where r_i is the distance of the ith mass point from the center of gravity of the molecule, in which the monomers are defined as mass points for the sake of simplicity. A simple argument, proposed by Zimm and Stockmayer,[7] leads to the transformation

$$R_n^{\,2} = \frac{1}{2n^2} \sum_{i,j} r_{ij}^{\,2} \tag{5}$$

where r_{ij} is the distance from the ith mass point to the jth mass point. With cyclic molecules being excluded, there is a unique path of bonds leading from the ith mass point to the jth mass point in the n-mer, which is one of the subchains in the n-mer. 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, is expressed as[9]

$$\langle R_n^{\,2}\rangle = \frac{1}{2n^2} \sum_{i,j} \langle r_{ij}^{\,2}\rangle \tag{6}$$

It should be noted that the subchain leading form the ith unit to the jth unit is a linear polymer chain, and therefore the mean square distance from the ith unit to the jth unit in the Θ state is $\langle r_{ij}^{\,2}\rangle_\Theta = b^2 l$, where b is the effective bond length formed during polymerization. By using the subchain number distribution, the mean square radius of gyration in the Θ state $\langle R_n^{\,2}\rangle_\Theta$ in above equation can be reformulated as

$$\langle R_n^{\,2}\rangle_\Theta = \frac{b^2}{n^2}\sum_{l<n} lN(n, l) \tag{7}$$

By combination of eqs 3 and 7, we can obtain the subchain number distribution $N(n,l)$ as

$$N(n,l) = \frac{(n - l)}{2C_n}\{(fl - l + 1)C_lC_{n-l} + [f(n - l) - (n - l) + 1]C_{n-l}C_l\} \tag{8}$$

Obviously, when $g = 1$, the combinatorial coefficient is $C_n = 1$, so the subchain number distribution is $N(n,l) = n - l$, which is the result of linear polymer chains. It is not difficult, by means of the decomposition formula of the combinatorial coefficient,[16] to prove that the summation over l in eq 8 gives the total number of subchains in the n-mer, $\sum_l N(n, l) = n(n - 1)/2$. It should be pointed out that the topological structure of hyperbranched polymer chains is unchanged in good solution as compared with that in Θ solution; therefore, the subchain number distribution is invariant. In the next section, the mean square radius of gyration of n-mer in good solvent is calculated by using the subchain number distribution.

The Mean Square Radius of Gyration in Good Solvent

To calculate the mean square radius of gyration of n-mer in good solvent, let us reconsider eq 6 in the above section. It is shown that the subchain leading form the ith unit to the jth unit is a linear polymer chain. When the polymer is dissolved in good solvent, it is sure that the mean square distance from the ith unit to the jth unit is $\langle r_{ij}^{\,2}\rangle_g = b^2l^{6/5}$, where the excluded volume effect is taken into consideration and presented through the Flory exponent, which is $^3/_5$ in three dimensions. Using the subchain number distribution again, the mean square radius of gyration in good solvent $\langle R_n^{\,2}\rangle_g$ is expressed as

$$\langle R_n^{\,2}\rangle_g = \frac{b^2}{n^2}\sum_{l<n} l^{6/5}N(n, l) = \frac{b^2}{2n^2C_n}\sum_{l<n} l^{6/5}(n - l)C_{n-l}C_l(fn - n + 2) \tag{9}$$

Here it should be noted that two approximations are adopted in obtaining the above equation. One is that mean square distance $\langle r_{ij}^{\,2}\rangle_g = b^2l^{6/5}$, which is valid only for linear chains and for the number of links much higher than unity, applies to the branched molecules and to short subchains. As being discussed above, the subchain leading from the ith unit to the jth unit is a linear polymer chain, and on the basis of this consideration, the results of linear chains can be used to calculate the physical quantities of branched polymers. Of course, as the length l of the subchain increases, $N(n,l)$ decreases, so that there exist many shorter subchains in the n-mer. But numerical calculations show that the longer subchains give the main contribution to the mean square radius of gyration $\langle R_n^{\,2}\rangle_g$. To see this more clearly, the contributions of the shorter subchains constituted by $l \le l_s = 25$ bonds denoted as $\langle R_n^{\,2}(25)\rangle_g$, where the Monte Carlo simulation for linear polymer chains give the well scaling argument when $l_s \ge 25$,[21,22] are calculated for the different n-mers. In Figure 1 the numerically calculated values of $\langle R_n^{\,2}(25)\rangle_g/\langle R_n^{\,2}\rangle_g$ is plotted vs n, where $f = 2$. It can be seen that as n increases, the quantity decreases significantly and has a value smaller than 0.1 as $n > 300$. Another approximation is that the effective bond length b is independent of the subchain length. Barrett had previously investigated this subject for the linear chain with excluded volume effect.[21] Since the main contributions of the mean square radius of gyration come from the longer subchain, in this case, the effective bond length has a slight dependence on the chain length in the viewpoint of scaling concept[24] and can be approximated as the constant.

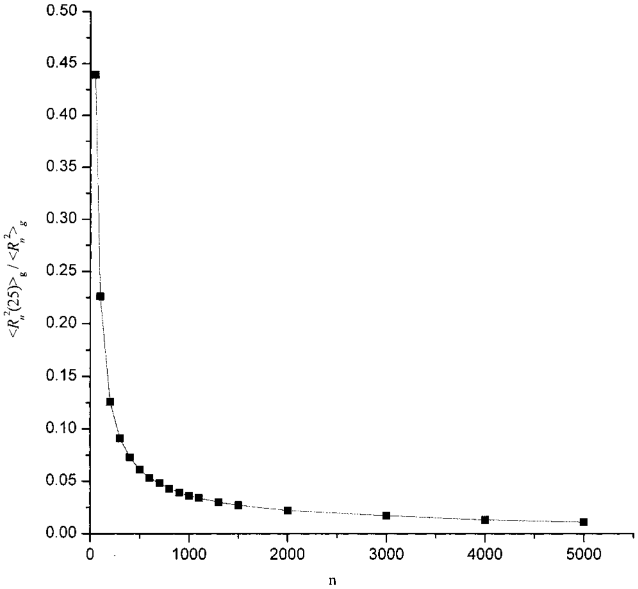

Figure 1. Dependence of $\langle R_n^{\,2}(25)\rangle_g/\langle R_n^{\,2}\rangle_g$ on n. $f = 2$.

In the experimental study, the light-scattering technique is used to determine the z-average mean square radius of gyration in good solvent. So the z-average mean square radius of gyration $\langle R^2\rangle_z$ is experimental accessible defined as

$$\langle R^2\rangle_z = \frac{\langle R^2\rangle_2}{\sum_n n^2P_n}, \quad \langle R^2\rangle_2 = \sum_n \langle R_n^{\,2}\rangle_g n^2P_n \tag{10}$$

where $\langle R^2\rangle_2$ can be calculated by means of the direct summation. Substituting eqs 9 and 1 into eq 10 yields $\langle R^2\rangle_2$ as follows

$$\langle R^2\rangle_2 = \frac{b^2x}{2W_0(1 - x)(1 - fx)}[(f - 1)M_2M_{6/5} + (f - 1)M_1M_{11/5} + 2M_1M_{6/5}] \tag{11}$$

where M_1 and M_2 are moments of distribution of polymerization degrees and can be given by the way of direct summation

$$M_1 = \sum_n nP_n = W_0, \quad M_2 = \sum_n n^2P_n = W_0\frac{1 - fx^2}{(1 - fx)^2} \tag{12}$$

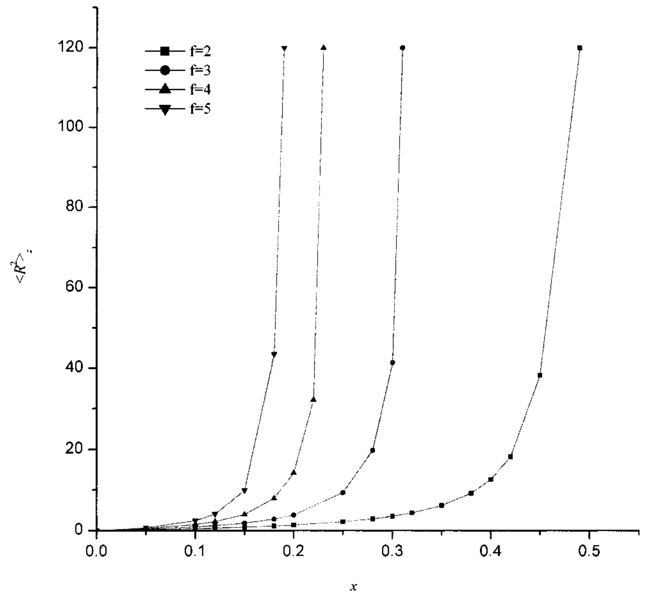

Figure 2. z-Average mean square radius of gyration $\langle R^2\rangle_z$ vs the conversion of B groups, x.

The first moment of distribution of polymerization degrees M_1 is the material balance condition. The other two quantities $M_{6/5}$ and $M_{11/5}$ are noninteger order moments of distribution of polymerization degrees defined as

$$M_{6/5} = \sum_n n^{6/5} P_n, \quad M_{11/5} = \sum_n n^{11/5} P_n \tag{13}$$

Unfortunately, the noninteger moments of distribution of polymerization degrees cannot be given analytically, but can be obtained by using numerical calculation. Substituting eqs 11−13 into eq 10 gives the z-average mean square radius of gyration

$$\langle R^2\rangle_z = \frac{b^2 x(1-fx)}{2W_0(1-x)(1-fx^2)}\left[\frac{(f-1)(1-fx^2)}{(1-fx)^2}M_{6/5} + (g-1)M_{11/5} + 2M_{6/5}\right] \tag{14}$$

Figure 2 shows the numerical calculations of $\langle R^2\rangle_z$ as a function of conversion of B groups, x, for $f = 2, 3, 4, 5$. It can be seen that the $\langle R^2\rangle_z$ values increase slowly at the beginning of the reaction and increase sharply at the end of the reaction. In fact $\langle R^2\rangle_z$ reaches infinity when the conversions of B groups are near the maximum value $x = 1/f$.

In experimental procedure, the low molecular weight materials, such as the residual monomers etc., are usually separated from the polymer systems by precipitation. The summations in above equations include the unreacted monomers, which are referring to summation index $n = 1$. The z-average mean square radius of gyration excluding the unreacted monomers can be expressed as follows

$$\langle R^2\rangle'_z = \frac{\sum_{n\neq 1}\langle R_n{}^2\rangle_g n^2 P_n}{\sum_{n\neq 1} n^2 P_n} = \frac{\langle R^2\rangle'_2}{\sum_{n\neq 1} n^2 P_n} \tag{15}$$

The summation in eq 15 does not include the unreacted monomers $n = 1$, and is the key difference comparing with eq 10. From eq 9, it can be seen that the mean square radius of gyration $\langle R_n{}^2\rangle_g$ equals zero for $n = 1$, which corresponds to the unreacted monomers, so $[\langle R_n{}^2\rangle_g n^2 P_n]_{n=1} = 0$. The $\langle R^2\rangle'_2$ can be obtained as

$$\begin{aligned}\langle R^2\rangle'_2 &= \sum_{n\neq 1}\langle R_n{}^2\rangle_g n^2 P_n \\ &= \Big[\sum_n \langle R_n{}^2\rangle_g n^2 P_n\Big] - [\langle R_n{}^2\rangle_g n^2 P_n]_{n=1} = \\ &\qquad \sum_n \langle R_n{}^2\rangle_g n^2 P_n = \langle R^2\rangle_2\end{aligned} \tag{16}$$

The second moments of distribution of polymerization degrees without the unreacted monomers can be evaluated as

$$M'_2 = \sum_{n\neq 1} n^2 P_n = W_0 \frac{1-fx^2}{(1-fx)^2} - W_0(1-fx)(1-x)^f \tag{17}$$

Substituting eqs 16 and 17 into eq 15 yields the z-average mean square radius of gyration, where the nureacted monomers are excluding

$$\langle R^2\rangle'_z = \frac{b^2 x}{2W_0(1-x)(1-fx)}\left[\frac{(f-1)(1-fx^2)}{(1-fx)^2}M_{6/5} + (f-1)M_{11/5} + 2M_{6/5}\right]\Big/\left[\frac{1-fx^2}{(1-fx)^2} - (1-fx)(1-x)^f\right] \tag{18}$$

Obviously, the z-average mean square radius of gyration excluding unreacted monomers in eq 18 is larger than that including the unreacted monomers in eq 14 of the same conversion of B groups, x. Furthermore, with the similar method mentioned above, the contribution of the low molecular weight materials, such as dimer, trimer, etc., to the z-average mean square radii gyration can be calculated without difficulty.

Summary and Conclusions

The results obtained in this work is expressed as the function of the conversion of B groups, x, so we can predict the variation of the z-average mean square radius of gyration during polymerization. Another important parameter characterized the topological structure of hyperbranched polymers is the branching density, which was dependent on the conversion of B groups, x.[4,14,15] Therefore, the z-average mean square radius of gyration can be rewritten as a function of branching density. From the chemical kinetic equation, the conversion of B groups, x, can be easily derived as a function of the reaction time, so the z-average mean square radius of gyration can also be rewritten as the functions of 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 to obtained the z-average mean square radius of gyration. The conversion of B groups, x, as well as reaction time and branching density, can be measured by means of NMR and FTIR and other techniques. Therefore, our results are convenient for comparison with experimental data since all quantities in the formulas are experimentally accessible. To our knowledge there has not yet been an experiment performed to study the conversion dependence of the mean size for the hyperbranched polymers during polymerization process. 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 or branching density during polymerization and to obtain the picture of growth kinetics and the elementary structure of hyperbranched polymers and so on.

The growth model leading to the molecular weight distribution given by eq 1 can be described by the Smoluchowski-like coagulation equation, where the coagulation kernel is proportional to the number of unreacted functional groups on both polymers. In obtaining the molecular weight distribution given by eq 1, the assumptions of ideal network polymerization were 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. These assumptions may not be fulfilled in reality.[13] The effects of statistical nonideal polymerization on the topological structure of hyperbranched polymers are not discussed in this work. In general, the mean size of polymer chains is dependent on topological structure, and therefore, certain deviations are to be expected when comparing with experimental results. Unfortunately, the *z*-average mean square radius of gyration cannot be calculated analytically whenever these imperfect factors are taken into account. In this case, computer simulation techniques should be powerful tools to investigate the molecular parameters,[17,18] and they are not further discussed in this paper. Although the statistical ideal polymerization whose kinetics is described by Smoluchowski-like coagulation equation is adopted, here we state that, as a basic model of 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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