Conversion Dependence of the Mean Size of the Star-Branched Polymers Made by AB + A_f Type Polycondensation

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ABSTRACT: The statistical method was used to give the number of bonds formed for the star-branched polymer chains made by the AB + A_f polymerization. On the basis of the kinetic model described by the Smoluchowski-like coagulation equation, the mean-square radii of gyration were given analytically. Furthermore, the *z*- and weight-average mean-square radii of gyration were investigated explicitly. The results were much different from that of the hyperbranched polymers made by the AB_f type monomers, where the former had the finite values when the reaction was quantitatively completed, and the latter reached the infinite values. In principle, by varying the number of the A_f type multifunctional core moieties, the average sizes, as well as the average degrees, can be controlled effectively.

Introduction

The star-branched polymers have received much attention as materials due to their novel physical properties, such as multiple end groups, high solubility, and reduced viscosities relative to their linear counterparts.[1] The most common method of preparing star-branched polymer is by linking active linear chains, which are usually pre-prepared by a chain polymerization, to core molecules. The star-branched polymers can also be synthesized by the approaches of the AB + A_f type polycondensation, where A and B are two different functional groups capable of reacting with each other, and *f* is the number of A groups in A_f type monomers.[2] As the reaction is quantitatively completed, the molecular weight distribution of the star-branched polymer becomes narrower with increasing functionality of the A_f type monomers. Under the assumptions of ideal network polymerization; 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 kinetic model of the AB + A_f type polycondensation was proposed to give the kinetic differential equation, which is a Smoluchowski-like coagulation equation. The coagulation kernel is proportional to the number of unreacted functional groups on the clusters. By the direct solutions of the differential equation, the molecular weight distribution and the average molecular weight were given explicitly.[3]

As is well-known, 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 treelike polymer systems, only the mean-square radius of gyration is meaningful.[4−7] From the architecture of a star-branched polymer, it can be seen 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. Since the number of the branching point in the star-branched polymer is only one, the mean-square radius of gyration should also have the much difference from that of the hyperbranched polymer systems, where many branched points exist inside the dendrimer or hyperbranched polymer skeleton. The presence of monomer A_f limits the mean-square radius of gyration and makes it proportional to the average length of linear part of macromolecules.

The average mean-square radius of gyration for the treelike polymer systems can be calculated by the computer simulation, such as MD and MC,[8] the analytical technique,[4−7] the kinetic approach method,[9,10] and so on. To our knowledge, no analytical method has been proposed to give the average mean-square radii of gyration for the star-branched polymers made by AB + A_f type polycondensation.

In this paper, the attention will be focused on a theoretical approach to calculate the average mean-square radius of gyration for the star-branched polymer systems made by the AB + A_f type polycondensation. The results should be treated as just the first approximation of real values. On the basis of the consideration of the architecture of the star-branched formed by AB and A_f type monomers, the statistical method is adopted to give the number of the bonds formed during the coagulation process. The decomposition formulas of the combinatorial coefficient, which count for the isomeric structures of the star-branched polymers, are determined to give the mean-square radii of gyration without the excluded-volume effect. Furthermore, the average mean-square radii of gyration are given analytically, where the assumptions of ideal network polymerization are retained. The average mean-square radius of gyration for star-branched polymers formed by the AB + A_f type polycondensation are quite different from that of the hyperbranched polymer systems made by the AB_f type monomers, where the former has the finite values and the latter reaches infinite values when the reaction was quantitatively completed.[10] The numerical calculations show that the *z*-average mean-square radius of gyration increases slowly at the beginning of the reaction and sharply increases at the end of

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reaction. Moreover, the average size of the star-branched polymers increases faster as the molar ratio of the multifunctional core moieties A_f to the AB type monomers decreases.

The Number of Bonds in the System

The star-branched polymers can be formed from the reversible linking of AB type monomers with a small amount of the A_f type monomers. From the architecture of the star-branched polymers, one can see that there are three kinds of molecules existing in the system. The first is the linear polymers made by the AB type monomers. The second is also the linear polymers made by the AB type monomers with one A_f monomer, in which only one functional group A in the A_f moiety was reacted. The third is the macromolecules with l arms, which can be formed by the AB type monomers with one A_f multifunctional core moiety. The difference is that l ($2 \le l \le f$) functional groups in the A_f core moiety were reacted. When $l = 2$, it is the linear polymer also, and when $l > 2$, it is the star-branched polymer. For an arbitrary linear n-mer without A_f type monomers in the ensemble of molecules, there should be in general $(n - 1)$ bonds linked by n monomers, in which the intramolecular reaction is being neglected. Let $C_n^{(0)}$ denote the number of isomeric structures of the linear polymer chains without A_f type monomers; then the total number of bonds of the linear n-mers without A_f type monomers in the ensemble of molecules is $(n - 1)C_n^{(0)}$. From another point of view, the linear polymer chains can be constructed as follows. If an arbitrary bond is considered in the n-mer, where the monomers are defined as the mass points for simplicity, there may be two moieties if this bond is imagined to be cut. The numbers of mass points found in the two moieties produced by cutting this bond are i and $(n - i)$. For the moiety with i mass points, where the numbers of the isomeric structures are $C_i^{(0)}$, there is one unreacted A group and one unreacted B group. The other moiety with $(n - i)$ mass points also has one unreacted A group and one unreacted B group, in which the numbers of the isomeric structures are $C_{n-i}^{(0)}$. Two moieties can be linked to form the linear n-mer without A_f type monomers, and the numbers of the bonds formed in this way are $C_i^{(0)}\, C_{n-i}^{(0)}$. Summation over i gives the total number of bonds for the linear n-mers without A_f type monomer

$$(n - 1)C_n^{(0)} = \sum_{i=1}^{n-1} C_i^{(0)}\, C_{n-i}^{(0)} \tag{1}$$

By way of the same argument mentioned above, one can obtain the result for the linear n-mer with one A_f type monomer

$$nC_n^{(1)} = f\, C_n^{(0)} + \sum_{i=1}^{n-1} C_i^{(0)} C_{n-i}^{(1)} \tag{2}$$

where $C_n^{(1)}$ stands for the number of isomeric structures of the linear polymer chains with one A_f type monomer. The first term on the right-hand side of the eq 2 is the number of the bonds formed by the two moieties, in which one moiety is the linear polymer chain with n monomers, and the other moiety is the A_f type monomer. The second term is also the number of the bonds connected by the two moieties, but one moiety is the linear polymer chain made by $(n - i)$ monomers with one A_f type monomer, and the other moiety is the linear polymer chain made by i monomers without A_f type monomer. In general, there should be n bonds linked by nAB type monomers and one A_f type monomer, in which the intramolecular reaction is being neglected. The decomposition formula of the combinatorial coefficient $C_n^{(l)}$, which is denoted as the number of isomeric structures of the macromolecules with l arms ($2 \le l \le f$), has some difference from that of the above argument. Considering an arbitrary bond in the n-mer, there may be two moieties if this bond is imagined to be cut. Here there are two ways that the moieties were formed. One is that the bond is linked to the A_f type monomer, so that the first moiety is the linear polymer chain without A_f type monomer, and the second moiety is the macromolecule with $(l - 1)$ arms. The two moieties can be linked to form the macromolecules with l arms. The numbers of the bonds formed by this way are $(f - l + 1)C_i^0 C_{n-i}^{(l-1)}$. The other way the moieties created is that the bond is not linked to the A_f type monomer, and in this case, the first moiety is also the linear polymer chain without A_f type monomer, and the second moiety is the polymer but with l arms. The numbers of the bonds formed by these two moieties are $lC_i^0 C_{n-i}^{(l)}$. The total numbers of the bonds formed by the two moieties are $nC_n^{(l)}$. Then the decomposition formula is

$$nC_n^{(l)} = \sum_{i=1}^{n-l+1} (f - l + 1)C_i^{(0)}\, C_{n-i}^{(l-1)} + \sum_{i=1}^{n-l} lC_i^{(0)}\, C_{n-i}^{(l)} \tag{3}$$

The decomposition formulas of the combinatorial coefficients are closely related to the conformational statistics of the AB + A_f type polymer systems. To interpret these equations more clearly, here eq 1 was taken as an example to rewrite it as follows:

$$n - 1 = \sum_{i=1}^{n-1} E(n,i)/C_n^{(0)} \tag{4}$$

with

$$E(n,i) = C_i^{(0)} C_{n-i}^{(0)} \tag{5}$$

The term $(n - 1)$ on the left-hand side of eq 4 is the number of bonds in the n-mer. The term $E(n,i)/C_n^0$ on the right-hand side of eq 4 should be the number of bonds in the n-mer, whose splitting produces two moieties of i and $(n - i)$ mass points. In the next section, the mean-square radius of gyration of n-mer is calculated by using the above formulas.

The Mean-Square Radii of Gyration

The mean-square radius of gyration for a star-branched polymer chain consisting of n mass points $\langle {R_n}^2 \rangle$, which averages over the fluctuations in time of ${R_n}^2$ due to Brownian motion, is defined as the following form:[4]

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

where r_{ij} is the distance in space from the ith to the jth unit. The monomers are defined as mass points for the

sake of simplicity. By use of the method proposed by Dobson and Gordon,[7] the mean-square radius of gyration $\langle R_n^2\rangle$ in eq 6 can be re-formulated as

$$\langle R_n^2\rangle = \frac{b^2}{n^2}\sum_{h=1}^{n-1}(n - n_h)n_h \tag{7}$$

The quantity b is determined by the detailed structure of chain, especially the length and flexibility, and can be named as the effective bond length. It should be noted that the assumption of all effective bond lengths in the n-mer being equal is taken. In obtaining eq 7, the excluded-volume effect is not taken into consideration, so the results are only suitable for the θ state of polymer solution. The index h in the summation is used to denote the hth bond in the n-mer. The terms n_h and $(n - n_h)$ on the right-hand side of eq 7 are the number of mass points associated with the two moieties which produced by imaginary cutting of the hth bond in the n-mer. The summation runs over all the bonds in the n-mer. According to the interpretation of eqs 1−3 mentioned above, the mean-square radii of gyration can be evaluated as

$$\langle R_n^2\rangle^{(0)} = \frac{b^2}{C_n^{(0)}n^2}\sum_{i=1}^{n-1} i(n - i)C_i^{(0)}C_{n-i}^{(0)} \tag{8}$$

$$\langle R_n^2\rangle^{(1)} = \frac{b^2}{C_n^{(1)}(n+1)^2}[fn + \sum_{i=1}^{n-1} i(n - i + 1)C_i^{(0)}C_{n-i}^{(1)}] \tag{9}$$

$$\langle R_n^2\rangle^{(l)} = \frac{b^2}{C_n^{(l)}(n+1)^2}[\sum_{i=1}^{n-l+1}(f - l + 1)i(n - i + 1)C_i^{(0)}C_{n-i}^{(l-1)} + \sum_{i=1}^{n-l} i(n - i + 1)lC_i^{(0)}C_{n-i}^{(l)}], \quad l = 2, 3, ..., f \tag{10}$$

where $\langle R_n^2\rangle^{(0)}$, $\langle R_n^2\rangle^{(1)}$, and $\langle R_n\rangle^{2)(l)}$ stand for the mean-square radii of gyration of the linear n-mer without A_f type monomer, the linear n-mer with one A_f type monomer, and the macromolecules with l arms ($2 \le l \le f$), respectively. Obviously, when the A_f type monomers are removed from the system, the results in eqs 9 and 10 can be reduced to the form of the linear polymer chain made by AB type monomers.

In obtaining the mean-square radii of gyration given by eqs 8−10, it is not needed to give the detailed forms of the combinatorial coefficients. These coefficients can be determined according to the kinetic model describing the AB + A_f type polymerization process. The analytical expressions of the mean-square radii of gyration can be obtained by use of the results of the combinatorial coefficients. Under assumption of the ideal network polymerization, the growth kinetic of AB + A_f type polycondensation can be modeled by Smoluchowski-like coagulation equation, and the combinatorial coefficients can be estimated as[3]

$$C_n^{(0)} = 1, \quad C_n^{(1)} = f, \quad C_n^{(l)} = \frac{f!\,(n-1)!}{l!\,(f-l)!\,(l-1)!\,(n-l)!} \tag{11}$$

Substituting eq 11 into eqs 8−10 yields

$$\langle R_n^2\rangle^{(0)} = b^2\frac{(n-1)(n+1)}{6n} \tag{12}$$

$$\langle R_n^2\rangle^{(1)} = b^2\frac{n(n+2)}{6(n+1)} \tag{13}$$

$$\langle R_n^2\rangle^{(l)} = b^2\frac{l(n+2)n}{(l+1)(l+2)(n+1)}, \quad l = 2, 3, ..., f \tag{14}$$

The results given by eqs 12−14 are reduced to that given by Zimm and Stockmayer by means of the statistics of chain configurations.[4] It should be noted that the asymptotic form of the star-branched polymers is $\langle R_n^2\rangle^{(l)} \sim n$, which has much difference from that of the hyperbranched polymer system, where the asymptotic form of the mean-square radius of gyration for hyperbranched polymers is $\langle R_n^2\rangle \sim n^{1/2}$. Therefore, the mean-square radius of gyration for star-branched polymers is smaller than that of a hyperbranched polymer chain of the same molecular weight.

The Average Mean-Square Radii of Gyration

For the synthesis of star-branched polymer made by AB + A_f type polycondensation, many different isomeric structures and a broad molecular weight distribution are obtained. Therefore, only the average statistical parameters, for instance, the z-average mean-square radius of gyration, can be experimentally accessible.[7] The molecular weight distributions can be obtained from the Smoluchowski-like coagulation equation[3]

$$P_n^{(0)} = N_0C_n^{(0)}(1 - x)(1 - rx)(rx)^{n-1} \tag{15}$$

$$P_n^{(1)} = A_0C_n^{(1)}(rx)^n(1 - rx)^f \tag{16}$$

$$P_n^{(l)} = A_0C_n{}^{(l)}(rx)^n(1 - rx)^f \tag{17}$$

where $P_n^{(0)}$, $P_n^{(1)}$, and $P_n^{(l)}$ represent the concentrations of the linear n-mer without A_f type monomers, the linear n-mer with one A_f type monomer, and the macromolecules with l arms ($2 \le l \le f$), respectively. x is the conversion of the B groups. N_0 is the total number of the AB type monomers in the system, and A_0 is the total number of the A_f type monomers, and $r = N_0/(N_0 + fA_0)$. The z-average mean-square radius of gyration $\langle R^2\rangle_z$ is defined as

$$\langle R^2\rangle_z = \frac{\langle R^2\rangle_2}{M_2} \tag{18}$$

with

$$\langle R^2\rangle_2 = \sum_n\langle R_n^2\rangle^{(0)}n^2P_n^{(0)} + \sum_n\langle R_n^2\rangle^{(1)}(n+1)^2P_n^{(1)} + \sum_n\sum_{l=2}^{f}\langle R_n^2\rangle^{(l)}(n+1)^2P_n^{(l)} \tag{19}$$

The second moment of distribution of polymerization

degrees M_2 is defined as

$$M_2 = \sum_n n^2 P_n^{(0)} + \sum_n (n+1)^2 P_n^{(1)} + \sum_n \sum_l (n+1)^2 P_n^{(l)}$$

$$= N_0 \frac{1 + 2x(1-r) + (f-3)rx^2 - (f-2)r^2x^2}{(1-rx)^2} + A_0[1-(1-rx)^f] \quad (20)$$

The quantity $\langle R^2\rangle_2$ can be obtained by direct summation. Substituting eqs 12−17 into eq 19 yields the explicit expression of the $\langle R^2\rangle_2$

$$\langle R^2\rangle_2 = \frac{N_0 b^2 x}{(1-rx)^3}[1 - rx + rx(f-1)(1-r)] \quad (21)$$

Substituting eqs 20 and 21 into eq 18 can give the explicit expression of the *z*-average mean-square radius of gyration depending on the conversion of B groups. The weight-average mean-square radius can be defined as

$$\langle R^2\rangle_w = \frac{\langle R^2\rangle_1}{M_1} \quad (22)$$

with

$$\langle R^2\rangle_1 = \sum_n \langle R_n{}^2\rangle^{(0)} n P_n^{(0)} + \sum_n \langle R_n{}^2\rangle^{(1)} (n+1) P_n^{(1)} + \sum_n \sum_{l=2}^{f} \langle R_n{}^2\rangle^{(l)} (n+1) P_n^{(l)} \quad (23)$$

The first moment of distribution of polymerization degrees M_1 is the material balance condition given by the following expression:

$$M_1 = \sum_n n P_n^{(0)} + \sum_n (n+1) P_n^{(1)} + \sum_n \sum_{l=2}^{f} (n+1) P_n^{(l)} = N_0 + A_0[1-(1-rx)^f] \quad (24)$$

The quantity $\langle R^2\rangle_1$ can also be obtained analytically by direct summation. Substituting eqs 12−17 into eq 23 yields

$$\langle R^2\rangle_1 = b^2 \frac{N_0 rx(1-x)(3-rx)}{6(1-rx)^2} + b^2 \frac{A_0 f}{rx}\left[\frac{f-1}{f} - \frac{2f-1}{(f+1)(1-rx)} + \frac{f}{(f+2)(1-rx)^2} - \frac{(f-2)(1-rx)^f}{f(f+1)(f+2)}\right] \quad (25)$$

In obtaining the above results, the residual groups of A_f are not taken into consideration, since the amount of the core molecules is very small compared with the AB type monomers. When the reaction is quantitatively completed, the conversion of the B groups reaches the maximum value 1. Substituting $x = 1$ into eq 18 yields the maximum value of the *z*-average mean-square radius of the gyration

$$\langle R^2\rangle_z^{\max} = b^2 \frac{fr(1+fr-r)}{fr(1-r)(3-2r+fr) + (1-r)^3[1-(1-r)^f]} \quad (26)$$

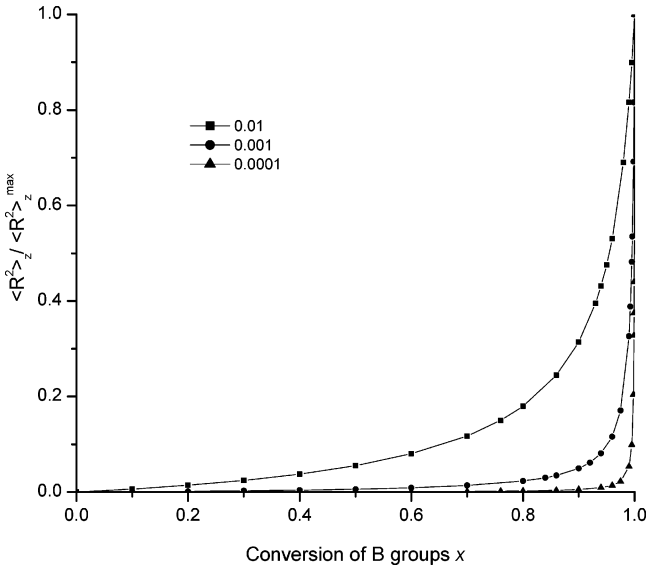

Figure 1. Dependence of $\langle R^2\rangle_z/\langle R^2\rangle_z{}^{\max}$ on the conversion of B groups x. $A_0/N_0 = 0.01$, 0.001, and 0.0001.

Here it is remarkable to point out that the maximum value of the *z*-average mean-square radius of the gyration is finite and is dependent on the r, which is the fraction of the A groups in the system. This result is quite different from that of the hyperbranched polymers made by the AB_f type monomers, where the *z*-average mean-square radius of gyration reaches infinite when the reaction is quantitatively completed.[10] The difference comes from the topological structure of the treelike polymers as mentioned above, in which the star-branched polymer has only one branched point, whereas the hyperbranched polymer has many branched points. The maximum values of the average size ($f = 4$) are $\langle R^2\rangle_z^{\max}/b^2 = 20.5$, 200.5, 2000, in which the fraction of the A groups are $r = 0.96$, 0.996, 0.9996, respectively. Figure 1shows the numerical calculations of $\langle R^2\rangle_z/\langle R^2\rangle_z^{\max}$ as a function of conversion of B groups x with $f = 4$. It can be seen that the quantities $\langle R^2\rangle_z/\langle R^2\rangle_z^{\max}$ increases slowly at the beginning of the reaction and increases sharply at the end of the reaction. The average size $\langle R^2\rangle_z$ increases faster as the number of the A_f type molecules decreases. In fact, it enlarges almost 100 times as the fraction of the A groups rise from 0.96 to 0.9996, where the molar ratio A_0/N_0 decreases from 0.01 to 0.0001. The existence of the maximum values means that the maximum average sizes are dependent only on the fraction of the A_f type molecules, and therefore, in principle, by varying the number of the multifunctional core moieties, the average size as well as the average degrees of polymerization can be controlled.

Summary and Conclusions

In the work the ideal network AB + A_f type polycondensation are assumed, which are normally retained in most theoretical consideration.[3,8] In general, the topological structures of treelike polymer chains are

affected by the imperfect factors, and therefore certain deviations are to be expected when comparing with experimental results.[6,8] Normally, the average sizes, as well as the average degrees, 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,[8] which are not further discussed in the paper. As a first approximation, the average mean-square radii of gyration for star-branched polymer system formed by AB + A_f type monomers are obtained as the function of the conversion of B groups and increase as the reaction time or the conversion of B groups increases. In accordance with the expressions given above, one can predict the variation of the average mean-square radii of gyration during polymerization. The interesting conclusion is that the average size, as well as the average degrees, of star-branched polymers can be controlled, in principle, by varying the number of the multifunctional core moieties. Furthermore, the average mean sizes increase sharply at the end of the reaction. Here it should be noted that excluded-volume effect is not taken into consideration in obtaining the mean-square radius of gyration,[5] so the results are only suitable for the θ state of polymer solution. The quantities given in the paper are all experimentally accessible.[6] In 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 obtain the *z*-average mean-square radius of gyration dependent on the conversion of the B groups. It should be pointed out that the topological structure of star-branched polymer chains is unchanged in the cell as that in the reaction bath, and therefore, understanding the *z*-average mean-square radius of gyration varying with the conversion may help to improve present knowledge about the architecture of the elementary structure and formation kinetic. Finally, it should be stressed that although the ideal statistical polymerization of AB + A_f type monomers, whose kinetics is described by Smoluchowski-like coagulation equation, is assumed, and 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 star-branched polymers during their formation. For instance, the prediction of the average sizes controlled by varying the number of the A_f type molecules can be investigated according to eqs 18, 22, and 26.

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