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Molecular Weight Distribution of Hyperbranched Polymers Generated from Polycondensation of AB_2 Type Monomers in the Presence of Multifunctional Core Moieties

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ABSTRACT: The molecular weight distribution and its moments for the hyperbranched polymer formed by the polycondensation of an AB_2 type monomer with a multifunctional core moiety were derived rigorously by means of the kinetic method. The variations of several molecular parameters of the growing polymer during the reaction were estimated. The presence of a small amount of multifunctional core molecules, RB_f, in the polycondensation system of AB_2 type monomers is found to lead to a marked reduction in the polydispersity index of the final polymer. During the polymerization process, the molecular weight distribution first becomes broader with increasing conversion of A groups and then abruptly becomes considerably more narrow as the reaction approaches completion. The greater the number of functional groups in the core moiety, the narrower the final molecular weight distribution of the polymer.

Introduction

Both the physical properties of polymer materials under application conditions and their processing behavior at elevated temperatures depend crucially on the average molecular weight and the molecular weight distribution (MWD). This is one reason that the polymer materials market contains different grades of each polymer which are often identical in chemical composition but only differ in molecular weight distributions. Therefore, it is an important research area for both academic interest and practical application. Flory's pioneering work[1] early in 1952 on the molecular weight distribution and its moments of so-called highly branched polymers generated from the polycondensation of AB_g type monomers has inspired many subsequent researchers since then. In Flory's expressions obtained by statistical method, A and B are the different functional groups capable of reacting with each other, and g is the number of B groups in a monomeric molecule. Thirty years later Kricheldof and co-workers[2] implemented the co-condensation of AB_2 type monomers. In 1988 Webster et al.[3] reported the synthesis of hyperbranched polyarylenes by using AB_2 type monomers. The highly branched architecture and numerous functional end groups of a hyperbranched polymer result in the special physical and chemical properties of the new sort of materials, which stimulated many polymer chemists[4−11] to make great efforts on the preparation of hyperbranched polymers. Recently, one of the authors of this paper and his co-workers[12] calculated the MWD and other molecular parameters by way of the kinetic approach for the hyperbranched polymer formed in either a self-condensing vinyl polymerization or a polycondensation of AB_2 type monomers. Both experimental data and theoretical estimation show that the MWD of a hyperbranched polymer is very wide. The character of the MWD of hyperbranched polymers may result from the fact that the rate of a given hyperbranched species adding to other ones is proportional to the number of its functional groups, and the number of functional groups is further proportional to its degree of polymerization. Therefore, large molecules grow faster than smaller ones, broadening the molecular weight distribution of the products.

It is interesting that the presence of a multifunctional core moiety in the star-branched polycondensation of AB type monomers leads to a considerable narrowing of MWD of the final polymer.[13] This trick can be used intentionally to synthesize hyperbranched polymers with narrow MWD. As a matter of fact Hult et al.[14] have already prepared such a polymer as mentioned above, i.e., the hyperbranched polymer with a core, from the polycondensation of 2,2-bis(hydroxymethyl)propionic acid in the presence of a small amount of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol. In this work, a kinetic model for the polycondensation of AB_2 type monomers in the presence of a multifunctional core moiety has been developed, and expressions for the number and the weight average degrees of polymerization and the MWD functions have been derived. Finally, the theoretical curves for MWD functions have been calculated according to our kinetic model.

Kinetic Model

If a small amount of a multifunctional compound, RB_f (f is the functionality and R is the core of the compound), is added into the condensation system of AB_2 type monomers, various species as shown in the architecture plots shown in Chart 1 will appear during the reaction. In the plots, $P_i^{(0)}$ represents the hyperbranched species with i monomeric units but without the core moiety, and $P_i^{(l)}$ stands for the hyperbranched species with i monomeric units and a residual core molecule in which l of the f B groups have reacted. For convenience, we assume that a $P_i^{(0)}$ species starts from a residual A group, and a $P_i^{(l)}$ species starts from a residual core. We can find that in a $P_i^{(l)}$ species there are l sectors with $(i + l)$ B groups in total, and $(f - l)$ B groups of the residual core unreacted. The kinetic differential equations ap-

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propriate for the polycondensation of AB$_2$ type monomers with a multifunctional core moiety are as follows:

$$\frac{\mathrm{d}(\mathrm{RB}_f)}{\mathrm{d}t} = -fk(\mathrm{RB}_f)\sum_{i=1}^{\infty}P_i^{(0)} \tag{1}$$

$$\frac{\mathrm{d}P_i^{(0)}}{\mathrm{d}t} = \frac{k}{2}\sum_{j=1}^{i-1}\{(j+1)P_j^{(0)}P_{i-j}^{(0)} + (i-j+1)P_{i-j}^{(0)}P_j^{(0)}\} - k\{(i+1)P_i^{(0)}\sum_{j=1}^{\infty}P_j^{(0)} + P_i^{(0)}\sum_{j=1}^{\infty}(j+1)P_j^{(0)}\} - fkP_i^{(0)}(\mathrm{RB}_f) - kP_i^{(0)}\sum_{l=1}^{f}\sum_{j=l}^{\infty}(j+f)P_j^{(l)} = \frac{k}{2}\sum_{j=1}^{i-1}(i+2)P_j^{(0)}P_{i-j}^{(0)} - k\{(i+2)P_i^{(0)}\sum_{j=1}^{\infty}P_j^{(0)} + P_i^{(0)}\sum_{j=1}^{\infty}jP_j^{(0)}\} - fkP_i^{(0)}\,(\mathrm{RB}_f) - kP_i^{(0)}\sum_{l=1}^{f}\sum_{j=1}^{\infty}(j+f)P_j^{(l)} \tag{2}$$

$$\frac{\mathrm{d}P_i^{(1)}}{\mathrm{d}t} = fk(\mathrm{RB}_f)P_i^{(0)} + k\sum_{j=1}^{i-1}(j+1)P_j^{(1)}P_{i-j}^{(0)} - k(i+f)P_i^{(1)}\sum_{j=1}^{\infty}P_j^{(0)} \tag{3}$$

$$\frac{\mathrm{d}P_i^{(l)}}{\mathrm{d}t} = (f-l+\mathrm{l})k\sum_{j=l-1}^{i-1}P_j^{(l-1)}P_{i-j}^{(0)} + k\sum_{j=l}^{i-1}(j+l)P_j^{(l)}P_{i-j}^{(0)} - k(i+f)P_i^{(l)}\sum_{j=l}^{\infty}P_j^{(0)}$$

$$l = 2, ..., f \tag{4}$$

The initial conditions are

$$(\mathrm{RB}_f)|_{t=0} = R_0$$

$$P_i^{(0)}|_{t=0} = \delta_{i,1}M_0$$

$$P_i^{(l)}|_{t=0} = 0, \quad l = 1, 2, ..., f$$

where R_0 and M_0 are the initial concentrations of the core moiety and the AB$_2$ type monomer, respectively; $\delta_{i,1}$ is the Kronecker symbol. In addition, the reaction system must fulfill the material balance conditions:

$$(\mathrm{RB}_f) + \sum_{l=1}^{f}\sum_{i=l}^{\infty}P_i^{(l)} = R_0 \tag{5}$$

$$\sum_{i=1}^{\infty}iP_i^{(0)} + \sum_{l=1}^{f}\sum_{i=l}^{\infty}iP_i^{(l)} = M_0 \tag{6}$$

The conversion of A groups is defined by

$$\alpha = \frac{M_0 - \sum_{i=1}^{\infty}P_i^{(0)}}{M_0} \tag{7}$$

It gives rise to

$$\sum_{i=1}^{\infty}P_i^{(0)} = M_0(1-\alpha) \tag{8}$$

Differentiating both sides of eq 8, we obtain

$$\frac{\mathrm{d}\sum_{i=1}^{\infty}P_i^{(0)}}{\mathrm{d}t} = -M_0\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{9}$$

Summing up the left and the right sides of eq 2, respectively, over the index i, we find

$$\frac{\mathrm{d}\sum_{i=1}^{\infty}P_i^{(0)}}{\mathrm{d}t} = -\frac{M_0{}^2}{r}k(1-\alpha)(1-r\alpha) \tag{10}$$

where

$$r = \frac{1}{2+f\lambda} \tag{11}$$

and λ is the ratio of R_0 to M_0. Comparing eq 9 with eq 10, we have

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{M_0}{r}k(\mathrm{l}-\alpha)(\mathrm{l}-r\alpha) \tag{12}$$

Dividing by eq 12, eqs 1–4 lead to the following ones:

$$\frac{\mathrm{d}(\mathrm{RB}_f)}{\mathrm{d}\alpha} = -\frac{f(\mathrm{RB}_f)}{2+f\lambda-\alpha} \tag{13}$$

$$\frac{\mathrm{d}P_i^{(0)}}{\mathrm{d}\alpha} = \frac{r}{M_0(1-\alpha)(1-r\alpha)}\left\{\frac{i+2}{2}\sum_{j=1}^{i-1}P_j^{(0)}P_{i-j}^{(0)} - M_0P_i^{(0)}[(i+2)(1-\alpha)+1+f\lambda]\right\} \tag{14}$$

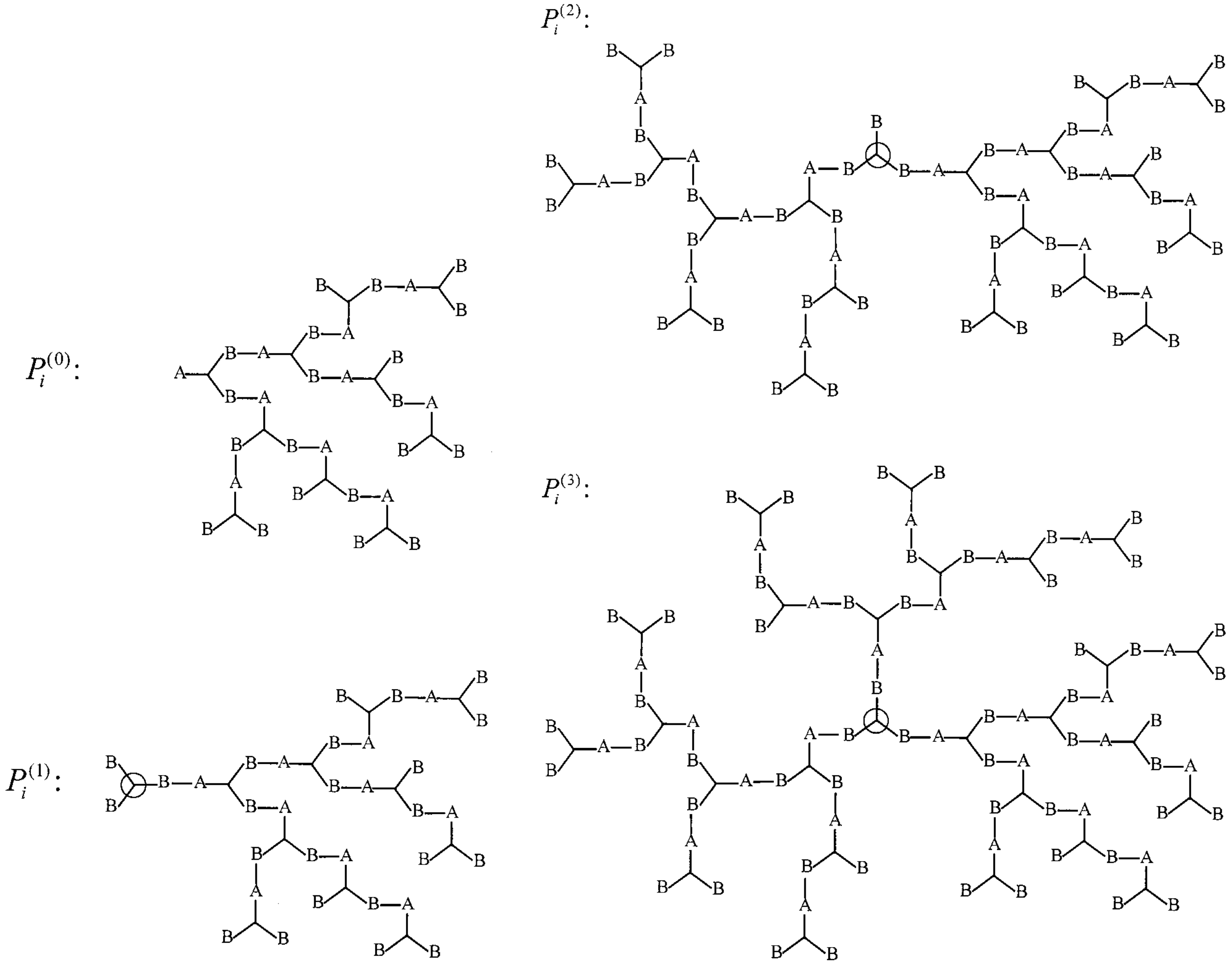
$$\frac{\mathrm{d}P_i^{(1)}}{\mathrm{d}\alpha} = \frac{r}{M_0(1-\alpha)(1-r\alpha)}\{f(\mathrm{RB}_f)P_i^{(0)} + \sum_{j=1}^{i-1}(j+1)P_j^{(1)}P_{i-j}^{(0)} - (i+f)P_i^{(1)}\sum_{j=1}^{\infty}P_j^{(0)}\} \tag{15}$$

$$\frac{\mathrm{d}P_i^{(l)}}{\mathrm{d}\alpha} = \frac{r}{M_0(1-\alpha)(1-r\alpha)}\{(f-l+1)\sum_{j=l-1}^{i-1}P_j^{(l-1)}P_{i-j}^{(0)} + \sum_{j=l}^{i-1}(j+l)P_j^{(l)}P_{i-j}^{(0)} - (i+f)P_i^{(l)}\sum_{j=1}^{\infty}P_j^{(0)}\}$$

$$l = 2, 3, ..., f \tag{16}$$

Equations 13–16 are a set of linear differential equations which can be solved rigorously.

Chart 1. Plots of Architecture



Molecular Parameters

The solutions of eqs 13−16 are

$$(\mathrm{RB}_f) = R_0(1 - r\alpha)^f \tag{17}$$

$$P_i^{(0)} = \frac{M_0}{i}\binom{2i}{i+1}(1-\alpha)(r\alpha)^{i-1}(1-r\alpha)^{i+1} \tag{18}$$

$$P_i^{(1)} = \frac{R_0 f}{i}\binom{2i}{i+1}(r\alpha)^i(1-r\alpha)^{i+f} \tag{19}$$

$$P_i^{(l)} = \frac{R_0 l}{i}\binom{f}{l}\binom{2i}{i+l}(r\alpha)^i(1-r\alpha)^{i+f} \quad l = 2, 3, ..., f \tag{20}$$

Equation 18 has been reported by Flory,[1] who derived it by using combinatorial arguments. This work presents a straightforward derivation using kinetic analysis. Other expressions given above have never been published.

The molecular weight distribution function of the total polymer generated from the polycondensation of AB_2 type monomers in the presence of a multifunctional core moiety is given by

$$P_i = \sum_{l=0}^{f} P_i^{(l)} \tag{21}$$

In order to obtain the number and weight average degree of polymerization, we must calculate the statistical moments of various species first:

$$\sum_i iP_i^{(0)} = M_0\frac{1-\alpha}{1-2r\alpha} \tag{22}$$

$$\sum_i i^2P_i^{(0)} = M_0\frac{(1-\alpha)[1-2(r\alpha)^2]}{(1-2r\alpha)^3} \tag{23}$$

The expression of the zeroth moment of $P_i^{(0)}$ is shown in eq 8. Substituting eq 17 into eq 5, we obtain

$$\sum_{l,j} P_i^{(l)} = R_0[1 - (1 - r\alpha)^f] \tag{24}$$

where the double summation notation $\sum_{l,j}$ means $\sum_{l=1}^{f}$ $\sum_{i=l}^{\infty}$. Further treatment leads to

$$\sum_{l,i} iP_i^{(l)} = \frac{fR_0r\alpha}{1-2r\alpha} \tag{25}$$

$$\sum_{l,i} i^2\, P_i^{(l)} = \frac{fR_0r\alpha}{(1-2r\alpha)^3}[1 + (f-1)r\alpha - 2f(r\alpha)^2] \tag{26}$$

Consequently, the expressions for various moments of the total products are hence

$$\sum_i P_i = M_0(1-\alpha) + R_0[1-(1-r\alpha)^f] \quad (27)$$

$$\sum_i iP_i = M_0 \quad (6')$$

$$\sum_i i^2 P_i = M_0(1-\alpha)\frac{1-2(r\alpha)^3}{(1-2r\alpha)^3} + R_0\frac{fr\alpha}{(1-2r\alpha)^3}[1 + (f-1)r\alpha - 2f(r\alpha)^2] \quad (28)$$

Finally, the number and the weight average degrees of polymerization can be ascertained:

$$\bar{P}_{\mathrm{n}} = \frac{1}{1-\alpha+\lambda[1-(1-r\alpha)^f]} \quad (29)$$

$$\bar{P}_{\mathrm{w}} = (1-\alpha)\frac{1-2(r\alpha)^3}{(1-2r\alpha)^3} + \frac{\lambda fr\alpha}{(1-2r\alpha)^3}[1 + (f-1)r\alpha - 2f(r\alpha)^2] \quad (30)$$

The polydispersity index is defined by:

$$D = \frac{\bar{P}_{\mathrm{w}}}{\bar{P}_{\mathrm{n}}} \quad (31)$$

In accordance with the expressions given above we can predict the variation of the molecular weight distribution and its averages of the resulting hyperbranched polymer during the polycondensation of AB_2 type monomers with a core moiety.

Numerical Results and Discussion

The normalized number-, weight-, and Z-distribution functions of various hyperbranched species and the total polymer formed are defined respectively by

$$N(l,i) = \frac{P_i^{(l)}}{\sum_{i=1}^{\infty} P_i}, \quad W(l,i) = \frac{iP_i^{(l)}}{\sum_{i=1}^{\infty} iP_i}, \quad Z(l,i) = \frac{i^2\, P_i^{(l)}}{\sum_{i=1}^{\infty} i^2\, P_i} \quad (32)$$

and

$$N(i) = \frac{P_i}{\sum_{i=1}^{\infty} P_i}, \quad W(i) = \frac{iP_i}{\sum_{i=1}^{\infty} iP_i}, \quad Z(i) = \frac{i^2\, P_i}{\sum_{i=1}^{\infty} i^2\, P_i} \quad (33)$$

The weight-distribution curves of hyperbranched polymers formed in the polycondensation with and without core moieties are shown in Figure 1, respectively. The Z-distribution curves of the same hyperbranched polymers are given in Figure 2. When the polycondensation is near to completion, the presence of a small amount of core moiety leads to a considerable narrowing of the molecular weight distribution. It is evident that the greater the number of the functional groups of the core, the narrower the molecular weight distribution of the final hyperbranched polymer. Parts A−C of Figure 3 show the evolution of Z-distributions of various hyperbranched species and the total resulting polymer with increasing the conversion of A groups in the polycondensation system of an AB_2 type monomer in the presence of trifunctional core molecules. Because the amount of core molecules is much less than that of the AB_2 type monomer, the hyperbranched species without core moiety is still predominant in the reaction system till the conversion of A groups reaching 99%. When the conversion approaches 99.9%, the hyperbrached species with two sectors becomes predominant in the reaction system. Finally, as the polycondensation approaches completion, the species without core moiety finally disappears from the reaction system, and the quantity of the hyperbranched species with two sectors equals the total amount of species with one and three sectors. Figure 4 demonstrates the variation of the Z-distribution with increasing the conversion of A groups for the polycondensation systems of AB_2 type monomers in the presence of the core moiety with $f = 10$. The dependence of the polydispersity index of the resulting polymer on the conversion of A groups, the functionality of the core moiety, and the mole ratio of the core compound to the monomer is shown in Figure 5. The molecular weight distribution first becomes wider and wider with increasing conversion of A groups and suddenly becomes considerably narrow by the end of the polycondensation. Figure 6 indicates the relationship between the polydispersity index and the functionality of the core at complete conversion ($\alpha = 1$). Similar to Figure 5, it is

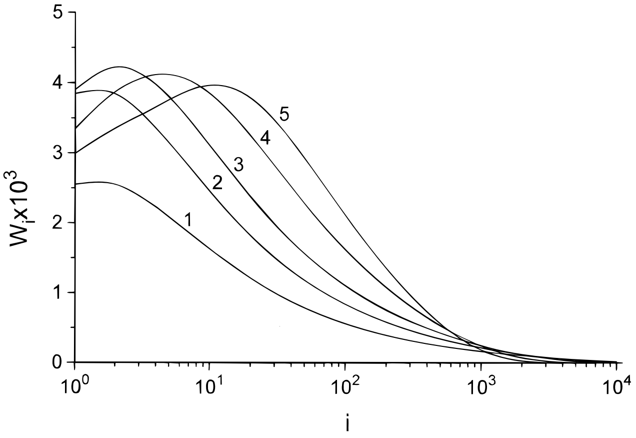


Figure 1. Comparison of the weight-distributions of hyperbranched polymers generated from polycondensation systems of AB_2 type monomers with and without core moieties, $\lambda = 0.01$, $\alpha = 0.99$: (1) $f = 0$; (2) $f = 1$; (3) $f = 2$; (4) $f = 4$; (5) $f = 6$.

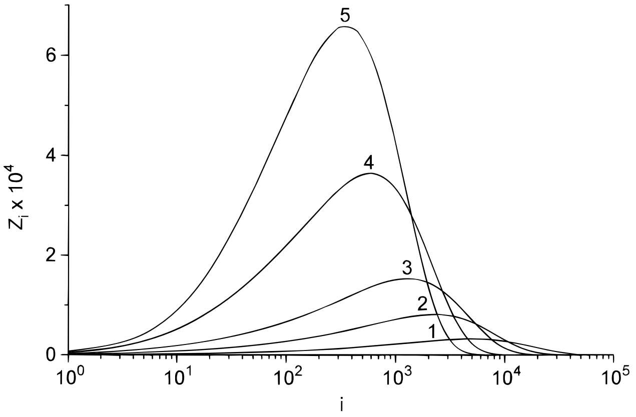


Figure 2. Comparison of the Z-distributions of hyperbranched polymers generated from polycondensation systems of AB_2 type monomers with and without core moieties, $\lambda = 0.01$, $\alpha = 0.99$: (1) $f = 0$; (2) $f = 1$; (3) $f = 2$; (4) $f = 4$; (5) $f = 6$.

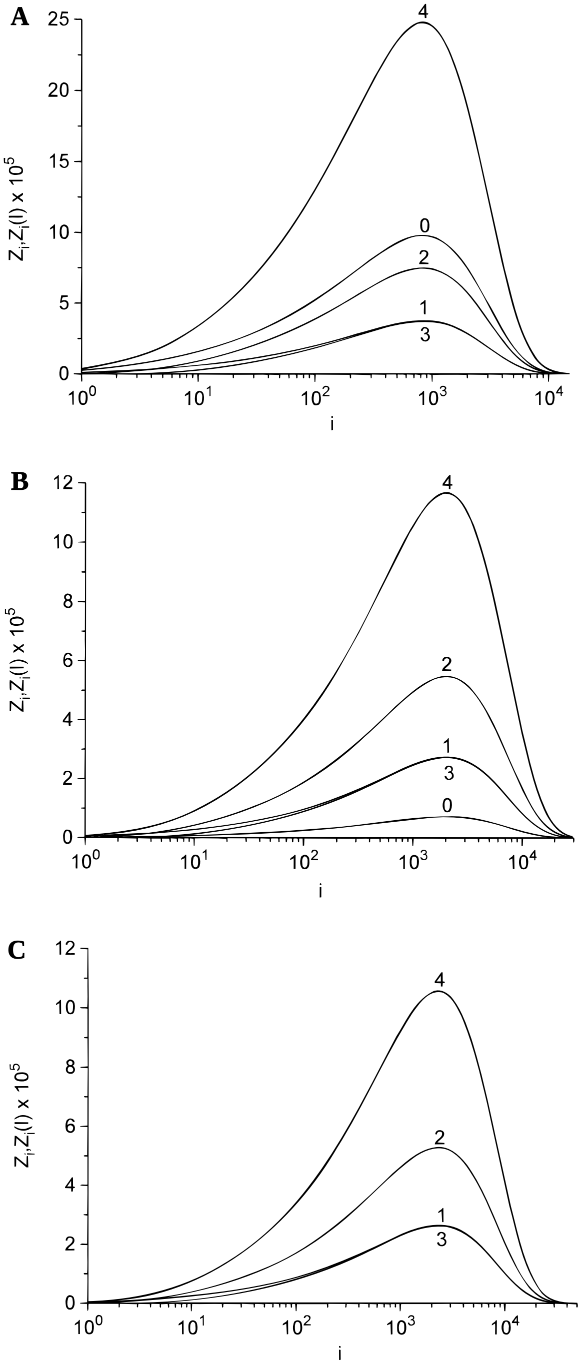


Figure 3. Evolution of *Z*-distributions of various hyperbranched species and total products formed during the polycondensation of AB_2 type monomers in the presence of a trifunctional core moiety: (A) $\lambda = 0.01$, $\alpha = 0.990$; (B) $\lambda = 0.01$, $\alpha = 0.999$; (C) $\lambda = 0.01$, $\alpha = 1$. Curves are numbered as follows: (0) $l = 0$; (1) $l = 1$; (2) $l = 2$; (3) $l = 3$. The thick curve (4) shows the total products.

clear that the larger the functionality of the core, the narrower the molecular weight distribution of the final hyperbranched polymer, whereas the influence of the mole ratio of the core compound to the monomer on the polydispersity index declines with increasing functionality of the core. From the above discussion, it can be seen that by adding a small amount of a core compound with a suitable functionality into the polycondensation systems of AB_2 type monomers, we can control the molecular weight distribution of the final hyperbranched polymers.

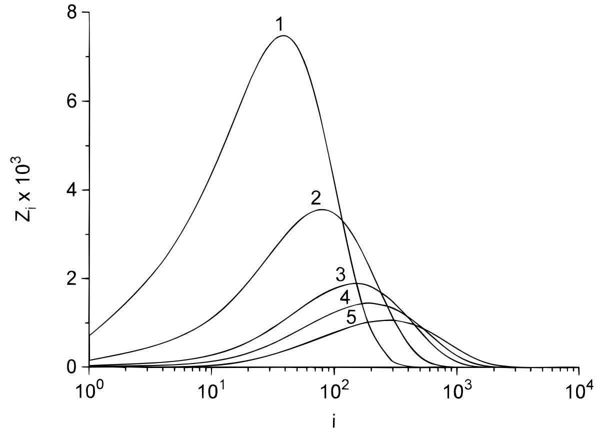


Figure 4. Variation of the *Z*-distribution of the hyperbranched polymer generated from the polycondensation of an AB_2 type monomer in the presence of a core moiety, $f = 10$, $\lambda = 0.01$: (1) $\alpha = 0.90$; (2) $\alpha = 0.95$; (3) $\alpha = 0.98$; (4) $\alpha = 0.99$; (5) $\alpha = 1$.

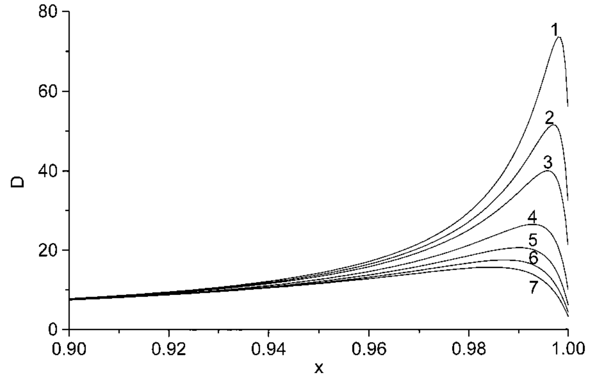


Figure 5. Plot of the polydispersity index varying with conversion of A groups, $\lambda = 0.001$: (1) $f = 6$; (2) $f = 8$; (3) $f = 10$; (4) $f = 15$; (5) $f = 20$; (6) $f = 25$; (7) $f = 30$.

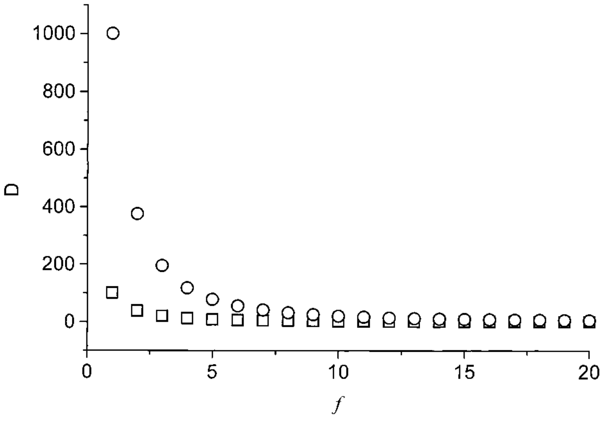


Figure 6. Relationship between the polydispersity index and the functionality of the core compound, $\alpha = 1$: (□) $\lambda = 0.01$; (○) $\lambda = 0.001$.

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