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Kinetic analysis of the polycondensation of ABg type monomer with a multifunctional core

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Abstract

This paper developed a kinetic model for the polycondensation of ABg type monomers with a multifunctional core (RB_f), giving the expressions of the molecular weight distribution function and average molecular weights of the resulting hyperbranched polymers. During the polycondensation both g and f markedly influence on the width of the molecular weight distribution of the products. When the reaction approaches completion, the molecular weight distribution of the resultant polymers is found to broaden with increasing g, and become narrower with increasing f. Hence the effect of increasing g on the polydispersity index can be offset by increasing f. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Hyperbranched polymers; Polycondensation; Kinetic model

1. Introduction

Since Webster et al. [1] first reported the preparation of hyperbranched polyarylenes a decade ago, varieties of hyperbranched polymers have been synthesized via the polycondensation of AB_2 type monomers [2–17]. Interestingly, Flory [18,19] had theoretically dealt with the polycondensation of ABg type monomers by means of statistics many years before the synthesis of the hyperbranched polyarylenes. Recently, the author of this work and co-workers [20,21] pointed out that the molecular weight distribution of the hyperbranched polymers resulting from the polycondensation of an AB_2 type monomer is extremely wide, and it becomes narrower if a small amount of multifunctional core molecules is added into the reaction system [22]. Similarly, the molecular weight distribution of star-shaped polymers generated from polycondensation systems of AB type monomers in the presence of multifunctional core moieties (RB_f) becomes narrower with increasing f [23,24]. Apparently, if an ABg ($g > 2$) type monomer is used in a polycondensation, there will be more functional end groups in the resulting polymers, which is attractive for polymer chemists. 2,4,6-tribromo phenol is an example of an AB_3 type of monomer [25], which can be polymerized with 1 equivalent of KOH and a catalytic amount of $K_3Fe(CN)_6$. The reaction scheme [26] is shown in Scheme 1. Recently Fréchet and coworker [27] have reported AB_3, AB_4 and AB_6 types of monomer for the synthesis of hyperbranched poly(siloxysilanes). It seems necessary to develop a kinetic model for the polycondensation of ABg type monomers in the presence of a core moiety, RB_f. This paper is devoted to the theoretical aspect of the reaction, and the experimental data will be reported elsewhere.

2. Kinetic model

Some authors [28,29] have concluded that cyclization is negligible in the polycondensation of ABg monomers. Therefore, this work takes no account of internal cyclization. In the polycondensation system of an ABg type monomer with a multifunctional core moiety, RB_f, there are various species. Let $P_i^{(0)}$ denote the hyperbranched species with i monomeric units and without the core, and $P_i^{(l)}$ represent the hyperbranched species with i monomeric units and a residual core in which l of the f B groups have reacted. As an example, the various species resulting from the polycondensation of AB_3 type monomer with a multifunctional core, RB_4, are shown in the plots of architecture.

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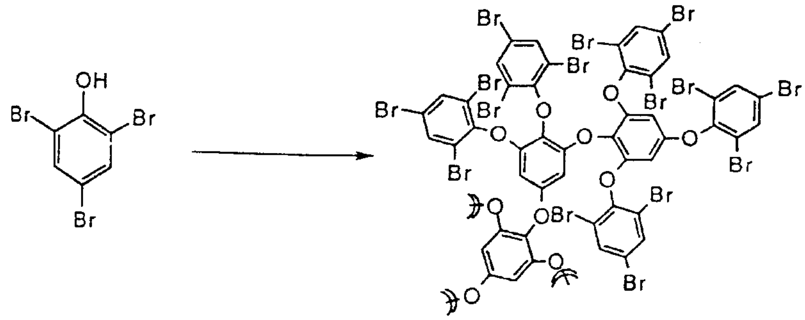


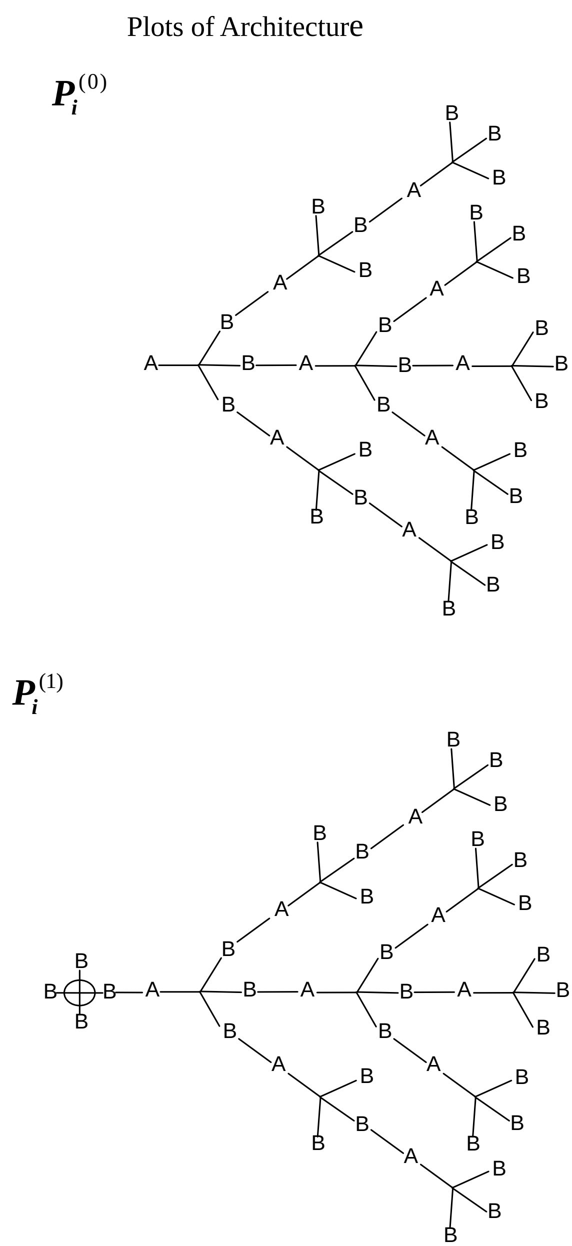
Scheme 1.

If the reactivities of all the functional groups are equal, the set of kinetic differential equations adapted to the reaction system under consideration reads:

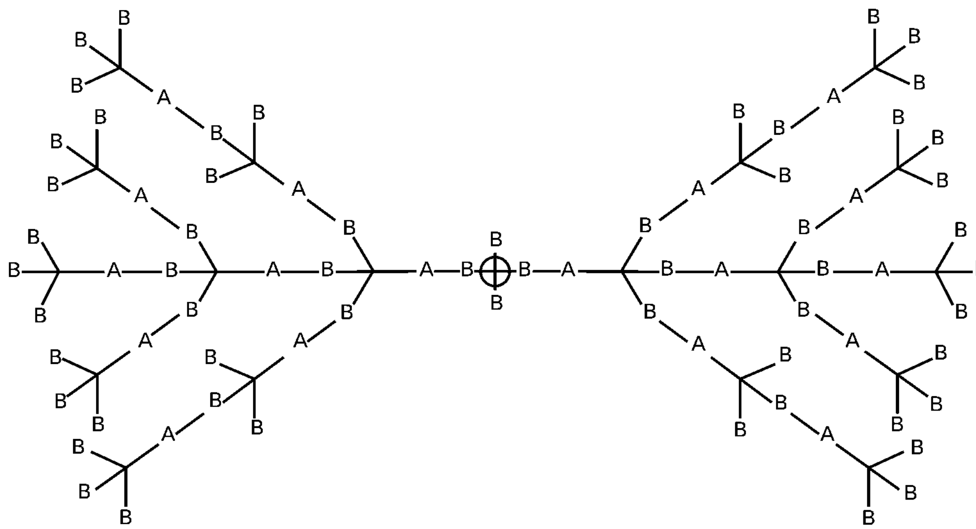
$$\frac{\mathrm{d}(\mathrm{RB}_f)}{\mathrm{d}t} = -fk(\mathrm{RB}_f)\sum_{i=1}^{\infty} P_i^{(0)} \tag{1}$$

$$\begin{aligned}\frac{\mathrm{d}P_i^{(0)}}{\mathrm{d}t} &= \frac{k}{2}\sum_{j=1}^{i-1}\{[j(g-1)+1]P_j^{(0)}P_{i-j}^{(0)} \\ &\quad + [(i-j)(g-1)+1]P_{i-j}^{(0)}P_j^{(0)}\} \\ &\quad - k\{[i(g-1)+1]P_i^{(0)}\sum_{j=1}^{\infty}P_j^{(0)} \\ &\quad + P_i^{(0)}\sum_{j=1}^{\infty}[j(g-1)+1]P_j^{(0)}\} - fkP_i^{(0)}(\mathrm{RB}_f) \\ &\quad - kP_i^{(0)}\sum_{l=1}^{f}\sum_{j=l}^{\infty}[j(g-1)+f]P_j^{(l)} \\ &= \frac{k}{2}\sum_{j=1}^{i-1}[i(g-1)+2]P_j^{(0)}P_{i-j}^{(0)} - k\{[i(g-1) \\ &\quad + 2]P_i^{(0)}\sum_{j=1}^{\infty}P_j^{(0)} + P_i^{(0)}\sum_{j=1}^{\infty}j(g-1)P_j^{(0)}\} - fkP_i^{(0)}(\mathrm{RB}_f) \\ &\quad - kP_i^{(0)}\sum_{l=1}^{f}\sum_{j=l}^{\infty}[j(g-1)+f]P_j^{(l)}\end{aligned} \tag{2}$$

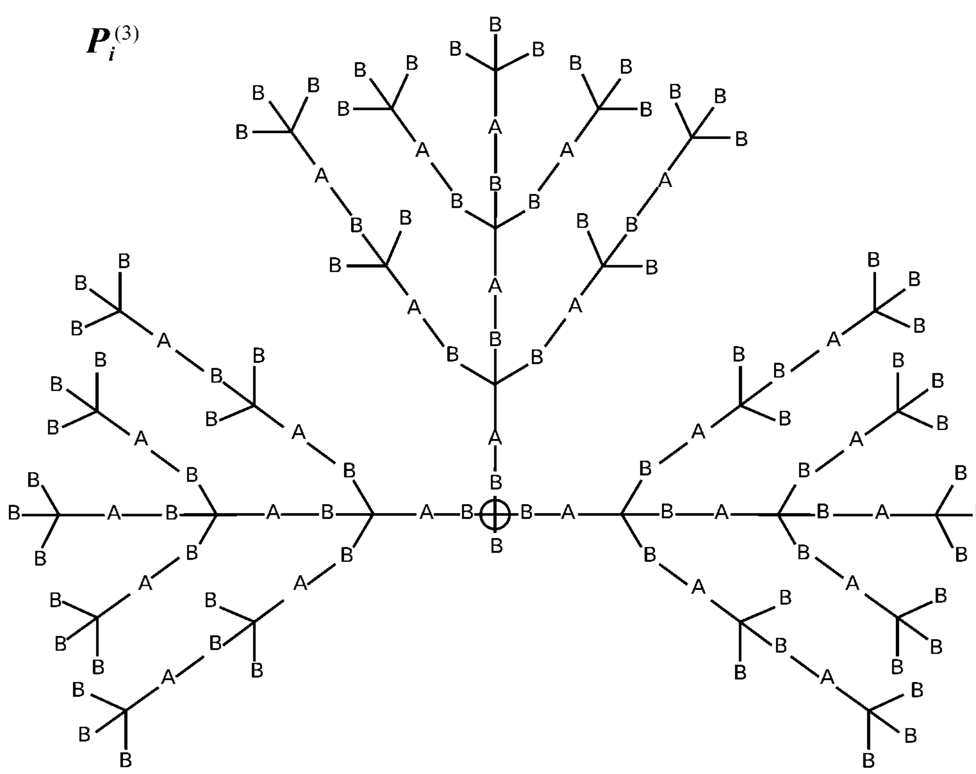
$$\begin{aligned}\frac{\mathrm{d}P_i^{(1)}}{\mathrm{d}t} &= fk(\mathrm{RB}_f)P_i^{(0)} + k\sum_{j=1}^{i-1}[j(g-1)+1]P_j^{(1)}P_{i-j}^{(0)} \\ &\quad - k[i(g-1)+f]P_i^{(1)}\sum_{j=1}^{\infty}P_j^{(0)}\end{aligned} \tag{3}$$



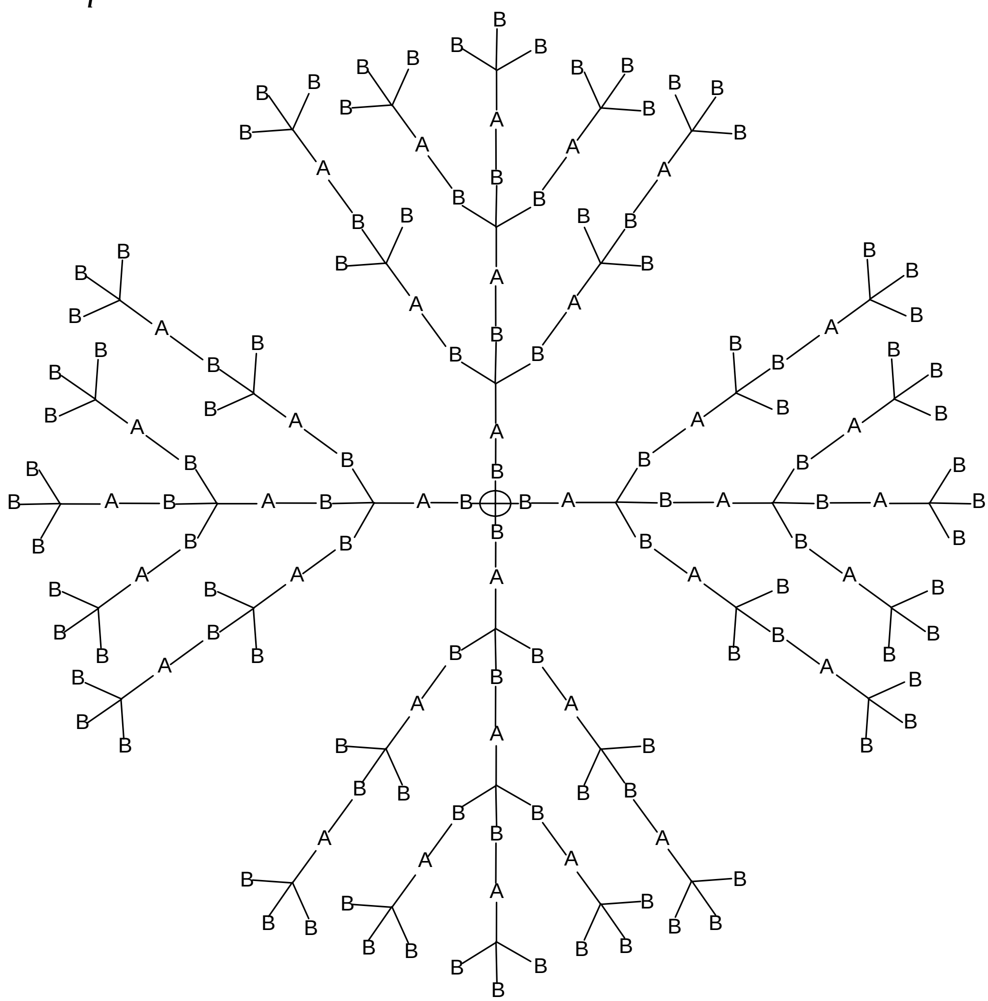
$P_i^{(2)}$



$P_i^{(3)}$



$\boldsymbol{P_i^{(4)}}$



$$\frac{dP_i^{(l)}}{dt} = (f - l + 1)k \sum_{j=l-1}^{i-1} P_j^{(l-1)} P_{i-j}^{(0)} + k \sum_{j=l}^{i-1} [j(g-1) + l] P_j^{(l)} P_{i-j}^{(0)} - k[i(g-1) + f] P_i^{(l)} \sum_{j=1}^{\infty} P_j^{(0)}$$

$$l = 2, 3, \ldots, f \tag{4}$$

The initial conditions of Eqs. (1)–(4) are:

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

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

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

where R_0 and M_0 are the initial concentrations of the core moiety and the ABg type monomer, respectively; $\delta_{i,1}$ is the Kronecker symbol. The constraint conditions can be written as:

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

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

Because there is an A group only in each of the species without the residual core (i.e. $P_i^{(0)}$), the conversion of A groups is defined by:

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

It results in

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

Differentiating both sides of Eq. (8), we got:

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

Summing up the left and the right sides of Eq. (2), respectively, over the index i, one finds:

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

where

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

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

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{M_0}{r} k(1-\alpha)(1-r\alpha) \tag{12}$$

If Eqs. (1)–(4) are divided by Eq. (12) and using the constraint conditions (Eqs. (5) and (6)), we obtain

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

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

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

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

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

Eqs. (13)–(16) can be solved rigorously.

3. Molecular parameters

After a laborious derivation, we can find the solutions of Eqs. (13)–(16):

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

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

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

$$P_i^{(l)} = \frac{R_0 l}{i} \binom{f}{l} \binom{gi}{i-l} (r\alpha)^i (1-r\alpha)^{i(g-1)+f} \tag{20}$$

$l = 2, 3, \ldots, f$

The details of derivation of Eqs. (18)–(20) are given in Appendices A–C. Eq. (18) has been reported by Flory [11] in 1952.

The molecular weight distribution function of the total polymers generated from the polycondensation of ABg type monomers in the presence of a multifunctional core moiety reads:

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

The statistical moments of various species are taken into account below. Besides Eq. (8) we can find the expressions of other moments of $P_i^{(0)}$:

$$\sum_i i P_i^{(0)} = M_0 \frac{1-\alpha}{1-gr\alpha} \tag{22}$$

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

The derivation procedures of Eqs. (22) and (23) are indicated in Appendix D. Substituting Eq. (17) into Eq. (5), one gains:

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

where the double summation $\sum_{l,i}$ denotes $\sum_{l=1}^{f} \sum_{i=l}^{\infty}$. Further treatment gives:

$$\sum_{l,i} i P_i^{(l)} = \frac{f R_0 r\alpha}{1-gr\alpha} \tag{25}$$

$$\sum_{l,i} i^2 P_i^{(l)} = \frac{f R_0 r\alpha}{(1-gr\alpha)^3} [1 + (f-1)r\alpha - gf(r\alpha)^2] \tag{26}$$

Appendix E shows the derivation of Eqs. (25) and (26).

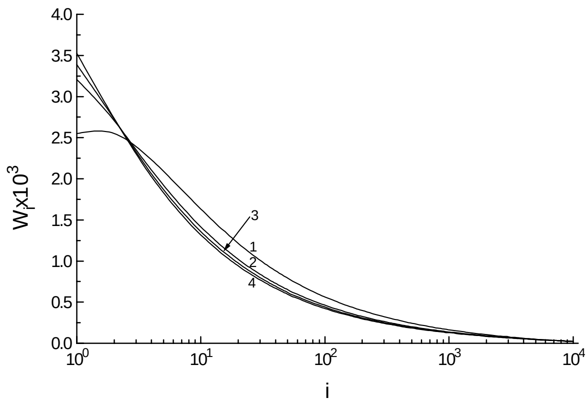


Fig. 1. Weight-distributions curves of hyperbranched polymers formed in polycondensation systems of ABg type monomers without core moiety, $\alpha = 0.99; 1: g = 2; 2: g = 4; 3: g = 6; 4: g = 10$.

Consequently, various moments of the total products read:

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

$$\sum_i iP_i = M_0 \tag{6'}$$

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

The number- and the weight-average degrees of polymerization can be expressed as:

$$\overline{P_n} = \frac{1}{1-\alpha+\lambda[1-(1-r\alpha)^f]} \tag{29}$$

$$\overline{P_w} = (1-\alpha)\frac{1-g(r\alpha)^2}{(1-gr\alpha)^3} + \frac{\lambda f r\alpha}{(1-gr\alpha)^3}[1+(f-1)r\alpha - gf(r\alpha)^2] \tag{30}$$

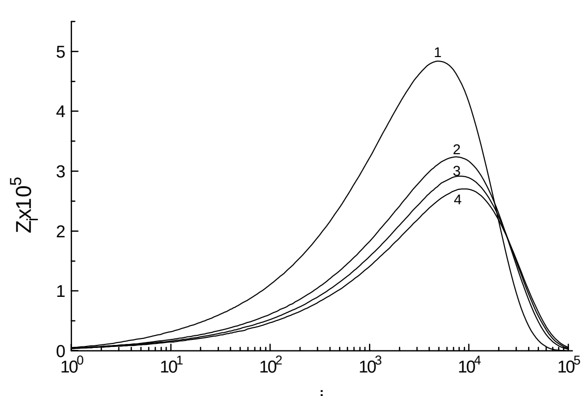


Fig. 2. Z-distributions curves of hyperbranched polymers formed in polycondensation systems of ABg type monomers without core moiety, other conditions are identical in Fig. 1.

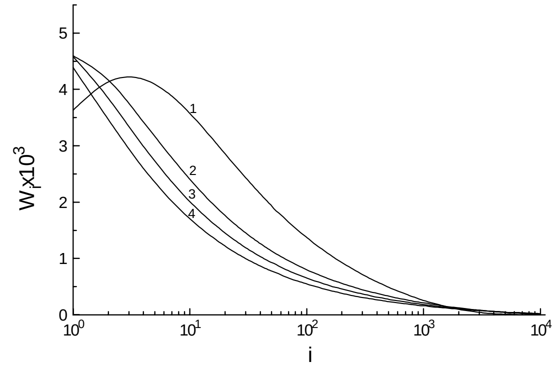


Fig. 3. Weight-distributions curves of hyperbranched polymers formed in polycondensation systems of ABg type monomers with a small amount core molecules, $\lambda = 0.01$, $\alpha = 0.99$, $f = 3; 1: g = 2; 2: g = 4; 3: g = 6; 4: g = 10$.

The polydispersity index is defined by:

$$D = \frac{\overline{P_w}}{\overline{P_n}} \tag{31}$$

Finally, we can predict the evolution of the molecular weight distribution and its averages of the resulting hyperbranched polymers during the polycondensation of ABg type monomers with a core moiety in accordance with the expressions given above.

4. Numerical results and discussion

It is necessary to define the normalized number-, weight-, and Z-distribution functions of various hyperbranched species and the total polymers formed, which are:

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

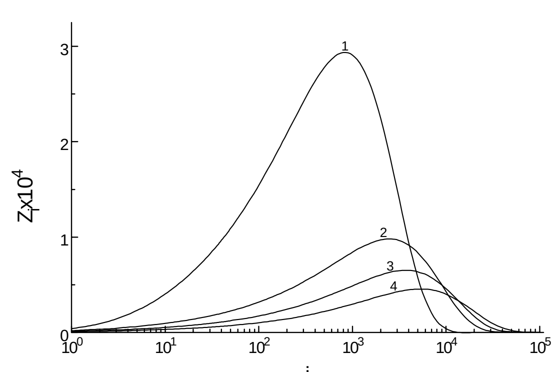


Fig. 4. Z-distributions curves of hyperbranched polymers formed in polycondensation systems of ABg type monomers with a small amount core molecules, other conditions are identical in Fig. 3.

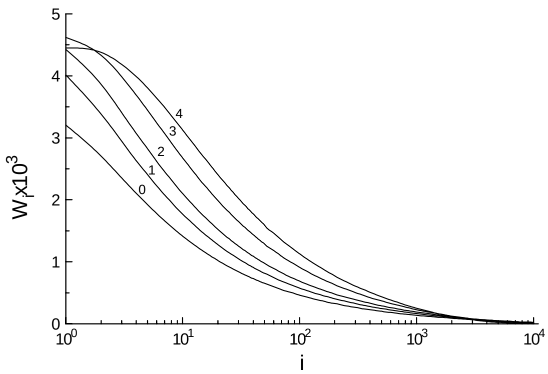


Fig. 5. Weight-distributions curves of hyperbranched polymers generated from the AB_4 type monomer in the presence of various core moieties respectively, $\lambda = 0.01$, $\alpha = 0.99, 0: f = 0; 1: f = 1; 2: f = 2; 3: f = 4; 4: f = 6$.

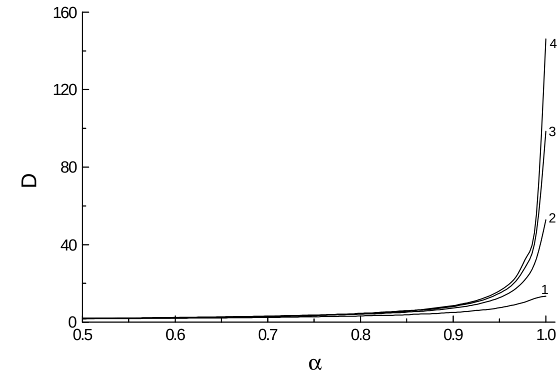


Fig. 7. The dependence of the polydispersity index on *g* and the conversion of A groups, $\lambda = 0.01$, $f = 4; 1: g = 2; 2: g = 4; 3: g = 6; 4: g = 8$.

and

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

The weight- and the *Z*-distribution curves of hyperbranched polymers generated from ABg type monomers without core moiety are given in Figs. 1 and 2, respectively. It can be seen that the molecular weight distribution of the hyperbranched polymers without core becomes wider with increasing *g* (the number of B groups in the monomer). Figs. 3 and 4, respectively, show the weight- and the *Z*-distribution curves of the hyperbranched polymers with a core moiety (RB_3). The same conclusion as aforementioned can be reached from the plots of the weight- and the *Z*-distribution of the hyperbranched polymers with a core. Figs. 5 and 6 show the weight- and the *Z*-distribution curves of hyperbranched polymers generated from the AB_4 type monomer with various core moieties. The molecular weight distribution becomes narrower with increasing the functionality of the core (*f*). During the polycondensation of ABg type monomers in the presence of a multifunctional core, the variation of the polydispersity index of the resulting hyperbranched polymers with the conversion of A groups is given in Figs. 7 and 8. It is evident that the greater the *g*, the broader the molecular weight distribution of the hyperbranched polymers, and the greater the *f*, the narrower the molecular weight distribution of the hyperbranched polymers. These tendencies are more obvious in Figs. 9 and 10, which show the dependencies of the polydispersity index on *g* and *f* when the reaction approaches completion. At the end of the polycondensation, i.e. all A groups being exhausted, the polydispersity index of the products monotonously increases with increasing *g*, and decreases with increasing *f*. Finally, we come to the conclusion: if an ABg ($g > 2$) type monomer is used in the polycondensation, the resultant hyperbranched polymers will have more functional end groups and possess wider molecular weight distribution than those generated from AB_2 type monomer, however, the disadvantage of broadening the molecular weight distribution can be offsetted by the presence of a multifunctional core moiety with a suitable functionality.

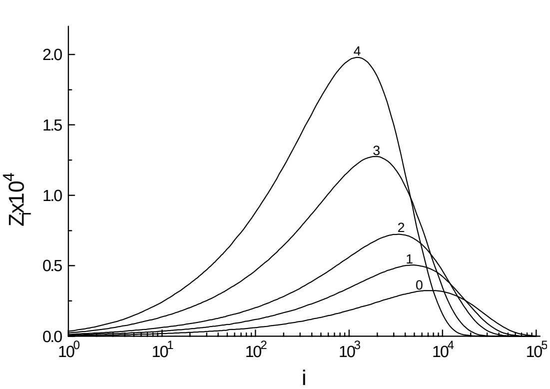


Fig. 6. *Z*-distributions curves of hyperbranched polymers generated from the AB_4 type monomer in the presence of various core moieties respectively, other conditions are identical in Fig. 5.

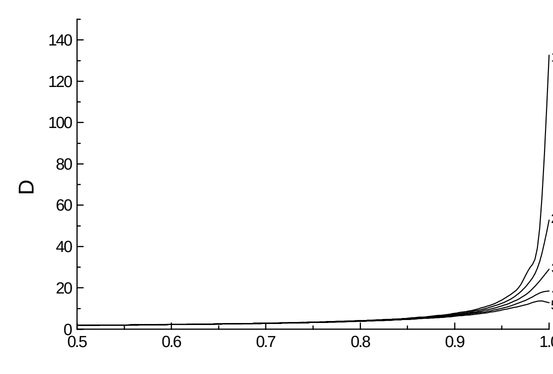


Fig. 8. The dependence of the polydispersity index on *f* and the conversion of A groups, $\lambda = 0.01$, $g = 4; 1: f = 2; 2: f = 4; 3: f = 6; 4: f = 8; 5: f = 10$.

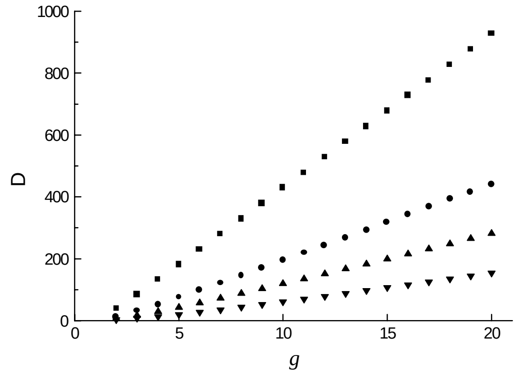


Fig. 9. Relationship between the polydispersity index and g, $\lambda = 0.01$, $\alpha = 1$; ■: $f = 2$; ◆: $f = 4$; ▲:$f = 6$; ▼: $f = 10$.

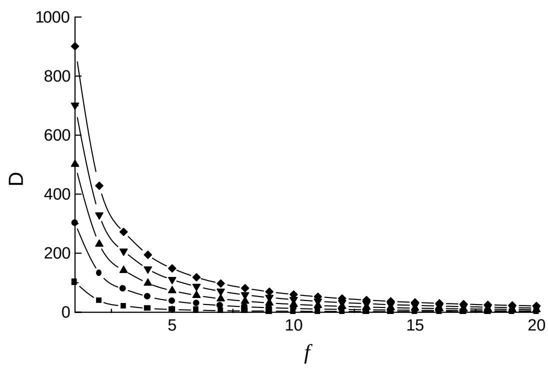


Fig. 10. Relationship between the polydispersity index and f, $\lambda = 0.01$, $\alpha = 1$; ■: $g = 2$; ●: $g = 4$; ▲: $g = 6$; ▼: $g = 8$; ◆: $g = 10$.

Acknowledgements

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Appendix A

Eq. (14) can be written as:

$$\frac{dP_i^{(0)}}{d\alpha} = -\frac{r\{[i(g-1)+2)(1-\alpha)+g-1+f\lambda\}}{(1-\alpha)(1-r\alpha)}P_i^{(0)} + \frac{r[i(g-1)+2]}{2M_0(1-\alpha)(1-r\alpha)}\sum_{j=1}^{i-1}P_j^{(0)}P_{i-j}^{(0)} \tag{A1}$$

The homogeneous equation corresponding to Eq. (A1) is

$$\frac{dP_i^{(0)}}{d\alpha} = -\frac{r\{[i(g-1)+2)(1-\alpha)+g-1+f\lambda]}{(1-\alpha)(1-r\alpha)}P_i^{(0)} \tag{A2}$$

The solution of Eq. (A2) is

$$P_i^{(0)} = C_i(1-r\alpha)^{i(g-1)+1}(1-\alpha) \tag{A3}$$

where C_i is a constant. Suppose the solution of Eq. (A1) to be:

$$P_i^{(0)} = C_i(\alpha)(1-r\alpha)^{i(g-1)+1}(1-\alpha) \tag{A4}$$

where $C_i(\alpha)$ is a function to be determined. Substituting Eq. (A4) into Eq. (A1), we obtain:

$$\frac{dC_i(\alpha)}{d\alpha} = \frac{[i(g-1)+2]r}{2M_0}\sum_{j=1}^{i-1}C_j(\alpha)C_{i-j}(\alpha) \tag{A5}$$

Let

$$C_i(\alpha) = M_0Q_i(r\alpha)^{i-1} \tag{A6}$$

and substituting Eq. (A6) into Eq. (A5), we have

$$Q_i = \frac{i(g-1)+2}{2(i-1)}\sum_{j=1}^{i-1}Q_jQ_{i-j} \tag{A7}$$

where Q_i is a constant, which is independent of α. From one of the initial conditions, i.e. $P_1^{(0)}|_{t=0} = M_0$, one gains:

$$Q_1 = 1 \tag{A8}$$

Then, it can be derived that

$$Q_i = \frac{(gi)!}{i![i(g-1)+1]!} \tag{A9}$$

and the solution of Eq. (A1) is

$$P_i^{(0)} = \frac{(gi)!}{i![i(g-1)+1]!}M_0(r\alpha)^{i-1}(1-\alpha)(1-r\alpha)^{i(g-1)+1} \tag{A10}$$

Appendix B

Combining Eq. (15) with Eq. (A10), we have

$$\frac{dP_i^{(1)}}{d\alpha} = -\frac{r[i(g-1)+f]}{M_0(1-r\alpha)}P_i^{(1)} + \frac{(gi)!}{i![i(g-1)+1]!}fR_0r(r\alpha)^{i-1}(1-r\alpha)^{i(g-1)+f} + r\sum_{j=1}^{i-1}[j(g-1) + 1]\frac{[g(i-j)]!}{(i-j)![(i-j)(g-1)+1]!}(r\alpha)^{i-j-1}(1 - r\alpha)^{(i-j)(g-1)}P_j^{(1)} \tag{B1}$$

The corresponding homogeneous equation of Eq. (B1) reads:

$$\frac{dP_i^{(1)}}{d\alpha} = -\frac{r[i(g-1)+f]}{1-r\alpha}P_i^{(1)} \tag{B2}$$

which results in

$$P_i^{(1)} = C_i(1-r\alpha)^{i(g-1)+f} \tag{B3}$$

where C_i is an integration constant. Supposing the solution of Eq. (B1) is

$$P_i^{(1)} = C_i(\alpha)(1 - r\alpha)^{i(g-1)+f} \tag{B4}$$

where $C_i(\alpha)$ is a function to be determined. Substituting Eq. (B4) into Eq. (B1), we have:

$$\frac{\mathrm{d}C_i(\alpha)}{\mathrm{d}\alpha} = \frac{(gi)!}{i![i(g-1)+1]!} fR_0 r(r\alpha)^{i-1} + r\sum_{j=1}^{i-1}[j(g-1)+1]\frac{[g(i-j)]!}{(i-j)![(i-j)(g-1)+1]!}C_j(\alpha)(r\alpha)^{i-j-1} \tag{B5}$$

Similar to Eq. (A6), let

$$C_i(\alpha) = (r\alpha)^i fR_0 Q_i \tag{B6}$$

then we find:

$$iQ_i = \frac{(gi)!}{i![i(g-1)+1]!} + \sum_{j=1}^{i-1}[j(g-1)+1]\frac{[g(i-j)]!}{(i-j)![(i-j)(g-1)+1]!}Q_j \tag{B7}$$

which leads to:

$$Q_i = \frac{(gi)!}{i![i(g-1)+1]!} \tag{B8}$$

Subsequently we gain:

$$P_i^{(1)} = \frac{(gi)!}{i![i(g-1)+1]!} fR_0(r\alpha)^i(1 - r\alpha)^{i(g-1)+f} \tag{B9}$$

Appendix C

Similar to the derivation of Eq. (B9), we have:

$$P_i^{(2)} = R_0 f(f-1)\frac{(i-1)(gi)!}{i![i(g-1)+2]!}(r\alpha)^i(1 - r\alpha)^{i(g-1)+f} \tag{C1}$$

$$P_i^{(3)} = R_0 f(f-1)(f-2)\frac{(i-1)!(gi)!}{2(i-3)!i![i(g-1)+3]!}(r\alpha)^i(1 - r\alpha)^{i(g-1)+f} \tag{C2}$$

$$P_i^{(4)} = R_0 f(f-1)(f-2)(f-3)\frac{(i-1)!(gi)!}{3!(i-4)!i![i(g-1)+4]!}(r\alpha)^i(1 - r\alpha)^{i(g-1)+f} \tag{C3}$$

By induction, we finally get:

$$P_i^{(l)} = R_0 \frac{f!(gi)!}{i(f-l)!(l-1)![i(g-1)+l]!(i-l)!}(r\alpha)^i \times (1 - r\alpha)^{i(g-1)+f} \tag{C4}$$

Appendix D

From Eq. (18) we have

$$\sum_{i=1}^{\infty} P_i^{(0)} = M_0(1-\alpha)\frac{1-r\alpha}{r\alpha}\sum_{i=1}^{\infty}\frac{(gi)!}{i![i(g-1)+1]!} \times [r\alpha(1-r\alpha)^{g-1}]^i \tag{D1}$$

Comparing Eq. (D1) with Eq. (8), we find:

$$\sum_{i=1}^{\infty}\frac{(gi)!}{i![i(g-1)+1]!}[r\alpha(1-r\alpha)^{g-1}]^i = \frac{r\alpha}{1-r\alpha} \tag{D2}$$

Putting

$$y = r\alpha(1-r\alpha)^{g-1} \tag{D3}$$

We further get from Eq. (D2):

$$\sum_{i=1}^{\infty} i\frac{(gi)!}{i![i(g-1)+1]!}y^i = y\frac{\mathrm{d}}{\mathrm{d}y}\sum_{i=1}^{\infty}\frac{(gi)!}{i![i(g-1)+1]!}y^i = \frac{r\alpha}{(1-r\alpha)(1-gr\alpha)} \tag{D4}$$

and

$$\sum_{i=1}^{\infty} i^2\frac{(2i)!}{i!(i+1)!}y^i = y\frac{\mathrm{d}}{\mathrm{d}y}\sum_{i=1}^{\infty} i\frac{(gi)!}{i![i(g-1)+1]!}y^i = \frac{r\alpha[1-g(r\alpha)^2]}{(1-r\alpha)(1-gr\alpha)^3} \tag{D5}$$

As the results we obtain:

$$\sum_i iP_i^{(0)} = M_0\frac{1-\alpha}{1-gr\alpha} \tag{D6}$$

$$\sum_i i^2 P_i^{(0)} = M_0\frac{(1-\alpha)[1-g(r\alpha)^2]}{(1-gr\alpha)^3} \tag{D7}$$

Appendix E

Substituting Eq. (17) into Eq. (5), one gains

$$\sum_{l,i} P_i^{(l)} = R_0[1-(1-r\alpha)^f] \tag{E1}$$

On the contrary, from Eq. (20), we can write:

$$\sum_{l,i} P_i^{(l)} = (1-r\alpha)^f \sum_{l,i} C_{l,i}y^i \tag{E2}$$

where

$$C_{l,i} = \frac{R_0 f!(gi)!}{i(f-l)!(l-1)![i(g-1)+l]!(i-l)!} \quad \text{(E3)}$$

Comparison of Eq. (E1) with Eq. (E2) results in

$$\sum_{l,i} C_{l,i} y^i = R_0 \left[\frac{1}{(1-r\alpha)^f} - 1 \right] \quad \text{(E4)}$$

Furthermore we can derive:

$$\sum_{l,i} iC_{l,i} y^i = y \frac{\mathrm{d}}{\mathrm{d}y} \sum_{l,i} C_{l,i} y^i = \frac{fR_0 r\alpha}{(1-gr\alpha)(1-r\alpha)^f} \quad \text{(E5)}$$

$$\sum_{l,i} i^2 C_{l,i} y^i = y \frac{\mathrm{d}}{\mathrm{d}y} \sum_{l,i} iC_{l,i} y^i$$

$$= \frac{fR_0 r\alpha[1+(f-1)r\alpha - gf(r\alpha)^2]}{(1-gr\alpha)^3(1-r\alpha)^f} \quad \text{(E6)}$$

Therefore we have

$$\sum_{l,i} iP_i^{(l)} = \frac{fR_0 r\alpha}{1-gr\alpha} \quad \text{(E7)}$$

$$\sum_{l,i} i^2 P_i^{(l)} = \frac{fR_0 r\alpha}{(1-gr\alpha)^3}[1+(f-1)r\alpha - gf(r\alpha)^2] \quad \text{(E8)}$$

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