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Effect of feed rate on structure of hyperbranched polymers formed by stepwise addition of AB_2 monomers into multifunctional cores

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Abstract

Hyperbranched polymers generated from the copolymerization of AB_2-type monomers slowly added into trifunctional C_3 cores under various feed rates were investigated by a kinetic model. The dependences of average molecular weight, polydispersity, degree of branching (DB), and number of structural units of the hyperbranched polymers on the feed rate were calculated by a generating function method. It was found that the final PDI can be attained below 1.5 by a slow addition with the parameter of feed rate, ϕ, less than 1. While the AB_2 monomers fed quickly, the system with a lower content of the C_3 cores results in a broader molecular weight distribution. A high DB, about 0.66, can be achieved by addition of a small amount of C_3 cores at ϕ lower than 10.

Keywords: Hyperbranched polymer; Generating function; Semibatch

1. Introduction

In recent years, dendrimers and hyperbranched polymers have been investigated with numerous structures and synthetic methods due to their unique dentritic architectures containing a large number of branching points and functional end groups [1–4]. Compared with the dendrimers having a perfectly regular structure, the hyperbranched polymers compose randomly branched and some linear structures. However, the hyperbranched polymers can be formed by simple one-pot polymerizations, such as polycondensation of AB_x-type monomers ($x \geq 2$); self-condensing vinyl polymerization, and radical alternating copolymerization [5–9]. And they also have similar properties as dendrimers. For example, the lack of entanglements results in a lower viscosity, and the large extent of end functional groups causes a higher solubility.

As shown in many theoretical and experimental results, the hyperbranched polymers formed in polymerization of AB_x monomers exhibit a very wide molecular weight distribution (MWD), at high conversion [10,11]. It was reported that copolymerization of AB_x monomers with multifunctional C_f cores can reduce the polydispersity of hyperbranched polymers [12–14]; either increment of the reactivity of core or slow addition of AB_x monomers can further make the MWD narrower [15–22]. Recently, the semibatch system was studied under extreme condition in which the AB_x monomers are added one after the other reacted, that is the feed rate is very slow, and near zero. Thus, the reaction between AB_x monomers is negligible, and the growth of the hyperbranched polymers is dominated by combining AB_x monomers with molecules containing core unit. According to the theoretical calculations at complete conversion of A groups, the polydispersity index of the hyperbranched polymers formed by copolymerization of AB_2 with C_3 can be reduced to be 1.333, and the degree of branching (DB), can also be increased to be 0.667 [15–20].

In a practical semibatch copolymerization process, the reaction occurs under a certain feed rate of monomers. Therefore, it is necessary to investigate the dependence of the feed rate on the structure parameters of the hyperbranched polymers. In this work, the generating function method based on the kinetic theory [21–27] will be applied to the copolymerization of multifunctional C_3 cores with AB_2 monomers added slowly into the reactor. This kinetic model will be adopted to examine the feed rate on the average degree of polymerization, polydispersity, DB, and number of structural units of the hyperbranched polymers during polymerization.

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2. Kinetic model of copolymerization of AB_2 monomers with multifunctional C_3 cores in a semibatch reactor

Hyperbranched polymers are generated in a semibatch system of which a definite number $N_T(AB_2)$ of AB_2 monomers is slowly fed under a constant molar flow, $F(AB_2)$, into a reactor containing multifunctional C_3 cores; then stopped at ratio λ, where $\lambda = N_0(C_3)/N_T(AB_2)$, and $N_0(C_3)$ is the initial number of C_3 in the reactor. Note that no AB_2 monomer is present in this reactor initially. The AB_2 monomer contains one A reactive group and two B groups, and C_3 possesses three functional groups. Assume that the reaction is bimolecular, both B and C groups can react with an A group: then becomes groups b,c and a, respectively, as follows:

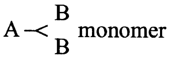
$$\mathrm{A} + \mathrm{B} \xrightarrow{k_{AB}} \mathrm{a} + \mathrm{b} \quad (1)$$

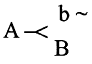
$$\mathrm{A} + \mathrm{C} \xrightarrow{k_{AB}} \mathrm{a} + \mathrm{c} \quad (2)$$

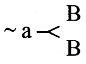
where k_{AB} and k_{AC} are reaction rate constants, and independent of the sizes of molecules [10]. And

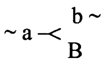
$$\beta = k_{AC}/k_{AB} \quad (3)$$

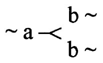
where β is assumed to be constant during polymerization. There are 10 different structural units involved in forming the hyperbranched polymers.

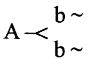
G(1):

$\mathrm{A}\prec\begin{matrix}\mathrm{B}\\ \mathrm{B}\end{matrix}$ monomer

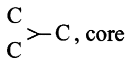
G(2):

$\mathrm{A}\prec\begin{matrix}\mathrm{b}\sim\\ \mathrm{B}\end{matrix}$

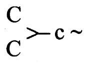
G(3):

$\sim\mathrm{a}\prec\begin{matrix}\mathrm{B}\\ \mathrm{B}\end{matrix}$

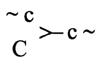
G(4):

$\sim\mathrm{a}\prec\begin{matrix}\mathrm{b}\sim\\ \mathrm{B}\end{matrix}$

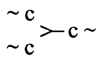
G(5):

$\sim\mathrm{a}\prec\begin{matrix}\mathrm{b}\sim\\ \mathrm{b}\sim\end{matrix}$

G(6):

$\mathrm{A}\prec\begin{matrix}\mathrm{b}\sim\\ \mathrm{b}\sim\end{matrix}$

G(7):

$\begin{matrix}\mathrm{C}\\ \mathrm{C}\end{matrix}\succ\mathrm{C}$, core

G(8):

$\begin{matrix}\mathrm{C}\\ \mathrm{C}\end{matrix}\succ\mathrm{c}\sim$

G(9):

$\begin{matrix}\sim\mathrm{c}\\ \mathrm{C}\end{matrix}\succ\mathrm{c}\sim$

G(10):

$\begin{matrix}\sim\mathrm{c}\\ \sim\mathrm{c}\end{matrix}\succ\mathrm{c}\sim$

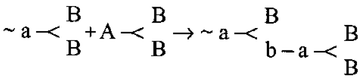
The reactions between various structural units (not functional groups or molecules) can be written as follows:

$$G(b_{i1}) + G(b_{i2}) \xrightarrow{k_i} G(b_{i3}) + G(b_{i4}) \qquad i = 1, 2, \ldots, 21 \quad (4)$$

The corresponding parameters, b_{ij} and k_i, are shown in Table 1. For example, The combination of the $G(1)$ with the $G(3)$ denotes the following reaction:

Table 1
The parameters of b_{ij} and k_i

$$\begin{bmatrix} b_{1\,1} & b_{1\,2} & b_{1\,3} & b_{1\,4} & k_1 \\ b_{2\,1} & b_{2\,2} & b_{2\,3} & b_{2\,4} & k_2 \\ b_{3\,1} & b_{3\,2} & b_{3\,3} & b_{3\,4} & k_3 \\ b_{4\,1} & b_{4\,2} & b_{4\,3} & b_{4\,4} & k_4 \\ b_{5\,1} & b_{5\,2} & b_{5\,3} & b_{5\,4} & k_5 \\ b_{6\,1} & b_{6\,2} & b_{6\,3} & b_{6\,4} & k_6 \\ b_{7\,1} & b_{7\,2} & b_{7\,3} & b_{7\,4} & k_7 \\ b_{8\,1} & b_{8\,2} & b_{8\,3} & b_{8\,4} & k_8 \\ b_{9\,1} & b_{9\,2} & b_{9\,3} & b_{9\,4} & k_9 \\ b_{10\,1} & b_{10\,2} & b_{10\,3} & b_{10\,4} & k_{10} \\ b_{11\,1} & b_{11\,2} & b_{11\,3} & b_{11\,4} & k_{11} \\ b_{12\,1} & b_{12\,2} & b_{12\,3} & b_{12\,4} & k_{12} \\ b_{13\,1} & b_{13\,2} & b_{13\,3} & b_{13\,4} & k_{13} \\ b_{14\,1} & b_{14\,2} & b_{14\,3} & b_{14\,4} & k_{14} \\ b_{15\,1} & b_{15\,2} & b_{15\,3} & b_{15\,4} & k_{15} \\ b_{16\,1} & b_{16\,2} & b_{16\,3} & b_{16\,4} & k_{16} \\ b_{17\,1} & b_{17\,2} & b_{17\,3} & b_{17\,4} & k_{17} \\ b_{18\,1} & b_{18\,2} & b_{18\,3} & b_{18\,4} & k_{18} \\ b_{19\,1} & b_{19\,2} & b_{19\,3} & b_{19\,4} & k_{19} \\ b_{20\,1} & b_{20\,2} & b_{20\,3} & b_{20\,4} & k_{20} \\ b_{21\,1} & b_{21\,2} & b_{21\,3} & b_{21\,4} & k_{21} \end{bmatrix} = \begin{bmatrix} 1 & 1 & 3 & 2 & 2k_{AB} \\ 1 & 2 & 3 & 6 & k_{AB} \\ 1 & 3 & 3 & 4 & 2k_{AB} \\ 1 & 4 & 3 & 5 & k_{AB} \\ 2 & 1 & 4 & 2 & 2k_{AB} \\ 2 & 2 & 4 & 6 & k_{AB} \\ 2 & 3 & 4 & 4 & 2k_{AB} \\ 2 & 4 & 4 & 5 & k_{AB} \\ 6 & 1 & 5 & 2 & 2k_{AB} \\ 6 & 2 & 5 & 6 & k_{AB} \\ 6 & 3 & 5 & 4 & 2k_{AB} \\ 6 & 4 & 5 & 5 & k_{AB} \\ 1 & 7 & 3 & 8 & 3k_{AC} \\ 1 & 8 & 3 & 9 & 2k_{AC} \\ 1 & 9 & 3 & 10 & k_{AC} \\ 2 & 7 & 4 & 8 & 3k_{AC} \\ 2 & 8 & 4 & 9 & 2k_{AC} \\ 2 & 9 & 4 & 10 & k_{AC} \\ 6 & 7 & 5 & 8 & 3k_{AC} \\ 6 & 8 & 5 & 9 & 2k_{AC} \\ 6 & 9 & 5 & 10 & k_{AC} \end{bmatrix}$$


$$\sim\mathrm{a}\prec\begin{matrix}\mathrm{B}\\ \mathrm{B}\end{matrix} + \mathrm{A}\prec\begin{matrix}\mathrm{B}\\ \mathrm{B}\end{matrix} \rightarrow \sim\mathrm{a}\prec\begin{matrix}\mathrm{B}\\ \mathrm{b}-\mathrm{a}\prec\begin{matrix}\mathrm{B}\\ \mathrm{B}\end{matrix}\end{matrix}$$

And a vector $\mathbf{E}$ is defined to characterize the molecule $\langle E \rangle$:

$$\mathbf{E} = (e_1, e_2, e_3, e_4, e_5, e_6, e_7, e_8, e_9, e_{10}, e_w) \quad (5)$$

where e_J denotes the number of structural unit $G(J)$ on a molecule $\langle E \rangle$, and e_w, equaling e_{11}, is the molecular weight of the molecule $\langle E \rangle$.

The changes of configuration and conformation are not taken into consideration. The influences of intramolecular reactions on the structure parameters of the hyperbranched polymers are also important for several cases discussed before [28,29]. However, in this study, the major object is to discuss the effect of feed rate of monomers for a semibatch system, and assume that no cyclization occurs during polymerization; thus the reactions between molecules are

$$\langle E' \rangle + \langle E'' \rangle \xrightarrow{k_i} \langle E' + E'' + L_i \rangle \qquad i = 1, 2, \ldots, 21 \quad (6)$$

The molecule $\langle E' + E'' + L_i \rangle$ is formed by combining molecule $\langle E'\rangle$ with $\langle E''\rangle$ in the ith reaction, and,

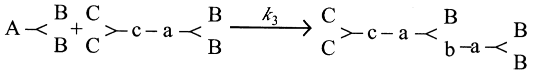
$$L_i = (l_1, l_2, ..., l_{10}, 0),$$

$$l_J = -\delta(b_{i1}, J) - \delta(b_{i2}, J) + \delta(b_{i3}, J) + \delta(b_{i4}, J), \quad J = l, 2, ..., 10 \tag{7}$$

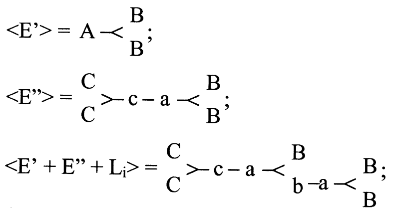
where $\delta(b_{ij}, J)$ is Kronecker delta, that is

$$\delta(b_{ij}, J) = 1, \ \text{for } b_{ij} = J; \qquad \delta(b_{ij}, J) = 0, \ \text{for } b_{ij} \neq J$$

For example, a molecule $\mathrm{A}\!\prec\!{}^{\mathrm{B}}_{\mathrm{B}}$ reacts with another molecule ${}^{\mathrm{C}}_{\mathrm{C}}\!\succ\!\mathrm{c-a}\!\prec\!{}^{\mathrm{B}}_{\mathrm{B}}$ by the following reaction:



in which



$$E' = (1, 0, 0, 0, 0, 0, 0, 0, 0, 0, W(\mathrm{AB_2}));$$

$$E'' = (0, 0, 1, 0, 0, 0, 0, 1, 0, 0, W(\mathrm{AB_2}) + W(\mathrm{C_3}));$$

$$L_3 = (-1, 0, -1 + 1, 1, 0, 0, 0, 0, 0, 0, 0);$$

$$E' + E'' + L_3 = (0, 0, 1, 1, 0, 0, 0, 1, 0, 0, 2W(\mathrm{AB_2}) + W(\mathrm{C_3});$$

$$k_3 = 2k_{\mathrm{AB}}$$

Then a dimensionless number fraction, [E], the ratio of the reaction rate constant, k'_i, and a scaled time, τ are defined as follows:

$$[E] = N(E)/N_0 \tag{8}$$

$$k'_i = k_i/k_0 \tag{9}$$

$$\tau = tk_0N_0/V_0 \tag{10}$$

where $N(E)$ is the number isomers $\langle E\rangle$, V the volume of the reaction system, t the reaction time, N_0 and V_0, the initial number and volume of $\mathrm{C_3}$ in the reactor, respectively and k_0 is an arbitrary reference rate constant.

For a constant-density reaction system according to Eq. (6), the rate equation of the isomers can be written as:

$$\frac{\mathrm{d}[E]}{\mathrm{d}\tau} = \Phi + \frac{1}{1+\phi\tau}\sum_{i=1}^{21} \times k'_i\left\{\sum_{E'+E''+L_i=E}([E'][E'']p''_{i1}p''_{i2}) - [E]p_{i1}\sum_{\text{all } E'}[E']p'_{i2} - [E]p_{i2}\sum_{\text{all} E'}[E']p'_{i1}\right\} \tag{11}$$

where

$$\Phi = \phi = \frac{F(\mathrm{AB_2})V_0}{N_0^2k_0}, \ \text{for } \mathbf{E} = \mathbf{E}^* = (1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 01),$$

$$\Phi = 0, \ \text{for } \mathbf{E} \neq \mathbf{E}^*$$

and $\sum_{\text{all } E}$ denotes the sum over all possible values of vector **E**, and $p_{ij} = e_J$ for $b_{ij} = J$, and ϕ is the parameter of feed rate of $\mathrm{AB_2}$ monomers. The positive term on the right side of Eq. (11) give the appearance the isomer $\langle E\rangle$ which formed by combination of smaller molecules $\langle E'\rangle$ and $\langle E''\rangle$, and the two negative terms denote the rates of disappearance of the isomer $\langle E\rangle$ which reacting with other molecule. Eq. (11) cannot be solved directly, but can be transformed into finite ordinary differential equations by a generating function, H, which is defined:

$$H(\tau, \omega_{j(j=1,2...,n+1)}) = \sum_{\text{all } E}\left(\prod_{j=1}^{n+1}\omega_j^{e_j}\right)[E] \tag{12}$$

where ω_j is a dummy variable, and H is dependent on τ and ω_j.

Eq. (11) can be multiplied by $\sum_{\text{all } E}(\prod_{j=1}^{n+1}\omega_j^{e_j})$ and summed over **E** to yield

$$\frac{\partial H}{\partial \tau} = \phi\omega_1\omega_{11} + \frac{1}{1+\phi\tau}\sum_{i=1}^{m}k'_i(H_{x_{i1}}H_{x_{i2}}x_{i3}x_{i4} - x_{i1}H_{x_{i1}}H_{i2} - x_{i2}H_{x_{i2}}H_{i1}) \tag{13}$$

where $m = 21$, and $n = 10$ in this study, and

$$x_{ij} = \omega_J \ \text{ for } b_{ij} = J, \qquad H_{x_{ij}} \equiv \frac{\partial H}{\partial x_{ij}},$$

$$H_{ij} \equiv H_{x_{ij}}(\omega_{q(q=1,2,...,n+1)} = 1)$$

that is, if $G(b_{ij}) = G(J)$,

$$b_{ij} = J, \qquad x_{ij} = \omega_J, \qquad \frac{\partial H}{\partial x_{ij}} = \frac{\partial H}{\partial \omega_J} = H_{\omega_J},$$

$$H_{ij} = H_{\omega_J}(\omega_{q(q=1,2,...,n+1)} = 1) \equiv H_J$$

By setting all dummy variables, $\omega_{q(q=1,2,...,n+1)}$ to 1, Eq. (13) can be written as:

$$\frac{\partial H^*}{\partial \tau} = \phi + \frac{1}{1+\phi\tau}\sum_{i=1}^{m}k'_i(-H_{i1}H_{i2}) \tag{14}$$

where $H^* = H(\omega_{q(q=1,2,...,n+1)} = 1)$. Furthermore, the partial derivatives of H along $\omega_{q(q=1,2,...,n+1)} = 1$ can be obtained by differentiating Eq. (13) with respect to ω_r, or to both ω_r and

ω_s :

$$\frac{\partial H_r}{\partial \tau} = \Phi + \frac{1}{1+\phi\tau}\sum_{i=1}^{m} \times k_i' H_{i1} H_{i2}\left(\frac{\partial x_{i3}x_{i4}}{\partial \omega_r} - \frac{\partial x_{i1}}{\partial \omega_r} - \frac{\partial x_{i2}}{\partial \omega_r}\right) \quad (15)$$

where

$\Phi = \phi$ for $H_r = H_1$, or H_{11},

$\Phi = 0$ for $H_r \neq H_1$ and $H_r \neq H_{11}$,

$$\begin{aligned}\frac{\partial H_{r,s}}{\partial \tau} &= \Phi + \frac{1}{1+\phi\tau}\sum_{i=1}^{m} \\ &\times k_i'\Bigg[H_{i1,r}H_{i2,s} + H_{i1,s}H_{i2,r} + (H_{i1,r}H_{i2} + H_{i1}H_{i2,r})\left(\frac{\partial x_{i3}x_{i4}}{\partial \omega_s}\right) \\ &+(H_{i1,s}H_{i2} + H_{i1}H_{i2,s})\left(\frac{\partial x_{i3}x_{i4}}{\partial \omega_r}\right) + (H_{i1}H_{i2})\left(\frac{\partial^2 x_{i3}x_{i4}}{\partial \omega_r\,\partial \omega_s}\right) \\ &-\left(\frac{\partial x_{i1}}{\partial \omega_r}H_{i1,s} + \frac{\partial x_{i1}}{\partial \omega_s}H_{i1,r}\right)H_{i2} \\ &-\left(\frac{\partial x_{i2}}{\partial \omega_r}H_{i2,s} + \frac{\partial x_{i2}}{\omega_s}H_{i2,r}\right)H_{i1}\Bigg]\end{aligned} \quad (16)$$

where

$\Phi = \phi$ for $H_{r,s} = H_{1,11} = H_{11,1}$,

$\Phi = 0$ for $H_{r,s} \neq H_{1,11}$ and $H_{r,s} \neq H_{11,1}$,

$$H_r = \frac{\partial H}{\partial \omega_r}(\omega_{q(q=1,2,\ldots,n+1)} = 1),$$

$$H_{r,s} = H_{s,r} = \frac{\partial^2 H}{\partial \omega_r\,\partial \omega_s}(\omega_{q(q=1,2,\ldots,n+1)} = 1),$$

$$H_{ij,r} = H_{r,ij} = \frac{\partial^2 H}{\partial x_{ij}\,\partial \omega_r}(\omega_{q(q=1,2,\ldots,n+1)} = 1),$$

$$H_{ij,s} = H_{s,ij} = \frac{\partial^2 H}{\partial x_{ij}\,\partial \omega_s}(\omega_{q(q=1,2,\ldots,n+1)} = 1)$$

and the initial conditions are

$$H^*(\tau = 0) = \sum_{\text{all } E}[E]_0 \quad (17)$$

$$H_r^*(\tau = 0) = \sum_{\text{all } E} e_r[E]_0 \quad (18)$$

$$H_{r,s}^*(\tau = 0) = \sum_{\text{all } E} e_r e_s[E]_0, \quad \text{for } r \neq s \quad (19)$$

$$H_{r,r}^*(\tau = 0) = \sum_{\text{all } E} e_r(e_r - 1)[E]_0 \quad (20)$$

$$[E]_0 = [E](\tau = 0) \quad (21)$$

The zeroth, first, and second moment of MWD can be calculated using the generating function [21–24]:

$$M_0 = \left(\frac{N_0}{N_\mathrm{T}}\right)H^* \quad (22)$$

$$M_1 = \left(\frac{N_0}{N_\mathrm{T}}\right)H_{11} \quad (23)$$

$$M_2 = \left(\frac{N_0}{N_\mathrm{T}}\right)(H_{11,11} + H_{11}) \quad (24)$$

The number average and weight average molecular weights, $\bar{M}_\mathrm{n}$, and $\bar{M}_\mathrm{w}$, are obtained:

$$\bar{M}_\mathrm{n} = \frac{M_1}{M_0} \quad (25)$$

$$\bar{M}_\mathrm{w} = \frac{M_2}{M_1} \quad (26)$$

According to the set of ODEs, Eqs. (14), (15) and (16), the relationships among the average molecular weight, concentration of unit, and reaction time can be obtained by $H^*(\tau)$, $H_r(\tau)$, and $H_{r,s}(\tau)$, which can be solved by the Rung-Kutta method or other solvers.

Furthermore, the number-average degree of polymerization also can be derived directly as follows:

$$\overline{\mathrm{DP}}_n = \frac{\text{total number of monomers and cores fed into the reactor}}{\text{total number of molecules in the reactor during polymerization}} \quad (27)$$

$$\overline{\mathrm{DP}}_n = \frac{N_0(\mathrm{C}_3) + N_\mathrm{f}(\mathrm{AB}_2)}{N_0(\mathrm{C}_3) + N_\mathrm{f}(\mathrm{AB}_2) - N_\mathrm{f}(\mathrm{AB}_2)\alpha(\mathrm{A})} \quad (28)$$

where $N_\mathrm{f}(\mathrm{AB}_2)$ is the total number of AB_2 monomers fed into the reactor; and

$$\alpha(\mathrm{A}) = 1 - N(\mathrm{AB}_2)/N_\mathrm{f}(\mathrm{AB}_2) \quad (29)$$

where $N(\mathrm{AB}_2)$ is the number of AB_2 monomers that remained in the system.

The final $\overline{\mathrm{DP}}_n$ is

$$\overline{\mathrm{DP}}_n = \frac{1+\lambda}{\lambda} \quad \text{at } \alpha(\mathrm{A}) = 1 \quad (30)$$

Therefore, the final number-average degree of polymerization, $\overline{\mathrm{DP}}_n$, can be controlled by the core/monomer ratio, λ, and increases with the number of the added AB_2 monomers.

3. Results and discussion

The influences of the parameter of feed rate of monomers AB_2, ϕ, on the polydispersity index (PDI), are shown in Fig. 1. In case of $\lambda = 0.1$, and low feed rate, for example $\phi = 0.1$, the PDI increases with the degree of the polymerization; then reaches a limiting value, about 1.47.

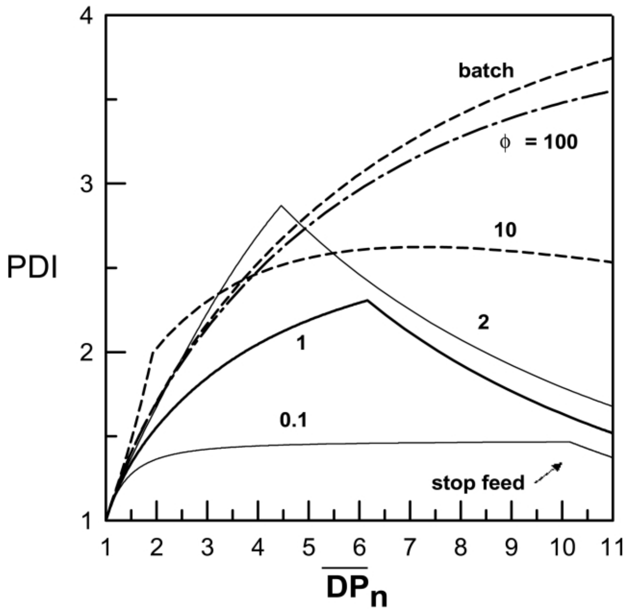


Fig. 1. The dependence of the polydispersity on degree of polymerization at various feed rates. ($\lambda = 0.1$).

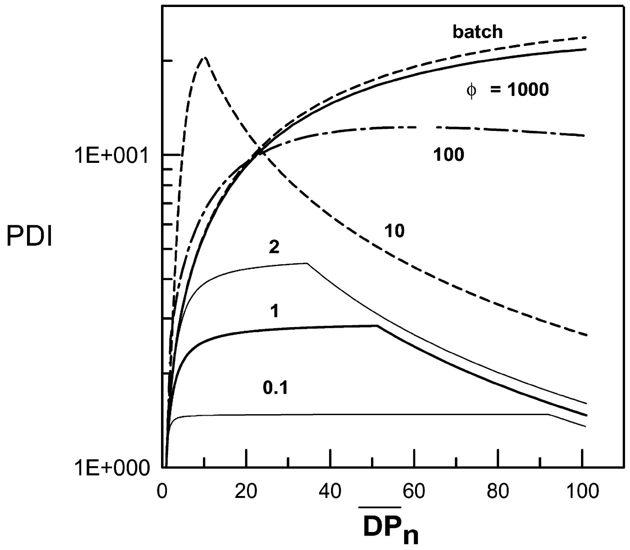


Fig. 3. The dependence of the polydispersity on degree of polymerization at various feed rates. ($\lambda = 0.01$).

After stopping the feed of AB_2 monomers, the PDI is further reduced to 1.37 at complete conversion of A groups. The result is very close to 1.33 obtained in the extreme case in which the AB_2 monomers are added one after the other reacted, i.e. ϕ is near zero [15,16,20]. On the other hand, when the AB_2 monomers were added quickly, for example $\phi = 100$, the profile of the PDI changed with $\overline{DP}_n$ is close to the result of batch system, in which the AB_2 monomers and C_3 cores were fed into a reactor at the same time. It is obvious that the higher feed rate causes the boarder distribution of molecular weight of the hyperbranched polymers.

While the concentration of AB_2 monomers is low in the reactor resulted from a slow feed, the probabilities of the formation of the focal units, ABb or Ab_2, are reduced as shown in Fig. 2. Therefore, the major growth of the hyperbranched polymers is contributed to the combinations of the molecule having a core unit, C_2c, Cc_2, or c_3, with AB_2 monomer added gradually; thus, the PDI is kept at a low value. After stopping the feed of AB_2, the remained molecules with ABb or Ab_2, in a small amount, will be further reacted with the molecules containing a core unit, and the distribution of the molecular weight of the hyperbranched polymer becomes narrower.

Figs. 3 and 4 show the changes of the PDI on the degree of polymerization under $\lambda = 0.01$ and 0.001, respectively. Furthermore, the dependences of the final PDI on the feed rate, ϕ, and core/monomer ratio, λ, are summarized in Fig. 5.

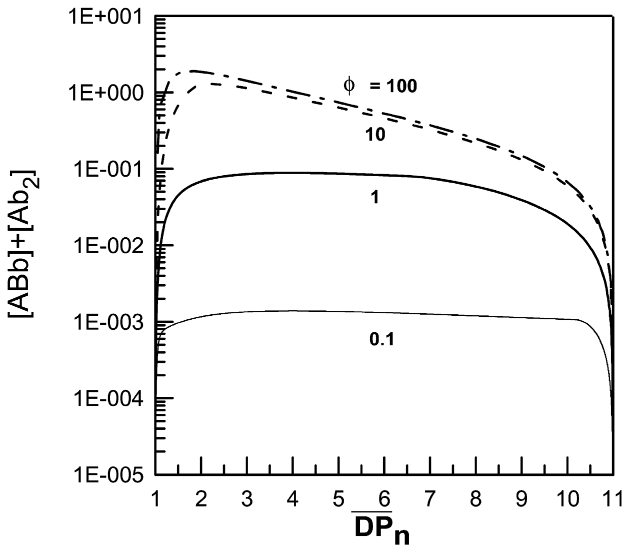


Fig. 2. The changes of the number of focal units during polymerization at various feed rates.

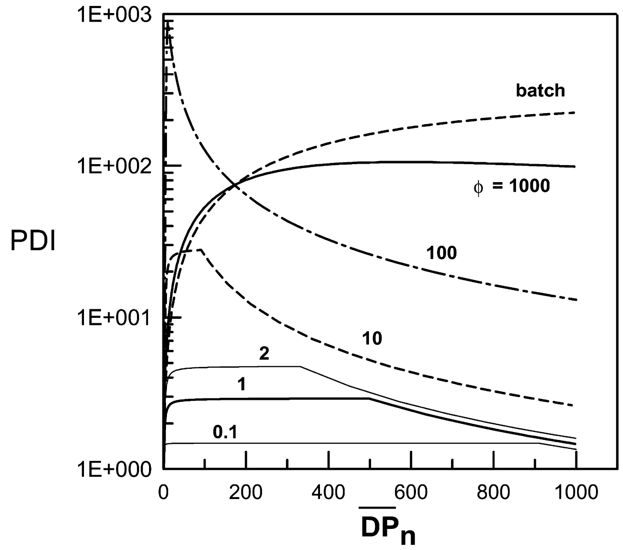


Fig. 4. The dependence of the polydispersity on degree of polymerization at various feed rates. ($\lambda = 0.001$).

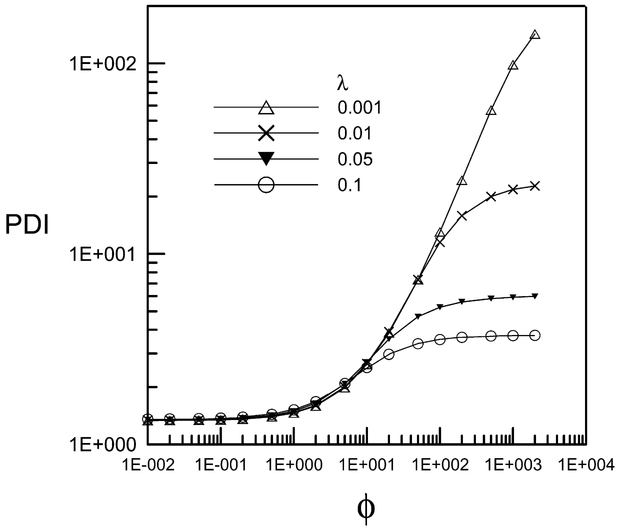


Fig. 5. The dependence of the final PDI on feed rate and core/monomer ratio, λ.

For the systems with $\lambda = 0.001-0.1$, the final PDI can be attained below 1.5 by a slow addition, $\phi < 1$. On the contrary, while the AB_2 monomers fed at quick rate, the system with a lower content of the C_3 cores results in a broader MWD. This result is similar to the batch system discussed before [12–14,21]. In the case of high value of λ, there are a large number of molecules with a core unit formed at early stage; thus the growth of polymers will be dominated by the reaction of the molecule containing a core unit with AB_2 monomers, and the MWD of the hyperbranched polymers becomes narrower.

Moreover, the DB, defined by Frechet et al. is a very important structural parameter in characterizing the hyperbranched polymers [30]:

$$\mathrm{DB} = \frac{\mathrm{ND}+\mathrm{NT}}{\text{total number of units}} \tag{31}$$

$$\mathrm{FB} = \frac{\mathrm{ND}}{(\text{total number of units}) - (\text{number of monomers})} = \frac{[G(5)]+[G(10)]}{[G(2)]+[G(3)]+[G(4)]+[G(5)]+[G(6)]+[G(8)]+[G(9)]+[G(10)]} \tag{34}$$

where ND is the number of dendritic units, and NT is the number of terminal units including monomers. Because the DB defined in Eq. (31) is overestimated for small molecules, Holter and Frey recently suggested an adjusted DB, DB(H.F.), based on the actual number over the maximum possible number of dendritic units [31]. Another parameter, the average number of branches (ANB) is defined as the deviation from the linear direction per non-terminal unit [32]. Muller et al. also suggested the fraction of branch points (FB), to characterize hyperbranched polymers [33]. Thus the DB(H.F.), ANB and FB of copolymerization of AB_2 monomers with C_3 cores are

$$\mathrm{DB(H.F.)} = \frac{2\mathrm{ND}}{2\mathrm{ND}+\mathrm{NL}} = \frac{[G(5)]+[G(10)]}{[G(5)]+[G(10)]+0.5[G(4)]+0.5[G(9)]} \tag{32}$$

$$\mathrm{ANB} = \frac{\mathrm{ND}}{\mathrm{ND}+\mathrm{NL}} = \frac{[G(5)]+[G(10)]}{[G(5)]+[G(10)]+[G(4)]+[G(9)]} \tag{33}$$

where ND is the number of dendritic units, $\sim a{-\!\!<}^{b\sim}_{b\sim}$ and ${}^{\sim c}_{\sim c}{>\!\!-}c\sim$ and NL is the number of linear units, $\sim a{-\!\!<}^{b\sim}_{B}$ and ${}^{\sim c}_{C}{>\!\!-}c\sim$.

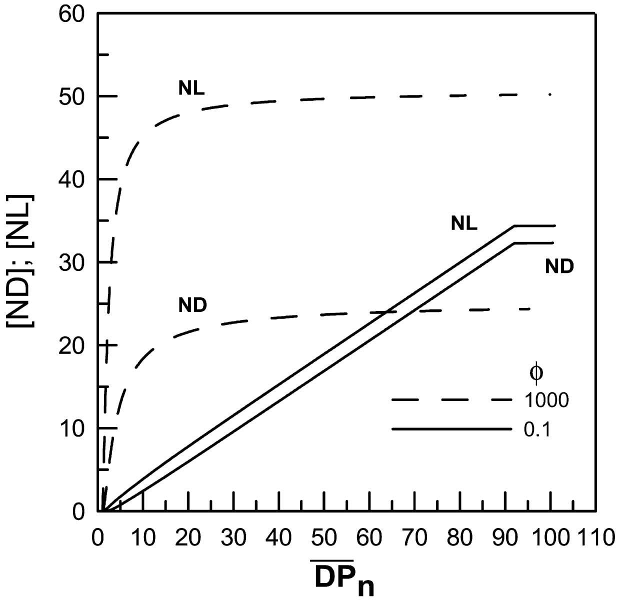


Fig. 6. The changes of the number of linear and dendritic units during polymerization at various feed rates at $\lambda = 0.01$, where $[\mathrm{ND}] = \mathrm{ND}/N_0(C_3)$; and $[\mathrm{NL}] = \mathrm{NL}/N_0(C_3)$.

The changes in the number of linear and dendritic units on the degree of polymerization under various feed rates are plotted in Fig. 6. For the quick addition of AB_2 monomers, $\phi = 1000$, the NL is far larger than ND during polymerization, and it causes a lower DB of the hyperbranched polymers. On the contrary, at low feed rate, $\phi = 0.1$, the ND is very close to the NL; thus

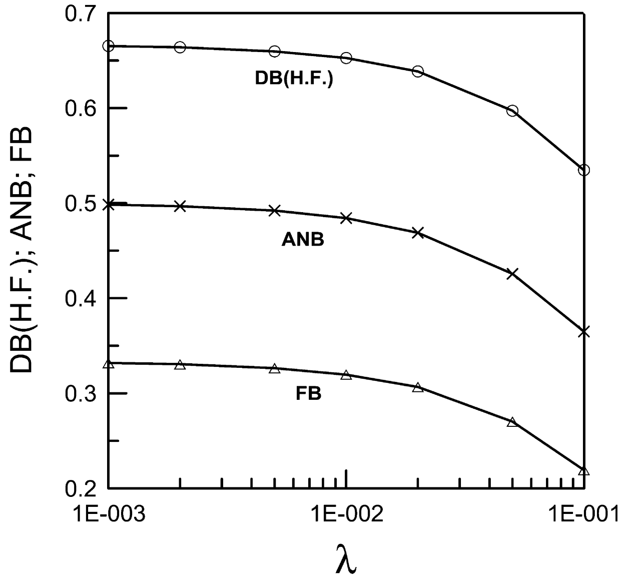


Fig. 7. The dependences of the final DB(H.F.); ANB; and FB units on core/monomer ratio λ ($\phi = 0.1$).

the DB increases. The probability of forming dentritic unit ab_2 decreases as the content of C_3 cores increases. Although the number of the dendritic units c_3 increases at the same time, it is not sufficient to compensate for the reduction of unit ab_2. Therefore, as shown in Fig. 7, the DB(H.F.), ANB and FB fall as C_3 cores increases. The dependences of the degree of branching, DB(H.F.), on the feed rate and core/monomer ratio λ are summarized in Fig. 8. For a low content of C_3 cores, for example $\lambda = 0.001$, while the parameter of feed rate ϕ is lower than 10, a high DB(H.F.), about 0.66, can be achieved.

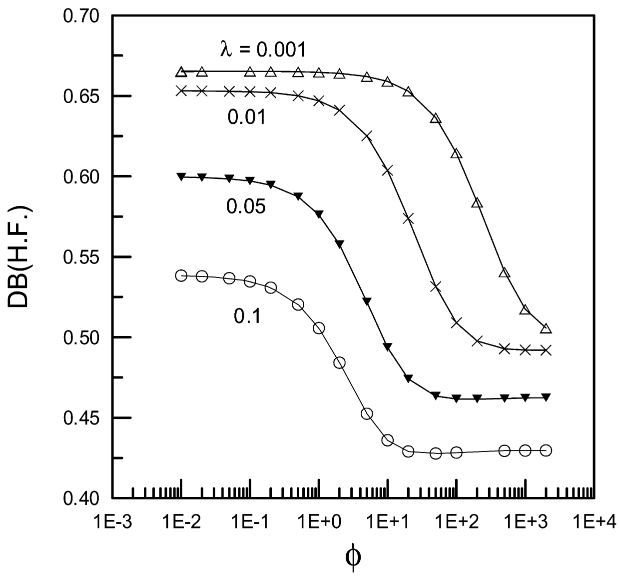


Fig. 8. The dependence of the final DB(H.F.) on feed rate and core/monomer ratio λ.

4. Conclusion

The generating function method has been extended to calculate the growth of hyperbranched polymers formed by copolymerization of AB_2 monomers added slowly into C_3 cores at various feed rates. The final number-average degree of polymerization can be controlled by the core/monomer ratio, and increases with the added AB_2 monomers. It was found that, under slower addition (parameter of feed rate $\phi < 1$), the low polydispersity index can be achieved below 1.5. A high DB, about 0.66, can be achieved at ϕ lower than 10, and small core/monomer ratio λ. For example, the hyperbranched polymers with high degree of polymerization, $\overline{\mathrm{DP}}_n = 1001$; high DB, DB(H.F.) = 0.66; and narrow MWD, PDI = 1.35, can be produced at $\lambda = 0.001$, and $\phi < 0.1$ in a semibatch reactor.

Acknowledgements

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