Polymer 51 (2010) 2763–2768

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Kinetic analysis of co-polycondensation of AB_2 and AB type monomers in presence of multi-functional cores

Zhiping Zhou [a,*], Zhengwei Jia [a], Deyue Yan [b]

[a] School of Materials Science and Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, China
[b] The State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

ARTICLE INFO

Article history:
Received 2 January 2010
Received in revised form
1 April 2010
Accepted 2 April 2010
Available online 14 April 2010

Keywords:
Hyperbranched polymer
Kinetic analysis
Molecular weight distribution

ABSTRACT

This work theoretically deals with the kinetics of the co-polycondensation of AB_2 and AB type monomers in the presence of multi-functional cores. The analytical expressions of the molecular size distribution function and the molecular parameters of the resultant hyperbranched polymers were derived. The general expressions are applicable for the copolymerization of AB_2 and AB monomers and the polymerization of homogeneous AB_2 or AB monomers in either presence or absence of cores. The feed ratio of the core molecules (β) or the AB_2 monomers (α) to the total monomers significantly affects the molecular weight distribution and the molecular parameters of the products. The polydispersity index of the copolymerization of AB_2 and AB monomers without cores is infinite when the reaction approaches to completion, while the presence of core molecules makes it become finite. The polydispersity index decreases with decreasing α, which also decreases with increasing β. The higher the functionality of the core (f), the lower the polydispersity index is as well.

1. Introduction

The hyperbranched polymers have been found more and more applications due to their highly branched structure and multitude of end groups. An easy approach to hyperbranched polymers is the polycondensation of AB_g-type monomers ($g \geq 2$)[1–3] and the broad molecular weight distribution (MWD) of the products formed can be avoided by adding a little amount of multi-functional core molecules into the reaction system [4]. In order to enhance the mechanical properties of hyperbranched polymers, one of the popular approaches is the copolymerization with AB and AB_g-type monomers, in which some linear segments can be incorporated into the hyperbranched polymers obtained. Experimental results show that, as the fraction of AB monomer increases, the degree of branching of the resultant products decreases and the mechanical properties are accordingly improved [5–7]. Theoretically, these polymerizations have been investigated systematically. Early in 1952, Flory[8] first derived the molecular size distribution for the polycondensation of AB_g monomers and the co-polycondensation of AB_g and AB monomers by means of statistical analysis. Hawker et al. [9] and Kim et al. [10] defined the degree of branching by comparing hyperbranched polymers with the perfectly branched analogues, dendrimers. Frey et al. [11–13] derived the expression of the degree of branching by both statistical and kinetic methods for the hyperbranched polymers made from AB_g monomers. Müller, Yan and co-workers[14,15] developed the kinetic theory of AB_2 polycondensation, giving the analytical expressions for the degree of branching and other molecular parameters. Litvinenko et al. [16,17], Moller et al. [18], Dusek et al. [19], Fawcett et al. [20,21] and Galina et al. [22] have also discussed the theoretical aspect of the related polycondensation systems in detail. We have reported the general kinetic model for the polycondensation of AB_g-type monomers[23,24] and the AB_g polycondensation in the presence of multi-functional core[25–27]. Cheng et al. [28,29] dealt with the similar topic by generating algebra method. The detailed kinetic analysis for the co-polycondensation of AB_2 and AB monomers has also been presented in our research group [30–32].

Recently, a series of poly(ether ketone) copolymers were prepared by nucleophilic aromatic polymerization reactions of the AB monomer 4-fluoro-4′-hydroxybenzophenone and the AB_2 monomer bis(4-fluoro-phenyl)-(4-hydroxyphenyl)phosphine oxide in the presence of a highly reactive core molecule, tris(3,4,5-trifluorophenyl)phosphine oxide (B_3) [33]. This can be denoted as the co-polycondensation of AB and AB_2 monomers in the presence of multi-functional core, by which the hyperbranched polymers with both narrow MWD and good mechanical properties can be prepared. To the best of our knowledge, there isn't a suitable theoretical investigation on the model. We aim to develop the kinetic analysis

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* Corresponding author. Tel.: +86 511 88791919.
E-mail address: zhouzp@ujs.edu.cn (Z. Zhou).

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doi:10.1016/j.polymer.2010.04.004

for the co-polycondensation of AB_2 and AB monomers in the presence of the multi-functional core and calculate the molecular parameters for the resultant products in this work.

2. Kinetic analysis

For the co-polycondensation system of AB_2 and AB type monomers in the presence of multi-functional core molecule, B_f, let N_0, L_0 and R_0 denote the initial concentration of AB_2 monomer, AB one and core molecule, respectively. The reaction only takes place between A and B groups. The species formed in the reaction system can be denoted by $P_{n,l}$ and $G_{n,l}$. The former represents the concentration of the species with n AB_2 units and l AB units (without core molecule) and the latter denotes the concentration of the species with n AB_2 units, l AB units and a core molecule. The chemical equations for the formation of species can be expressed as:

$$P_{i,j} + P_{n-i,l-j} \rightarrow P_{n,l}$$

$$G_{i,j} + P_{n-i,l-j} \rightarrow G_{n,l}$$

It can be known that there are exactly an unreacted A and $n+1$ B groups in every $P_{n,l}$ species and there are $n+f$ B groups in every $G_{n,l}$ species. If the reactivities of all the functional groups are identical and the intramolecular cyclization reactions are negligible, the set of kinetic differential equations adapting to above chemical equations read:

$$\frac{dG_{0,0}}{dt} = -fkG_{0,0}\sum_{i+j>0} P_{i,j} \tag{1}$$

$$\begin{aligned}\frac{dP_{n,l}}{dt} &= \frac{k}{2}\sum_{0<i+j<n+l}\left[(i+1)P_{i,j}P_{n-i,l-j} + (n-i+1)P_{n-i,l-j}P_{i,j}\right] \\ &\quad - kP_{n,l}\left[(n+1)\sum_{i+j>0}P_{i,j} + \sum_{i+j>0}(i+1)P_{i,j} + \sum_{i+j>0}(i+f)G_{i,j}\right] \\ &= \frac{k}{2}\sum_{0<i+j<n+l}(n+2)P_{i,j}P_{n-i,l-j} - kP_{n,l}\left[(n+1)\sum_{i+j>0}P_{i,j}\right. \\ &\quad \left. + \sum_{i+j>0}(i+1)P_{i,j} + \sum_{i+j>0}(i+f)G_{i,j}\right]\end{aligned} \tag{2}$$

$$\frac{dG_{n,l}}{dt} = k\sum_{0\le i+j<n+l}(i+f)G_{i,j}P_{n-i,l-j} - k(n+f)G_{n,l}\sum_{i+j>0}P_{i,j} \tag{3}$$

where k represents the reactivity between an A group and a B group. In Eqs. (2) and (3), the first term represents the generation rate of the corresponding species and the second negative one denotes the consumption.

The initial conditions of these equations are:

$$\begin{aligned}&P_{1,0}|_{t=0} = N_0;\ P_{0,1}|_{t=0} = L_0;\ P_{i,j}(i+j>1)|_{t=0} = 0 \\ &G_{0,0}|_{t=0} = R_0;\ G_{i,j}(i+j>0)|_{t=0} = 0\end{aligned} \tag{4}$$

The constraint conditions can be written as:

$$\sum_{n+l>0} n(P_{n,l}+G_{n,l}) = N_0 \tag{5}$$

$$\sum_{n+l>0} l(P_{n,l}+G_{n,l}) = L_0 \tag{6}$$

$$\sum_{n+l\ge 0} G_{n,l} = R_0 \tag{7}$$

Since every $P_{i,j}$ species, including both the residual monomers and the polymer species, has only one A group, the conversion of A groups is defined as:

$$x = \frac{N_0 + L_0 - \sum_{i+j>0} P_{i,j}}{N_0 + L_0} \tag{8}$$

that is, the total concentration of A groups in the reaction system is

$$A = \sum_{i+j>0} P_{i,j} = (N_0+L_0)(1-x) \tag{9}$$

The concentration of the residual B groups is

$$B = 2N_0 + L_0 + fR_0 - (N_0+L_0)x \tag{10}$$

Differentiating both sides of Eq. (9) leads to:

$$\frac{dA}{dt} = -(N_0+L_0)\frac{dx}{dt} \tag{11}$$

On the other hand, the consumption of A groups fits:

$$\frac{dA}{dt} = -kAB = -k(N_0+L_0)^2(1-x)(1-x+r) \tag{12}$$

with

$$r = \frac{N_0 + fG_0}{N_0 + L_0} = \alpha + f\beta \tag{13}$$

The $\alpha = N_0/(N_0 + L_0)$is the initial mole fraction of the AB_2 monomers to the total monomers and β the mole ratio of cores to total monomers. Comparing Eq. (11) with Eq. (12) yields

$$\frac{dx}{dt} = k(N_0+L_0)(1-x)(1+r-x) \tag{14}$$

Dividing Eqs. (1)–(3) by Eq. (14) and using the constraint conditions [Eqs. (5)–(7)], we can transfer the variable from the time (t) to the conversion of A groups (x) for the kinetic differential equations.

$$\frac{dG_{0,0}}{dx} = -\frac{fG_{0,0}}{1+r-x} \tag{15}$$

$$\begin{aligned}\frac{dP_{n,l}}{dx} = \frac{1}{(1-x)(1+r-x)}\left\{\frac{1}{2}\frac{1}{N_0+L_0}\sum_{0<i+j<n+l}(n+2)P_{i,j}P_{n-i,l-j}\right. \\ \left. - P_{n,l}[(n+2)(1-x)+r]\right\}\end{aligned} \tag{16}$$

$$\begin{aligned}\frac{dG_{n,l}}{dx} = \frac{1}{1+r-x}\left\{\frac{1}{(N_0+L_0)(1-x)}\sum_{0\le i+j<n+l}(i+f)G_{i,j}P_{n-i,l-j}\right. \\ \left. - (n+f)G_{n,l}\right\}\end{aligned} \tag{17}$$

3. Molecular size distribution and molecular parameters

After a laborious derivation, we can find the solutions to Eqs. (15)–(17):

$$\begin{aligned}P_{n,l} &= (N_0+L_0)\frac{(2n+l)!}{n!l!(n+1)!}\frac{(1-x)(1+r-x)}{x}\left[\frac{\alpha x(1+r-x)}{(1+r)^2}\right]^n \\ &\quad \left[\frac{(1-\alpha)x}{1+r}\right]^l\end{aligned} \tag{18}$$

$$G_{n,l} = (N_0+L_0)\frac{f\beta(f+2n+l-1)!}{n!l!(f+n)!}\left(\frac{1+r-x}{1+r}\right)^f\left[\frac{\alpha x(1+r-x)}{(1+r)^2}\right]^n \left[\frac{(1-\alpha)x}{1+r}\right]^l \quad (19)$$

The solution of $G_{0,0}$ has been included in the general expression of Eq. (19). Eqs. (18) and (19) are just the molecular size distribution functions of the species formed from AB_2 and AB type monomers in the presence of multi-functional cores. If $\beta = 0$ and $0<\alpha<1$, Eq. (18) degenerates into the size distribution function reported for the co-polycondensation of AB_2 and AB type monomers[31]; If $\beta = 0$ and $\alpha = 0$ or $\alpha = 1$, it is reduced to linear polymerization of AB monomer or the polycondensation of AB_2 monomers[14,15]; If $\beta \neq 0$ and $\alpha = 0$ or $\alpha = 1$, these expressions reduce to that of the star-branched polycondensation[25] or the polycondensation of AB_2 monomers in the presence of multi-functional cores [16,26].

The various molecular parameters can be obtained from these distribution functions. Eqs. (7) and (9) are the respective zeroth moments of $G_{n,l}$ and $P_{n,l}$ distributions, that is, $\sum_{n+l>0} P_{n,l} = (N_0+L_0)(1-x)$ and $\sum_{n+l\geq 0} G_{n,l} = R_0 = \beta(N_0+L_0)$. The first and second moments are given in Appendix.

For the sake of simplicity, the core molecules can be neglected when we investigate the molecular size distribution and the average molecular size because it is just a small fraction. Then, the normalized number-, weight-, and z-distribution of the molecular size can be defined as:

$$N(i) = \frac{\sum_{j\leq i}(P_{j,i-j}+G_{j,i-j})}{\sum_{i\geq 0, j\leq i}(P_{j,i-j}+G_{j,i-j})} \quad (20)$$

$$W(i) = \frac{\sum_{j\leq i} i(P_{j,i-j}+G_{j,i-j})}{\sum_{i>0, j\leq i} i(P_{j,i-j}+G_{j,i-j})} \quad (21)$$

$$Z(i) = \frac{\sum_{j\leq i} i^2(P_{j,i-j}+G_{j,i-j})}{\sum_{i>0, j\leq i} i^2(P_{j,i-j}+G_{j,i-j})} \quad (22)$$

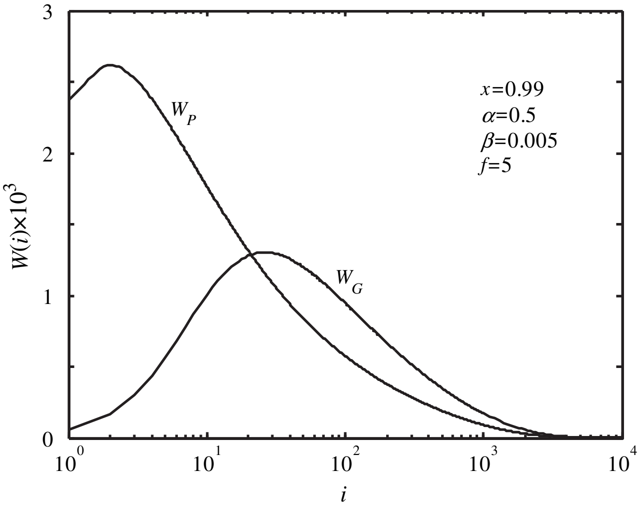

Fig. 2. Typical weight distributions of the hyperbranched polymers formed from AB_2 and AB type monomers in the presence of multi-functional cores with $x = 0.99$, $\alpha = 0.5$ and $\beta = 0.005$ at the specified value of $f = 5$. W_P: the distribution of $P_{n,l}$ species; W_G: the distribution of $G_{n,l}$ species.

The number-distribution curves usually decrease monotonously when $x < 1$. The pictorial relationships of the weight distribution of the products are shown in Fig. 1, with $x = 0.99$, $\alpha = 0.5$, $\beta = 0.005$ and the specified values of $f = 1$, 3, 5 and 10, respectively. A bimodal appears in some distribution curves, which should contribute to that the products consist of two clusters, one is the group of $P_{n,l}$ species and the other is that of $G_{n,l}$ species. Fig. 2 is a typical example of the weight distributions of these two types of species, in which the low molecular weight distribution results from the $P_{n,l}$ species and the high molecular weight distribution from the $G_{n,l}$ species. Higher f values and fraction of the core favour the formation of the $G_{n,l}$ species. Therefore, with the increase in f and β, the peak of the $G_{n,l}$ species drifts toward the right (high degree of polymerization), and the other drifts toward the left. The higher the value of f, the larger the space between the two peaks is. For a low f, the distribution curve only has a monomodal, due to a major overlap of these two distributions.

Fig. 3 shows the total z-distribution curves under the same parameter conditions as those used in Fig. 1. Every z-distribution curve has only a monomodal regardless of the value of f. It is evident that the larger the functionality of the core, the narrower the molecular weight distribution is, which is in agreement with that of AB_g-type polycondensation with multi-functional cores [26,27].

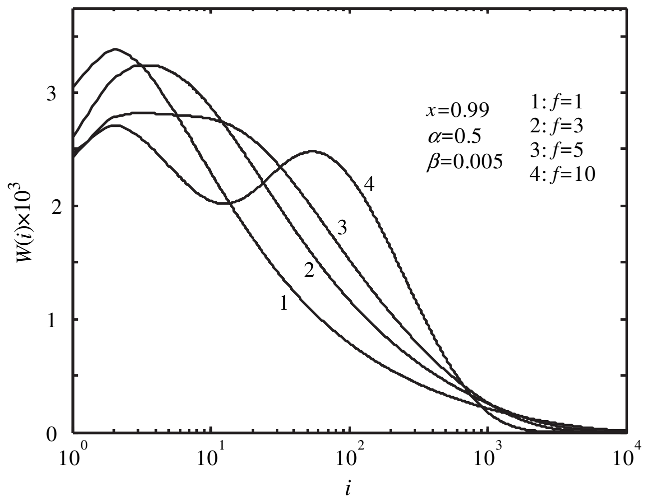

Fig. 1. Weight distributions of the hyperbranched polymers formed from AB_2 and AB type monomers in the presence of multi-functional cores with $x = 0.99$, $\alpha = 0.5$ and $\beta = 0.005$ at the specified values of f. 1: $f = 1$; 2: $f = 3$; 3: $f = 5$; 4: $f = 10$.

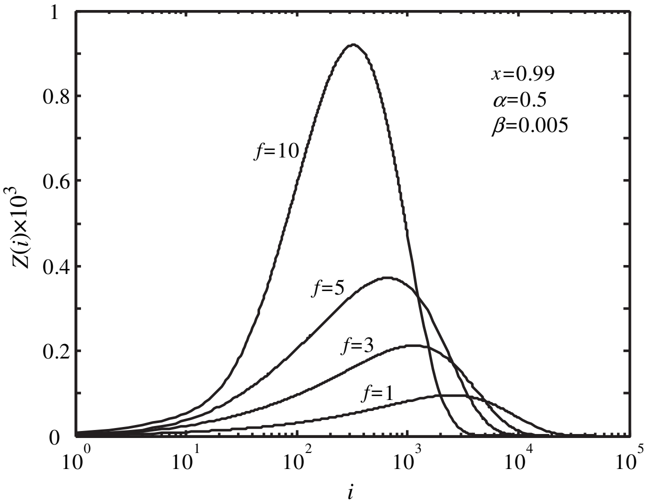

Fig. 3. z-Distribution of the hyperbranched polymers formed from AB_2 and AB type monomers in the presence of multi-functional cores under the identical conditions used in Fig. 1.

The possibility of forming $G_{n,l}$ species also decreases with the increase in α. So it can be known that the weight distribution of the molecular size varies from dimodal to monomodal by increasing the fraction of AB_2 type monomers, when the other reaction conditions are specified.

Shown in Fig. 4 are the total *z*-distribution curves of the products obtained, with $x = 0.99$, $\beta = 0.005$, $f = 5$, and the several α values margined. The lower the α value, the narrower the molecular weight distribution is.

When the molecular weight and the molecular weight distribution of the products are investigated, the masses of the various units and the core molecule should be involved. The number- and the weight-average molecular weight are defined as, respectively:

$$\overline{M_n} = \frac{\sum_{i,j}\left[(im_1+jm_2)P_{i,j}+(im_1+jm_2+m_R)G_{i,j}\right]}{\sum_{i,j}(P_{i,j}+G_{i,j})} = \frac{m_1\alpha+m_2(1-\alpha)+m_R\beta}{1-x+\beta} \tag{23}$$

$$\overline{M_w} = \frac{\sum_{i,j}\left[(im_1+jm_2)^2P_{i,j}+(im_1+jm_2+m_R)^2G_{i,j}\right]}{\sum_{i,j}\left[(im_1+jm_2)P_{i,j}+(im_1+jm_2+m_R)G_{i,j}\right]} \tag{24}$$

Where m_1 and m_2 represents the mass of AB_2 and AB unit, respectively, and m_R denotes the mass of a core molecule. Accordingly, the polydispersity index is $PI = \overline{M_w}/\overline{M_n}$. The number- and the weight-average molecular weights and the resultant polydispersity index are easy to calculate by the various moments derived above and the masses of units. When the masses of AB_2 and AB units are assumed to be identical, the average molecular weights can be simplified as the average degree of polymerizations.

$$\overline{P_n} = \frac{\sum_{i>0,j\le i} i\left(P_{j,i-j}+G_{j,i-j}\right)}{\sum_{i>0,j\le i}\left(P_{j,i-j}+G_{j,i-j}\right)} = \frac{1}{1-x+\beta} \tag{25}$$

$$\overline{P_w} = \frac{\sum_{i>0,j\le i} i^2\left(P_{j,i-j}+G_{j,i-j}\right)}{\sum_{i>0,j\le i} i\left(P_{j,i-j}+G_{j,i-j}\right)} = \frac{(1+r)^2+\left[f(f-1)\beta-1-\alpha^2\right]x^2}{(1+r-x-\alpha x)^2} \tag{26}$$

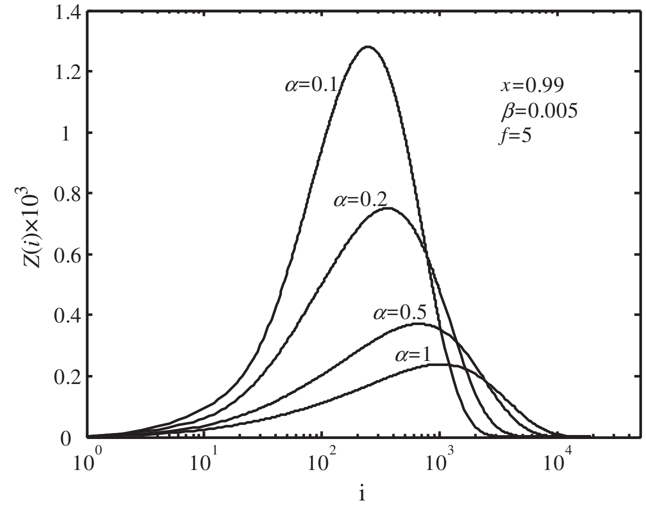

Fig. 4. *z*-Distribution of the hyperbranched polymers formed from AB_2 and AB type monomers in the presence of multi-functional cores with $x = 0.99$, $\beta = 0.005$ and $f = 5$ at the specified values of α: 0.1, 0.2, 0.5 and 1.

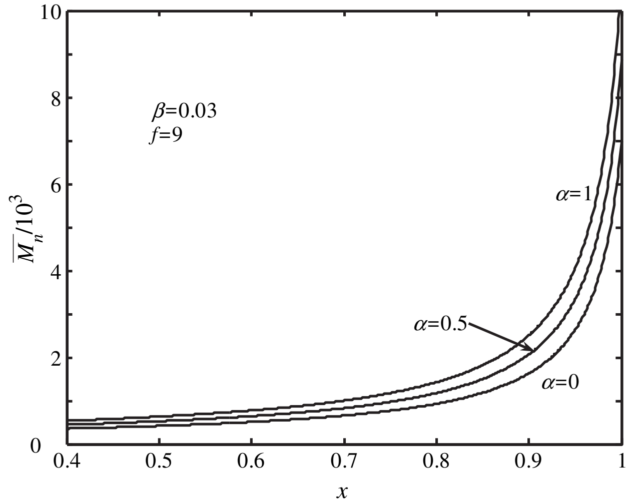

Fig. 5. The dependence of the number-average molecular weight on the conversion of A groups, with $\beta = 0.03$, $f = 9$, and $\alpha = 0$, 0.5 and 1, respectively.

Accordingly, it has:

$$PI' = \overline{P_w}/\overline{P_n} = \frac{1-x+\beta}{(1+r-x-\alpha x)^2}\left\{(1+r)^2+\left[f(f-1)\beta-\left(1+\alpha^2\right)\right]x^2\right\} \tag{27}$$

Taking the example of the polymerization reaction of the 4-fluoro-4′-hydroxybenzophenone (AB monomer) and the bis-(4-fluorophenyl)-(4-hydroxyphenyl)phosphine oxide (AB_2 monomer) in the presence of a tris-(3,4,5-trifluorophenyl)phosphine oxide (core molecule) [33], the dependence of the number-average molecular weight of the resultant hyperbranched polymers calculated by Eq. (23) on the reaction extent of A groups and the fraction of AB_2 type monomers are shown in Fig. 5. The number-average molecular weight increase slowly when $x < 0.8$ and it rises sharply when the reaction approaches to completion. Shown in Figs. 6 and 7 is the dependence of polydispersity index on the reaction extent. Initially the molecular weight distribution gets wider and wider with the increase in *x*. When the reaction approaches to completion, it turns downwards and becomes considerably narrow

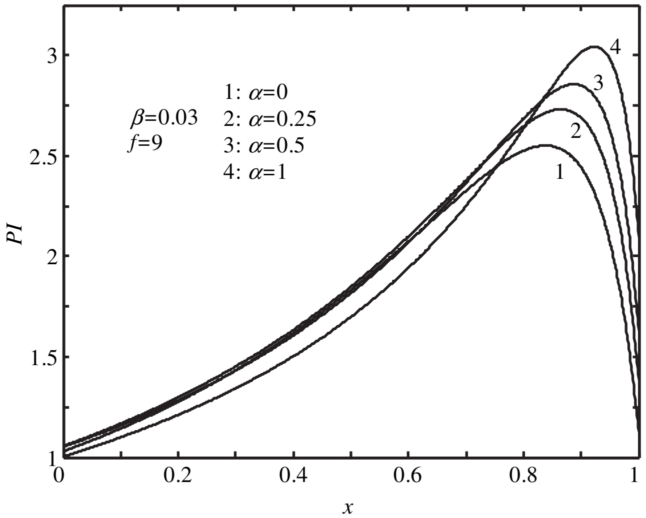

Fig. 6. The dependence of the polydispersity index on the conversion of A groups, with $\beta = 0.03$, $f = 9$ at the several specified values of α.

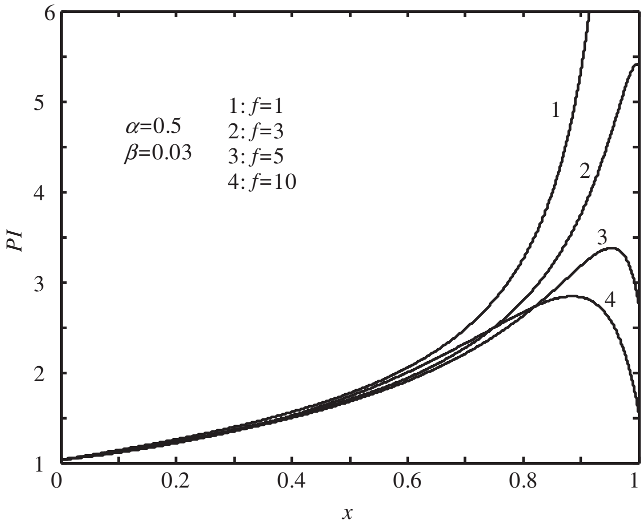

Fig. 7. The dependence of the polydispersity index on the conversion of A groups, with $\alpha = 0.5$, $\beta = 0.03$ at the several specified values of f.

ultimately. This may contribute to the fact that the species $P_{n,l}$ gradually disappear at that time. Before the end of the reaction, polydispersity index increases with the increase in the faction of AB_2 monomers and it also increase with the decrease in f. Higher β narrows the molecular weight distribution as well. Calculations show that the difference of the polydispersity index between *PI* and *PI'* is negligible.

At the end of reaction, the polydispersity reads:

$$PI = \frac{1}{f^2\beta}[2\alpha(f\beta+1)+f\beta(f\beta+f+1)] \tag{28}$$

The dependence relationship is identical with that of the general self-condensing vinyl polymerization in the presence of the multi-functional cores [34].

4. Conclusion and discussion

For the reaction system of co-polycondensation of AB_2 and AB type monomers in the presence of multi-functional cores, the feed ratio of core molecules and AB_2 monomers to the total monomers considerably affects the molecular weight distribution and molecular parameters of the resultant hyperbranched polymers. If $\alpha = 1$, the reaction system degenerates to that of AB_2 polycondensation with core molecules[16,26] and, if $\alpha = 0$, it is the star-branched polycondensation [25]. The molecular parameters of the hyperbranched polymers can be controlled by adjusting the value of α. Compared with the general copolymerization of AB_2 and AB monomer without core molecule, in which the polydispersity index of the resultant polymers increases monotonously with the increase in x, the presence of core molecules makes the polydispersity index go down fast when the reaction approaches to completion and it becomes very low ultimately. Higher concentrations of core molecules and AB monomers favour the formation of $G_{n,l}$ species and afford the products with lower polydispersity as well.

The effect of the core molecules on the molecular parameters of hyperbranched polymerization have been investigated theoretically by many authors [16,25,26,28,29,34–39]. In the recent work [34] on the theoretical treatment of the general self-condensing vinyl polymerization in the presence of multi-functional core molecules, we have reported that the distribution curve of molecular size appears a bimodal structure for the low stimulus concentration and it varies from bimodal to monomodal with the increase in the fraction of stimulus. A stimulus can activate an AB monomer into an AB* inimer, so the reaction system also can be taken as self-condensing vinyl copolymerization of AB monomer and AB* inimer in the presence of core molecules. The calculated results in this work for the co-polycondensation of AB_2 and AB monomers with core molecules have the similar characteristics with it. For a lower fraction of AB_2 type monomer, the weight distribution curve of the total products has a bimodal structure and it changes from bimodal to monomodal with the increase in the fraction of AB_2 monomer or the decrease in the fraction of core molecules. These theoretical analysis can explain the experimental molecular weight distribution of hyperbranched phenylacetylene polymers formed from 3,5-diiodophenylacetylene (AB_2 monomer) in the presence of multi-functional core [40], in which monomodal distributions were observed at low monomer/core ratios and, as this ratio increases, a bimodal molecular weight distribution was observed consisting of a sharp peak at high molecular weight and a broad tail at low molecular weights.

At specified α and β, the number-average molecular weights increase monotonously with increase in x. Experimental values reported by Sennet et al. [33] show that they increase slightly with the increase in the reaction temperature as well and are less than that of ultimate theoretical results, which means that the ultimate conversion of A groups may not approach 1 experimentally and it may increases with the increase in temperature. In comparison with the theoretical calculations, the conversion of A groups may ranges from 0.97 to 0.99 in these experiments. The calculated values of *PI* within the range of x are in good agreement with the experimental data, 1.41–4.07, with α from 0.05 to 0.25.

Acknowledgement

This work was sponsored by NSF of China (20774038, 50633010) and the fund of The State Key Laboratory of Metal Matrix Composites.

Appendix. The first and second moments of the distribution functions

$$\sum_{n+l>0} nP_{n,l} = (N_0+L_0)\frac{\alpha(1+r)(1-x)}{1+r-x-\alpha x} \tag{A1}$$

$$\sum_{n+l>0} lP_{n,l} = (N_0+L_0)\frac{(1-\alpha)(1+r)(1-x)}{1+r-x-\alpha x} \tag{A2}$$

$$\sum_{n+l>0} n^2P_{n,l} = (N_0+L_0)\frac{\alpha(1+r)(1-x)}{(1+r-x-\alpha x)^3}\Big[\Big(1-2\alpha-\alpha^2\Big)x^2 - 2(1-\alpha)(1+r)x+(1+r)^2\Big] \tag{A3}$$

$$\sum_{n+l>0} l^2P_{n,l} = (N_0+L_0)\frac{(1-\alpha)(1+r)(1-x)}{(1+r-x-\alpha x)^3}\Big[\Big(\alpha^2+4\alpha-1\Big)x^2 - 4\alpha(1+r)x+(1+r)^2\Big] \tag{A4}$$

$$\sum_{n+l>0} nlP_{n,l} = (N_0+L_0)\frac{\alpha(1-\alpha)(1+r)(1-x)x}{(1+r-x-\alpha x)^3}[3(1+r) - (3+\alpha)x] \tag{A5}$$

$$\sum_{n+l\geq 0} nG_{n,l} = (N_0+L_0)\frac{f\beta\alpha x}{1+r-x-\alpha x} \tag{A6}$$

$$\sum_{n+l\geq 0} lG_{n,l} = (N_0+L_0)\frac{f\beta(1-\alpha)x}{1+r-x-\alpha x} \tag{A7}$$

$$\sum_{n+l\geq 0} n^2G_{n.l} = (N_0+L_0)\frac{f\beta\alpha x}{(1+r-x-\alpha x)^3}\Big\{\Big[1-(f+1)\alpha-f\alpha^2\Big]x^2 - [2-(f+1)\alpha](1+r)x+(1+r)^2\Big\} \tag{A8}$$

$$\sum_{n+l\geq 0} l^2G_{n,l} = (N_0+L_0)\frac{f\beta(1-\alpha)x}{(1+r-x-\alpha x)^3}\Big\{\Big(f\alpha^2+4\alpha-f\Big)x^2 - [(f+3)\alpha-f+1](1+r)x+(1+r)^2\Big\} \tag{A9}$$

$$\sum_{n+l\geq 0} nlG_{n,l} = (N_0+L_0)\frac{f\beta\alpha(1-\alpha)x^2}{(1+r-x-\alpha x)^3}[(2+f)(1+r) - (2+f+f\alpha)x] \tag{A10}$$

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