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Theoretical investigation on the polyaddition of A_2 and CB_2 monomers with non-equal reactivity

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ABSTRACT

Taking account of the difference of reactivities between C and B group, the evolution of the monomers and the various structural units formed from the polyaddition of A_2 and CB_2 monomers was investigated by the kinetic mechanism. The calculated results theoretically explain the experimental data observed in our previous works very well, if the reactivity ratio of C to B groups is 200. The critical conversion of gelation for the $A_2 + CB_2$ type polymerization depends on the reactivity ratio. The lower the ratio, the earlier the gelation appears. Compared with the $A_2 + B_3$ type polymerization, the disappearance of gelation for the $A_2 + CB_2$ type polymerization should attribute to the much higher reactivity of C group than that of B one. The analytical expression of the degree of branching was derived as well. If the reactivity of C group is much higher than that of B group and the substitution effect is neglected, the value of the degree of branching for the hyperbranched polymers obtained is equal to the value of conversion of B groups and it may exceed 0.5, with the feed ratio of monomers varying from 1 to 3/2.

1. Introduction

The techniques to prepare hyperbranched polymers could be divided into two major categories. The one is the single monomer methodology (SMM), which mainly consists of the AB_g type polycondensation [1–3], the self-condensing vinyl-polymerization [4] and the self-condensing ring-opening polymerization [5,6]. The other adopts the double monomer methodology (DMM). One of the merits is the commercial availability of monomers for the DMM. The typical representative is the copolymerization of A_2 and B_3 type monomers [7,8]. However, it is a bit troublesome to avoid gelation for the reaction system. Recently, a novel strategy to synthesize hyperbranched polymers by one-step polymerization, based on the non-equal reactivity of functional groups in specific monomer pairs (A_2 and BB'_2 or CB_2 monomers), has been invented in our laboratory [9–15]. A series of new hyperbranched polymers are synthesized with cheap and commercially available raw materials, such as poly(sulfone-amine)s with divinyl sulfone (DV, A_2 monomer) and 1-(2-aminoethyl)piperazine (AP, BB'_2 monomer), N-ethylethylene-diamine (NDA, BB'_2 monomer) or N-methylpropane-1,3-diamine (NPA, BB'_2 monomer), respectively, poly(ester-amine)s with ethylene diacrylate (A_2) and BB'_2 monomers mentioned above, and poly(urea-urethane)s with diisocyanates (A_2) and CB_n monomers suspending single amine and multi-hydroxyls. As a denotation, the BB'_2 monomer also can be expressed as CB_2 one when a theoretical investigation is carried out. In this work, for convenience, we uniformly denote the polymerizations mentioned above as $A_2 + CB_n$ methodology, that is, the BB'_2 monomer is denoted as CB_2 monomer correspondingly.

For the copolymerization of A_2 and CB_2 monomers, the reaction takes place between group A and group C or B. A notable characteristic is that the reactivity between A and C groups is much higher than that between A and B groups. So one of A groups of A_2 monomer always reacts fast with the C group, generating dominantly an intermediate with one active A group and two active B groups during the initial period of the reaction. The intermediate is a new kind of AB_2-type monomer. Further polycondensation of the intermediates results in hyperbranched polymers. In addition, a small amount of AB_2 may couple with CB_2 monomers, resulting in the species with four active B functional groups. This species can play the role of "core" in the polymerization. Thus, the molecular weight distribution of the resulting hyperbranched polymers may get narrow. Usually, the maximum average degree of branching (DB) of the hyperbranched polymers formed from AB_2-type monomers does not exceed 0.5 [16,17]. However, the average degree of branching of these polymers is higher than 0.5, according to the experimental observation.

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Theoretical analysis is helpful to understand the reaction mechanism and control the molecular structures for the species obtained. The kinetic model is successful to derive the analytical expressions of molecular size distribution and calculate the various molecular parameters for the hyperbranched polymers formed from the SMM [16–25]. In this work, taking account of the difference in reactivities between C and B groups, we carry out theoretical investigation on the evolution of monomers and various structural units resulted from the polyaddition of A_2 and CB_2 type monomers, through which the degree of branching can be calculated and some experimental results can be explained.

2. Kinetic analysis

Let M_0 and N_0 denote the respective initial concentration of A_2 and CB_2 monomer. The reaction takes place only between group A and group B or C and the reactivity of group B and C is represented by k_B and k_C, respectively. An example of oligomer formed from A_2 and CB_2 type polyaddition is shown in Fig. 1, in which the various structural units incorporated in the products are shown. Where the capital A, B and C denotes the active groups and the minuscule a, b and c represents the reacted A, B and C groups, respectively. It can be known from Fig. 1 that there are seven types of possible structural units in the species formed, which including three linear units (a_2, bcB, b_2C), three terminal units (aA, cB_2, bBC) and a dendritic unit (cb_2). Together with the residual A_2 and CB_2 monomers, the corresponding specifications of these units are listed in Table 1.

According to the kinetic mechanism, the evolution of these monomers and units fits the following differential equations:

$$\frac{dM}{dt} = -2(k_C C + k_B B)M \tag{1}$$

$$\frac{dN}{dt} = -(k_C + 2k_B)AN \tag{2}$$

$$\frac{dT_1}{dt} = k_C AN - k_B 2AT_1 \tag{3}$$

$$\frac{dT_2}{dt} = 2k_B AN - (k_C + k_B)AT_2 \tag{4}$$

$$\frac{dT_3}{dt} = 2(k_C C + k_B B)M - (k_C C + k_B B)T_3 \tag{5}$$

$$\frac{dL_1}{dt} = (k_C T_2 + 2k_B T_1)A - k_B AL_1 \tag{6}$$

$$\frac{dL_2}{dt} = k_B T_2 A - k_C L_2 A \tag{7}$$

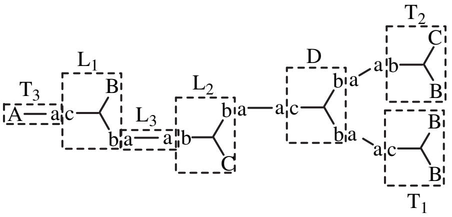

Fig. 1. An example of oligomer formed from A_2 and CB_2 type polyaddition.

Table 1
The residual monomers and the various structural units resulted from the polyaddition of A_2 and CB_2 monomers.

Structural unit	Type of the unit	Symbol
A_2	Residual A_2 monomer	M
CB_2	Residual CB_2 monomer	N
cB_2	Terminal unit 1	T_1
bCB	Terminal unit 2	T_2
aA	Terminal unit 3	T_3
cbB	Linear unit 1	L_1
b_2C	Linear unit 2	L_2
a_2	Linear unit 3	L_3
cb_2	Dendritic unit	D

$$\frac{dL_3}{dt} = (k_C C + k_B B)T_3 \tag{8}$$

$$\frac{dD}{dt} = (k_B L_1 + k_C L_2)A \tag{9}$$

The initial conditions read: $M|_{t=0} = M_0$, $N|_{t=0} = N_0$, and all the structural units are zero at $t = 0$. Let x denote the conversion of B groups, then

$$x = \frac{2N_0 - B}{2N_0} \tag{10}$$

That is,

$$B = 2N_0(1 - x) \tag{11}$$

Differentiating both sides of Eq. (11) leads to

$$\frac{dB}{dt} = -2N_0\frac{dx}{dt} \tag{12}$$

On the other hand, the consumption of B groups fits

$$\frac{dB}{dt} = -k_B BA \tag{13}$$

By comparing Eq. (12) with Eq. (13), it yields

$$\frac{dx}{dt} = k_B\frac{AB}{2N_0} = k_B A(1 - x) \tag{14}$$

The consumption of A and C groups fits, respectively:

$$\frac{dC}{dt} = -k_C CA \tag{15}$$

$$\frac{dA}{dt} = -(k_B B + k_C C)A \tag{16}$$

with the initial conditions: $A|_{t=0} = 2M_0$ and $C|_{t=0} = N_0$.

By dividing Eqs. (15) and (16) by Eq. (14) and solving the resulting equations, we obtain:

$$C = N_0(1 - x)^r \tag{17}$$

$$A = 2N_0\left\{\alpha - x - \frac{1}{2}\left[1 - (1 - x)^r\right]\right\} \tag{18}$$

where r represents the reactivity ratio of C to B group, and α the initial feed ratio of A_2 to CB_2 monomer.

$$r = k_C/k_B \tag{19}$$

$$\alpha = M_0/N_0 \tag{20}$$

By dividing Eqs. (1)–(9) by Eq. (14), we can transfer the variable from the time (t) to the conversion of B group (x) for these equations:

$$\frac{\mathrm{dM}}{\mathrm{d}x} = -4\frac{\mathrm{N_0}}{\mathrm{AB}}(r\mathrm{C}+\mathrm{B})\mathrm{M} \tag{21}$$

$$\frac{\mathrm{dN}}{\mathrm{d}x} = -2(r+2)\mathrm{N_0}\frac{\mathrm{N}}{\mathrm{B}} \tag{22}$$

$$\frac{\mathrm{dT_1}}{\mathrm{d}x} = \frac{2\mathrm{N_0}}{\mathrm{B}}(r\mathrm{N}-2\mathrm{T_1}) \tag{23}$$

$$\frac{\mathrm{dT_2}}{\mathrm{d}x} = \frac{\mathrm{N_0}}{\mathrm{B}}[2r\mathrm{N}-(1+r)\mathrm{T_2}] \tag{24}$$

$$\frac{\mathrm{dT_3}}{\mathrm{d}x} = \frac{4\mathrm{N_0}}{\mathrm{AB}}(r\mathrm{C}+\mathrm{B})\mathrm{M}-\frac{2\mathrm{N_0}}{\mathrm{AB}}(r\mathrm{C}+\mathrm{B})\mathrm{T_3} \tag{25}$$

$$\frac{\mathrm{dL_1}}{\mathrm{d}x} = \frac{2\mathrm{N_0}}{\mathrm{B}}(r\mathrm{T_2}+r\mathrm{T_1}-\mathrm{L_1}) \tag{26}$$

$$\frac{\mathrm{dL_2}}{\mathrm{d}x} = \frac{2\mathrm{N_0}}{\mathrm{B}}(\mathrm{T_2}-r\mathrm{L_2}) \tag{27}$$

$$\frac{\mathrm{dL_3}}{\mathrm{d}x} = \frac{2\mathrm{N_0}}{\mathrm{AB}}(r\mathrm{C}+\mathrm{B})\mathrm{T_3} \tag{28}$$

$$\frac{\mathrm{dD}}{\mathrm{d}x} = \frac{2\mathrm{N_0}}{\mathrm{B}}(\mathrm{L_1}+r\mathrm{L_2}) \tag{29}$$

Solving these equations, we can get:

$$\mathrm{M} = \frac{\mathrm{N_0}}{\alpha}\left[\alpha-x-1/2+(1-x)^r/2\right]^2 \tag{30}$$

$$\mathrm{N} = \mathrm{N_0}(1-x)^{(2+r)} \tag{31}$$

$$\mathrm{T_1} = \mathrm{N_0}(1-x)^2\left[1-(1-x)^r\right] \tag{32}$$

$$\mathrm{T_2} = 2\mathrm{N_0}x(1-x)^{1+r} \tag{33}$$

$$\mathrm{T_3} = \frac{\mathrm{N_0}}{\alpha}\left[2x+1-(1-x)^r\right]\left[\alpha-x-1/2+(1-x)^r/2\right] \tag{34}$$

$$\mathrm{L_1} = 2\mathrm{N_0}x(1-x)\left[1-(1-x)^r\right] \tag{35}$$

$$\mathrm{L_2} = \mathrm{N_0}x^2(1-x)^r \tag{36}$$

$$\mathrm{L_3} = \frac{\mathrm{N_0}}{\alpha}\left[x+1/2-(1-x)^r/2\right]^2 \tag{37}$$

$$\mathrm{D} = \mathrm{N_0}x^2\left[1-(1-x)^r\right] \tag{38}$$

3. Results and discussions

The concentrations of the residual functional groups, monomers and various structural units in the reaction system depend on x, α and r. Fig. 2 shows the relationships between the residual fractions of functional groups ($f_\mathrm{A} = \mathrm{A}/2\mathrm{M_0}, f_\mathrm{B} = \mathrm{B}/2\mathrm{N_0}, f_\mathrm{C} = \mathrm{C}/\mathrm{N_0}$) and the conversion of B groups at the specified reactivity ratio, $k_\mathrm{C}/k_\mathrm{B} = 200$. The residual fraction of A groups is related to the value of the feed ratio and two curves are given in Fig. 2 for it with $\alpha = 1$ and 3/2, respectively. The residual fractions of C and A groups show a fast drop during the initial short stage. Then they decrease smoothly. In the previous work [9], the reaction process of DV and AP with $\alpha = 1$ was investigated in situ with FTIR and it has been known that the absorption peak assigned to the secondary amino (C) groups rapidly decreases with the reaction and totally disappears in about 15 s. However, during this period, the peaks assigned to the primary amino (B) groups changed a little and the area of the absorption band assigned to carbon–carbon double bonds (A groups) decreased to about a half. In order to compare the experimental data with the theoretical results, we investigated the evolution of the residual fractions of functional groups at the various r values. The results show that the higher the reactivity ratio r, the steeper the decrease of the curve is during the initial period. Only when $r = 200$, the evolutions of these functional groups calculated theoretically, as shown in the Fig. 2, are in good agreement with the experimental results.

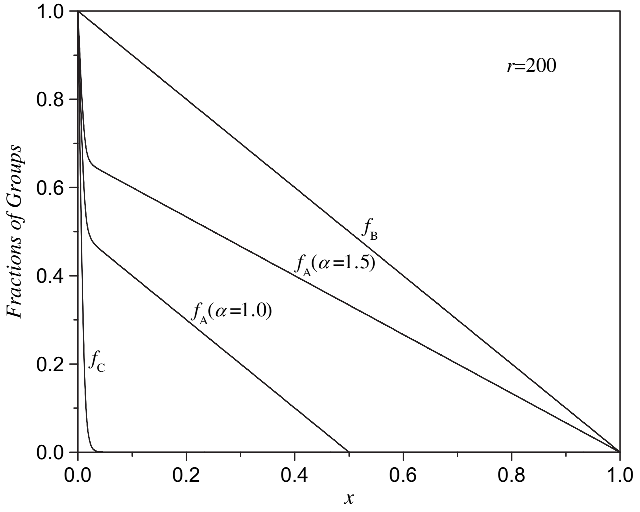

Fig. 2. The relationships between the residual fractions of functional groups and the conversion of B groups with $r = 200$.

Shown in Figs. 3 and 4 are the evolutions of the fractions of the residual monomers ($f_\mathrm{M} = \mathrm{M}/\mathrm{M_0}$, $f_\mathrm{N} = \mathrm{N}/\mathrm{N_0}$) and the various structural units ($f_{\mathrm{T_1}} = \mathrm{T_1}/\mathrm{N_0}$, $f_{\mathrm{T_2}} = \mathrm{T_2}/\mathrm{N_0}$, $f_{\mathrm{T_3}} = \mathrm{T_3}/\mathrm{M_0}$, $f_{\mathrm{L_1}} = \mathrm{L_1}/\mathrm{N_0}$,

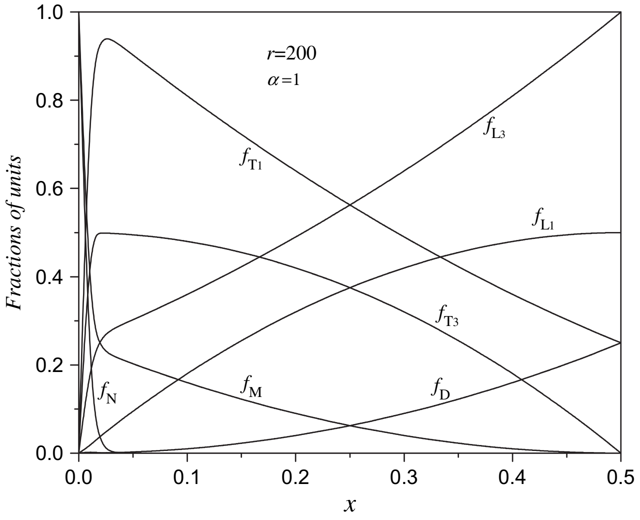

Fig. 3. The evolutions of fractions of residual monomers and structural units with $r = 200$ and $\alpha = 1$.

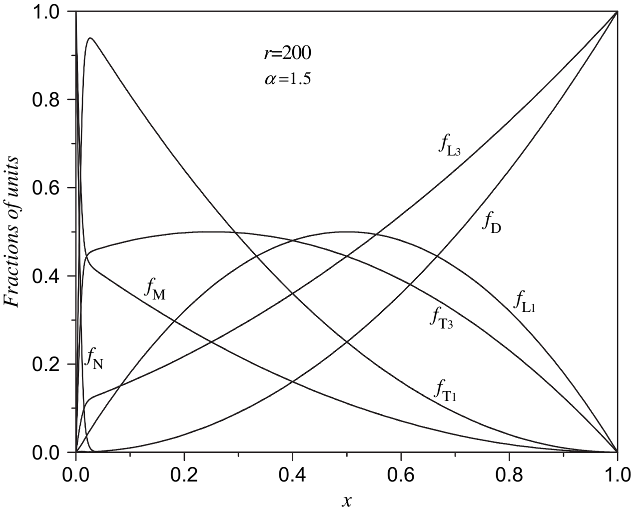

Fig. 4. The evolutions of fractions of residual monomers and structural units with $r = 200$ and $\alpha = 3/2$.

$f_{L_2} = L_2/N_0, f_{L_3} = L_3/M_0, f_D = D/N_0$) at the special reactivity ratio, $r = 200$, and the feed ratios, $\alpha = 1$ and 3/2, respectively. The CB_2 monomers were almost used up when the conversion of B groups is about 3%. At the beginning of the initial period, the fractions of terminal T_1 and T_3 units increase synchronously and the fraction of other units are negligible, which represents the formation of Aa–cB_2 intermediates. When CB_2 monomers were almost used up, with the feed ratio being equal to 1, about 94% of the monomers were converted into terminal T_1, which is the maximum value of f_{T_1} obtained under the condition of $r = 200$. Meanwhile, about 50% of the A_2 monomers were converted into T_3 units, which should exist mainly in the Aa–cB_2 intermediates, and about 27% of the monomers into L_3 units, which may constitute the B_2c–aa–cB_2 trimer. After the initial period, the reaction takes place principally between A and B groups. The fractions of T_1 and T_3 descend and the fractions of linear L_1 and branched D units keep increasing. These evolution processes also show a good agreement with those observed experimentally [9,10]. The maximum conversion of B groups with $\alpha = 1$ should be only a little higher than 50% for a high value of r. Therefore, the reaction is about to end when the conversion of B reaches 0.5. So it is enough for the x to be ranged from 0 to 0.5 in Fig. 3. According to the FTIR spectra, the absorption peak assigned to A groups totally disappears in about 5 h, which indicates that the A groups can react completely and the conversion of B groups can reach 0.5 (or a little higher than 0.5). At the end of the reaction the fraction of linear L_1 and branched D unit converge to 0.5 and 0.25, respectively, for the feed ratio of 1. The fractions of L_2 and T_2 are extremely small and the corresponding curves press close to the abscissa at the present scale of Fig. 3. The conversion of B groups permits to reach 100% when the feed ratio is equal to 3/2 and there are only two kinds of units, L_3 and D, theoretically at the end of the reaction, as shown in Fig. 4. However, the experimental observation indicated that the secondary amino (C) groups totally disappeared in about 12 s and the amino and vinyl groups were still present in 6 h. The hyperbranched polymers obtained contains amino and vinyl end functional groups, which implies that the B groups had not been used up and the reaction will stop at a certain value of the B groups conversion in solution [9,10,13].

It can be known from the structure of the product shown in Fig. 1 that there are two more number of the terminal units than that of the branched units. Therefore we can calculate the total concentration of macromolecule species formed by

$$\begin{aligned} N' &= \frac{T_1 + T_2 + T_3 - D}{2} \\ &= \frac{N_0}{\alpha}\left\{\alpha - x - x^2 - 1/4 - (1-x)^r\left[\alpha(1-x)^2 - x - 1/2\right]\right. \\ &\quad \left. - (1-x)^{2r}/4\right\} \end{aligned} \tag{39}$$

It is useful to draw the dependence of the fraction of macromolecule species formed to the total initial monomers [$f_{N'} = N'/(M_0 + N_0)$] on the conversion of C groups, P_C [$=1-(1-x)^r$], which is printed in Fig. 5 with three specified reactivity ratios, 1, 10 and 100, and two feed ratios, 1 (solid lines) and 3/2 (dash lines), respectively. A universal phenomenon is that the fraction of macromolecules increases initially and then becomes to decrease. The particular location of the turning point depends on the reactivity ratio (r) and the feed ratio (α). For an enough high value of r (>10), the fraction of macromolecules keeps increasing until the conversion of C groups approaches to unity. While in the situation of $r = 1$, it has already decreased to null at $P_C \approx 0.65$ (for $\alpha = 1$) and $P_C \approx 0.81$ (for $\alpha = 3/2$), which, undoubtedly, results in the formation of gelation. Further calculations indicate that the fraction of macromolecule species is easy to reach 0 if $r < 10$. For $r = 1$, the reaction system reduces to that of $A_2 + B_3$ type. In truth, the gelation is easy to take place for the experiment of $A_2 + B_3$ type copolymerization, while no gelation occurs for the $A_2 + CB_2$ type polymerization in solution [9–12]. The reaction process becomes very slow after a large part of C groups is consumed, according to above analysis and experimental investigations. Therefore it needs a long time to reach the critical conversion of gelation if the reactivity ratio is high. In other words, the avoidance of the gelation for the polyaddition of A_2 and CB_2 type monomers should be attributed to the large difference in reactivities between C and B groups, as pointed in the previous works [9,13]. The theoretical investigations in this work exclude the intramolecular cyclization for the species formed, which may reduce the formation of crosslink and gelation. Solvent is also one of the important factors about it. However, it seems not easy in theory to solve the problems thoroughly at present.

The degree of branching is one of the most important parameters for the structural characterization of hyperbranched polymers. Usually, the DB of a linear polymer is defined as 0 and a perfectly branched dendrimer as unity. In the previous works [9–12], the

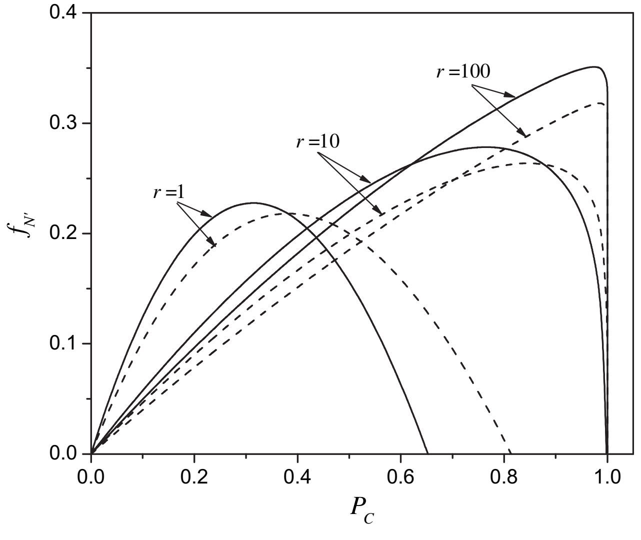

Fig. 5. The relationship between fraction of macromolecule species and conversion of C groups with three specified reactivity ratio, 1, 10 and 100, as printed, and two feed ratio, 1 (solid curves) and 3/2 (dash curves), respectively.

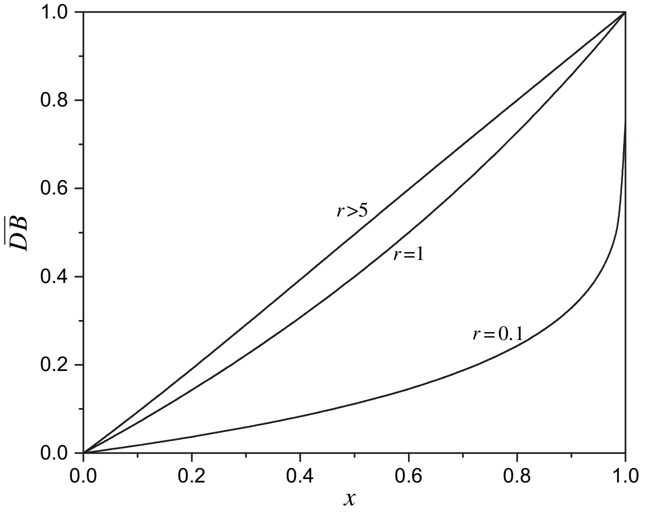

Fig. 6. The dependence of average degree of branching on the conversion of B groups.

combination of one A_2 and one CB_2 monomer was regarded as an intermediate and the linear L_3 was not taken as a separate unit. Thus a reasonable definition of the average degree of branching for the products of polyaddition of A_2 and CB_2 type mentioned in this work should be as follows:

$$\overline{\mathrm{DB}} = \frac{\mathrm{D} + \mathrm{T}_1 + \mathrm{T}_2 + \mathrm{T}_3 - 2\mathrm{N}'}{\mathrm{D} + \mathrm{T}_1 + \mathrm{T}_2 + \mathrm{T}_3 + \mathrm{L}_2 + \mathrm{L}_3 - 2\mathrm{N}'} = \frac{2x\left[1-(1-x)^r\right]}{x+(2-x)\left[1-(1-x)^r\right]} \qquad (40)$$

Fig. 6 prints the evolution of average degree of branching with the increase in conversion of B group. It increases by increasing x at any specified r and the effect of r on the relationship between average degree of branching and x is negligible when it is greater than 5. This may contribute to that the C groups are used up fast under the condition. Then the reaction becomes the polycondensation of the AB_2 intermediates and the B_4 cores. The feed ratio determines the maximum conversion of B groups and the average degree of branching for the ultimate products, though Eq. (40) is independent of the value of α. If the reactivity of C group is much higher than that of B group, the C groups are used up rapidly, that is, $P_C = 1-(1-x)^r \to 1$. Then $\overline{\mathrm{DB}} \to x$. Therefore, the average degree of branching may range from 0.5 to 1 with the variation of feed ratio from 1 to 3/2, according to theoretical calculations. However, it has already been pointed out that the reaction will stop at a certain value of the conversion of B groups and the x should be less than 1 for the feed ratio of 3/2. Here the reactivities of the two B groups of CB_2 monomer are assumed to be identical in the theoretical deduction. In fact, when one of the hydrogen atoms of primary amino reacts, the primary amino degenerates to a secondary amino and the other hydrogen can react rather faster with a vinyl group, which favors the enhancement of degree of branching. Experimental data indicate that the average DB is in the range from 0.53 to 0.71 and generally the degree of branching of the products with $\alpha = 3/2$ is higher than that with $\alpha = 1$ [9,10]. It shows a qualitative agreement with the theoretical calculations. However, the substitution effect should be considered for the more quantitative comparison.

4. Conclusion

The kinetic model has been successfully applied to the polyaddition of A_2 and CB_2 monomers with non-equal reactivities between C and B group, which has been proved to be effective in the theoretical investigation on the hyperbranched polymers [16–25]. Taking the conversion of B groups as the variable, the evolution expressions of the functional groups, monomers and various structural units formed from the reaction system were derived. The experimental observation for the evolution of monomers and functional groups in the previous works can be explained by the theoretical calculations. For a high reactivity ratio (r) of C to B group, the residual fractions of C and A groups have a fast drop during the initial short stage of the reaction. Then they decrease smoothly. By comparison with the experimental results in our previous works and the theoretical calculations, the reactivity ratio, r, is about 200. If $r = 1$, the $A_2 + CB_2$ type polymerization degenerates to $A_2 + B_3$ type one and the gelation takes place before the conversion of C groups reaches about 0.65 and 0.81 for the feed ratio 1 and 1.5, respectively. The large difference of reactivity between C and B group results in the disappearance of the gelation for the polyaddition of A_2 and CB_2 monomers. The analytical expression of the degree of branching was also derived. If the reactivity of C group is much higher than that of B group and the substitution effect is neglected, the value of average degree of branching for the hyperbranched polymers obtained is equal to the value of conversion of B groups, and it may exceed 0.5 with the feed ratio varying from 1 to 3/2. The effect of r on the average degree of branching is negligible when it is greater than 5.

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