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Distribution function of hyperbranched polymers formed by AB_2 type polycondensation with substitution effect

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Abstract

By kinetic model, the analytical expression of the distribution function for the hyperbranched polymers formed from AB_2 type polycondensation with substitution effect was derived. The results are compared to those for self-condensing vinyl polymerization of AB* monomers. Reaction becomes faster with the increasing reactivity of a linear B group. At any finite conversion of A group, both average degree of polymerization and dispersity increase with the increase of low rate constant, r (ratio of the reactivity of a linear B group to that of a terminal B group). However, the variation of these parameters is moderate if $r>100$ and they converge to respective limiting value. The average degree of polymerization and dispersity are much smaller than that of self-condensing vinyl polymerization of AB* monomers at the same conversion.

Keywords: MWD; Hyperbranched polymer; Kinetics

1. Introduction

Due to their unique physical and chemical properties as well as potential applications, hyperbranched polymers have drawn much attention and a variety of hyperbranched polymers have been prepared [1–4]. Hyperbranched polymers are imperfect dendritic macromolecules with a randomly branched structure and various molecular weight or degree of polymerization. Therefore, molecular weight distribution (MWD) describing the molecular weight composition of the molecules and degree of branching (DB), a ratio of the number of dendritic and terminal units to that of total units, are the two most important parameters for the hyperbranched polymers. There are attempts to maximize degree of branching and minimize dispersity, which describes the degree of molecular weight deviation from the average value and is defined as the ratio of the weight-average molecular weight to the number-average molecular weight. The dispersity can be improved by employing the copolymerization scheme of monomers with multifunctional core moieties B_f [5–11], here f represents the number of B groups in every core molecule. The MWD of the resultant polymer can become narrow with increasing f. As for the DB, according to the kinetic analysis based on the assumption of equal reactivity (i.e. random polymerization), the maximum value does not exceed 0.5 for the hyperbranched polymers obtained by one-step polycondensation of AB_2-type monomers [12–15] and 0.465 for that formed by self-condensing vinyl polymerization (SCVP) of AB* type monomers [13]. However, high degree of branching (>0.5) can often be observed experimentally. In the polycondensation of 3,5-bis(trimethylsioxy)-benzoyl chloride, Hawker et al. [16] and Wooley et al. [17] found DB = 0.55–0.60. Malmstrom et al. [18] found DB = 0.7–0.8 for hyperbranched aliphatic polyesters. Recently, our laboratory [19] developed a new strategy for synthesis of hyperbranched polymers from A_2 type and BB'_2 type monomers. The polymerization of divinyl sulfone(A_2) and 1-(2-aminoethyl)piperazine(BB'_2) without any catalysts are used to prepare hyperbranched polysulfone-amines. During polymerization, secondary amino groups of 1-(2-aminoethyl)-piperazine react fast with vinyl groups of divinyl sulfone forming dominant dimmers, which can be regarded as a new AB'_2 type intermediate monomer. Resultant polymerization of this monomer results in hyperbranched polysulfone-amine. The DB reaches 0.5–0.6 in this system.

Holter and Frey [20] supposed several possibilities to enhance DB: (1) higher reactivity of linear vs terminal units (i.e. substitution effect); (2) polymerization of prefabricated, dendritic units; and (3) slow addition/dilution techniques.

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DB also increases with the reactivity of the core molecule in the case of copolycondensation [9–11].

Intuitively, higher reactivity of the B group in a linear unit favors the formation of branched units. The reactivity change after the first B group has reacted was termed 'substitution effect' by Gordon [21]. By combining kinetic analysis with numeral calculation, Holter and Frey [20] investigated the evolution of DB with the conversion of A group at the various values of k_L/k_T for AB_2 type polymerization, where k_L and k_T represent the reactivity of B groups in linear and terminal units, respectively. A large increase in the ratio k_L/k_T will lead to strongly enhance DB values. DB can come close to a value of 1 at the full conversion of A groups only if k_L/k_T is large enough. The effect of non-equal reactivity on DB also was investigated by Galina [22] for the generalized AB_f type polymerization. For SCVP of AB* monomer with non-equal rate constants, Yan et al. [13] derived an analytical expression for DB by variable transformation. It can increase up to 0.5 if $k_A/k_B = 2.59$ and 2/3 by using multifunctional initiators and adding monomer slow enough [13,23], where k_A and k_B represent the reactivity of A* and B* group, respectively.

The partial differential equations that describe evolution of the size distribution of polymer species formed in the polycondensation of AB_2 monomer with substitution effect was developed by Galina et al. [24,25]. The model can be applied to calculate various molecular parameters in polymerizing systems, including various average degrees of polymerization, size distribution of polymers, degree of branching, etc. However, the kinetic treatment of such a non-equal reactivities problem is extremely complex and, to our knowledge, there is no any analytical solution for distribution function and weight-average molecular weight, although numerical calculations can be carried out.

Muller et al. [26] also calculated weight-average molecular weight and dispersity for non-equal rate SCVP by numerical method. In this work, we develop the kinetic model of AB_2 type polycondensation with substitution effect, and drive the analytical expressions for the various parameters of the resultant hyperbranched polymers, such as distribution function, average molecular weights, and dispersity.

2. Kinetic differential equations

There are six types of structural units in the polymerization system of AB_2 type monomers, i.e. linear units abB and AbB, terminal units AB_2 and aB_2, and dendritic units Ab_2 and ab_2. Here capital letters A and B represent the unreacted A and B groups, while lowercase letters a and b the reacted A and B groups, respectively. Reaction takes place between A and B groups. The residual unreacted B groups can be divided into two catalogues. One is termed linear B groups, which are those attached on the linear units AbB and abB, and another is termed terminal B groups, which are those attached on the terminal units AB_2 and aB_2. At the assumption of equal reactivity, the difference of reactivities between these two catalogues B groups is neglected. As the notation in Ref. [20], taking account for the substitution effect, we let k_L represent the reactivity of a linear B group and k_T be that of a terminal B group.

We can set up the following simple reaction schemes for the reaction between two molecules:

$$P_{i,j} + P_{n-i,l+1-j} \xrightarrow{k_L} P_{n,l}$$

$$P_{i,j} + P_{n-i,l-1-j} \xrightarrow{k_T} P_{n,l}$$

where $P_{n,l}$ denotes both the molecule and concentration of the n-mer species including l linear units (abB + AbB). There is an increase by 1 for linear units if an A group reacts with a terminal B group of another molecule, while a decrease by 1 for linear units if an A group reacts with a linear B group of another molecule. In every $P_{n,l}$ species, there is an unreacted A group, l linear B groups and $(n-l+1)$ terminal B groups. If the intramolecular reactions are prohibited, the reaction scheme above leads to the kinetic differential equations

$$\begin{aligned}
\frac{dP_{n,l}}{dt} = & \frac{k_L}{2}\sum_{i,j}\{jP_{i,j}P_{n-i,l+1-j} + (l+1-j)P_{n-i,l+1-j}P_{i,j}\} \\
& + \frac{k_T}{2}\sum_{i,j}\{(i+1-j)P_{i,j}P_{n-i,l-1-j} + [n-i+1 \\
& -(l-1-j)]P_{n-i,l-1-j}P_{i,j}\} \\
& -k_L\left\{lP_{n,l}\sum_{i,j}P_{i,j} + P_{n,l}\sum_{i,j}jP_{i,j}\right\} \\
& -k_T\left\{(n+1-l)P_{n,l}\sum_{i,j}P_{i,j} + P_{n,l}\sum_{i,j}(i+1-j)P_{i,j}\right\} \\
= & \frac{k_L}{2}\sum_{i,j}(l+1)P_{i,j}P_{n-i,l+1-j} + \frac{k_T}{2}\sum_{i,j}(n-l+3)P_{i,j}P_{n-i,l-1-j} \\
& -k_L\left\{lP_{n,l}\sum_{i,j}P_{i,j} + P_{n,l}\sum_{i,j}jP_{i,j}\right\} \\
& -k_T\left\{(n+1-l)P_{n,l}\sum_{i,j}P_{i,j} + P_{n,l}\sum_{i,j}(i+1-j)P_{i,j}\right\}
\end{aligned} \tag{1}$$

The first and second term of Eq. (1) are related to the formation of $P_{n,l}$ species, and the last two terms represent the consumption of $P_{n,l}$ species during the reaction process. From the architecture of a hyperbranched polymer $P_{n,l}$ formed in AB_2 polycondensation, we can know $(n-l)$ is an odd number. Therefore, the index of i can run from 1 to $n-1$ (at the former two terms) or infinite (at the last two terms) in Eq. (1), and the index j should guarantee $(i-j)$ to be odd. For the formation of $P_{n,l}$ species (former two terms), the double summation for i and j makes every species be counted twice. Therefore, we divide it by the factor 2. The initial condition of Eq. (1) is

$$P_{1,0}(t=0)=M_0, \qquad P_{n>1,l\geq 0}(t=0)=0 \tag{2}$$

where M_0 is the initial concentration of AB_2 monomers. If A also represents the concentration of residual A groups in the reaction system, then

$$\sum_{n,l} P_{n,l}=A \tag{3}$$

due to there being only one A group per molecule. Just this is the zeroth moment of the distribution function. From the material balance condition, we have

$$\sum_{n,l} nP_{n,l}=M_0 \tag{4}$$

$$\sum_{n,l} lP_{n,l}=L \tag{5}$$

$$\sum_{n,l}(n+1-l)P_{n,l}=2T \tag{6}$$

where $L(=\mathrm{abB}+\mathrm{AbB})$ and $T(=\mathrm{aB}_2+\mathrm{AB}_2)$ denote concentration of linear and terminal units, respectively. Eq. (4) also is called the first moment of the distribution function.

From the kinetic principle we can derive the differential equations as follows:

$$\frac{\mathrm{d}A}{\mathrm{d}t}=-(k_L L+2k_T T)A \tag{7}$$

$$\frac{\mathrm{d}T}{\mathrm{d}t}=-2k_T TA \tag{8}$$

$$\frac{\mathrm{d}L}{\mathrm{d}t}=2k_T TA-k_L LA \tag{9}$$

The initial conditions of these equations are

$$A(t=0)=M_0, \qquad T(t=0)=M_0, \qquad L(t=0)=0 \tag{10}$$

By substituting Eqs. (3)–(9) into Eq. (1), it gives

$$\begin{aligned}\frac{\mathrm{d}P_{n,l}}{\mathrm{d}t}=&\frac{k_L}{2}\sum_{i,j}(l+1)P_{i,j}P_{n-i,l+1-j}+\frac{k_T}{2}\sum_{i,j}(n-l\\&+3)P_{i,j}P_{n-i,l-1-j}\\&-\left\{-\frac{\mathrm{d}A}{A\mathrm{d}t}+k_L lA+k_T(n+1-l)A\right\}P_{n,l}\end{aligned} \tag{11}$$

In order to solve Eq. (11), we introduce the variable transformation

$$z=k_T\int_0^t A\mathrm{d}t, \quad \text{i.e.} \quad \frac{\mathrm{d}z}{\mathrm{d}t}=k_T A \tag{12}$$

Dividing Eqs. (7)–(9) by Eq. (12), we have

$$\frac{\mathrm{d}A}{\mathrm{d}z}=-(rL+2T) \tag{13}$$

$$\frac{\mathrm{d}T}{\mathrm{d}z}=-2T \tag{14}$$

$$\frac{\mathrm{d}L}{\mathrm{d}z}=2T-rL \tag{15}$$

where r denotes the reactivity ratio of k_L and k_T. The solutions of these equations are

$$T=M_0\,\mathrm{e}^{-2z} \tag{16}$$

$$L=\frac{2}{r-2}M_0[\mathrm{e}^{-2z}-\mathrm{e}^{-rz}] \tag{17}$$

$$A=\frac{M_0}{r-2}[(r-1)(2\,\mathrm{e}^{-2z}-1)+1-2\,\mathrm{e}^{-rz}] \tag{18}$$

The conversion of A groups is defined as

$$x=\frac{M_0-A}{M_0}=\frac{2}{r-2}[(r-1)(1-\mathrm{e}^{-2z})+\mathrm{e}^{-rz}-1] \tag{19}$$

From this relationship, we can determine the value of parameter z. Fig. 1 gives the relationship between x and z with various r values. The variation range of z values monotonously decreases with the increase in r. In the limitation of $r=\infty$, which trends to result in the product of perfect dendritic polymers, the maximum z is ln 2/2 at the full conversion of A group. While it trends to infinite if $r=0$, which represents a linear polymerization.

The reaction time, t, is related to the parameter z and it is given by Eqs. (12) and (18):

$$t=\frac{1}{k_T M_0}\int_0^z\frac{(r-2)\mathrm{d}u}{(r-1)(2\,\mathrm{e}^{-2u}-1)+1-2\,\mathrm{e}^{-ru}} \tag{20}$$

This equation, together with Eq. (19), gives a relation between the conversion of A groups, x, and a reduced time, $\tau=k_T M_0 t$, which is shown in Fig. 2. Obviously, the reaction becomes faster and faster with increasing r.

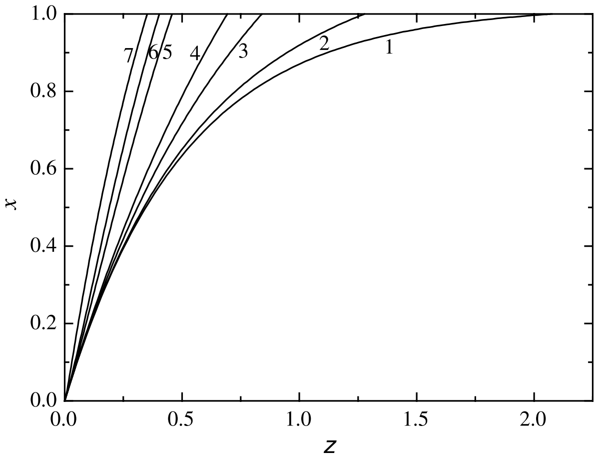

Fig. 1. Relationship of conversion of A groups, x, vs parameter z for AB_2 type polycondensation with various reactivity ratios, $r=k_L/k_T$. (1) $r=0.01$; (2) $r=0.1$; (3) $r=0.5$; (4) $r=1$; (5) $r=5$; (6) $r=10$; (7) $r=100$.

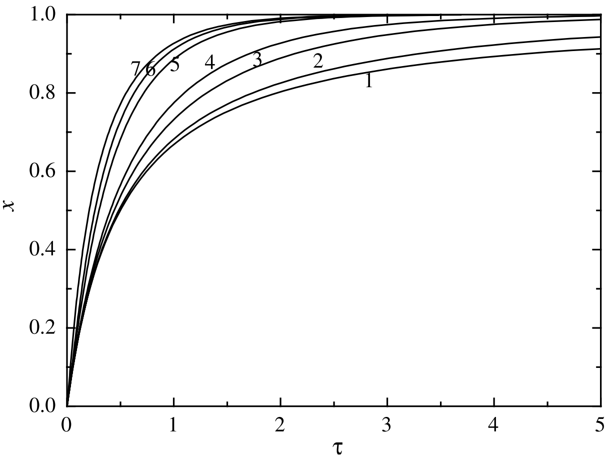

Fig. 2. Plot of conversion of A groups, x, vs reduced time, $\tau = k_T M_0 t$, for AB_2 type polycondensation with various reactivity ratios. Also see the legend of Fig. 1.

Eq. (11) also can be transformed into the following one:

$$\frac{dP_{n,l}}{dz} = \frac{1}{2A}\left\{ r(l+1)\sum_{i,j} P_{i,j}P_{n-i,l+1-j} + (n-l+3) \times \sum_{i,j} P_{i,j}P_{n-i,l-1-j} \right\} - \left\{ (r-1)l + n + 1 - \frac{d\ln A}{dz} \right\} P_{n,l} \tag{21}$$

Correspondingly, the initial conditions are transformed as:

$$P_{1,0}(z=0) = M_0, \qquad P_{n>1,l\geq 0}(z=0) = 0$$

3. Distribution function and average degree of polymerization

After a laborious derivation, we can get the distribution function of concentration from Eq. (21):

$$P_{n,l} = \frac{1+(-1)^{n-l+1}}{2} \frac{2^l (n-1)!}{l!\left(\frac{n-l-1}{2}\right)!\left(\frac{n-l+1}{2}\right)!} A \left[\frac{e^{(r-2)z}-1}{r-2}\right]^l \times \left[\frac{2(e^{-rz}-1) - r(e^{-2z}-1)}{r-2}\right]^{(n-l-1)/2} e^{-[(r-1)l+n+1]z} \tag{22}$$

In order to guarantee that $(n-l)$ is odd for the species in the reaction system, we introduce the factor $[1+(-1)^{n-l+1}]/2$ in Eq. (22).

The zero and the first moments of the distribution function were expressed by Eqs. (3) and (4), respectively, and the second moment reads

$$\sum_{n,l} n^2 P_{n,l} = \frac{(r-2)M_0}{[(1-r)(1-2e^{-2z}) + 1 - 2e^{-rz}]^2} \times \left\{ 2 - r + 2(3r-4)e^{-2z} - 4e^{-rz} - \frac{4}{r-2}[e^{-rz} - (r-1)e^{-2z}]^2 \right\} \tag{23}$$

Now we can give the expressions of the number-, the weight-average degrees of polymerization, and the dispersity:

$$\bar{P}_n = \frac{\sum_{n,l} nP_{n,l}}{\sum_{n,l} P_{n,l}} = \frac{r-2}{(1-r)(1-2e^{-2z}) + 1 - 2e^{-rz}} = \frac{1}{1-x} \tag{24}$$

$$\bar{P}_w = \frac{\sum_{n,l} n^2 P_{n,l}}{\sum_{n,l} nP_{n,l}} = \frac{(r-2)\left\{2-r+2(3r-4)e^{-2z} - 4e^{-rz} - \frac{4}{r-2}[e^{-rz}-(r-1)e^{-2z}]^2\right\}}{[(1-r)(1-2e^{-2z})+1-2e^{-rz}]^2} \tag{25}$$

$$D = \frac{\bar{P}_w}{\bar{P}_n} = \frac{2-r+2(3r-4)e^{-2z} - 4e^{-rz} - \frac{4}{r-2}[e^{-rz}-(r-1)e^{-2z}]^2}{\left[(1-r)(1-2e^{-2z})+1-2e^{-rz}\right]^2} \tag{26}$$

In experimental procedure, the low molecular weight materials, such as the residual monomer, are usually separated from the polymer samples by precipitation. The low molecular weight part of the products plays an important role for the dispersity. If the contribution of unreacted monomer, $P_{1,0}$, is excluded from the various moments, the expressions of number- and weight-average degrees of polymerization can be written as

$$\bar{P}'_n = \frac{\sum_{n,l} nP_{n,l} - P_{1,0}}{\sum_{n,l} P_{n,l} - P_{1,0}} \tag{27}$$

$$\bar{P}'_w = \frac{\sum_{n,l} n^2 P_{n,l} - P_{1,0}}{\sum_{n,l} nP_{n,l} - P_{1,0}} \tag{28}$$

and

$$D' = \frac{\bar{P}'_w}{\bar{P}'_n} \tag{29}$$

with

$$P_{1,0} = \frac{M_0}{r-2}[(1-r)(1-2e^{-2z}) + 1 - 2e^{-rz}]e^{-2z} \tag{30}$$

From the distribution function of Eq. (22), we can extract the number- and weight-distribution function of the hyperbranched polymers formed by AB_2-type polycondensation:

$$M_n = \frac{\sum_l P_{n,l}}{\sum_{n,l} P_{n,l}} \tag{31}$$

$$W_n = \frac{n\sum_l P_{n,l}}{\sum_{n,l} nP_{n,l}} \tag{32}$$

Fig. 3(a) and (b) indicate the weight-distributions for the various values of r at two defined conversions of A group, 0.95 and 0.99, respectively. It is seen that the weight-distributions show a maximum only at $r < 1$, while the number-distributions (not given in figure) decrease monotonously with n in this case.

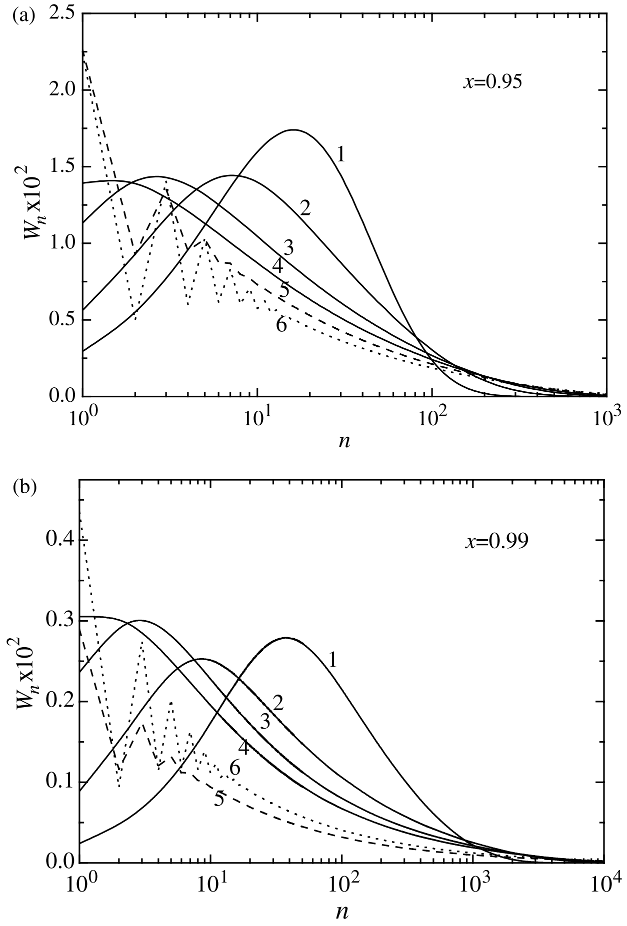

Fig. 3. Semilogarithmic weight distribution of hyperbranched polymers generated from AB_2 type polycondensation with various reactivity ratios at two specified conversions. (a) $x=0.95$; (b) $x=0.99$. Also see the legend of Fig. 1.

For $r>1$, when the polymerization system trends to form dendritic polymers, the distributions curves show the property of odd–even oscillation for the low degree of polymerization. This is due to the fact that the second B group reacts as soon as the first B group reacts in the same structural unit if r is large and the concentration of these molecules with linear units is very low. Therefore, the concentration of these molecules with even degree of polymerization is low, which includes one linear unit at least.

Figs. 4 and 5 are the number- and weight-average degree of polymerization as functions of monomer conversion, respectively. $\bar{P}_n(=1/(1-x))$ is independent of the ratio of reactivities, r. However, at any specified monomer conversion, both weight-average degree of polymerization and $\bar{P}'_n$ increase with increasing r. The larger the r is, the faster the average degree of polymerization trends to infinite. This also can be shown clearly by the relationship between average degree of polymerization and the reduced time, such as Fig. 6. The relationships between weight-average degree of polymerization and the conversion also were indicated by pictures in Ref. [24]. However, the effect of residual monomer was not considered there.

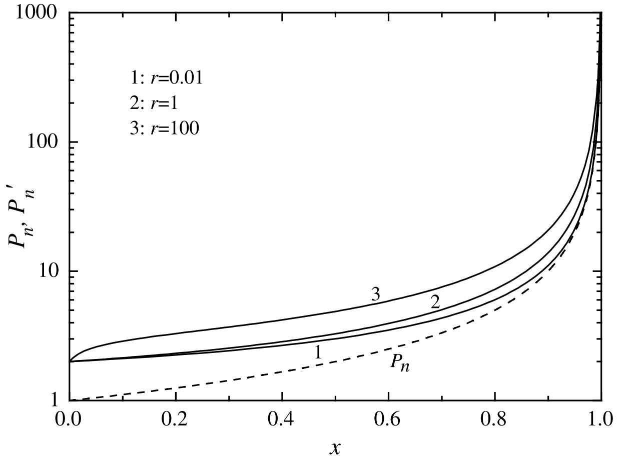

Fig. 4. Dependence of number-average degree of polymerization on conversion of A groups for AB_2 polycondensation system including monomers (dashed lines, which is independent of values of r) and excluding monomers (solid lines) with various reactivity ratios. (1) $r=0.01$; (2) $r=1$; (3) $r=100$.

In order to explain further the relationship between average degree of polymerization and the conversion, we derive the expressions for two special cases, $r=0$ and ∞, as follows:

$$\lim_{r\to 0} \bar{P}'_n = \frac{2-x}{1-x} \tag{33}$$

$$\lim_{r\to \infty} \bar{P}'_n = \frac{3-x}{1-x} \tag{34}$$

$$\lim_{r\to 0} \bar{P}_w = \frac{1+x}{1-x} \tag{35}$$

$$\lim_{r\to \infty} \bar{P}_w = \frac{1+x-x^2}{(1-x)^2} \tag{36}$$

$$\lim_{r\to 0} \bar{P}'_w = \frac{4-3x+x^2}{(1-x)(2-x)} \tag{37}$$

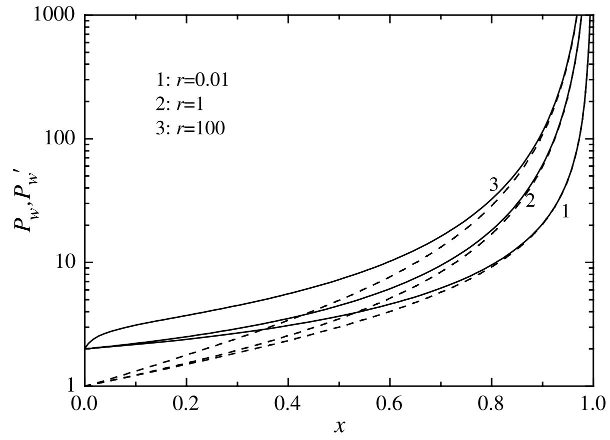

Fig. 5. Dependence of weight-average degree of polymerization on conversion of A groups for AB_2 polycondensation system including monomers (dashed lines) and excluding monomers (solid lines) with various reactivity ratios. (1) $r=0.01$; (2) $r=1$; (3) $r=100$.

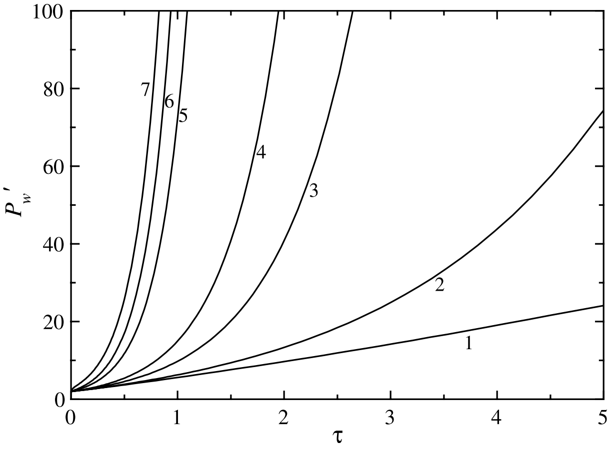

Fig. 6. Plot of weight-average degree of polymerization without including monomers vs reduced time, $\tau = k_T M_0 t$, for AB_2 type polycondensation with various reactivity ratios. Also see the legend of Fig. 1.

$$\lim_{r\to\infty} \bar{P}_w' = \frac{9-11x+5x^2-x^3}{(1-x)^2(3-x)} \tag{38}$$

The dependence of degree of polymerization on reactivities at specified conversion for AB_2 type polycondensation is different from that for SCVP of AB* monomers. From Fig. 8 or Fig. A3–1 in supporting information of Ref. [26], we can learn that $\bar{P}_n'$ quickly increases with increasing r at defined conversion for SCVP, where $r = k_A/k_B$. However, the enhancement of $\bar{P}_n'$, $\bar{P}_w$ and $\bar{P}_w'$ is negligible only if $r > 100$ for the AB_2 type polycondensation considered in this work. The given relationship by Eqs. (34), (36) and (38) for $r = \infty$ almost coincide with the corresponding curve 3 in Figs. 4 and 5, respectively. At the same conversion, the average degree of polymerization of AB_2 polycondensation is much smaller than that of SCVP. $\bar{P}_n'$ converges to 201 ($x = 0.99$) and 41 ($x = 0.95$) at infinite r for the AB_2 polycondensation, while it already exceeds 4000 ($x = 0.95$) and 10000 ($x = 0.99$) in Fig. 8 of Ref. [26] for SCVP with $r < 10^5$.

A plot of dispersity vs conversion of A groups for the various values of r is given in Fig. 7. The dispersity does not exceed 10 in the range of $x < 0.95$ for these excluding the residual monomers (solid curves). Then it increases quickly and reaches infinite at the full conversion ($x = 1$) for $r > 0$. The dispersity is 2 at the full conversion for a linear polymerization with $r = 0$. In the two special cases for $r = 0$ and ∞, the dispersity can be expressed as follows:

$$\lim_{r\to 0} D = 1 + x \tag{39}$$

$$\lim_{r\to 0} D = \frac{1+x-x^2}{1-x} \tag{40}$$

$$\lim_{r\to 0} D' = \frac{4-3x+x^2}{(2-x)^2} \tag{41}$$

$$\lim_{r\to 0} D' = \frac{9-11x+5x^2-x^3}{(1-x)(3-x)^2} \tag{42}$$

Without excluding the residual monomers, the dispersity also was shown in the work of Galina et al. [24]. For comparison, a curve including the residual monomers at $r = 100$ is also printed in Fig. 7 (dashed line). At any finite conversion, the dispersity including the residual monomer is higher than the one excluding them.

Shown in Fig. 8 is the dependence of dispersity on r at two specified monomer conversions. At $x = 0.99$, D and D' increase monotonously with increasing r from 1.99 and 1.97 to 100.99 and 50.50 with the variation in r from 0 to ∞, respectively. However, enhancement of dispersity is moderate with the further increase of r. The corresponding values of dispersity at $r = 100$ are already very close to these values for infinite r. Similar to the average degree of polymerization, the dispersity of AB_2 type polycondensation is much smaller than that of SCVP of AB* monomers at the same conversion of A groups. For the latter, D' exceeds 400 at $x = 0.99$ and $r = 100$. Moreover, the dispersity increase with increasing r and can reach very large values at the defined conversion for SCVP [26].

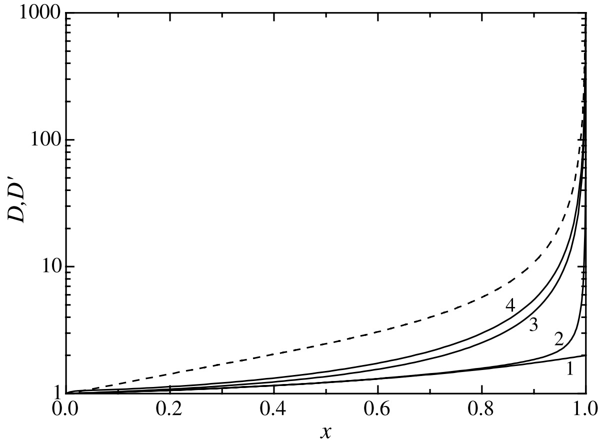

Fig. 7. Dependence of dispersity on conversion of A groups for AB_2 polycondensation system including monomers (dashed curve, $r = 100$) and excluding monomers (solid curves), (1) $r = 0$; (2) $r = 0.01$; (3) $r = 1$; (4) $r = 100$.

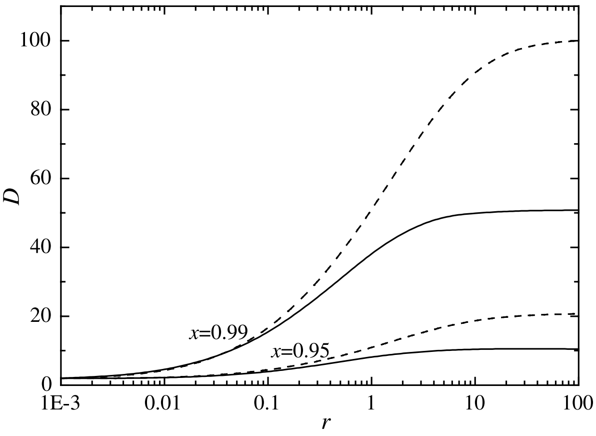

Fig. 8. Dependence of dispersity on reactivity ratios for AB_2 polycondensation system including monomers (dash lines) and excluding monomers (solid lines) with the defined conversion of A groups. (1) $x = 0.95$; (2) $x = 0.99$.

4. Conclusions

By the explicit expression of the distribution function derived in this paper for AB_2 type polycondensation, the molecular parameters can be calculated easily, taking account of the substitution effect, i.e. the difference of the reactivity between a linear B group and a terminal one. The average molecular weight increases with the increase of the reactivity ratio, r, at any specified conversion. In comparison with the SCVP of AB* monomers, however, this variation of average molecular weight with r is moderate. When reaction comes to completion, the weight-distribution shows a maximum at $r < 1$. The corresponding degree of polymerization of the peak decreases with increasing r. The average degree of polymerization of AB_2 type polycondensation is much smaller than that of SCVP at any finite conversion. The dispersity shows a fast increase with the variation of r from 0.1 to 10. At other ranges, the effect of the variation in r on dispersity is moderate. However, for a high value of $r(>10)$, the dispersity including residual monomer is almost twice as broad as that excluding residual monomers. Only if $r>0$, the dispersity trends to infinite at $x=1$ for both AB_2 type condensation and SCVP of AB* monomers. However, at a finite value of conversion, the dispersity for the system of AB_2 type condensation is much smaller than that for SCVP of AB* monomers.

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