Kinetic Model of Hyperbranched Polymers Formed by Self-Condensing Vinyl or Self-Condensing Ring-Opening Polymerization of AB Monomers Activated by Stimuli with Different Reactivities

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ABSTRACT: Hyperbranched polymers (HBPs) formed by the self-condensing vinyl polymerization (SCVP) or self-condensing ring-opening polymerization (SCROP) of monomer AB activated by stimuli with various reactivities were investigated by the generating function method. Two different cases were discussed: in case I, the concentration of the stimulus decayed during the activating reaction, and in case II, the stimulus acted as a catalyst to activate the monomer AB, and the change in stimulus concentration was neglected. The reduced number- and weight-average degree of polymerization ($\overline{DP}_n^*$ and $\overline{DP}_w^*$) and degree of branching (DB) of the HBPs were found to depend not only on the mole ratio of stimulus to monomer AB (λ) but also on the reactivity ratio of the stimulus (β). The $\overline{DP}_n^*$, $\overline{DP}_w^*$ and polydispersity index of the reduced degree of polymerization increased with decreasing reactivity of the stimulus. In case II, when $\lambda\beta > 1$, there were only a few influences on the average degree of polymerization by $\lambda\beta$, and the results were similar to those of case I. However, when $\lambda\beta < 1$, the degree of polymerization differed significantly between the two cases. The maximum degree of branching of about 0.5 was obtained with near full conversion of A, and the degree of branching depended on the amount and reactivity ratio of the stimulus.

Introduction

Highly branched polymers have unique dendritic architectures, a large number of branching points and can have functional end groups. Hyperbranched polymers (HBPs) contain more random branched architectures with some linear structures and a less regular structure than dendrimers, which exhibit repetitive branching in the manner of a tree and comprise a perfectly regular structure with a well-defined shape and size.[1-6] HBPs can be prepared via a simple one-pot stepwise polymerization of AB_g-type monomers, in which $g > 1$,[7,8] or by self-condensing vinyl polymerization (SCVP), which involves monomer AB* consisting of a vinyl group A and an initiating group B*.[9] The chain reaction in SCVP results from the active B* reacting with the double bond A on another monomer; a dimer is then formed with one group A and two active groups, B* and A*. The new active center A* can also react with the double bond A on any other molecule and produce a branch point on the resulting larger molecule. Consequently, hyperbranched polymers can be prepared via further SCVP reaction.

Many theoretical models have been reported to express the molecular parameters of hyperbranched polymers: the molecular size distribution, the average degree of polymerization (DP), and the degree of branching (DB).[10-15] In a previous work, we used the generating function method to investigate the effects of the different reactivities of trifunctional core molecules and the feed rate of a semibatch reactor on the molecular structures of hyperbranched polymers.[16,17] Actually, inimer AB* could be formed from monomer AB, in which the A group contains a double bond and B is a pendant group that can be transformed into an initiating center by an external stimulus, S. In those

theoretical investigations, the activation reaction is assumed to be very fast and to reach completion in a short period of time. If the initial mole ratio of stimulus S to monomer AB is equal to or larger than one, the residual of the unreacted AB is neglected during calculation. Self-condensing ring-opening polymerization (SCROP) and SCVP based on metal complex-mediated atom transfer radical polymerization (ATRP) were also intensively studied.[18-21] For example, branched polyether can be synthesized via cationic polymerization of 3-methyl-3-(hydroxymethyl)oxetane (MHO) activated by the catalyst $BF_3 \cdot OEt_2$. The self-condensing vinyl polymerization of 4-(chloromethyl)styrene using metal-catalyzed living radical polymerization catalyzed by the complex CuCl/2,2*-bipyridyl has been reported. The molecular structures of the resulting polymers, such as the degree of branching and the fraction of linear units, were observed to depend on either the monomer-to-catalyst ratio or the reaction temperature. Therefore, Zhou and Yan suggested a kinetic model for the influences of nonequal molar concentrations of stimulus and monomer in self-condensing vinyl polymerization.[22,23] If the concentration of stimulus is less than that of the monomer and the activation reaction is assumed to reach completion instantaneously, the polymerization starts from a mixture of monomer AB and inimers AB*. These authors found that the initial ratio of residual monomer and inimer has a significant influence on the molecular parameters of the hyperbranched polymers. Because it was found that the molecular structures of the hyperbranched polymers are also dependent on the reaction temperature in SCROP,[19] the reaction rate of the stimulus S to monomer AB is believed to have a significant effect on the molecular parameters of the HBPs prepared by self-condensing vinyl or ring-opening polymerization.

This study further expands the generating function method to investigate the influences of the reactivity of the stimulus S with group B in SCVP or SCROP reactions. In case I, the stimulus S is assumed to be deactivated after initiating group B. In contrast, in
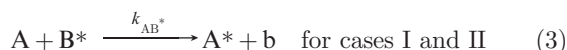
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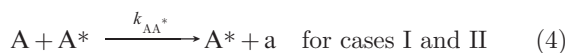
Table 1. Parameters b_{ij} and k_i

Case I:					**Case I:**			
b_{11}	b_{12}	b_{13}	k_1		1	2	3	k_{SB}
b_{21}	b_{22}	b_{23}	k_2		1	5	6	k_{SB}
b_{31}	b_{32}	b_{33}	k_3		1	8	9	k_{SB}
Case II:					**Case II:**			
b_{11} b_{12} b_{13} b_{14}	k_1				1 2	1	3	k_{SB}
b_{21} b_{22} b_{23} b_{24}	k_2				1 5	1	6	k_{SB}
b_{31} b_{32} b_{33} b_{34}	k_3				1 8	1	9	k_{SB}
Cases I and II:					**Cases I and II:**			
b_{41} b_{42} b_{43} b_{44}	k_4				2 3	5	4	k_{AB*}
b_{51} b_{52} b_{53} b_{54}	k_5				2 6	5	7	k_{AB*}
b_{61} b_{62} b_{63} b_{64}	k_6		=		2 9	5	10	k_{AB*}
b_{71} b_{72} b_{73} b_{74}	k_7				3 3	6	4	k_{AB*}
b_{81} b_{82} b_{83} b_{84}	k_8				3 6	6	7	k_{AB*}
b_{91} b_{92} b_{93} b_{94}	k_9				3 9	6	10	k_{AB*}
$b_{10,1}$ $b_{10,2}$ $b_{10,3}$ $b_{10,4}$	k_{10}				4 3	7	4	k_{AB*}
$b_{11,1}$ $b_{11,2}$ $b_{11,3}$ $b_{11,4}$	k_{11}				4 6	7	7	k_{AB*}
$b_{12,1}$ $b_{12,2}$ $b_{12,3}$ $b_{12,4}$	k_{12}				4 9	7	10	k_{AB*}
$b_{13,1}$ $b_{13,2}$ $b_{13,3}$ $b_{13,4}$	k_{13}				2 5	5	8	k_{AA*}
$b_{14,1}$ $b_{14,2}$ $b_{14,3}$ $b_{14,4}$	k_{14}				2 6	5	9	k_{AA*}
$b_{15,1}$ $b_{15,2}$ $b_{15,3}$ $b_{15,4}$	k_{15}				2 7	5	10	k_{AA*}
$b_{16,1}$ $b_{16,2}$ $b_{16,3}$ $b_{16,4}$	k_{16}				3 5	6	8	k_{AA*}
$b_{17,1}$ $b_{17,2}$ $b_{17,3}$ $b_{17,4}$	k_{17}				3 6	6	9	k_{AA*}
$b_{18,1}$ $b_{18,2}$ $b_{18,3}$ $b_{18,4}$	k_{18}				3 7	6	10	k_{AA*}
$b_{19,1}$ $b_{19,2}$ $b_{19,3}$ $b_{19,4}$	k_{19}				4 5	7	8	k_{AA*}
$b_{20,1}$ $b_{20,2}$ $b_{20,3}$ $b_{20,4}$	k_{20}				4 6	7	9	k_{AA*}
$b_{21,1}$ $b_{21,2}$ $b_{21,3}$ $b_{21,4}$	k_{21}				4 7	7	10	k_{AA*}

case II, the stimulus maintains its activity, so the stimulus concentration is assumed to remain constant during polymerization. The effects of the reactivity and the mole ratio of the stimulus on the degree of polymerization and degree of branching of the HBPs will also be discussed.

Kinetic Model of Self-Condensing Vinyl Polymerization of Monomers AB. Both self-condensing vinyl and ring-opening polymerization involve monomers AB, in which group A is a double bond or a heteroring group. A stimulus, S, can transform group B into an initiating center B*, that is, the AB* inimer can be formed by the reaction of the AB monomer with S. The chain reaction then occurs with the active B* reacting with group A of monomer AB or with another inimer AB*, forming a dimer Ab-A*B or Ab-A*B*. The new active center A* can also react with group A of any other molecule and form a branch point on the resulting larger molecule. Consequently, further polymerization in this way will result in the synthesis of hyperbranched polymers. Two possibilities will be discussed. First, in case I, the stimulus S loses its activity after initiating group B. In case II, the activity of the stimulus can be preserved, and the stimulus concentration is assumed to remain constant during polymerization. The mechanisms of the initiation and addition reactions among the stimulus and functional groups A, B, A*, and B* can be described as the follows:
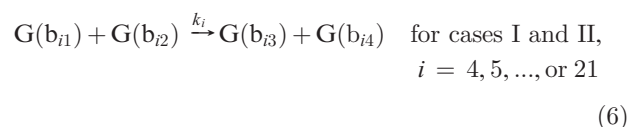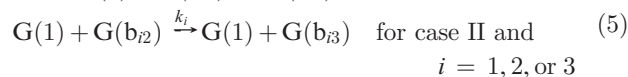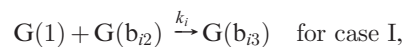
$$S + B \xrightarrow{k_{SB}} B* \quad \text{for case I} \tag{1}$$

$$S + B \xrightarrow{k_{SB}} S + B* \quad \text{for case II} \tag{2}$$

$$A + B* \xrightarrow{k_{AB*}} A* + b \quad \text{for cases I and II} \tag{3}$$

and

$$A + A* \xrightarrow{k_{AA*}} A* + a \quad \text{for cases I and II} \tag{4}$$

where b is the product group of B*, and group A* can react with group A and becomes group a.

We assume that the reaction is bimolecular and that no intramolecular reactions occur during polymerization, and

k_{SB}, k_{AB*}, and k_{AA*} are the reaction rate constants. The reactions between various structural units can be expressed in the following kinetic scheme:

$$G(1) + G(b_{i2}) \xrightarrow{k_i} G(b_{i3}) \quad \text{for case I,}$$

$$G(1) + G(b_{i2}) \xrightarrow{k_i} G(1) + G(b_{i3}) \quad \text{for case II and} \tag{5}$$
$$i = 1, 2, \text{ or } 3$$

$$G(b_{i1}) + G(b_{i2}) \xrightarrow{k_i} G(b_{i3}) + G(b_{i4}) \quad \text{for cases I and II,}$$
$$i = 4, 5, ..., \text{ or } 21 \tag{6}$$

where

$$G(1) = S \text{ (stimulus)}$$
$$G(2) = AB \text{ (monomer)}$$
$$G(3) = AB* \text{ (inimer)}$$
$$G(4) = Ab{\sim}$$
$$G(5) = {\sim}A*B$$
$$G(6) = {\sim}A*B*$$
$$G(7) = {\sim}A*b{\sim}$$
$$G(8) = {\sim}\overset{a}{\underset{\wr}{}}{}^{B}$$
$$G(9) = {\sim}\overset{a}{\underset{\wr}{}}{}^{B*}$$
$$G(10) = {\sim}\overset{ab}{\underset{\wr}{}}{\sim}$$

and

$$\beta = k_{SB}/k_{AB*} \tag{7}$$

in which β is assumed to be a constant and independent of the extent of reaction. Table 1 presents the corresponding parameters b_{ij} and k_i.

Furthermore, a vector **E** is defined to characterize the molecule $\langle E \rangle$:

$$\mathbf{E} = (e_1, e_2, e_3, e_4, e_5, e_6, e_7, e_8, e_9, e_{10}, e_w) \tag{8}$$

where e_J represents the number of structural units $G(J)$ on a molecule $\langle E \rangle$, and e_w, equal to e_{11}, is the molecular weight of the molecule $\langle E \rangle$. For example, $\mathbf{E} = (0, 1, 0, 0, 0, 0, 0, 0, 0, 0, W(AB))$ denotes monomer AB, and $W(AB)$ is the molecular weight of this monomer; the molecule Ab−A*B formed by combining AB* and AB can be specified by $\mathbf{E} = (0, 0, 0, 1, 1, 0, 0, 0, 0, 0, 2W(AB))$ when no condensates are produced during polymerization.

According to mean-field theory, the effects of configuration and conformation are not considered in the calculation. The effects of intramolecular cyclization on the structures of the hyperbranched polymers are also important for non-linear polymerization systems.[24−26] In this study, we focus on the reactivity and mole ratio of the stimulus and assume that all reactions are chemically controlled and that there are no intramolecular reactions.[27−29]
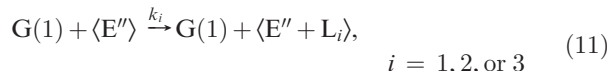
In case I, the molecule $\langle E'' \rangle$ with group B can be activated by the stimulus S, $G(1)$:

$$G(1) + \langle E'' \rangle \xrightarrow{k_i} \langle E'' + L_i \rangle$$
$$i = 1, 2, \text{ or } 3 \tag{9}$$
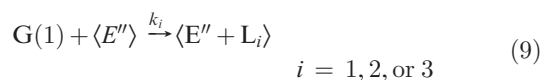
where

$$L_1 = (-1, -1, 1, 0, 0, 0, 0, 0, 0, 0, 0)$$
$$L_2 = (-1, 0, 0, 0, -1, 1, 0, 0, 0, 0, 0) \qquad (10)$$
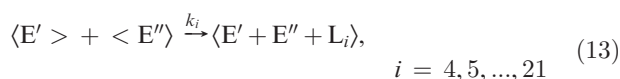$$L_3 = (-1, 0, 0, 0, 0, 0, 0, -1, 1, 0, 0)$$

On the other hand, in case II, the molecule $\langle E'' \rangle$ with group B can be stimulated by a catalyst S, G(1), and the catalyst S does not disappear during polymerization:

$$G(1) + \langle E'' \rangle \xrightarrow{k_i} G(1) + \langle E'' + L_i \rangle,$$
$$i = 1, 2, \text{ or } 3 \qquad (11)$$

where

$$L_1 = (0, -1, 1, 0, 0, 0, 0, 0, 0, 0, 0)$$
$$L_2 = (0, 0, 0, 0, -1, 1, 0, 0, 0, 0, 0) \qquad (12)$$
$$L_3 = (0, 0, 0, 0, 0, 0, 0, -1, 1, 0, 0)$$

Furthermore, the reactions between molecules are

$$\langle E' > + < E'' \rangle \xrightarrow{k_i} \langle E' + E'' + L_i \rangle,$$
$$i = 4, 5, ..., 21 \qquad (13)$$

where $\langle E' + E'' + L_i \rangle$ is the molecule formed by combining $\langle E' \rangle$ with $\langle E'' \rangle$ in the ith reaction, and
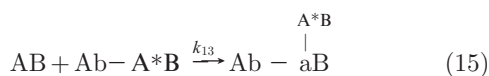
$$L_i = (l_1, l_2, ..., l_{10}, 0)$$
$$l_J = -\delta(b_{i1}, J) - \delta(b_{i2}, J) + \delta(b_{i3}, J) + \delta(b_{i4}, J), \qquad (14)$$
$$J = 1, 2, ..., 10$$

in which $\delta(b_{ij}, J)$ is Kronecker delta such that

$$\delta(b_{ij}, J) = 1, \quad \text{for } b_{ij} = J, \text{ and}$$

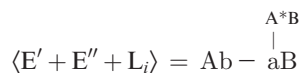$$\delta(b_{ij}, J) = 0, \quad \text{for } b_{ij} \neq J$$

For example, a monomer AB reacts with another molecule Ab−A*B as follows:

$$AB + Ab-A*B \xrightarrow{k_{13}} Ab - \overset{\overset{\displaystyle A*B}{\displaystyle |}}{aB} \qquad (15)$$

then

$$\langle E' \rangle = AB$$

$$\langle E'' \rangle = Ab-A*B*$$

$$\langle E' + E'' + L_i \rangle = Ab - \overset{\overset{\displaystyle A*B}{\displaystyle |}}{aB}$$

$$E' = (0, 1, 0, 0, 0, 0, 0, 0, 0, 0, W(AB))$$

$$E'' = (0, 0, 0, 1, 1, 0, 0, 0, 0, 0, 2W(AB))$$

$$L_{13} = (0, -1, 0, 0, 0, 0, 0, +1, 0, 0, 0)$$

$$E' + E'' + L_3 = (0, 0, 0, 1, 1, 0, 0, 1, 0, 0, 3W(AB))$$

$$k_{13} = k_{AA*}$$

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

$$[E] = N(E)/N(AB)_o \qquad (16)$$

$$k_i' = k_i V_o/(k_{AB*} V) \qquad (17)$$

$$\tau = t k_o N(AB)_o / V_o \qquad (18)$$

where $N(E)$ is the number of isomers of the molecule $\langle E \rangle$, V is the volume of the reaction system, V_o is the initial volume of the reaction system, and t is the reaction time.

If the change in the reaction volume is negligible, then $k'_{AB*} = 1$. According to eqs 9−14, the rate equations of the isomers can be written as,

$$\frac{d[E]}{d\tau} = \sum_{i=1}^{21} k_i' \{ \sum_{E' + E'' + L_i = E} ([E'][E''] p_{i1}' p_{i2}'') $$
$$- [E] p_{i1} \sum_{\text{all } E'''} [E'''] p_{i2}''' - [E] p_{i2} \sum_{\text{all } E'''} [E'''] p_{i1}''' \} \qquad (19)$$

where $\sum_{\text{all E}}$ denotes the sum over all possible values of vector $\mathbf{E}$, and $p_{ij} = e_J$ for $b_{ij} = J$. The positive and negative terms on the right side of eq 19 give the total rates of appearance and disappearance of the isomer $\langle E \rangle$, respectively. Equation 19 cannot be solved directly, but it can be transformed into finite ordinary differential equations using a generating function.[30,31] The average degree of polymerization and the fractions of the structural units, G(I), can be calculated from the generating function using the previously described algorithm.[16,17]

Results and Discussion

First, in case I, group B is activated by the stimulus S, which becomes deactivated or disappears after the reaction. Figure 1 shows the profiles of the reduced weight-average degree of polymerization, $\overline{DP}_w^*$. The term "reduced average degree of polymerization" denotes the residual S, and AB and AB* are excluded in the calculation of average degree of polymerization, which is performed by setting the molecular weight of AB to one, and that of stimulus S to zero.[16,17] The growth of hyperbranched polymers (HBPs) was found to depend on the reactivity ratio of k_{SB} to k_{AB*}, β, according to eqs 1 and 3. With a lower value of β, few AB monomers are immediately initiated by the stimulus, and the HBPs grow quickly. On the contrary, if monomers AB can be activated by S in a short time under an equal mole ratio of S to AB, $\lambda = 1$, the major portion of AB becomes AB*. This results in a lower average degree of polymerization of HBPs at any conversion of A. For example, when $\beta = 100$, the profiles of the average degree of polymerization are very close to the results calculated by Zhou and Yan.[22] They assume that the activation reaction in eq 1 reaches completion instantaneously and that all the AB* species are formed at the beginning of the reaction.

Figure 2 illustrates the effects of the ratio of stimulus S, λ, on the degree of polymerization of HBPs. At reactivity ratio $\beta = 1$, the reduced weight-average degree of polymerization decreases with an increasing ratio of stimulus S. Under lower values of λ such as 0.01 and 0.1, the profiles of $\overline{DP}_w^*$ are almost the same as those calculated by the Zhou−Yan model. This implies that the assumption proposed by that model is reasonable at low amounts of the stimulus S. However, at $\lambda = 1$, the average degrees of polymerization proposed by the Zhou−Yan model are lower than those determined when considering the limit of the
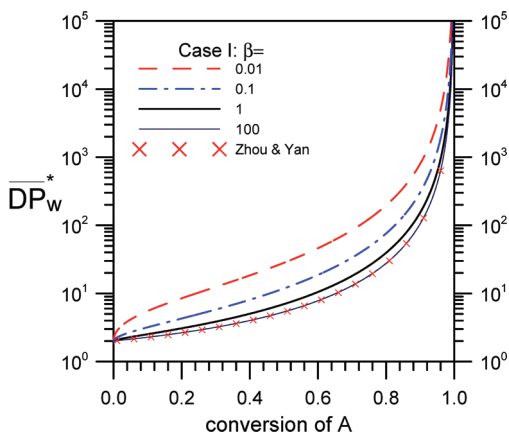
Figure 1. Reduced weight-average degree of polymerization versus conversion of A groups under various stimulus reactivities (case I, the mole ratio of stimulus to monomer AB: $\lambda = 1$).
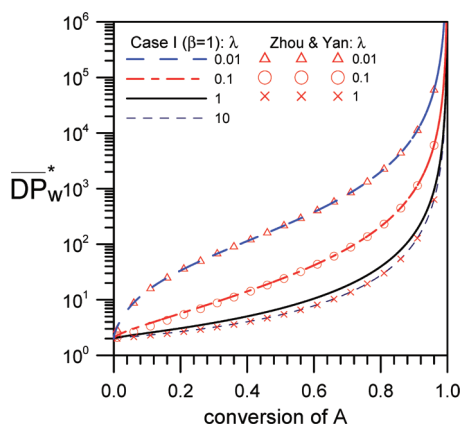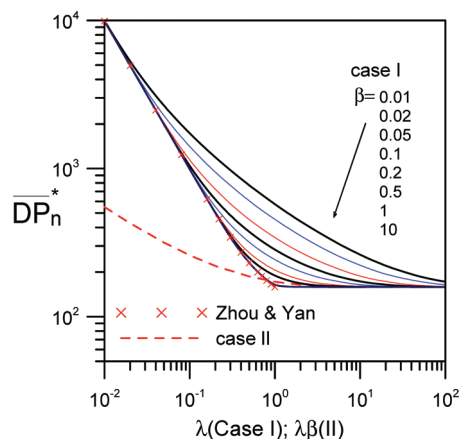

Figure 2. Reduced weight-average degree of polymerization versus conversion of A groups under various amounts of stimulus (case I, $\beta = 1$).

Figure 3. Dependence of the reduced number-average degree of polymerization of hyperbranched polymers on the mole ratio and reactivity of the stimulus at the conversion of $A = 0.99$.

Figure 4. Dependence of the reduced weight-average degree of polymerization of hyperbranched polymers on the mole ratio and reactivity of the stimulus at the conversion of $A = 0.99$.
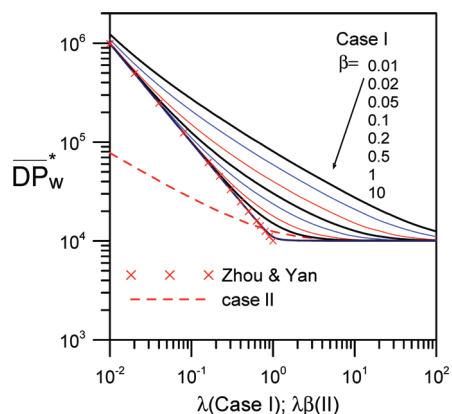
activating reaction rate. When the ratio of the stimulus is increased to 10, the results are close to the values determined by the Zhou–Yan model at $\lambda = 1$. That is, although the reaction rate of the activation is limited at $\beta = 1$, the 10-fold excess of stimulus results in the rapid activation of the AB monomers.

Figures 3 and 4 plot the dependence of the average degrees of polymerization of hyperbranched polymers on λ and β at 0.99 conversion of A. The addition of a low content of stimulus such as $\lambda = 0.01$ results in a high $\overline{DP}_n^*$ of about 10 000, and $\overline{DP}_n^*$ decreases to about 170 at high values of λ such as 100. At low or high ratios of stimulus, the number- and weight-average degrees of polymerization are little affected by the reactivity ratio β. In contrast, near the equal ratio of stimulus to monomer AB, $\lambda = 1$, the degree of polymerization of HBPs decreases with increasing β. If the reactivity ratio β is 10, the $\overline{DP}_n^*$ and $\overline{DP}_w^*$ are higher at lower λ. When λ is larger than one, $\overline{DP}_n^*$ and $\overline{DP}_w^*$ tend to be constant values of around 160 and 10 000, respectively.

Figure 5 shows the dependence of the reduced polydispersity index (PDI*) of the degree of polymerization on λ and β at the conversion of 0.99. At the same ratio of λ, the molecular weight distribution of the hyperbranched polymers becomes narrower when the stimulus has a higher reactivity. When β is lower than one, 0.01–0.5, the PDI first increases with an increasing amount of stimulus and then reaches a maximum, and the molecular weight distribution becomes narrower by adding more of the stimulus. At a high reactivity ratio of $\beta = 10$ and a low λ of 0.01–0.1, the PDI reaches a high plateau of 100. With an increasing stimulus amount, the PDI decreases to 67 at $\lambda = 1$ and then reaches a low plateau region after a λ of about 2. Moreover, as shown in Figures 3–5, the results calculated for case I at a high reactivity ratio of $\beta = 10$ are very close to those of the Zhou–Yan model.

The parameter degree of branching (DB) was suggested by Holter and Frey to characterize the structure of hyperbranched polymers.[32,33] DB is based on the actual number over the maximum possible number of dendritic units:

$$DB = \frac{2ND}{2ND + NL} = \frac{G(10)}{G(10) + 0.5[G(7) + G(8) + G(9)]} \quad (20)$$

where ND denotes the number of dendritic units and NL is the number of linear HBP units. For example, at $\beta = 1$ in Figure 6, the growth of the dendritic units increases with the addition of the stimulus S, thus the DB increases with λ. The DB reaches a maximum of about 0.50 at $\lambda = 0.8$, and then declines slightly to 0.46 above λ values of 1.5; later, it reaches a plateau and remains unchanged by additional stimulus. Increasing the reactivity ratio β, the highest degree of branching appears at lower ratios of λ. At $\beta = 10$, the maximum of DB is 0.5 at $\lambda = 0.627$, and this result is consistent with the report of the Zhou–Yan model, which assumes that the initiation reaction in eq 1 is extremely fast and β is very high.

In case II, group B can be catalyzed by the stimulus, S, and activated to B*. Thus, the change in the concentration of S can be neglected in the calculation. The reaction rate of eq 2 is
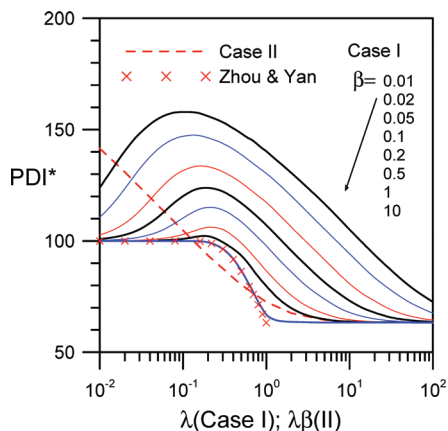
Figure 5. Dependence of the reduced PDI of degree of polymerization on the mole ratio and reactivity of the stimulus at the conversion of $A = 0.99$.
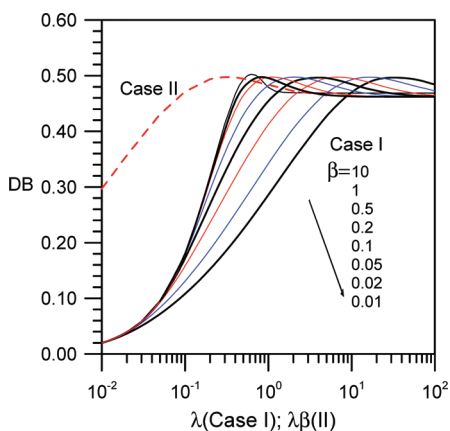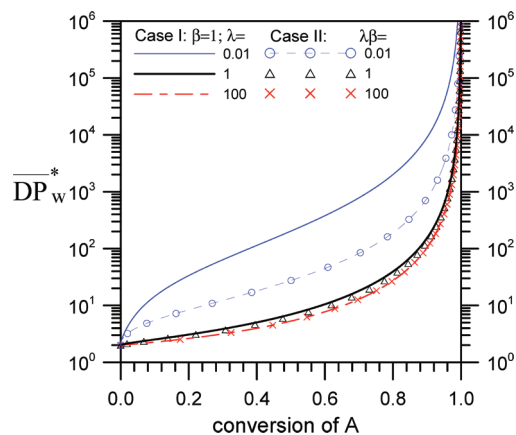

Figure 6. Dependence of the degree of branching of HBP on the mole ratio and reactivity of the stimulus at the conversion of $A = 0.99$.

described as

$$\frac{d[B]}{d\tau}_{eq2} = -k'_{SB}[S]_0[B] = -k'_{AB*}\beta\lambda[AB]_0[B]$$

$$= -\lambda\beta[B] \qquad (22)$$

Therefore, the effects of the amount and reactivity of the stimulus S on the molecular structure of the HBPs can be combined as the product of λ and β. Figure 7 shows the dependence of the reduced weight-average degree of polymerization on $\lambda\beta$. At the same conversion of A, the degree of polymerization decreases with increasing $\lambda\beta$. When $\lambda\beta > 1$, the DP profiles are relatively constant over $\lambda\beta$, and the results are similar to those of case I. On the other hand, if $\lambda\beta < 1$, $\lambda\beta$ has different effects for the two cases. For example, at $\beta = 1$ and $\lambda = 0.01$ in case I, most of the stimulus is consumed in the early stage of the reaction as shown by eq 1, and few active sites are formed, resulting in a higher degree of polymerization. In case II, although the ratio of the stimulus is low, it does not disappear during the reaction. Group B can be activated continuously, resulting in a lower DP.

The reduced average degrees of polymerization at conversion A of 0.99 in case II are also presented in Figures 3 and 4. The $\overline{DP}_n^*$ and $\overline{DP}_w^*$ are 549 and 77700 at $\lambda\beta = 0.01$, respectively, decrease to 172 and 12500 at $\lambda\beta = 1$, and then reach low plateaus of about 159 and 10100 at high values of $\lambda\beta$. The PDI also declines from 142 at $\lambda\beta = 0.01$ to 63 at $\lambda\beta = 100$ as shown in Figure 5. The degree of branching of the HBPs increases with $\lambda\beta$

Figure 7. Dependence of the reduced weight-average degree of polymerization on $\lambda\beta$ in case II.

in case II, and reaches a maximum of about 0.5 at $\lambda\beta = 0.3$ (Figure 6). At low $\lambda\beta$ values such as 0.01, the DB is 0.3 in case II, higher than that in case I, which is about 0.02 at $\lambda = 0.01$. Because the stimulus does not disappear during the reaction in case II, more linear units aB, G(8) in eq 20, could be turned into dendritic units ab, G(10). This results in a higher degree of branching.

Conclusion

In self-condensing vinyl or ring-opening polymerizations of monomers AB, the molecular structures of hyperbranched polymers are not only affected by the amount ratio of the stimulus, λ, but also by its reactivity ratio, β. In case I, the stimulus S reacts and is exhausted after activating group B. If the stimulus has a high reactivity ratio β, then the reduced average degree of polymerization and the degree of branching of the HBPs calculated by the generating function in this work are similar to those suggested by Zhou and Yan.[22] However, at low β values, there are differences between the two studies. The reduced average degree of polymerization, and polydispersity indices of HBPs decrease with increasing reactivity ratio β. In case II, the change of the stimulus concentration can be neglected during polymerization. For $\lambda\beta > 1$, $\lambda\beta$ has little influence on the DP profiles, and the results are similar to those of case I. On the other hand, when $\lambda\beta < 1$, $\lambda\beta$ has different effects for the two cases. The maximum degree of branching of about 0.5 can be obtained at a high conversion of A and is dependent on the amount and the reactivity ratio of the stimulus as well as on the different cases.

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