Kinetic Model of Hyperbranched Polymers Formed in Copolymerization of AB_2 Monomers and Multifunctional Core Molecules with Various Reactivities

Kuo-Chung Cheng*,† and Lee Y. Wang‡

Department of Chemical Engineering, National Taipei University of Technology, Taipei 106, Taiwan, and Center for Condensed Matter Sciences, National Taiwan University, Taipei 106, Taiwan

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ABSTRACT: Hyperbranched polymers generated from the polymerization of AB_2-type monomers and trifunctional cores with various reactivities were examined by means of the kinetic theory. The average molecular weight, polydispersity, degree of branching, and structural units of the hyperbranched polymers, which all changed with time or conversion, were calculated by a generating function method. Growth of the hyperbranched polymers was limited by adding C_3 monomers because no reactions occur among molecules with a core unit. The presence of multifunctional core monomers can reduce the polydispersity of the hyperbranched polymers but leads to less branching and more residual of unreacted core monomers. Increment of the reactivity of core monomers results in a lower weight-average degree of polymerization and a narrower molecular weight distribution of the hyperbranched polymers.

Introduction

The properties of dendrimers and hyperbranched polymers have been shown to be very different from those of linear polymers. For example, the lack of entanglements results in a lower viscosity, and the large extent of end functional groups causes higher solubility in various solvents for hyperbranched polymers compared with linear structure at a given molecular weight.[1−3] In contrast to dendrimers with a perfectly regular structure, hyperbranched polymers contain randomly branched and some linear structures. However, they can be synthesized by simple one-pot polymerizations, such as self-condensation of AB_g-type monomers, while retaining properties very similar to those of dendrimers. Accordingly, many various hyperbranched polymers have been recently synthesized, and numerous applications, such as surface modification, tougheners, coatings, and drug delivery systems, have been suggested.[4−9]

To understand the formation−structure−property relationships of these novel polymers, the development of adequate theoretical models for investigating how polymerization conditions affect the molecular weight, polydispersity index, PDI, and degree of branching of polymers, becomes very important. The theoretical calculation of the statistical model and the experimental results[10,11] have shown that the molecular weight distribution, MWD, of a hyperbranched polymer is extremely broad at high conversion. This disadvantage can be improved by adding monomers in several batches or by reacting them with a little multifunctional core to reduce the polydispersity of the final hyperbranched polymers.[12−17]

A kinetic model of the polycondensation of AB_2-type monomers with B_f cores has been established to examine the MWD of hyperbranched polymers.[18,19] According to those results, the DPI of the resultant hyperbranched polymer decreased as the functionality of the core molecule increased. To our knowledge, the changes of the degree of branching with various content or types of cores have not yet been analyzed. In some practical circumstances, the reactivity of functional groups of the core molecule may differ from that of the AB_2 monomer. Therefore, it is interesting to examine the dependence of the molecular weight and PDI of hyperbranched polymers on the differences between the reactivities of AB_2-type monomers and that of the core molecule.

In this work, we use the generating function method,[20−24] based on kinetic theory, to the copolymerization of AB_2 monomers with trifunctional cores of C_3. This kinetic model is adopted to examine the effects of different amounts of cores with various reactivities on the average molecular weight of polymers, degree of branching, DB, and the fractions of structural units and residual unreacted monomers.

Kinetic Model of Copolymerization of AB_2 Monomers with Multifunctional C_3 Cores

First, a polymerization system is considered with AB_2 monomers and multifunctional C_3 cores, in which the AB_2 monomer contains one A reactive group and two B groups and the C_3 core possesses three functional groups, C. Assume that the reaction is bimolecular; both B and C groups can react with an A group as follows:

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

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

where k_{AB} and k_{AC} are reaction rate constants, which are independent of the sizes of the molecules according to the principle of equal reactivity, PER,[10] and

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

in which β is assumed to be constant and independent of the extent of reaction. There are 10 various structural

* To whom correspondence should be addressed.
† National Taipei University of Technology.
‡ National Taiwan University.

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units involved in this polymerization:

G(1): A–≺(B,B) monomer G(6): A–≺(b~, b~)

G(2): A–≺(b~, B) G(7): (C, C)≻–C, core monomer

G(3): ~a–≺(B, B) G(8): (C, C)≻–c~

G(4): ~a–≺(b~, B) G(9): (~c, C)≻–c~

G(5): ~a–≺(b~, b~) G(10): (~c, ~c)≻–c~

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

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

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

A–≺(B,B) + ~a–≺(B,B) → ~a–≺(B, b–a–≺(B,B))

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

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

where e_J represents the number of structural unit G(J) on a molecule $\langle E \rangle$, and e_w, equaling e_{11}, is the molecular weight of the molecule $\langle E \rangle$. For example, **E** = (1, 0, 0, 0, 0, 0, 0, 0, 0, 0, $W(AB_2)$) denotes monomer AB_2, and $W(AB_2)$ is the molecular weight of this monomer; **E** = (0, 0, 0, 0, 0, 0, 0, 1, 0, 0, 0, $W(C_3)$) denotes core monomer C_3, and $W(C_3)$ is the molecular weight of the core; and **E** = (0, 0, 1, 0, 0, 0, 0, 0, 1, 0, 0, $W(AB_2) + W(C_3)$) is the molecule

(C, C)≻–c–a–≺(B,B)

formed by combining a monomer AB_2 with a core C_3, if there are no condensates produced during polymerization. The system with condensate molecules formed can also be treated by the generating function method.[22]

The effects of configuration and conformation are not considered in the calculation. Assuming that all reactions are chemically controlled and that no intramolecular reaction occurs,[25,26] the reactions between molecules are

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

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

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

$$l_J = -\delta(b_{i1},J) - \delta(b_{i2},J) + \delta(b_{i3},J) + \delta(b_{i4},J), \quad J = 1, 2, ..., 10 \quad (7)$$

Table 1. Parameters of b_{ij} and k_i

b_{11}	b_{12}	b_{13}	b_{14}	k_1		1	1	3	2	$2k_{AB}$
b_{21}	b_{22}	b_{23}	b_{24}	k_2		1	2	3	6	k_{AB}
b_{31}	b_{32}	b_{33}	b_{34}	k_3		1	3	3	4	$2k_{AB}$
b_{41}	b_{42}	b_{43}	b_{44}	k_4		1	4	3	5	k_{AB}
b_{51}	b_{52}	b_{53}	b_{54}	k_5		2	1	4	2	$2k_{AB}$
b_{61}	b_{62}	b_{63}	b_{64}	k_6		2	2	4	6	k_{AB}
b_{71}	b_{72}	b_{73}	b_{74}	k_7		2	3	4	4	$2k_{AB}$
b_{81}	b_{82}	b_{83}	b_{84}	k_8		2	4	4	5	k_{AB}
b_{91}	b_{92}	b_{93}	b_{94}	k_9		6	1	5	2	$2k_{AB}$
b_{101}	b_{102}	b_{103}	b_{104}	k_{10}		6	2	5	6	k_{AB}
b_{111}	b_{112}	b_{113}	b_{114}	k_{11}	=	6	3	5	4	$2k_{AB}$
b_{121}	b_{122}	b_{123}	b_{124}	k_{12}		6	4	5	5	k_{AB}
b_{131}	b_{132}	b_{133}	b_{134}	k_{13}		1	7	3	8	$3k_{AC}$
b_{141}	b_{142}	b_{143}	b_{144}	k_{14}		1	8	3	9	$2k_{AC}$
b_{151}	b_{152}	b_{153}	b_{154}	k_{15}		1	9	3	10	k_{AC}
b_{161}	b_{162}	b_{163}	b_{164}	k_{16}		2	7	4	8	$3k_{AC}$
b_{171}	b_{172}	b_{173}	b_{174}	k_{17}		2	8	4	9	$2k_{AC}$
b_{181}	b_{182}	b_{183}	b_{184}	k_{18}		2	9	4	10	k_{AC}
b_{191}	b_{192}	b_{193}	b_{194}	k_{19}		6	7	5	8	$3k_{AC}$
b_{201}	b_{202}	b_{203}	b_{204}	k_{20}		6	8	5	9	$2k_{AC}$
b_{211}	b_{212}	b_{213}	b_{214}	k_{21}		6	9	5	10	k_{AC}

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

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

For example, a molecule

A–≺(B,B)

reacts with another molecule

(C, C)≻–c–a–≺(B,B)

by the following reaction:

A–≺(B,B) + (C, C)≻–c–a–≺(B,B) $\xrightarrow{k_3}$ (C, C)≻–c–a–≺(B, b–a–≺(B,B))

in which

<E'> = A–≺(B,B);

<E"> = (C, C)≻–c–a–≺(B,B);

<E' + E" + L_i> = (C, C)≻–c–a–≺(B, b–a–≺(B,B));

E' = (1, 0, 0, 0, 0, 0, 0, 0, 0, 0, W(AB_2));

E"= (0, 0, 1, 0, 0, 0, 0, 1, 0, 0, W(AB_2)+W(C_3));

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

E'+E'+L_3 = (0, 0, 1, 1, 0, 0, 0, 1, 0, 0, 2W(AB_2)+W(C_3), and

$k_3 = 2k_{AB}$

Furthermore, a dimensionless number fraction, [E], the ratio of the reaction rate constant, k_i', and a scaled

time, τ, are defined as

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

$$k_i' = (k_i/k_0)(V_0/V) \tag{9}$$

$$\tau = tk_0(N_0/V_0) \tag{10}$$

where $N(E)$ is the number isomers $\langle E\rangle$, V is the volume of the reaction system, N_0, k_0, and V_0 are arbitrary reference numbers, rate constant, and volume, respectively, and t is the reaction time.

If the change of the volume of the reaction system is negligible, then according to eq 6, the rate equation of the isomers can be written as

$$\frac{d[E]}{d\tau} = \sum_{i=1}^{21} k_i'\{\sum_{E'+E''+L_i=E}([E'][E'']p'_{i1}p''_{i2}) - [E]p_{i1}\sum_{\text{all } E'''}[E''']p'''_{i2} - [E]p_{i2}\sum_{\text{all } E'''}[E''']p'''_{i1}\} \tag{11}$$

where $\sum_{\text{all } E}$ denotes the sum over all possible values of vector **E**, and $p_{ij} = e_J$ for $b_{ij} = J$. The one positive and two negative terms on the right side of eq 11 give the total rates of appearance and disappearance of the isomer $\langle E\rangle$, respectively. Equation 11 cannot be solved directly, but it can be transformed into finite ordinary differential equations using a generating function.[20−24] The profiles of the average molecular weights of polymers and the fractions of the structural units, $G(I)$, can be calculated from the generating function; the relevant algorithm is described in the Appendix.

Moreover, the degree of branching, DB, is a very important structural parameter in characterizing the hyperbranched polymers. Flory proposed the "coefficient of branching", which is defined as the probability that a given functional group of a branch unit leads via a chain to another branch unit. It was shown that the coefficient of branching of the polycondensation of AB_g monomer is identical to the conversion of B groups.[11,27] Then, Hawker and Frechet defined the degree of branching:[28]

$$\text{DB} = \frac{\text{ND} + \text{NT}}{\text{total number of units}} \tag{12}$$

where ND is the number of dendritic units and NT is the number of terminal units including monomers. DB is overestimated for small molecules; for example, according to eq 12, the DB of AB_2 monomer always takes the highest value of one.[29−31] Holter and Frey recently suggested an adjusted degree of branching, DB(HF), based on the actual number over the maximum possible number of dendritic units.[29] Another parameter, the average number of branches (ANB), is defined as the deviation from the linear direction per nonterminal unit.[30] Thus, DB(HF) and ANB of the copolymerization of AB_2 monomers with C_3 cores are as follows:

$$\text{DB(HF)} = \frac{2\text{ND}}{2\text{ND} + \text{NL}} = \frac{G(5) + G(10)}{G(5) + G(10) + 0.5[G(4) + G(9)]} \tag{13}$$

$$\text{ANB} = \frac{\text{ND}}{\text{ND} + \text{NL}} = \frac{G(5) + G(10)}{G(5) + G(10) + G(4) + G(9)} \tag{14}$$

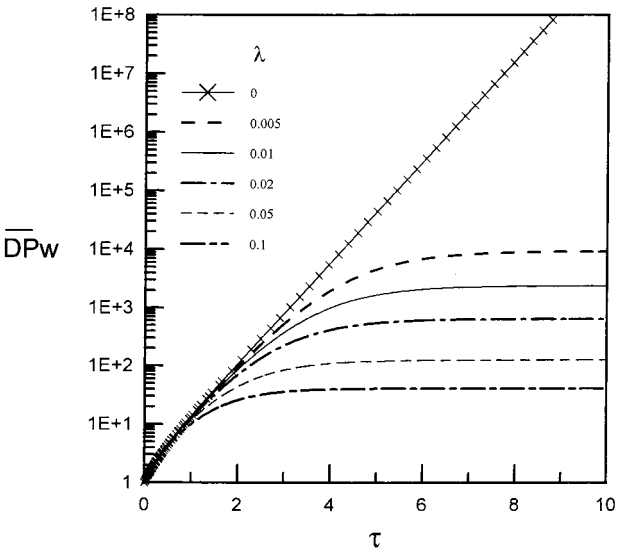
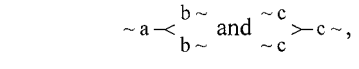
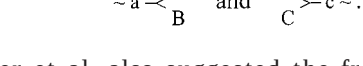


Figure 1. Weight-average degree of polymerization vs reaction time for the systems added with various contents of C_3 core monomers ($\beta = 1$).

where ND is the number of dendritic units,



and NL is the number of linear units,



Muller et al. also suggested the fraction of branch points, FB, to characterize hyperbranched polymers:[32]

$$\text{FB} = \frac{\text{ND}}{(\text{total number of units}) - (\text{number of monomers})} = \frac{G(5) + G(10)}{G(2) + G(3) + G(4) + G(5) + G(6) + G(8) + G(9) + G(10)} \tag{15}$$

Results and Discussion

Figures 1 and 2 show the weight-average degree of polymerization, $\overline{DP}_w$, of the system to which has been added various ratios of C_3 cores to AB_2 monomers, λ. The figures plot these values against the scaled time and the conversion of A, α(A), respectively. The value of β, the ratio of reactivity of group C to that of B, is set at unity, and $\overline{DP}_w$ is determined by setting the molecular weights of C_3 and AB_2 also to one. Notice that the C_3 core is also counted as a monomer in the calculation. The $\overline{DP}_w$ of the system without trifunctional cores was found to increase more rapidly than that of other systems and tends to infinity at full conversion of A but converges to a finite value for a reaction system in the presence of core monomers. The final $\overline{DP}_w$ decreases as the concentration of C_3 monomers increases. The $\overline{DP}_w$ profiles vary with reactivity ratio, β, reaction time, and conversion, as shown in Figures 3 and 4. The core with higher reactivity yields a lower weight-average degree of polymerization.

Figure 5 gives the curves of the number-average degree of polyermerization, $\overline{DP}_n$, according to the gen-

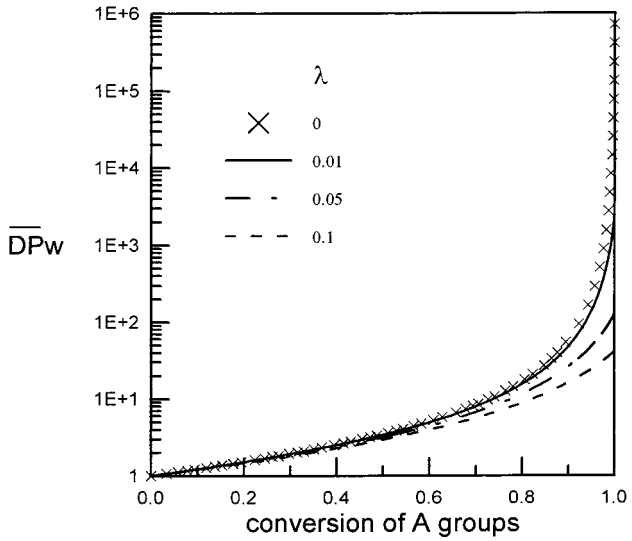


Figure 2. Weight-average degree of polymerization vs conversion of A groups for the systems added with various contents of C_3 core monomers ($\beta = 1$).

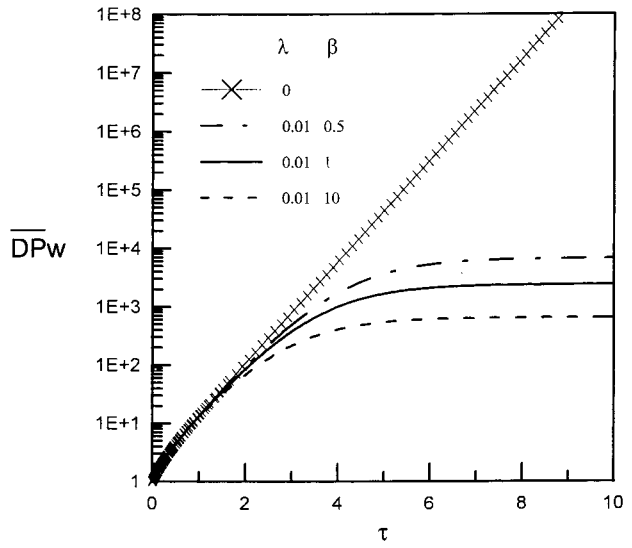


Figure 3. Weight-average degree of polymerization vs reaction time for core with various reactivities.

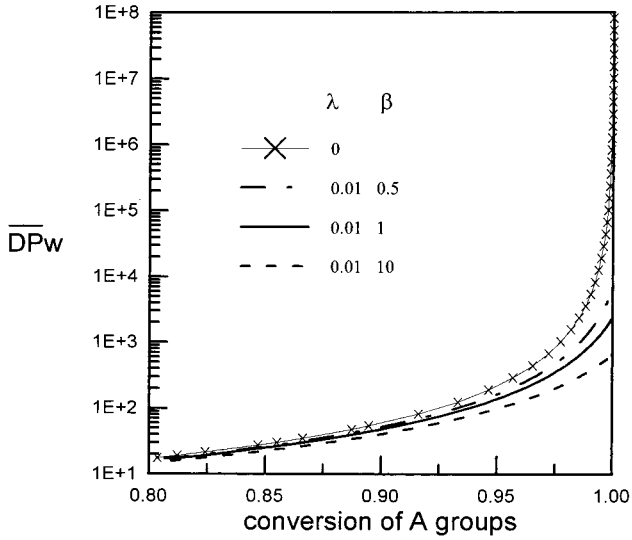


Figure 4. Weight-average degree of polymerization vs conversion of A groups for the core with various reactivities.

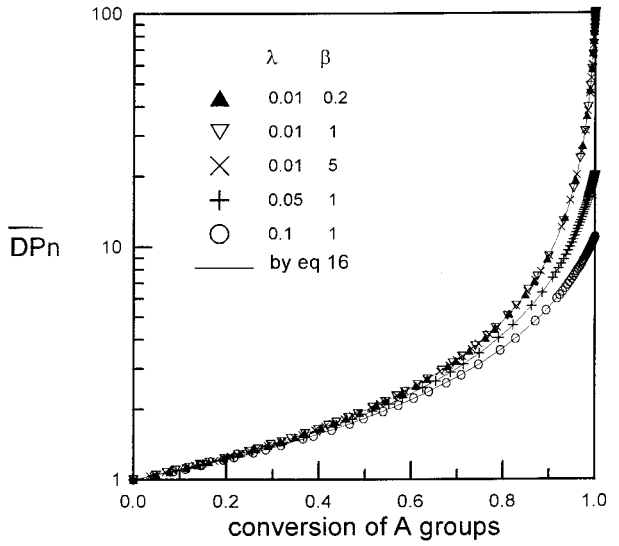


Figure 5. Dependence of the number-average degree of polymerization on conversion of A groups under various formations.

erating function method, for hyperbranched polymers with various values of λ and β. In this polymerization system, the relationship between the number-average degree of polymerization and the conversion of A groups can be derived directly:

$$\overline{DP}_n = \frac{\text{initial no. of monomers}}{\text{total no. of molecules during polymerization}}$$

$$= \frac{N_0(AB_2) + N_0(C_3)}{N_0(AB_2) + N_0(C_3) - N_0(AB_2)\,\alpha(A)}$$

$$= \frac{1+\lambda}{1+\lambda-\alpha(A)} \qquad (16)$$

And the final $\overline{DP}_n$ is

$$\overline{DP}_n = \frac{1+\lambda}{\lambda} \quad \text{at } \alpha(A) = 1 \qquad (17)$$

where $N_0(AB_2)$ and $N_0(C_3)$ are the initial numbers of AB_2 and C_3, respectively; $\alpha(A)$ is the conversion of A groups, and λ is the ratio of $N_0(C_3)$ to $N_0(AB_2)$. As shown in eqs 16 and 17 and in Figure 5, a higher core ratio leads to a lower $\overline{DP}_n$, but the number-average degree of polymerization is independent of the reactivity of C_3.

Figure 6 indicates the dependence of the polydispersity index, PDI, of the hyperbranched polymer on conversion. With lower reactivitive core units, for example $\beta = 0.01$, the system contains a higher ratio of core units, $\lambda = 0.05$, resulting in a higher PDI of polymers before full conversion. When the reactivity of the core increases, the PDI decreases with increasing of the core monomers. During polymerization, the growing molecules can be classified into two major types: the first includes molecules with a focal unit, (ABb) or (Ab_2); the other group includes molecules with a reacted core unit, (C_2c), (Cc_2), or (c_3). The molecules without a core unit can be combined with each other, or reacted with one containing core unit to form, in both cases, a larger product. Because the larger molecules contain a higher number of unreacted B groups, it is easy to combine two large molecules into an even larger

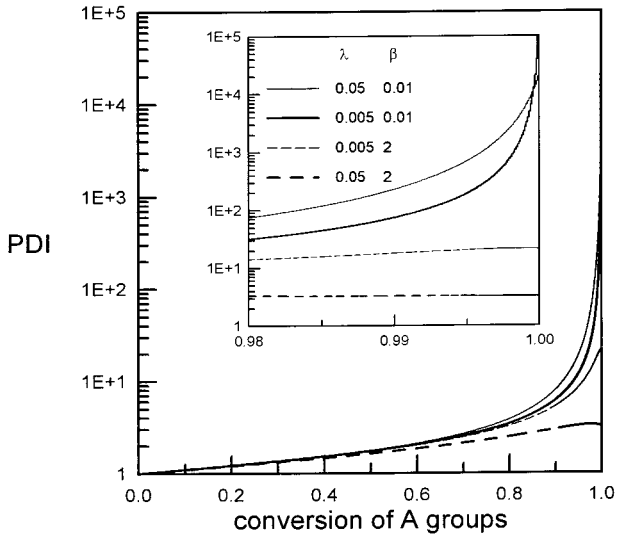


Figure 6. Dependence of the polydispersity index on conversion of A groups under various formations.

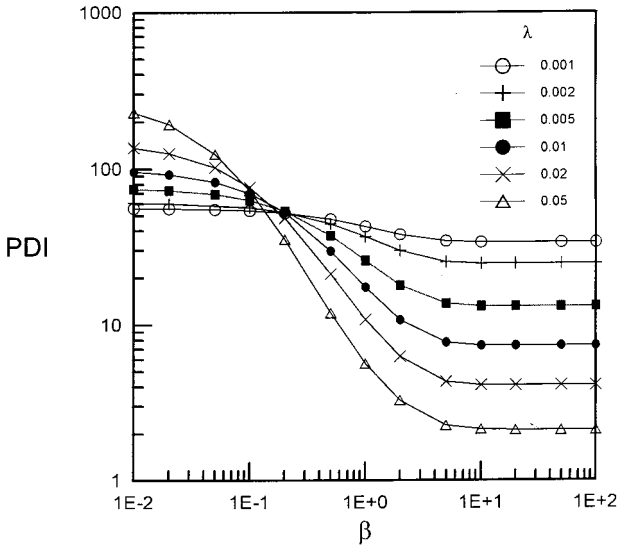


Figure 7. Dependence of the polydispersity index of the hyperbranched polymers on the reactivity ratio and contents of C_3 cores at the conversion of 0.99.

one, and this causes a broad molecular weight distribution of the hyperbranched polymers. On the other hand, no reactions occur among the molecules with a core unit; the degree of polymerization is thus limited by adding C_3 monomers. In the case of high values of β and λ, there are a large number of molecules with a core unit formed at early stage, the polymerization will be dominated by the combination of the molecule with a core unit with a monomer AB_2, and the PDI of the hyperbranched polymers becomes narrower as illustrated in Figure 7.

Figure 8 shows that, even when all A groups have been consumed, around 13% of unreacted C_3 cores remain in the system, for which $\lambda = 0.01$ and $\beta = 1$. However, adding a highly reactive C_3 can reduce the fraction of the unreacted core monomers. Figure 9 presents the changes in the degree of branching, and the number of linear and dendritic units, with conversion at various contents of C_3 cores in the system with $\beta = 1$. The number of linear and dendritic units and DB increase with conversion. Furthermore, both the number of dendritic unit and the degree of branching decline as the amount of C_3 increases. Figure 10 shows

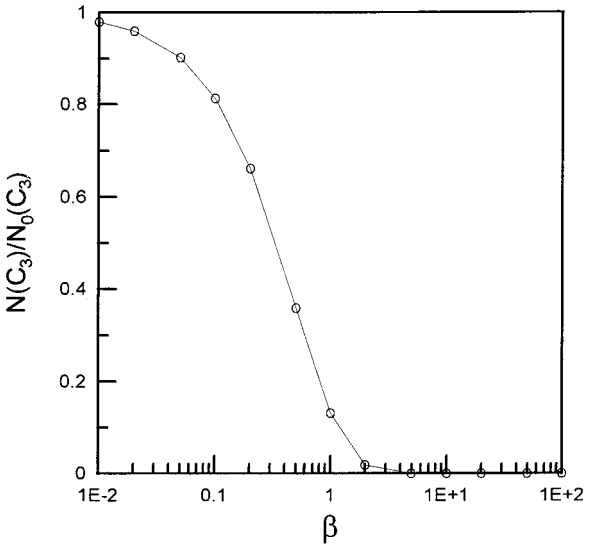


Figure 8. Dependence of the number of unreacted residual cores, which remain after all A groups being consumed, on the reactivity ratio, β, at $\lambda = 0.01$.

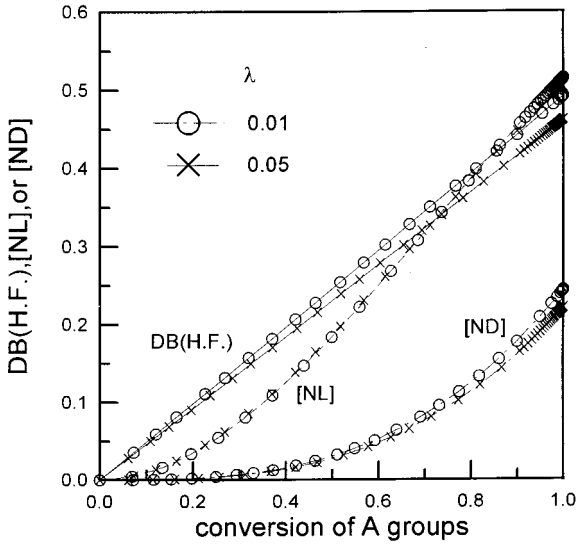


Figure 9. Dependence of the degree of branching and the number of linear and dendritic units on conversion under various contents of C_3 cores, at $\beta = 1$, where [ND] = $ND/N_0(A)$, [NL] = $NL/N_0(A)$.

the dependence of both the final DB(HF) and the number of dendritic units composed of (ab_2) and (c_3) on the core ratio for the system with $\beta = 1$. The probability of forming (ab_2) unit decreases as the content of C_3 cores increases due to competition between the reactions of functional groups A with B and A with C. Although the number of dendritic (c_3) units increases at the same time, the increase is insufficient to compensate for the reduction of (ab_2) units. Consequently, the total number of dendritic units, ND, and the degree of branching fall as the content of C_3 increases.

Figure 11 gives the changes of the final number of dendritic units and DB with the reactivity of the core in the case which $\lambda = 0.05$. With a higher value of β, the opportunity for reactions between groups A and C rises, and the number of dendritic (c_3) units increases, but the number of (ab_2) units decreases. For systems with $\lambda = 0.01$, 0.02, and 0.05, the total number of dendritic units and the degree of branching first decrease as the reactivity of C_3 increases and reach a

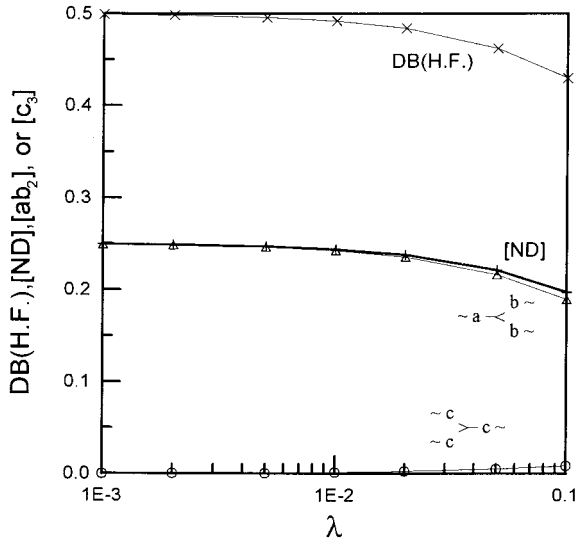


Figure 10. Dependence of final DB(HF) and the number of dendritic units on the contents of core, at $\beta = 1$.

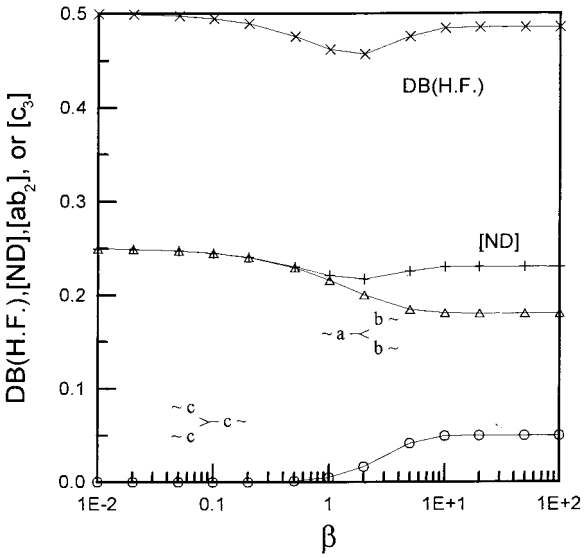


Figure 11. Dependence of final DB(HF) and the number of dendritic units on the reactivity ratio, β, at $\lambda = 0.05$.

minimum at a β ratio of about 2, before increasing, as shown in Figure 12.

Conclusion

This study has expanded the generating function method to elucidate the growth of hyperbranched polymers formed by copolymerization of AB_2 monomers with trifunctional cores C_3. Use of this kinetic model revealed that the more reactive core monomers yield a lower weight-average degree of polymerization and a narrower MWD. Furthermore, the degree of branching changes with the reactivity of the core molecule and decreases as the content of C_3 of increases. A hyperbranched polymer can be tailored by tuning the formation as suggested by this model; for example, the PDI of the hyperbranched polymers can be reduced to about two by adding higher reactive C_3 monomers in 0.05 molar ratio of the C_3 to AB_2 monomer.

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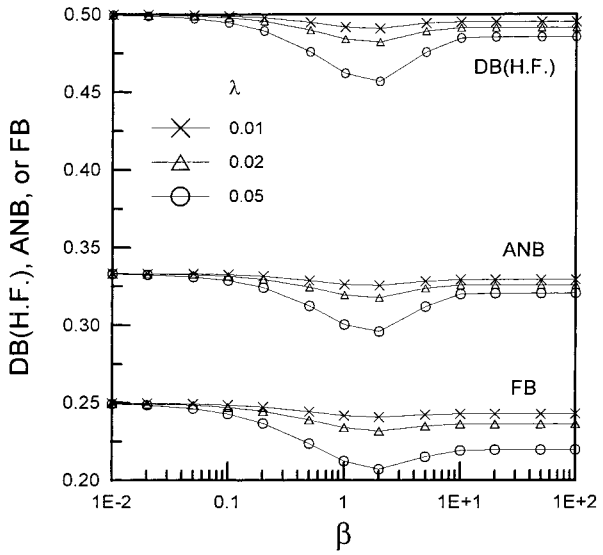

Figure 12. Dependence of the final DB(HF), ANB, and FB of the hyperbranched polymers on the reactivity ratio, β, under various contents of C_3 cores.

Appendix: Generating Function Method

The generating function method is applied to obtain the relationship between the average molecular weight and the reaction time. First, a generating function, H, is defined:

$$H(\tau,\omega_{j(j=1,2...,n+1)}) = \sum_{\text{all } E} \left(\prod_{j=1}^{n+1} \omega_j^{e_j}\right)[E] \qquad \text{(A1)}$$

where ω_j is a dummy variable and H is a function of τ and ω_j.

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

$$\frac{\partial H}{\partial \tau} = \sum_{i=1}^{m} k_i'(H_{x_{i1}} H_{x_{i2}} x_{i3} x_{i4} - x_{i1} H_{x_{i1}} H_{i2} - x_{i2} H_{x_{i2}} H_{i1}) \qquad \text{(A2)}$$

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

$$x_{ij} = \omega_J \quad \text{for } b_{ij} = J$$

$$H_{x_{ij}} \equiv \frac{\partial H}{\partial x_{ij}}$$

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

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

$$b_{ij} = J$$

$$x_{ij} = \omega_J$$

$$\frac{\partial H}{\partial x_{ij}} = \frac{\partial H}{\partial \omega_J} = H_{\omega_J}$$

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

By setting all dummy variables, $\omega_{q(q=1,2,...,n+1)}$ to 1, eq

A2 can be written as

$$\frac{\partial H^*}{\partial \tau} = \sum_{i=1}^{m} k_i'(-H_{i1}H_{i2}) \tag{A3}$$

where $H^* = H(\omega_{q(q=1,2,....,n+1)} = 1)$. Furthermore, the partial derivatives of H along $\omega_{q(q=1,2,....,n+1)} = 1$ can be obtained by differentiating eq A2 with respect to ω_r or to both ω_r and ω_s:

$$\frac{\partial H_r}{\partial \tau} = \sum_{i=1}^{m} k_i' H_{i1}H_{i2}\left(\frac{\partial x_{i3}x_{i4}}{\partial \omega_r} - \frac{\partial x_{i1}}{\partial \omega_r} - \frac{\partial x_{i2}}{\partial \omega_r}\right) \tag{A4}$$

$$\begin{aligned}\frac{\partial H_{r,s}}{\partial \tau} = \sum_{i=1}^{m} k_i' \Bigg[& H_{i1,r}H_{i2,s} + H_{i1,s}H_{i2,r} + (H_{i1,r}H_{i2} + H_{i1}H_{i2,r})\left(\frac{\partial x_{i3}x_{i4}}{\partial \omega_s}\right) + (H_{i1,s}H_{i2} + H_{i1}H_{i2,s})\left(\frac{\partial x_{i3}x_{i4}}{\partial \omega_r}\right) + \\ & (H_{i1}H_{i2})\left(\frac{\partial^2 x_{i3}x_{i4}}{\partial \omega_r \partial \omega_s}\right) - \left(\frac{\partial x_{i1}}{\partial \omega_r}H_{i1,s} + \frac{\partial x_{i1}}{\partial \omega_s}H_{i1,r}\right)H_{i2} - \\ & \left(\frac{\partial x_{i2}}{\partial \omega_r}H_{i2,s} + \frac{\partial x_{i2}}{\omega_s}H_{i2,r}\right)H_{i1}\Bigg]\end{aligned} \tag{A5}$$

where

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

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

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

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

and the initial conditions are

$$H^*(\tau{=}0) = \sum_{\text{all } E}[E]_0 \tag{A6}$$

$$H_r^*(\tau{=}0) = \sum_{\text{all } E} e_r[E]_0 \tag{A7}$$

$$H_{r,s}^*(\tau{=}0) = \sum_{\text{all } E} e_r e_s[E]_0, \quad \text{for } r \neq s; \tag{A8}$$

$$H_{r,r}^*(\tau{=}0) = \sum_{\text{all } E} e_r(e_r - 1)[E]_0 \tag{A9}$$

$$[E]_0 = [E](\tau{=}0) \tag{A10}$$

This set of ordinary differential equations, eqs A3−A5, dependent on variable τ, can be solved by the Runge−Kutta method to determine $H^*(\tau)$, $H_r(\tau)$, and $H_{r,s}(\tau)$. The ath moment of the molecule weight distribution, MWD, is defined as

$$M_a = \left(\frac{N_0}{N_T}\right)\sum_{\text{all } E} W^a(E)[E] \tag{A11}$$

where N_T is he total number of molecules in the reaction system, and $W(E)$ is the molecular weight of isomer, $\langle E \rangle$. The zeroth, first, and second moment of MWD can be calculated using the generating function:

$$M_0 = \left(\frac{N_0}{N_T}\right)H^* \tag{A12}$$

$$M_1 = \left(\frac{N_0}{N_T}\right)H_{n+1} \tag{A13}$$

$$M_2 = \left(\frac{N_0}{N_T}\right)(H_{n+1,n+1},+H_{n+1}) \tag{A14}$$

The number-average and weight-average molecular weights, $\bar{M}_n$ and $\bar{M}_w$, are obtained:

$$\bar{M}_n = \frac{M_1}{M_0} \tag{A15}$$

$$\bar{M}_w = \frac{M_2}{M_1} \tag{A16}$$

The conversion of $G(J)$ units can also be calculated as

$$\begin{aligned}\text{conversion of } G(J) &= 1 - N(G(J))/N_0(G(J)) \\ &= 1 - \sum_{\text{all } E} e_J[E] = 1 - H_J\end{aligned} \tag{A17}$$

where $N_0(G(J)) = N(G(J))$ at $\tau = 0$.

The relationships among the average molecular weight, conversion, and reaction time can be calculated by the following algorithm:

1. Calculate the initial conditions, $H^*(0)$, $H_r(0)$, and $H_{r,s}(0)$, from the concentrations of the reactants at $\tau = 0$, according to eqs A6−A10.
2. Set $\tau \leftarrow \tau + \Delta\tau$, where $\Delta\tau$ is the specified step time.
3. Solve the set of ODEs, eqs A3−A5, and obtained the values of $H^*(\tau)$, $H_r(\tau)$, and $H_{r,s}(\tau)$ by the Runge−Kutta method or other solvers.
4. Calculate the average molecular weights and conversions according to eqs A15−A17.
5. Repeat procedures 2−4 until the specified time.

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