



Model of hyperbranched polymers formed by monomers A_2 and B_g with end-capping molecules

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ABSTRACT

Hyperbranched polymers, HBPs, formed via a stepwise polymerization of A_2 , B_g type monomers with the addition of end-capping molecules, AR, were investigated by means of recursive and kinetic models. First, gelation curves were established based on the initial compositions of reactants at various functionalities, g , of monomers B_g . According to this guide, the hyperbranched polymers without gel fraction can be obtained. The molecular structures of HBPs, such as molecular weight and the degree of branching were calculated as related to conversion. It is shown that they can be controlled by the composition of reactants. With the addition of molecules AR, the gelation can be avoided at high conversion, and the distribution of molecular weights of polymers becomes narrower.

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1. Introduction

Because highly branched polymers show distinguishing characteristics resulted from their unique dendritic architectures containing a large number of branching points and functional end groups, the synthesis of dendrimers and hyperbranched polymers has become a major research interest [1–7]. The dendrimers have well-defined shape and size, and prepared by multi-step reactions with complicated purifying processes [8–11]. On the contrary, the hyperbranched polymers, HBPs, have more random branched architectures with some linear structures, and less regular structure than that of dendrimers, but they can be formed by simple one-pot polymerizations, such as stepwise polymerization of AB_g -type monomers ($g > 2$); self-condensing vinyl polymerization, and self-condensing ring-opening polymerization [1,12–15]. However, the commercial monomers used in those methodologies are still limited. Another method is the direct stepwise polymerization of difunctional monomers, A_2 , with

multi-functional monomers, B_g ($g > 2$) [9,16–18]. Many commercial monomers, A_2 and B_g , are available, but the major problem of this polymerization is how to avoid gelation. It can be achieved by stopping the reaction before gelation, or choosing appropriate composition of monomers [19,20]. The kinetics of hyperbranched polymers formed by monomers A_2 and B_3 were investigated theoretically, and the model of degree of branching, DB changed with the initial composition of monomers and conversion was proposed [21].

In our previous work, the systems of diepoxides cured with primary amine in the presence of monoepoxide were discussed. The critical epoxy conversion increases with increasing monofunctional reactive diluents. At higher ratio of monoepoxide, the system cannot reach a gel point. It implies that hyperbranched polymers under 100% sol fraction can be obtained by the addition of end-capping molecules, AR [22,23]. Therefore, it is worthy to examine the dependence of the molecular structure of hyperbranched polymers on the composition of monomers, A_2 and B_g , and monofunctional molecules. In this study, we use recursive and kinetic models to investigate the molecular weights and degree of branching, DB, of HBPs formed

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by the stepwise polymerization of the monomers, A_2 and B_g , with the addition of end-capping molecules. Furthermore, the initial composition of reactants that can avoid gelation at high conversion is proposed. The effect of non-equal reactivity of functional group on the structure parameters of the hyperbranched polymers are also important for several cases discussed before [5,8,21–24]. However, in this work we focus on the molecular structure changed with initial composition, and assume that the reactivities of all functional groups of the same type are equal, and the reaction is bimolecular, i.e. there is no cyclization occurring before gelation [19].

2. Average molecular weight and gel point of polymers formed by A_2 , B_g monomers, and AR

A stepwise polymerization system is considered with bifunctional A-type monomers, A_2 , monofunctional A-type monomers, AR, and g functional B-type monomers, B_g , in which the groups A and B cannot react with themselves, but group A can react with B; then the two molecules combine to form a large molecule. If there is no by-product eliminated, the number-average molecular weight of polymers at the conversion of group A, p_A , can be calculated by the total mass over the number of polymers [24]:

$$\begin{aligned} \bar{M}_n &= \frac{(B_g)_0 M_{B_g} + (AR)_0 M_{AR} + (A_2)_0 M_{A_2}}{(B_g)_0 + (AR)_0 + (A_2)_0 - (AR)_0 p_A - 2(A_2)_0 p_A} \\ &= \frac{M_{B_g} + \lambda_1 M_{AR} + \lambda_2 M_{A_2}}{1 + \lambda_1 + \lambda_2 - (\lambda_1 + 2\lambda_2) p_A} \end{aligned} \quad (1)$$

where

$$\lambda_1 = (AR)_0 / (B_g)_0;$$

$$\lambda_2 = (A_2)_0 / (B_g)_0.$$

$(AR)_0$, $(A_2)_0$, and $(B_g)_0$ are the initial moles of monomers AR, A_2 and B_g , respectively. M_i is the molecular weight of monomer i . Furthermore, according to the equation derived by Macosko and Miller [25], the weight-average molecular weight of the copolymers can be obtained as follows

$$\begin{aligned} \bar{M}_w &= \frac{p_B m'_a + p_A m'_b}{p_B m_a + p_A m_b} \\ &+ \frac{p_A p_B [p_A (f_e - 1) M_{B_g}^2 + p_B (g - 1) M_a^2 + 2 M_a M_{B_g}]}{(p_B m_a + p_A m_b) [1 - p_A p_B (f_e - 1) (g - 1)]} \end{aligned} \quad (2)$$

where the conversion of group B is $p_B = r p_A$;

$$\begin{aligned} r &= \frac{(AR)_0 + 2(A_2)_0}{g(B_g)_0} = \frac{\lambda_1 + 2\lambda_2}{g} \\ a_1 &= \frac{(AR)_0}{(AR)_0 + 2(A_2)_0} = \frac{\lambda_1}{\lambda_1 + 2\lambda_2} \\ a_2 &= \frac{2(A_2)_0}{(AR)_0 + 2(A_2)_0} = \frac{2\lambda_2}{\lambda_1 + 2\lambda_2} \\ f_e &= a_1 + 2a_2 = \frac{\lambda_1 + 4\lambda_2}{\lambda_1 + 2\lambda_2} \end{aligned}$$

$$M_a = M_{AR} a_1 + M_{A_2} a_2$$

$$M_b = M_{B_g}$$

$$m_a = M_{AR} a_1 + \frac{M_{A_2} a_2}{2}$$

$$m'_a = M_{AR}^2 a_1 + \frac{M_{A_2}^2 a_2}{2}$$

$$m_b = \frac{M_{B_g}}{g}$$

$$m'_b = \frac{M_{B_g}^2}{g}$$

when

$$r(p_A)_{\text{gel}}^2 = \frac{(p_B)_{\text{gel}}^2}{r} = \frac{1}{(f_e - 1)(g - 1)} \quad (3)$$

that is

$$(p_A)_{\text{gel}}^2 = \frac{g}{2\lambda_2(g - 1)}; \quad (4)$$

or

$$(p_B)_{\text{gel}}^2 = \frac{(\lambda_1 + 2\lambda_2)^2}{2\lambda_2 g (g - 1)}, \quad (5)$$

the weight-average weight becomes infinite, at which a gel occurs.

Case (a): $r < 1$ in the case of the initial concentration of groups B is greater than that of groups A, that is

$$r = \frac{\lambda_1 + 2\lambda_2}{g} < 1 \quad \text{and} \quad p_B < p_A.$$

If $\lambda_2 > \frac{g}{2(g-1)}$, as shown as “region II” in Fig. 1, the gel point occurs at the conversion p_A less than 100%. On the contrary, when $\lambda_2 < \frac{g}{2(g-1)}$, the $(p_A)_{\text{gel}} > 1$, and even though the groups A are consumed entirely, the gelation does not take place. Therefore, branched polymers without gel portion, i.e., 100% of sol fraction, can be synthesized as long as $\lambda_1 + 2\lambda_2 < g$, and $\lambda_2 < \frac{g}{2(g-1)}$. The limitation is presented as “region I”; and in this rang the average-molecular weights of polymers at $p_A = 1$ are

$$\bar{M}_n = \frac{M_{B_g} + \lambda_1 M_{AR} + \lambda_2 M_{A_2}}{1 - \lambda_2}; \quad (6)$$

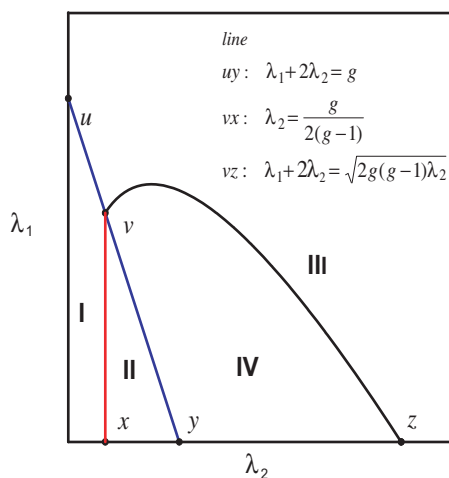


Fig. 1. The regions of the gelation and 100% of sol fraction dependent on the initial compositions of reactants.

and

$$\overline{M}_w = \frac{rm'_a + m'_b}{rm_a + m_b} + \frac{r[(f_e - 1)M_{B_g}^2 + r(g - 1)M_a^2 + 2M_a M_{B_g}]}{(rm_a + m_b)[1 - r(f_e - 1)(g - 1)]} \quad (7)$$

Case (b): $r > 1$

The initial A groups is in excess as compared with B, i.e.,

$$r = \frac{\lambda_1 + 2\lambda_2}{g} > 1 \quad \text{and} \quad p_A < p_B.$$

when $\lambda_1 + 2\lambda_2 > \sqrt{2g(g-1)\lambda_2}$, according to the Eq. (5), the $(p_B)_{\text{gel}} > 1$, and the gelation can be avoided. In the “region III” indicated in Fig. 1, at $p_B = 1$, the average-molecular weights of polymers are

$$\overline{M}_n = \frac{M_{B_g} + \lambda_1 M_{AR} + \lambda_2 M_{A_2}}{1 + \lambda_1 + \lambda_2 - g} \quad (8)$$

and

$$\overline{M}_w = \frac{m'_a + \frac{1}{r}m'_b}{m_a + \frac{1}{r}m_b} + \frac{\frac{1}{r}[(f_e - 1)M_{B_g}^2 + (g - 1)M_a^2 + 2M_a M_{B_g}]}{(m_a + \frac{1}{r}m_b)[1 - \frac{1}{r}(f_e - 1)(g - 1)]} \quad (9)$$

On the other hand, in the region IV:

$$\lambda_1 + 2\lambda_2 > 1 \quad \text{and} \quad \lambda_1 + 2\lambda_2 < \sqrt{2g(g-1)\lambda_2},$$

$(p_B)_{\text{gel}} < 1$, and the infinite network can be formed during polymerization.

Case (c): $r = 1$ when the initial groups A and B is equal, and

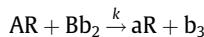
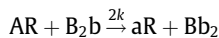
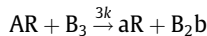
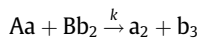
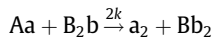
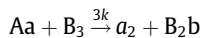
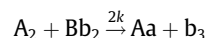
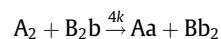
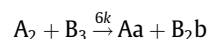
$$\lambda_1 + 2\lambda_2 = g; \text{ then}$$

$$(p_A^2)_{\text{gel}} = (p_B^2)_{\text{gel}} = \frac{g}{2\lambda_2(g-1)} \quad (10)$$

Therefore, in case $\lambda_1 > \frac{g(g-2)}{(g-1)}$, of which the value is higher than the “v” point as shown in Fig. 1, the $(p_A)_{\text{gel}}$ and $(p_B)_{\text{gel}} > 1$; then 100% of sol fraction can be obtained at $p_A = p_B = 1$. The molecular weight can be calculated by Eqs. (6) and (7) at $r = 1$. On the contrary, if $\lambda_1 < \frac{g(g-2)}{(g-1)}$, the gel could be formed during polymerization. At point “v”, that is $\lambda_1 = \frac{g(g-2)}{(g-1)}$; and $\lambda_2 = \frac{g}{2(g-1)}$, the critical conversion is 100%.

3. Degree of branching of polymers formed by A_2 , B_3 monomers, and AR

In this study, only group A can react with B. For example, monomer A_2 can react with B_3 to form product $Aa-bB_2$, in which a and b are the reacted groups of A and B. Therefore, the reactions between various structural units (not functional groups or molecules) can be written in the following kinetic scheme [22,24]:



where k is the reaction rate constant of reaction of groups A and B.

Furthermore, a dimensionless number fraction, $[U_i]$, and a scaled time, τ , are defined

$$[U_i] = N_i/N_0;$$

$$\tau = tkN_0/V$$

where N_i is the number of units of U_i ; V is the volume of the reaction system; N_0 is the arbitrary reference number; and t is the reaction time. If the change of the reaction volume is negligible, according to the principle of equal reactivity, PER [19], the reaction rate of monomers A_2 can be expressed as

$$\frac{d[A_2]}{d\tau} = -6[A_2][B_3] - 4[A_2][B_2b] - 2[A_2][Bb_2]$$

where the negative terms denote the disappearance rates of the monomers A_2 , which reacts with other units and becomes units Aa . In the same way, the rate of equations of the other units can be written as follows, and solved by the Runge–Kutta method or other solvers.

$$\begin{aligned} \frac{d[Aa]}{d\tau} &= 6[A_2][B_3] + 4[A_2][B_2b] + 2[A_2][Bb_2] - 3[Aa][B_3] \\ &\quad - 2[Aa][B_2b] - [Aa][Bb_2] \end{aligned}$$

$$\frac{d[a_2]}{d\tau} = 3[Aa][B_3] + 2[Aa][B_2b] + [Aa][Bb_2]$$

$$\frac{d[B_3]}{d\tau} = -6[B_3][A_2] - 3[B_3][Aa] - 3[B_3][AR]$$

$$\begin{aligned} \frac{d[B_2b]}{d\tau} &= 6[B_3][A_2] + 3[B_3][Aa] + 3[B_3][AR] - 4[B_2b][A_2] \\ &\quad - 2[B_2b][Aa] - 2[B_2b][AR] \end{aligned}$$

$$\begin{aligned} \frac{d[Bb_2]}{d\tau} &= 4[B_2b][A_2] + 2[B_2b][Aa] + 2[B_2b][AR] - 2[Bb_2][A_2] \\ &\quad - [Bb_2][Aa] - [Bb_2][AR] \end{aligned}$$

$$\frac{d[b_3]}{d\tau} = 2[Bb_2][A_2] + [Bb_2][Aa] + [Bb_2][AR]$$

$$\frac{d[AR]}{d\tau} = -3[AR][B_3] - 2[AR][B_2b] - [AR][Bb_2]$$

$$\frac{d[aR]}{d\tau} = 3[AR][B_3] + 2[AR][B_2b] + [AR][Bb_2]$$

The degree of branching, DB, of HBPs is another important parameter of the molecular structure [26]. Holter and Frey suggested a modified degree of branching based on the actual number over the maximum possible number of dendritic units [27]:

$$DB = \frac{ND}{ND + 0.5NL} \quad (11)$$

where ND and NL are the number of dendritic, and linear units, respectively. In this study, three reacted B-functionalities, b_3 , denotes the dendritic units, and two reacted B-functionalities, Bb_2 , presents the linear units [21]. The numbers of dendritic, and linear units are changed with reaction time and conversion that can be calculated by the kinetic model and numerical method mentioned above. Moreover, Muller et al. suggested the use of the fraction of branch points, FB, to characterize the hyper-branched polymers [28]:

$$FB = \frac{ND}{(\text{total number of units}) - (\text{number of monomers and AR})} \quad (12)$$

4. Results and discussion

Fig. 2 shows the gelation curves of $(p_A)_{\text{gel}} = 1$ for $r < 1$, or $(p_B)_{\text{gel}} = 1$ for $r > 1$ depending on the functionality, g , of monomer B_g . At $r < 1$, if $\lambda_2 < \frac{g}{2(g-1)}$, on the left side of the gelation line, the gel cannot occur at $p_A = 1$. At higher functionality, g , the system needs feeding fewer monomers A_2 to keep away from the gelation. On the other hand, while $r > 1$, if $\lambda_1 + 2\lambda_2 > \sqrt{2g(g-1)\lambda_2}$, in which λ_1 and λ_2 are above the gelation curve, at $p_B = 1$, the polymerization system can still avoid gelation. With increasing the functionality of B_g , more end-capping molecules, AR, are needed to produce totally soluble polymers at high conversion.

In this work, the polymerization system of B_3 mixed with monomers A_2 with the addition of AR are discussed as an example. The gelation curves of various critical conversions are plotted in Fig. 3. It suggests that, once the initial composition of the reactants is outside of the “xvz” region, that is $\lambda_2 < 0.75$ or $\lambda_1 + 2\lambda_2 - 2\sqrt{3\lambda_2} > 0$, at $p_A = 1$ or $p_B = 1$, polymers can be formed under 100% of sol fraction. In other words, when the polymerization stops automatically caused by the complete consumption of groups A or B, the products without a gel can be obtained.

Fig. 4 shows the degree of polymerization, DP, at $p_A = 1$ or $p_B = 1$, without the addition of AR. In this study, the DP

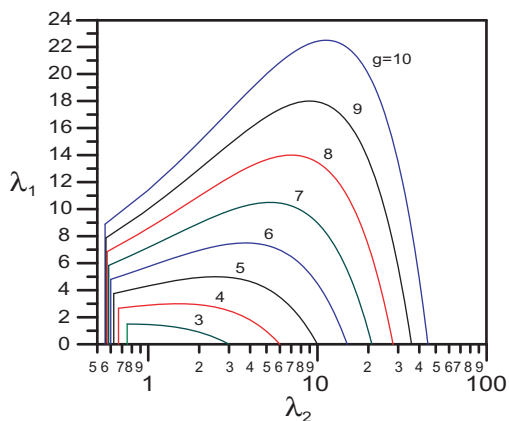


Fig. 2. The gelation curves of $(p_A)_{\text{gel}} = 100\%$ or $(p_B)_{\text{gel}} = 100\%$ under various functionality, g , of monomers B_g .

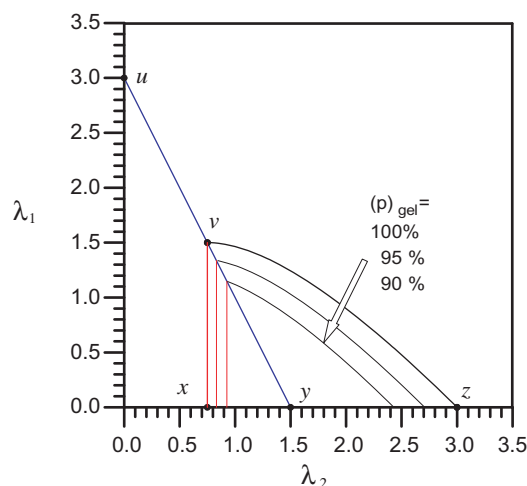


Fig. 3. The gelation curves of critical conversion of 90, 95, or 100% for $A_2 + B_3 + AR$ system. [$(p)_{\text{gel}} = (p_A)_{\text{gel}}$ at $r < 1$; $(p)_{\text{gel}} = (p_B)_{\text{gel}}$ at $r > 1$].

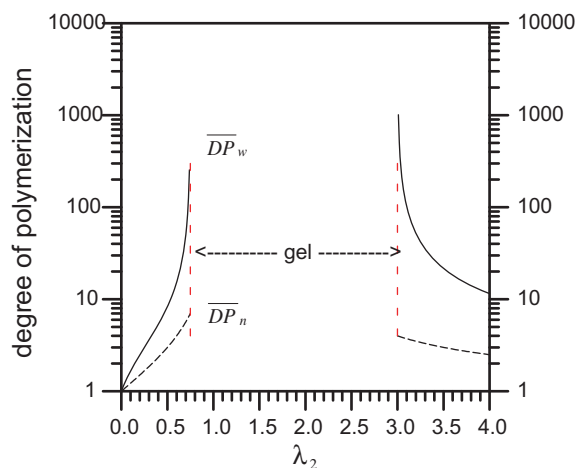


Fig. 4. Degree of polymerization, DP, changed with λ_2 at $\lambda_1 = 0$. ($p_A = 100\%$ at $\lambda_2 < 0.75$; $p_B = 100\%$ at $\lambda_2 > 3$).

was calculated by setting the molecular weight of AR, A_2 , or B_3 to be one. If $r < 1$, the degree of polymerization increases with increasing A_2 . At $\lambda_2 = 0.75$, the weight-average degree of polymerization, \overline{DP}_w calculated by the Eq. (7) becomes infinite, and the gelation occurs. When the value of the λ_2 is larger than 0.75, $(p_A)_{\text{gel}}$ is less than 100%, an infinite network can be formed during the polymerization. After which, when λ_2 is 1.5, the groups A are in excess; and when $\lambda_2 < 3$, the value of $(p_B)_{\text{gel}}$ is lower than 100%. It implies that cross-linking can take place during the polymerization when λ_2 is in the range of $0.75 \leq \lambda_2 \leq 3$. At $\lambda_2 = 3$, the value of $(p_B)_{\text{gel}}$ is equal to 100%. It means that the weight-average degree of polymerization is divergent at $p_B = 1$. If more monomers A_2 are added into the system, and λ_2 becomes larger than 3, the polymerization can keep away from the gelation; then the weight-average degree of polymerization returns to finite values, but both \overline{DP}_n and \overline{DP}_w are decreased with the increase of monomers A_2 .

Fig. 5 shows the profiles of average degree of polymerization with the addition of AR at $\lambda_2 = 0.75$. In case of the $\lambda_1 \leq 1.5$, “line vx” in Fig. 3, the critical conversion $(p_A)_{\text{gel}}$ calculated by the Eq. (4) is equal to 100%. Therefore, the weight-average degree of polymerization becomes infinite at $p_A = 100\%$. Once $\lambda_1 > 1.5$, within the region III in Fig. 1, the value of $(p_B)_{\text{gel}}$ calculated by Eq. (5) is greater than 100%, i.e. there is no cross-linking occurs when the growth of the polymers stops at full consumption of groups B. For example, at $\lambda_1 = 1.6$ and $\lambda_2 = 0.75$, as plotted in Fig. 5, the \overline{DP}_w increases with the conversion of A, p_A . The growing profiles of \overline{DP}_n and \overline{DP}_w are very close to the system of $\lambda_1 = 1.5$ ($r = 1$), but they are terminated at $p_B = 100\%$ and $p_A = 96.8\%$; then finite branched polymers can be obtained, of which $\overline{DP}_n = 9.6$, and $\overline{DP}_w = 64$.

Because, in the actual stepwise polymerization, the conversion is difficult to reach 100%, it is worthy to calculate the molecular weight of the polymers that are close to the full consumption of groups A or B. At $\lambda_2 = 0.75$ and $r < 1$, $(p_A)_{\text{gel}} = 100\%$, and the degree of polymerization near the critical conversion increases with increasing AR as indicated in Fig. 6. It was found that at $p_A = 95\%$, the \overline{DP}_w is 34 through 40, and grows to 171–207 at $p_A = 99\%$; then 1714–2076 at $p_A = 99.9\%$. Finally, the \overline{DP}_w tends towards infinite when p_A approaches 100%. On the other hand, if more AR is added into the system and λ_1 becomes larger than 1.5, at which $r > 1$, the degree of polymerization, DP, decreases suddenly. Because the polymers can react with end-capping molecules AR to form dead dangling chains: aR, it can retard the growth of polymers, and avoid gelation. With increasing AR, the DP and polydispersity index, PDI, decrease as shown in Figs. 6 and 7. At $r = 1$, and $p_A = p_B = 99\%$, the \overline{DP}_w is 207, \overline{DP}_n is 12, and PDI is very broad, about 18. With the addition of more end-capping molecules AR, for example, at $\lambda_1 = 1.6$, and $p_B = 99\%$, of that $r = 1.03$, the weight- and number-average degree of polymerization are reduced as 49, and 8.8, respectively; thus the distribution of the degree of polymerization becomes narrower, PDI is 5.6. Moreover, after the p_B is about 99%, the value of DP is less sensitive to the conversion. In other words, it can be

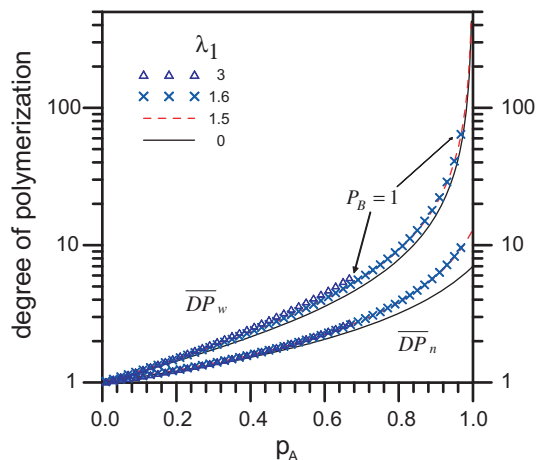


Fig. 5. Degree of polymerization changed with conversion of A group at $\lambda_2 = 0.75$, and $\lambda_1 = 0; 1.5; 1.6$; and 3.

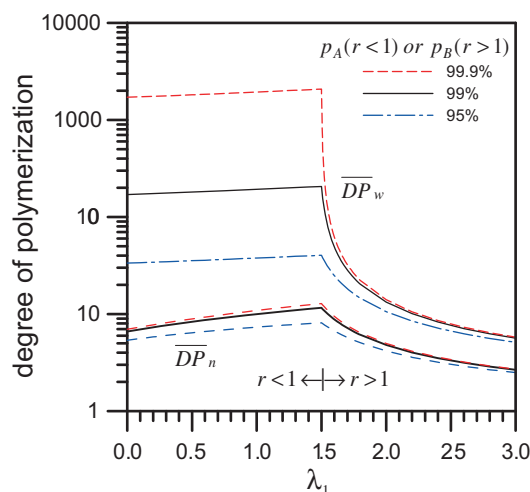


Fig. 6. Degree of polymerization changed with λ_1 at $\lambda_2 = 0.75$, and p_A or $p_B = 95, 99$, and 99.9%.

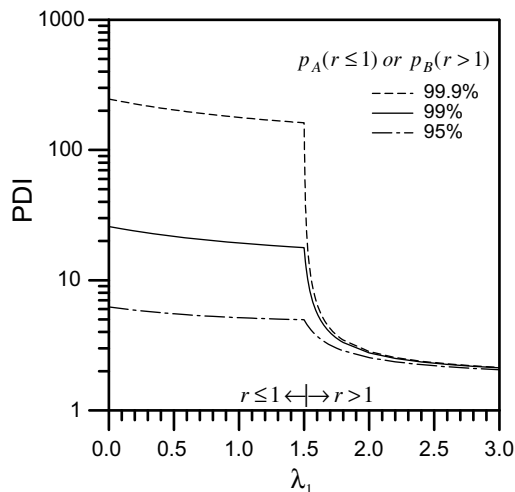


Fig. 7. Polydispersity index, PDI, of polymers changed with λ_1 at $\lambda_2 = 0.75$, and p_A or $p_B = 95, 99$, and 99.9%.

easier to control the molecular weight of polymers at a high conversion.

When λ_1 is smaller than 1.5, and $r = 1$, the gelation occurs at the conversion of 100% or less, as shown in “vy” line of Fig. 3. After the λ_1 of 1.5, “v” point, even the functional groups of A and B are consumed totally, it cannot reach a gel point. Therefore, the soluble hyperbranched polymers could be formed. In this case, the average degree of polymerization near the full conversion can be calculated by Eqs. (1) and (2). Fig. 8 indicates the average degree of polymerization changes with λ_1 at $r = 1$. It was found that, after the λ_1 of 1.5, the DP decreases with the increasing of the end-capping molecules AR.

The degree and the fraction of branching of the polymerization system, Eqs. (11) and (12), can be further calculated by the kinetic model and numerical method.

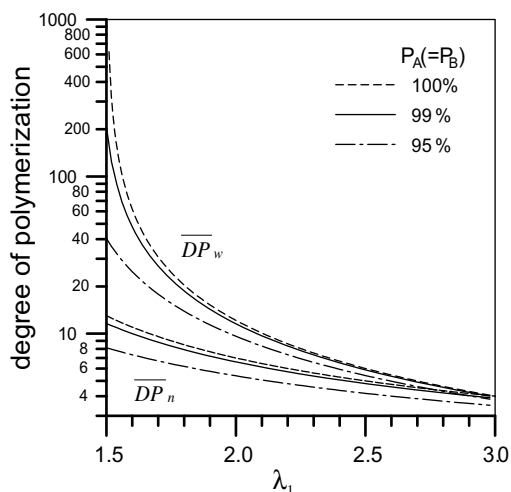


Fig. 8. Degree of polymerization changed with λ_1 at $r = 1$, and $p_A = p_B = 95, 99$, and 100%.

Fig. 9 shows the degree and the fraction of branching of the polymerization system, Eqs. (11) and (12), of B_3 mixed with A_2 monomers, and without the addition of AR, $\lambda_1 = 0$. It was found that, with the increase of monomers A_2 , the number of dendritic units, b_3 , increases, and the DB increases to 0.4 at $\lambda_2 = 0.75$, and $p_A = 99\%$. When the λ_2 is up to 0.75, the gel could be formed during the polymerization. When the λ_2 is larger than 3 and $p_B = 99\%$, because most of functional groups B are reacted, the DB of HBPs is increased to 0.99. Actually, in the case of $r = 1$ or $r > 1$, the DB could reach to 100% when the groups B are reacted completely with A. As shown in Fig. 9, at a low content of monomers A_2 , $\lambda_2 < 0.75$, the FB also increases with λ_2 , resulted from the increase of dendritic units. At the λ_2 of 0.75, and $p_B = 99\%$, the FB is 0.075. After the λ_2 of 3,

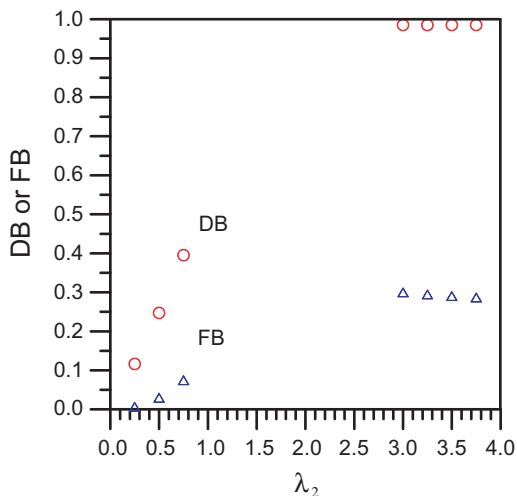


Fig. 9. Degree and fraction of branching, DB and FB, changed with λ_2 at $\lambda_1 = 0$, and $p_A = 99\%$ ($\lambda_2 < 0.75$); or $p_B = 99\%$ ($\lambda_2 > 3$).

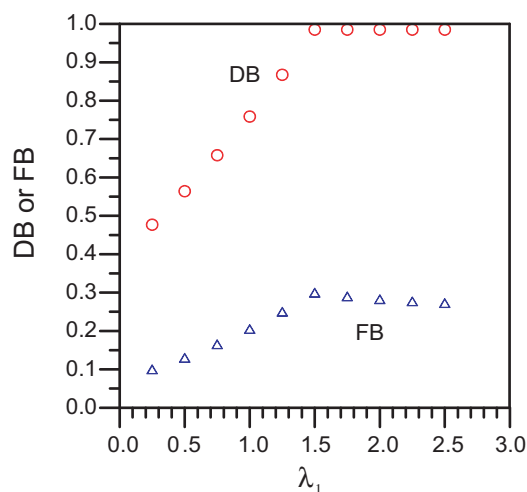


Fig. 10. Degree and fraction of branching changed with λ_1 at $\lambda_2 = 0.75$, and $p_A = 99\%$ ($\lambda_1 < 1.5$); or $p_B = 99\%$ ($\lambda_1 > 1.5$).

the FB rises to 0.3, and it would be reduced slightly to 0.29 at $\lambda_2 = 3.5$. The DB and the FB of the system of $\lambda_2 = 0.75$ with the addition of the end-capping molecules AR are plotted in Fig. 10. At $r < 1$, that is $\lambda_1 < 1.5$, both of DB and FB increase with increasing λ_1 . When $r = 1$, and $\lambda_1 = 1.5$, the DB is 0.99, and the FB is 0.29 at the conversion of 99%. After $\lambda_1 = 1.5$, the DB is kept as 0.99, but the FB is down slightly to be 0.27 at $\lambda_1 = 2.5$. Under an equal stoichiometric system, $r = 1$, at the conversion of 99%, the DB is 0.99, and the FB is about 0.3, which would be a little less by increasing λ_1 .

5. Conclusions

The stepwise polymerization of a mixture of bifunctional A-type monomers, A_2 , and g functional B-type monomers, B_g , with the addition of the end-capping molecules AR have been investigated by the recursive model. A diagram of gel region depends on the molar ratios of $(AR)_0/(B_g)_0$ and $(A_2)_0/(B_g)_0$, λ_1 and λ_2 , has been plotted by the model. The degree and the fraction of branching, DB and FB, were calculated by the kinetic model. It was found that, by the addition of molecules AR, a gelation can be avoided at high conversion, and the hyperbranched polymers, HBPs, can be synthesized. The molecular structures of HBPs, such as molecular weight and the degree of branching, can be manipulated by the initial composition of reactant. Moreover, with the excess of groups A or B, the functional groups can be remained on the prepared hyperbranched polymers. We can also introduce the other functional groups resulted from the reaction of groups A and B on the HBPs. For example, hyperbranched polymers with hydroxyl groups would be synthesized by epoxy resin, D.E.R. 332 (A_2), and diethylene triamine (B_5) with the addition of phenyl glycidyl ether (AR) as the end-capping molecules under bulk polymerization [29].

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