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## First shell substitution effects on hyperbranched polymers formed from monomers $A_2$ and $B_3$ with end-capping molecules

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#### ABSTRACT

Hyperbranched polymers obtained by the polymerization of monomers  $A_2$  and  $B_3$  in the presence of end-capping molecules AR with a first shell substitution effect, FSSE, on the monomer  $B_3$  were investigated by a kinetic model. The profiles of the average degree of polymerization, degree of branching, and critical conversion under various compositions were calculated by a generating function method. It was found that, if groups B in excess of A, the curves of critical conversion A of 100%, at which a gelation occurs, based on the initial compositions with substitution effect differ from that with equal reactivity of the groups B. The weight-average degree of polymerization,  $\overline{DP}_w$ , and degree of branching, DB, increase with increasing of the reactivity ratio of B. On the other hand, when the initial groups B are lower than A, there is no apparent difference of the curves of critical conversion B of 100% between the polymerizations with and without FSSE. At high conversion of B, 99%, for example, the  $\overline{DP}_w$  and DB decrease with increasing of the end-capping molecules AR, but the  $\overline{DP}_w$  and DB are less influenced by the FSSE.

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#### 1. Introduction

Synthesis of dendrimers or hyperbranched polymers has become a major research interest due to their highly branched structure with very different characteristic features from linear polymers, such as relatively low viscosity, high solubility, and having a large amount of pending, peripheral or side functional groups [1–6]. Dendrimers are similar to star polymers except that each arm of the star exhibits repetitive branching in the manner of a tree, and have a perfectly regular structure, well-defined shape and size. Yet, dendrimers are prepared by multi-step reactions with complicated and often expensive processes [7,8]. On the other hand, the hyperbranched polymers, HBPs, are not fully branched, and have less regular structure than that of dendrimers, but the HBPs can be prepared by simple onepot polymerizations on a larger scale, such as stepwise polymerization of  $AB_g$ -type monomers (g > 2); self-condensing

\* Corresponding author. *E-mail address:* gordon@ntut.edu.tw (K.-C. Cheng). vinyl polymerization, and self-condensing ring-opening polymerization [9–13]. However, the commercial monomers are still restricted. On the contrary, because difunctional monomers  $A_2$  and multi-functional monomers  $B_g$  (g > 2) are more readily available, the direct step-wise polymerization of,  $A_2$ , with  $B_g$  to produce the hyperbranched polymers is worthy to be studied [14–18]. In order to keep away from the formation of network during polymerization, we can choose appropriate composition of monomers, or stop the reaction before gelation.

Furthermore, it was found that, in the polymerization of diepoxides with primary amine in the presence of monoepoxide, the gelation can be avoided by the addition of monofunctional reactive diluents [19,20]. It makes possible to prepare the hyperbranched polymers under 100% sol fraction by the addition of end-capping molecules. A kinetic Monte Carlo simulations was applied to interpret experimental measurements in the polymerization of hyperbranched poly(ether esters)s in a melt condensation of  $A_2$ oligomers and  $B_3$  monomers and monofunctional reagents. However, there are only few cases were reported, and the

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gel point dependent on the composition was not discussed [21,22]. The stepwise polymerization of a mixture of bifunctional A-type monomers, A<sub>2</sub>, and g functional B-type monomers, B<sub>g</sub>, with the addition of the end-capping molecules AR were investigated by a recursive model [23,24]. A diagram of the critical conversion of 100%, at which a gel forms, depends on the molar ratios of  $AR/B_g$  and  $A_2/B_g$  has been proposed. The molecular structures of the HBPs, such as molecular weight and the degree of branching, can be controlled by the initial composition of reactants. Those theoretical models of the stepwise polymerization of a mixture of monomers A<sub>2</sub> and B<sub>g</sub> with the addition of the end-capping molecules AR are base on the assumption that all functional groups of the same type are equally reactive, and react independently of one another. In other words, all the A or B groups in the monomer have the same reactivity. Yet, the equal reactivity might not be valid when first shell substitution effect is taken into consideration due to the steric effects or other reasons [25-28]. Therefore, in a polymerization with the substitution effect, the reactivity of unreacted group is dependent on the number of already reacted on the same unit. For example, for the polymerization of a diepoxide with amine, the reactivity of the primary hydrogen is higher than that of secondary hydrogen. Therefore some chain extension occurs before the branching reaction and delays the gel point [19,29-31].

In this study, we extended the generating function method [11,32–34], based on the kinetic theory, to the stepwise polymerization of a mixture of monomers of  $A_2$  and  $B_3$  in the presence of end-capping molecules AR with first shell substitution effect on  $B_3$  units but not on  $A_2$  (FSSE) [35]. The effects of reactivity on the degree of polymerization, critical conversion of *A* or *B*, and degree of branching of the hyperbranched polymers were further discussed.

### 2. Average degree of polymerization and gel point of polymers formed by A<sub>2</sub>, B<sub>3</sub> monomers, and AR

A stepwise polymerization system is considered with bifunctional A-type monomers,  $A_2$ , monofunctional A-type monomers, AR, and three functional B-type monomers,  $B_3$ , in which the groups A and B can not react with themselves, but group A can react with B; then the two molecules can combine to form a large molecule. There are nine various structural units, G(i), involved in this polymerization:

G(1): A<sub>2</sub> monomer G(2): Aa ~ G(3): ~ aa ~ or a<sub>2</sub> G(4): B<sub>3</sub> monomer G(5): B<sub>2</sub>b ~ G(6): ~ bBb ~ or Bb<sub>2</sub> G(7):  $b > b ~ or b_3$ G(8): AR G(9): ~ aR

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

$$\begin{array}{l} A_{2} + B_{3} \longrightarrow Aa + B_{2}b \quad G(1) + G(4) \stackrel{6k_{AB}}{\longrightarrow} G(2) + G(5) \\ A_{2} + B_{2}b \longrightarrow Aa + Bb_{2} \quad G(1) + G(5) \stackrel{4k'_{AB}}{\longrightarrow} G(2) + G(6) \\ A_{2} + Bb_{2} \longrightarrow Aa + b_{3} \quad G(1) + G(6) \stackrel{2k''_{AB}}{\longrightarrow} G(2) + G(7) \\ Aa + B_{3} \longrightarrow a_{2} + B_{2}b \quad G(2) + G(4) \stackrel{3k_{AB}}{\longrightarrow} G(3) + G(5) \\ Aa + B_{2}b \longrightarrow a_{2} + Bb_{2} \quad G(2) + G(5) \stackrel{2k'_{AB}}{\longrightarrow} G(3) + G(6) \\ Aa + Bb_{2} \longrightarrow a_{2} + b_{3} \quad G(2) + G(6) \stackrel{k''_{AB}}{\longrightarrow} G(3) + G(7) \\ AR + B_{3} \longrightarrow aR + B_{2}b \quad G(8) + G(4) \stackrel{3k_{AB}}{\longrightarrow} G(9) + G(5) \\ AR + B_{2}b \longrightarrow aR + Bb_{2} \quad G(8) + G(5) \stackrel{2k'_{AB}}{\longrightarrow} G(9) + G(6) \\ AR + Bb_{2} \longrightarrow aR + b_{3} \quad G(8) + G(6) \stackrel{k''_{AB}}{\longrightarrow} G(9) + G(7) \\ \end{array}$$

or

$$G(b_{i1}) + G(b_{i2}) \xrightarrow{k_i} G(b_{i3}) + G(b_{i4}) \quad i = 1, 2, \dots, 9$$
(1)

The corresponding parameters,  $b_{ij}$  and  $k_i$ , are shown in Table 1, and

$$\rho = \frac{k'_{AB}}{k_{AB}} = \frac{k''_{AB}}{k'_{AB}} \tag{2}$$

in which  $\rho$  is reactivity ratio. In this study, we focus on the changes in the reactivity at the B-sites, but not A-sites, with polymerization, and  $\rho$  is assumed to be constant and independent of the extent of reaction. If the reactivity of group B increases after reaction of the first or second one, it is a positive substitution effect on B; then  $\rho > 1$ . On the contrary, when a negative substitution effect leads to a decrease of the reactivity of B on the unit  $B_2b$  or  $Bb_2$ , and  $\rho < 1$ .

The initial composition is defined by parameters  $\lambda_1$  and  $\lambda_2$ :

$$\lambda_1 = (AR)_0 / (B_3)_0$$
; and  
 $\lambda_2 = (A_2)_0 / (B_3)_0$ ,

where  $(AR)_0$ ,  $(A_2)_0$ , and  $(B_3)_0$  are the initial moles of monomers AR,  $A_2$  and  $B_3$ , respectively. Therefore, the molar ratio of group A to B becomes

$$r = \frac{\lambda_1 + 2\lambda_2}{3} \tag{3}$$

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

$$\mathbf{E} = (e_1, e_2, e_3, e_4, e_5, e_6, e_7, e_8, e_9, e_w)$$
(4)

where  $e_J$  represents the number of structural unit G(J) on a molecule  $\langle E \rangle$ , and  $e_w$ , equaling  $e_{10}$ , is the molecular weight

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The	parameters	of	bii	and	ki.

$\begin{bmatrix} b_{11} \\ b_{21} \\ b_{31} \\ b_{41} \\ b_{51} \\ b_{61} \\ b_{71} \end{bmatrix}$	b <sub>12</sub> b <sub>22</sub> b <sub>32</sub> b <sub>42</sub> b <sub>52</sub> b <sub>62</sub> b <sub>72</sub>	b <sub>13</sub> b <sub>23</sub> b <sub>33</sub> b <sub>43</sub> b <sub>53</sub> b <sub>63</sub> b <sub>73</sub>	b <sub>14</sub> b <sub>24</sub> b <sub>34</sub> b <sub>44</sub> b <sub>54</sub> b <sub>64</sub> b <sub>74</sub>	$k_1 \\ k_2 \\ k_3 \\ k_4 \\ k_5 \\ k_6 \\ k_7$	=	1 4 1 5 1 6 2 4 2 5 2 6 8 4	2 2 3 3 9	5 6 7 5 6 7 5	
b <sub>61</sub> b <sub>71</sub>	b <sub>62</sub> b <sub>72</sub>	b <sub>63</sub> b <sub>73</sub>	b <sub>54</sub> b <sub>64</sub> b <sub>74</sub>	$k_6 \\ k_7$		2 5 2 6 8 4	3 9	7 5	$\left  \begin{array}{c} Z_{AB} \\ K_{AB}'' \\ 3k_{AB} \end{array} \right $
$b_{81}$ $b_{91}$	b <sub>82</sub> b <sub>92</sub>	b <sub>83</sub> b <sub>93</sub>	b <sub>84</sub> b <sub>94</sub>	$\frac{k_8}{k_9}$		85 86	9 9	6 7	$\begin{bmatrix} 2k'_{AB} \\ k''_{AB} \end{bmatrix}$

of the molecule  $\langle E \rangle$ . For example, **E** = (1,0,0,0,0,0,0,0,0,  $W(A_2)$ ) denotes monomer A<sub>2</sub>, and  $W(A_2)$  is the molecular weight of this monomer; **E** = (0,0,0,1,0,0,0,0,0, $W(B_3)$ )) denotes monomer B<sub>3</sub>, and  $W(B_3)$  is the molecular weight of the monomer; and **E** = (0,1,0,0,1,0,0,0,0, $W(A_2)$ +  $W(B_3)$ ) is the molecule  $Aa - bB_2$ , formed by combining monomers A<sub>2</sub> and B<sub>3</sub>, if there are no condensates produced during polymerization. The system with condensate molecules formed can also be treated by the generating function method.

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 [10,11], the reactions between molecules are

$$\langle E' \rangle + \langle E'' \rangle \xrightarrow{\kappa_i} \langle E' + E'' + L_i \rangle \quad i = 1, 2, \dots, 9$$
 (5)

where  $\langle E' + E'' + L_i \rangle$  is the molecule formed by combining  $\langle E' \rangle$  with  $\langle E'' \rangle$  in the i-th reaction, and,

$$\begin{split} L_{i} &= (l_{1}, l_{2}, \dots, l_{9}, 0) \\ l_{J} &= -\delta(b_{i1}, J) - \delta(b_{i2}, J) + \delta(b_{i3}, J) + \delta(b_{i4}, J), \quad J = 1, 2, \dots, 9 \end{split}$$

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

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

For example, a monomer  $A_2$  reacts with another molecule  $Aa - bB_2$  by the following reaction:

$$A_2 + Aa - bB_2 \longrightarrow Aa - bBb - aA$$

in which

$$\begin{split} \langle E' \rangle &= A_2 \\ \langle E'' \rangle &= Aa - bB_2 \\ \langle E' + E'' + L_i \rangle &= Aa - bBb - aA \\ E' &= (1,0,0,0,0,0,0,0,W(A_2)); \\ E'' &= (0,1,0,0,1,0,0,0,0,W(A_2) + W(B_3)); \\ L_2 &= (-1,1,0,0,-1,1,0,0,0,0); \\ E' + E'' + L_2 &= (0,2,0,0,0,1,0,0,0,2W(A_2) + W(B_3), \text{ and } \\ k_2 &= 4k'_{AB} \end{split}$$

Furthermore, a dimensionless number fraction, [*E*], the ratio of the reaction rate constant,  $k_i^*$ , and a scaled time,  $\tau$ , are defined:

$$[E] = N(E)/N_0 \tag{7}$$

 $k_{i}^{*} = (k_{i}/k_{o})(V_{o}/V)$ (8)

$$\tau = tk_o(N_o/V_o) \tag{9}$$

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. (5), the rate equation of the isomers can be written as,

$$\frac{d[E]}{d\tau} = \sum_{i=1}^{9} k_i^* \left\{ \sum_{E'+E''+L_i=E} ([E'][E'']p'_{i1}p''_{i2}) - [E]p_{i1} \sum_{\text{all } E''} [E''']p''_{i2} - [E]p_{i2} \sum_{\text{all } E''} [E''']p''_{i1} \right\}$$
(10)

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. (10) give the total rates of appearance and disappearance of the isomer  $\langle E \rangle$ , respectively. Eq. (10) cannot be solved directly, but it can be transformed into finite ordinary differential equations using a generating function [27,34,35]. 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 A.

Moreover, the degree of branching, DB, is a very important structural parameter in characterizing the hyperbranched polymers. Holter and Frey suggested a modified degree of branching based on the actual number over the maximum possible number of dendritic units [36]:

$$DB = \frac{ND}{ND + 0.5NL}$$
(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 Bfunctionalities,  $Bb_2$ , presents the linear units [18]. 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 hyperbranched polymers [13]:

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

#### 3. Results and discussion

In the previous work, we reported the gel points of polymerization changed by the molar ratios of  $AR/B_{\rm g}$  and  $A_2/B_g$ ,  $\lambda_1$  and  $\lambda_2$  [24]. It suggested that, under no substitution effect, if the initial composition is outside of the "xvz" region, the polymerization stops automatically caused by the complete consumption of groups A or B, and the hyperbranched polymers under 100% sol fraction can be obtained. For example, at  $\lambda_1 = 0$  and  $\lambda_2 = 0.75$ , that is on the point "x" in Fig. 1, the gelation forms at conversion of A =100 % and that of B=50%. If  $\lambda_2$  was increased to be 0.76, the critical conversion of A would be reduced as 99.3%. It implies that a gel could occur before the full consumption of groups A. On the contrary, in the case that  $\lambda_2$  is decreased to be 0.74, even though the groups A are totally reacted, the polymerization system still keeps away from the gelation. Furthermore, if there is an increase in the rate constant after one or two of the group(s) B of the monomer  $B_3$  has reacted, the rate constant ratio,  $\rho$ , is great than one. First, we consider the case of *r* < 1, that is  $\lambda_1 + 2\lambda_2 < 3$  as shown on the left and down side of line "uy" in Fig. 1, of which the initial number of groups B is larger than that of A, and conversion of A,  $p_A$ , is always larger than that of B,  $p_{\rm B}$ . Fig. 2 shows the critical conversion of group A, at which the weight-average degree of polymerization tends toward a divergence, dependent on the value of  $\lambda_1$  at



**Fig. 1.** The curves of critical conversion A or B of 100% dependent on the initial compositions of reactants under various reactivity ratios,  $\rho$ .

 $\lambda_2 = 0.6$ . It was found that the critical conversion of A,  $p(A)_{gel}$ , increases with increasing of end-capping molecules AR. Under  $\rho = 2$ , that is  $k_{AB'}/k_{AB} = k_{AB''}/k_{AB'} = 2$  in Eq. (2),  $p(A)_{gel}$  is 0.928 at  $\lambda_1 = 0$ , and is raised to 100% at  $\lambda_1 = 0.534$ . It implies that if more reactants AR are added into the system, and  $\lambda_1$  becomes larger than 0.534, the polymerization can keep away from the gelation. With higher reactivity ratio  $\rho$ , the positive substitution effect leads to increasing the probability of three sides of monomer B<sub>3</sub> combined with group A, and there are more effective branching points formed; then a gelation might occur easily. Therefore, it needs more end-capping molecules AR to avoid formation of cross-linking networks during polymerization. For example, if  $\rho = 10$ , the critical conversion of A becomes 100% at  $\lambda_1 = 1.16$ . After that, the polymer products without a gel can be prepared. The



Fig. 2. The critical conversion of A changed with  $\lambda_1$  and reactivity ratio  $\rho$  at  $\lambda_2 = 0.6$ .

gelation curves of the  $p(A)_{gel}$  of 100% for  $A_2 + B_3 + AR$  system at r < 1 are plotted as lines "vi", "vj", and "vk" at  $\rho = 10, 4$  and 2, respectively, in Fig. 1. When the initial composition of reactants is on the left upper side of the gelation curves, the polymerization stops automatically resulted from the complete consumption of groups A, and the gelation cannot occur.

Fig. 3 indicates the critical conversion of A changed with the addition of end-capping molecules AR at  $\lambda_2 = 0.85$  and r < 1. Under no substitution effect, i.e.,  $\rho = 1$ , the critical conversion of A is about 94%, and it seems not be changed by the addition of AR. In the case of  $\rho > 1$ , the  $p(A)_{opl}$  increases with increasing of  $\lambda_1$ . On the contrary, when ho < 1, the critical conversion of A decreases with the addition of AR, for example, if  $\rho = 0.5$ , the critical conversion of A is 100% at  $\lambda_1 = 0.22$ , and reduced to be 0.94 at  $\lambda_1 = 1.3$  (r = 1). It suggests that, at  $\lambda_1$  less than 0.22, the soluble polymers without a gel would be produced after total consumption of groups A. The gelation curves of the system of  $p(A)_{gel} = 100\%$  at r < 1 are shown as lines "vm" and "vn" in Fig. 1. If the initial composition is on the left side of lines "vm" or "vn", the gelation can be avoided.

Furthermore, the polymerization systems with the groups A in excess of B, i.e., r > 1, and  $p_A < p_B$ , were calculated at  $\lambda_2 = 2$ . Fig. 4 shows the critical conversion of B,  $p(B)_{gel}$ , dependent on the addition of end-capping molecules AR. It was found that the value of  $p(B)_{oel}$  increases with the increase of AR. At the same initial composition, the higher reactivity ratio,  $\rho$ , results in a lower critical conversion. The difference of the critical conversion becomes smaller at higher value of  $\lambda_1$ . Finally, at  $\lambda_1 = 0.90$ , the  $p(B)_{gel}$  is 100%, and it is independent of the reactivity ratio,  $\rho$ . We calculated the profile of the degree of polymerization changed with conversion, and obtain the critical conversion under different  $\lambda_1$  and  $\lambda_2$ . It was found that, when r > 1, the  $p(B)_{gel}$  of 100% of the system with substitution effect occurs at the same composition of that without substitution effect as shown on the curve "vz" in Fig. 1. The



**Fig. 3.** The critical conversion of A changed with  $\lambda_1$  and  $\rho$  at  $\lambda_2 = 0.85$ .



**Fig. 4.** The critical conversion of B changed with  $\lambda_1$  and  $\rho$  at  $\lambda_2 = 2$ .

function of that curve is  $\lambda_1 + 2\lambda_2 = 2\sqrt{3\lambda_2}$ , which was derived from the recursive model [23,24]. If  $\lambda_1$  and  $\lambda_2$  are above the curve "vz", i.e.,  $\lambda_1 + 2\lambda_2 > 2\sqrt{3\lambda_2}$ , at  $p_{\rm B} = 100\%$ , the polymerization can still keep from a gelation.

We further discuss the polymerization system with the equal initial number groups A and B, i.e., r = 1, and alone the line "yu" in Fig. 1. Fig. 5 shows the profile of weight-average degree of polymerization versus conversion. For the system of  $\lambda_1 = 0.6$ ;  $\lambda_2 = 1.2$ ; and  $\rho = 0.1$ , the  $\overline{\text{DP}}_{w}$  becomes infinite at conversion of 0.79 as indicated in Fig. 6, and the critical conversion is reduced to 0.65 at  $\rho = 10$ . Before  $\lambda_1$  of 1.5, the critical conversion decreases with increase of the value of  $\rho$ . However, when the initial composition is on the point "v" in Fig. 1, where  $\lambda_1 = 1.5$  and  $\lambda_2 = 0.75$ , the critical conversion is increased to 100%, and it seems independent of the reactivity ratio,  $\rho$ . In the actual polymerization, the conversion of A or B is dif-



**Fig. 5.** The profile of degree of polymerization changed with reactivity ratio  $\rho$  at r = 1.



**Fig. 6.** The critical conversion of A or B changed with  $\lambda_1$  and  $\rho$  at r = 1.

ficult to reach 100%, thus we calculated the degree of polymerization that is close to the full conversion. Fig. 7 shows the degree of polymerization changed with the initial composition at conversion of 99%. The number-average degree of polymerization,  $\overline{DP}_n$ , can be calculated by the generation function method or by the following equation [23,24]:

$$\overline{DP}_n = \frac{1 + \lambda_1 + \lambda_2}{1 + \lambda_1 + \lambda_2 - (\lambda_1 + 2\lambda_2)p_A}$$
(13)

Apparently, it is independent of the reactivity ratio,  $\rho$ . On the contrary, at  $\lambda_1 = 1.5$  and  $\lambda_2 = 0.75$ , the weight-average degrees of polymerization, which changed with reactivity, are about 206, 207, and 388 at  $\rho = 0.1$ , 1 and 10, respectively. It decreases with increase of end-capping molecules AR. As shown in Fig. 8, if the value of  $\lambda_1$  is 1.6, at early stage of the reaction, the weight-average degree of



**Fig. 7.** The degree of polymerization changed with  $\lambda_1$  and  $\rho$  at r = 1, and  $p_A = p_B = 99\%$ .



**Fig. 8.** The profile of degree of polymerization changed with reactivity ratio  $\rho$  at  $\lambda_1 = 1.6$  and  $\lambda_2 = 0.7$  (r = 1).

polymerization,  $\overline{\text{DP}}_{w}$ , grows faster for the system with a higher reactivity ratio,  $\rho$ , than that with a lower one. But, when the functional groups A and B are nearly full reacted, the weight-average degrees of polymerizations of the products are similar under different reactivity ratio. For example, at conversion of 99%, the weight-average degrees of polymerization are about 48, 48, and 53 at  $\rho = 0.1$ , 1 and 10, respectively.

Fig. 9 indicates the degree of polymerization changed with the addition of AR at  $\lambda_2 = 0.75$  and conversion of A (r < 1) or B (r > 1) of 99%. For the polymerization system without substitution effect, i.e.,  $\rho = 1$ , if r < 1,  $\overline{\text{DP}}_w$  is about 171 through 207. On the other hand, if the substitution effect is taken into account, the weight-average degree of polymerization is different. Under positive FSSE,  $\rho = 10$  and r < 1, for example, the critical conversion of A is less than 99%, that is, before that, the weight-average degree



**Fig. 9.** The degree of polymerization changed with  $\lambda_1$  and  $\rho$  at  $\lambda_2 = 0.75$  and  $p_A$  (r < 1) or  $p_B$  (r > 1) = 99%.

of polymerization would tend to be infinite. However, with addition of the AR of  $\lambda_1 = 1.5$ , the critical conversion becomes 99.7%, and the weight-average degree of polymerization is about 387. On the contrary, at  $\rho = 0.1$  and  $\lambda_1 = 0$ , the  $\overline{DP}_w$  is only 10. But, with addition of the molecules AR of  $\lambda_1 = 1.5$ , that is r = 1, it is raised to 206, which is very close to that without substitution effect. Once more end-capping molecules AR are added into the polymerization, and the  $\lambda_1$  becomes larger than 1.5, at which r > 1, the degree of polymerization decreases rapidly for all systems with various reactivity ratios of 0.1 through 10. It is resulted from that the end-capping molecules can react with polymers and form dead dangling chains, which could retard the growth of polymers. Under an equal stoichiometric system, r = 1, the weight-average degree of polymerization is 387 at  $\rho = 10$ , which is apparently higher than that without substitution effect. After  $\lambda_1$  of 1.5; then r > 1, the degree of polymerization decreases with addition of AR. If the  $\lambda_1$  increases to 1.7, for example, the  $\overline{\text{DP}}_{\text{w}}$  is reduced to 30 at  $\rho = 10$ , and 28 at  $\rho = 1$  or 0.1. It implies that, if groups A in excess of groups B and at high conversion, the reactivity ratio,  $\rho$ , has only slight effects on the degree of polymerization.

According to the Eqs. (11) and (12), the degree and fraction of branching, DB and FB, can be calculated by the generating function method. Fig. 10 shows the DB and FB of the system of  $\lambda_2 = 0.75$  with the addition of the end-capping molecules AR. It was found that both DB and FB increase with the addition of AR. If there is no substitution effect, the degree of branching is 0.395 at  $\lambda_1 = 0$ , and raised to 0.985 at r = 1. Because, it is difficult to form dendritic units,  $b_3$ , for the polymerization at a low reactivity ratio, when  $\rho = 0.1$ , the degree of branching are only 0.035 at  $\lambda_1 = 0$ . But, it also increases to 0.985 at r = 1; then keeps at the same value after that. The DB of the system with high reactivity ratio of  $\rho = 10$  is near 100% at  $r \ge 1$  as shown in Fig. 10. 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. It could be misleading from short range effects. The dendritic



**Fig. 10.** The degree and fraction of branching changed with  $\lambda_1$  and  $\rho$  at  $\lambda_2 = 0.75$  and  $p_A$  (r < 1) or  $p_B$  (r > 1) = 99%.

unit,  $b_3$ , is just capped with monomer  $A_2$  or AR. The longer range effects of  $A_2 + B_3$  polymerization system were discussed by Schmaljohann and Voit [18]. The change of the fraction of branching, FB, shows the similar trend. At r = 1, the FB is about 0.3. It would be a little less by increasing the end-capping molecules AR.

#### 4. Conclusions

The first shell substitution effects, FSSEs, on the polymerization of monomers A<sub>2</sub> and B<sub>3</sub> with end-capping molecules AR have been investigated by the kinetic model. First, the diagram of the critical conversion of 100% depends on the molar ratios of  $AR/B_g$  and  $A_2/B_g$ ,  $\lambda_1$  and  $\lambda_2$ , has been proposed. When the initial number of groups A is less than that of B, that is  $\lambda_1 + 2\lambda_2 < 3$ , and r < 1, the curve of conversion A of 100%, at which the gelation occurs, is dependent on the reactivity ratio,  $\rho$ . With the positive substitution effect and higher reactivity ratio, the polymerization system needs more end-capping molecules to keep away from gelation. Under the negative substitution effect. i.e.,  $\rho < 1$ , the initial composition region which leads to 100% sol fraction at conversion of A of 100% is a little larger than that of polymerization without substitution effect. On the contrary, if the initial groups A is in excess of B, r > 1, there is no difference of the curve of critical conversion B of 100% between the polymerizations with and without FSSE. At the same initial composition of reactants, at r < 1, both of the weight-average degree of polymerization,  $\overline{DP}_{w}$ , and degree of branching, DB, increase with increasing of the reactivity ratio. At r > 1 and high conversion of B, the  $\overline{DP}_{w}$  and DB decrease with the addition of end-capping molecules AR, but they are less affected by the reactivity ratio of groups B.

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#### Appendix A. 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:

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

where  $\omega_j$  is a dummy variable, and H is a function of  $\tau$  and  $\omega_j$ .

Eq. 10 can be multiplied by  $\sum_{\text{all } E} \left( \prod_{j=1}^{n+1} \omega_j^{e_j} \right)$  and summed over E to yield,

$$\frac{\partial H}{\partial \tau} = \sum_{i=1}^{m} k_i^* (H_{x_{i1}} H_{x_{i2}} x_{i3} x_{i4} - x_{i1} H_{x_{i1}} H_{i2} - x_{i2} H_{x_{i2}} H_{i1})$$
(A.2)

where m = 9, and n = 9 in this study, and

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

$$H_{ij} \equiv H_{x_{ij}}(\omega_{q(q=1,2,\dots,n+1)} = 1),$$
that is, if  $G(b_{ij}) = G(J),$ 

$$b_{ij} = J;$$

$$x_{ij} = \omega_J;$$

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

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

 $x_{ii} = \omega_i$  for  $b_{ii} = I$ :

By setting all dummy variables,  $\omega_{q(q=1,2,\dots,n+1)}$  to 1, Eq. (A.2) can be written as,

$$\frac{\partial H^*}{\partial \tau} = \sum_{i=1}^m k_i^* (-H_{i1} H_{i2}) \tag{A.3}$$

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. (A.2) with respect to  $\omega_r$ , or to both  $\omega_r$  and  $\omega_s$ :

$$\frac{\partial H_r}{\partial \tau} = \sum_{i=1}^m k_i^* H_{i1} H_{i2} \left( \frac{\partial x_{i3} x_{i4}}{\partial \omega_r} - \frac{\partial x_{i1}}{\partial \omega_r} - \frac{\partial x_{i2}}{\partial \omega_r} \right)$$
(A.4)

$$\begin{aligned} \frac{\partial H_{r,s}}{\partial \tau} &= \sum_{i=1}^{m} k_{i}^{*} \left[ H_{i1,r} H_{i2,s} + H_{i1,s} H_{i2,r} + (H_{i1,r} H_{i2} + H_{i1} H_{i2,r}) \right. \\ & \times \left( \frac{\partial \chi_{i3} \chi_{i4}}{\partial \omega_{s}} \right) + (H_{i1,s} H_{i2} + H_{i1} H_{i2,s}) \left( \frac{\partial \chi_{i3} \chi_{i4}}{\partial \omega_{r}} \right) + (H_{i1} H_{i2}) \\ & \times \left( \frac{\partial^{2} \chi_{i3} \chi_{i4}}{\partial \omega_{r} \partial \omega_{s}} \right) - \left( \frac{\partial \chi_{i1}}{\partial \omega_{r}} H_{i1,s} + \frac{\partial \chi_{i1}}{\partial \omega_{s}} H_{i1,r} \right) H_{i2} \\ & - \left( \frac{\partial \chi_{i2}}{\partial \omega_{r}} H_{i2,s} + \frac{\partial \chi_{i2}}{\omega_{s}} H_{i2,r} \right) H_{i1} \right] \end{aligned}$$
(A.5)

where

$$\begin{split} H_r &= \frac{\partial H}{\partial \omega_r} (\omega_{q(q=1,2,\dots,n+1)} = 1); \\ H_{r,s} &= H_{s,r} = \frac{\partial^2 H}{\partial \omega_r \partial \omega_s} (\omega_{q(q=1,2,\dots,n+1)} = 1); \\ H_{ij,r} &= H_{r,ij} = \frac{\partial^2 H}{\partial x_{ij} \partial \omega_r} (\omega_{q(q=1,2,\dots,n+1)} = 1); \\ H_{ij,s} &= H_{s,ij} = \frac{\partial^2 H}{\partial x_{ij} \partial \omega_s} (\omega_{q(q=1,2,\dots,n+1)} = 1); \text{ and} \end{split}$$

and the initial conditions are

$$H^{*}(\tau = 0) = \sum_{\text{all } E} [E]_{0}; \tag{A.6}$$

$$H_r^*(\tau = 0) = \sum_{\text{all } E} e_r[E]_0;$$
(A.7)

$$H^*_{r,s}(\tau = 0) = \sum_{\text{all } E} e_r e_s[E]_0, \text{ for } r \neq s;$$
(A.8)

$$H_{r,r}^{*}(\tau = 0) = \sum_{\text{all } E} e_r(e_r - 1)[E]_0; \text{ and }$$
(A.9)

$$[E]_0 = [E](\tau = 0) \tag{A.10}$$

This set of ordinary differential equations, Eqs. (A.3)–(A.5), dependent on variable  $\tau$ , can be solved by the Runge-Kutta

method to determine  $H^*(\tau)$ ,  $H_r(\tau)$ , and  $H_{r,s}(\tau)$ . The a-th moment of the molecule weight distribution, MWD, is defined as,

$$M_a = \left(\frac{N_0}{N_T}\right) \sum_{\text{all } E} W^a(E)[E]$$
(A.11)

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 zero-th, first, and second moment of MWD can be calculated using the generating function:

$$M_0 = \left(\frac{N_0}{N_T}\right) H^* \tag{A.12}$$

$$M_1 = \left(\frac{N_0}{N_T}\right) H_{n+1} \tag{A.13}$$

$$M_2 = \binom{N_0}{N_T} (H_{n+1,n+1}, +H_{n+1})$$
(A.14)

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

$$\overline{M}_n = \frac{M_1}{M_0} \tag{A.15}$$

$$\overline{M}_{w} = \frac{M_{2}}{M_{1}} \tag{A.16}$$

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

Conversion of 
$$G(J) = 1 - N(G(J))/N_0(G(J))$$
  
=  $1 - \sum_{\text{all } E} e_J[E] = 1 - H_J$  (A.17)

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. (A.6)–(A.10).
- 2. Set  $\tau \leftarrow \tau + \Delta \tau$ , where  $\Delta \tau$  is the specified step time.
- 3. Solve the set of ODEs, Eqs. (A.3)–(A.5), and obtained the values of  $H^*(\tau)$ ,  $H_r(\tau)$ , and  $H_{r,s}(\tau)$ , by the Rung–Kutta method.
- 4. Calculate the average molecular weights and conversions according to Eqs. (A.15)–(A.17),
- 5. Repeat procedures 2-4 until the specified time.

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