

DEGREE OF BRANCHING OF THE HYPERBRANCHED POLYMERS RESULTED FROM AB₂ POLYCONDENSATION WITH SUBSTITUTION EFFECT*

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Abstract The analytical expressions of the various structural units and the average degree of branching for the hyperbranched polymers resulted from AB₂ polycondensation with substitution effect were derived by the kinetic mechanism. The reactivity difference between the B group in linear unit and that in terminal group has great effect on the molecular parameters of the products obtained. The concentration of terminal units has a maximum with the increase of the conversion of A groups (x). The higher the reactivity ratio (r) of linear B group to branched one is, the later the maximum appears and the larger it is. The degree of branching of the hyperbranched polymers obtained is controllable by adjusting the parameters of r and x , which increases with increasing both x and r .

Keywords: Degree of branching; Polycondensation; Hyperbranched polymers; Substitution effect.

INTRODUCTION

Highly branched structure that contains a large number of terminal groups is the typical characteristics of hyperbranched polymers. The degree of branching (DB) is one of the most important molecular parameters that can represent the architecture of hyperbranched polymers. DB is related to the physical properties of polymers, such as the glass transition temperature (T_g)^[1], the crystallinity^[2] and the viscosity in solution or melt. According to the kinetic analysis based on the assumption of equal reactivity (*i.e.* random polymerization), the maximum value of the average DB doesn't exceed 0.5 for the hyperbranched polymers obtained by one-step polycondensation of AB₂-type monomers^[3–6]. However, high degree of branching (> 0.5) can often be observed experimentally^[7–10]. It means that the assumption of equal reactivity has to be revised theoretically. Obviously, DB may increase if the reactivity of the groups in linear units is higher than that in terminal units. In addition, slow monomer addition technique also is an effective method to enhance DB of the products^[11, 12].

Under the approximation of high degree of polymerization, Müller *et al.*^[11] derived that the average degree of branching may approach 2/3 by the slow monomer addition technique for the AB₂ polycondensation. Frey *et al.*^[12] also obtained the same result by the assumption that the number ratio of linear units and terminal ones is equal to that of their respective forming rates. Recently, taking the conversion of monomer (x) as a variable, we^[13] derived the analytic expressions of molecular size distribution function, average degree of polymerization, polydispersity index and degree of branching for the slow monomer addition process of AB₂ polycondensation. The reactivity changes after the first B group having reacted was termed “substitution effect”.

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Frey *et al.*^[12] and Galina^[14–16] discussed the topic by kinetic mechanism and carried out the numeral calculations for the DB. However, due to the complex of the differential equation with the substitution effect, it is short in analytical expression for DB still. In our previous work^[17], the kinetic model of the AB₂ type polycondensation with substitution effect has been developed in detail. The distribution functions and the average degree of polymerization of the products have been derived successfully. Reaction becomes faster with the increase of the reactivity of linear B group. At any specified conversion of A groups, both average degree of polymerization and polydispersity index increase with the increase of the reactivity ratio (r) of a linear B group to a terminal B group. However, the variation of these parameters becomes moderate when $r > 10$ and they will converge to respective limiting value. In this work, we pay attention on the investigation on the degree of branching of AB₂ polymerization with substitution effect.

STRUCTURAL UNITS

In order to determine the degree of branching, the various structural units of the products and their concentration should be examined at first. There are five types of possible structural units that incorporate in the hyperbranched polymers generated from the polycondensation of AB₂ monomers. These structural units and their symbols, together with the residual monomer, are tabulated in Table 1. In this work, as used usually, every group or unit is represented by a symbol (or letter) and its concentration or number is denoted by the corresponding italics.

Table 1. Various structural units incorporated in hyperbranched polymers made of AB₂ polycondensation

Structural unit	Type of the unit	Symbol	Remark
AB ₂	Residual monomer	M	
AbB	Initial unit 1	I ₁	Can be regarded as a terminal unit
Ab ₂	Initial unit 2	I ₂	Can be regarded as a linear unit
abB	Linear unit	L	
ab ₂	Dendritic unit	D	
aB ₂	Terminal unit	T	

For the convenience of theoretical treatment, the structural units carrying only one and two unreacted B groups are denoted as U₁ and U₂, respectively. The former includes AbB and abB units, and the latter is composed of AB₂ and aB₂ units. Taking account of the substitution effect, the rate constant of the reaction between A and B of U₁ is denoted as k_1 and that between A and B of U₂ as k_2 . The evolution of the U₁ and U₂ fits the following equations:

$$\frac{dU_1}{dt} = 2k_2U_2A - k_1U_1A \quad (1)$$

$$\frac{dU_2}{dt} = -2k_2U_2A \quad (2)$$

The initial conditions are

$$U_1(t=0) = 0 \text{ and } U_2(t=0) = M_0 \quad (3)$$

Where M_0 is the initial concentration of AB₂ monomer.

Let

$$z = k_2 \int_0^t A dt, \quad i.e. \quad \frac{dz}{dt} = k_2 A \quad (4)$$

Dividing Eqs. (1) and (2) by Eq. (4) leads to

$$\frac{dU_1}{dz} = 2U_2 - rU_1 \quad (5)$$

$$\frac{dU_2}{dz} = -2U_2 \quad (6)$$

where r ($= k_1/k_2$) denotes the reactivity ratio. Previously, we have got the relationship between z and the concentration of A group^[17]:

$$A = \frac{M_0}{r-2}[(r-1)(2e^{-2z} - 1) + 1 - 2e^{-rz}] \quad (7)$$

The conversion of A groups is

$$x = 1 - A/M_0 = \frac{2}{r-2}[(r-1)(1 - e^{-2z}) + e^{-rz} - 1] \quad (8)$$

Solving Eqs. (5) and (6) yields

$$U_1 = \frac{2}{r-2}M_0[e^{-2z} - e^{-rz}] \quad (9)$$

$$U_2 = M_0e^{-2z} \quad (10)$$

According to the distribution function^[17], the concentration of residual monomers is

$$M = Ae^{-2z} \quad (11)$$

Taking account of the substitution effect, the evolution equations of the various structural units can be derived as follows:

$$\frac{dI_1}{dt} = 2k_2MA - k_1I_1A - I_1(k_1U_1 + 2k_2U_2) \quad (12)$$

$$\frac{dT}{dt} = M(k_1U_1 + 2k_2U_2) - 2k_2TA \quad (13)$$

$$\frac{dL}{dt} = I_1(k_1U_1 + 2k_2U_2) + 2k_2TA - k_1LA \quad (14)$$

$$\frac{dI_2}{dt} = k_1I_1A - I_2(k_1U_1 + 2k_2U_2) \quad (15)$$

$$\frac{dD}{dt} = k_1LA + I_2(k_1U_1 + 2k_2U_2) \quad (16)$$

Dividing these equations by Eq. (4) and solving the resultant equations obtain:

$$I_1 = M_0 \frac{2(1-x)}{r-2}(e^{-2z} - e^{-rz}) \quad (17)$$

$$T = M_0xe^{-2z} \quad (18)$$

$$L = M_0 \frac{2x}{r-2}(e^{-2z} - e^{-rz}) \quad (19)$$

$$I_2 = M_0 \frac{1-x}{r-2} (2e^{-rz} - re^{-2z} + r - 2) \quad (20)$$

$$D = M_0 \frac{x}{r-2} (2e^{-rz} - re^{-2z} + r - 2) \quad (21)$$

The concentrations of these structural units are dependent on the three variable parameters, r , x , and z , two of which are independent, due to the link condition of Eq. (8). With the variation of A groups conversion, at the various values of r margined, the evolution of the fraction of terminal units (T/M_0 , solid curves) and that of dendritic units (D/M_0 , dash curves) is shown in Fig. 1. The fraction of dendritic units always increases with increasing x monotonously. The higher the r value, the faster it increases. While the fraction of terminal units increases initially and it decreases after a maximum. The higher the r value is, the later the maximum appears and the larger it is. When the reaction approached to the end ($x \rightarrow 1$), the concentrations of both I_1 and I_2 become very small and it leads to $D \approx T$. The concentration of the linear units increases with increasing x monotonously as well. However, it decreases with increasing r .

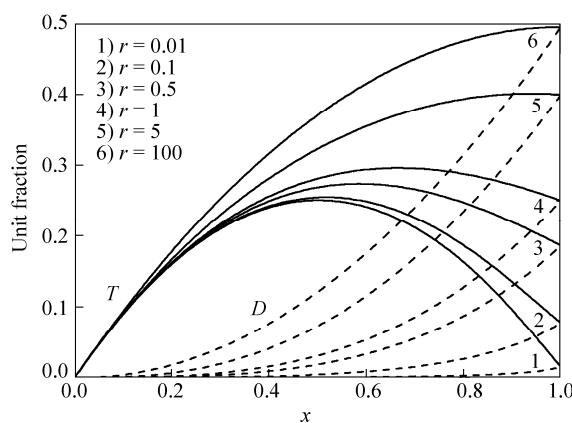


Fig. 1 Evolution of the fractions of terminal units (T/M_0 , solid curves) and that of dendritic units (D/M_0 , dash curves) with the increase of the conversion of A groups

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Hawker *et al.*^[7], Holter *et al.*^[5, 11] and Yan *et al.*^[4] respectively presented the definition of DB. In order to make that $DB = 0$ for a linear chain molecule and $DB = 1$ for a perfect dendremer, the definition has been improved effectively in dealing with copolymerization system with AB and AB_2 monomers^[3, 18, 19]. Accordingly, AbB unit is taken as terminal one and Ab_2 as linear one. Thus, for the hyperbranched polymers obtained from the polycondensation of AB_2 monomers, it has:

$$\overline{DB} = \frac{D + T + I_1 - 2A'}{M_0 - M - 2A'} \quad (22)$$

where $A' (= I_1 + I_2)$ denotes the concentration of oligomers or macromolecules formed. There are two terminal units (aB_2 and/or AbB) and there is no branched one for every linear chain molecule. Any linear unit may become a dendritic one by addition of a monomer, which becomes a new terminal one simultaneously. Therefore, the number of the terminal units always is 2 more than that of dendritic ones for any hyperbranched polymer formed. For the whole reaction system, it has:

$$D = T + I_1 - 2A' \quad (23)$$

Substituting the related expresses into Eq. (22) yields

$$\overline{DB} = \frac{2M_0x(r-2+2e^{-rz}-re^{-2z})}{(r-2)[M_0-A(2-e^{-2z})]} \quad (24)$$

The average DB depends on the three parameters x , r and z . The high r value favors to form the dendritic units and the low value to the linear ones. Figure 2 is the pictorial illustration of the dependence of $\overline{DB}$ on the reactivity ratio and the conversion of A groups. It reveals that the average DB increases with increasing both r and x . When r approaches to zero, linear polymers can be obtained. $\overline{DB}$ may reaches 1 while r tends to infinity. Thus the topology of the hyperbranched polymers can be designed by adjusting the parameters of r and x .

Shown in Fig. 3 is the relationship between the average DB and r at the end of reaction ($x = 1$). With the increase of r , the evolution of the fraction of terminal units (F_T) and linear units (F_L) also is printed in Fig. 3. The concentration of terminal units monotonously increases and that of linear ones decreases always. The reactivity ratio of the reaction system can be determined by the observable value of F_L , F_T or F_D by the pictorial relationships.

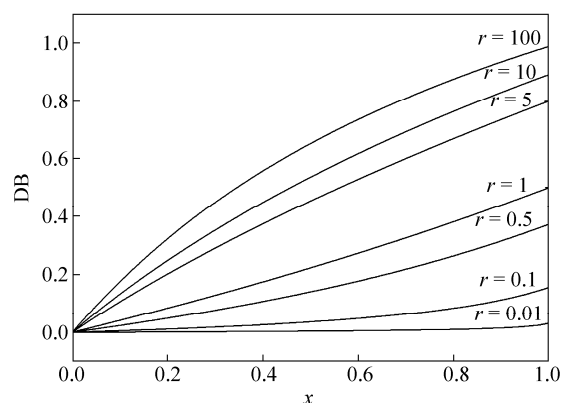


Fig. 2 Degree of branching as a function of conversion of A groups in AB₂ type polycondensation with substitution effect

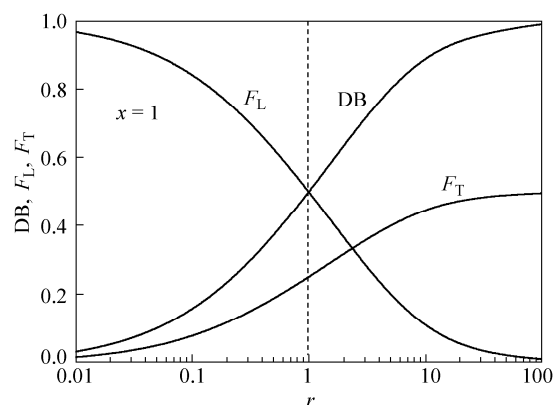


Fig. 3 The dependence of average DB, fraction of linear and terminal units on r at the end of reaction

In the condition of $r = 1$, the reaction system under consideration degenerates into the AB₂ type polycondensation with equal reactivity. Thus the expression of $\overline{DB}$ is simplified into:

$$\overline{DB}|_{r=1} = \frac{2x}{5-x} \quad (25)$$

It increases monotonously with increasing x and reaches 0.5 when the reaction is close to completion, when the fraction of linear units reaches 0.5 and that of both terminal and dendritic approach 0.25, respectively.

CONCLUSIONS

The analytical expressions of the various structural units and the average degree of branching of the hyperbranched polymers obtained from AB₂ polycondensation with substitution effect have been derived, which are subject to the reactivity ratio of linear group to the terminal one and the conversion of A groups. The high average degree of branching (> 0.5) of the products of AB₂ polycondensation observed experimentally can be understood that the reactivity of linear B group is higher than that of terminal B group, due to the substitution effect. Various architectures of the products can be designed by suitable reaction conditions. The reactivity ratio can be determined by the concentration of the structural units in the reaction system.

REFERENCES

- 1 Mai, Y., Zhou, Y. and Yan, D., Chem. J. Chin. Univs. (in Chinese), 2004, 25: 1373
- 2 Mai, Y., Zhou, Y., Yan, D. and Hou, J., New J. Phys., 2005, 7: Art. No. 42
- 3 Zhou, Z., Yu, M., Yan, D. and Li, Z., Macromol. Theory Simul., 2004, 13: 724
- 4 Yan, D., Muller, A.H.E. and Matyjaszewski, K., Macromolecules, 1997, 30: 7024
- 5 Holter, D., Burgath, A. and Frey, H., Acta Polym., 1997, 48: 30
- 6 Frey, H. and Holter, D., Acta Polym., 1999, 50: 67
- 7 Hawker, C.J., Lee, R. and Frechet, J.M.J., J. Am. Chem. Soc., 1991, 113: 4583
- 8 Wooley, K.L., Hawker, C.J., Lee, R. and Frechet, J.M.J., Polym. J., 1994, 26: 187
- 9 Malmstrom, E., Johansson, M. and Hult, A., Macromolecules, 1995, 28: 1698
- 10 Yan, D. and Gao, C., Macromolecules, 2000, 33: 7693
- 11 Radke, W., Litvinenko, G. and Müller, A.H.E., Macromolecules, 1998, 31: 239
- 12 Holter, D. and Frey, H., Acta Polym., 1997, 48: 298
- 13 Zhou, Z., Jia, Z. and Yan, D., Chin. Sci. Chem., 2010, 53: 891
- 14 Galina, H., Polimery, 2003, 48(nr9): 24
- 15 Galina, H., Lechowicz, J.B. and Walczak, M., Macromolecules, 2002, 35: 3253
- 16 Galina, H., Lechowicz, J.B. and Walczak, M., Macromolecules, 2002, 35: 3261
- 17 Zhou, Z. and Yan, D., Polymer, 2006, 47: 1473
- 18 Yu, M., Zhou, Z., Yan, D. and Li, Z., Chem. J. Chin. Univs. (in Chinese), 2003, 24: 1332
- 19 Yu, M., Zhou, Z. and Yan, D., Chinese J. Polym. Sci., 2004, 22(2): 155