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Kinetic model of hyperbranched polymers formed by self-condensing vinyl polymerization of AB* monomers in the presence of multifunctional core molecules with different reactivities

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Abstract

Hyperbranched polymers formed by the self-condensing vinyl polymerization, SCVP, of AB* monomers in presence of trifunctional C_3^* cores with various reactivities were studied by means of the kinetic model. The changes of the degree of polymerization, polydispersity, degree of branching, and structural units of the hyperbranched polymers with the conversions were all investigated by the generating function method. By the addition of the cores with higher reactivity, the molecular weight distribution of the hyperbranched polymers can be further narrowed, and the degree of branching is only slightly lower than that without core monomers. At full conversion of A, the polydispersity index of the hyperbranched polymers formed by the SCVP is lower than that by the AB_2–C_3 copolymerization studied before.

Keywords: Hyperbranched polymer; Self-condensing vinyl polymerization; Generating function

1. Introduction

Highly branched polymers exhibit very different characteristic features from linear polymers: relatively low viscosity, high solubility, and having a large amount of pending or peripheral or side functional groups, for example. Therefore, toughening, molecular sensors, rheology modifiers, and drug delivery systems all have been suggested [1–7]. There are two major approaches of the highly branched polymers: dendrimers and hyperbranched polymers. 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. Hyperbranched polymers have more random branched architectures with some linear structures, and do not emanate from a central core [8]. The hyperbranched polymers have a less regular structure than the dendrimers, but, compared with the complicated and expensive procedures for the synthesis of dendrimers, they can be obtained by a simpler one-pot polymerization, such as polycondensation of AB_g-type monomer in which g is greater than one, and self-condensing vinyl polymerization, SCVP [9–15].

The SCVP involves a monomer AB*, such as *p*-(chloromethyl) styrene, consisting a vinyl group A and an initiating group B* [10,15]. The chain reactions is the active B* reacting with the double bond A of another monomer; then a dimer is formed with one group A and two active groups: B* and A*. The new active center A* converted from the group A by reacting with B* can also react with the double bond of any other molecules, and form a branch point on the resulting larger molecule. Consequently, the hyperbranched polymers can be synthesized under further polymerization.

However, according to the theoretical models and the experimental results [16,17], the molecular weight distribution, MWD, of the hyperbranched polymer formed by either the stepwise polymerization of monomers AB_g or the SCVP 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 index (PDI) of the final products [18–24].

Several kinetic studies of the polycondensation of AB_g monomers with C_f cores as well as the SCVP in presence of

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multifunctional C_f^* initiators has been used to investigate the molecular-weight distribution (MWD) and the degree of branching of the hyperbranched polymers during reaction [15,25,26]. For both cases, the PDI of the hyperbranched polymers can be reduced by addition with multifunctional cores or initiators. In the previous work, we had adopted a kinetic model of the AB_2 system to evaluate the dependences of different amounts of C_3 cores with various reactivities on the molecular weight and the degree of branching during the polymerization [27]. It was found that increment of the reactivity of core monomers leads to not only a narrower MWD, but also to keeping the high degree of branching of the hyperbranched polymers.

In this study, the generating function method [27–31] will be further expanded to investigate the SCVP in presence of trifunctional cores, and to evaluate the effects of the core monomers and various reactivities on the average degree of polymerization, polydispersity, degree of branching, and structural units of the hyperbranched polymers. Furthermore, the difference between the structures formed by the SCVP with cores and by the copolymerization of AB_2 with C_3 will be discussed.

2. Kinetic model of self-condensing vinyl polymerization of monomers AB^* with multifunctional C_3^*

The SCVP involves monomers AB^* with core C_3^*, of which active group B^* and C^*can initiate the polymerization of vinyl group, A

$$A + B^* \xrightarrow{k_{AB^*}} A^* + b \tag{1}$$

$$A + C^* \xrightarrow{k_{AC^*}} A^* + c \tag{2}$$

where the double bond, A, is converted into a new active group, A^*; and b and c are the product groups of B^* and C^*, respectively. The group A^* can also react with vinyl group A and becomes group a:

$$A + A^* \xrightarrow{k_{AA^*}} A^* + a \tag{3}$$

Assume that the reaction is bimolecular, and there are no intramolecular reactions occurring during polymerization, and k_{AB^*}, k_{AC^*} and k_{AA^*} are the reaction rate constants. The reactions between various structural units (not functional groups or molecules) can be expressed in the following kinetic scheme

$$G(b_{i1}) + G(b_{i2}) \xrightarrow{k_i} G(b_{i3}) + G(b_{i4}) \qquad i = 1, 2, \ldots, 16 \tag{4}$$

where

$G(1) = AB^*$ monomer

$G(2) = Ab\sim$

$G(3) = \sim A^*B^*$

$G(4) = \sim A^*b\sim$

$G(5) = \sim aB^*$

$G(6) = \sim \underset{\wr}{ab} \sim$

$G(7) = C_3^*$

$G(8) = C^* \prec \begin{matrix} c\sim \\ C^* \end{matrix}$

$G(9) = C^* \prec \begin{matrix} c\sim \\ c\sim \end{matrix}$

$G(10) = \sim c \prec \begin{matrix} c\sim \\ c\sim \end{matrix}$

and

$$\beta = k_{AC^*}/k_{AB^*} = k_{AC^*}/k_{AA^*} \tag{5}$$

in which β is assumed to be a constant and independent of the extent of reaction. Furthermore, a vector $\mathbf{E}$ is defined to characterize the molecule $\langle E\rangle$

$$\mathbf{E} = (e_1, e_2, e_3, e_4, e_5, e_6, e_7, e_8, e_9, e_{10}, e_w) \tag{6}$$

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

According to the mean-field theory, the effects of configuration and conformation are not considered in the calculation. The effects of intramolecular cyclization on the structures of the hyperbranched polymers are also important for non-linear polymerization systems, which were discussed before [32–34]. However, in this study, we focus on the core molecules with different reactivities, and assume that no cyclization occurs during polymerization [27–29]; thus the reactions between molecules are

$$\langle E'\rangle + \langle E''\rangle \xrightarrow{k_i} \langle E' + E'' + L_i''\rangle \qquad i = 1, 2, \ldots, 16 \tag{7}$$

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,

$$L_i = (l_1, l_2, \ldots, l_{10}, 0) \tag{8}$$

$$l_J = -\delta(b_{i1}, J) - \delta(b_{i2}, J) + \delta(b_{i3}, J) + \delta(b_{i4}, J),$$

$$J = 1, 2, \ldots, 10$$

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

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

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

For example, a molecule C_3^* reacts with another molecule

Ab–A*B* as follows:

$$C_3^* + \text{Ab-A*B*} \xrightarrow{k_{14}} C^* \prec \begin{matrix} \text{c - A*b - A*B*} \\ C^* \end{matrix} \quad (9)$$

then

$\langle E' \rangle = C_3^*$

$\langle E'' \rangle = \text{Ab–A*B*}$

$$\langle E' + E'' + L_i \rangle = C^* \prec \begin{matrix} \text{c - A*b - A*B*} \\ C^* \end{matrix}$$

$E' = (0,0,0,0,0,0,1,0,0,0, W(C_3^*))$

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

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

$E' + E'' + L_3 = (0,0,1,1,0,0,0,1,0,0, W(C_3^*) + 2W(AB^*))$

$k_{14} = 3k_{AC^*}$

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

$$[E] = N(E)/N_0 \quad (10)$$

$$k_i' = (k_i/k_0)(V_0/V) \quad (11)$$

$$\tau = tk_0(N_0/V_0) \quad (12)$$

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

If the change of the reaction volume is negligible, then according to Eq. (7), the rate equation of the isomers can be written as

$$\frac{d[E]}{d\tau} = \sum_{i=1}^{16} k_i' \left\{ \sum_{E'+E''+L_i=E} ([E'][E'']p_{i1}'p_{i2}'') - [E]p_{i1} \sum_{\text{all } E'''} \times [E''']p_{i2}''' - [E]p_{i2} \sum_{\text{all } E'''} [E''']p_{i1}''' \right\} \quad (13)$$

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. (13) give the total rates of appearance and disappearance of the isomer $\langle E \rangle$, respectively. Eq. (13) cannot be solved directly, but it can be transformed into finite ordinary differential equations using a generating function [27–31]. 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, and the algorithm was described in the previous papers [27].

3. Results and discussion

Fig. 1 show the profiles of the weight-average degree of polymerization, $\overline{DP}_w$, at different values of β and λ, of which β is the ratio of k_{AC^*} to k_{AB^*}, and λ is the initial molar ratio of core C_3^* to monomer AB^*. The degree of polymerization is determined by setting both the molecular weights of AB^* and C_3^* to be one. In the case of the polymerization system without core monomers the $\overline{DP}_w$ increases more quickly than the system with cores; then it diverges at full conversion of A. On the other hand, with C_3^* cores, it converges to finite values. As shown in Fig. 1, either the higher content of trifunctional C_3^* cores or increasing the rate constant ratio β leads to a lower $\overline{DP}_w$ at the complete conversion of A groups.

In the SCVP of monomers AB^* with core C_3^*, the relationship between the number-average degree of polymerization and the conversion of A groups can be derived easily as follows

$$\overline{DP}_n = \frac{\text{initial number of monomers}}{\text{total number of molecules during polymerization}} = \frac{N_0(AB^*) + N_0(C_3^*)}{N_0(AB^*) + N_0(C_3^*) - N_0(AB^*)\alpha(A)} = \frac{1+\lambda}{1+\lambda-\alpha(A)} \quad (14)$$

where $N_0(AB^*)$ is the initial number of monomer AB^*; $N_0(C_3^*)$ is the initial number of core C_3^*; and $\alpha(A)$ is the conversion of A group. Furthermore, the final number-average degree of polymerization is

$$\overline{DP}_n(\alpha = 1) = \frac{1+\lambda}{\lambda} \quad (15)$$

The profiles of the number-average degree of polymerization calculated by the generating function are also plotted in Fig. 2. Obviously, as can be seen from Eq. (14) and Fig. 2,

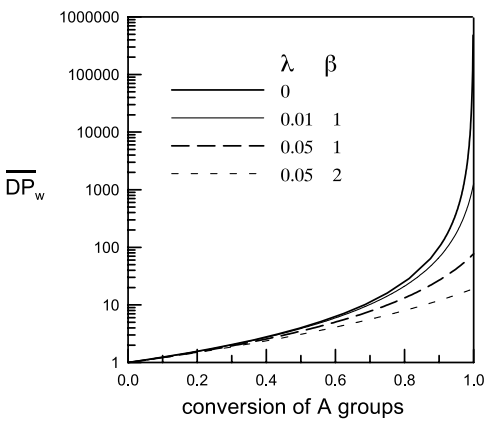

Fig. 1. Weight-average degree of polymerization versus conversion of A groups for the systems with various contents of cores and rate constant ratios.

the $\overline{DP}_n$ decreases with increasing of the cores, but is independent of the reactivity of the core C_3^*.

In the SCVP of AB^* with C_3^*, there are two types of the growing molecules: one is the molecule with a focal unit A–b ~ , the other one includes a reacted core unit, cC_2^*, c_2C^*, or c_3. The molecules with a core unit cannot be combined with each other to form a larger one due to no reactive group A ~ on these molecules. Therefore, the increasing rate of the degree of polymerization is retarded by adding the multifunctional cores. For a higher content of the C_3^* with higher reactivity, $\lambda = 0.05$ and $\beta = 2$ in Fig. 3 as an example, a lot of molecules each of which contains a core unit are formed at early stage, and the PDI of the hyperbranched polymers becomes narrow. On the other hand, in the absence of cores, it is easy to combine two large molecules into an even larger one; then leads to a broad molecular weight distribution. For a low reactivity of core, $\beta = 0.01$, both the number-average and weight-average degree of polymerization decrease with increasing of core monomers, and before full conversion, the higher content of C_3^* results in the higher value of PDI as shown in Fig. 4. However, near the complete conversion of A groups, the effect of the increasing $\overline{DP}_w$ of the system with lower content of cores overcomes that with higher one; thus the PDI decreases with increasing C_3^* cores.

The dependences of the PDI of the hyperbranched polymers on the λ and β at the conversion of 0.99 and 1.0 are plotted in Figs. 5 and 6, respectively. It was found that the molecular weight distribution of the hyperbranched polymers becomes narrower by adding cores with higher reactivity. Compared with the copolymerization of AB_2 monomer with multifunctional cores [27] under these conditions, the polydispersity index of the hyperbranched polymers formed by the SCVP is lower than that of the AB_2–C_3 system at full conversion of A.

The degree of branching, DB, is a very important structural parameter in characterizing the hyperbranched polymers [35]. Holter and Frey [23] suggested a modified degree of branching, DB(HF), which is based on the actual

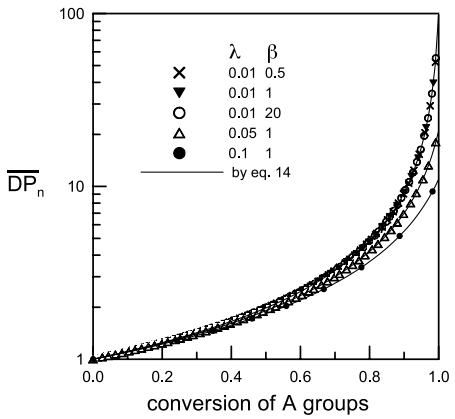

Fig. 2. Number-average degree of polymerization versus conversion of A groups for the systems with various contents of cores and rate constant ratios.

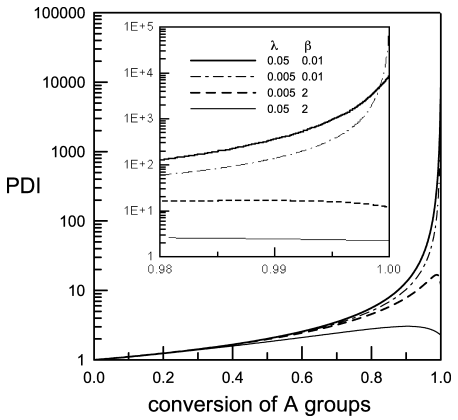

Fig. 3. Polydispersity index versus conversion of A groups for the systems under different formations.

number over the maximum possible number of dendritic units:

$$\mathrm{DB(HF)} = \frac{2\mathrm{ND}}{2\mathrm{ND} + \mathrm{NL}} = \frac{\mathrm{G}(6) + \mathrm{G}(10)}{\mathrm{G}(6) + \mathrm{G}(10) + 0.5[\mathrm{G}(4) + \mathrm{G}(5) + \mathrm{G}(9)]} \quad (16)$$

Muller et al. [11] also suggested the use of the fraction of branch points, FB, to characterize the hyperbranched polymers

$$\mathrm{FB} = \frac{\mathrm{ND}}{(\text{total number of units}) - (\text{number of monomers})} = \frac{\mathrm{G}(6) + \mathrm{G}(10)}{\mathrm{G}(2) + \mathrm{G}(3) + \mathrm{G}(4) + \mathrm{G}(5) + \mathrm{G}(6) + \mathrm{G}(8) + \mathrm{G}(9) + \mathrm{G}(10)} \quad (17)$$

According to Eqs. (16) and (17), the changes of the degree of branching and FB, can be calculated from the numbers of the units. For example, λ is 0.05 in Fig. 7, the growth of the

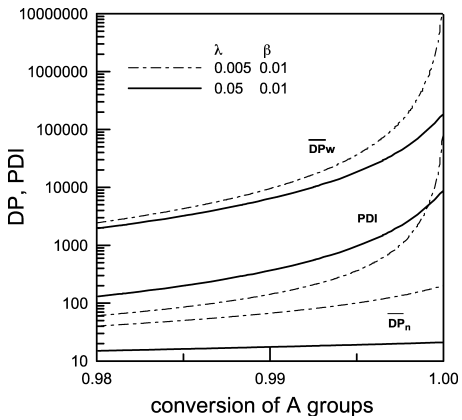

Fig. 4. Dependence of the average degree of polymerization or the polydispersity index under different formations at high conversion of A groups.

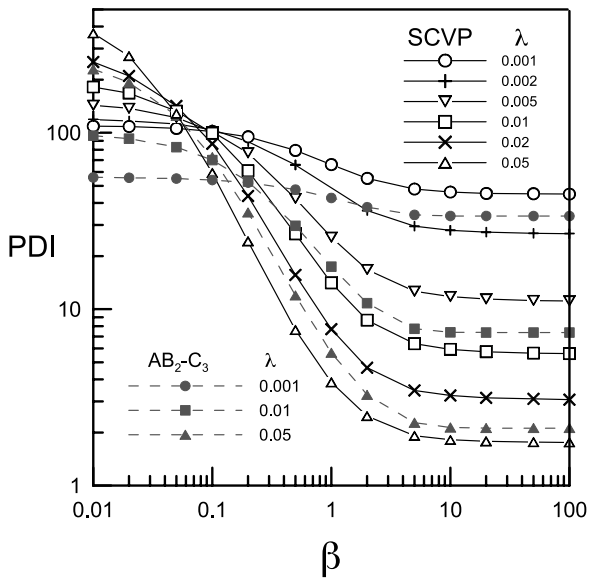

Fig. 5. Dependence of the PDI of the hyperbranched polymers on the reactivity ratio and contents of cores at the conversion of $A = 0.99$.

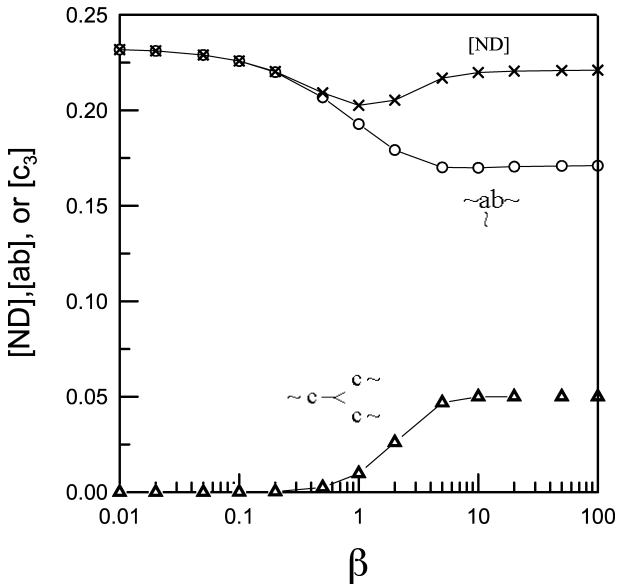

Fig. 7. Dependence of the final number of dendritic units of the hyperbranched polymers on the reactivity ratio, β at $\lambda = 0.05$.

dendritic (ab) units is retarded by the reacting of A with C^*, and the dendritic (c_3) units increase with adding the C_3^* cores with high reactivity. Therefore, as shown in Figs. 7–9, the total number of dendritic units, ND, DB(HF), and FB first decrease with the value of β, and reach a minimum at a β of about one; then rise with β. The results show that, the DB(HF) of the SCVP system without core monomers is 0.5, and in the system containing the C_3^* cores with high reactivity, $\beta = 10$, for example, at $\lambda = 0.01$, 0.02, or 0.05, it falls slightly to about 0.46. Under the same values of β and λ, the DB(HF) of the AB_2–C_3 system studied before is higher than the SCVP of AB^* with C_3^*.

4. Conclusion

In SCVP of AB^*, the molecular weight distribution and the degree of branching of the hyperbranched polymers are affected by adding the multifunctional C_3^* cores. It was found that the molecular weight distribution of the hyperbranched polymers can be further reduced by adding cores with higher reactivity. For the C_3^* cores with high reactivity, $\beta = 10$, and $\lambda = 0.01$, 0.02, or 0.05, the degree of branching, DB(HF), falls to about 0.46, whereas, in absence of cores, the DB(HF) is 0.5. Under the same condition, the polydispersity index of the hyperbranched

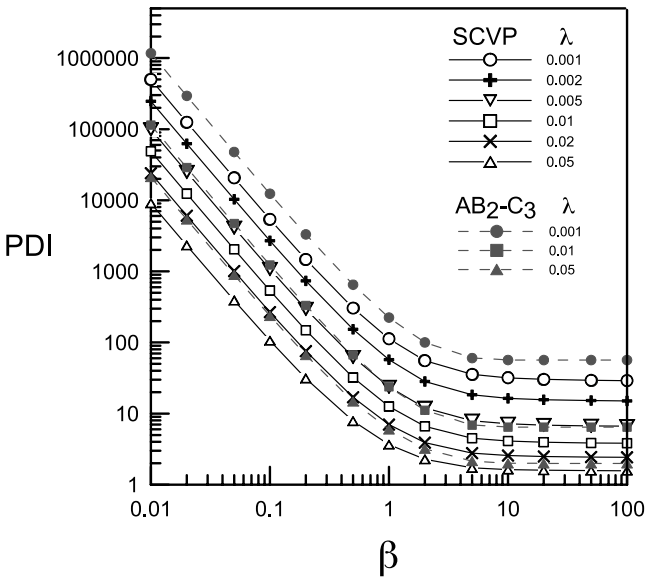

Fig. 6. Dependence of the PDI of the hyperbranched polymers on the reactivity ratio and contents of cores at the full conversion.

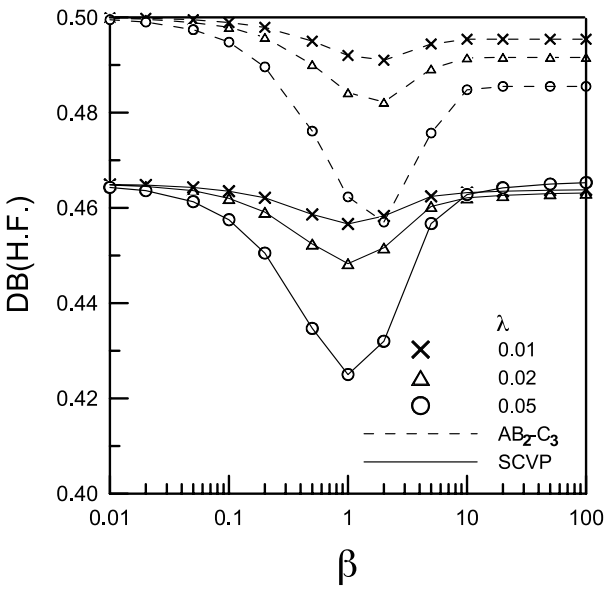

Fig. 8. Dependence of the final DB(HF) of the hyperbranched polymers on the reactivity ratio, β under various contents of cores for the SCVP and AB_2–C_3 systems.

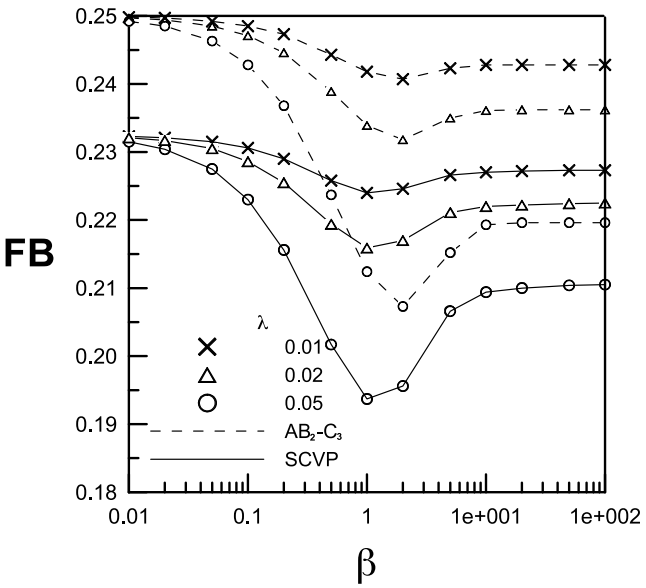

Fig. 9. Dependence of the final FB of the hyperbranched polymers on the reactivity ratio, β under various contents of cores for the SCVP and AB_2-C_3 systems.

polymers formed by the SCVP is lower than that of the AB_2-C_3 system at full conversion of A.

Acknowledgements

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References

[1] Hult A, Johansson M, Malmstrom E. Adv Polym Sci 1999;143:2.
[2] Uhrich K. Trends Polym Sci 1997;5:388.
[3] Kim YH. J Polym Sci, Part A: Polym Chem 1998;36:1685.
[4] Kim YH, Webster OW. Macromolecules 1992;25:5561.
[5] Davis N, Rannard S. Polym Mater Sci Engng 1997;77:158.
[6] Laibinis PE, Whitesides GM. J Am Chem Soc 1992;114:9022.
[7] Shi W, Ranby B. J Appl Polym Sci 1996;59:1951.
[8] Stevens MP. Polymer chemistry, 3rd ed. New York: Oxford University Press; 1999.
[9] Frechet JMJ, Henmi M, Gitsov I, Aoshima S, Leduc MR, Grubbs RB. Science 1995;269:1080.
[10] Muller AHE, Yan D, Wulkow M. Macromolecules 1997;30:7015.
[11] Yan D, Muller AHE, Matyjaszewski K. Macromolecules 1997;30:7024.
[12] Radke W, Litvinenko GI, Muller AHE. Macromolecules 1998;31:239.
[13] Yan D, Zhou Z, Muller AHE. Macromolecules 1999;32:245.
[14] Litvinenko GI, Simon PFW, Muller AHE. Macromolecules 2001;34:2418.
[15] Litvinenko GI, Muller AHE. Macromolecules 2002;35:4577.
[16] Flory PJ, Principles of polymer chemistry, Ithaca, NY: Cornell University Press; 1953.
[17] Beginn U, Drohmann C, Moller M. Macromolecules 1997;30:4112.
[18] Yang Y, Zhang H, He J. Macromol Theory Simul 1995;4:953.
[19] Hanselmann R, Holter D, Frey H. Macromolecules 1998;31:3790.
[20] Johansson M, Malmstrom E, Hult AJ. J Polym Sci, Part A: Polym Chem 1993;31:619.
[21] Feast WJ, Stainton NM. J Mater Chem 1995;5:404.
[22] Bharathi P, Moore JS. Macromolecules 2000;33:3212.
[23] Frey H, Holter D. Acta Polym 1999;50:67.
[24] Sunder A, Heinemann J, Frey H. Chem Eur J 2000;6:2499.
[25] Yan D, Zhou Z. Mocromolecules 1999;32:819.
[26] Zhou Z, Yan D. Polymer 2000;41:4549.
[27] Cheng KC, Wang LY. Macromolecules 2002;35:5657.
[28] Galina H, Szustalewicz A. Macrmolecules 1990;23:3833.
[29] Cheng KC, Chiu WY. Macromolecules 1993;26:4658.
[30] Cheng KC, Chiu WY. Macromolecules 1993;26:4665.
[31] Cheng KC. J Polym Sci, Part B: Polym Phys 1998;36:2339.
[32] Dusek K, Somvarsky J, Smrckova M, Simonsick Jr. WJ, Wilczek L. Polym Bull 1999;42:489.
[33] Cameron C, Fawcett AH, Hetherington CR, Mee RAW, McBride FV. J Chem Phys 1998;108:8235.
[34] Burgath A, Sunder A, Frey H. Macromol Chem Phys 2000;201:782.
[35] Hawker CJ, Frechet JMJ. J Am Chem Soc 1991;113:4583.