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Self-condensing vinyl polymerization in the presence of multifunctional initiator with unequal rate constants: Monte Carlo simulation

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Abstract

Monte Carlo method was applied to simulate self-condensing vinyl polymerization (SCVP) in the presence of multifunctional initiator with unequal reactive rate constants. Simulations showed that, with the increase of reactivity of multifunctional initiator, the molecular weight distribution decreases, the fraction of multi-armed hyperbranched polymers increases, and the best reactivity ratio of multifunctional initiator to inimor is 10/1; the reactivity difference of two active sites in inimer has strong effects on the molecular weight distribution and degree of branching. The branch degree and fraction of branch-points depend on both the conversion of double bonds and reactivity difference of two active centers in inimer, and have no relation with the adding of multifunctional initiator. The density distribution of degree of branching further shows common self-similarity in SCVP.

Keywords: SCVP; Multifunctional initiator; Monte Carlo simulation

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1. Introduction

An active field in polymer chemistry is the synthesis of complex polymers, such as hyperbranched polymers and dendrimers, due to their specific properties and potential applications in industrial fields [1–5]. Therefore, finding the proper synthetic routes and selecting the suitable polymerization conditions have been, in the past years, interesting subjects both in theories and experiments [6–16]. One method, so-called self-condensation polymerization of AB_n ($n \geq 2$) type monomers origin from Flory [9], was used in synthesis of hyperbranched polymers [6–8]. Since, Fréchet et al. suggested a new method, named 'self-condensing vinyl polymerization' (SCVP) in 1995 [10], synthesis of hyperbranched polymers has been inspired by many subsequence researches [11–16].

In general, SCVP starts from the specific monomers, i.e. inimer A–B*, where A is a double bond and B* is an initiating group, respectively. The active B* group first initiates A double bond in another inimer leading to a dimer with two active sites, A* and B*, which still have capabilities of further reacting with other inimers or oligomers having double bonds. As a result, the successive propagation reactions result in the desired hyperbranched polymers. Various types of living polymerization, such as atom transfer living free radical polymerization [11–13], cationic polymerization [14], group transfer polymerization [15], nitroxide mediated living polymerization [16], have been applied to the synthesis of hyperbranched polymers by SCVP. Generally, hyperbranched polymers prepared by SCVP have a broad molecular weight distribution. Müller and co-workers [17] suggested that adding a few percent of multifunctional initiator, G, with f_G initiation groups, into the reaction system in order to synthesize hyperbranched polymer with relatively narrow molecular weight distribution [18,19]. Müller et al. reported the detailed numerical calculations of SCVP in the presence of multifunctional initiators with the rate constant equal to that of inimer [17, 20]. Although several experimental attempts were taken to understand SCVP in the presence of multifunctional initiator [15,21,22], up to date, the influences of the reactivity difference between inimer and multifunctional initiator on the molecular structural parameters of final

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hyperbranched polymers, such as molecular weight distribution, still remain unclear due to the difficulty of characterizing the polymers obtained. Therefore, analysis of such specific polymerization with a suitable theoretical method becomes more important. In this paper, Monte Carlo method has been applied to study the SCVP using inimer and multifunctional initiator with unequal reactive rate constants. In comparison with the numerical calculation method, solving the complex kinetic differential equations is not necessary [23,24], and more helpful information can be obtained. In Section 3.1, we consider the case that two active sites of inimer have equal reactivity, but are different from that of multifunctional initiator. In Section 3.2, inimer with two unequally reactive sites are discussed.

2. Model description and Monte Carlo algorithm

For SCVP in the presence of multifunctional initiator, G, all possible reactions between the functional groups with different structural patterns are considered and shown in Scheme 1. The description of Monte Carlo algorithm of SCVP is following.

Supposing that the volume V contains a spatially homogeneous mixture of multifunctional initiator, G, and inimer, A–B*, and these species are able to react each other through reaction channels R_q $(q = 1, 2, 3, 4, \ldots, 16)$ listed in Scheme 1. In a Monte Carlo time interval, the channel n that exactly happens is determined by a unit-interval uniformly distributed random number, r, $r \in [0, 1]$, according to the following relation [25,26]:

$$\sum_{q=1}^{n-1} R_q < r \sum_{q=1}^{16} R_q \leq \sum_{q=1}^{n} R_q \tag{1}$$

where R_q is the rate of qth reaction in a total of 16 reaction channels. As a bimolecular second-order reaction, R_q can be generally written as

$$R_q = k_{lm} X_l Y_m \tag{2}$$

where k_{lm} is the microscopic reaction rate constant between species of l and m in Monte Carlo simulation and X_l is the molar concentration of active centers in the molecular structure l, and Y_m is the molar concentration of double bond in the molecular structure m. So the reaction probability of reaction channel R_q, P_q, is defined as:

$$P_q = \frac{R_q}{\sum\limits_{q=1}^{16} R_q} \tag{3}$$

and it satisfies the relation

$$\sum_{q=1}^{16} P_q = 1 \tag{4}$$

then Eq. (3) can be expressed as:

$$P_q = \frac{k_{lm} X_l Y_m}{\sum\limits_{q=1}^{16} k_{lm} X_l Y_m} \tag{5}$$

it should be noted that the equations of reaction rates are established based on the functional groups, i.e. active centers and double bonds, instead of the molecules in the system because there may be two or more active centers in one molecule. In this study, the intramolecular cyclization reactions in the polymerization were neglected.

From Scheme 1, all the reactions involve three kinds of active centers, G*, B* and A*, and a double bond A, although branched polymers involved are different such as molecular weight, degree of branching and the length of each branch chain etc. Then there should be three kinds of reactive constants, k_{lm} (k_{GA}, k_{BA}, k_{AA}), in SCVP with unequal reactive constants Eq. (6). Here, G*/B*/A* was used to express the rate constant ratios, $k_{\mathrm{GA}}/k_{\mathrm{BA}}/k_{\mathrm{AA}}$, as a short hand.

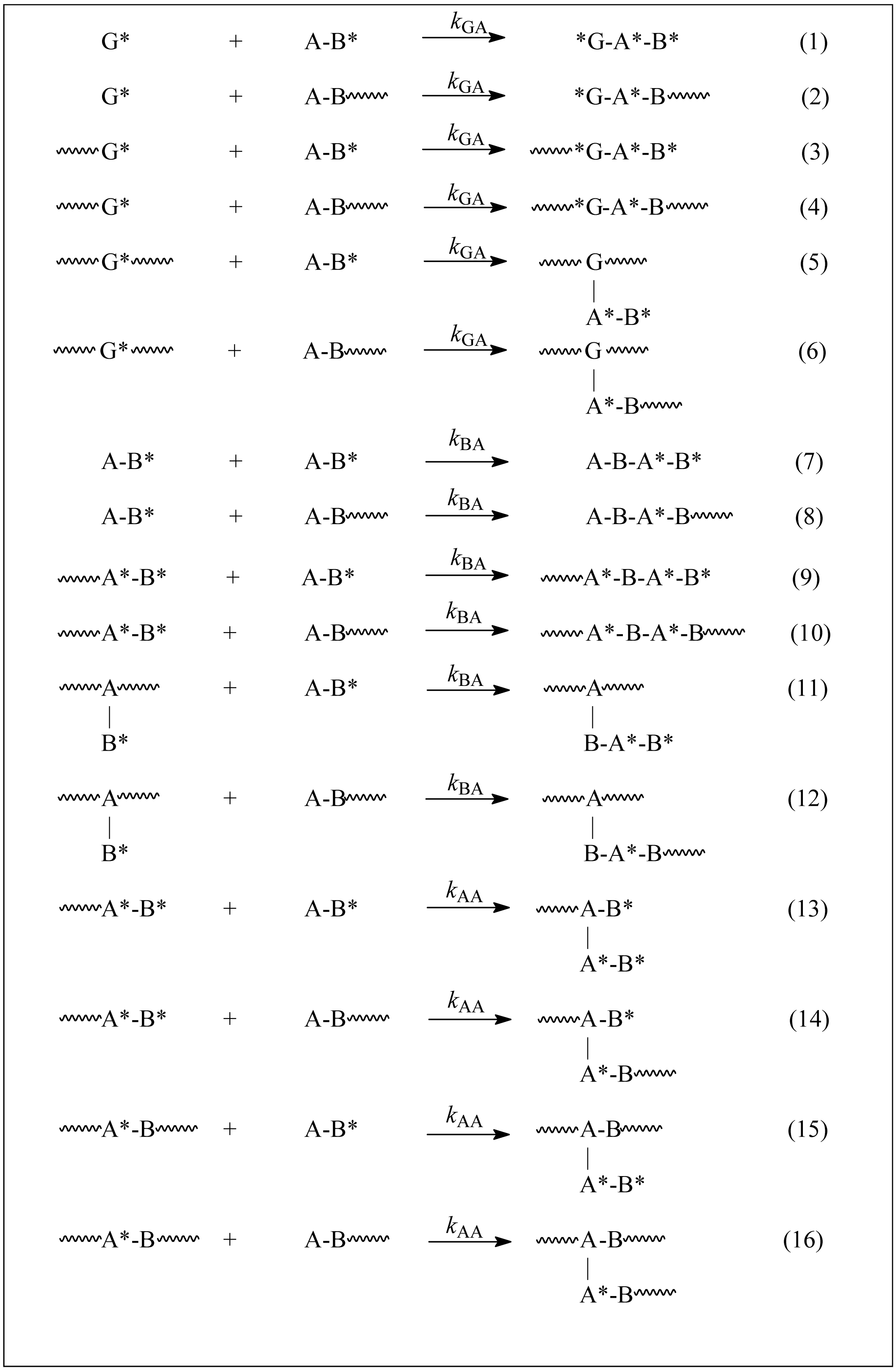
$$\mathrm{G}^* + \mathrm{A} \xrightarrow{k_{\mathrm{GA}}} \mathrm{A}^* \qquad \mathrm{B}^* + \mathrm{A} \xrightarrow{k_{\mathrm{BA}}} \mathrm{A}^* \qquad \mathrm{A}^* + \mathrm{A} \xrightarrow{k_{\mathrm{AA}}} \mathrm{A}^* \tag{6}$$

Radke et al. obtained the results of the number-average degree of polymerization, P_{n}, and the weight-average degree of polymerization, P_{w}, of the hyperbranched polymer prepared from SCVP in the presence of multifunctional initiators with equal reactive constants, G*/B*/A* = 1/1/1 [17].

$$P_{\mathrm{n}} = \frac{1 - (1 - c_x)\exp\left(-\dfrac{\gamma c_x}{\gamma + 1}\right)}{(1 - c_x)\left[1 - \exp\left(-\dfrac{\gamma c_x}{\gamma + 1}\right)\right] + \dfrac{1}{f_{\mathrm{G}}\gamma}\left[1 - \exp\left(-\dfrac{f_{\mathrm{G}}\gamma c_x}{\gamma + 1}\right)\right]} \tag{7}$$

$$P_{\mathrm{w}} = \frac{(\gamma + f_{\mathrm{G}})\left[\dfrac{1 + \gamma}{1 + \gamma(1 - c_x)}\right]^2 - 2f_{\mathrm{G}}\left[\dfrac{1 + \gamma}{1 + \gamma(1 - c_x)}\right] + f_{\mathrm{G}} - \gamma(1 - c_x)\exp\left(-\dfrac{\gamma c_x}{\gamma + 1}\right)}{\gamma\left[1 - (1 - c_x)\exp\left(-\dfrac{\gamma c_x}{\gamma + 1}\right)\right]} \tag{8}$$

where $\gamma = M/(f_{\mathrm{G}} \times G)$, f_G is the number of initial active groups in multifunctional initiator; M and G are the initial number of the inimer and multifunctional initiator; and c_x is



A-B* and G* are respectively inimer and multifunctional initiator with three initiating groups

Scheme 1. Reactions (*q*) of structural units in SCVP. A–B* and G* are, respectively, inimer and multifunctional initiator with three initiating groups.

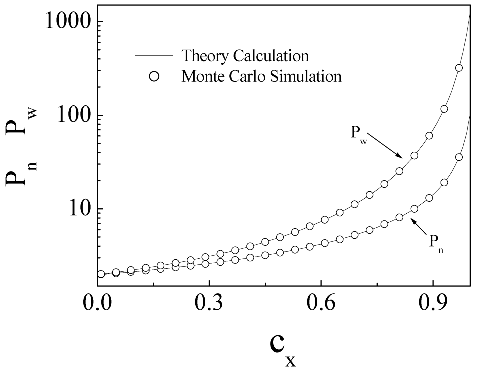


Fig. 1. Theoretical data (solid line) and simulation data (open circle) for the number-average degree of polymerization, P_n, and the weight-average degree of polymerization, P_w, in simulation. The number of functional group of multifunctional initiator, f_G, equals to 3. The content of multifunctional initiator, G/inimer, equals 0.01, G*/B*/A* = 1/1/1.

the double bond conversion. All simulations are carried out in reaction systems containing 10^8 monomers at starting. Using larger system did not affect the final results. Fig. 1 shows that the results of Monte Carlo simulation are in well agreement with theory results, indicating the correctness of the computing algorithm and the program. The unreacted inimer and multifunctional initiator core on the chain were not taken into account for the final statistical calculation of molecular parameters, such as P_w and P_n.

3. Results and discussion

3.1. Equal reactivities of A* and B*

In order to study the effect of reactivity of multifunctional initiator on the hyperbranched polymerization, we firstly consider the simple case, in which A* and B* have equal reactivity, i.e. B*/A* = 1/1. In SCVP without multifunctional initiators, hyperbranched polymers are formed only through the reactions of active centers, A* or B*, in a polymer and double bond in another inimer or polymer when the intramolecular reactions are neglected. In the presence of multifunctional initiators, however, the active centers, G*, of multifunctional initiators will also react with double bonds. As a result, competition between the reactions of double bond with A* and B* in inimer and G* in multifunctional initiator should occur in the system. The number of multifunctional initiators attached to the hyperbranched polymers through reactions should reasonably increase with the increase of reactivity of multifunctional initiator, and further influence on the molecular weight and molecular weight distribution of the final polymers.

In Fig. 2, the number-average degree of polymerization, P_n, exponentially increase with the double bond conversion, c_x. In comparison with the systems having multifunctional initiators with low reactivity, higher reactivity of the initiator leads to lower molecular weight. In Fig. 3, the polydispersity index, PI (PI = P_w/P_n, the unreacted inimer and multifunctional initiator on the chain are not taken into account), also increases with double bond conversion, which is the character of SCVP. Detailed analysis of Fig. 3 shows that in higher double bond conversion ($c_x > 70\%$), the systems with higher reactivity of multifunctional initiator have relatively narrower molecular weight distribution, i.e. the PI values are always lower than 4. In contrast, for the systems with lower reactivity of multifunctional initiators, the PI values reach nearly 20 when $c_x > 90\%$, indicating that higher reactivity multifunctional initiators will be more beneficial to the preparation of lower PI hyperbranched polymers. Fig. 4 shows the dependence of molecular weight distribution, PI, on the reactivity ratio, G*/B*, at various double bond conversions, c_x. Its clear that, PIs decrease with the increase of G*/B*, and in particular in the range of G*/B* = 0.01/1 ∼ 10/1, PIs depend strongly on G*/B*. After G*/B* = 10, the PI values remain steady. All results above are obtained under the case of molar ratio of multifunctional initiator to inimer, G/inimer = 0.01.

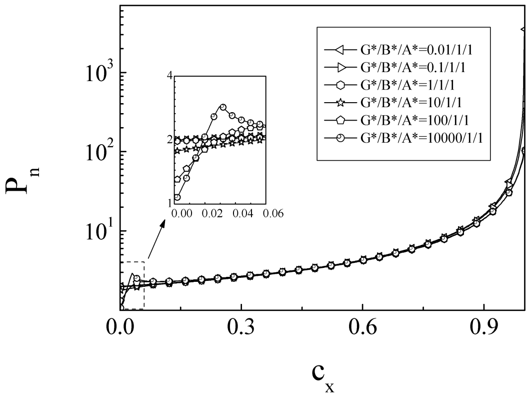


Fig. 2. Dependence of the number-average degree of polymerization, P_n, on conversion of double bonds, c_x, in simulation. The number of functional group of multifunctional initiator, f_G, equals to 3; G/inimer = 0.01.

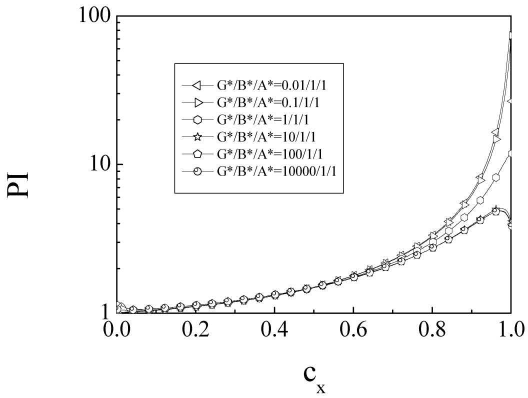


Fig. 3. Dependence of the molecular weight distribution, PI(P_w/P_n), on conversion of double bonds, c_x, in simulation. The other parameters are the same as those in Fig. 2.

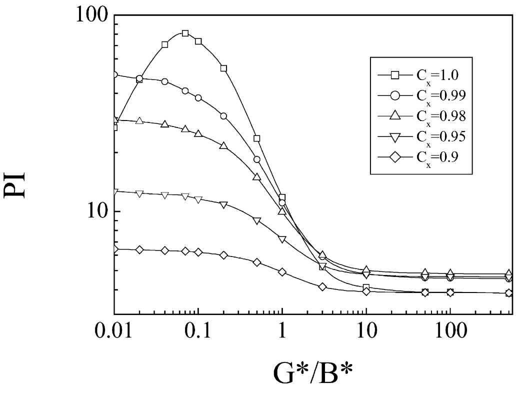


Fig. 4. Dependence of the molecular weight distribution, PI, on reactivity ratio, G*/B*, in simulation, when B* have the same reactivity with A*. The other parameters are the same as those in Fig. 2.

From the simulation, the best reactivity ratio of multifunctional initiator to inimor is about 10/1, and more higher reactivity ratio has less effect on decrease of molecular weight distribution of the final polymer. It means that the range to decrease PI is limited through batch polymerization in the presence of multifunctional initiator. The semi-batch polymerization, i.e. inimors are added enough slowly to the system containing multifunctional initiators, can decrease further the PI, however, the process in experiments is more complicated and needs to be well controlled [20].

Obviously, the reactivity of multifunctional initiator significantly influences on the molecular weight and polydispersity of the polymers, implying the difference of polymerization behavior. In statistical calculation of average degree of polymerization, the multifunctional initiator joined on polymer chain was not taken into account due to its less quantities, less than 1%. In this case, under the high reactivity ratio, such as $G^*/B^* = 10000$, at initial polymerization, the double bond A on inimer prefers to react with G*. As shown in Fig. 2, in the lower double bond conversion ($c_x < 3\%$), the number-average degree of polymerization P_n increases rapidly from 1 to 3 (here there are three active centers G* on one multifunctional initiator G). At the very beginning of initiations, i.e. c_x is close to 0, when $G^*/B^* = 1/1$, the high probability of reactions between two inimers, A–B*, is typical because of its high concentration, which leads to the $P_n \approx 2$; When $G^*/B^* = 10000/1$, i.e. multifunctional initiator has extremely high reactivity, most multifunctional initiators G should firstly participate the initiations, which leads to the $P_n \approx 1$ (Fig. 2, the unreacted inimer and multifunctional initiator on the chain are not taken into account). After the active centers G* in the multifunctional initiators G were mostly consumed, propagation reactions between active centers in oligomers and inimers will be dominated in the polymerization.

It is reasonable that for $G^*/B^* \rightarrow \infty$, all active centers G* on multifunctional initiators should firstly react with inimer, A–B*, to form new multifunctional initiators, on each of which there are six active centers, i.e. 3A* and 3B*. In this case, the polymerization behavior will become the same with SCVP in the presence of multifunctional initiators with equal reactivity since $B^*/A^* = 1/1$, while the number of active center in G increases two times. Again, the P_w and P_n can be expressed with Eq. (7) and (8), but f_G should multiply a parameter which equals to 2. In contrary, when $G^*/B^* \rightarrow 0$, the polymerization should behave like the pure SCVP without multifunctional initiator since, no multifunctional initiator take part in the polymerization. [20]

In Fig. 5, the weight fraction of the polymers with multifunctional initiator core in polymers obtained, H_{core}, i.e. the weight ratio of polymers attached with multifunctional initiator core to that of total polymers, increases with the reactivity of multifunctional initiator. In the case of the higher reactivity of multifunctional initiator, such as $G^*/B^*/A^* = 100/1/1$ or 500/1/1, the polymerization at the beginning are mainly due to the initiation of active sites on multifunctional initiator, so higher H_{core} is observed. When most of multifunctional initiator molecules are consumed and active sites G* are converted to low active site A*, the reactions between the inimers, or between the inimer and the oligomer without initiator core become dominant since, high concentration of inimer, H_{core} rapidly decreases, which is observed before conversion $c_x < 20\%$ as shown in Fig. 5. With the proceeding of polymerization, more and more oligomers and inimers react with hyperbranched polymers having multifunctional initiator residue because they have larger amount of active centers. As a result, the H_{core} increases slightly. At the end of polymerization, the combinations between polymers with initiator core and without core will rapidly increase, and the total number of macromolecules reduces, resulting in rapid increase of H_{core}. On the basis of above analysis, we conclude that increasing the reactivity of multifunctional initiator will favor the formation of the multi-armed hyperbranched polymers. From Fig. 6, we are able to know the relative contents of hyperbranched polymers with different arm numbers in the total polymers. For $G^*/B^*/A^* = 10/1/1$ at

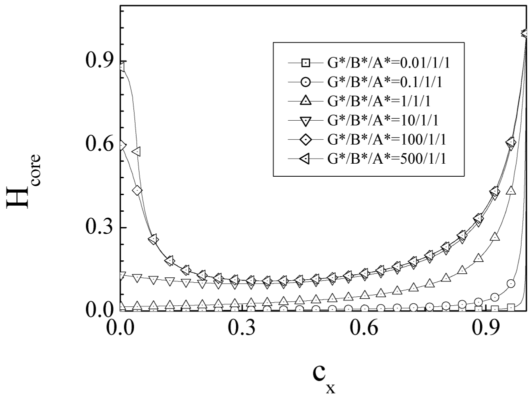


Fig. 5. Dependence of the weight content of macromolecules with initiator core, H_{core}, on conversion of double bonds in simulation. The other parameters are the same as those in Fig. 2.

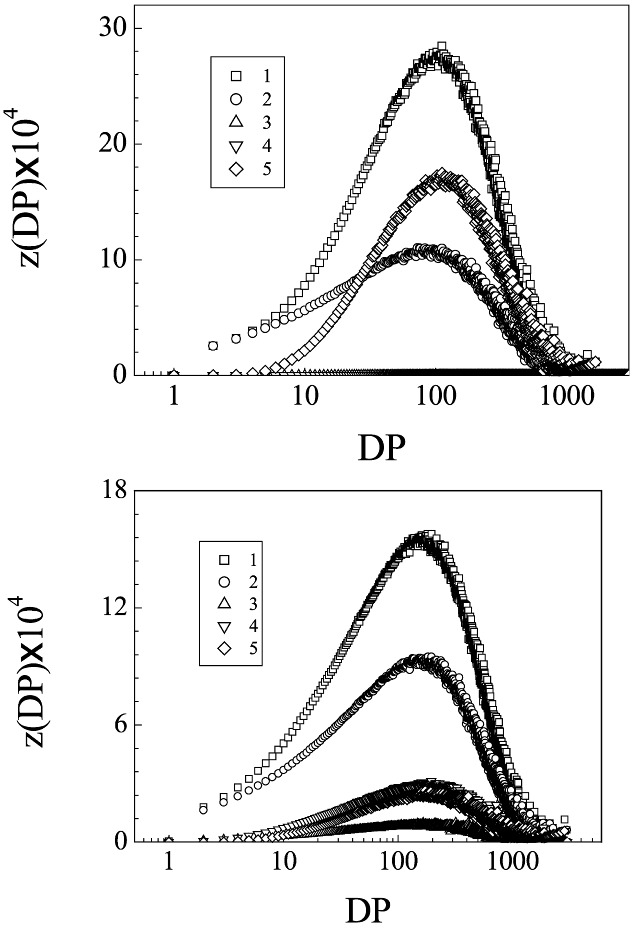


Fig. 6. z-distribution (GPC distribution) curves of various species of polymers based on different multifunctional initiator situation and total products obtained, z(DP), in simulation. DP is the degree of polymerization. $f_G = 3$, $c_x = 0.95$. (a) G*/B*/A* = 10/1/1; (b) G*/B*/A* = 1/1/1. (1) Total products; (2) product without initiator core; (3) product with initiator core in which one functional group has been reacted; (4) product with initiator core in which two functional groups have been reacted; (5) product with initiator core in which three functional groups have been reacted.

$c_x = 0.95$, the major part of the polymers is the hyperbranched polymers with three arms (Fig. 6(a)), while G*/B*/A* = 1/1/1 at $c_x = 0.95$ the major part of the polymer is hyperbranched polymer without multifunctional initiator (Fig. 6(b)). So the increase of reactivity of G* not only leads to the narrower molecular weight distribution but also increases the content of multi-armed hyperbranched polymer, which is an important role to improve final hyperbranched polymer properties. The final polymer with much multi-armed hyperbranched polymer will have better rheological properties due to symmetrical shape of macromolecule and optic-electronic property when the optically responsive core have been introduced [1–3].

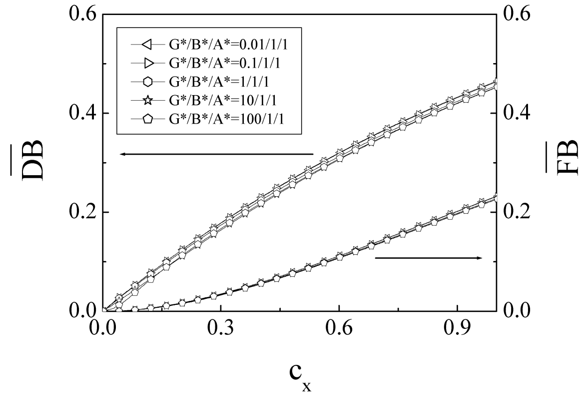


Fig. 7. Dependence of average degree of branching, $\overline{DB}$, and average fraction of branch-points, $\overline{FB}$, on conversion of double bonds in simulation. All the other parameters are the same as those in Fig. 2.

For consistence with previous works of other groups, we used the definitions of average degree of branching, $\overline{DB}$, and average fraction of branch-points, $\overline{FB}$, in literatures [17,24].

$$\overline{FB} = \frac{\text{number of branched units}}{(\text{total number of inimers}) - (\text{number of inimers remaining})} \tag{10}$$

here, N is the total number of polymers formed. Fig. 7 shows that $\overline{DB}$ and $\overline{FB}$ are almost not affected by reactivity of multifunctional initiator, and only depend on the conversion of double bond ($\overline{DB} = 0 - 0.465$, $\overline{FB} = 0 - 0.232$). In order to further understand branching structure of polymers, we obtained, for the first time, the density distribution of branch degree, n_{DB}, through the simulation (Fig. 8(a)), in which $n_{DB} = N_{DB}/N_{total}$, N_{DB} is the number of polymer molecules with DB, and N_{total} is the total number of polymer molecules. Due to the reaction mechanism of SCVP, the molecules with different DBs can react with each other, and their numbers will correlate each other during the polymerization. It is reasonable that there is a density distribution of DB, which should be responsible for the essential characters of SCVP. From Fig. 8(a), we know that the final polymer system obtained is the blend of polymers with various DB from linear (DB = 0) to dendrimer polymers (DB = 1). The study on density distribution of branch degree, n_{DB}, is particularly interesting. As shown in Fig. 8(a), the features of density distribution of branch degree between DB = 0.4–0.5 are similar to that between DB = 0–1, we defined this as the self-similarity of the density distribution of branch degree in SCVP. The study on origin of this particular feature is undergoing.

Fig. 9(a) shows the dependence of DB and FB on the degree of polymerization. DB′ and FB′ are, respectively,

$$\overline{DB} = \frac{2(\text{number of branched units})}{(\text{total number of inimers}) - (\text{number of inimers remaining}) - N} \tag{9}$$

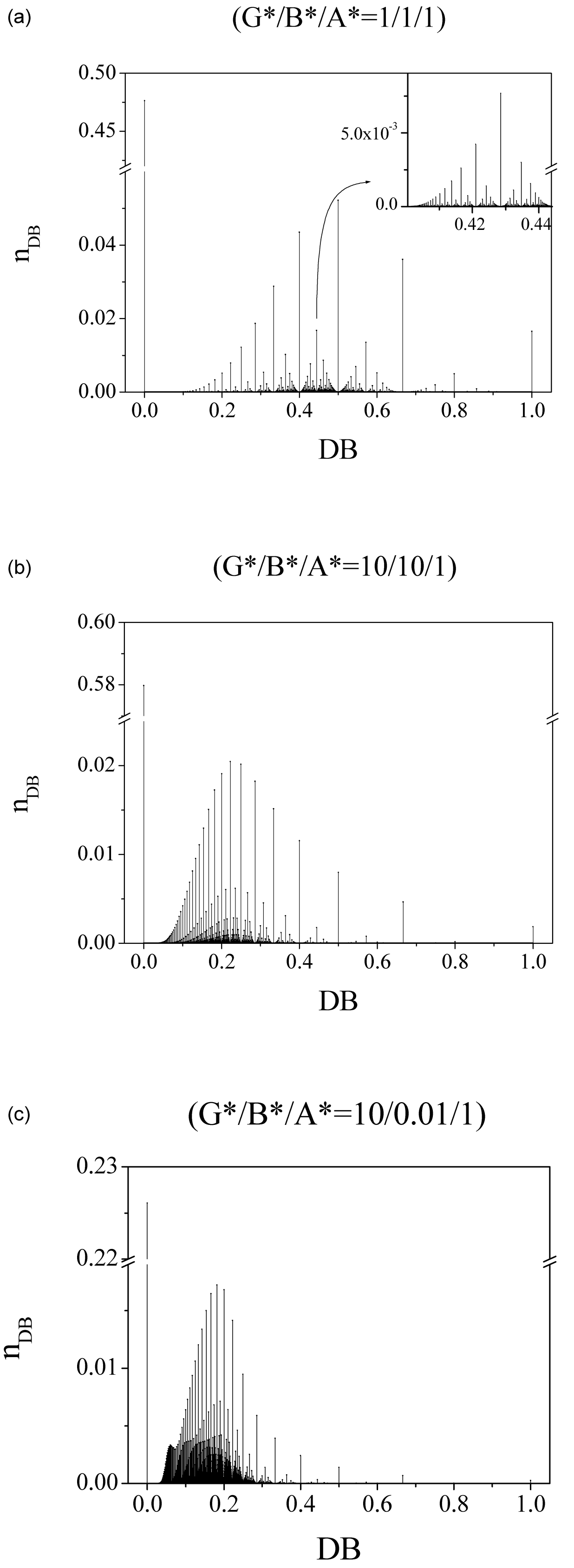


Fig. 8. Density distribution of DB with different reactivity ratio, G*/B*/A*, at $c_x = 0.95$ in simulation, all other parameters are the same as those in Fig. 2. (a) G*/B*/A* = 1/1/1; (b) G*/B*/A* = 10/10/1; (c) G*/B*/A* = 10/0.01/1.

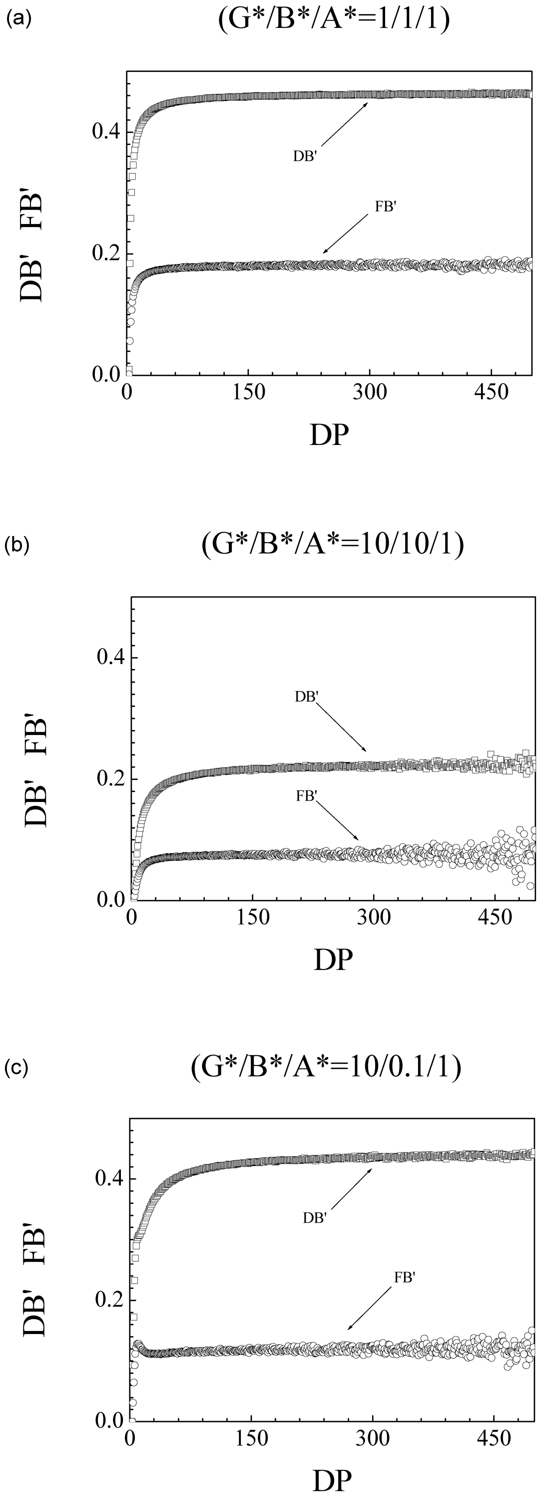


Fig. 9. Dependence of branch degree, DB′, and fraction of branch points, FB′, on the degree of polymerization, DP, in simulation. All the other parameters are the same as those in Fig. 2. (a) G*/B*/A* = 1/1/1; (b) G*/B*/A* = 10/10/1; (c) G*/B*/A* = 10/0.1/1.

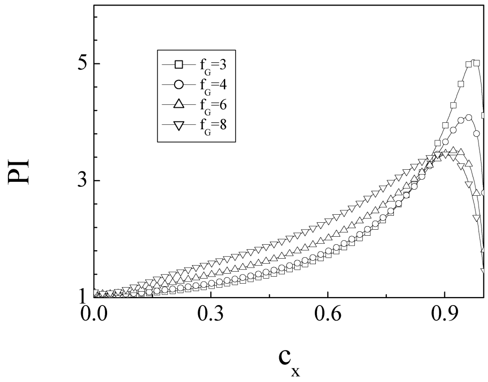


Fig. 10. Dependence of molecular weight distribution, PI, on conversion of double bonds, c_x, at various f_G ($f_{G=}3,4,6,8$) and G*/B*/A* = 10/1/1 in simulation. All the other parameters are the same as those in Fig. 2.

average degree of branching and average fraction of branch-points with a certain DP. Their definitions are as following.

$$\mathrm{DB}' = \frac{\sum_{i=1}^{n_{\mathrm{DP}}} \mathrm{DB}_{\mathrm{DP}}^{i}}{n_{\mathrm{DP}}} \tag{11}$$

$$\mathrm{FB}' = \frac{\sum_{i=1}^{n_{\mathrm{DP}}} \mathrm{FB}_{\mathrm{DP}}^{i}}{n_{\mathrm{DP}}} \tag{12}$$

Here n_{DP} is the number of polymers with DP. $\mathrm{DB}_{\mathrm{DP}}^{i}$ and $\mathrm{FB}_{\mathrm{DP}}^{i}$ are, respectively, the DB and FB of the ith polymer with a certain DP. When A* and B* have the equal reactivity, the DB′ and FB′ increase rapidly before DP ≈ 30, and then level off with the increase of DP indicating that the hyperbranched polymers with different DP (DP > 70) have almost the same DB′ and FB′. The data shown in Fig. 10 demonstrate that increasing the initiation sites in the multifuctional initiator will narrow the molecular weight distribution, especially at high conversion of double bond. This phenomenon is similar to the case of increasing the reactivity of multifunctional initiator, because more initiation sites in multifunctional initiator will enhance the propagating possibility of polymer chain with initiator core, and reduce the formation of polymer chain without initiator core. Thus, the final molecular weight distribution depends not only on adding of multifunctional initiator but also on the reactivity of active sites on multifunctional initiator.

3.2. Unequal reactivities of A* and B*

In this section, we will focus on investigation of SCVP system with B*/A* ≠ 1/1, while the reactivity of G* is higher than that of A* or B*. At first we consider two extreme cases, i.e. $G^* > B^* \gg A^*$ and $G^* > A^* \gg B^*$. In the first case, as shown by reaction channels 1 and 9 in Scheme 1, G* initially reacts with the double bond of inimer A–B*, forming G*–A*–B*. Successively, the double bond A on the inimer A–B* will prefer to react with active center B* instead of A* because $B^* \gg A^*$. Thus, the SCVP in this case behaves like characteristics of common condensation polymerization of A–B in the presence of B_n. However, for later case, due to $A^* \gg B^*$, reaction channel 13 in the Scheme 1 will be the most favorable reaction in the system, which leads to the star vinyl polymerization resulting in star polymer. Remember above knowledge in mind, it will be easy to understand our following results. To clearly reveal the effects of reactivity difference of A* and B* on the SCVP polymerization, in this part, G*/A* keeps constant and equals to 10.

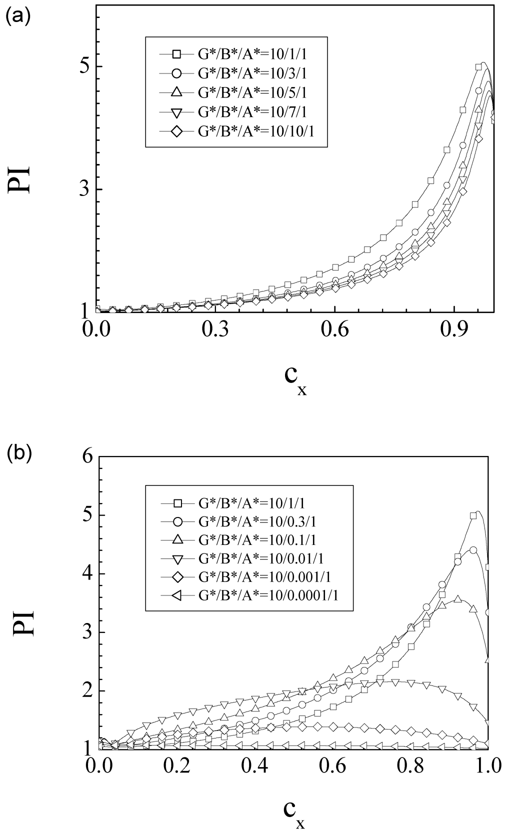


Fig. 11. Dependence of molecular weight distribution, PI, on conversion of double bonds, c_x, at various reactivity ratio of A* and B* in simulation. All the other parameters are the same as those of Fig. 2. (a) B*/A* ≥ 1; (b) B*/A* ≤ 1; $f_G = 3$; G/inimer = 0.01.

When $B^* > A^*$, the relationship between conversion and PI at various reactivity ratios of B*/A* are shown in Fig. 11(a). At conversion <70%, the PIs slightly increase with the increase of conversion. Above 70% conversion, we will observe the rapid increase of PI. Different from nonlinear condensation polymerization of A–B and B_n, in SCVP the double bond A reacted transforms into the active site A* which is able to initiate the polymerization of another double bond although its reactivity is low. Below 70% conversion, propagation reactions occurred mainly between active chain ends and inimers, so PI slightly increase. Above 70% conversion, most of inimers are consumed. The reaction possibility between various oligomers with different chain lengths gradually increases, resulting in rapid increase of PI. The maximum values in the curves of PI vs c_x are due to the reaction of polymer chains capped with vinyl group, with the star branched polymer. At last, all vinyl polymer chains link to the polymers with initiator core, resulting in decrease of PIs.

When $B^* < A^*$, the evolution of PI with conversion is shown in Fig. 11(b). Due to $G^* > B^*$ and $B^* < A^*$, at early stage of polymerization, most of active sites G* participate in the initiation, and the propagation takes place mainly between active sites A* and double bond A. Only very few of polymers with double bond are formed due to the initiation and propagation reaction among inimer molecules, A–B*. Greater the reactivity ratio of A* to B* is, less is the content of vinyl polymers formed. The behavior of the polymerization is closer to that of star polymerization of vinyl monomers using multifunctional initiator. Thus, with the decrease of B*/A*, the PIs of molecular weight distribution become low (see Fig. 11(b)).

It should be interesting to note that the ratio of B*/A* influences the $\overline{DB}$ and $\overline{FB}$ of hyperbranched polymers prepared from SCVP. The $\overline{DB}$ and $\overline{FB}$ have the maximum values at $B^*/A^* \approx 0.5/1$ for all double bond conversions (see Figs. 12 and 13). The large reactivity difference between A* and B*, i.e. the reactivity of B* is too low or too high compared with A*, will lead the polymerization close to the nonlinear condensation polymerization of A–B and B_n or close to star polymerization of vinyl monomer with multifunctional initiator. Thus the polymers formed have low DB and FB. DB' and FB' of the hyperbranched polymers are not affected by degree of polymerization obviously as shown in Fig. 9(b) and (c). The self-similarity character of the density distribution of branch degree in SCVP with $B^*/A^* \neq 1/1$ is also appear in this system as shown in Fig. 8(b) and (c). As we stated above, the final product through SCVP in the presence of multifunctional initiator will be a mixture of branched polymers from linear polymer (DB = 0) to dendrimer (DB = 1). The values of DB in the system with unequal reactivities of A* and B* concentrate in the range of 0.05–0.5 (Fig. 8(b) and (c)) instead of 0.1–0.8 as in the cases of equal reactivity of A* and B* as shown in Fig. 8(a).

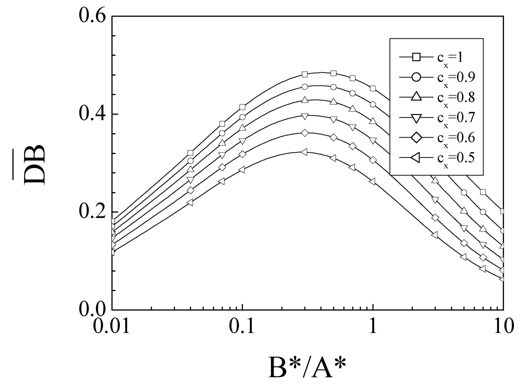


Fig. 12. Dependence of average degree of branching, $\overline{DB}$, on reactivity ratio, B*/A*, at various conversion of double bond, c_x, in simulation. $G^*/A^* = 10/1$. All the other parameters are the same as those in Fig. 2.

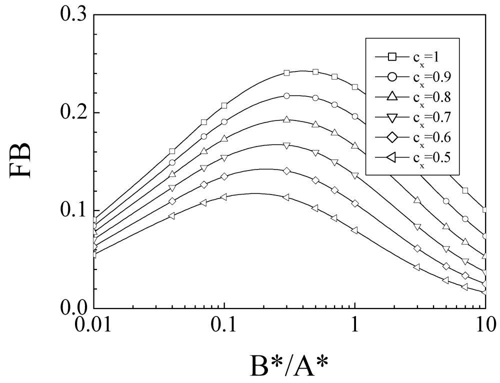


Fig. 13. Dependence of average fraction of branch points, $\overline{FB}$, on reactivity ratio, B*/A*, at various conversion of double bond, c_x, in simulation. $G^*/A^* = 10/1$; all the other parameters are the same as those in Fig. 2.

The phenomena of $\overline{DB}$ and $\overline{FB}$ depending only on the reactivity difference of A* and B* and double bond conversion as shown in Figs. 12 and 13 can be understood from the mechanism of SCVP. When both A* and B* in one unit are reacted, a branch point is formed. So all the parameters related with branch points, such as $\overline{DB}$ and $\overline{FB}$ should depend on the reactivity ratio of A* to B*, and their amounts in the polymers, which must be related with the conversion. Generally, the increase of reactivity difference of A* and B* will narrow the molecular distribution, but will decrease the branched degree, vise verse, decreasing reactivity difference of A* and B* will enhance branched degree, but will broaden molecular weight distribution of the polymers obtained.

4. Conclusion

Monte Carlo method was used to study the SCVP in the presence of multifunctional initiator with various reactive ratio of G*/B*/A*. The molecular weight distribution becomes narrow with the increase of reactivity of multifunctional initiator, especial at high double bond conversion. The reactivity of multifunctional initiator has little effects on the branched degree and branch point fraction. The higher reactivity of the initiator does enhance the contents of multi-armed hyperbranched polymers. The best reactivity ratio G*/B*/A* is about 10/1/1. The branched degree depends only on the double bond conversion and reactivity ratio of B*/A*, and is almost not dependent on multifunctional initiator. B*/A* corresponding to the highest DB is about 0.5/1. When $DP > 70$, the hyperbranched polymers with different DP have almost the same DB and FB. The density distribution of degree of branching further shows common self-similarity in SCVP.

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