Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 4047–4052 **4047**
DOI: 10.1021/ma900443u

Effect of Multifunctional Initiator on Self-Condensing Vinyl Polymerization with Nonequal Molar Ratio of Stimulus to Monomer

Zhiping Zhou*,† and Deyue Yan‡

†*School of Materials Science and Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, China, and* ‡*The State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China*

Received March 1, 2009; Revised Manuscript Received April 13, 2009

ABSTRACT: This work theoretically dealt with the effect of multifunctional initiators on the self-condensing vinyl polymerization (SCVP) with nonequal molar ratio of stimulus to monomer (α). The molecular size distribution function and other molecular parameters of the resulting hyperbranched polymers were derived analytically. The feed ratio of stimulus to monomer significantly affects the molecular parameters of the products. At the specified conversion of monomer (x), 99%, the number distribution curve of the total species formed appears as a bimodal structure for the low stimulus-to-monomer ratio, and it changes from bimodal to monomodal with increasing fraction of stimulus. When the polymerization is completed, the polydispersity index of the product increases with increasing α value, which is opposite for the polymerization without the core initiator. The higher the functionality of the core initiator (f), the lower the polydispersity index. However, unlike the homo-SCVP with core initiator, the polydispersity index does not always monotonously decrease with increasing fraction of core initiators (β). If $\beta > \sqrt{\alpha/f}$, then it increases with increasing β; otherwise, it decreases monotonously.

Introduction

Since Frèchet and coworkers[1−3] reported the self-condensing vinyl polymerization (SCVP) in 1995, theoretical investigations have been made systematically. Müller, Yan, and coworkers[4,5] developed the kinetic theory for the SCVP in 1997 and derived the analytical expressions of the molecular size distribution function and other molecular parameters for the hyperbranched polymers obtained. In addition, Müller et al. [6] suggested an approach to narrow the molecular weight distribution, which can be conducted in two ways: (i) the semibatch process: monomer molecules were added so slowly to the additional multifunctional initiator solution that they could react only with the core initiators or the macromolecules formed already but not with each other and (ii) the batch process: the additional multifunctional initiator and monomer molecules were mixed instantaneously. The authors gave the expressions of the molecular weight distribution and its averages for the semibatch process and those of molecular weight averages for the batch process. Then, the authors of this work and Müller[7] reported the molecular weight distribution function for the batch process. Using generating function, Cheng et al.[8,9] evaluated the influence of the trifunctional cores with nonequal reactivities on various molecular parameters of hyperbranched polymers. Monte Carlo simulation was also used to treat SCVP in the presence of multifunctional initiator with nonequal reaction rate constants.[10,11] Müller et al.[12,13] presented the technology of the self-condensing vinyl copolymerization (SCVCP) to design the molecular structure and parameters. Theoretical calculation shows that the average degree of branching strongly depends on the feed ratio of comonomers and the relative reactivities of the monomer and inimer.[12,13]

SCVP involves AB-type monomers. The A group is a double bond, and B is a pendent group that can be transformed into an initiating center by an external stimulus. Therefore, the B group becomes activated, and the AB monomer is transferred to an AB* molecule, which had been coined as the "inimer".[4] Chain initiation is the addition of the active B* group to the double bond of other inimers and residual monomers. If all AB monomers are transferred to AB* inimers, then it is the homo-SCVP. If the mole number of stimulus is less than the initial mole number of the monomer, then there are both AB* inimers and AB monomers in the reaction system at the beginning of the polymerization. The activation reaction is usually assumed to be finished instantaneously. All aforementioned kinetic theories are confined to the homo-SCVP. In the last year, we[14] have reported the molecular size distribution function and calculated various molecular parameters for the general model of SCVP with nonequal ratio of stimulus to monomer. The self-condensing ring-opening polymerization of 3-ethyl-3-(hydroxymethyl)oxetane is another example for this model. A series of hyperbranched poly[3-ethyl-3-(hydroxymethyl)oxetane]s with various degrees of branching have been synthesized by adjusting the feed ratio of catalyst to monomer.[15−19] The experimental data showed that the molecular structures and parameters of the hyperbranched polymers obtained are indeed related to the feed ratio of catalyst to monomer. In this work, we further investigate the kinetics of the general SCVP in the presence of a small amount of multifunctional initiator molecules, giving the expressions of molecular size distribution function and various molecular parameters, which may facilitate molecular design of the product and control of the polymerization process.

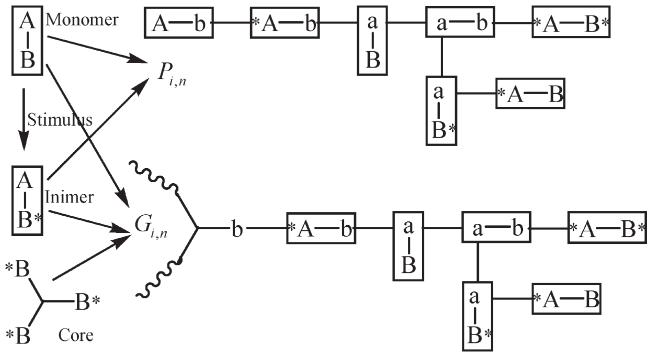
Kinetic Analysis

The reaction mechanism can be described by Scheme 1 with a trifunctional core initiator. The AB monomers are partially transformed into AB* inimers by the stimulus. Let M_0 be the initial concentration of AB monomers and α (≤ 1) be the mole ratio of stimulus to monomers. Usually, the active reaction

---

*Corresponding author. Tel: +86-511-88791919. Fax: +86-511-88791947. E-mail: zhouzp@ujs.edu.cn.

Scheme 1



finishes instantaneously. Therefore, at the beginning of polymerization, the concentration of AB* inimers is αM_0, and that of residual monomers is $(1-\alpha)M_0$. To reduce the polydispersity of the resulting hyperbranched polymer, a small amount of multifunctional core initiator, B_f* (f represents the functionality, i.e., the number of active B* groups in the initiator), is present in the reaction system, and its concentration is denoted as βM_0.

The double bond A can react with any active group (B* or A*), and the A becomes active A* group after it reacts. The polymerization results in two types of species. One is those without core initiator and the other includes a core initiator. Let $P_{i,n}$ denote the concentration of the species consisting of n inimer units and $(i-n)$ monomer units without core and $G_{i,n}$ denote the concentration of the species with a core and n inimer units and $(i-n)$ monomer units. If the core initiator is neglected, then the degrees of polymerization of both $P_{i,n}$ and $G_{i,n}$ are i. According to the kinetic mechanism,[4,7,14] there is exactly a double bond and n active centers (A* + B*) in every $P_{i,n}$ species, and there are $n + f$ active centers in every $G_{i,n}$ species. The chemical equations for the formation of species read $P_{l,j} + P_{i-l,n-j} \rightarrow P_{i,n}$ and $P_{l,j} + G_{i-l,n-j} \rightarrow G_{i,n}$.

If the rate constants of the various active groups are assumed to be identical and the intramolecular cyclization reactions are excluded, then the kinetic differential equations for the evolution of species with respect to time are

$$\frac{\mathrm{d}P_{i,n}}{\mathrm{d}t} = \frac{k}{2}\sum_{l<i,j\leq l}[jP_{l,j}P_{i-l,n-j} + (n-j)P_{i-l,n-j}P_{l,j}] - k\left[nP_{i,n}\sum_{l>0,j\leq l}P_{l,j} + P_{i,n}\left(\sum_{l>0,j\leq l}jP_{l,j} + \sum_{l>0,j\leq l}(f+j)G_{l,j}\right)\right] = \frac{k}{2}\sum_{l<i,j\leq l}nP_{l,j}P_{i-l,n-j} - k\left[nP_{i,n}\sum_{l>0,j\leq l}P_{l,j} + P_{i,n}\left(\sum_{l>0,j\leq l}jP_{l,j} + \sum_{l>0,j\leq l}(f+j)G_{l,j}\right)\right] \quad (1)$$

$$\frac{\mathrm{d}G_{i,n}}{\mathrm{d}t} = k\sum_{l<i,j\leq l}(f+n-j)P_{l,j}G_{i-l,n-j} - k(f+n)G_{i,n}\sum_{l>0,j\leq l}P_{l,j} \quad (2)$$

where k represents the reactivity between a double bond and an active site. In these two equations, the first term represents the generation rate of the corresponding species and the second negative term denotes the consumption.

The initial conditions of species read

$$P_{1,1}|_{t=0} = \alpha M_0; \quad P_{1,0}|_{t=0} = (1-\alpha)M_0; \ P_{l,j}(l>1)|_{t=0} = 0$$
$$G_{0,0}|_{t=0} = \beta M_0; \quad G_{l,j}(l>0)|_{t=0} = 0 \quad (3)$$

The constraint conditions can be written as

$$\sum_{i>0,n\leq i} n(P_{i,n} + G_{i,n}) = \alpha M_0 \quad (4)$$

$$\sum_{i>0,n\leq i}(i-n)(P_{i,n} + G_{i,n}) = (1-\alpha)M_0 \quad (5)$$

$$\sum_{i\geq 0,n\leq i} G_{i,n} = \beta M_0 \quad (6)$$

Because every inimer, AB*, or monomer, AB, has a double bond, A, the conversion of double bonds is defined as

$$x = \frac{M_0 - \sum_{i>0,n\leq i}P_{i,n}}{M_0} \quad (7)$$

that is, the total number of double bonds in the reaction system is

$$A = \sum_{i>0,n\leq i}P_{i,n} = M_0(1-x) \quad (8)$$

Differentiating both sides of eq 8 leads to

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -M_0\frac{\mathrm{d}x}{\mathrm{d}t} \quad (9)$$

However, the consumption of the double bonds fits

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -kA(\mathrm{A}^* + \mathrm{B}^*) = -kM_0^2(\alpha + f\beta)(1-x) \quad (10)$$

where the total concentration of active site, A* + B*, always remains constant, $M_0(\alpha + f\beta)$. Comparing eqs 9 and 10 leads to

$$\frac{\mathrm{d}x}{\mathrm{d}t} = kM_0\gamma(1-x) \quad (11)$$

with

$$\gamma = \alpha + f\beta \quad (12)$$

By dividing eqs 1 and 2 by eq 11 and using the constraint conditions (eqs 4–6), we can transfer the variable from the time, t, to the double conversion, x, for the kinetic differential equations.

$$\frac{\mathrm{d}P_{i,n}}{\mathrm{d}x} = \frac{1}{2M_0\gamma(1-x)}\sum_{l,j}nP_{l,j}P_{i-l,n-j} - \left(\frac{n}{\gamma} + \frac{1}{1-x}\right)P_{i,n} \quad (13)$$

$$\frac{\mathrm{d}G_{i,n}}{\mathrm{d}x} = \frac{1}{M_0\gamma(1-x)}\sum_{l,j}(f+n-j)P_{l,j}G_{i-l,n-j} - \frac{1}{\gamma}(f+n)G_{i,n} \quad (14)$$

Molecular Size Distribution and Molecular Parameters

Solving eqs 13 and 14 yields

$$P_{i,n} = M_0\frac{n^{i-1}}{n!(i-n)!}\alpha^n(1-\alpha)^{i-n}(1-x)(x/\gamma)^{i-1}\mathrm{e}^{-nx/\gamma} \quad (15)$$

$$G_{i,n} = M_0\beta\frac{f(f+n)^{i-1}}{n!(i-n)!}\alpha^n(1-\alpha)^{i-n}(x/\gamma)^i\mathrm{e}^{-(f+n)x/\gamma} \quad (16)$$

Equations 15 and 16 are just the molecular size distribution function of the species formed from the general SCVP in the presence of multifunctional initiators. If $\beta = 0$, then eq 15 degenerates into the size distribution function reported for general SCVP,[14] and if α = 0, then these two expressions can be reduced to that for homo-SCVP in the presence of multifunctional core initiators.[7] If both α and β are zero, then eq 15 degenerates into the size distribution function for homo-SCVP without core initiators.[5] The various molecular parameters can be obtained from these two expressions. Equations 6 and 8 are the respective zeroth moments of $P_{i,n}$ and $G_{i,n}$ distributions; that is, $\mu_0^P = \Sigma_{i\geq 0,n\leq i} P_{i,n} = M_0(1-x)$ and $\mu_0^G = \Sigma_{i>0,n\leq i} \mathrm{G}_{i,n} = \beta M_0$. The first and second moments can be derived as

$$\mu_1^P = \sum_{i>0,\, n\leq i} iP_{i,n} = M_0 \frac{1-x}{1-\alpha x/\gamma} \tag{17}$$

$$\mu_2^P = \sum_{i>0,\, n\leq i} i^2 P_{i,n} = M_0 \frac{\gamma(1-x)}{(\gamma-\alpha x)^3}[\gamma^2 + \alpha(1-\alpha)x^2] \tag{18}$$

$$\mu_1^G = \sum_{i>0,\, n\leq i} iG_{i,n} = M_0 \frac{f\beta x}{\gamma - \alpha x} \tag{19}$$

$$\mu_2^G = \sum_{i>0,\, n\leq 0} i^2 G_{i,n} = M_0 f\beta x \frac{\gamma^2 + f\gamma x - f\alpha x^2 + \alpha(1-\alpha)x^2}{(\gamma-\alpha x)^3} \tag{20}$$

For the sake of simplicity, the core initiators can be neglected when we investigate the molecular size and average molecular weight because it is only a small fraction. Then, the normalized number-, weight-, and z-distribution of the molecular size can be defined as

$$N(i) = \frac{\sum_{n\leq i}(P_{i,n} + G_{i,n})}{\sum_{i\geq 0,\, n\leq i}(P_{i,n} + G_{i,n})} = \frac{1}{1-x+\beta}\left(\frac{x(1-\alpha)}{\gamma}\right)^i \sum_{n\leq i}\left[\frac{\gamma(1-x)n^{i-1}}{x} + \beta f(f+n)^{i-1}\mathrm{e}^{-fx/\gamma}\right]\frac{1}{n!(i-n)!}\left(\frac{\alpha}{1-\alpha}\mathrm{e}^{-x/\gamma}\right)^n \tag{21}$$

$$W(i) = \frac{\sum_{n\leq i} i(P_{i,n} + G_{i,n})}{\sum_{i>0,\, n\leq i} i(P_{i,n} + G_{i,n})} = i\left(\frac{x(1-\alpha)}{\gamma}\right)^i \sum_{n\leq i}\left[\frac{\gamma(1-x)n^{i-1}}{x} + \beta f(f+n)^{i-1}\mathrm{e}^{-fx/\gamma}\right]\frac{1}{n!(i-n)!}\left(\frac{\alpha}{1-\alpha}\mathrm{e}^{-x/\gamma}\right)^n \tag{22}$$

$$Z(i) = \frac{\sum_{n\leq i} i^2(P_{i,n} + G_{i,n})}{\sum_{i>0,\, n\leq i} i^2(P_{i,n} + G_{i,n})} \tag{23}$$

Figure 1 shows the number distribution of the products, with $x = 0.99$, $\beta = 0.01$, and α = 0.1 at the specified values of $f = 0$, 1, 2, and 5, respectively. A particular feature is that the distribution curve has a bimodal when $f > 1$. It should contribute to the fact that the products consist of two clusters. One is the group of $P_{i,n}$ species and the other is that of $G_{i,n}$ species. Figure 2 is a typical example of the number distributions of these two types of species in which the low molecular weight distribution comes from the $P_{i,n}$ species and the high molecular weight distribution comes from the $G_{i,n}$ species. In consequence, it results in the total dimodal distribution curve. When $f = 1$, there is a major overlap of the two distributions, which composes a monomodal for the total distribution curve. The large value of f favors the formation of $G_{i,n}$ species. Therefore, with the increase in f, the peak of the $P_{i,n}$ species drifts toward the left (low degree of polymerization), and the other drifts toward the right. The higher the value of f, the larger the space between the two peaks.

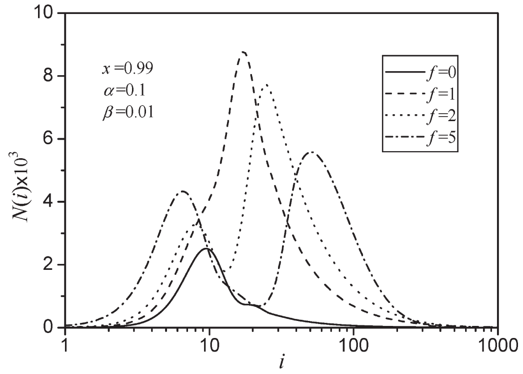


Figure 1. Number distributions of the hyperbranched polymers formed from general SCVP in the presence of multifunctional cores with $x = 0.99$, $\beta = 0.01$ and α = 0.1 at the specified values of f: 0 (—), 1 (– – –), 2 (· · ·), and 5 (– · –).

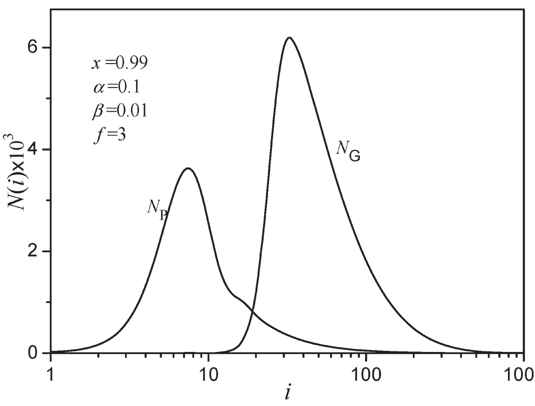


Figure 2. Typical number distributions of the hyperbranched polymers formed from general SCVP in the presence of multifunctional cores with $x = 0.99$, $\beta = 0.01$, and α = 0.1 at the specified values of $f = 3$. N_P: the distribution of $P_{i,n}$ species; N_G: the distribution of $G_{i,n}$ species.

Shown in Figure 3 are the total z-distribution curves under the same parameter conditions as those used in Figure 1. Every z-distribution curve has only a monomodal regardless of the values of f. It is evident from Figure 3 that the larger the functionality of the core, the narrower the molecular weight distribution, which is in agreement with that of homo-SCVP[7] and $\mathrm{AB_g}$ type polycondensation[21,22] in the presence of a multifunctional initiator. For the general SCVP without core initiators, that is, $f = 0$, the molecular size distribution is extremely broad, and the z-distribution curve presses close to the abscissa on the present scale of Figure 3.

With the increase in α values, the fraction of inimers increases, and the probability of forming $G_{i,n}$ species decreases. The typical number distribution curves, with $x = 0.99$, $\beta = 0.01$, and $f = 3$ at the specified values α = 0.5 and 1, are given in Figures 4 and 5, respectively. The dashed lines (N_P) denote the number distribution of $P_{i,n}$ species, and the dotted lines (N_G) represent the distribution of $G_{i,n}$ species. The solid lines (N) represent the total distribution of products. The respective

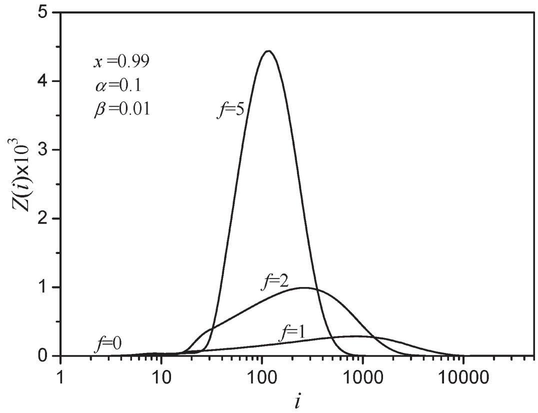


Figure 3. *z*-Distributions of the hyperbranched polymers formed from general SCVP in the presence of multifunctional cores under the identical conditions in Figure 1.

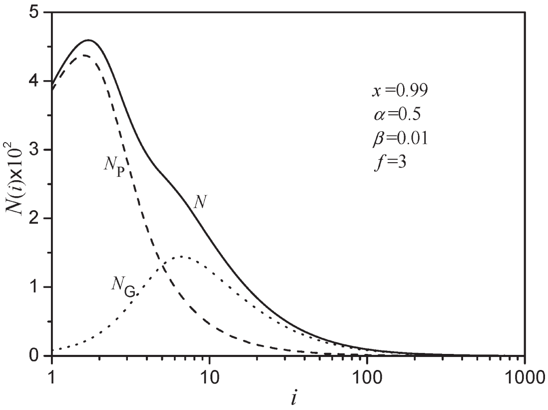


Figure 4. Number distributions of the hyperbranched polymers formed from general SCVP in the presence of multifunctional cores with $x = 0.99$, $\beta = 0.01$, $f = 3$, and $\alpha = 0.5$. N_P: the distribution of $P_{i,n}$ species; N_G: the distribution of $G_{i,n}$ species; N: the total distribution of products.

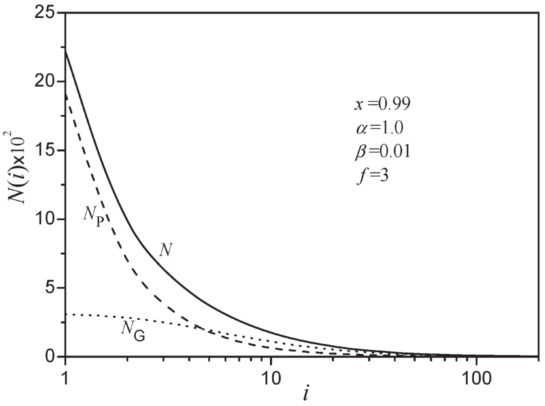


Figure 5. Number distributions of the hyperbranched polymers formed from general SCVP in the presence of multifunctional cores with $x = 0.99$, $\beta = 0.01$, $f = 3$, and $\alpha = 1.0$. N_P: the distribution of $P_{i,n}$ species; N_G: the distribution of $G_{i,n}$ species; N: the total distribution of products.

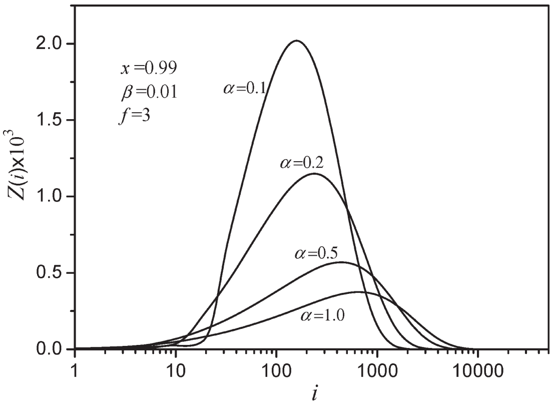


Figure 6. *z*-Distributions of the hyperbranched polymers formed from general SCVP in the presence of multifunctional cores with $x = 0.99$, $\beta = 0.01$, and $f = 3$ at the specified values of α: 0.1, 0.2, 0.5, and 1.0.

peak of $P_{i,n}$ and $G_{i,n}$ species still appears at $\alpha = 0.5$, but there is no dimodal for the total distribution. There is even no peak for the respective distribution curve at $\alpha = 1$. Therefore, it can be known that the total number distribution changes from dimodal to monomodal by increasing the fraction of stimulus, that is, α values, and there is no peak at a high value of α. Shown in Figure 6 is the *z*-distribution curves at $f = 3$, $x = 0.99$, $\beta = 0.01$, and the several α values margined. The lower the α value, the narrower the molecular weight distribution.

The molecular weight of $P_{i,n}$ species with n inimers and $(i-n)$ monomers is $[nw_I + (i - n)w_M]$ and that of $G_{i,n}$ species is $[nw_I + (i - n)w_M + w_G]$, where w_I, w_M, and w_G denotes the mass of inimer, monomer, and core initiator, respectively. Therefore, the kth molecular weight distribution (MWD) moment is

$$\mu_k = \sum_{i,n} [nw_I + (i-n)w_M]^k P_{i,n} + \sum_{i,n} [nw_I + (i-n)w_M + w_G]^k G_{i,n} \quad (24)$$

The number- and weight-average molecular weights of the products formed are defined as $\overline{M}_n = \mu_1/\mu_0$ and $\overline{M}_w = \mu_2/\mu_1$, that is

$$\overline{M}_n = \frac{\sum_{i,n}[nw_I + (i-n)w_M](P_{i,n} + G_{i,n}) + w_G \sum_{i,n} G_{i,n}}{\sum_{i,n}(P_{i,n} + G_{i,n})} \quad (25)$$

$$\overline{M}_w = \frac{\sum_{i,n} [nw_I + (i-n)w_M]^2 P_{i,n} + \sum_{i,n} [nw_I + (i-n)w_M + w_G]^2 G_{i,n}}{\sum_{i,n}[nw_I + (i-n)w_M](P_{i,n} + G_{i,n}) + w_G \sum_{i,n} G_{i,n}} \quad (26)$$

As a matter of fact, the inimer was formed by activating monomer, and they have same mass. Furthermore, the molecular weight of the hyperbranched polymers always remains large when the reaction approaches completion, and the mass of the core initiator may be negligible. The average molecular weight can be substituted by the average degree of polymerization.

$$\overline{P_n} = \frac{\sum_{i,n} i(P_{i,n} + G_{i,n})}{\sum_{i,n}(P_{i,n} + G_{i,n})} = \frac{1}{1-x+\beta} \quad (27)$$

$$\overline{P_w} = \frac{\sum_{i,n} i^2(P_{i,n} + G_{i,n})}{\sum_{i,n} i(P_{i,n} + G_{i,n})} = \frac{1}{\gamma^2(1-\alpha x/\gamma)^3}\{\gamma^2 - x(\gamma^2 - f\beta\gamma) + x^2(\alpha - \alpha^2 + f^2\beta) - x^3\alpha[1 - \alpha + f\beta(f-1+\alpha)/\gamma]\} \quad (28)$$

The polydispersity index of the products reads

$$\mathrm{PI} = \overline{P_\mathrm{w}}/\overline{P_\mathrm{n}} = \frac{1-x+\beta}{\gamma^2(1-\alpha x/\gamma)^3}\{\gamma^2 - x(\gamma^2 - f\beta\gamma) + x^2(\alpha - \alpha^2 + f^2\beta) - x^3\alpha[1-\alpha+f\beta(f-1+\alpha)/\gamma]\} \quad (29)$$

If the residual monomers, inimers, and core initiators are excluded, then the revised number- and weight-average degrees of polymerization and the polydispersity index read

$$\overline{P}_\mathrm{n}' = \frac{1-(1-\alpha)(1-x)-\alpha(1-x)\mathrm{e}^{-x/\gamma}-\beta\mathrm{e}^{-fx/\gamma}}{1-x+\beta-(1-\alpha)(1-x)-\alpha(1-x)\mathrm{e}^{-x/\gamma}-\beta\mathrm{e}^{-fx/\gamma}} \quad (30)$$

$$\overline{P}_\mathrm{w}' = \frac{\mu_2/M_0-(1-\alpha)(1-x)-\alpha(1-x)\mathrm{e}^{-x/\gamma}-\beta\mathrm{e}^{-fx/\gamma}}{1-(1-\alpha)(1-x)-\alpha(1-x)\mathrm{e}^{-x/\gamma}-\beta\mathrm{e}^{-fx/\gamma}} \quad (31)$$

$$\mathrm{PI}' = \frac{\overline{P}_\mathrm{w}'}{\overline{P}_\mathrm{n}'} \quad (32)$$

Shown in Figure 7 is the evolution of the number-average degree of polymerization. The solid line denotes the total average degree of polymerization calculated from eq 27, which is independent of *f* and α, and the dashed line is the average degree of polymerization of $G_{i,n}$ species for the specified α values, 0.01, 0.5, and 1.0, respectively, calculated according to $G_n = \mu_1^G/\mu_0^G$. For the low value of α, the average degree of polymerization of $P_{i,n}$ species is very small. At any specified *x*, the lower the α, the larger the average degree of polymerization of $G_{i,n}$ species formed. At the end of the reaction ($x = 1.0$), the $P_{i,n}$ species disappears, and the total average degree of polymerization reaches $1/\beta$ regardless of the α values. Similar to the homo-SCVP in the presence of multifunctional initiators, the polydispersity index of the products initially increases with increasing reaction extent of A groups and decreases after a maximum. Here, however, the location of the maximum of the polydispersity index depends on the value of α. The lower the value of α, the earlier the maximum appears, as shown in Figure 8.

At the end of reaction, the polydispersity index reads

$$\mathrm{PI} = \frac{1}{f^2\beta}[(2f\beta+1)\alpha + f^2\beta(1+\beta)] \quad (33)$$

The pictorial relationship of eq 33 is shown in Figure 9. The polydispersity index increases linearly with the increase in α at the specified *f* and β, and the slope decreases with increasing functionality of core initiator. The polydispersity index always decreases with increasing *f*. As for the dependence of the polydispersity index on β, it can be known from the equation that it decreases with increasing fraction of core initiator if $\beta < \sqrt{\alpha}/f$. Otherwise, it increases monotonously. The number-average degree of polymerization remains constant at the specified *x*. Therefore, the corresponding relationship of the weight-average degree of polymerization can be understood from eq 33 and Figure 9 as well.

Conclusions and Discussion

For the general SCVP in the presence of multifunctional core initiators, the feed ratio of stimulus to monomer considerably affects the molecular weight distribution and molecular parameters for the resulting hyperbranched polymers. For a low ratio of stimulus/monomer, the number distribution curve of the total product has a dimodal structure. The peak in low molecular weight distribution belongs to the species without the core initiator ($P_{i,n}$), and the peak in high molecular weigh distribution belongs to the $G_{i,n}$ species. The space between the two peaks increases with the increase in the functionality of core, *f*. The total number distribution changes from dimodal to monomodal with increasing fraction of stimulus, and there is no peak at a high value of α. For the ultimate products, the polydispersity index increases with increasing α value. It can be understood that the

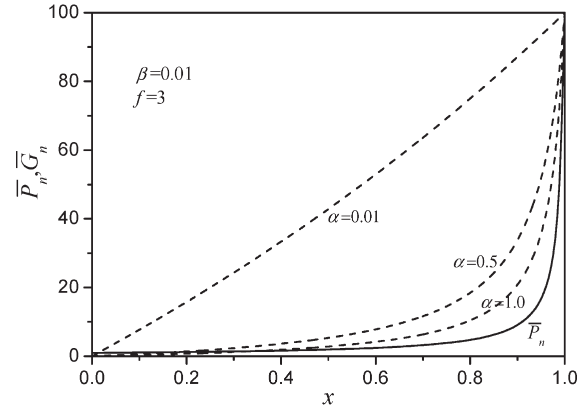


Figure 7. Evolution of the number-average degree of polymerization with $f = 3$ and $\beta = 0.01$. Solid line: the number-average degree of polymerization of total products; dashed lines: the number- average degree of polymerization of the $G_{i,n}$ species with $\alpha = 0.01$, 0.5, and 1.0, respectively.

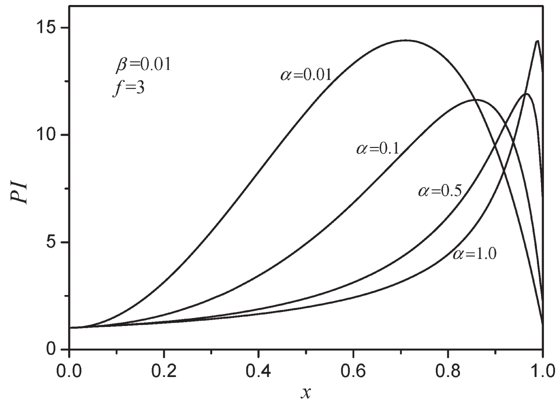


Figure 8. Dependence of polydispersity on *x* with $f = 3$ and $\beta = 0.01$ at the values of $\alpha = 0.01$, 0.1, 0.5, and 1.0, respectively.

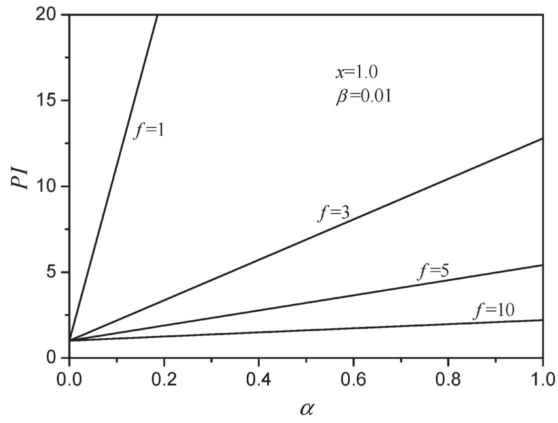


Figure 9. Dependence of polydispersity on the ratio of stimulus-to-monomer at $x = 1$, $\beta = 0.01$, and the several specified values of *f*.

large fraction of inimers results in a high probability of forming the $P_{i,n}$ species, which enhances the polydispersity index. Oppositely, the polydispersity decreases with increasing α for the general SCVP without core initiator.[14] For the homo-SCVP with core initiator, the polydispersity index of the product always decreases with increasing fraction of core initiator.[7] However, it depends on both the fraction of stimulus (α) and that of core initiator (β) for the polymerization model in this work. It can be known from eq 33 that the polydispersity index decreases with increasing β on the condition that $\beta < \sqrt{\alpha/f}$; otherwise, it increases monotonously.

Experiment[17,23] and Monte Carlo simulation[10,11] have confirmed the theoretical prediction that the polydispersity index is slightly low when a core molecule was used in the polymerization. However there is very little experimental detail of the molecular weight distribution in the literature. In the synthesis of hyperbranched phenylacetylene polymers by 3,5-diiodophenylacetylene (AB_2 monomer) in the presence of multifunctional core, monomodal molecular weight distributions were observed at low monomer/core ratios. As this ratio increases, a bimodal molecular weight distribution was observed, which consists of a sharp peak at high molecular weight and a broad tail at low molecular weight.[24] It is thought that the low molecular weight distribution comes from the self-polymerization of added AB_2 monomer. The calculated number distributions in this work are in good agreement with their experimental results.

The theoretical treatment in this work is limited to the assumption that the reactivities of A* and B* functional groups are identical and the intramolecular cyclization is absent. Taking into account the effect of nonequal reactivities, some investigations have been reported for the SCVP;[25,26] however, further endeavor is needed still to interpret the results fully.

Acknowledgment. This work was sponsored by the NSF of China (20774038, 50633010).

References and Notes

(1) Frèchet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *269*, 1080.
(2) Aoshima, S.; Frèchet, J. M. J.; Grubbs, R. B.; Henmi, M.; Leduc, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*, 531.
(3) Hawker, C. J.; Frèchet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763.
(4) Müller, A. H. E.; Yan, D.; Wulkow, M. *Macromolecules* **1997**, *30*, 7015.
(5) Yan, D.; Müller, A. H. E.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7024.
(6) Radke, W.; Litvinenko, G.; Müller, A. H. E. *Macromolecules* **1998**, *31*, 239.
(7) Yan, D.; Zhou, Z.; Müller, A. H. E. *Macromolecules* **1999**, *32*, 245.
(8) Cheng, K. C. *Polymer* **2003**, *44*, 877.
(9) Cheng, K. C.; Wang, L. Y. *Macromolecules* **2002**, *35*, 5657.
(10) He, X.; Liang, H.; Pan, C. *Macromol. Theory Simul.* **2001**, *10*, 196.
(11) He, X.; Liang, H.; Pan, C. *Polymer* **2003**, *44*, 6697.
(12) Litvinenko, G. I.; Simon, P. F. W.; Müller, A. H. E. *Macromolecules* **1999**, *32*, 2410.
(13) Litvinenko, G. I.; Simon, P. F. W.; Müller, A. H. E. *Macromolecules* **2001**, *34*, 2418.
(14) Zhou, Z.; Yan, D. *Macromolecules* **2008**, *41*, 4429.
(15) Bednarek, M.; Biedron, T.; Helinski, J.; Kaluzynski, K.; Kubisa, P.; Penczek, S. *Macromol. Rapid Commun.* **1999**, *20*, 369.
(16) Bednarek, M.; Kubisa, P.; Penczek, S. *Macromolecules* **2001**, *34*, 5112.
(17) Magnusson, H.; Malmstrom, E.; Hult, A. *Macromolecules* **2001**, *34*, 5786.
(18) Yan, D.; Hou, J.; Zhu, X.; Kosman, J. J.; Wu, H. S. *Macromol. Rapid Commun.* **2000**, *21*, 557.
(19) Mai, Y.; Zhou, Y.; Yan, D.; Hou, J. *New J. Phys.* **2005**, *7*, 42.
(20) Litvinenko, G. I.; Müller, A. H. E. *Macromolecules* **2002**, *35*, 4577.
(21) Yan, D.; Zhou, Z. *Macromolecules* **1999**, *32*, 819.
(22) Zhou, Z.; Yan, D. *Polymer* **2000**, *41*, 4549.
(23) Parker, D.; Feast, W. J. *Macromolecules* **2001**, *34*, 5792.
(24) Bharathi, P.; Moore, J. S. *Macromolecules* **2000**, *33*, 3212.
(25) Zhou, Z.; Zhang, J.; Sheng, W.; Yan, D. *Acta Chim. Sin.* **2008**, *66*, 2547.
(26) Zhou, Z.; Wang, G.; Yan, D. *Chin. Sci. Bull.* **2008**, *53*, 3516.