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A General Model for the Kinetics of Self-Condensing Vinyl Polymerization

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ABSTRACT: The kinetic model of the self-condensing vinyl polymerization (SCVP) with nonequal molar concentrations of stimulus and monomer was developed in this work. The molecular size distribution function and other molecular parameters of the resulting hyperbranched polymers were derived. The feed ratio of stimulus to monomer significantly affects the molecular parameters of the products. The residual monomer and inimer in the reaction system have an important influence on the molecular parameters of the hyperbranched polymers obtained even at a high double-bond conversion. Similarly to the SCVP with nonequal reactivities and self-condensing vinyl copolymerization, the maximum of the degree of branching is 0.5 for the SCVP with nonequal molar concentrations of stimulus and monomer. In other words, when the molar ratio of stimulus to monomer approaches 0.627 and the vinyl conversion reaches 1, we can get the hyperbranched polymers with the highest degree of branching.

Introduction

The discovery of self-condensing vinyl polymerization (SCVP)[1] makes it easy to synthesize hyperbranched polymers using vinyl monomers. Since Frèchet et al.[1] reported the SCVP in 1995, various types of living polymerization, such as living/controlled radical polymerization,[2–5] cationic polymerization,[1,6] group transfer polymerization,[7] and anionic polymerization,[8–10] have been applied to synthesize hyperbranched polymers via the strategy. In addition, SCVP was extended to the self-condensing ring-opening polymerization (SCROP).[11–16]

In 1997, one of the authors in this work and co-workers[17,18] dealt with the kinetics of the SCVP with equal molar concentrations of stimulus and monomer, giving the analytic expressions of all molecular parameters for the resulting hyperbranched polymers, such as the degree of branching, the molecular size distribution, the average molecular weights, and the polydispersity index. Afterward, Müller et al.[19,20] investigated the effect of core molecules on the molecular weight averages of hyperbranched polymers generated from SCVP. The molecular size distribution functions for the same polymerization system and the AB_g-type polycondensation with multifunctional core molecules were derived by the authors of this work.[21–23] One of the basic assumptions adopted by all of the works aforementioned is the equal molar concentrations of stimulus and monomer in SCVP. In fact, this is not a prerequisite for the SCVP, and special architecture can be formed if less stimulus is used. Experimental data showed that molecular parameters of the hyperbranched polymers made from SCVP are related to the feed ratio of stimulus to monomer.[13,15] Therefore, it is high time to develop a general model for the kinetics of SCVP with nonequal concentrations of stimulus and monomer.

Kinetic Analysis

Both self-condensing vinyl polymerization and self-condensing ring-opening polymerization involve in an AB-type monomer. The A group is a double bond or a heteroring, and B is a pendent group that can be transformed into an initiating center by an external stimulus. The activation of B groups by the stimulus was assumed to be completed instantaneously.[17–20] Then the AB monomer becomes the AB*-type inimer.[17] Inimer combines features of an initiator and a monomer. Chain initiation is the addition of active B* groups to double bonds of other inimers. In this way, the double bond A of the second monomer is converted into the σ bond with a fresh active center, A*. So the dimer formed has two active sites (A* and B*) and only one vinyl group. Both the initiating group B* and the newly created propagating center A* can react with the double bonds of other molecules including inimers, monomers, and polymeric species. Further polymerization results in hyperbranched polymers. As mentioned before, in previous work AB-type monomers were always assumed to be activated completely by an equal concentration of stimulus for the convenience of theoretical treatment. If the concentration of stimulus is less than that of the monomer, not only inimers but also monomers are present in the SCVP system after the activation of B groups, and both inimers and monomers can polymerize through double-bond addition. So the architecture of the resulting polymer depends on the stimulus to monomer ratio. The quantitative relationships between the stimulus to monomer ratio and various molecular parameters are seriously derived below.

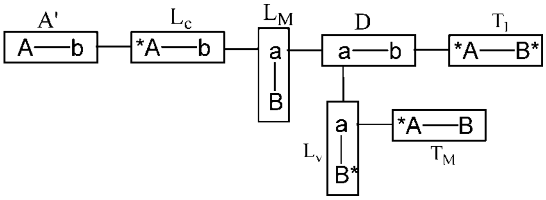

Figure 1. A typical example of branched heptamer.

Let M_0 be the initial concentration of AB monomer, S_0 the initial concentration of stimulus, and α (≤ 1) the molar ratio of stimulus to monomer. The activation reaction is assumed to complete instantaneously. Hence, at the beginning of polymerization, the concentration of AB* inimer is αM_0, and that of residual AB monomer is $(1 - \alpha)M_0$. The hyperbranched species formed in this reaction system is composed of both inimer units and monomer units. Figure 1 is a typical example of the

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branched heptamer obtained. Let $P_{n,m}$ denote the species consisting of n AB* inimer units and m AB monomer units. Obviously, there are n active centers (A* + B*) and only one vinyl group in $P_{n,m}$ species. The chemical equation for the formation of this species reads

$$P_{i+j} + P_{n-i,m-j} \rightarrow P_{n,m}$$

If the reactivities of various active sites are assumed to be identical and the intramolecular cyclization is absent, correspondingly, the set of kinetic differential equations describing the evolution of species are

$$\frac{\mathrm{d}P_{n,m}}{\mathrm{d}t} = \frac{k}{2}\sum_{i+j<m+n}[iP_{i,j}P_{n-i,m-j} + (n-i)P_{n-i,m-j}P_{i,j}] - k\left[nP_{n,m}\sum_{i,j}P_{i,j} + P_{n,m}\sum_{i,j}iP_{i,j}\right] \quad (1)$$

where k represents the reactivity between a double bond and one active site. The initial conditions are

$$P_{1,0t=0} = \alpha M_0; \quad P_{0,1t=0} = (1-\alpha)M_0; \quad P_{i,jt=0} = 0 \quad i+j>1 \quad (2)$$

The constraint condition yields

$$\sum_{n+m\geq 1} nP_{n,m} = \alpha M_0 \quad (3)$$

$$\sum_{n+m\geq 1} mP_{n,m} = (1-\alpha)M_0 \quad (4)$$

Since every molecule (inimer AB*, monomer AB, or polymeric species) has only one double bond, the conversion of double bonds is defined as

$$x = \frac{M_0 - \sum_{n+m\geq 1} P_{n,m}}{M_0} \quad (5)$$

The total concentration of molecules (or double bonds) in the reaction system is

$$A = \sum_{n+m\geq 1} P_{n,.m} = M_0(1-x) \quad (6)$$

Differentiating both sides of eq 6 leads to

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -M_0\frac{\mathrm{d}x}{\mathrm{d}t} \quad (7)$$

On the other hand, according to the kinetic mechanism, the consumption of double bonds fits:

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -kA(A^* + B^*) = -k\alpha M_0^2(1-x) \quad (8)$$

where A^* and B^* represents the concentration of the two active sites, respectively. The total concentration of active groups is αM_0, i.e.

$$\alpha M_0 = A^* + B^* \quad (9)$$

Comparing eq 7 with eq 8 yields

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k\alpha M_0(1-x) \quad (10)$$

Dividing eq 1 by eq 10 and substituting eqs 3 and 6 into it, we can obtain a set of linear differential equations with the new variable x:

$$\frac{\mathrm{d}P_{n,m}}{\mathrm{d}x} = \frac{n}{2\alpha M_0(1-x)}\sum_{i,j}P_{i,j}P_{n-i,m-j} - \left(\frac{n}{\alpha} + \frac{1}{1-x}\right)P_{n,m} \quad (11)$$

Equation 11 looks much simpler than eq 1, which can be solved rigorously (see Supporting Information).

Distribution Function and Molecular Parameters

The solution of eq 11 is the molecular size distribution function of the hyperbranched polymers formed in SCVP with nonequal feed ratio of stimulus to monomer:

$$P_{n,m} = \alpha M_0\frac{n^{n+m-1}}{n!m!}\left(\frac{1-\alpha}{\alpha}\right)^m(1-x)x^{n+m-1}\mathrm{e}^{-nx/\alpha} \quad (12)$$

Various molecular parameters of the resulting hyperbranched polymers can be calculated from eq 12. Generally, in experiment researchers usually added some termination agent into the SCVP system to deactivate the active sites by the end of the polymerization. After deactivation, we cannot discriminate whether the structural units come from inimer or monomer; i.e., the inimer units and the monomer units in the final products become the same. Therefore, we can define the number distribution function of the final hyperbranched polymers as

$$P_i = \sum_{n=0}^{i}P_{n,i-n} = \alpha M_0\frac{1-x}{x}\left(\frac{1-\alpha}{\alpha}x\right)^i\sum_{n=0}^{i}\frac{n^{i-1}}{n!(i-n)!}\left(\frac{\alpha}{1-\alpha}\mathrm{e}^{-x/\alpha}\right)^n \quad (13)$$

If $\alpha = 1$ ($n \equiv i$ for this case) eq 13 degenerates into the distribution function reported for SCVP with equal feed concentrations of stimulus and monomer (eq 10 in ref 17).

The zero and the first moments of P_i have been given in eq 6 and eqs 3 and 4, respectively:

$$\sum_{i>0}P_i = M_0(1-x) \quad (14)$$

$$\sum_{i>0}iP_i = M_0 \quad (15)$$

The second moment can be derived from eq 13 (see Supporting Information):

$$\sum_{i>0}i^2P_i = \frac{M_0(1-x^2+x^2/\alpha)}{(1-x)^2} \quad (16)$$

According to the definitions[21–23] of the normalized number-, weight- and Z-distributions, we find respectively

$$N(i) = \frac{P_i}{\sum_{i>0}P_i} = \frac{\alpha}{x}\left(\frac{1-\alpha}{\alpha}x\right)^i\sum_{n=0}^{i}\frac{n^{i-1}}{n!(i-n)!}\left(\frac{\alpha}{1-\alpha}\mathrm{e}^{-x/\alpha}\right)^n \quad (17)$$

$$W(i) = \frac{iP_i}{\sum_{i>0}iP_i} = \frac{i\alpha(1-x)}{x}\left(\frac{1-\alpha}{\alpha}x\right)^i\sum_{n=0}^{i}\frac{n^{i-1}}{n!(i-n)!}\left(\frac{\alpha}{1-\alpha}\mathrm{e}^{-x/\alpha}\right)^n \quad (18)$$

$$Z(i) = \frac{i^2P_i}{\sum_{i>0}i^2P_i} = \frac{i^2\alpha^2(1-x)^3}{x(\alpha+x^2-\alpha x^2)}\left(\frac{1-\alpha}{\alpha}x\right)^i\sum_{n=0}^{i}\frac{n^{i-1}}{n!(i-n)!}\left(\frac{\alpha}{1-\alpha}\mathrm{e}^{-x/\alpha}\right)^n \quad (19)$$

Figures 2a–c diagram the number-, weight- and Z-distribution at $x = 0.95$ and specify three values of stimulus to monomer ratios, $\alpha = 0.1$, 0.5, and 1.0, respectively. For the low stimulus to monomer ratio, there are only a few active sites in the SCVP system, which essentially grow into linear macromolecules, and all of number-, weight-, and Z-distributions have a maximum. Numerical calculation indicates that the location of maximum is related to the stimulus to monomer ratio and the double-bond conversion. For the high stimulus to monomer ratio, only the

Z-distribution shows a maximum and both number- and weight-distributions decrease monotonously with the degree of polymerization. At a higher value of x, the fraction of low molecular weight products decreases and the distribution curves drift toward the right. The results are contrary at a lower x, and, moreover, the peaks of the distribution curves will disappear.

In accordance with the definitions[21–23] of the number- and weight-average degrees of polymerization and the polydispersity index (PI), we get

$$\overline{P_n} = \frac{\sum_{i>0} iP_i}{\sum_{i>0} P_i} = \frac{1}{1-x} \tag{20}$$

$$\overline{P_w} = \frac{\sum_{i>0} i^2P_i}{\sum_{i>0} iP_i} = \frac{\alpha + x^2 - \alpha x^2}{\alpha(1-x)^2} \tag{21}$$

$$\mathrm{PI} = \frac{\overline{P_w}}{\overline{P_n}} = \frac{\alpha + x^2 - \alpha x^2}{\alpha(1-x)} \tag{22}$$

From the distribution function eq 12, it is easily to obtain the concentrations of residual inimers (I) and monomers (M) in the reaction system:

$$I = P_{1,0} = M_0\alpha(1-x)\mathrm{e}^{-x/\alpha} \tag{23}$$

$$M = P_{0,1} = M_0(1-\alpha)(1-x) \tag{24}$$

The concentration of macromolecules in the polymerization system is

$$A' = \sum_{i>1} P_i = M_0\alpha(1-x)(1-\mathrm{e}^{-x/\alpha}) \tag{25}$$

In experiment, the low molecular weight materials, such as residual monomers and inimers, are usually removed from the reaction system by reprecipitation, and the low molecular weight part of the products has an important effect on average degree of polymerization and polydispersity index. If the residual monomers and inimers are excluded from the system, the expressions of average degree of polymerization and polydispersity index should be improved by subtracting the monomer and inimer concentrations from both numerators and denominators of related equations:

$$\overline{P_n}' = \frac{\sum_{i>1} iP_i}{\sum_{i>1} P_i} = \frac{1-(1-x)(1-\alpha+\alpha\mathrm{e}^{-x/\alpha})}{\alpha(1-x)(1-\mathrm{e}^{-x/\alpha})} \tag{26}$$

$$\overline{P_w}' = \frac{\sum_{i>1} i^2P_i}{\sum_{i>1} iP_i} = \frac{\alpha + x^2 - \alpha x^2 - \alpha(1-x)^3(1-\alpha+\alpha\mathrm{e}^{-x/\alpha})}{\alpha(1-x)^2[1-(1-x)(1-\alpha+\alpha\mathrm{e}^{-x/\alpha})]} \tag{27}$$

$$\mathrm{PI}' = \frac{[\alpha + x^2 - \alpha x^2 - \alpha(1-x)^3(1-\alpha+\alpha\mathrm{e}^{-x/\alpha})](1-\mathrm{e}^{-x/\alpha})}{(1-x)[1-(1-x)(1-\alpha+\alpha\mathrm{e}^{-x/\alpha})]^2} \tag{28}$$

Figure 3 demonstrates the dependence of polydispersity index on the ratio of stimulus to monomer with the specified double-bond conversion, $x = 0.99$. The solid curve shows the variation of PI with α in the presence of residual monomers and inimers, and the dashed curve denotes the relationship between PI′ and α in the absence of residual monomers and inimers. Evidently, the influence of α on PI′ is much less than that on PI. On the contrary, the number-average degree of polymerization excluding the residual inimers and monomers is much larger than that including the low materials, as shown in Figure 4. $\overline{P_n}$ is independent of α and equals $1/(1-x)$ (see solid line), whereas $\overline{P_n}$ decreases with increasing α (dashed line), especially for low α value. Further calculation indicates that the effect of residual monomers and inimers on the weight-average degree of po-

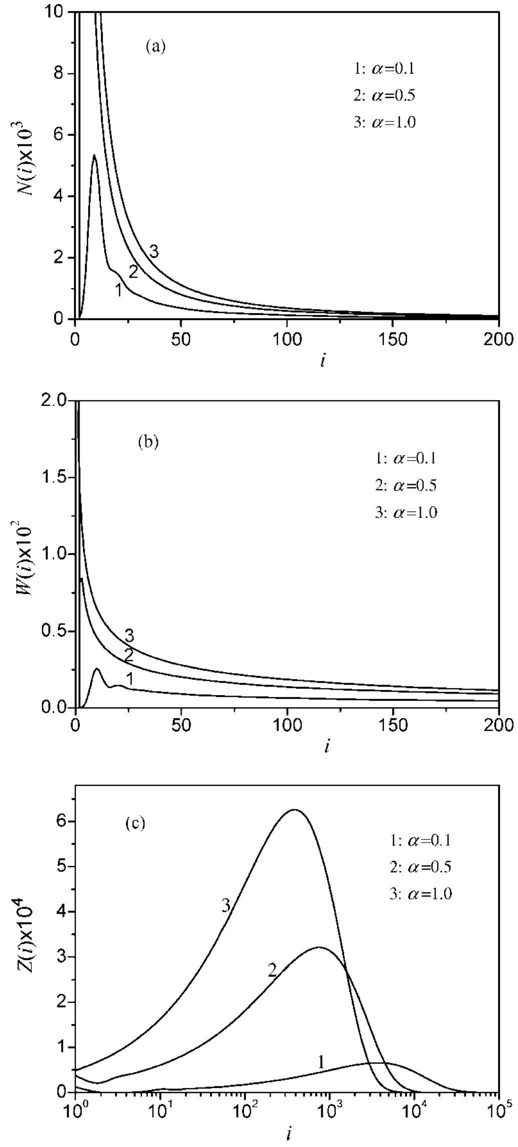

Figure 2. Distribution curves of hyperbranched polymer formed from general SCVP: (a) number-distribution; (b) weight-distribution; (c) *Z*-distribution. 1: α = 0.1; 2: α = 0.5; 3: α = 1.0.

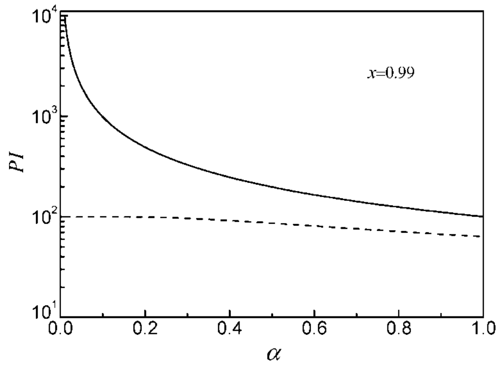

Figure 3. Dependence of polydispersity index on the ratio of activators/monomers at $x = 0.99$. Solid curve: including residual inimers and monomers; dashed curves: excluding residual inimers and monomers.

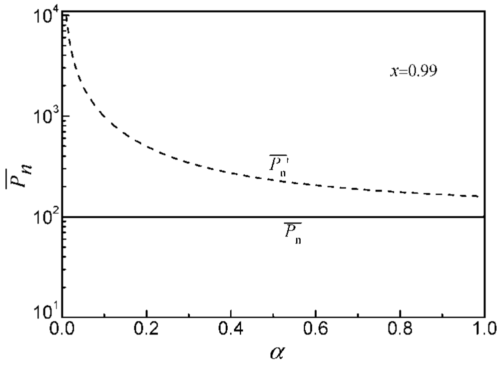

Figure 4. Dependence of number-average degree of polymerization on the ratio of activators/monomers at $x = 0.99$. Solid curve: including residual inimer and monomers; dashed curves: excluding residual inimers and monomers.

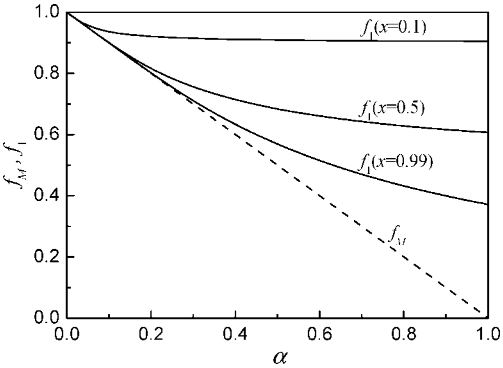

Figure 5. Dependence of the fractions of residual monomers and inimers on the ratio of activators/monomers. $f_M = M/A$; $f_I = P_1/A$.

lymerization is negligible at the same conversion of double bonds.

Similarly to the self-condensing vinyl copolymerization (SCVCP) of AB* inimer with a conventional vinyl monomer,[24,25] the inimers are consumed almost instantaneously at very low α, and it much like a fast initiation process in the normal living polymerization. However, the concentration of residual monomers always maintains a high level for very low α value. Figure 5 shows the relationship of the number fraction of residual monomers and inimers vs α. The total concentration of molecules in the reaction system is A, which equals $M_0(1 - x)$. The residual monomer fraction is defined as $f_M = M/A$ and that of both residual monomers and inimers as $f_I = P_1/A$. The solid curves represent the dependences of f_I on α at three specified double-bond conversions, $x = 0.1$, 0.5, and 0.99, and the dashed line denotes that of f_M on α, which is independent of x and equal to $(1 - \alpha)$. At low α value, the difference between f_M and f_I is very small because only a small amount of monomers are activated into inimers by the stimulus.

Degree of Branching

One of the advantages of the reaction system under consideration is tunable in degree of branching of the products. There are seven types of structural units incorporated in the polymeric species, as shown in Figure 1, which include initial units (A′), terminal units (T_I and T_M), linear units (L_c, L_v, and L_M), and dendritic units (D), respectively. Table 1 tabulates these units and their symbols. Units A′, T_I, L_c, L_v, and D come from inimers and units T_M and L_M from monomers. In order to calculate the degree of branching, it is necessary to know the number or concentration of these units and monomers.

Table 1. Various Structural Units in Polymeric Species and Residual Inimers and Monomers

structural unit	type of unit	symbol	remark
A−B*	residual inimer	I	
A−B	residual monomer	M	
A−b	initial unit	A′	can be regarded as a terminal unit
A*−B*	terminal inimer unit	T_I	
A*−B	terminal monomer unit	T_M	
A*−b	condensation type linear unit	L_c	
a−B*	vinyl type linear unit	L_v	
a−B	monomer type linear unit	L_M	
a−b	dendritic unit	D	

I, M, and A′ have been given by eqs 23–25, respectively. In accordance with the reaction mechanism, we can list the kinetic differential equations that describe the formation and consumption of various structural units and active centers (A* and B*), respectively.

$$\frac{dT_I}{dt} = kI(A^* + B^*) - 2kT_IA \tag{29}$$

$$\frac{dT_M}{dt} = kM(A^* + B^*) - kT_MA \tag{30}$$

$$\frac{dL_c}{dt} = kT_IA + k(A^* + B^*)A' - kL_cA \tag{31}$$

$$\frac{dL_v}{dt} = kA(T_I - L_v) \tag{32}$$

$$\frac{dL_M}{dt} = kT_MA \tag{33}$$

$$\frac{dD}{dt} = kA(L_c + L_v) \tag{34}$$

$$\frac{dA^*}{dt} = kAB^* \tag{35}$$

$$\frac{dB^*}{dt} = -kB^*A \tag{36}$$

Dividing these equations by eq 10, the variable can be transferred into double-bond conversion, x, from the reaction time, t. It is easy to solve these resulting equations and obtain the solutions, respectively.

$$T_I = M_0\alpha^2 e^{-x/\alpha}(1 - e^{-x/\alpha}) \tag{37}$$

$$T_M = M_0\alpha(1 - \alpha)(1 - e^{-x/\alpha}) \tag{38}$$

$$L_c = M_0\alpha^2(1 - e^{-x/\alpha})^2 \tag{39}$$

$$L_v = M_0\alpha e^{-x/\alpha}(x - \alpha + \alpha e^{-x/\alpha}) \tag{40}$$

$$L_M = M_0(1 - \alpha)(x - \alpha + \alpha e^{-x/\alpha}) \tag{41}$$

$$D = M_0\alpha(1 - e^{-x/\alpha})(x - \alpha + \alpha e^{-x/\alpha}) \tag{42}$$

$$A^* = M_0\alpha(1 - e^{-x/\alpha}) \tag{43}$$

$$B^* = M_0\alpha e^{-x/\alpha} \tag{44}$$

According to the definition,[26] the degree of branching of hyperbranched polymers formed from SCVP with nonequal concentrations of stimulus and monomer can be derived as follows:

$$\begin{aligned}\overline{\mathrm{DB}} &= \frac{D + T_I + T_M + A' - 2\sum_{i>1} P_i}{\sum_{i>1} iP_i - 2\sum_{i>1} P_i} \\ &= \frac{2(1 - e^{-x/\alpha})[x - \alpha(1 - e^{-x/\alpha})]}{1 + (1 - \alpha)x/\alpha - (1 - x)(2 - e^{-x/\alpha})}\end{aligned} \tag{45}$$

Let α = 1, eq 45 can be reduced as

$$\overline{\mathrm{DB}}|_{\alpha=1} = \frac{2(1-\mathrm{e}^{-x})(x-1+\mathrm{e}^{-x})}{1-(1-x)(2-\mathrm{e}^{-x})} \qquad (46)$$

It is just the degree of branching for the SCVP with equal concentrations of stimulus and monomer.[18] After variable transformation, eq 45 is conformed to that reported by Müller et al. for the self-condensing vinyl copolymerization.[24]

According to eq 45, the degree of branching of hyperbranched polymers formed from SCVP can be controlled by adjusting the feed concentration of stimulus. Figure 6 shows the dependence of $\overline{\mathrm{DB}}$ on α at four specified double-bond conversions, $x = 0.1$, 0.4, 0.7, and 1. For any specified double-bond conversion, $\overline{\mathrm{DB}}$ increases with increasing α initially, and after a maximum, it decreases slightly. The maximum and their location can be obtained by solving equation $\partial\overline{\mathrm{DB}}/\partial\alpha = 0$. For example, when the reaction approaches to completion ($x = 1$), we have

$$\overline{\mathrm{DB}}_{\infty} = 2\alpha(1-\mathrm{e}^{-1/\alpha})[1-\alpha(1-\mathrm{e}^{-1/\alpha})] \qquad (47)$$

Its maximum is 0.5 at $\alpha \approx 0.627$. The higher the double-bond conversion, the larger the maximum. So 0.5 is the highest one of the degree of branching for SCVP.

Conclusions and Discussion

For the SCVP with stimulus/monomer <1, the monomer molecules were activated partly by the stimulus. In this case, both AB monomers and AB* inimers are present in the reaction system. According to the kinetic theory developed in this work, the feed ratio of stimulus to monomer considerably affects the molecular parameters of the resulting hyperbranched polymers. For low ratio of stimulus/monomer, number-, weight-, and *Z*-distributions all show maxima and reach minimums at $i = 2$. However, for high ratio of stimulus/monomer, *Z*-distribution appears a maximum only. The fraction of residual monomers and inimers always maintains high even though at a high double-bond conversion. If the residual inimers and monomers are excluded, at any specified double-bond conversion, the number-average degree of polymerization decreases with increasing α, especially for low α value, whereas the polydispersity index only shows a modest variation. The degree of branching shows a maximum with the variation of α. The higher the double-bond conversion is, the larger the maximum, and the largest value of degree of branching can reach 0.5 at $x = 1$ and $\alpha \approx 0.627$, which is a little higher than that for homo-SCVP (0.465).[18]

The kinetics of general SCVP is applicable for the self-condensing vinyl copolymerization. In comparison with the copolycondensation of AB- and AB_2-type monomers,[26] with the increase of α values, the appearance of maximum for $\overline{\mathrm{DB}}$ is the characteristic of general SCVP. The $\overline{\mathrm{DB}}$ keeps to monotonously increase with increasing fraction of AB_2 monomers in the copolycondensation of AB- and AB_2-type monomers.

The general model of SCVP developed in this work is of great significance to practical applications. Experimentally, Frèchet et al.[27] reported that a high catalyst to monomer ratio favors the formation of a branched structure in the SCVP of [4-(chloromethyl)styrene]. A series of hyperbranched poly[3-ethyl-3-(hydroxymethyl)oxetane]s and poly(3-methyl-3-oxetanemethanol)s with various degree of branching have been synthesized by adjusting the feed ratio of catalyst to monomer in our laboratory.[13,15] Therefore, the architecture of the resulting polymer is tunable through the ratio of stimulus to monomer, and experimental data are in accordance with the theoretical expectation. Except for the feed ratio of catalyst to monomer, however, experimental results are dependent on the other reaction conditions as well, such as temperature and reactivities ratio. Recently, we have set about the quantitative investigations on the relationship between the degree of branching and the ratio of stimulus to monomer experimentally and expect a quantitative comparison of theory with experiments in the subsequent paper.

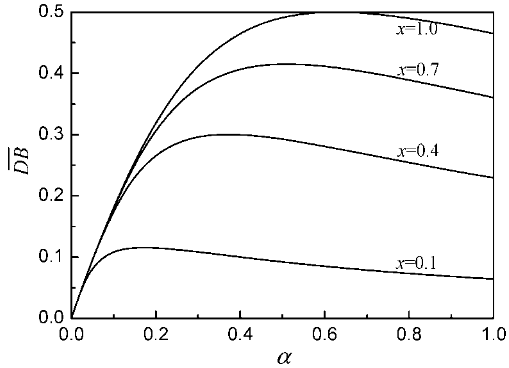

Figure 6. Dependence of the average degree of branching on the ratio of activators/monomers at specified x values, 0.1, 0.4, 0.7, and 1.

The theoretical investigations in this work are based on the assumption of the equal reactivities of all active sites and absence of intramolecular cyclization. Taking account of the intramolecular cyclization, Frey et al.[28] and Dusek et al.[29] have made an improvement in theory for AB_g-type polycondensation. In a previous work,[30] we derived an analytic expression of distribution function for AB_2-type polycondensation with nonequal reactivities. Turning to the case of SCVP, it is clear that different reactivities of the two types of active sites (A* and B*) will have a strong effect on molecular parameters of the resulting hyperbranched polymers. Müller et al.[17,18] derived the analytic expression for the degree of branching of SCVP with nonequal reactivities and carried out the numeral calculations for the polydispersity index. The Monte Carlo method has been applied to simulate this case by Pan et al.[31,32] Using the generating function, Cheng et al.[33,34] evaluated the influence of trifunctional cores and nonequal reactivities on various molecular parameters of hyperbranched polymers. However, it is too tedious to derive the analytic molecular weight distribution function for SCVP with nonequal reactivities due to the complexity of the kinetic differential equations. Anyway, it seems clear that in an accounting for nonequal reactivities in the SCVP scheme would involve significant work.

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Supporting Information Available: Text giving derivations of eqs 12 and 16. This material is available free of charge via the Internet at http://pubs.acs.org.

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