Model of Hyperbranched Polymerization Involving AB_2 Monomer and B_3 Core Molecules both Reacting with Substitution Effect

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ABSTRACT: A kinetic model of hyperbranched polymerization is presented where an AB_2 monomer reacts with up to 10% of a B_3 one (A and B are functional groups) to yield a hyperbranched polymer. The model consists of two compact rate equations for entire distributions of two kinds of molecules that are formed in the system. Changes in reactivity of B groups in the form of the so-called *first shell substitution effect* are taken into account. Molecular parameters, namely the number and weight averages of polymerization degree as well as the average degree of branching of hyperbranched molecules, are extracted out from the rate equations and plotted against conversion.

Introduction

The hyperbranched polymer are obtained in a one-step synthesis from multifunctional monomers of general formula AB_f (see also ref 1) where A and B stand for functional groups reacting with each other. The polymers consisting of highly branched molecules are reported to have interesting properties as consisting of compact molecules containing numerous functional groups that can easily be modified.[2] However, as follows from the early works of Flory,[3] as well as from studies by Ziff[4] and more recent papers,[5−10] the size distribution of hyperbranched polymers is prohibitively broad when obtained directly from the monomer in one step. This is because the number of functional groups in hyperbranched polymers is roughly proportional to their polymerization degree, and hence, big molecules react faster than small ones. In particular, polydispersity of hyperbranched molecules rapidly increases as the conversion of minority groups (A groups) approaches unity.

The polydispersity of hyperbranched molecules can be reduced by introducing a multifunctional monomer, preferably having the same B groups as AB_f monomer,[11−13] or by applying a multifunctional initiator in the case of chain reactions.[14] Another trick is to apply a multifunctional monomer and gradually add the AB_f monomer to the polymerization vessel.[15,16]

Several theoretical descriptions of the systems consisting of $AB_f + B_g$ monomers have already been published.[11−16] Yan and Zhou[11] and Radke et al.[13] presented appropriate kinetic analyses, whereas Hanselmann et al.[16] performed Monte Carlo simulations in order to assess the effect of the presence of multifunctional monomers on the molecular parameters of the system, namely, the polymerization degree and polydispersity index in the system. In all these works, all reactions in the system were considered equally probable; i.e., any reaction between groups A and B had the same rate constant or probability of occurring.

In this work, we present an alternative analysis of the system where monomer AB_2 reacts with B_3 core-forming molecules. Additionally, we take into account changes of reactivity of B groups in both kinds of molecules. The changes are due to the so-called first shell substitution effect. In other words, in AB_2 molecules both B groups have the same reactivity, but as the first group reacts, the second B group may have different one. The same applies to the reactivity of B groups in B_3 monomer. Initially, all three groups have the same reactivity. The reactivity changes as the first reacts (and then it is equal to the reactivity of B groups in AB_2 monomer). It may then change again, when the second group reacts. Hence, three different rate constants are taken into account describing the reactivity of groups B in B_3, $-B_2$, or AB_2, and in $>-B$ or $-AB$ units, respectively.

Theory

Consider a system where functional groups A in an AB_2 monomer react with groups B. Some B_3 monomer is also present in the system with identical B groups as in AB_2. Monomer B_3 plays the role of a core of hyperbranched molecules, and the system is referred to as the hyperbranched polymerization with core molecules.

Unlike in our previous papers,[10] we will consider just branched molecules and disregard the presence of cycle-containing molecules. Systems with intramolecular linking will be the subject of a forthcoming paper. In our models of AB_2 polymerization, the fraction of cycle-containing molecules turned out to be rather small except in the vicinity of full monomer conversion.

Two types of molecules are present in the ideal $AB_2 + B_3$ system. There are the “reactive” molecules, each containing one A group, and the “inactive” molecules that do not bear an A group. The reactive molecules may react with both reactive and inactive ones, whereas the inactive molecules react via their B groups only with an A group of a reactive one. In fact the terms “reactive” and “inactive” serve rather as labels to distinguish the two kinds of molecules and do not refer to their actual reactivity.

The structure of an individual molecule is coded with just two parameters. Thus, an m,n-mer is a molecule containing m terminal units, i.e., the units with two B groups still unreacted, and n linear units, i.e., units with one B group unreacted. An AB_2 monomer molecule is a special terminal molecule. B_3 monomer molecules are

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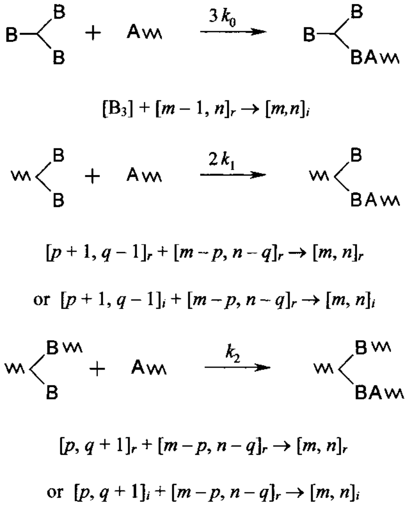
considered separately. The number of branch units, i.e., the units with all B groups reacted (including the linear units with A group unreacted, if present) is simply $m - 1$ for reactive and $m - 2$ for inactive molecule, respectively.

Certainly, in the reacting system there are many structural isomers that share the same set of m and n values. The concentration of an m,n-mer, $[m,n]_r$ or $[m,n]_i$, is expressed as the number of (moles of) molecules of the same kind (**r**eactive or **i**nactive) that share their m and n values, divided by the total number of (moles of) units. At the start of polymerization we have $[1,0]_r + [B_3] = 1$; i.e., concentrations of monomers sum up to unity.

B groups react with the first shall substitution effect defined as in the paper by Gordon and Scantlebury.[17] Thus, all groups B in a unit have the same reactivity until one of the groups has reacted. Then the remaining B group(s) may have different reactivities. This is illustrated in the following scheme where all elementary reactions are presented.



$[B_3] + [m-1,n]_r \rightarrow [m,n]_i$

$[p+1,q-1]_r + [m-p,n-q]_r \rightarrow [m,n]_r$

or $[p+1,q-1]_i + [m-p,n-q]_r \rightarrow [m,n]_i$

$[p,q+1]_r + [m-p,n-q]_r \rightarrow [m,n]_r$

or $[p,q+1]_i + [m-p,n-q]_r \rightarrow [m,n]_i$

The component molecules that combine to form an m,n-mer are shown below each elementary reaction scheme. The elementary reactions are second-order reactions. The rate of reaction between a B group in a terminal unit of a reactive p,q-mer and A group of an u,v-mer is assumed to be

$$2k_1 p[p,q]_r[u,v]_r \tag{1}$$

It is convenient to define the relative rate constants

$$\alpha = \frac{2k_1}{3k_0}; \quad \beta = \frac{k_2}{3k_0} \tag{2}$$

and rescale the time units according to $\tau = 3k_0t$. In this new time units, the monomer B_3 reacts with rate 1 and the rate constant in front of eq 1 is α. Note that in the random case, i.e., in the absence of any substitution effect, $\alpha = {}^2/_3$ and $\beta = {}^1/_3$.

Now, it is just a matter of algebra to write down all terms describing the rate at which m,n-mers appear in, and disappear from, the system both for the reactive and inactive molecules. The resulting rate equations are multiplied by $(\alpha x)^m(\beta y)^n$ for each m,n-mer and summed up over all m's and n's. The variables x and y are dummy quantities that have no physical meaning and are used to facilitate mathematical manipulations. The procedure yields the following master Smoluchowski-like rate equations:

$$\frac{\partial H}{\partial \tau} = \left[(\beta y)\frac{\partial H}{\partial x} + \frac{\partial H}{\partial y}\right]H - \left[(\alpha x)\frac{\partial H}{\partial x} + (\beta y)\frac{\partial H}{\partial y}\right]H_1 - (H_x + H_y + G_0 + G_x + G_y)H \tag{3}$$

$$\frac{\partial G}{\partial \tau} = \left[(\alpha x)G_0 + (\beta y)\frac{\partial G}{\partial x} + \frac{\partial G}{\partial y}\right]H - \left[G_0 + (\alpha x)\frac{\partial G}{\partial x} + (\beta y)\frac{\partial G}{\partial y}\right]H_1 \tag{4}$$

for the functions

$$H(\tau,x,y) = \sum_{m=1}^{\infty}\sum_{n=0}^{\infty}[m,n]_r(\alpha x)^m(\beta y)^n \tag{5}$$

$$G(\tau,x,y) = G_0(\tau) + \sum_{m=2}^{\infty}\sum_{n=0}^{\infty}[m,n]_i(\alpha x)^m(\beta y)^n \tag{6}$$

The functions H and G carry all information on the size distribution of reactive and inactive molecules, respectively. The remaining symbols in eqs 3 and 4 are all functions derived from H and G, thus

$$H_1 = H_1(\tau) \equiv H(\tau,1/\alpha,1/\beta) \tag{7}$$

$$H_\xi = H_\xi(\tau) \equiv \left.\frac{\partial H}{\partial \xi}\right|_{x=1/\alpha,y=1/\beta}; \quad \xi = x,y \tag{8}$$

Similarly,

$$G_\xi = G_\xi(\tau) \equiv \left.\frac{\partial G}{\partial \xi}\right|_{x=1/\alpha,y=1/\beta}; \quad \xi = x,y \tag{9}$$

and, finally

$$G_0 = G_0(\tau) \equiv [B_3] \tag{10}$$

The master equations, eqs 3 and 4, can be used to follow changes of size distribution in polymerizing systems at different initial mole fractions of AB_2 and B_3. In particular, the moments of distribution and the average degrees of polymerization are available after solving a few ordinary differential equations obtained by elementary manipulation with eqs 3 and 4. Thus, H_1 is obtained after solving ordinary differential equation obtained from eq 3 by setting $x = 1/\alpha$ and $y = 1/\beta$. The functions H_ξ or G_ξ ($\xi = x$ or y) are obtained by differentiating (3) or (4), respectively, with respect to ξ followed again by setting $x = 1/\alpha$ and $y = 1/\beta$. G_0 can similarly be obtained after solving the differential equation obtained from (4) by introducing $x = y = 0$. Further differentiation of (3) or (4) with respect to ξ followed by setting $x = 1/\alpha$ and $y = 1/\beta$ provides ordinary differential equations for functions H_{xx}, H_{xy}, etc. All differential equations sufficient to calculate the weight- and number-average degrees of polymerization are presented in the Appendix.

The moments of distribution are defined thus

$$M_{k,r} = \sum_{m=1}^{\infty}\sum_{n=0}^{\infty}(2m + n - 1)^k[m,n]_r \tag{11}$$

and

$$M_{k,i} = G_0 + \sum_{m=2}^{\infty}\sum_{n=0}^{\infty}(2m + n - 2)^k[m,n]_i \qquad (12)$$

The terms in parentheses are the degrees of polymerization of m,n-mers. Note that the zeroth moment of distribution of "inactive" molecules, $M_{0,i}$, i.e., the total number of inactive molecules, remains constant and, as follows from the definition of concentration, equals to the initial mole fraction of monomer B_3 [$=G_0(0)$] times the total number of all units. This is because each inactive molecule contains exactly one unit originating from B_3 monomer.

The number-average degree of polymerization in the whole system is calculated as the total number of units in the system divided by the total number of molecules; thus

$$P_{\mathrm{n}} = \frac{1}{H_1 + G_0(0)} \qquad (13)$$

One can also consider the partial number-average polymerization degrees for the reactive and inactive polymer molecules. These are

$$P_{\mathrm{n,r}} = \frac{M_{1,\mathrm{r}}}{M_{0,\mathrm{r}}} = \frac{2H_x}{\alpha H_1} + \frac{H_y}{\beta H_1} - 1 \qquad (14)$$

and

$$P_{\mathrm{n},i} = \frac{M_{1,i}}{G_0(0)} = \frac{1}{G_0(0)}(3G_0(\tau) + 2G_x/\alpha + G_y/\beta) - 2 \qquad (15)$$

respectively.

The weight-average degree of polymerization is the ratio of the second and first moments of distribution. Since the terms in moment equations can be expressed by successive derivatives of H and G with respect to dummy variables calculated at $x = 1/\alpha$ and $y = 1/\beta$, for example

$$\sum_{m}^{\infty}\sum_{n}^{\infty} m^2[m,n]_{\mathrm{r}} = H_{xx}/\alpha^2 + H_x/\alpha \qquad (16)$$

the second derivatives of H and G, available in the form of ordinary differential equations are required (see Appendix).

Here again we express the global weight-average polymerization degree for the whole system and separately for the reactive and inactive molecules. For the latter case, the respective moment equations are

$$M_{2,\mathrm{r}} = 4H_{xx}/\alpha^2 + 4H_{xy}/\alpha\beta + H_{yy}/\beta^2 - H_y/\beta + H_1 \qquad (17)$$

$$M_{2,i} = 4G_0(0) + 4G_{xx}/\alpha^2 + 4G_{xy}/\alpha\beta + G_{yy}/\beta^2 - 4G_x/\alpha - 3G_y/\beta - 3G_0 \qquad (18)$$

The global weight-average polymerization degree is simply the sum of the two quantities, whereas the partial averages are obtained by dividing the second moments by the respective first moments.

The results of modeling at different input parameters ($G_0(0)$, α, β) are conveniently compared by plotting molecular parameters of the system vs the extent of reaction. We adopt the conversion degree of A groups as a measure of the extent. The number of A groups that have not yet reacted is equal to the number of active molecules. Thus, the conversion degree of groups A is

$$p = 1 - \frac{H_1}{H_1(0)} \qquad (19)$$

The entire distribution can be obtained by solving the set of rate equations for every m,n-mer. In the appropriate rate equations at most the first derivatives of H and G appear.

Results and Discussion

In this report, we limit ourselves to the system where a B_3 monomer (core) is added to an AB_2 monomer and the polymerization is carried out in one batch. A system where AB_2 monomer is added gradually[15,16] is left to a forthcoming paper.

As already known,[11-13] the presence of core molecules in the reacting system reduces both the average polymerization degree and polydispersity of the resulting polymer product.

The influence of changes in reactivity of groups due to substitution effect on the molecular parameters of the system is presented in Figure 1. B groups in the model systems react with (rather strong) positive substitution effect, strong negative substitution effect or without any change in reactivity (random system). In the system reacting with positive substitution effect, the rate constant at which B group on a terminal unit reacts is 10 times larger than that of a B group on B_3 monomer. Furthermore, a B group on a linear unit reacts 10 times faster than that on a terminal unit ($k_0 = 1$; $k_1 = 10$; $k_2 = 100$). In the system reacting with negative substitution effect, the rate constants at which B groups react reduces by a factor of 10 on passing from B_3 monomer to the terminal and again 10 times on passing from the terminal to linear unit ($k_0 = 1$; $k_1 = 0.1$; $k_2 = 0.01$).

It is interesting to notice that for the system reacting with positive substitution effect, the presence of core molecule affects the molecular parameters of the system very little. The reduction of polydispersity is much better pronounced for the random system or for the system reacting with negative substitution effect as the fraction of core molecules increases from 0 through 0.05 to 0.1.

The degree of branching in hyperbranched polymers can be characterized by using a single quantity, e.g., a parameter proposed by Frey's group.[18] The Frey's degree of branching is a quantity relatively easy to measure. It helps to locate a product structure on the branching scale. The branching index is zero for linear polymers and assumes unity for ideal dendrimers. It is defined as the ratio of twice the number of branching units divided by the same plus the number of linear units. Twice the number of branching units is, for reactive molecules, the same as the number of terminal units plus the number of branching units minus one. In terms of quantities used in this work the degree of branching (DB) expresses as

$$DB_{\mathrm{Frey}} = \frac{\left(\frac{H_x}{\alpha} - H_1\right)M_{1,\mathrm{r}} + \left[\frac{G_x}{\alpha} + 2(G_0 - G_0(0))\right]M_{1,i}}{\left(\frac{H_x}{\alpha} + \frac{H_y}{2\beta} - H_1\right)M_{1,\mathrm{r}} + \left[\frac{G_x}{\alpha} + \frac{G_y}{2\beta} + 2(G_0 - G_0(0))\right]M_{1,i}} \qquad (20)$$

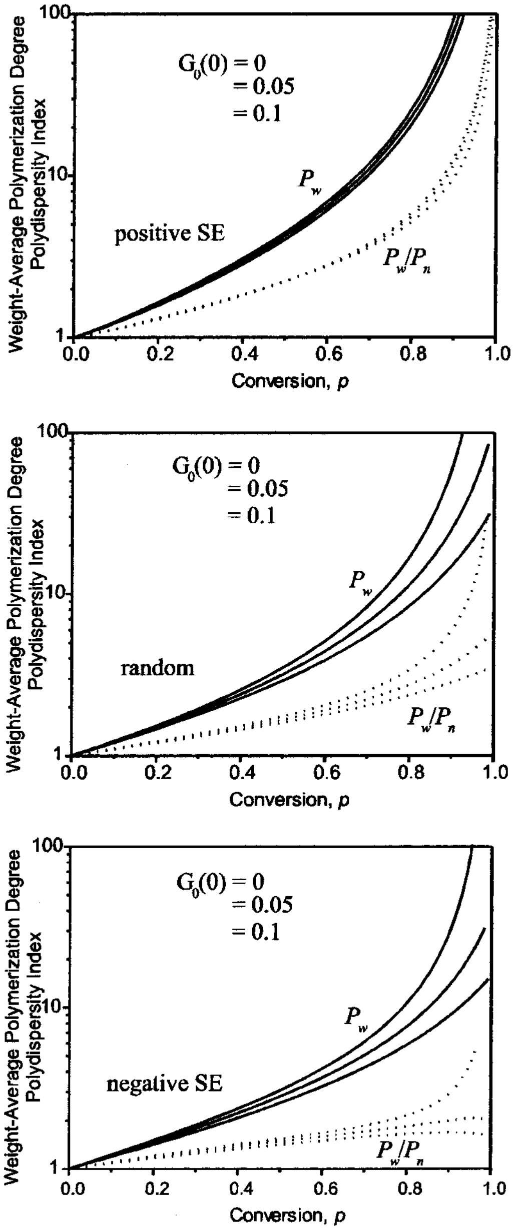


Figure 1. Effect of the presence of B_3 core molecules on the weight-average polymerization degree and polydispersity index for systems containing AB_2 monomer reacting with different substitution effects (see text for definition of the effect). The top curves in each series correspond to the system without B_3 monomer, $G_0(0) = 0$, and the bottom to the initial mole fraction of B_3, $G_0(0) = 0.1$.

The dependence of Frey's degree of branching on conversion of A groups is shown in Figure 2 for three initial mole fractions of the core monomer. It can be seen that for the positive substitution effect ($k_0 = 1$; $k_1 = 10$; $k_2 = 100$), DB practically does not depend on the fraction of core monomer in the system. In the random system or in the system reacting with the negative substitution effect ($k_0 = 1$; $k_1 = 0.1$; $k_2 = 0.01$) the degree of branching decreases with increasing amount of B_3 core monomer.

In conclusion, one may state that the presence of core-forming multifunctional monomer reduces both the average polymerization degree and polydispersity index of hyperbranched polymers. Similar modification of size distribution can also be achieved by selecting AB_2 monomers reacting with a negative substitution effect. Obviously, the latter method of modification might not be easy to perform.

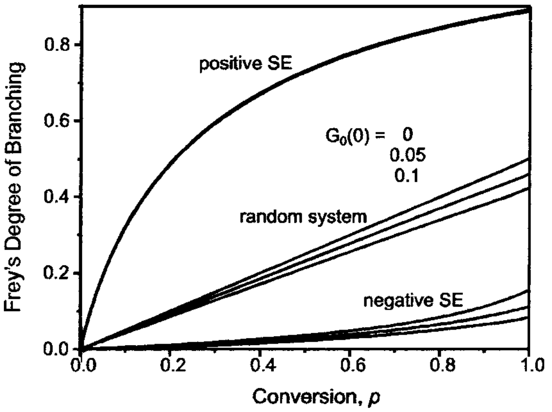


Figure 2. Average Frey's degree of branching vs conversion of A groups in hyperbranched molecules obtained by polymerization of AB_2 monomer in the presence of B_3 core molecules. The top curves in each series correspond to the system without B_3 monomer, $G_0(0) = 0$, and the bottom to the initial mole fraction of B_3, $G_0(0) = 0.1$.

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Appendix

The set of ordinary differential equations obtained from (3) and (4) needed to calculate moments of distribution reads as follows:

$$\dot{H}_1 = -(H_x + H_y + G_0 + G_x + G_y)H_1 \tag{A1}$$

$$\dot{H}_x = -\alpha H_x H_1 - (G_0 + G_x + G_y)H_x \tag{A2}$$

$$\dot{H}_y = -\beta(H_y - H_x) - (G_0 + G_x + G_y)H_y \tag{A3}$$

$$\dot{G}_0 = -G_0 H_1 \tag{A4}$$

$$\dot{G}_x = -\alpha(G_x - G_0)H_1 + (G_0 + G_x + G_y)H_x \tag{A5}$$

$$\dot{G}_y = -\beta(G_y - G_x)H_1 + (G_0 + G_x + G_y)H_y \tag{A6}$$

$$\dot{H}_{xx} = 2(H_{xx} + H_{xy})H_x - 2\alpha H_{xx}H_1 - (G_0 + G_x + G_y)H_{xx} \tag{A7}$$

$$\dot{H}_{xy} = [\beta(H_{xx} - H_{xy}) - \alpha H_{xy}]H_1 + (\beta H_x + H_{xy} + H_{yy})H_x + (H_{xx} + H_{xy})H_y - (G_0 + G_x + G_y)H_{xy} \tag{A8}$$

$$\dot{H}_{yy} = 2\beta(H_{xy} - H_{yy})H_1 + 2(\beta H_x + H_{xy} + H_{yy})H_y - (G_0 + G_x + G_y)H_{yy} \tag{A9}$$

$$\dot{G}_{xx} = -2\alpha G_{xx}H_1 + 2(\alpha G_0 + G_{xx} + G_{xy})H_x + (G_0 + G_x + G_y)H_{xx} \tag{A10}$$

$$\dot{G}_{xy} = [\beta(G_{xx} - G_{xy}) - \alpha G_{xy}]H_1 + (\beta G_x + G_{xy} + G_{yy})H_x + (\alpha G_0 + G_{xx} + G_{xy})H_y + (G_0 + G_x + G_y)H_{xy} \tag{A11}$$

$$\dot{G}_{yy} = 2\beta(G_{xy} - G_{yy})H_1 + 2(\beta G_x + G_{xy} + G_{yy})H_y + (G_0 + G_x + G_y)H_{yy} \tag{A12}$$

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