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Kinetic Modeling of Hyperbranched Polymerization Involving an AB2 Monomer Reacting with Substitution Effect

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ABSTRACT: A model is developed in the form of one or two partial differential equations (master Smoluchowski-like equations) that describe evolution of the size distribution of polymer species formed in a step-growth polymerization of an AB_2 monomer. Groups B react with a substitution effect; i.e., they are initially equally reactive, but the reactivity of the second B group changes as the first has reacted. One master equation is sufficient to model formation of branched molecules only. Two are needed to take into account intramolecular cyclization. Monte Carlo simulations of the same process are used to verify the results of applying the kinetic model. The model can be applied to calculate various molecular parameters in polymerizing systems, including various average degrees of polymerization, size distribution of acyclic and cycle-containing polymer molecules, degree of branching, etc. Explicit formulas describing the dependence of some of these quantities on time or conversion degree are derived for the random system, i.e., the system reacting without substitution effect.

Introduction

Hyperbranched polymerization is a process that leads to highly branched (dendritic) polymers in essentially one pot reaction system. The interest in hyperbranched polymerization and in its products significantly increased in the past decade following the considerable attention focused on the perfectly branched dendrimers. Reviews on the subject have already been published[1,2] where the types of monomers and techniques of polymerization applied so far are discussed. The one pot technique is advantageous compared to the laborious multistage synthesis of dendrimers, but the hyperbranched polymerization yields usually very polydisperse products in terms of both molecular weight and topology of macromolecules. The principles of hyperbranched polymerization are known since the pioneering works of Flory.[3] He presented a statistical analysis of the size distribution in condensation polymerization of an AB_2 type monomer. A and B are the functional groups that react with each other. Ziff[4] was the first to present an alternative kinetic analysis of the same process. His approach was based on the Smoluchowski coagulation equation.[5] Later, the kinetic description of the polymerization of an AB_f monomer ($f > 2$) was shown[6] to be mathematically equivalent to that of network homopolymerization of an A_f monomer, i.e., to the classical network polymerization of the Flory−Stockmayer type.

More recently, several authors modeled the hyperbranched polymerization in relation to certain real systems.[7−19] All the models were based on the classical assumptions and had a form of either analytical equations or numerical simulations. Accordingly, all reactions were considered ideal with no interference of physical nature such as changes in viscosity, volume contraction, or local variation of temperature. In particular, single rate constants or the same probabilities of reaction were usually applied for all types of elementary polymerization steps. In all cases, but a few[7,20] intramolecular reactions that led to cycle formation were disregarded. The molecular parameters sought for in the modeling were those characterizing the size distribution in the polymerizing systems as well as the average degree of branching of the molecules. The systems analyzed were the polymerization of AB_f monomer by stepwise[7,11,14,18] or self-condensing vinyl reaction.[8,9,12] The models were also used to demonstrate how the presence of "core-forming" molecules (extra B_f -type monomers) or the slow monomer addition techniques resulted in narrowing the molecular weight distribution of hyperbranched molecules.[10,12−14,16]

In this paper, we present an alternative model of condensation polymerization of an AB_2 monomer. The model is a classical-type kinetic one that makes it possible to take into account rigorously different reactivities of functional groups (more strictly, the differences due to substitution effect) and, in approximate way, the possibility of closing intramolecular cycles. Calculations based on the analytical derivations are compared with results of Monte Carlo simulations developed to model the same types of reactions.

The Models

System without Intramolecular Linking. From the point of view of reactivity of functional groups, the structure of hyperbranched molecules is conveniently coded with two parameters. Thus, let i be the number of units with both groups B unreacted (terminal unit) and j be the number of units with one reacted, and one unreacted, B group (linear unit). Hence, an i,j-mer is a molecule with i terminal units and j units in the linear parts of the molecule. The monomer, $[1,0]_b$ is a special molecule with just one terminal unit ("b" means that monomer is a treelike branched molecule). The two parameters are sufficient to characterize the size of molecules, since isomers of any connectivity of a treelike i,j-mer have necessarily the polymerization degree, $n = 2i + j - 1$ (the number of branching units, i.e., those with all groups reacted, is exactly $i - 1$). An i,j-mer

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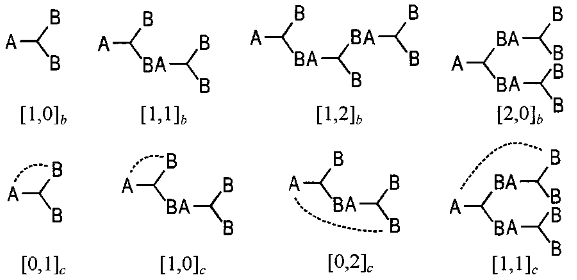
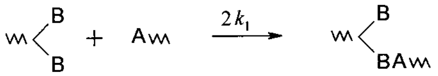
Scheme 1. Examples of AB$_2$ Polymer Hyperbranched Molecules, Both Acyclic (subscript *b*) and Cycle-Containing Ones (Subscript *c*), along with Codes Describing Their Structure



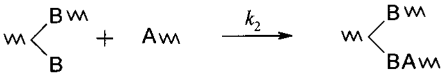
containing cycle has the polymerization degree $n = 2i + j$; the molecule may have only one cycle (intramolecular link) and does not contain an A group, anymore. Examples of AB$_2$ polymer molecules along with their respective codes are shown in Scheme 1.

The symbol $[i,j]_b$ (or $[i,j]_c$ for the cycle-containing species) is used to identify the molecules as in Scheme 1 and also stands for the concentration of an *i,j*-mer, expressed as the number of all isomers sharing the same code divided by the number of units in the whole system. The double meaning of the same notation should not, however, lead to confusion. The concentrations are used only in rate equations. In the rate equations the subscripts "b" or "c" are omitted in places where the type of reacting species is irrelevant.

Two elementary reactions of growth are considered in the system (∿ stands for a part of the molecule):



$$[i-p+1,j-q-1] + [p,q]_b \rightarrow [i,j]$$



$$[i-p,j-q+1] + [p,q]_b \rightarrow [i,j]$$

The constants k_1 and k_2 describe the rates of reaction of groups B with group A in terminal and linear units, respectively. The symbols under the reactions show the component molecules that combine to form an *i,j*-mer.

In this analysis, we limit ourselves to symmetric AB$_2$ monomers, i.e., to monomers with both B groups in terminal units equally reactive. The groups, however, react with the substitution effect.[21] It means that the reactivity of B group in a linear unit may be different than that in terminal ones. Protons of primary amino group provide a good example of the idea.

The general formula describing the rate at which *i,j*-mers disappear from the system in reactions with other molecules reads:

$$-(2ik_1 + k_2j)[i,j]\sum_{p=1}^{\infty}\sum_{q=0}^{\infty}[p,q]_b - [i,j]_b\sum_{p=1}^{\infty}\sum_{q=0}^{\infty}(2k_1p + k_2q)[p,q] \quad (1)$$

Equation 1 has four terms. The first two are the rates at which B groups on a terminal or linear *i,j*-mer, respectively, react with an A group on any other molecule $[p,q]$. The next two terms are the rates at which an A group of an *i,j*-mer reacts with terminal or linear groups in any other molecule in the system.

It is convenient to define the relative rate constant $\alpha \equiv k_2/2k_1$. For the random reaction (no change of reactivity of B groups) $\alpha = {}^1/_2$. Then eq 1 can be rewritten in the form

$$\left.\frac{d[i,j]_b}{d(2k_1t)}\right|_{\text{disapp}} = -(i + \alpha j)[i,j]_b\sum_{p,q}[p,q]_b - [i,j]_b\sum_{p,q}(p + \alpha q)[p,q] \quad (2)$$

with the abbreviation: $\sum_{p,q} \equiv \sum_{p=1}^{\infty}\sum_{q=0}^{\infty}$.

The general equation describing the rate at which an *i,j*-mer is formed from matching components is derived in the same way by referring to the equations in Scheme 1. It reads

$$\left.\frac{d[i,j]_b}{d(2k_1t)}\right|_{\text{app}} = \sum_{p}^{i-1}\sum_{q}^{j-1}\{(i-p+1)[i-p+1,j-p-1] \times [p,q]_b + \alpha(j-q+1)[i-p,j-q+1][p,q]_b\} \quad (3)$$

The rate at which *i,j*-mers appear and disappear from reacting system is now the sum of eqs 2 and 3. Note that this sum is in fact the Smoluchowski-type equation[5,20] for AB$_2$ polymerization and with the substitution effect taken into account.

For clarity of notation, the time t can be rescaled and new units introduced according to the relation $\tau = 2k_1t$.

It is now the matter of algebra to show that the Smoluchowski-like equation (3) + (2) can be transformed into a more convenient form by multiplying it by $x^i(\alpha y)^j$ for each i and j and summing the result for all i and j. A relatively compact equation is thus obtained

$$\frac{\partial H}{\partial \tau} = H\left[(\alpha y)\frac{\partial H}{\partial x} + \frac{\partial H}{\partial y}\right] - H_1\left[x\frac{\partial H}{\partial x} + (\alpha y)\frac{\partial H}{\partial y}\right] - H(H_x + H_y) \quad (4)$$

for the counting function

$$H(\tau,x,y) = \sum_{i}^{\infty}\sum_{j}^{\infty}[i,j]_b x^i(\alpha y)^j \quad (5)$$

representing the whole size distribution of all branched molecules in the system. The other functions that appear in (4) are derived from H:

$$H_1 = H_1(\tau) \equiv H[\tau,1,(1/\alpha)] \quad (6)$$

$$H_\xi = H_\xi(\tau) \equiv \left.\frac{\partial H}{\partial \xi}\right|_{x=1,y=1/\alpha};\ \xi = x,y \quad (7)$$

The origin of individual terms in (4) is shown in the Appendix.

As compared with the analogous equation defined in ref 20 for the same system, but reacting without substitution effect (random case), the time units in (4) are the half of those used previously.

The functions H_1, H_x, and H_y can easily be extracted from (4). The first one is obtained in the form of an ordinary differential equation after removing dummy variables by putting $x = 1$ and $y = 1/a$. The other two functions become available, again in the form of ordi-

Table 1. Explicit Solutions of Some Differential Equations Derived from the Master Eq 4 for the Random Case, $a = {}^1/_2$, and Some Molecular Parameters of the System[a]

$H_1 = \dfrac{1}{2e^{\tau/2} - 1}$	$p = 1 - H_1 = \dfrac{e^{\tau/2} - 1}{e^{\tau/2} - 1/2}$
$H_x = \dfrac{e^{\tau}}{(2e^{\tau/2} - 1)^2}$	$H_y = \dfrac{e^{\tau/2}}{2e^{\tau/2} - 1} - \dfrac{e^{\tau}}{(2e^{\tau/2} - 1)^2}$
$H_{xx} = H_{yy} = 2H_x^{\,2}(e^{\tau/2} - 1)^2$	$H_{xy} = H_x^{\,2}\,\dfrac{(e^{\tau/2} - 1)(2e^{\tau} - 2e^{\tau/2} + 1)}{e^{\tau/2}}$
$P_n = M_0^{\,-1} = 2e^{\tau/2} - 1$	$P_w = M_2 = 2e^{\tau} - 1$
$P_n = \dfrac{1}{1 - p}$	$P_w = \dfrac{1 - p^2/2}{(1 - p)^2}$

[a] The meaning of symbols is explained in text. Unlike in papers by Flory[3] and Ziff,[4] the conversion degree p is the fraction of groups A that reacted.

nary differential equations, by differentiating (4) with respect to x and y, respectively, followed by putting $x = 1$ and $y = 1/a$. The system of equations thus obtained reads

$$\begin{cases} \dot{H}_1 = -H_1(H_x + H_y) \\ \dot{H}_x = -H_1 H_x \\ \dot{H}_y = \alpha H_1(H_x - H_y) \end{cases} \tag{8}$$

(the upper dot denotes differentiation with respect to time τ.)

The explicit forms of the functions for $a = {}^1/_2$ (random case) are listed in Table 1.

The average polymerization degrees of molecules in the system are conveniently expressed through the moments of size distribution. The latter are defined for any integer k as

$$M_k = \sum_{i=1}^{\infty}\sum_{j=0}^{\infty}(2i + j - 1)^k[i,j]_b \tag{9}$$

The advantage of expressing concentrations in terms of the number of i,j-mers per monomeric unit is that the zeroth moment, the sum of concentrations of all molecules, is at the same time the reciprocal of the number average polymerization degree:

$$P_n = M_0^{-1} = 1/H_1 \tag{10}$$

For the same reason, the first moment

$$M_1 = \sum_{i=1}^{\infty}\sum_{j=0}^{\infty}(2i + j - 1)[i,j]_b = 2H_x + H_y/\alpha - H_1 = 1 \tag{11}$$

is necessarily equal to 1. It may serve as a convenient check for the equations. Using eq 8 a reader may wish to verify that the time derivative of M_1 expressed, according to (11), as $2\dot{H}_x + \dot{H}_y/\alpha - \dot{H}_1$ is zero, as it should be.

The weight-average polymerization degree in the system is

$$P_w = M_2/M_1 = M_2 = 4H_{xx} + H_{yy}/\alpha^2 + 4H_{xy}/\alpha - H_y/\alpha + H_1 \tag{12}$$

(see Appendix) where

$$H_{\xi\zeta} \equiv \left.\frac{\partial^2 H}{\partial\xi\partial\zeta}\right|_{x=1,y=1/\alpha}; \quad \xi,\zeta = x,y \tag{13}$$

The functions $H_{\xi\zeta}$ are again obtained from the master eq 4 by differentiating it twice with respect to dummy variables x and y followed by putting $x = 1$ and $y = 1/\alpha$. The ordinary differential equations obtained in this way are presented in the Appendix.

The explicit size distribution of i,j-mers becomes available after solving successive ordinary differential equations for individual species. Thus, as follows from eqs 2 and 3

$$\frac{d[1,0]_b}{d\tau} = -[1,0]_b(H_1 + H_x + H_y) \tag{14}$$

$$\frac{d[1,1]_b}{d\tau} = [1,0]_b^{\,2} - [1,1]_b[(1 + \alpha)H_1 + H_x + H_y] \tag{15}$$

$$\frac{d[2,0]_b}{d\tau} = \alpha[1,0]_b[1,1]_b - [2,0]_b[2H_1 + H_x + H_y] \tag{16}$$

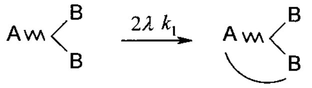
etc.

Finally, it is possible to calculate the average degree of branching of molecules in the system. Several definitions have been proposed of a parameter that measures quantitatively the degree of branching of a molecule.[9,22,23] All are quite easy to express in terms of quantities used in this model. We limit ourselves to the analysis of the degree of branching (DB) proposed by Frey's group. According to definition,[23] DB is twice the number of branching (trifunctional) units divided by the number of units in linear parts of the molecule plus again twice the number of branching units. As already stated, twice the number of branching points is the same as the sum of terminal and branching units minus one. The Frey's degree of branching is zero for linear molecules and unity for a perfect dendrimer.

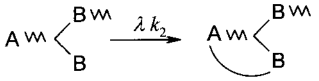
$$\mathrm{DB}_{\mathrm{Frey}} = \frac{2\sum(i - 1)[i,j]_b}{2\sum(i - 1)[i,j]_b + \sum j[i,j]_b} = \frac{2(H_x - H_1)}{2(H_x - H_1) + H_y/\alpha} \tag{17}$$

The System With Cyclization. Intramolecular reactions are inevitable in AB_2 polymerization because it produces highly branched molecules. The reactions lead to formation of intramolecular cycles. Obviously, in the ideal AB_2 polymerization, the cyclization reaction engages the only A group in the molecule. Hence, an AB_2 molecule may contain at most one intramolecular link. Reactions between two cycle-containing molecules are impossible. The cycle-containing molecules may grow only in reactions with acyclic ones. Each reaction produces another "cyclic" molecule. One should also bear in mind that both acyclic and cycle-containing species remain hiperbranched molecules with lots of unreacted B groups.

We consider just two elementary cyclization reactions:



$$[i+1,j-1]_b \rightarrow [i,j]_c$$



$$[i,j+1]_b \rightarrow [i,j]_c$$

The same rate constants as in the respective intermolecular reactions are used, except that they are premultiplied by factor λ weighing the chance of cycle-closing reaction relative to the respective intermolecular one in which the same group A takes part.

The rate equation describing disappearance of acyclic molecules (eq 2) has to be extended to include two extra terms for the rate of cycle formation (for terminal and linear units). The respective rates constants in rescaled time units are equal to λ and $\alpha\lambda$. Two more terms account for disappearance of branched molecules in their reactions with cycle-containing molecules. The rate of appearance term for acyclic molecules (eq 3) remains unchanged.

An extra rate equation is needed both for appearance and disappearance of cyclic molecules. These are formed either in cyclization reactions or in reactions between cycle-containing and acyclic molecules (four positive terms in rate equation). The rate equation contains two negative terms for the rate of disappearance of cyclic molecules in reactions with acyclic ones (two terms).

Algebraic manipulation analogous to that described for branched molecules converts the rate equation written for cyclic i,j-mers into

$$\frac{\partial h}{\partial \tau} = \left[(\alpha y)\frac{\partial H}{\partial x} + \frac{\partial H}{\partial y}\right]\lambda + \left[(\alpha y)\frac{\partial h}{\partial x} + \frac{\partial h}{\partial y}\right]H - \left[x\frac{\partial h}{\partial x} + (\alpha y)\frac{\partial h}{\partial y}\right]H_1 \quad (18)$$

for the counting function:

$$h(\tau,x,y) = \sum_{i=0}^{\infty}\sum_{j=0}^{\infty}[i,j]_c x^i (\alpha y)^j \quad (19)$$

The master rate equation for the branched molecules (extended eq 4) reads

$$\frac{\partial H}{\partial \tau} = \left[(\alpha y)\frac{\partial H}{\partial x} + \frac{\partial H}{\partial x}\right]H - \left[x\frac{\partial H}{\partial x} + (\alpha y)\frac{\partial H}{\partial x}\right](H_1 + \lambda) - (H_x + H_y + h_x + h_y)H \quad (20)$$

with

$$h_\xi = h_\xi(\tau) \equiv \left.\frac{\partial h}{\partial \xi}\right|_{x=1,y=1/\alpha};\ \xi = x,y \quad (21)$$

(meaning of all other symbols remains unchanged).

Clearly, the use of the single cyclization parameter λ is a crude simplification. However, the nature of rate equations in the present model makes the actual probability of closing a cycle in an i,j-mer proportional to the number of B groups in the molecule. In other words, big molecules have a higher chance to form an intramolecular link than small ones.

Intramolecular linking introduces the so-called long-range correlations into the system considered. The present kinetic approach, being a classical mean-field model, necessarily fails when tackling long-range correlations. Only an approximate prediction becomes possible of the changes in molecular parameters of the system with time or conversion.

Mathematically, the models fail because the set of ordinary differential equations derived from the master rate eqs 18 and 20 by successive differentiation of these equations followed by setting $x = 1$ and $y = 1/\alpha$ never closes down. The first derivatives of functions H and h with respect to dummy variables x and y are expressed in terms of second derivatives of H. The second derivatives of H and h are expressed in terms of third derivatives of H etc. The equations needed to calculate averages of polymerization degree in the system up to the weight averages of the whole system and separately for branched and cyclic molecules are presented in Appendix (eqs B1−B16, Table 2). In our calculations, we closed up the set (B13−B16) by neglecting the terms containing fourth derivatives of H. The accuracy of this approximation was the better the smaller was the cyclization parameter λ. A comparison of calculations with Monte Carlo experiments proved that the approximation was fairly good up to the conversion above 0.95.

The conversion degree p is defined as the fraction of groups A that reacted. Its value is twice the conversion degree of B groups defined by Flory[3] and used also by Ziff.[4] Since every molecule, acyclic or cycle-containing has $2i + j - 2$ or $2i + j$ links, respectively, each involving reacted group A, the fraction of all reacted A groups is

$$p = \sum_{i,j}(2i + j - 2)[i,j]_b + \sum_{i,j}(2i + j)[i,j]_c = M_1 - \sum_{i,j}[i,j]_b = 1 - H_1 \quad (22)$$

Monte Carlo Calculations. To assess the quality of approximations made in modeling the system with the classical kinetic method, we have performed simulations of the polymerization system by a Monte Carlo technique. The mechanism of polymerization carried out in virtual space was exactly the same as in the analytical model. All reactions took place according to rules and assumptions usually adopted in the classical analysis. The kind of Monte Carlo modeling of that type can be referred to as the pseudoclassical modeling. Its advantage is that one may relax some of the assumptions impossible to modify or neglect in the classical approaches. Good example is the effect of long-range correlations that lead to cyclization. In the Monte Carlo simulations, one simply sets a probability of intramolecular reaction.

In our calculations, a million of AB_2 monomers were placed in the memory of a computer and all possible elementary reactions between functional groups on units of different substitution, including cycle forming ones, were predefined. The rate constant for each of the reaction was an input parameter. The pairs of reacting functional groups were selected at random and let to react provided the conditions for the particular type of reaction had been met. A given type of reaction was allowed to continue when it happened to be selected at least that many times as the ratio of the rate of the fastest reaction in the system to that of the selected type of reaction. The rate constant of an elementary reaction was premultiplied by an extra parameter L when the selected functional groups happened to belong to the same molecule (cyclization reaction). We took the value of L divided by the total number of units (10^6) to correspond to the cyclization parameter λ used in the kinetic model. Details of the algorithm used by us can be found elsewhere.[24] For each set of input parameters, the simulations were performed at least three times at different seed values of the random number generator and the results were averaged.

Results and Discussion

In the model considered in this work, groups A react with B groups of an AB_2 monomer in a stepwise manner. Both groups in the monomer molecule as well as in the terminal units have the same reactivity. The reactivity of the "second" B group, i.e., the group in linear units, may have the same or different reactivity compared to that of B groups in terminal units. The change of reactivity is controlled by the rate constant ratio α. The latter serves as a measure of the substitution effect. The value of α equal to $^1/_2$ corresponds to the random reaction, the case considered in most papers published so far (cf., however, refs 17 and 18) We have changed the value of α in a quite broad range from 0.005 to 50. These limiting values correspond to dramatic changes of reactivity of the "second" group B in a unit relative to the initial reactivity of the same group. The respective rate constant drops down or rise by 2 orders of magnitude, respectively.

It should be pointed out that in the systems with kinetically controlled elementary reaction steps that react with substitution effect, the size distribution of polymer species carries information on the history of formation of molecules. In other words, the size distribution cannot be compounded up from the distribution of unit substitution degrees as it is done in the most of statistical methods of modeling, including the method described in ref 18. Any changes in reactivity, including the substitution effects, introduce the so-called time correlations into the distribution. Then, kinetic calculations usually yield different results than simple statistical methods applied to identical system.[5,23,24]

From practical point of view, it is desirable that hyperbranched polymer obtained in a one-pot synthesis contained highly branched molecules, i.e., high degree of branching[16,17] and, possibly, limited polydispersity of sizes.

Intuitively, when α is less than $^1/_2$, formation of long linear fragments is preferred. On the other hand, the values of α higher than $^1/_2$ favor branching and molecules containing more terminal units are formed. In Figure 1, the change of the average degree of branching of AB_2 molecules with conversion is shown for a series of α values. The situation does not change in the system where cyclization takes place. In fact, similar plots as that in Figure 1 made at different values of cyclization parameter (in the range of λ from 10^{-2} to 10^{-6}) are very similar. As already known,[17] for the random system, DB linearly depends on conversion and approaches 0.5 at $p \to 1$.

The effect of α on the ratio P_w/P_n for polymers containing no cycles is illustrated in Figure 2. It is evident that as the conversion approaches unity, polydispersity of the system rapidly increases. The reason is that, similar to what is seen in network polymerization, the big molecules react and grow much faster than the small ones. The increase becomes dramatic at the end of reaction. Here again, the system behaves as the network polymerization system approaching the gel point.

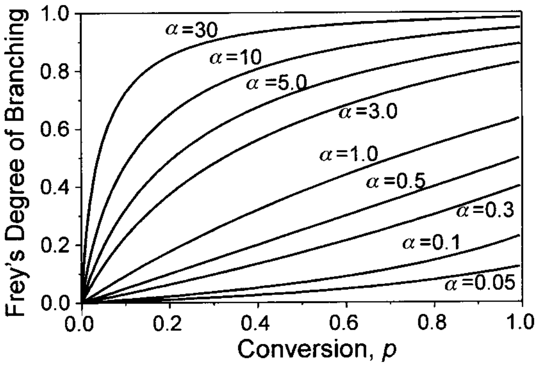


Figure 1. Frey's degree of branching as a function of conversion of A groups in hyperbranched polymerization of AB_2 monomers reacting with the substitution effect α. Definitions and the meaning of symbols are explained in the text.

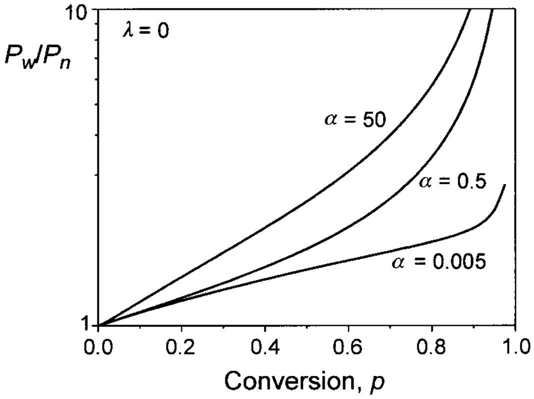


Figure 2. Polydispersity index P_w/P_n of hyperbranched polymer molecules containing no intramolecular cycles calculated from eq 4 as a function of degree of conversion of groups A in AB_2 monomers reacting with the substitution effect α.

Clearly, the system reacting with a strong positive substitution effect ($\alpha = 50$) yields product much more polydisperse than the randomly reacting system ($\alpha = 0.5$) or the system with preferred formation of linear chains (negative substitution effect, $\alpha = 0.005$). Again, the presence of cycle-containing molecules generated at various λ does not affect the picture.

The conclusion is that having a choice of monomers reacting with different substitution effects, we can either select a monomer yielding a highly branched, but also a highly polydisperse, polymer system or select one reacting with a negative effect that will produce moderately polydisperse macromolecules rather rich in linear parts.

For acyclic molecules ($\lambda = 0$) the results of calculations based on the Smoluchowski-like eq 4 are exactly the same as the results of Monte Carlo modeling. The averages of polymerization degree calculated in both ways coincide, including the weight averages calculated at various values of α. One should recall that the weight and higher averages are sensitive to the time correlations and would probably be different when calculated statistically,[5,26] e.g., from diads content.[18]

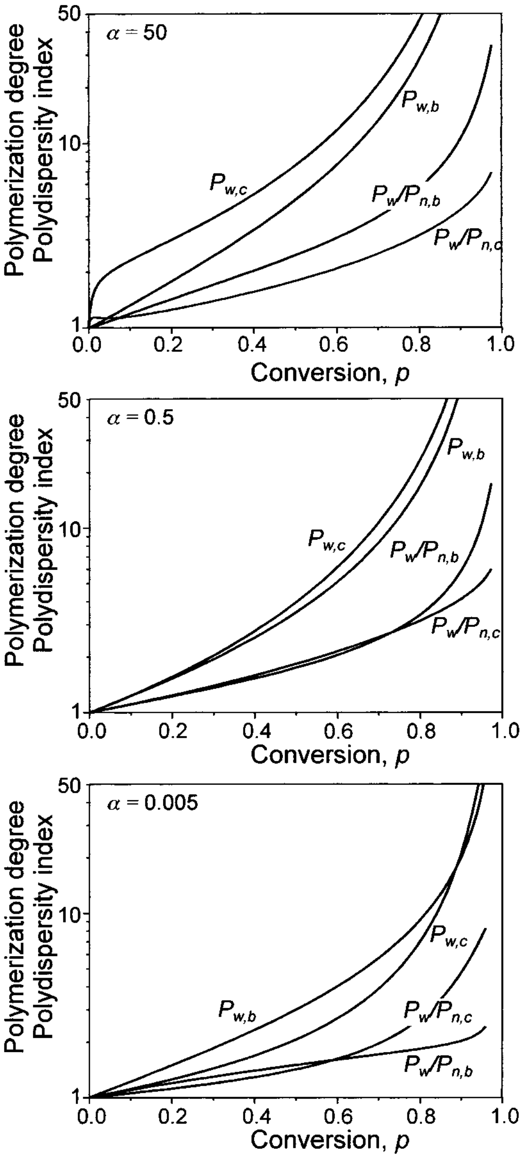


Figure 3. Weight-average degrees of polymerization and polydispersity indices of branched and cycle-containing molecules vs conversion as calculated using the kinetic model. The cyclization parameter $\lambda = 10^{-3}$. The shape of curves does not depend on the extent of cyclization, but on the substitution effect α.

The average degrees of polymerization in hyperbranched polymerization based on calculations made using eqs 18 and 20, i.e., with intramolecular cyclization taken into account, are plotted in Figure 3. It is interesting that the shape of curves depends on the magnitude of substitution effect, but not on the value of cyclization parameter. The average degrees of polymerization for branched and cyclic molecules presented in the plots are calculated separately as the ratios of appropriate moments. The equations used in calculations are presented in Appendix (Table 2, eq B17). It should be pointed out that the curves in Figure 3 present the sizes of molecules, specifically the average sizes of cycle-containing molecules, but are not related to the contents of respective types of species. The fractions of cycle-containing molecules at various magnitudes of the cyclization parameters are shown in Figure 4.

Here, the shapes of curves are practically independent of the substitution effect. In general, the fraction of cyclic containing molecules is rather small in the adopted range of cyclization parameters (10^{-2}–10^{-6}) and substantially increases as the conversion of groups A approaches unity. It remains close to zero for small conversion degree. Unfortunately, the simplifications used in the present calculations make the results very close to $p = 1$ not very reliable. At large λ values, the fraction of cycle-containing molecules rapidly peaks, while the average polymerization degree of acyclic molecules falls below zero. This numerical instability, however, is observed only at the conversion exceeding 0.95 and should not invalidate the results obtained below that value. The results of Monte Carlo calculations provide an evidence for that. For the random system (α = 0.5), the fractions of units in cycle-containing molecules calculated by using two methods of modeling are compared in Figure 4. The dashed lines obtained by Monte Carlo simulations (average results from six runs) remain fairly close to lines calculated from differential equations. Similar comparison is presented in Figure 5 where weight-average degrees of polymerization calculated by using both methods are plotted against conversion. The curves representing the polymerization degree of all molecules in the system coincide for any set of input parameters (α or λ). The curves representing $P_{w,c}$ and $P_{w,c}/P_{n,c}$, i.e., the average polymerization degrees of cycle-containing molecules and their polydispersity indexes, respectively, are slightly different for the two methods of calculations.

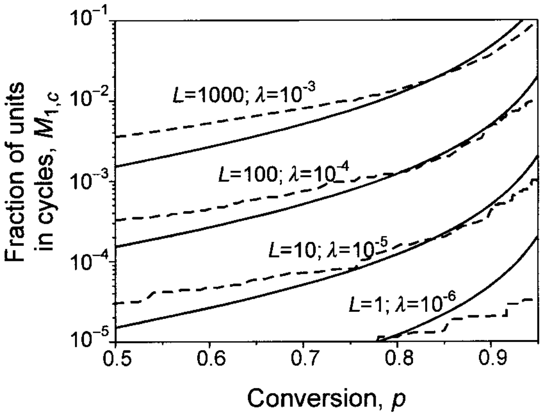


Figure 4. Fractions of units in cycle-containing molecules as calculated from the kinetic model (eqs 18 and 20) (solid lines) and by Monte Carlo simulations. The parameters controlling the extent of cyclization are shown.

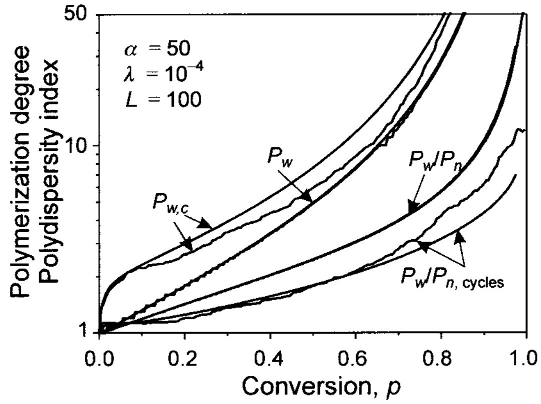


Figure 5. Comparison of calculated properties of all molecules and of those containing cycles in hyperbranched polymerization of an AB_2 monomer reacting with a strong positive substitution effect.

The curves from Monte Carlo experiments are easy to identify because of the noise of numerical calculations in the relatively small system. The curves in Figure 5 were obtained by averaging results of 16 simulation runs. One should bear in mind while analyzing Figures 4 and 5 that in Monte Carlo simulations the number of cyclic molecules is relatively small and rarely exceeds a few hundred even at as high a conversion as 0.95. Therefore, we believe the results obtained by the two methods of modeling to be quite consistent despite differences in results obtained at certain values of input parameters.

Concluding, one may state that however crude the simplifications adopted by us during kinetic modeling of AB_2 monomer polymerization and despite of numerical tricks used, the results well agree with those of numerical simulations performed by the Monte Carlo method with the same mechanism of growth steps and principles of cycle closing reactions.

The extent of cyclization in the reaction has been found to be relatively small. At a strong positive substitution effect ($\alpha = 50$), the average size of cycle-containing molecules exceeds that of acyclic molecules, at least at small conversion. In other words, although intramolecular cyclization takes place rather scarcely at the beginning of reaction, if it happened, it occurred in rather large molecules.

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Appendix

A. Master Equations. The method of deriving the terms of master eqs 4, 18, and 20 is outlined by two examples. Consider the first term in eq 3

$$\sum_{p}^{i-1}\sum_{q}^{j-1}(i - p + 1)[i - p + 1, j - p - 1]_{\mathrm{b}}[p,q]_{\mathrm{b}} \qquad \text{(A1)}$$

multiplication of the term by $x^i(\alpha j)^j$ and summation over all i's and j's yield

$$\sum_{i}^{\infty}\sum_{j}^{\infty}\sum_{p}^{i-1}\sum_{q}^{j-1}(i - p + 1)[i - p + 1, j - q - 1]_{\mathrm{b}}x^{i-p}(\alpha y)^{j-q} [p,q]_{\mathrm{b}}x^{p}(\alpha y)^{q} = (\alpha y)\left(\frac{\partial H}{\partial x}\right)H \qquad \text{(A2)}$$

for the function H defined by eq 5. The reader may wish to verify this result by writing down the terms of the sum. There are four running indices so the verification is rather tedious. Generally, the derivative on the right-hand side appears because the concentration is premultiplied by the number of units of given kind (the term $(i - p + 1)$ in (A1)). Since the number of linear units in the concentration terms is one less than in the exponent of αy, one αy has to be extracted out from the sum. It appears in front of the right-hand side of (A2).

The use of a dummy (αy) rather than just y is very convenient, since differentiation of H with respect to y automatically introduces the substitution effect parameter in front of the appropriate concentration term.

Easier to derive (and to verify) are the terms of the negative, disappearance terms of the master equations. Thus, when multiplied by $x^i(\alpha j)^j$ and summed over all i's and j's, the terms in eq 2 become

$$-\sum_{i}^{\infty}\sum_{j}^{\infty}[(i + \alpha j)[i,j]x^{i}(\alpha y)^{j}\sum_{p}^{\infty}\sum_{q}^{\infty}[p,q]_{\mathrm{b}} + [i,j]_{\mathrm{b}}x^{i}(\alpha y)^{j}\sum_{p}^{\infty}\sum_{q}^{\infty}(p + \alpha q)[p,q]] = -\left(x\frac{\partial H}{\partial x} + (\alpha y)\frac{\partial H}{\partial y}\right)H_1 - H(H_x + H_y) \qquad \text{(A3)}$$

B. The Set of Ordinary Differential Equations. The master Smoluchowski-like eqs 18 and 20 are used to derive the following set of ordinary differential eqs by differentiating (20) and (18) with respect to x and y followed by setting $x = 1$ and $y = 1/\alpha$

$$\dot{H}_1 = -(H_x + H_y)\lambda - (H_x + H_y + h_x + h_y)H_1 \qquad \text{(B1)}$$

$$\dot{h}_1 = (H_x + H_y)\lambda \qquad \text{(B2)}$$

$$\dot{H}_x = -(H_{xx} + H_{xy})\lambda - (H_1 + \lambda)H_x - (h_x + h_y)H_x \qquad \text{(B3)}$$

$$\dot{H}_y = -(H_{xy} + H_{yy})\lambda - (h_x + h_y)H_y - \alpha(H_y - H_x)H_1 + \alpha H_y\lambda \qquad \text{(B4)}$$

$$\dot{h}_x = (H_{xx} + H_{xy})\lambda + (h_x + h_y)H_x - h_xH_1 \qquad \text{(B5)}$$

$$\dot{h}_y = (H_{xy} + H_{yy})\lambda + (h_x + h_y)H_y - \alpha(h_y - h_x)H_1 + \alpha H_x\lambda \qquad \text{(B6)}$$

$$\dot{H}_{xx} = -(H_{xxx} + H_{xxy})\lambda + 2(H_{xx} + H_{xy})H_x - [2(H_1 + \lambda) + (h_x + h_y)]H_{xx} \qquad \text{(B7)}$$

$$\dot{H}_{xy} = -(H_{xxy} + H_{xyy})\lambda - (1 + \alpha)H_{xy}(H_1 + \lambda) + \alpha H_{xx}H_1 + (\alpha H_x + H_{xy} + H_{yy})H_x + (H_{xx} + H_{xy})H_y - (h_x + h_y)H_{xy} \qquad \text{(B8)}$$

$$\dot{H}_{yy} = -(H_{xyy} + H_{yyy})\lambda + 2\alpha H_1H_{xy} + 2(\alpha H_x + H_{xy} + H_{yy})H_y - [2\alpha(H_1 + \lambda) + (h_x + h_y)]H_{yy} \qquad \text{(B9)}$$

$$\dot{h}_{xx} = (H_{xxx} + H_{xxy})\lambda - 2h_{xx}H_1 + 2(h_{xx} + h_{xy})H_x + (h_x + h_y)H_{xx} \qquad \text{(B10)}$$

$$\dot{h}_{xy} = (H_{xxy} + H_{xyy} + \alpha H_{xx})\lambda - [(1 + \alpha)h_{xy} - \alpha h_{xx}]H_1 + (\alpha h_x + h_{xy} + h_{yy})H_x + (h_{xx} + h_{xy})H_y + (h_x + h_y)H_{xy} \qquad \text{(B11)}$$

$$\dot{h}_{yy} = (H_{xyy} + H_{yyy} + 2\alpha H_{xy})\lambda - 2\alpha(h_{yy} - h_{xy})H_1 + 2(\alpha h_x + h_{xy} + h_{yy})H_y + (h_x + h_y)H_{yy} \qquad \text{(B12)}$$

$$\dot{H}_{xxx} = [3H_x - 3(H_1 + \lambda) - (h_x + h_y)]H_{xxx} + 3H_xH_{xxy} + 3(H_{xx} + H_{xy})H_{xx} \qquad \text{(B13)}$$

$$\dot{H}_{xxy} = (\alpha H_1 + H_y)H_{xxx} + [2H_x + H_y - (2 + \alpha)(H_1 + \lambda) - (h_x + h_y)]H_{xxy} + 2H_xH_{xyy} + [3\alpha H_x + 3H_{xy} + H_{yy}]H_{xx} + 2H_{xy}^{\;2} \qquad \text{(B14)}$$

$$\dot{H}_{xyy} = 2(H_y + \alpha H_1)H_{xxy} + [H_x + 2H_y - (1 + 2\alpha)(H_1 + \lambda) - (h_x + h_y)]H_{xyy} + H_xH_{yyy} + (2\alpha H_y + H_{yy})H_{xx} + (4\alpha H_x + 2H_{xy} + 3H_{yy})H_{xy} \qquad \text{(B15)}$$

$$\dot{H}_{yyy} = 3(H_y + \alpha H_1)H_{xyy} + [3H_y - 3\alpha(H_1 + \lambda) - (h_x + h_y)]H_{yyy} + 3(\alpha H_x + H_{xy} + H_{yy})H_{yy} + 6\alpha H_yH_{xy} \qquad \text{(B16)}$$

Table 2. Moments and Average Degrees of Polymerization

quantity	branched molecules	cycle-containing molecules	whole system
M_0	$1/H_1$	$1/h_1$	$(H_1 + h_1)^{-1}$
M_1	$2H_x + h_y/\alpha - H_1$	$2h_x + h_y/\alpha_1$	$M_{1,b} + M_{1,c} = 1$
M_2	$4H_{xx} + 4H_{xy}/\alpha + H_{yy}/\alpha^2 - H_y/\alpha + H_1$	$4h_{xx} + 4h_{xy}/\alpha + h_{yy}/\alpha^2 + 4h_x - h_y/\alpha$	$M_{2,b} + M_{2,c}$

In fact, eqs B13–B16 do not contain the terms with fourth derivatives of H (H_{xxxx}, H_{xxxy}, etc.) that are multiplied by λ. This is a simplification that helps one to close the system of equations down. The system without cyclization ($\lambda = 0$) does close down without any simplifications.

The derivatives up to $H_{\xi\zeta}$ and $h_{\xi\zeta}$ with $\xi,\zeta = x,y$ are needed to calculate averages of degree of polymerization up to the weight averages. The explicit formulas for respective moments of distribution are presented in Table 2. They are simply the developed moment expressions, eq 9 for acyclic molecules and

$$M_{k,cycl} = \sum_{i=1}^{\infty}\sum_{j=0}^{\infty}(2i + j)^k[i,j]_c \qquad \text{(B17)}$$

for cycle-containing ones.

The averages are expressed in terms of moments calculated for the respective type of molecules (branched or cycle-containing), thus:

$$P_{n,type} = \frac{M_{1,type}}{M_{0,type}};\ P_{w,type} = \frac{M_{2,type}}{M_{1,type}} \qquad \text{(B18)}$$

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