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A Monte Carlo model of hyperbranched polymerization

RAPID COMMUNICATION

Summary — A Monte Carlo computer model of is described for hyperbranched polymerization involving AB_2 monomers. The structure of algorithm used in the model and selected results of its application are presented. The results are compared with those obtained by using an analytical kinetic model. For analogous polymerization systems, the two models were found to yield identical molecular parameters, *viz.*, the average degrees of polymerization as the degree of conversion was varied, and polydispersity index for the reacting systems involving different substitution effects.
Key words: Monte Carlo modeling, hyperbranched polymers, size distribution, polymerization degree.

A considerable interest in highly branched polymers forming non-gelling systems has been observed in the recent fifteen years [1, 2]. Two groups of such polymers have been studied most widely. These are dendrimers, *i.e.*, highly branched, nearly monodisperse oligomers obtained in sophisticated multistage processes [3] and hyperbranched polymers obtained in one-pot reactions. The latter are much easier to prepare than dendrimers by *e.g.*, homopolymerization of AB_2 monomers, but the products are polydisperse both with respect to the size of molecules and to their structure. Symbols A and B stand for functional groups that react with each other in elementary growth reactions. Since the pioneering works of Flory [4] published nearly 50 years ago, the theory of polymerization of AB_2 monomers has not attracted much attention until very recently (*cf.*, *e.g.*, [5—8]). In our theoretical work, we concentrate on the study on an influence of variations in the reactivity of functional groups, known as the first shell substitution effect [9, 10], on the size distribution of hyperbranched polymers obtained by polymerization of an AB_2 monomer [11, 12]. In this work, we present some results obtained by using an alternative Monte Carlo model of the same type of polymerization as well as the principles of the model itself.

THE MODEL

We consider a pseudoclassical model of hyperbranched polymerization involving an AB_2 monomer. The reacting system is a graph-like one with no volume

ascribed to the units. The units have no definite position in space and any pair of functional groups is as likely to be selected to react as any other. Hence, no physical effects influencing the reactions are taken into account such as temperature or rate constant variations, restrictions to diffusion of species, *etc.* The cycle closing reactions occur at random and the extent of cyclization in the typical systems consisting of 10^6 units is negligibly small, but not eliminated from the present model.

Three states of a unit with unreacted A group can be distinguished. For unreacted B groups, the number of unit reaction states is four. The states are presented schematically in Table 1. Each reaction state has its own elementary rate constant. The actual rate constant of a reaction is a product of the appropriate elementary constants multiplied by the symmetry factor. The rate constants for all twelve possible growth reactions are listed

Table 1. The types of units bearing reactive groups A and B (small zigzags denote the remaining fragment of the molecule to which the unit is attached)

Reactive A groups		Reactive B groups	
unit	elementary rate constant	unit	elementary rate constant
A—⟨ B B	k_{1A}	Λ—⟨ B B	k_{1B}
A—⟨ B~ B	k_{2A}	~A—⟨ B B	k_{2B}
A—⟨ B~ B~	k_{3A}	Λ—⟨ B B~	k_{3B}
		~A—⟨ B B~	k_{4B}

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in Table 2. The product form of the rate constants is equivalent to the assumption that the contributions from both reacting units to the activation energy are additive. The approach makes it possible to model the so-called first shell substitution effect at which the units react [9].

T a b l e 2. The rate constants in the elementary growth reactions taking place in hyperbranched polymerization involving an AB_2 monomer reacting with the first shell substitution effect.

Reagent A / Reagent B	$A{-}{<}^B_B$	$A{-}{<}^{B\text{---}}_B$	$A{-}{<}^{B\text{---}}_{B\text{---}}$
$A{-}{<}^B_B$	$2\,k_{1A}k_{1B}$	$2\,k_{2A}k_{1B}$	$2\,k_{3A}k_{1B}$
$\text{---}A{-}{<}^B_B$	$2\,k_{1A}k_{2B}$	$2\,k_{2A}k_{2B}$	$2\,k_{3A}k_{2B}$
$A{-}{<}^B_{B\text{---}}$	$k_{1A}k_{3B}$	$k_{2A}k_{3B}$	$k_{3A}k_{3B}$
$\text{---}A{-}{<}^B_{B\text{---}}$	$k_{1A}k_{4B}$	$k_{2A}k_{4B}$	$k_{3A}k_{4B}$

The algorithm on which calculations were based consisted of the following steps:

— **Initialization of the system.** For the number of units introduced by the operator (typically 10^6) a table is generated in computer memory that contains information on the state of every unit. All parameters and variables are set to their initial values.

— **Choice of units to react.** A pair of units to react is selected (random number generator points at the positions of units in the unit table). First a unit with unreacted A group is selected and then follows a unit with a free B group. Hence, the choice of a unit is at the same time the choice of functional groups to react.

— **Determination of rate constants.** By using the data on the unit states, the rate constant is ascribed to the event as shown in Table 2. The ratio of the resulting value to the rate constant of the fastest reaction in the system determines the 'probability' of whether or not the selected units actually react. The 'probabilities' add up each time a given type of pair happened to be selected. As the sum for a pair exceeds unity, the reaction is allowed to proceed. Otherwise, a new pair of units is selected without introducing any changes into the system.

— **Modification of system parameters.** The reaction that takes place between units is equivalent to introducing appropriate modifications of the states of units in the table and to altering global parameters of the system, such as conversion degree.

— **Results.** At certain values of conversion degree, the reacting system is analyzed. The molecules of different polymerization degrees are identified and the average polymerization degrees calculated. The parameters are written to disk.

— **End of simulation.** The simulation ends when the conversion degree reaches a predetermined value. For practical purposes, the end value is usually set to be slightly smaller than 1, typically 0.995.

The results obtained by the Monte Carlo simulations were confronted with the molecular parameters evaluated by using the newly developed kinetic model of the same hyperbranched polymerization [12]. The kinetic model has a form of a single compact Smoluchowski-like rate equation. In its present form, the rate equation also tackles the systems reacting with the first shell substitution effect, but to a limited extend as compared to the Monte Carlo model. Namely, only two different rate constants are distinguished: $K_1 = k_A k_{1B} = k_A k_{2B}$ and $K_2 = k_A k_{3B} = k_A k_{4B}$ with $k_A = k_{1A} = k_{2A} = k_{3A}$. In other words, in units with two unreacted B groups, the latter react with the rate constant K_1, whereas in the units with just one B group unreacted, the rate constant of its reaction with any A group is K_2.

The Smoluchowski-like rate equation is

$$\frac{\partial H}{\partial \tau} = H\left[(\alpha y)\frac{\partial H}{\partial x} + \frac{\partial H}{\partial y}\right] - H_1\left[x\frac{\partial H}{\partial x} + (\alpha y)\frac{\partial H}{\partial y}\right] - H(H_x + H_y) \tag{1}$$

for the counting function

$$H(\tau, x, y) = \sum_i^\infty \sum_j^\infty [i, j]_b\, x^i (\alpha y)^j \tag{2}$$

which is a polynomial representation of the entire size distribution in polymerization system. The coefficients: $[i, j]_b$ at the dummy variables x and y are the concentrations of molecules composed of i units with two unreacted B groups (terminal units) and j units with one unreacted B group (linear units). The functions H_1, H_x, and H_y are functions of time, τ, also derived from H, thus:

$$H_1 = H(\tau, 1, 1/\alpha) \tag{3}$$

$$H_\xi = \frac{\partial H}{\partial \xi}\bigg|_{x=1, y=1/\alpha} \quad ; \xi = x, y \tag{4}$$

The rate constants are present in the rate equation in the form of a ratio

$$\alpha = \frac{K_2}{2K_1} \tag{5}$$

and the time units are rescaled relative to the real time t according to

$$\tau = 2K_1 t \tag{6}$$

Details of derivation of the rate equation (1) as well as the methods of extracting molecular parameters of polymerizing systems out of it can be found elsewhere [11].

RESULTS AND DISCUSSION

In order to compare the results of calculations obtained by the two methods, i.e., the results of Monte Carlo simulations with those of kinetic calculations, we have limited ourselves to the sets of rate constants that can be set the same in both methods. In the Monte Carlo calculations we have set

$$k_{1A} = k_{2A} = k_{3A} = 1$$
$$k_{1B} = k_{2B} = K_1 \qquad (7)$$
$$k_{3B} = k_{4B} = K_2$$

The relative rate constant of the kinetic model, α, was calculated as in eqn. (5).

For the typical size of reacting system consisting of 10^6 monomer units, the time needed for a single simulation on a PC equipped with an 800 MHz processor ranged from half an hour (for random system, $K_1 = K_2 = 1$) to several hours. Simulations were repeated for a given set of input parameters to smooth out the results. The results presented below are averages from at least five simulations.

The number- and weight-average polymerization degrees in the system, P_n and P_w, respectively, as well as polydispersity indices P_w/P_n, were essentially identical in both methods. The lines on the plots obtained by the two methods were indistinguishable. Since in the Monte Carlo simulations cycle formation was allowed to proceed at random (*i.e.*, whenever the functional groups selected to react happened to belong to the same unit, the reaction was allowed to proceed at the same rate as in the case of reaction between same groups on different units), the identical values of the averages suggest that the extent of cyclization in all systems was very small. Indeed, only the presence of a few cyclic molecules was recorded in the simulation outputs.

As found also earlier [11, 12], in all cases, the average degrees of polymerization grew quite rapidly as the conversion approached unity. For a large rate constant ratio α, the average polymerization degrees grew faster with conversion than they did at small α. This was the result of the increased rate of formation of branched molecules in the system. The reactions between large molecules were faster than those involving monomer. This can be observed in Fig. 1, where the fraction of monomer units is plotted against conversion of groups A. At any conversion p, the monomer fraction n_1/N is the
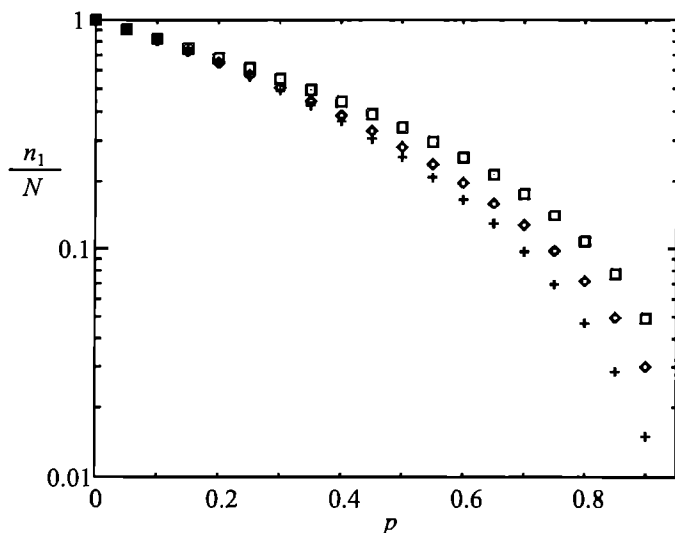
larger, the larger is α. Note that, for the random reaction (all rate constants are the same), $\alpha = 0.5$.

It is also interesting to observe the changes in the entire size distribution of polymer species calculated at different conversions p at various rate constant ratios (Fig. 2). To calculate the entire distribution from the ki-
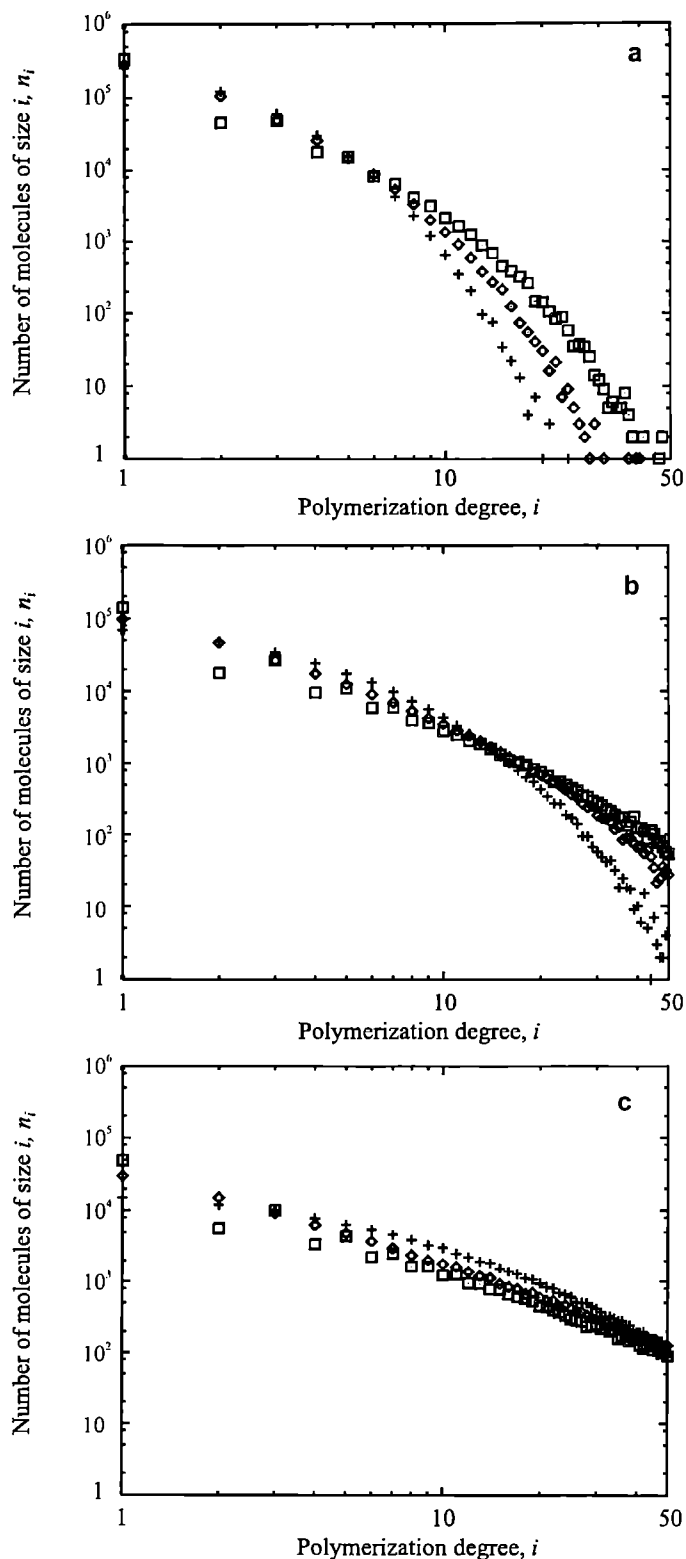

Fig. 2. *The number distribution of polymer species in homopolymerization of an AB_2 monomer in relation to conversion, p, at various rate constant ratio α; conversion p: a — 0.5, b — 0.75, c — 0.9; constant ratio α: + — 0.05, $\diamond$ — 0.5, $\square$ — 5*

Fig. 1. *The change of monomer concentration in homopolymerization of an AB_2 monomer; the concentration is expressed as the ratio of monomer, n_1, to the total of all units in the system, N: constant ratio α: + — 0.05, $\diamond$ — 0.5, $\square$ — 5*

netic model (eqn.1) one has to derive and solve roughly twice as many differential equation as there are polymer sizes taken into account. In this respect, the advantage of the Monte Carlo model is unquestionable. From the plots one can see that the concentrations of small molecules of odd polymerization degree is at large α somewhat smaller than concentrations of the neighboring even counterparts. This is explained by the fact that the even molecules have more units in linear fragments that tend to react rapidly to form branches.

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