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Percolation Model of Hyperbranched Polymerization

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Summary: Computer simulations of the step-growth homopolymerization of an AB_2 monomer have been carried out on a square lattice. No rearrangements of units were made between reaction events. Instead, the capture radius, i.e., the maximum distance between the randomly selected unit and its reaction partner was changed. The reaction was considered as controlled either by diffusion and local concentration fluctuations or by the law of mass action (classical limit). The size distribution of polymer species and the extent of cyclization reactions in the polymerization are discussed.

Keywords: AB2 monomer; cyclization; homopolymerization; hyperbranched polymerization; non-classical approach

Introduction

In the early days of polymer science, Flory[1] demonstrated that polymerization of an AB_2 monomer, where groups A reacted with groups B, led to a polymer consisting of highly branched molecules and that the system did not undergo gelation. Later, Ziff et al.[2] pointed out the similarities and differences between AB_2 polymerization and network polymerization involving an f-functional B_f monomer (with B groups able to react with each other). Interest in hyperbranched polymerization and hyperbranched polymers rose considerably in recent years, along with the spectacular 'explosion' of publications on dendrimers. A good illustration of the state of the art is provided by the review by Sunder et al.[3]

Hyperbranched polymers obtained in one batch by polymerization of AB_2 monomer are polydisperse in terms of both molecular size and the structure of individual molecules. Both highly branched molecules resembling dendrimers and almost linear structures are formed.[4,5]

The attempts to control polydispersity of hyperbranched polymers consist of (i) modification of reactivity of functional groups (by selection of the chemical structure of the monomer),[6] (ii) carrying out polymerization of an AB_f monomer in the presence of a minor quantity of monomer B_g[7] (f and g are the numbers of functional groups of B-type on the respective monomer species), or (iii) gradual introduction of monomer AB_f into a polymerization vessel where the B_g monomer is also present.[8,9]

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In their quantitative analyses, most authors have neglected the intramolecular cyclization that necessarily accompanies polymerization.[1,2,4,10,11] Some, however, have taken this possibility into account.[4, 12-14] When modelling hyperbranched polymerization, most authors, apart from a few (cf. e.g.[12]), tackled the problem in the classical way, simply modifying the rate constants to harness the intramolecular, cycle-closing reactions. The approaches had intrinsic limitations since intramolecular cyclization is a form of the long-range correlations that in principle cannot be tackled rigorously within the framework of classical mean-field theory. The same applies to concentration fluctuations that affect the resulting size distribution and can be related to, say, the diffusion-restricted mobility of reacting species as their size increases.[15] Slow diffusion may also influence the extent of cyclization by modifying ring-chain competition in the polymerization system.[16]

Classical modelling usually treats a polymerizing system as graph-like and no spatial information is taken into account. Intuitively, one can expect that when highly branched molecules are formed, the high local concentration of B groups belonging to a molecule may favour cycle closing reactions, in which one of B groups reacts with the A group belonging to the same molecule.

In our previous papers,[14] we have developed a (classical) kinetics model of hyperbranched polymerization where the rate of the cycle-closing reaction was set proportional to the number of B groups in a molecule. The fraction of cycle-containing molecules in the system was found to be relatively small, apparently smaller than observed for real systems.[4] By simulating hyperbranched polymerizations on a square lattice, for a system consisting of 10^6 monomer molecules,[13] we have arrived at exactly the same size distributions and very similar fractions of cycle-containing molecules as those calculated by using the kinetics model. In the Monte-Carlo simulation procedure used, any pair of units had the same probability of undergoing reaction.

In this paper, we report on the changes in size distribution of polymer species and in the structure of hyperbranched polymers that are generated by Monte-Carlo simulations on a square lattice with limited capture radius, so that, at least in principle, the effects of concentration fluctuations and diffusion hindrance on the size distribution of polymer species and cycle containing molecules can be analysed.

The Model

The idea of long-range percolation was applied to study the effects of availability restrictions imposed on units in the polymerization of an AB_2 monomer.[17] In comparison with the usual nearest-neighbour percolation,[15] the longest distance between reacting units was extended. This distance, called the capture radius,[18] determined the area to which both reacting units were confined.

The idea of a capture radius is illustrated in Figure 1. In the square lattice composed of 10^6 nodes, the size of lattice is 1000×1000 nodes. Hence, 500 lattice steps constitute the highest possible capture radius, provided advantage is taken of the usual periodic boundary conditions.[15] At this radius, the system corresponds to a mean-field one since any pair of functional groups has the same chance of entering reaction.

A pair of AB_2 units is selected at random to react. The first must have an unreacted **A** group, and the second, a **B** group. To take into account possible substitution effects, one may distinguish three states of a unit with respect to the reaction ability of its **A** group and four states of reactivity of a unit from the point of view of a **B** group. The states are shown schematically in Table 1.

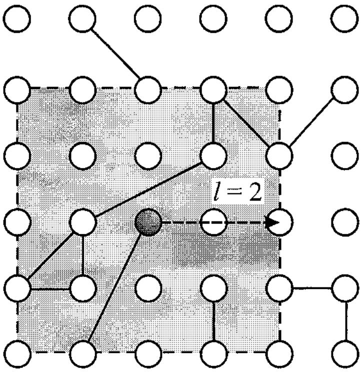


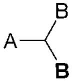
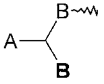
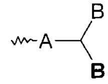
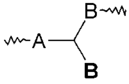
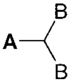
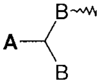
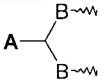
Fig. 1. Illustration of the idea of a capture radius in the percolation experiment on a square lattice. A reaction partner for the unit selected to react (dark) has to be found in the shaded square area determined by the distance l (capture radius).

The product form of the 12 rate constants in Table 1 is equivalent to the assumption that contributions from units to the activation energy of the specific reaction are additive.[19] The contributions correspond to the elementary rate constants. To simplify the system of equations and to concentrate on the accessibility of functional groups rather than on their reactivity, we assume that $k_{1A} = k_{2A} = k_{3A}$, $k_{1B} = k_{3B}$, and $k_{2B} = k_{4B}$ so that the substitution effect is limited the changes of reactivity of B groups only. By introducing the ratio:[20]

$$\alpha = \frac{k_{2B}}{k_{1B}} \qquad (1)$$

the number of different rate constants is further reduced. The same simplification was introduced to the kinetics model based on the Smoluchowski coagulation equation described elsewhere.[14] All elementary reactions are considered irreversible and a link once formed remains so.

Table 1. Elementary states of reactivity of units and the contributions from the units to the rate constants of the reactions taking place in the system.

				
	$2k_{1A}k_{1B}$	$k_{1A}k_{2B}$	$2k_{1A}k_{3B}$	$k_{1A}k_{4B}$
	$2k_{2A}k_{1B}$	$k_{2A}k_{2B}$	$2k_{2A}k_{3B}$	$k_{2A}k_{4B}$
	$2k_{3A}k_{1B}$	$k_{3A}k_{2B}$	$2k_{3A}k_{3B}$	$k_{3A}k_{4B}$

∿∿ means that the group has reacted – linked to the rest of a molecule.

Results and Discussion

As the capture radius *l* (see Figure 1) is reduced in the long-range percolation model, the unit selected to react 'sees' fewer and fewer potential reaction partners. It can react only with units present in the reaction area. A reduction of *l* corresponds to the situation where the reaction is either very fast or the distance that a unit travels before reacting is limited by, say, high viscosity of the system slowing down or restricting free movements of units. Furthermore, the meanconcentration of units that belong to a given molecule drops as the size of the system (or capture radius) increases. It is zero in the thermodynamic limit to which the mean-field models refer. In a system confined to a limited domain, the probability of an intramolecular cycle-closing reaction is larger. Cycle formation is a typical feature of percolation models. Confinement to a restricted reaction volume is also equivalent to the presence of local concentration fluctuations.[15]

The disadvantage of the percolation model is that it remains graph-like and any changes in the capture radius (as well as in lattice geometry) are difficult to interpret in terms of the behaviour of real systems.

In the present work we studied principally the extent of cyclization. The elementary reactions that lead to cycle formation were not 'weighted' in any way, i.e., they occurred whenever the second selected unit happened to belong to the same molecule as the first. The rate of reaction was the same as in the case of analogous intermolecular reaction. One should bear in mind, however, that, unlike in the thermodynamic limit, even for the highest capture radius (the whole lattice) the probability of cycle-closing reaction is non-zero because of the limited size of the lattice.[13]

The weight-average degree of polymerization of polymer species vs. conversion of **A** groups is shown in Figure 2 for a series of relative rate constants α defined by eq. (1). The monomers reacted randomly, i.e., without any substitution effect, at $\alpha = 1$. For a positive substitution effect ($\alpha > 1$) the weight-average polymerization degree grows faster than in the random case. The opposite is observed for the systems with a negative substitution effect ($\alpha < 1$). The negative (positive) substitution effect means that the second **B** group on a unit reacts more slowly (faster) than the first one.

In the simulations performed to obtain the results presented in Figure 2, the capture radius was set to its highest value ($l = 500$). Any unit in the entire system could be selected as the reaction partner for any other unit, just as in the classical systems. It is worth noting that only a few cycle-containing molecules were formed in the simulations carried out at $l = 500$. No effect of kinetics constants on their amount was observed. Simply, the lattice was sufficiently large for cyclic molecules to form at random. The weight-average degree of polymerization obtained in percolation simulations over all the lattice and with monomers reacting with zero substitution effect was identical to that calculated using the kinetics model based on the Smoluchowski equation.[14] Although it may come as a surprise, the long-range percolation model with a large capture radius, even in two-dimensions and for the simplest lattice geometry, reproduces very well the molecular parameters of a polymerization system generated using classical models.

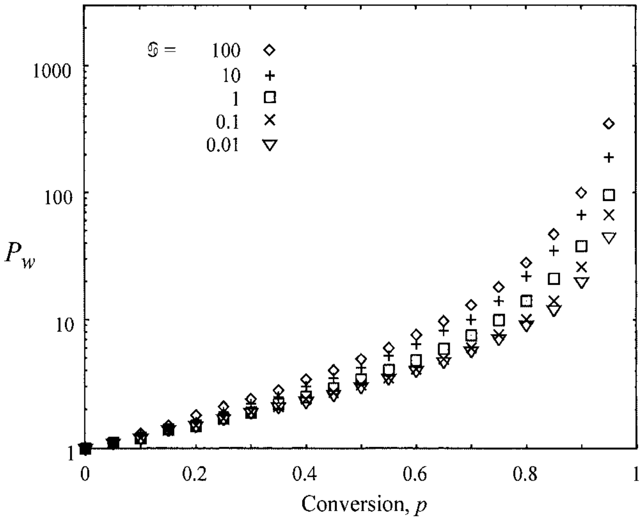


Fig. 2. Weight-average degree of polymerization vs. conversion degree for several values of the relative rate constant α.

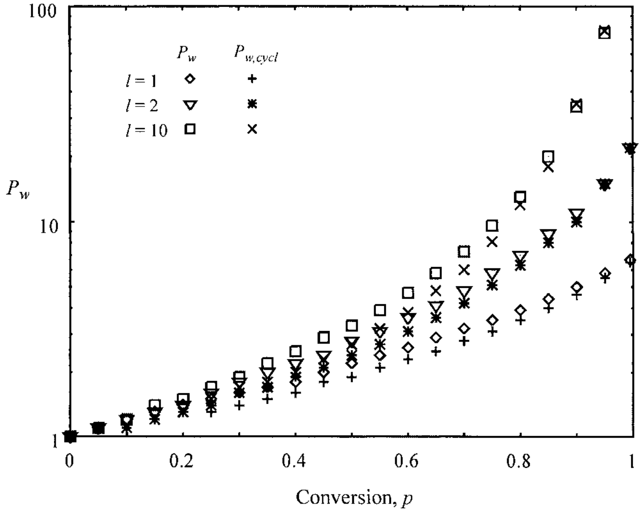


Fig. 3. The weight-average polymerization degree of the whole system, P_w, and that of the cycle-containing fraction, $P_{w,cycl}$, vs. conversion of **A** groups in percolation experiments carried out at small capture radii, l.

As the number of reaction partners is reduced with decreasing capture radius, local conditions start to have an effect on the reaction. The weight-average degree of polymerization of the whole system shown in Figure 3 is compared with the value for cycle-containing molecules. Each curve was constructed as an average from at least 5 simulations. The deviations of results around the average values increased with conversion, but did not exceed 5 % at full conversion. As can be seen in Figure 3, the weight-average degrees of polymerization of cycle-containing molecules do not differ much from those of the whole system. This is because in systems with small capture radii most molecules contain a cycle. Note that in an AB_2 polymer only one cycle may be present in one molecule. A molecule may become the cycle-containing one by reacting intermolecularly with a smaller molecule already containing a cycle.

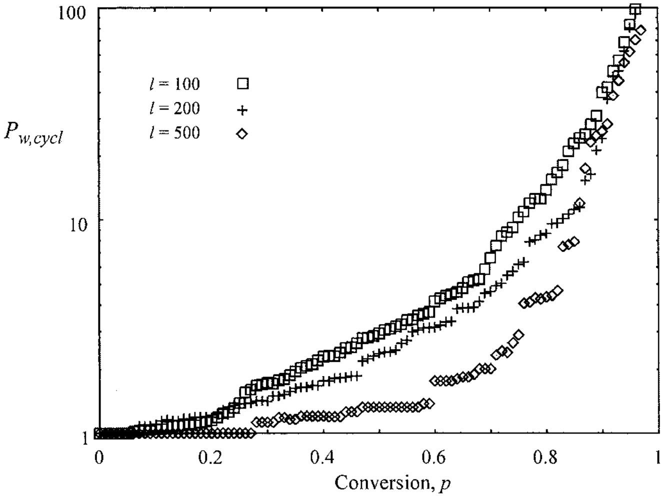


Fig. 4. The weight-average degree of polymerization of cycle-containing molecules, $P_{w,cycl}$, vs. conversion of **A** groups in percolation experiments carried out at large capture radii, l.

In systems with small capture radii, small cycles are most likely to appear. Consequently, the sizes of molecules become small; smaller that in classical systems or in systems with larger capture radii. It is clearly seen from Figure 3 that the increase in capture radius results in increasing weight-average degree of polymerization of the system over the whole range of conversions. However, this trend is true only for very small capture radii. For moderate values, starting from l = 10, the average degree of polymerization for the whole system becomes similar to that obtained in the classical limit. Nevertheless, the average size of cycle-containing species is roughly the same as that of the whole system.

Further increase of the capture radius does not affect the overall size of species, but reduces both the fraction of cycle-containing molecules and their size. This is illustrated in Figure 4 where the weight-average degree of polymerization of cycle containing molecules is plotted against conversion for l changing from 100 to 500. As can be seen, the data obtained for large values of l are not very smooth, although each curve was constructed as an average from at least 20 simulation runs. The standard deviations of the calculated values from the average increased with conversion in some cases reaching several tens of percent. For the largest capture radius irregular noise is clearly seen, as is usual in the simulation of small-valued quantities. Since the number of cycle-containing molecules is very small, the random appearance of a large cyclic molecule is clearly visible in the output data-sheet or in the plot. For large capture radii the amounts of cyclic molecules formed become reduced and should go to zero for infinite systems.

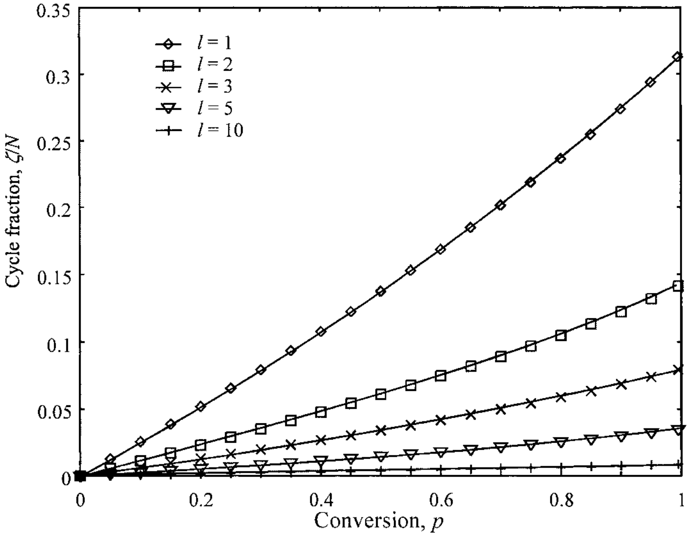


Fig. 5. The reduced contents of cyclic bonds, ζ/N, vs. conversion for various capture radii, l, in long-range percolation experiments. Since any molecule may contain only one cycle, the cycle rank, ζ is equal to the number of cycle-containing molecules.

In order to analyse the changes in cycle content in polymerizing systems at various capture radii, the fraction of links engaged in cycles, ζ/N, is plotted against conversion in Figure 5.

More specifically, ζ is the cycle rank, i.e., the number of links that have to be split to restore the tree-like structure of the system. Since each acyclic molecule contains just one A group, Figure 5 also presents the number of cycle-containing molecules in the system divided by the number of units. The values of ζ/N change with conversion almost linearly and, for given conversion, are highest for $l = 1$. Already for $l = 10$ the fraction of cyclic molecules drops to ca. 1%. Note that the highest value of cycle rank is above $0.3 \cdot 10^6$ for $l = 1$ and $p \to 1$. The largest number-average degree of polymerization of molecules obtained under these conditions is only 3.0. These numbers show how small are the molecules obtained at low capture radius and how suppressed is the growth of polymer in the ordinary (nearest-neighbour) percolation model. One of the reasons is that monomer molecules are not excluded from consideration and are assumed to undergo the cyclization reaction:

$$AB_2 \xrightarrow{2\,k_{1A}k_{1B}} \overset{\frown}{BAB} \qquad (2)$$

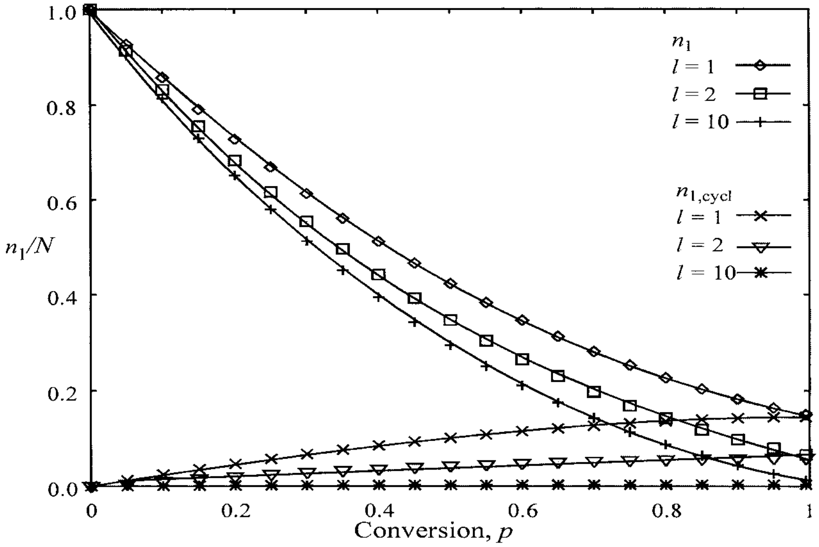


Fig. 6. Fraction of monomer molecules, n_1/N, both in the starting AB_2 form and in the cyclic $\overset{\frown}{BAB}$ form, $n_{1,\mathrm{cycl}}$/N, vs. conversion of **A** groups for different capture radii, l. N is the total number of units in a system.

In Figure 6, the fraction of monomeric units in a system belonging to species of degree of polymerization 1 is plotted against conversion for various capture radii. As can be seen, the number of monomers not having an **A** group available for reaction, $n_{1,cycl}$, is most substantial in the system simulated with the smallest capture radius. These molecules react through the remaining **B** group, but this reaction is less likely than that with bigger molecules. For capture radii $l = 1$ or 2, a significant proportion of the cyclized monomer molecules remain, even at full conversion. The number becomes small for large values of capture radius and for $l \geq 10$ it can be considered negligible.

Conclusions

The results obtained using long-range percolation modelling of AB_2 systems reacting with various substitution effects and large capture radius confirmed our earlier observations concerning changes in the size distributions of hyperbranched polymers.[13] Changes in the reactivity of functional groups seem not to affect the extent of intramolecular cyclization in a system. The proportion of cycle-closing links is relatively small.

Restriction of the reaction area by adjusting the capture radius had a decisive effect on the extent of cyclization. For small capture radii $l \leq 10$ lattice units, the plot of the weight-average degree of polymerization for cycle-containing molecules vs. conversion was almost the same as that for the whole system. This suggests that most of the molecules formed under these conditions (small capture radius) are cycle-containing molecules. Consequently, the average size of molecules present in the systems simulated also decreased with decreasing capture radius.

Since intramolecular reaction within monomer molecules was not excluded, a substantial proportion of cyclized monomer was present after the simulation was completed ($p \to 1$). At the smallest capture radius ($l = 1$) the proportion of these cyclized monomer molecules was as high as ca. 18%.

The proportion of cycle-containing molecules increases nearly linearly with conversion of **A** groups, independently of the magnitude of the capture radius.

Acknowledgments

One of us (JBL) dedicates this work to Maksymilian on the occasion of his zero-th birthday. Financial support of this work by the Polish Committee of Scientific Research (KBN), grants no. 3T09A 069 19 and 4T09B 125 22 is gratefully acknowledged.

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[20] The same ratio was slightly differently defined in refs. 13 and 14. In this work it is twice the value defined there.