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Random homopolymerization of an AB_2 monomer as studied by Monte Carlo methods

Summary — Monte Carlo simulations were carried out to model the molecular size distribution in a hyperbranched polymerization involving a monomer of AB_2 type, where A and B were functional groups reacting with each other only. Three approaches were tested: the off-lattice percolation, classical percolations on square or cubic lattices with adjustable reaction range, and the dynamic lattice liquid (DLL) simulation. The latter was used also to investigate dependence of the average radii of gyration of hyperbranched macromolecules on the conversion.

Key words: AB_2 monomers, hyperbranched homopolymerization, Monte Carlo simulations.

BADANIE METODAMI SYMULACJI MONTE-CARLO PROCESU STATYSTYCZNEJ HOMOPOLIMERYZACJI MONOMERU TYPU AB_2

Streszczenie — Przeprowadzono symulacje Monte Carlo w modelowaniu rozkładu wymiarów (makro)cząsteczek podczas homopolimeryzacji monomeru typu AB_2, gdzie A i B stanowią grupy funkcyjne, które mogą reagować wyłącznie naprzemiennie. Wykorzystano trzy typy przybliżeń: modele bezkratowe, modele perkolacyjne na kracie dwu- i trójwymiarowej z regulowanym zakresem przereagowania oraz modele DLL (*Dynamic Lattice Liquid* = dynamiczna ciecz sieciowa, por. rys. 1 i tabela 1). Na rysunku 2 przedstawiono zmiany liczbowo średnich stopni polimeryzacji (P_n), wraz z rosnącym stopniem przereagowania układu. Metoda DLL pozwoliła na określenie średniego promienia bezwładności (R_g) hiperrozgałęzionych cząsteczek w układzie reakcyjnym. Rysunek 3 ilustruje podwójnie logarytmiczną zależność tego promienia żyracji od P_n. Stwierdzono, że wymiar fraktalny $d_f = 2{,}55$ jest zbliżony do wartości uzyskanych w typowych układach perkolacyjnych ($d_f = 2{,}53$).

Słowa kluczowe: monomer AB_2, homopolimeryzacja hiperrozgałęziona, symulacje Monte Carlo.

Polymerization of AB_{f-1} type (or ARB_{f-1}) monomers (f = 3, 4, ...), with A and B being reactive groups, was studied theoretically by Flory [1] more than half a century ago. By using statistical arguments he derived a function linking the number fraction of molecules of a given polymerization degree with the conversion of majority B groups. Then the interest in hyperbranched polymers practically disappeared, as this type of polymers was found less attractive materials. Only after publicizing and commercializing dendrimers [2] — another kind of highly branched oligomers and polymers — the synthesis of hyperbranched polymers regained its significance as a much simpler and less expensive method of preparing polymers of highly ramified dendritic structure [3]. The hyperbranched polymers are hence considered a cheaper substituent of the regular dendrimers [4—7]. The main advantage of these both groups of polymers is the high content of terminal groups that provide them with certain unique properties and allow for further extensive modification.

At first, the direct synthesis of AB_2-type monomers was extensively studied [8—16]. However, for many applications, the products, particularly those of high molecular weight, had too broad molecular weight distribution. Soon, methods of reducing this dispersity have been proposed. Thus, Hölter and Frey [17] proposed to carry out polymerization of an AB_n monomer (usually with n = 2,3) in the presence of some amount of a B_m type monomer (with, again, m = 2,3) acting as core forming units [18—20]. Certainly, both monomers had to share the same reactive groups.

Another possibility was to use, among others, systems such as $A_n + B_m$ [*e.g.* 21—23], AB_n + AB [24—27]. To reduce the broad molecular size distribution of hyperbranched polymers still further, the polymerization procedure was modified by dividing the total of AB_n monomer into portions and introducing the portions at different stages of polymerization process [28—32].

To model the hyperbranched polymerization, mostly the mean-field approaches were used. These models usu-

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ally disregarded the possibility of intramolecular link formation, *i.e.* formation of cycle-containing molecules. Indeed, in all simulations of hyperbranched polymerization, the amount of cycle-containing molecules was negligible up to a substantial conversion of functional groups. In the simulations on reaction lattices [14, 33], on the other hand, the cycle formation steps were imminent events usually reducing the final polymerization degree in the system [34]. Such a behavior was observed in some experimental systems [35].

In this work we compare the results of modeling the hyperbranched polymerization using different simulation methods, namely the off-lattice, 2D or 3D lattice, and the dynamic liquid lattice (DLL) models.

THE MODELS

The details of chemical structure of monomers and polymer molecules were disregarded in all models. The unit was the elementary structure considered. Its status changed as a result of conversion of its functional (reactive) groups A and B. These groups reacted with each other only. Each reaction step resulted in irreversible formation of a link that reduced the number of molecules in the system by one. The changes in the size distribution of molecules present in the system were monitored as changed with the conversion degree. The reactivity of functional groups (probability of being selected to react) was considered to be constant (no substitution effects were taken into account [*cf.* 8—13]).

Off-Lattice Model

The monomer molecules were placed in a virtual reaction space without defining its size or dimensions. The molecules were dimensionless and had neither coordinates nor specific positions in space. The reaction took place between a pair of groups A and B selected at random from among all these groups available in the system. Physically, the model corresponds to the mean-field classical approach where many collisions between molecules occur before an active collision leading to bond formation can take place.

Lattice (Percolation) Model

The monomer molecules are placed in the vertices of a 2D (square) or 3D (simple cubic) reaction lattice. As in the original percolation model [36], only the functional groups belonging to the neighboring vertices can react with each other. Hence, for lattices of low dimensionality and small coordination number, the number of reaction partners is very limited. In the long range percolation [37], the effect of the steric factor is relaxed. The availability of functional groups is controlled by the range parameter (l) providing access to the shells distant from that of a selected unit [29]. For the simple (classical) percolation, the $l = 1$, since only the units from the first shell are reaction partners for the selected unit. The largest value of l corresponds to the full accessibility to reaction of all functional groups in the lattice. The range parameter is, in some respect, equivalent to the so called capture radius used in some polymerization models [38].

The number of reaction partners of a given unit depends directly on the value of l, and on the type and dimensionality of lattice. For the square lattice the number of nearest neighbors of a unit is 8, whereas for the simple cubic lattice is 26. Generally, the number of neighbors in the simple lattices depends on dimensionality (d) according to the expression $(2l + 1)^d - 1$.

Dynamic Lattice Liquid (DLL) Model

The DLL [39, 40] model bases on a lattice structure with beads representing atoms or small molecules. Positions of beads are regarded as coinciding with lattice sites. The assumption about dense packing of molecules corresponds to considering the system with all lattice sites occupied by (beads) molecules (density factor $\rho = 1$). It is also assumed, that the system has small excess volume, so that each molecule has enough space to vibrate around its equilibrium position defined by its location at the lattice. However, the molecules cannot move freely over a larger distance, because all neighboring lattice sites are occupied by similar elements. Nevertheless, the DLL model ensures conditions for molecular translation over distances exceeding the vibrational range (long range mobility). Each large enough displacement of the molecule from the mean position is considered as an attempt to move to a neighboring lattice site. For simplicity, directions of the attempts are assumed only along the coordination lines, but are independent and randomly distributed among q directions, where q is the lattice coordination number. Only those attempts can be successful, which coincide in such a way that along a path including more than two molecules, the sum of displacements is close to zero (condition of continuity). This results in displacements of beads along self-avoiding closed paths.

The DLL model described above was implemented as a dynamic simulation algorithm for simple liquids in two or three dimensions [41]. Systems of beads on the triangular or face-centered cubic lattice were considered. Generally, it is possible to regard one molecule as represented by two or more beads connected by non-breakable bonds. In this study a single bead represents a substrate or product molecule; only in few cases the product is represented as two connected beads. A field of randomly chosen unit vectors represents motion attempts. These vectors are assigned to beads and point in the directions of attempted motions. An example of such assignment of attempted directions of motion is shown in Fig. 1, for a system representing a liquid on the triangular lattice.

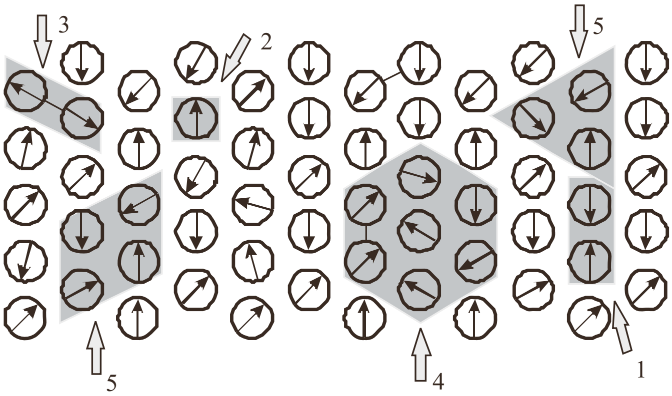
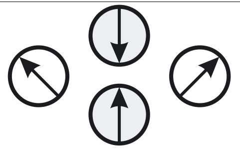
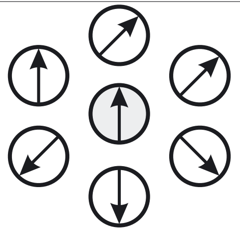
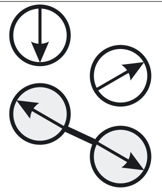
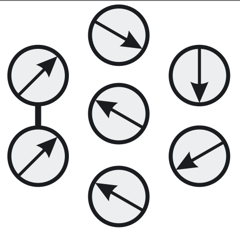
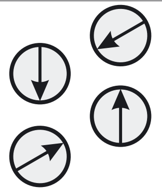


Fig. 1. An illustration of the vector field representing attempts of molecular displacements towards neighboring sites in the DLL model; numbers 1—5 correspond to variants of movement from Table 1

All beads which do not contribute to correlated sequences (circuits) are immobilized. This occurs in cases 1—4 illustrated in Table 1.

T a b l e 1. Special cases of movement toward neighboring lattice sites

	Variant of movement	Description
1.		Two neighbouring beads try to move in opposite directions
2.		An attempt of motion starts from a lattice site towards which no other beads are attempting to move, at the same time
3.		Attempted move would lead to a bond breaking
4.		Particle would jump through a bond
5.		Cooperative rearrangement along a closed loop

After setting to zero all vectors giving failed attempts, only these vectors remain that contribute to the closed loops. They constitute traces for the possible rearrangements (case 5 in Table 1). For an athermal system, all possible rearrangements are performed by shifting beads along the closed loop traces, each bead to a neighboring lattice site. Thus, the following steps can be distinguished: a) random generation of the vector field representing attempts of movement, b) elimination of non-successful attempts and c) replacing beads within closed loop paths.

Molecular systems treated this way can be regarded as provided with the dynamics consisting of local vibrations and occasional diffusion steps resulting from coincidence of attempts by the neighboring elements to displace beyond the occupied positions. Within a longer time interval, this kind of dynamics leads to displacements of individual beads along the random walk trajectories with steps distributed randomly in time.

RESULTS AND DISCUSSION

The results of the off-lattice percolation and DLL simulations representing a model hyperbranched polymerization are compared to each other. All simulations were started with 10^6 molecules of an AB_2 monomer.

The conversion dependence of the number-average polymerization degrees calculated in simulations of one-pot systems is shown in Fig. 2. In order to avoid an overlap of curves, the changes in P_n obtained by percolation are shown for the whole system only. For other simu-

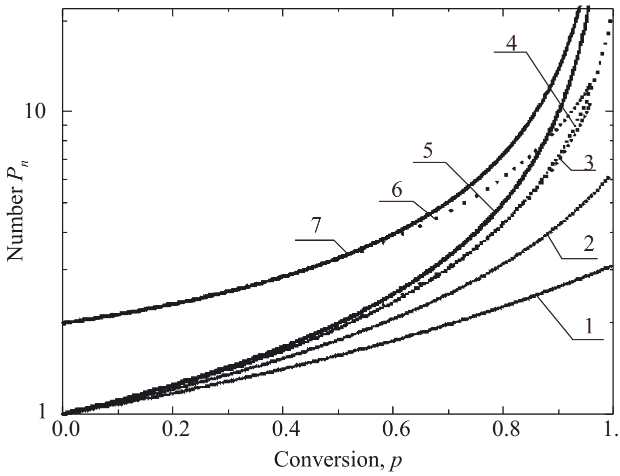


Fig. 2. The conversion dependence of the number average polymerization degree (P_n) in polymerization of an AB_2 monomer. The curves represent the calculated moments of distribution obtained by using the off-lattice model (uncorrected and corrected: curves 5 and 7, respectively), percolation on 2D square lattice (uncorrected moments: curve 1), percolation on 3D cubic lattice (uncorrected moments: curve 2), percolation on 3D cubic lattice with the range parameter equal 2 (uncorrected moments: curve 4), DLL simulations (uncorrected and corrected moments: curves 3 and 6, respectively)

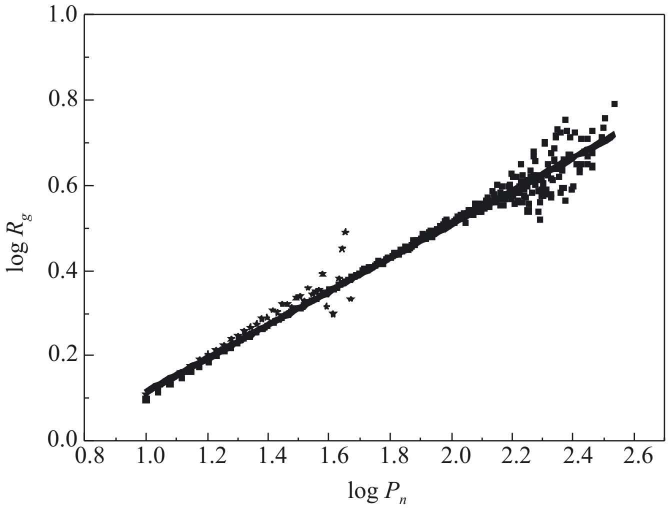


Fig. 3. The average radii of gyration (R_g) versus polymerization degree (P_n) of hyperbranched polymers, obtained in DLL simulation at the conversion degree of AB_2 monomer: $p = 0.6$ (∗) and 0.95 (■), linear fit (–) at $p = 0.95$

lations, corrected average polymerization degrees ($P_{n,corr}$) are shown in Fig. 2, for illustration, along with the values for the whole system (P_n). The corrected values were obtained by subtracting the contributions from unreacted monomer. The reason was that in real experiments (to be described in a forthcoming paper), the polymer isolation step made the smallest molecules, mostly monomer, lost in the isolation procedure. Furthermore, the detectors used in evaluation of molecular weight are the least sensitive towards the smallest molecules. Hence, the results of direct measuring the averages of polymerization degrees led to overestimations.

As expected, the moments of molecular size distribution calculated with the percolation method with the range parameter limited to one, as in the original simple percolation (curves 1 and 2 for 2D and 3D percolations, respectively), depart from those evaluated by other simulation methods. Substrate availability limited to the units from the closest neighborhood results in a reduction of the average size of molecules as compared to other simulations. Formation of a molecule of even a moderate size in the vicinity of another one, reduces or even halts altogether the chance of growing the latter. The lack of reaction partners in the vicinity of a unit leads to formation of cyclic molecules [14, 29]. In the percolation simulation applied to hyperbranched polymerization, the availability of reactive groups for reaction seemed much more limited than in crosslinking homopolymerization of an A_n monomer. The neighbor-neighbor percolation models seem to be suitable only for rapidly reacting systems with a diffusion controlled mechanism.

An increase in the availability of reaction substrates in the percolation models, by extending the range of finding a partner for reaction beyond the nearest neighbor shell, very quickly makes the results of modeling coincident with those obtained by classical methods (curve 4). When the range parameter reaches 5 or more, the moments calculated with the percolation method become identical with those obtained by classical calculations within the range of calculation accuracy.

Interesting are the new results of modeling, obtained by applying the dynamic liquid lattice (DLL) method (curves 3 and 6). The resulting moments are close to those obtained from 3D percolation on a cubic lattice with the range parameter equal to 2 (curve 4). This means that DLL model is only slightly less affected by the diffusion control of polymerization as compared to the simple percolation model. The reason is that although the monomer molecules have limited mobility, they can move around their average positions.

The advantage of the DLL model over the other procedures used in this work is that it provides the average dimensions of the hyperbranched molecules. In evaluating the radii of gyration of the simulated polymer particles, the data were used for the system generated at certain conversion levels, namely at $p = 0.6$ and 0.95. The results are presented in Fig. 3 which is the double-logarithmic plot of the radius of gyration *vs*. the polymerization degree. The solid line is the regression line for the points collected at $p = 0.95$. Each point in the plot is the average value from 5 simulation runs. Most of the points deviating from the trend line correspond to the average dimensions of molecules that are scarcely represented in the whole population. Hence, for the system with $p = 0.6$ one can see the points (stars) deviating from the regression line at log (P_n) of about 1.6 representing molecules of polymerization degree above 35. Only very few molecules of that size are present in the system at that conversion. Similar situation occurs in the case of the system with $p = 0.95$ (dots) for log $P_n > 2,3$ ($P_n > 160$).

The slope of the line in Fig. 3 defines the reciprocal of fractal dimension d_f of the hyperbranched molecules. The result obtained in this work ($d_f = 2.55$) well corresponds to the value obtained in other percolation experiments ($d_f = 2.53$) [42].

The straight line shown in Fig. 3 contradicts the recent finding that highly branched polymers have no fractal dimension and log (R_g) is proportional to log[log (P_n)] rather than to log (P_n) [43].

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