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Monte-Carlo simulation of random hyperbranched polymers with flexible branches

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Monte-Carlo simulation of random hyperbranched polymers with flexible branches was conducted. It was shown that such polymers demonstrate universal conformational properties. In particular, there exist a critical hyperbranched polymer generation number $G_{cr} \approx 6$ at which the transfer occurs from coil-type structure with scaling properties similar to those of linear polymer coil to fractal structure. The fractal dimension $d_{fr} \approx 3$ is universal independently on details of random hyperbranched polymer internal building. It is shown that system entropy is of Tsallis type.

Обсуждаются результаты компьютерного моделирования методом Монте-Карло гиперразветвлённых полимеров со случайным ветвлением с гибкими ветвями. Показано, что такие дендримеры демонстрируют универсальное поведение независимо от деталей их внутреннего строения. Так, существует критический номер поколения $G_{cr} \approx 6$, при котором происходит переход от структуры типа клубок со свойствами, подобными свойствам линейных полимеров, к фрактальной структуре. Фрактальная размерность $d_{fr} \approx 3$ является универсальной величиной независимо от деталей внутреннего строения гиперразветвлённого полимера. Показано, что энтропия системы имеет форму Цалеса.

Recently, highly branched dendritic macromolecules have attracted much interest due to their structural characteristics. Dendritic macromolecules can be classified into two types: one is a monodisperse macromolecule with well defined and defect-free structure, a so-called dendrimer, and the other one is a polydisperse macromolecule with imperfect structure, a so-called hyperbranched polymer. Since dendrimers are costly and due to many synthetic steps the rapid preparation of a large amount of polymers is not possible. Hyperbranched polymers show structural characteristics of dendrimers such as low viscosity and high functionality and can be prepared in a much simpler way (one-pot polymerization) compared to the synthesis of dendrimers (see, e.g. [1–4]).

Such structures combine properties of linear polymers and solid particles, which makes them unusual nanoobjects. Number of branches in such molecules grows exponentially with generation number, that makes them compact particles with low interpenetrability. At the same time, hyperbranched polymers possess typical traits of polymers, such as ability to change their shape in dependence of environment properties. All this makes researching hyperbranched polymers an important part of molecular nanoscience with highly promising applications in nanomedicine, creation of high quality surfaces, liquid crystal screens etc (see e.g.[1–4]).

Present work is dedicated to the computer modeling of random hyperbranched polymers. Random hyperbranched polymer is a polymer, each repeat unit of which can become branching point with equal probability. Schematic representation of random hyperbranched polymer with degree of branching equal to 2 is given in Fig. 1. The properties of random hyperbranched poly-

mers have been studied theoretically and via computer simulation since first works of Flory [5, 6]. Flory established universal scaling low for the molecular weight distribution of hyperbranched polymers [5, 6]. However, the drawback of this theory consists in the assumption that there are no excluded volume interactions. In reality, however, excluded volume interactions that lead to fluctuation effects can not be neglected in 3D case. This has been demonstrated via computer simulation by Cameron [7–8] and shown theoretically as well as via computer simulations by Buzza [9, 10]. Both theoretical studies [9] and simulation results [10] predicted, in particular, that the fractal dimension of hyperbranched polymer chains in the reaction melt equals to 3 that is significantly different from the mean-field result $d_{fr} = 4$ and the percolation result $d_{fr} = 2.53$ [9, 10]. It was also found that molecular weight distribution of random hyperbranched polymers has a universal form that does not depend on degree of branching and is different from that found via mean-field approximation [5, 6].

Since Flory's works [5, 6], most of the studies employed the mean-field method [11–21], where excluded volume interactions are taken into account in spatially-averaged way via introducing mean field and fluctuations are neglected. In these works statistical properties of hyperbranched polymers in melt such as the molecular weight distribution and fractal structure were studied. However, the applicability of these results is limited due to the fact that they neglect excluded volume interactions, as it was shown in [7–10].

Besides mentioned works [7–10], there have been a few theoretical and simulation studies of random branching in hyperbranched systems where excluded volume interactions effects have also been included. Galina et al. [22] have performed a Monte Carlo simulation of a 2D percolation type model with a variable capture radius to mimic the effects of diffusion. However, Buzza [9] has shown that in the non-mean-field regime the large-scale properties of hyperbranched polymers depend critically on spatial dimension. Thus, theoretical and simulation studies performed in [7–10] are more experimentally relevant.

The principal difference of the present work from the previous computer simulation studies of random hyperbranched polymers is that the average number spacers per branch $<M>$ is taken quite large (up to 60) and, simultaneously, excluded volume interactions are taken into account. To the best author's knowledge, in all previous works on computer simulations of random hyperbranched polymers the branch length was restricted to several (up to seven) spacers. In theoretical works [5, 6, 18, 19] hyperbranched polymers with long branches were considered, however excluded volume interactions were not taking into account [5, 6] or accounted for via mean-field approximation that rendered the results non-realistic, as it was shown in [7–10].

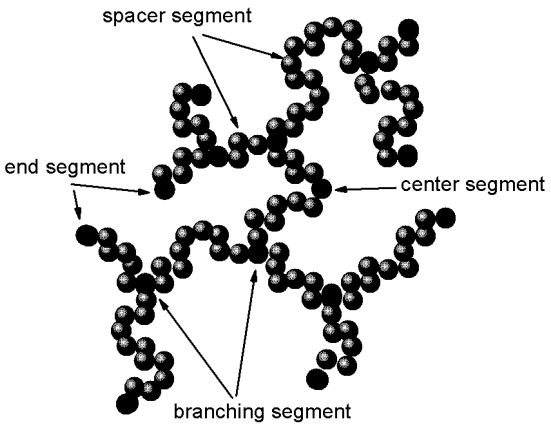

Fig. 1. Schematic representation of third generation hyperbranched polymer with random branching.

However, only considering hyperbranched polymers with long flexible branches that include many spacers allows to obtain universal scaling properties, that characterize individual polymer, not a polymer melt as a whole, in a way similar to linear polymers (see e.g. [23]). Thus, considering random hyperbranched polymers with long flexible branches, and, simultaneously, taking into account excluded volume interactions allowed to find polymer density profiles and dependence of polymer size on generation number as well as fractal dimension of individual polymer in solvent, not of polymer melt. All these characteristics at large enough average number of spacers per branch $<M>$ accept universal form not depending on the details of polymer building. These results, described in details below, are new as compared to the previous works.

The purpose of the present work is finding via computer simulation universal scaling laws, describing conformational properties of random hyperbranched polymers. For this purpose, hyperbranched polymers with long flexible branches are modeled by Monte-Carlo method via random walks on

3-dimensional cubic lattice. Simulation relates to hyperbranched polymers in solvent, where repulsive part of interaction potential between non-connected spacers much exceeds the attractive part. The details of the method, applied for modeling dendrimers are described in the work of the author [24]. The average number of spacers per branch $<M>$ was varied from 20 to 60, and generation number G taken from 1 to 9.

In the present model, each spacer of model hyperbranched polymer represents part of molecular chain of real hyperbranched polymer longer then so-called persistent length, at which correlation between orientations of periodic molecular units, constituing each branch, vanishes. The end of each spacer can became a bifurcation point with equal probability p. The average number of spacers per brunch $<M> = 1/p$. In the present work only $p << 1$ are considered that corresponds to long flexible polymer branches with $<M> > 1$. The total number of consecutive branchings of a polymer is called hyperbranched polymer generation. All branches, that are separated by the same Q number of branching points from the central spacer form Qth shell of polymer.

The number of hyprbranched polymer spacers grows exponentially with generation number, while hyperbranched polymer size increases much slower, and, as a consequence some of branches can get stack and stop growing. However, in the present work only such hyperbranched molecules are considered, where number of bifurcations separating each end point, where polymer growth is terminated, from the central node is the same. In other words all endpoints belong to the same shell. This type of random hyperbranched polymers is the most interesting from the application point of view due to compact structure and large number of end segments, which can be modified according to various practical needs [1–4].

Computational difficulties connected with peculiarities of hyperbranched polymer topology, were overcome via building structures with highly extended inner branches that allowed more space for the growth of exponentially larger number of outer ones. From all possible randomly built branches, consisting of M spacers, and belonging to the shell Q, are selected those with the length larger or equal to $L(M,Q)$. ($L(M,Q)$ is the parameter of the problem over which system entropy should be optimized). For this purpose, a number n_{tries} of random attempts should be made (some of these attempts are unsuccessful because the obtained branch is not of the right length or its growth is prohibited by other branches).

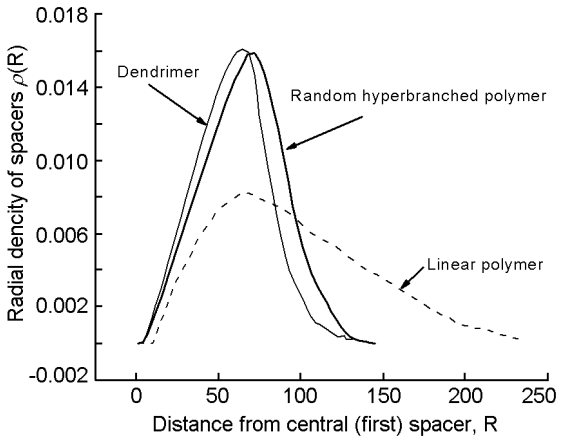

Fig. 2. Radial density $c(R)$ of spacers for random hyperbranched polymer (bold line), dendrimer (thin line) and linear polymer (dashed line).

After j-th structure is built, the probability $p_j(G)$ to obtain the same structure as a result of unbiased random growth ($L(M,Q)\equiv 0$), can be estimated as

$$p_j(G) \equiv p_j\{L(M,Q)\} = \left[Z(G) \prod_{\substack{\text{all branches} \\ \text{of the } j\text{th structure}}} n_{tries} \right]^{-1} \quad (Q = 1,2...G), \tag{1}$$

where

$$Z(G) = \sum_{\text{all structures}} \left[\prod_{\text{all branches}} n_{tries} \right]^{-1} \tag{2}$$

(2)

is the statistical sum of the system.

System entropy $S(G)$ was calculated according to Shannon-Gibbs formula as

$$S(G) = -\sum_{\text{all structures}} p_j(G) \ln[p_j(G)], \tag{3}$$

where p_j are calculated according to Eqs.(1), (2). System entropy $S(G)$ was maximized over parameter $L(<M>,Q)$ ($<M> = 30, 35,...60$, $Q = 1,2...G$)) so that most probable conformations of the system were found. The results were averaged with account of probabilities $p_i(G)$ over more then 10^4 conformations for each hyperbranched polymer generation. The dependence of system size R (equal to average distance from polymer spacers to the central one) on hyperbranched polymer generation G is presented

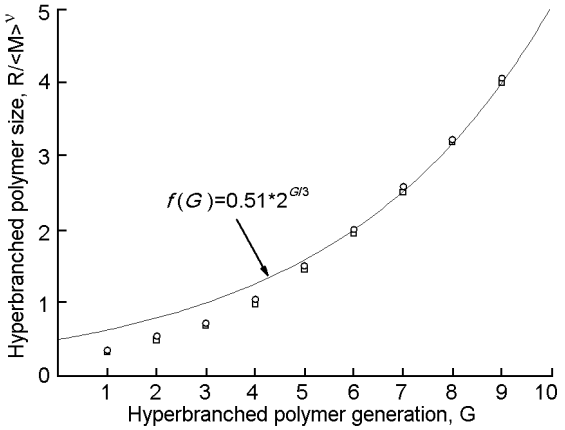

Fig. 3. Dependence $R(G)$ of random hyperbranched polymer size on its generation for $<M>$ = 60 (squares) and approximating function $f(G) = 6.9 \cdot 2^{G/3}$.

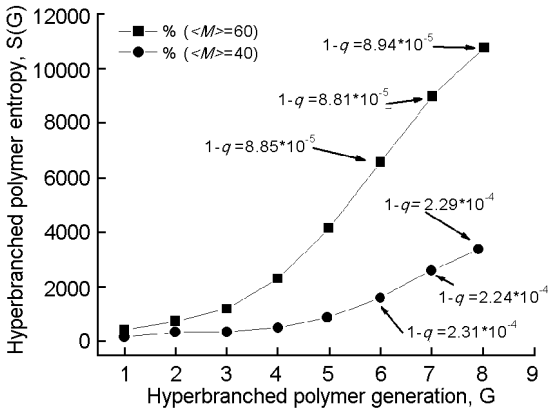

Fig. 4. Dependences $S(G)$ of random hyperbranched polymer entropy on its generation for average branch length $<M>$ = 40 (circles) and $<M>$ = 60 (squares); arrows show the values of Tsallis parameter $1-q$, calculated according to Eq. 4.

in Fig. 3 for various $<M>$. For $G > 6$ and $<M> > 40$ it takes universal form

$$R(G) \sim <M>^{\nu} 2^{G/3}, \quad \nu = 0.6. \qquad (4)$$

The fractal dimension d_{fr} of hyperbranched polymers is found to be equal to 3, which is in excellent agreement with the hyperscaling prediction [9]. Let us note, that fractal dimension $d_{fr} = 3$ of random hypebranched polymers is larger than that of dendrimers ($d_{fr} \approx 2.57$ [24]). Evidently, random branching allows a more compact organization of hyperbranched molecule due to existence of a small fraction of very long branches.

Examples of radial spacer density profiles for random hyperbranched polymers, dendrimers and linear polymers with the same number of spacers are presented in Fig. 2. It can be seen from the figure that hyperbranched polymer is essentially more compact system than linear polymer in a coil state. It was shown that such polymers have filled core. At long enough branches ($<M> > 35$) the density profiles take universal shape that does not depend on $<M>$ and G. *Dependence of system entropy* $S(G)$ (calculated according to Eq. 3) on generation number G is shown in Fig. 4 for various $<M>$. Simulation results demonstrated that, for polymer generations $G > 6$, this dependence is well approximated by recursive formula

$$S(G) = 2S(G-1) - (1-q)S(G-1)^2 \qquad (5)$$

with relative error less than 2 %. (Here $1-q \approx 2.24 \cdot 10^{-4}$ for $<M> = 40$, $1-q \approx 8.85 \cdot 10^{-5}$ for $<M> = 60$). Such form of dependence $S(G)$ is evidently determined by the fractal properties of hyperbranched macromolecules. It can be seen from Fig. 1, that each hyperbranched polymer H_G of generation G with entropy $S(G)$ consists of two hyperbranched polymers H_{G-1} of generation $G-1$ that are connected to each other by a single branch. Thus, entropy $S(G)$ of polymer H_G consists of the sum of entropies of its parts (polymers H_{G-1}) with the subtraction of the term, corresponding to their interaction. The closer is value of q in Eq. 4 to unity, the smaller is interaction between sub-polymers H_{G-1}.

Eq. (4) is a particular case of Tsallis form of entropy [25] a system under investigation consists of two equivalent subsystems. It should be noted that, although parameter $(1-q)$ is much smaller than unity, the non-additive term makes significant contribution to the total system entropy.

Thus, it was shown in the present work that random hyperbranched polymers with long enough branches demonstrate universal scaling properties. In particular, there exist a critical hyperbranched polymer generation number $G_{cr} \approx 6$ at which the transfer occurs from coil-type structure with scaling properties similar to those of linear polymer coil to fractal structure. It was shown that such polymers have filled core. At long enough branches ($<M> > 35$) the density profiles take universal shape that does not depend on $<M>$ and $<G>$. The fractal dimension $d_{fr} \approx 3$ is universal independently

on details of random hyperbranched polymer internal building. It was shown that system entropy is of Tsallis type.

The result that random hyperbranched polymers with long flexible branches possess filled core (terminal spacers reach polymer center) qualitatively agree with theoretical predictions [18, 19], that takes into account excluded volume interactions via mean-field approximation and contradicts to theoretical works [5, 6] that do not take into account excluded volume interactions at all. However, found in the present work fractal dimension $d_{fr} \approx 3$ differs from mean field predictions [17, 18] that give $d_{fr} \approx 4$. This fact is, evidently, due to the limited applicability of the mean field method to random hyperbranched polymers, shown in the works [7–10].

References

1. S.Sheiko, M.Moller, Hyperbranched Macromolecules: Soft Particles with Adjustable Shape and Persistent Motion Capability S. Topics in Current Chemistry, **212**, Springer-Verlag Berlin Heidelberg (2001).
2. G.R.Newkome, C.N.Moorefield, F.Vogtle, Dendritic Molecules: Concepts, Syntheses, Perspectives, VCH, Weinheim (1996).
3. D.A.Tomalia, A.M.Naylor, W.A.Goddard III Angew, *Chem.,Int. Ed. Engl.*, **29**, 138 (1990).
4. O.A.Matthews, A.N.Shipway, J.F.Stoddart, *Prog. Polym. Sci.*, **23**, 1 (1998).
5. P.J.Flory, *J.Am. Chem. Soc.*, **74**, 2718 (1952).
6. P.J.Flory, Principles of Polymer Chemistry; Cornell University Press, Ithaca, NY (1953).
7. C.Cameron, A.H.Fawcett, C.R.Hetherington et al., *J. Chem. Phys.*, **108**, 8235 (1998).
8. C.Cameron, A.H.Fawcett, C.R.Hetherington et al., *Macromolecules*, **33**, 6551 (2000).
9. D.M.A.Buzza, *Eur. Phys. J. E*, **13**, 79 (2004).
10. E.L.Richards, D.M.A.Buzza, G.R.Davies, *Macromolecules*, **40**, 2210 (2007).
11. Y.Beginn, C.Drohmann, M.Moller, *Macromolecules*, **30**, 4112 (1997).
12. A.H.E.Muller, D.Yan, M.Wulkow, *Macromolecules*, **30**, 7015 (1997).
13. D.Yan, A.H.E.Muller, K.Matyjaszewski, *Macromolecules*, **30**, 7024 (1997).
14. D.Holter, A.Burgath, H.Frey, *Acta Polym.*, **48**, 30 (1997).
15. D.Holter, H.Frey, *Acta Polym.*, **48**, 298 (1997).
16. W.Radke, G.Litvinienko, A.H.E.Muller, *Macromolecules*, **31**,145 **(1998).**
17. D.Yan, Z.Zhou, A.H.E.Muller, *Macromolecules*, **32**, 245 (1999).
18. D.Yan, Z.Zhou, *Macromolecules*, **32**, 8194 (1999).
19. D.Schmaljohann, J.G.Barrat, H.Komber et al., *Macromolecules*, **33**, 6284 (2000).
20. Z.Zhou, D.Yan, *Polymer*, **41**, 4549 (2000).
21. S.Unala, C.Oguzb, E.Yilgorc et al., *Polymer*, **46**, 4533 (2005).
22. H.Galina, J.Lechowicz, M.Walczak, *Macromolecules*, **35**, 3253 (2002).
23. A.Yu.Grosberg, A.V.Khohlov, Statistical Physics of Macromolecules, Moscow, Nauka (1989) [in Russian].
24. M.Ratner, *Functional Materials*, **14**, 171 (2007).
25. A.Plastino, A.R.Plastino, *Brazilian J. Phys.*, **29**, 50 (1999).

Моделювання методом Монте-Карло гіперрозгалужених полімерів з гнучкими сегментами

М.Ратнер

Обговорюються результати комп'ютерного моделювання методом Монте-Карло гіперрозгалужених полімерів із випадковим розгалуженням з гнучкими гілками. Показано, що такі дендримери демонструють універсальну поведінку незалежно від деталей внутрішньої будови. Так, існує критичний номер покоління $G_{cr} \approx 6$, за якого відбувається перехід від ланцюгового типу структури з властивостями, подібними до лінійних полімерів, до фрактальної структури. Фрактальна розмірність $d_{fr} \approx 3$ є універсальною величиною незалежно від деталей внутрішньої будови гіперрозгалуженого полімера. Показано, що ентропія системи має Цалісовську форму.