

## Nanocontainer properties of flexible dendrimers

*M.Ratner*

Institute for Single Crystals, STC "Institute for Single Crystals",  
National Academy of Sciences of Ukraine,  
60 Lenin Ave., 61001 Kharkiv, Ukraine

*Received June 19, 2008*

Monte-Carlo simulation of solvophobic interactions of flexible dendrimers with small molecules was conducted. It was shown that universal scaling properties of such dendrimers apply also to the case of interaction with small molecules. The dependence of conformational entropy on molecule size was found.

Проведено моделювання методом Монте-Карло взаємодіяння дендримерів з гнучкими гілками з невеликими молекулами. Показано, що властивості масштабної інваріантності дендримерів проявляються і в цьому випадку. Знайдено залежність конфігураційної ентропії від розміра молекули.

Dendrimers are hyperbranched macromolecules that combine properties of 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 dendrimers possess typical traits of polymers, such as ability to change their shape in dependence of environment properties. All this makes researching dendrimers 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]). A considerable number of researches were dedicated to computer simulations of dendrimers (see e.g.[1-4]). However length of dendrimer branches of the researched structures was restricted to several (up to seven) spacers. Such dendrimers demonstrated dependence of their properties on the details of concrete model. The origin of such dependence lies, evidently, in dendrimer topology: the number of spacers grows exponentially with dendrimer generation, while dendrimer size increases much slower. Thus, as dendrimer

generation grows, dendrimer quickly becomes very rigid system, whose properties strongly depend on details of its structure.

In [5] of the author, the search of the universal scaling law was conducted for dendrimers with large enough number of spacers per branch (i.e. for flexible dendrimers). Such dendrimers can adjust to high spacer density by stretching their branches which at low generation are in entangled "coil" state, similar to that of linear polymer chains.

It was shown [5], that such dendrimers demonstrate universal conformational properties. In particular, there exist critical dendrimer generation number  $G_{cr} \approx 4$  at which the transfer occurs from coil-type structure with scaling properties similar to those of linear polymer coil to fractal structure with fractal dimension  $D_{fr} \approx 2.56$ .

Both critical generation number  $G_{cr} \approx 4$  and fractal dimension  $D_{fr} \approx 2.56$  are universal values, independent on details of dendrimer internal building. Dendrimer size  $R$  depends on its generation number  $G$  as  $(MG)^v$  at  $G < G_{cr}$  and  $(MG_{cr})^v 2^{(G-G_{cr})/D_{fr}}$  at  $G > G_{cr}$  (here  $M$  is the number of periodic

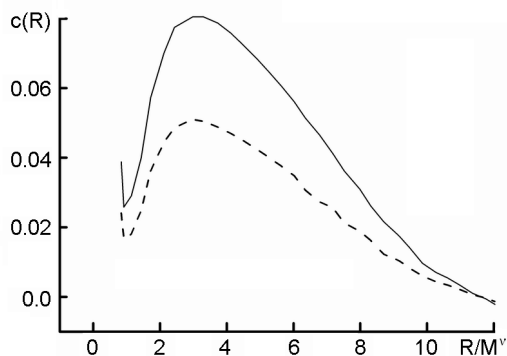


Fig.1. Dependences of dendrimer nodes concentration  $c$  on normalized distance from central node  $R/M^v$  (solid line relates to  $M=60$ , dashed one to  $M=40$ ).

units in the model dendrimer branch,  $v \cong 0.6$  is critical index for linear polymer chain. The periodic unit length is taken equal to unity).

The purpose of the present work is computer simulation of solvophobic interactions of flexible dendrimers with small molecules. An example of concentration distribution of dendrimer nodes is presented in Fig.1. As it follows from [5], fractal structure of dendrimers leads to the fact that concentration distribution of dendrimer nodes is not spherically symmetrical, but rather forms islands and cavities. Such structure can facilitate formation of the complexes of dendrimers with small particles. In the present work such dendrimers are modeled by Monte-Carlo method via random walks on 3-dimensional cubic lattice. The details of the simulation are described in [5] of the author. The number of spacers per branch  $M$  was varied from 20 to 60, and generation number  $G$  taken from 1 to 9. Computational difficulties were overcome via building dendrimers with highly extended inner branches that allowed more space for the growth of exponentially larger number of outer ones.

Small molecules, interacting with dendrimer were modelled as solid spheres, that can not be penetrated by dendrimer nodes. For all molecule sizes, an equal number of attempts to grow dendrimer in a random way, starting from the central node, was made. The statistical weight  $W$  of the dendrimer, interacting with a small particle of given radius  $L$ , was assumed to be proportional to the number  $N_{structures}$  of dendrimers, successfully grown up to maximal

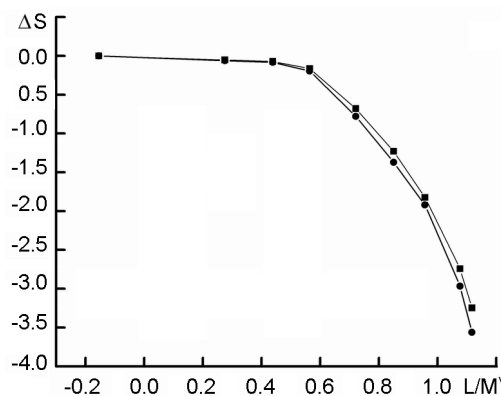


Fig.2. Dependences of configurational entropy of dendrimer on normalized radius  $L/M^v$  of the molecule, placed at distance  $R/M^v = 2.5$  from the central node; (squares relate to  $M=60$ , circles to  $M=40$ ).

(9th) generation. The configurational entropy  $S(L)$  of such system thus is

$$S = \ln(N_{structures}) \quad (1)$$

The results were averaged over 1000 conformations for each dendrimer generation. Simulation conducted in the present work relates to dendrimers in solvent, where repulsive part of interaction potential between non-connected spacers much exceeds the attractive part.

The example of the calculated dependence of conformational entropy on molecule radius  $L$  is given in Fig.2. This dependence was found to be independent both on number of spacers per branch  $M$  and on dendrimer generation  $G$  (at  $M > 30$ ,  $G > 4$ ).

As it can be seen from Fig.2, conformational entropy starts decrease sharply at molecule radius

$$L_{cr} \approx 0.6M^v \quad (2)$$

Entropy decrease at  $L > L_{cr}$  is accompanied by growth of dendrimer size, while at  $L < L_{cr}$  dendrimer size practically does not change with  $L$ . This allows to suppose that at  $L < L_{cr}$  small molecule fits into cavities formed due to fractal structure of dendrimer. Thus, universal scaling properties of dendrimers with flexible branches apply also to the case of interaction with small molecules.

One can roughly estimate attractive energy dendrimer and small particle required to form stable complex as  $T(S(L) - S(0))$ , where  $T$  is system temperature,  $S(L)$  is configurational entropy, defined above. As it

can be seen from Fig.2, the characteristic energy of hydrophobic interactions of about thousand Kelvins provides formation of stable complexes with particles with sizes smaller than  $L_{cr}$ , defined by Eq.2. Thus fractal structure of dendrimers facilitates formation of complexes with small particles making them perspective materials for nanocontainer applications.

### References

1. B.Klajnert, M. Bryszewska, *Acta Biochemica Polonica*, **48**, 199 (2001).
2. D.A.Tomalia, J.M.J.Frechet, *Dendrimers and Other Dendritic Polymers*, Wiley, Chichester (2002).
3. I. O. Goltze, C. N.Likos, *Macromolecules*, **36**, 8189 (2003).
4. A.N.Rissanou, I.G.Economou, A.Z.Panagiotopoulos, *Macromolecules*, **39**, 6298 (2006).
5. M.Ratner, *J. Theor. and Computat. Nanoscience*, **5**, 2284 (2008).

## Наноконтейнерні властивості дендримерів з гнучкими гілками

*М.Ратнер*

Проведено моделювання методом Монте-Карло взаємодії дендримерів з гнучкими гілками з невеликими молекулами у розчиннику. Показано, що масштабна інваріантність дендримерів має місце і в такому випадку. Знайдено залежність конфігураційної ентропії від розміру молекули.