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Computer simulation of intramolecular mobility of dendrimers

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Structure and intramolecular mobility of a carbosilane dendrimer of the 5th generation has been analysed in a wide temperature range by molecular dynamics. It is shown that in a "poor" solvent, the frequency of conformational transitions, f_{rot}, is independent on the conformer position in the macromolecule with the exception of chain end fragments. For the latter, the frequency was 2-3 times higher at all temperatures. In a "good" solvent, f_{rot} uniformly increases with a conformer distance from the centre of the molecule. Intramolecular diffusion of chain ends was highly temperature dependent. This allowed to suggest the existence of "liquid-like" and "glassy" states of individual dendrimer molecules.

1. INTRODUCTION

Dendrimers - regular high-branched dendritic polymer structures - have been actively studied because of their unique chemical and physical properties (see reviews [1-5]). The main attention in both real and numerical experiments has been paid to such properties as melt and intrinsic viscosity, glass transition, solubility, adsorption on a macroscopic surface as well as dendrimer space structure (size and intramolecular density distribution).

A smaller number of works is dedicated to the intramolecular mobility of dendrimers, which ought to be qualitatively different from both mobility of linear or star polymers and mobility in polymer networks due to the structure of dendrimer molecules with many chain ends. The available experimental data are scarce; two papers on NMR spectroscopy [6,7] and a recent paper on thermomechanical analysis [8] can be mentioned. Theoretical analysis of dendrimer mobility is in its initial stage now. It was performed only in the approximations of Rouse [9] and Rouse-Zimm [10] models.

Earlier we used molecular dynamics (MD) simulations to investigate the effect of branching and molecular sizes on the structure of carbosilane dendrimers consisting of silicon (Si) branching sites connected by propyl spacers and containing methyl end groups [4,11,12]. Our interest for carbosilane dendrimers is encouraged by the versatility of organosilicon chemistry that makes it possible to synthesise molecules with different degrees of branching and end

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groups [13,14]. These compounds, consequently, have a wide range of potential applications [15-17].

In References [4,11,12], calculations have been performed for molecules of a maximum degree of branching (core functionality, $f_c = 4$ and branch junction multiplicity, $f = 3$) and for two less branched dendrimers ($f_c = 4$, $f = 2$ and $f_c = 3$, $f = 2$). It is shown that from the 3rd generation for the maximum-branched dendrimer and from the 5th generation for two other dendrimers, the systems consist of molecular particles of a rather spherical shape, relatively dense central region and more loose periphery. In a "poor" solvent, the dendrimers form dense globules. In a "good" solvent, the radius of gyration of dendrimers increases by 30%, and their average density is two times lower. End fragments are located mainly on the surface of molecules, but a number of them is distributed over the whole inner region of the dendrimer that can essentially influence the rate of chemical reactions involving these fragments. Thus, an analysis of the intramolecular mobility of end fragments is of special interest.

In this study, MD simulations are used for analysing in detail intramolecular mobility of carbosilane dendrimers of the 5th generation, C_{94}^{144} (Me) according to the terminology of [8,13]. Main attention is paid to the conformational mobility of the polymer since it is the mobility which is responsible for large-scale intramolecular rearrangements. Some preliminary results have been published earlier [17].

2. MOLECULAR MODEL AND METHOD OF SIMULATION

The carbosilane dendrimer studied has core functionality, $f_c = 3$ and branch junction multiplicity $f = 2$, it comprises 94 Si atoms (including 48 Si atoms in terminal groups) and has a molecular weight of 9373 a.e. (Figure 1). Methyl and methylene groups have been considered as united atoms in the mass point approximation.

The DREIDING force field [18] comprising potential terms of stretching, bending, torsion and van der Waals interactions has been used. Van der Waals interactions, U_{VW} are determined by a modified Lennard-Jones (6-12) potential with a finite radius of interaction, r_c,

$$U_{VW}(r_{ij}) = \begin{cases} U_{LJ}(r_{ij}) - U_{LJ}(r_c), & r_{ij} < r_c, \\ 0, & r_{ij} \geq r_c, \end{cases} \qquad (1)$$

where r_{ij} is the distance between ith and jth atoms, r_c being the cut-off distance. Two extreme cases concerning solvent quality have been considered depending on the r_c value. For a "good" solvent, r_c is equal to the distance of minimum U_{VW} (r) ($r_c = r_{min}$) and the resulting potential is only repulsive. By increasing r_c up to 2.5 r_{min}, the attractive term was taken into account as well. The absence of implicit solvent atoms in the model effectively represented "poor" solvent conditions.

Standard MD techniques [19,20] and the method of Berendsen et al. [21,22] have been applied for the relaxation processes and simulation of dendritic structures at constant temperature. Depending on temperature, the elementary integration time step was in the range

of 0.0005 ps - 0.001 ps. Special measures have been taken to preserve the system from rotation and translation motions.

Initial dendrimer structure should be prescribed to start MD simulations. The construction of these configurations is one of the basic problems in the computer simulation of dense polymer systems. The configurations should have correct valent lengths and valent angles, and the atoms should not overlap. Furthermore, they should be representative and hence should be near equilibrium at the prescribed temperature.

In this study, the initial dendrimer configuration for MD simulations has been established in two steps. First, a special procedure has been used to assemble the dendrimer structure which resembled a dandelion: all end fragments were rather uniformly located in the periphery of a molecule, lengths of valent bonds and valent angles were close to the equilibrium values whereas the angles of internal rotation of linear fragments corresponded to trans-conformations. In general, this procedure allows to obtain sufficiently large dendrimers, since the overlapping and the entanglements of end fragments are significantly lower than upon assembling structures of "baobab" type [12].

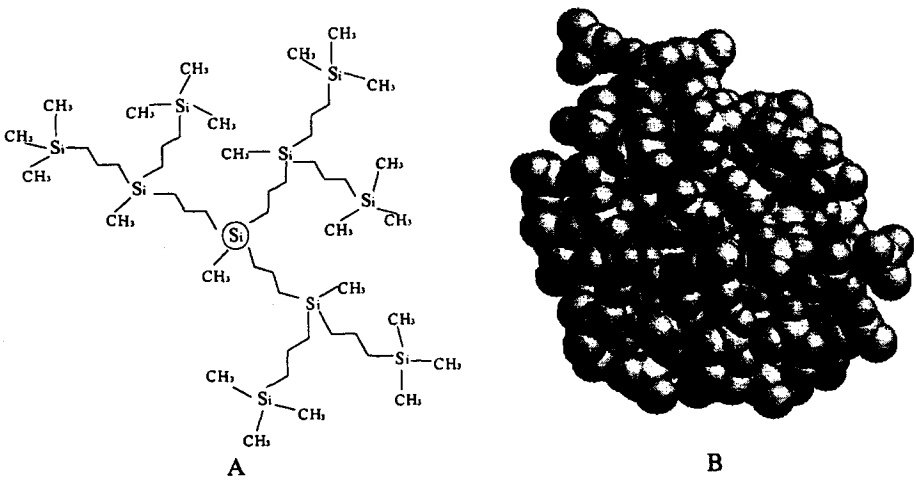

Figure 1. A. Schematic drawing of a dendrimer of the 2nd generation. B. Computer image of the dendrimer simulated.

At the second step, the system relaxed at high constant temperature of 600 K, when the radial mobility of end fragments in the equilibrium state was observed. The equilibrium state has been defined using energy parameters (potential energy U_{pot} and its components) and structure parameters (radius of gyration R_G, main inertia moments). It is found that the relaxation of structure parameters is the slowest process, but the period of the slowest fluctuations of the radius of gyration does not exceed 100 ps - 200 ps.

Once equilibrium configurations of molecules in "good" and "poor" solvents at 600 K have been obtained, the systems were cooled at a constant rate. The cooling was stopped at given moments, and the calculations were accomplished at a constant temperature. Moreover, to

analyse the dendrimer relaxation behaviour, numerical experiments were carried out with jump-like temperature changes.

3. STRUCTURE AND RELAXATION BEHAVIOUR AT DIFFERENT TEMPERATURES

In a "good" solvent, a linear temperature dependence of U_{pot} and its components was observed, R_G strongly fluctuated even at low temperatures and the temperature coefficient of the linear expansion α_l was slightly negative (Figure 2A). Thus these quantities in a "good" solvent do not indicate a transition from the liquid-like to the glassy state. In contrast, for a "poor" solvent, two temperature regions are clearly seen in the R_G (T) curve (Figure 2B). At $T > 350$ K, $\alpha_l = 1.9 \times 10^{-4} K^{-1}$ and significant low frequency fluctuations of R_G are observed. In the low temperature range ($T < 200$ K), the coefficient of temperature expansion is essentially lower: $\alpha_l = 0.8 \times 10^{-4} K^{-1}$, R_G fluctuations are low and include a high-frequency component only. Similar changes are observed for the van der Waals component of potential energy, but the slope of the U_{pot} value in the range of 250 K < T < 400 K is slightly decreased, hindering the determination of the glass temperature T_g.

As shown in Figure 2, a tenfold decrease in the cooling rate does not generally change the type of R_G (T) and U_{pot} (T) curves, but a more relaxed state of the molecule with lower average R_G and U_{pot} values was obtained, the lower limit of the high-temperature region being slightly reduced.

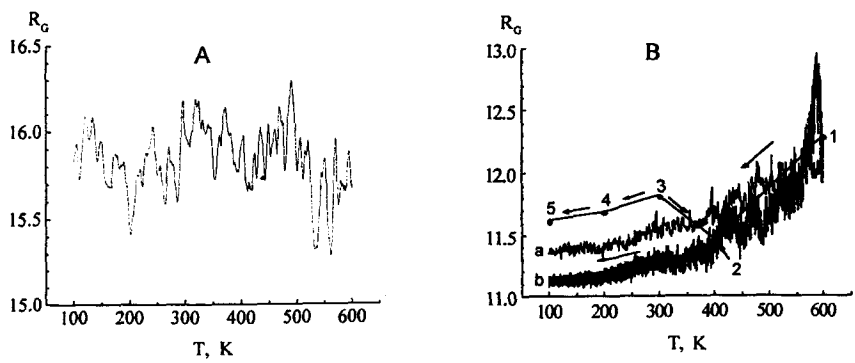

Figure 2. Radius of gyration R_G versus temperature. A. Uniform cooling in a "good" solvent, 2 K/ps. B. Uniform cooling in a "poor" solvent: a. 2 K/ps; b. 0.2 K/ps. ● Data of computer experiments at constant temperature; arrows indicate directions of temperature jumps (1→2; 1→3→4→5; 3→2).

On the base of the data obtained, it is believed that the dendrimer is glassy in a "poor" solvent at $T < 200$ K and is liquid-like at $T > 400$ K. Additional calculations have been performed to obtain the limits of the glassy region: Molecules were jump cooled from 600 K to 300 K and 400 K followed by aging at these temperatures until full relaxation of the parameters studied.

The dendrimer structure obtained at 400 K did not differ from the structure formed at slow cooling by the energy parameters, whereas superfast cooling to 300 K has resulted in an energetically less favourable structure of the higher R_G value (Figure 2). Further jump cooling to 200 K and 100 K did not change the dendrimer internal structure, whereas the heating up to 400 K resulted in relaxation to the equilibrium structure. Upon the annealing at 350 K both U_{pot} and R_G values did not achieve the equilibrium values; that suggests a significant increase in the dendrimer intrinsic viscosity at this temperature. Thus is believed that the glassy region for the dendrimer is between 300 K to 350 K.

These results agree well with the data on radial mobility of end silicon atoms. At $T > 400$K, the atoms move significantly, some atoms managed to move from the centre to the periphery of a molecule in 2×10^{-9} ps even at 400 K. However, at 300 K, fluctuations of the ends with an amplitude not exceeding 3 Å - 4 Å are observed.

Glass temperatures of close structure dendrimers with more extended end groups obtained in a physical experiment are shown to be slightly lower: they come to 167 K [14]. This can be related both to different structures of end groups (their effect on T_g is essential) and to peculiar features of MD experiments. It is believed that the shift of the glassy region is also due to the relative roughness of the selected potential values (mainly for U_{rot}). To determine the real source of T_g shift additional MD experiments are necessary. They are now being carried out in our laboratory.

The above α_l values are slightly lower than the calculated ones based on the results of thermomechanical experiments [14], where $\alpha_l = 2.3 \times 10^{-4} K^{-1}$ ($150 K < T < 185 K$) and $\alpha_l = 8.2 \times 10^{-4} K^{-1}$ ($185 K < T < 215 K$). This discrepancy is probably related to the fact that the MD experiments deal with the size analysis of an individual molecule, whereas intermolecular interactions can obviously contribute to the α_l value.

4. INTRAMOLECULAR DISTRIBUTION AND MOBILITY OF END GROUPS

Solvent quality and temperature have a slight effect on the molecular shape, the shape nearest to the spherical one being observed in a "poor" solvent at low temperature, ratios of main inertia moments I_2/I_1 and I_3/I_1 being equal to 0.98 and 0.97, respectively ($I_1 > I_2 > I_3$). In a "good" solvent, these ratios were equal to 0.95 and 0.91, and in a "poor" solvent at high temperature, the ratios were equal to 0.92 and 0.70. The low values of the relative shape anisotropy $æ^2$ [23]

$$æ^2 = \left[b^2 + (3/4)c^2\right] / R_G{}^4; \qquad b = I_1 - 0.5(I_2 + I_3); \qquad c = I_2 - I_3 \tag{2}$$

which is equal to 0.0003, 0.003 and 0.04, respectively, are indicative of a good sphericity as well.

In Figure 3A, the radial distribution of density near the centre of mass of a molecule is shown for these three cases. The calculations have been accomplished with a 0.1 Å step, atoms being considered as spheres of constant density and mass corresponding to the atom mass. The sphere diameter was equal to the corresponding van der Waals radius of the DREIDING force field. A denser inner region with a radius of 11 Å - 12 Å in a "poor" solvent and approximately 15 Å in a "good" solvent with 3 maxima related to the intramolecular distribution of the existing denser branching centres is clearly seen in Figure 3A. The peripheral region of density drop is rather extended (8 Å - 11 Å). This drop corresponds to the real density drop near the surface of a slightly aspheric molecule.

Radial distribution of end methyl groups near the centre of mass is shown in Figure 3B. As can be seen, most of these groups are located in the periphery, but 20 - 30 end groups (14% - 20%) are positioned within the globule, some groups being rather near the molecule centre.

Since the structure of the dendrimer discussed corresponds to the rigid bonding of end groups to the Si atoms of the last, 5th layer, the analysis of large-scale mobility of ends can be limited by considering dynamics of chain and silicon atoms. A molecule consists of 48 end Si atoms, their movements within the globule being at least limited by the globule size and being dependent on the bonding in pairs with the common branching centre of the 4th layer and weaker bonds via common branching centres of the 3rd and 2nd layers. As far as we know, theoretical analysis of the mobility of such branching structures has not been accomplished. It essentially hinders the interpretation of computer simulation results.

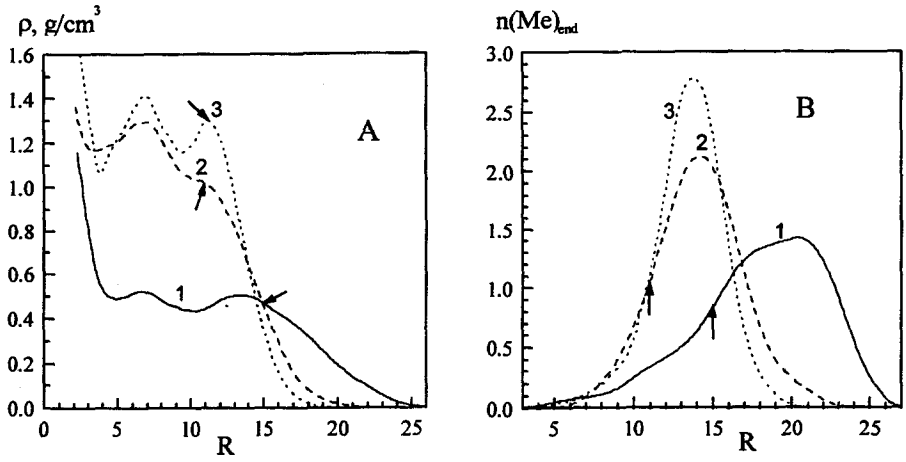

Figure 3. Radial distributions of density ρ (A) and number of end methyl groups $n(Me)_{end}$ (B) inside the dendrimer (distance from the centre of masses R is given in Å). 1: "good" solvent; 2: "poor" solvent, T = 600 K; 3: "poor" solvent, T = 100 K. Arrows show the position of the boundary between the inner and peripheral regions.

As mentioned above, a significant mobility of chain ends in the radial direction (radial mobility to ends) is observed at T = 600 K. In a "poor" solvent at T > 400 K, several end groups move to considerable distances; particularly, one group managed to transfer from the centre to the periphery of the molecule in 2×10^{-9} ps even at 400 K. In this case, the correlation in the mobility of ends having a common branching centre in the 4th layer is obvious. However, at 300 K, all but fluctuations of the molecule ends of an amplitude not exceeding 3 Å - 4 Å along the molecule radius are observed. This confirms the earlier conclusion about liquid-like behaviour of the dendrimer in a "poor" solvent at T > 300 K. In a "good" solvent, the radial mobility does also depend on the temperature, but even at T = 200 K, it was sufficiently high to make the deformation of the glassy region impossible.

The relatively small durations of numerical experimence (or high intramolecular viscosity, which is the same thing) do not allow to carry out a reliable statistical analysis of end group mobility. To estimate the mobility of end groups, the mean-square deviation of the ends during time τ:

$$<\Delta r^2> = <[\mathbf{r}_i (t+\tau) - \mathbf{r}_i (t)]^2> \qquad (3)$$

was calculated. The averaging was performed through the total run after establishing equilibrium and by all 144 end groups (Figure 4).

As can be seen from Figure 4A, in a "poor" solvent, mean-square deviations $<\Delta r^2>$ of chain ends are very small at 350 K and 400 K, but they grow with time. The heating up to 500 K results in a marked increase in the mobility of the ends. Their large mean-square deviations at 200 ps - 300 ps suggest that most of the ends are involved in an intensive intramolecular diffusion.

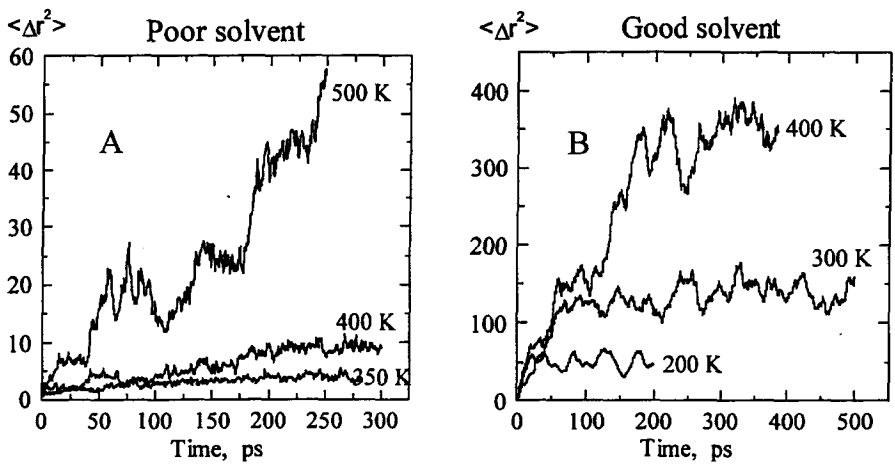

Figure 4. Mean-square deviation of end Si atoms $<\Delta r^2>$ (Å^2) versus time at different temperatures in a "poor" solvent (A) and in a "good" solvent (B).

A different temperature dependence of $<\Delta r^2>$ occurs in a "good" solvent (Figure 4B): For 3 temperatures studied, a fast, nearly linear growth in $<\Delta r^2>$ is observed at the initial portion of the curve followed by a flattening out. The length of the initial portion and the limiting $<\Delta r^2>$ value increase with temperature; even at the minimum temperature of 200 K, the limiting value of 50 $Å^2$ is achieved in 20 ps. It seems likely that for a "good" solvent, a different picture of intramolecular diffusion is observed due to the absence of a real solvent in the model system. In this case, time averaged structure parameters can be close to the ensemble of averaged parameters without taking into account the solvent contribution into the intramolecular viscosity.

5. CONFORMATIONAL MOBILITY

Detailed analysis of the conformational mobility of a molecule has been accomplished by account that any large-scale movements of polymer chains within the dendrimer were related to the conformational transitions. In Figure 5, a repeated fragment of the dendrimer is schematically shown; as can be seen, only 4 different angles of internal rotation (conformers) are present in the molecule discussed. The torsion potentials of the angles φ_1 and φ_4, which are adjacent to the branching centre, are similar:

$$U_{rot} = B\,[1+\cos(3\varphi)]; \qquad B = 1 \text{ kcal / mol} \tag{4}$$

and the 3 minima are equivalent. It becomes obvious in Figure 6, where the distribution of values of the angle φ_1 is shown in a "good" solvent at different temperatures. Analogous distributions have been obtained for φ_1 in a "poor" solvent and for φ_4 in both solvents. In all cases, 3 equivalent minima at 0°, 120°, 240° and maxima at 60°, 180°, 300° slightly broadening with temperature are observed. It is found that the same distributions take place for the angles φ_1 and φ_4 and for discrete layers of the dendrimer.

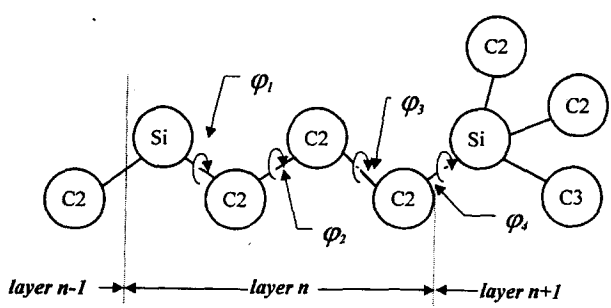

Figure 5. Schematic diagram of a repeated fragment of a dendrimer. C2 and C3 are methylene and methyl groups respectively.

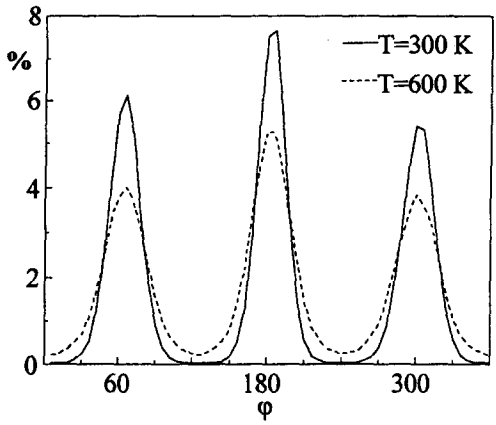

Figure 6. Histograms of the distribution of φ_1 for a fragment of a dendrimer in a "good" solvent at 300 K and 600 K.

During the time of the numerical experiment, several types of rotational dynamics of the angles φ_1 and φ_4 (see Figure 7, where examples of rotational dynamics are given for a "poor" solvent at T = 400 K) are observed: Conformational transitions are absent (3), individual transitions take place (1) and multiple transitions in a wide angular range take place (4). Unstable states (when the angle shows irregular high-frequency oscillations between neighbour potential minima) have rarely occured in a "poor" solvent (2).

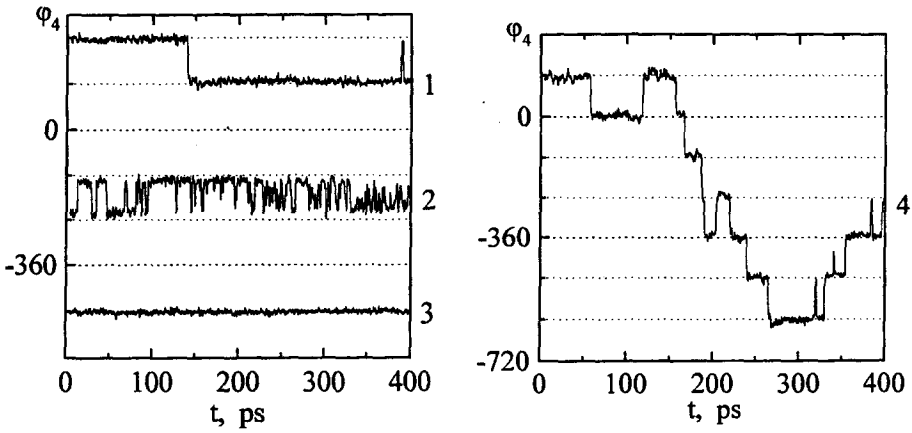

Figure 7. Time behaviour of φ_1 and φ_4 (see details in the text).

The frequency of these jumps f_{rot} defined as the number of jumps in 100 ps was selected as a measure of conformational mobility; only the jumps when previous and following stable states persisted more than 2 ps were taken into account. The dependence of the conformational mobility on the topological distance (number of chemical bonds) d_{top} between the dendrimer core and the chemical bond related to the rotation angle considered is of special interest. The values $<f_{rot}>$ averaged for every dendrimer layer are presented in Figure 8 for "poor" and "good" solvents at different temperatures.

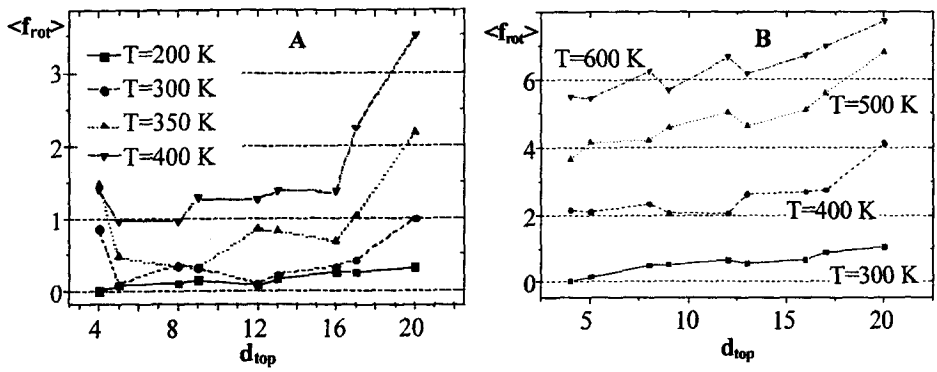

Figure 8. The conformational mobility $<f_{rot}>$ averaged for every dendrimer layer versus the topological distance d_{top} at different temperatures for a "poor" solvent (A) and a "good" solvent (B). Standard deviation for the calculations is essentially dependent on the layer number and on the temperature and amounts to 0.6 - 1.1 for a "poor" solvent and to 0.08 - 0.2 for a "good" solvent.

It is seen that in a "poor" solvent, conformer mobility increases with temperature, being practicallly independent on d_{top} except for the end angles φ_4 with a frequency being 2 - 3 times higher (Figure 8A). These results correlate well with the experimental data [6,7], where the ^2H and ^{13}C NMR relaxation measurements are presented for specifically labeled poly(amidoamine) dendrimers in D_2O and $DMSO-d_6$ solutions. Another feature of $<f_{rot}>_1$ dependence of d_{top} is observed in a "good" solvent (Figure 8B). In this case, the $<f_{rot}>_1$ value shows a relatively uniform growth with d_{top} at all temperatures, increasing by 30% near the molecular ends.

The effect of temperature on the conformatinal mobility of inner and end rotation angles is shown in Figure 9. As can be seen, the mobility of end groups is slightly different in "good" and "poor" solvents (by 10%), whereas the mobility of inner angles differs by a factor of two.It is of interest that the temperature dependence of the transition frequency closes to linear in the range of 300 K - 500 K.

6. CONCLUSIONS

The calculations carried out in this work show that MD simulations could be used to analyse the intramolecular mobility of dendrimers at high temperatures. However, because of the high intramolecular viscosity of dendrimers numerical experiments require several hundreds of picoseconds to reach the equilibrium structure even at a high temperature (T > 400 K for the dendrimers considered). As shown, statistical analysis of large-scale intramolecular mobility requires even more time. It should be noticed that the mobility simulation in a "good" solvent requires taking into account the real solvent either directly or in an indirect manner using the method of Brownian or collision dynamics [19, 24].

It is established that dendrimers demonstrate "liquid-like" behaviour at high temperatures and "glassy" behaviour at low temperatures. At high temperatures, both the significant diffusion mobility of end fragments in the radial direction and the conformational mobility are observed, which are rather absent at low temperatures. The presence of the "glassy" state at low temperatures imposes essential limitations on simulations of equilibrium thermodynamic and structure by both MD and Monte Carlo methods. Because of this analysis the conclusion is drawn that a dendrimer consists of the uniform (by density and local molecular mobility) inner region and the less dense and more mobile periphery.

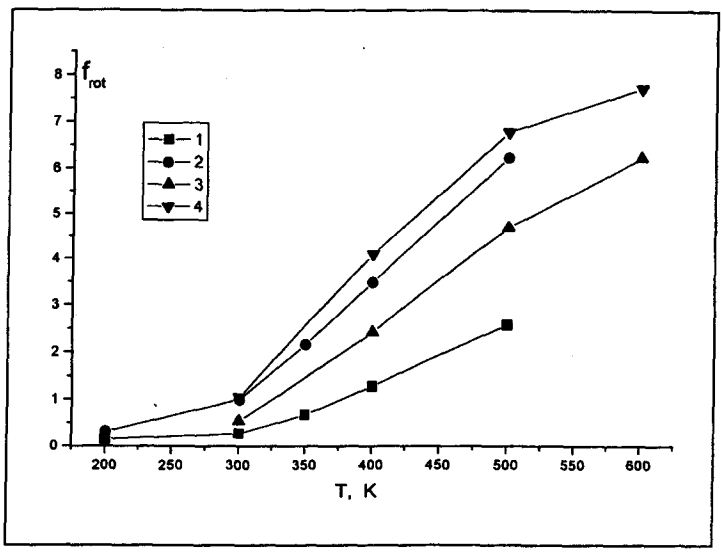

Figure 9. Temperature dependence of the conformational mobility of inner and end rotation angles:

■ inner rotation angles, "poor" solvent; ▼ inner rotation angles, "good" solvent;
● end rotation angles,"poor" solvent; ▲ end rotation angles, "good" solvent.

7. ACKNOWLEDGMENTS

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