# Computer Simulation of Spatial Structure and Intramolecular Mobility of Two Types of Siloxane Dendrimers of Different Generations in a Wide Range of Temperatures

Kurbatov A. O.[a], Balabaev N. K.[b], Mazo M. A.[c] , Kramarenko E. Yu.[a]
[a] *Faculty of Physics, Lomonosov Moscow State University, Moscow 119991, Russia*
[b] *Institute of Mathematical Problems of Biology, Keldysh Institute of Applied Mathematics RAS, Pushchino, Moscow Region 142290, Russia*
[c] *Semenov Institute of Chemical Physics RAS, Moscow 119991, Russia*
E-mail: kurbatov@polly.phys.msu.ru

## Model and Simulation Details

**A molecular dynamic simulation of single siloxane dendrimers (from the 2nd to the 8th generation) with a trifunctional $Si(CH_3)$ nucleus, the terminal $CH_3$ groups, and two types of trifunctional repeating groups: $OSi(CH_3)$ (temperatures 150, 250, 300, 350 , 400, 500, 600 K) and $OSi(CH_3)_2$-$OSi(CH_3)$ (temperature 150, 350, 600 K) have been performed.**
**The force field PCFF was used.**
**The equilibration was checked by autocorrelation functions for the gyration radius and by the graphs of various types of energy.**
**For each system, the calculations were performed on an ensemble of 10 independent structures. Averaging simmulation time was up to 1 ns for dendrimers with $OSi(CH_3)$ and up to 3 ns for dendrimers with $OSi(CH_3)_2$-$OSi(CH_3)$ .**
**To study intramolecular mobility, trajectories of up to 50 ns were obtained.**

### I. Parameters of the force field for the atoms:

**Table 1.** Bond potential

$$U_{bond} = \varepsilon_b (l - l_0)^2$$

| Bond type | $\varepsilon_b$, kc·mol$^{-1}$A$^{-2}$ | $l_0$, A |
|---|---|---|
| Si-$CH_3$ | 238.0 | 0.1809 |
| O-Si | 392.8 | 0.16650 |

**Table 2.** Valence angle

$$U_{angle} = \varepsilon_{angle} (\theta - \theta_0)^2$$

| Atom type | $\varepsilon_{angle}$, kcal·mol$^{-1}$grad$^{-2}$ | $\theta_0$, grad |
|---|---|---|
| Si-O-Si | 31.1 | 149.8 |
| X-Si-X | 44.4 | 113.5 |

**Table 3**. Lennard-Jones potential

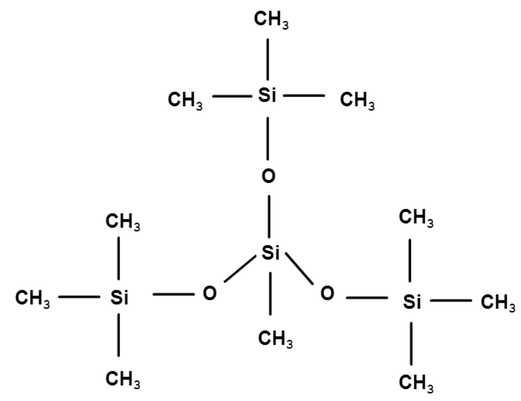
$$U_{ij} = \varepsilon_{ij}\left[2\left(\frac{R_{min,ij}}{r_{ij}}\right)^9 - 3\left(\frac{R_{min,ij}}{r_{ij}}\right)^6\right]$$

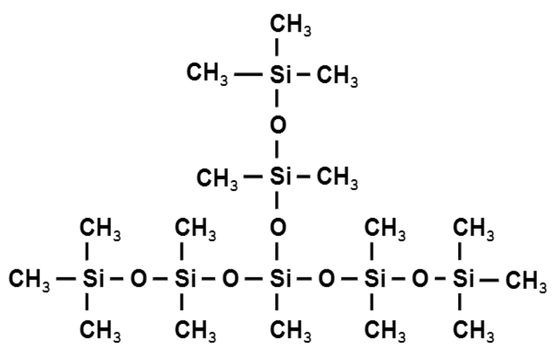
$$\varepsilon_{ij} = 2(\varepsilon_i\varepsilon_j)^{1/2}\frac{r_i^3 r_j^3}{r_i^6 + r_j^6},\quad R_{min,ij} = \left(\frac{R_{min,i}^6 + R_{min,j}^6}{2}\right)^{1/6}$$

| Atom type | $\varepsilon_i$, kc·mol$^{-1}$ | $R_{min}$, A |
|---|---|---|
| $CH_3$ | 0.054 | 4.010 |
| Si | 0.070 | 4.284 |
| O | 0.240 | 3.350 |

**Table 4.** Atomic masses and partial charges of the atoms

| Atom type | m, am u | q, e |
|---|---|---|
| $CH_3$-Si-3O | 28 | 0.760 |
| $2CH_3$-Si-2O | 28 | 0.640 |
| $3CH_3$-Si-O | 28 | 0.520 |
| O | 16 | -0.440 |
| CH3 | 15 | -0.100 |

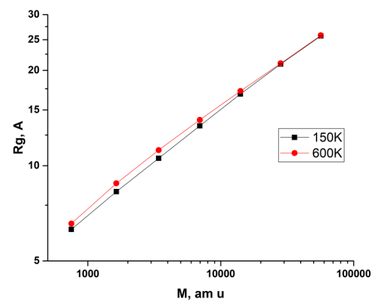




Molecular structure of the first generation siloxane dendrimers with short (top) and longer (bottom) spacers.

## Gyration Radius

**Si-O**



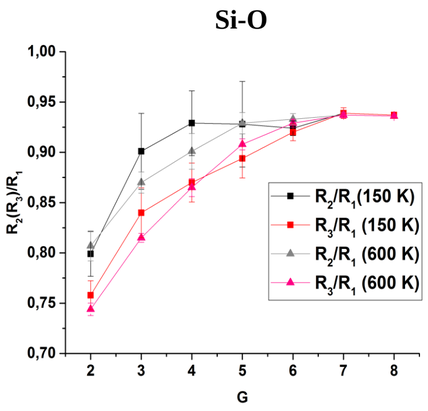

$$R_g \sim M^a$$

| Dendrimer type | 150 K | | 600 K | |
|---|---|---|---|---|
| | $a$ | d$a$ | $a$ | d$a$ |
| Si-O | 0,321 | 0,004 | 0,303 | 0,004 |
| O-Si-O-Si | 0,324 | 0,002 | 0,305 | 0,003 |

- The dependence of the gyration radius on the temperature is weak over a wide temperature range.
- As the length of the spacer increases, the values of the gyration radius increase, but the general form of the dependencies remains the same.

## Shape Factor

**Si-O**

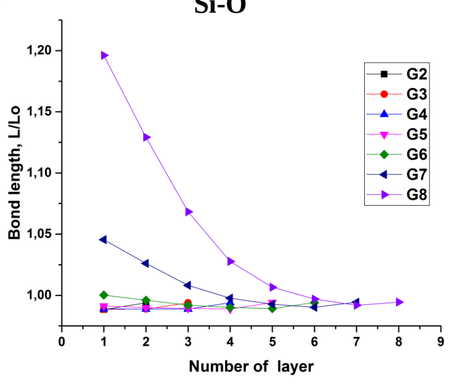



The form factor is the ratio of the principal moments of the gyration tensor of the dendrimer.

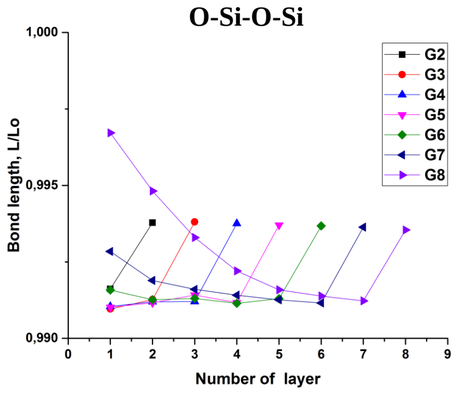
- Dendrimers have a shape close to the sphere
- The sphericity depends weakly on temperature and increases significantly with increasing generation number.
- Asymmetry for small generation numbers
- Small generations of dendrimers with a long spacer form a more asymmetric structure

## Bond Length and Valence Angle

**Si-O**

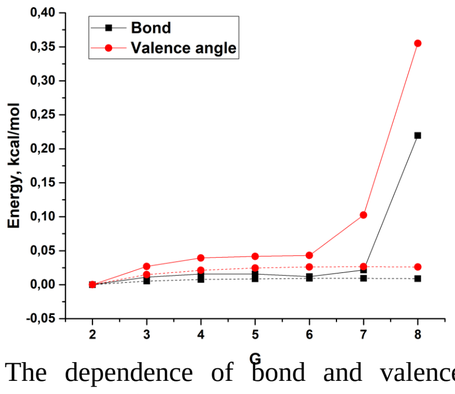



**O-Si-O-Si**




The dependence of average relative values of the bond length on the number of dendrimer layer for various generations of siloxane dendrimers with short (left) and longer (right) spacers at T=350 K.

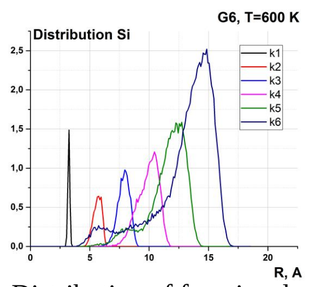
- The bond energy, $U_b$, and the angle energy, $U_a$, behave differently with generation for Si-O and O-Si-O-Si dendrimers
- The bond and angle energies stay practically constant for O-Si-O-Si dendrimers
- The noticeable growth of both $U_b$ and $U_a$ takes place for the seventh and eighth generations of Si-O dendrimers
- The equilibrium length of all the bonds is slightly smaller than L0 due to van der Waals attraction between dendrimer atoms
- The bonds in the last layer are less compressed since the terminal Si atoms in this layer experience more freedom
- The considerable stretching of the bonds takes place for high generation Si-O dendrimers, due to conformational restrictions, i.e. packing conditions



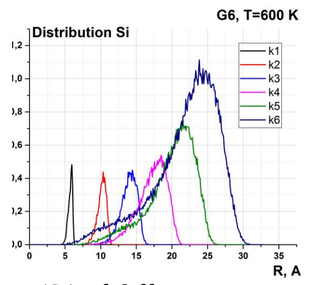

The dependence of bond and valence angle relative energies per atom on generation for siloxane dendrimers with short (solid line) and longer (dotted line) spacers at T=350 K. (the curves are shifted with respect to the energy of G2 dendrimers)

## Distribution of Si Atoms

**Si-O**



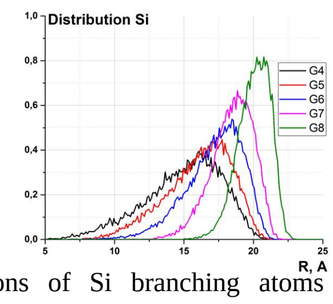

**O-Si-O-Si**




Distribution of functional groups (Si) of different layers. $k_i$ is the number of the layer.

- The branching groups in the dendrimers are distributed over the radial layers.
- As the generation number increases, the layers begin to mix. As the length of the spacer increases, this mixing is much more noticeable.
- On large generations, there is a noticeable tendency to shift the functional groups of the first few layers from the center of the dendrimer.

**O-Si-O-Si**

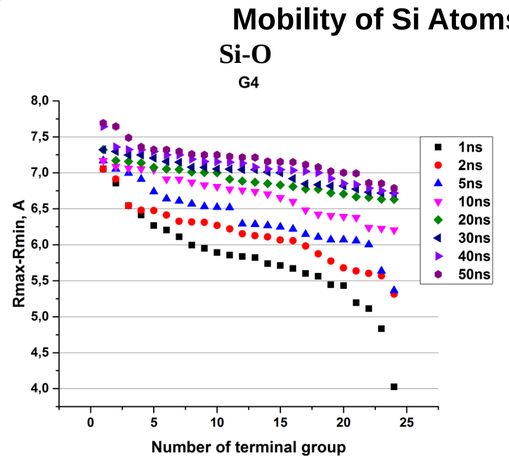



Distributions of Si branching atoms of the fourth layer in dendrimers of various generations with long spacers at T = 600 K.

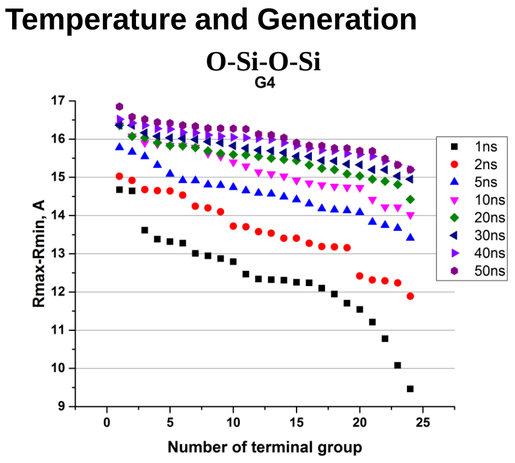
- A strong displacement from the center of the right boundary of the inner layers for the seventh and eighth generations is due to the stretching of the first several layers of the dendrimer, which results from an increase in the length of the bonds and an increase in the valence angles.

## Mobility of Si Atoms vs Temperature and Generation

**Si-O**



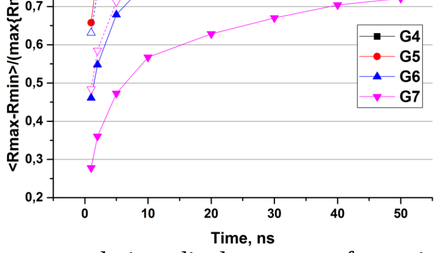

**O-Si-O-Si**




The difference between the maximum, $R_{max}$, and minimum, $R_{min}$, radial position of each terminal Si atom reached at various time trajectories of G4 dendrimers with the short (left) and longer (right) spacers. T=600 K.

To study intramolecular mobility, the qualitative behavior of the radial displacement of the end groups of each generation was considered.

- One part of terminal Si atoms demonstrate high mobility moving within the whole dendrimer molecule, while some others are “frozen” on this timescale
- The mobility of these frozen groups decreases with increasing dendrimer generation
- Typical mixing times are tens of ns.
- As the generation number increases, the mobility decreases
- The mobility of terminal groups does not depend on their positions within dendrimer molecule




Average relative displacement of terminal Si atoms vs time for various generation dendrimers with the short (solid lines) and longer (dotted lines) spacers at T=600 K.

## Conclusion

A comparative analysis of the structure of two types of dendrimers (with different spacer lengths) is performed depending on the generation number and temperature. The behavior of the gyration radius and the shape factor of dendrimers is studied. It is shown that the temperature dependence is weak, and that the dendrimers are predominantly spherical. The density distributions of all monomer units and individual distributions for silicon atoms of different structural layers of the molecule are obtained, and the characteristic features of the reduced distributions for dendrimers of this type are studied. The phenomenon of the backfolding was found and quantitatively evaluated, and the nature of the mobility of silicon atoms was studied.

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