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New sparse polymethylsiloxane dendrimers

Elena Yu. Katarzhnova,*[a] Elena A. Tatarinova,[a] Galina M. Ignat'eva,[a] Nataliya G. Vasilenko,[a] Ivan B. Meshkov[a] and Aziz M. Muzafarov[a,b]

[a] *N. S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 117393 Moscow, Russian Federation. Fax: +7 495 718 3404; e-mail: elena.katarzhnova@ispm.ru*
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 6549*

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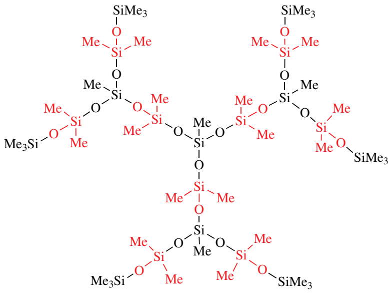
New non-functional methylsiloxane dendrimers possessing a sparse structure with a trimethylsiloxy outer layer containing a flexible dimethylsiloxane link between branch points have been synthesized. Two alternative synthetic protocols were employed, namely, a divergent scheme comprising an additional stage of generating a spacer –OSiMe$_2$– group with sodium ethoxy(dimethyl)silanolate, and a hybrid method using monofunctional dendrons with a sparse structure.

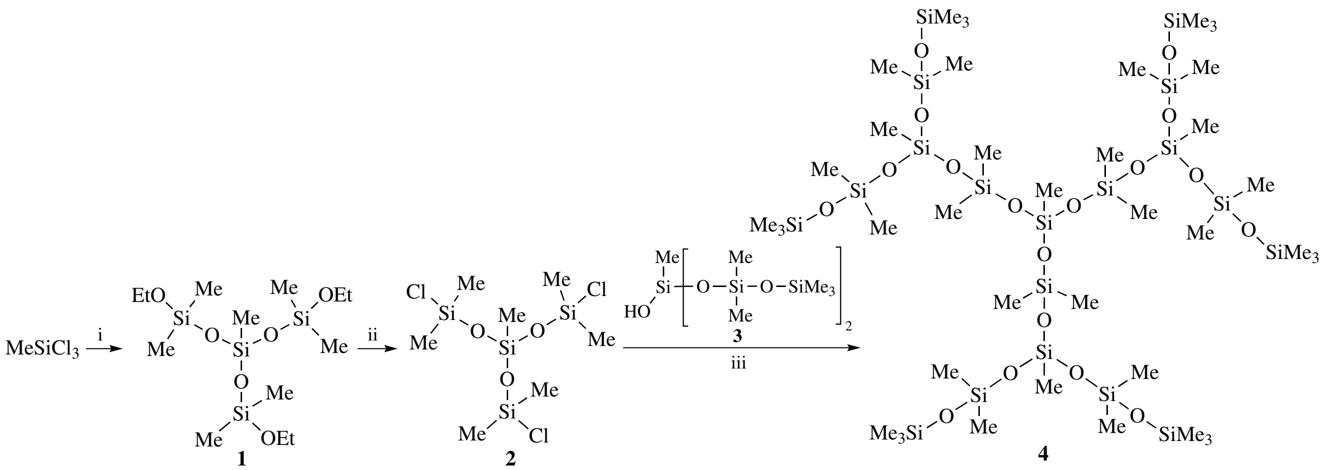


Keywords: polymethylsiloxane, dendrimers, macromolecule particles, alkoxysilanes, silanols.

Organoelement dendrimers occupy a special place among the new polymer forms. In particular, polyphosphazene dendrimers[1,2] are in demand in catalysis[3] and a number of medicinal applications.[4] At the same time, polymethylsilsesquioxane dendrimers, the first objects of a new type of organic element polymers[5–8] synthesized 30 years ago, were nearly forgotten until a new impulse was given by computer simulations of dendrimers[9,10] as well as recent syntheses of methylsilsesquioxanes.[11–16]

Polymethylsilsesquioxane dendrimers are popular due to a wide range of operating temperatures, thermooxidative and electrical stability, and biological inertness. The specific architecture of dendrimeric macromolecules gives them properties that differ significantly from those of classical polymers.[17–20] The properties of the former tend towards those of so-called 'macromolecule particles', with anomalously low viscosity and the 'α' coefficient in the Mark–Kuhn–Houwink equation close to zero,[21] while the solvent nature weakly affects the hydrodynamic radius of their macromolecules.[22] The glass transition temperature of dendrimers is generally dependent on the nature of their terminal groups.[23–25] Interestingly, high-generation dendrimers manifest nonclassical intermolecular interactions. In such dense structures, the formation of entanglements similar to those in classical polymers is impossible due to the architecture of the dendrimeric macromolecule. An increase in the molecular mass does not affect viscosity, however an abrupt change in the properties of the compound and an unprecedented increase in the melt viscosity by eight orders of magnitude are observed at a certain generation.[26] It was assumed that this could be explained by the formation of a physical network of intermolecular entanglements of the terminal groups in the surface layer of high-generation dendrimers. However, these studies were carried out with rather rigid carbosilane dendrimers. Hence, studying dendrimers with differing mobility of the macromolecule frameworks are required for better understanding of the mechanism of this unusual phenomenon. Methylsiloxane dendrimers with flexible Si–O–Si bonds should possess the required flexible internal structure. Although the first representatives of such compounds were synthesized about 30 years ago,[5] they remained poorly explored. Apparently, a large variety of non-functional siloxane dendrimers was not synthetically accessible due to the absence of necessary pool of special blocking agents. The use of conventional blocking agents such as chlorotrimethylsilane disrupted the integrity of the macromolecule's siloxane skeleton. Recently, the synthesis of anhydrous siloxanols by catalytic aerobic oxidation of hydridosilyl groups[27] and their use as blocking agents made it possible to prepare a representative series of polymethylsilsesquioxane dendrimers with trimethylsilyl terminal groups.[28] It was found that the viscosity of their melt and their T_g increased with an increase in the dendrimer generation number. The activation energy of viscous flow of polymethylsilsesquioxane dendrimers significantly exceeded the E_a of classical polydimethylsiloxanes, and its value increased monotonously with the generation number. On the example of carbosilane dendrimers with a rigid core structure and a methylsiloxane outer layer, the effect of the structural features of the outer layer on the properties of dendrimers was studied. An obvious dependence of T_g of the polymer on the mobility of the siloxane terminal groups of the dendrimer branches was revealed. If the dendrimer surface contained flexible linear oligomers –SiMe–[OSiMe$_2$]$_4$–OSiMe$_3$, the results were as follows: T_g(G3) = –110 °C,[29] T_g(G3) = –83 °C with less mobile external –SiMe[OSiMe$_3$]$_2$ groups[30] and T_g(G3) = –66 °C in the case of most rigid cyclotetrasiloxanes.[31] At the same time, no studies on the effect of the mobility of the internal structure of the dendrimer, that is, the flexibility of its siloxane skeleton, on its properties were performed due to the lack of samples of siloxane dendrimers with different internal architectures for comparison.

Since the known polymethylsilsesquioxane dendrimers contained only methylsilsesquioxane units in the inner sphere, the



Scheme 1 *Reagents and conditions*: i, NaOSi(OEt)Me$_2$, ii, SOCl$_2$, DMF; iii, hexane, Py, –40 °C.

purpose of this work was to obtain new dendrimers with sparse structures containing flexible linear spacer –Me$_2$SiO–, along with the –MeSiO$_{1.5}$– units, in each generation. The availability of such objects would make it possible to carry out a comparative study of the behaviour of a dense structure with branching centers bound *via* oxygen atoms and with the properties of sparse structures, and to make a reliable conclusion about the nature of the formation of a physical network in high-generation dendrimers.

An additional interest is related to the fact that similar structures are studied in detail by computer modeling methods;[32,33] with the appearance of real compounds, it will be possible to correlate these results with each other.

Two approaches to the synthesis of such compounds were herein suggested. In the first one (Scheme 1), we intended to start building the skeleton (compound **1**) with the use of sodium ethoxy(dimethyl)silanolate, the difunctional Rebrov's salt.[34] The terminal functional groups in trichloride **2** were blocked using a monodendron reactant **3** with a sparse structure bearing a focal hydroxy group. Thus, a branching element is simultaneously introduced in the final dendrimer **4** while the number of generations is increased by one step (see Scheme 1).

The key sparse monofunctional dendron **3** was prepared from dichloro(methyl)phenylsilane as outlined in Scheme 2. In the course of step iv, the phenyl substituent was replaced by bromine atom capable of further functionalization. The most difficult stage involved the Si–Br → Si–OH functionality conversion (step v). If the hydrolysis was carried out at 0 °C in the presence of various HBr acceptors, a considerable number of side processes occurred that disrupted the dendron structure to give a complex mixture of products. A more successful approach involved the replacement of bromine with an acetate group followed by hydrolysis. However, that material also contained admixtures and required additional purification.

Taking these results into account, we recognized the synthetic protocol for dendrimer **4** employing monodendron **3** (see Schemes 1 and 2) to be laborious, and turned our attention to the divergent stepwise construction of the dendrimer skeleton. The new protocol involved two main stages: branching of the structure by means of an AB$_n$ reagent ($n \geqslant 2$) followed by the functionality replacement. To create a molecule with a sparse architecture type, an additional intermediate stage had to be included using the difunctional Rebrov's salt,[34] which provided the possibility of generating the –OSiMe$_2$– spacer group between the branch points. Initially, in this way a model comparative compound **5**, a non-functional zero-generation dendrimer G-0(sp)(OSiMe$_3$), was synthesized using trimethylsilanol as the blocking reagent (Scheme 3).[35] GPC analysis showed the formation of a product with a narrow MMD in 80% yield. Compound **5** was purified by preparative liquid chromatography, its structure was confirmed by ^{29}Si, ^{13}C and ^{1}H NMR spectroscopy (see Online Supplementary Materials, Figures S1–S4).

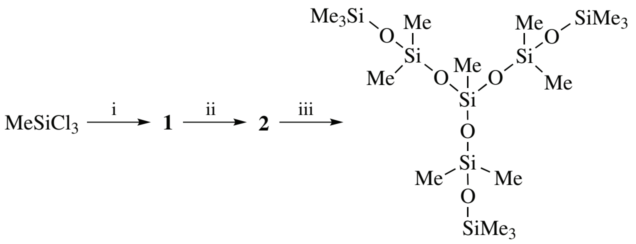
Sparse first generation dendrimer **4** was synthesized analogously (Scheme 4). However, at the first stage when

$$\mathrm{PhSiMeCl_2} \xrightarrow{\text{i}} \mathrm{PhSiMe(OSiMe_2OEt)_2} \xrightarrow{\text{ii}} \mathrm{PhSiMe(OSiMe_2Cl)_2}$$

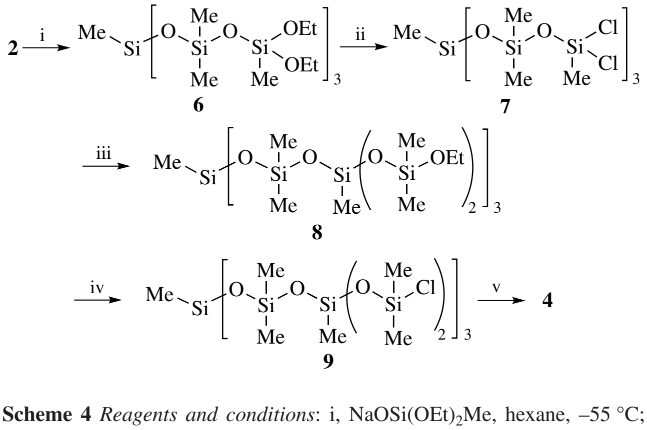
$$\xrightarrow{\text{iii}} \mathrm{PhSiMe(OSiMe_2OSiMe_3)_2} \xrightarrow{\text{iv}} \mathrm{BrSiMe(OSiMe_2OSiMe_3)_2}$$

$$\xrightarrow{\text{v}} \underset{\mathbf{3}}{\mathrm{HOSiMe(OSiMe_2OSiMe_3)_2}}$$

Scheme 2 *Reagents and conditions*: i, NaOSi(OEt)Me$_2$, hexane, –45 °C; ii, SOCl$_2$, DMF, 90 °C; iii, Me$_3$SiOH, hexane, Py, –30 °C; iv, Br$_2$, CCl$_4$; v, H$_2$O, hexane, Et$_2$O, Py, from –3 to 0 °C.



Scheme 3 *Reagents and conditions*: i, NaOSi(OEt)Me$_2$, hexane, –55 °C; ii, SOCl$_2$, DMF, 90 °C; iii, Me$_3$SiOH, hexane, Py, –40 °C.



Scheme 4 *Reagents and conditions*: i, NaOSi(OEt)$_2$Me, hexane, –55 °C; ii, SOCl$_2$, DMF, 90 °C; iii, NaOSi(OEt)Me$_2$, hexane, –55 °C; iv, SOCl$_2$, DMF, 90 °C; v, Me$_3$SiOH, hexane, Py, –40 °C.

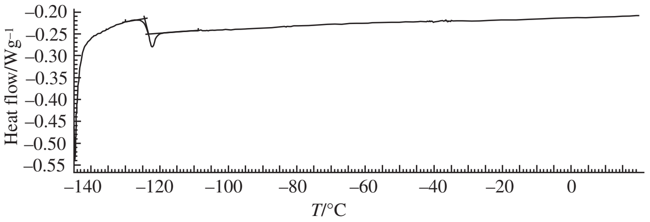
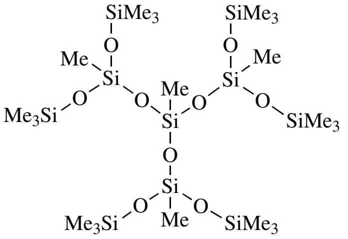


Figure 1 DSC curve of dendrimer **4**.



10

G-1(dense)(OSiMe$_3$)

Table 1 Properties of polymethylsilsesquioxane dendrimers with sparse (**4**, **5**) and dense (**10**) structures.

Dendrimer	M/g mol^{-1}	d_4^{25}/g cm^{-3}	n_D^{25}	T_g/°C
4	1423.00	0.961	1.4026	–123
5	533.15	0.924	1.3956	–134
10	755.6	0.948	1.4010	–123

obtaining compound **6**, sodium diethoxy(methyl)silanolate (the trifunctional Rebrov's salt) was used to create branching points of the structure. The resulting compound **4** was purified by preparative chromatography and its structure was confirmed by NMR spectroscopic data (see Online Supplementary Materials, Figures S4–S6).

Sparse dendrimers G-1(sp)(OSiMe$_3$) **4** and G-0(sp)(OSiMe$_3$) **5** possess methylsilsesquioxane structures with the same trimethylsilyl terminal groups and differ in the skeleton. It seemed reasonable to compare their properties with those of their analogue G-1(dense)(OSiMe$_3$) **10** having a dense structure.[28] Analysis of the main properties of dendrimers **4** and **5** showed some increase in the density and refractive indices with the growth of generation number (Table 1), which is similar to the variation in these parameters in the case of non-sparse dendrimers.[28]

Comparison of the properties of dendrimers **4** and **10** revealed that, with the same Me$_3$SiO/MeSiO$_{1.5}$ ratio, incorporation of the –OSiMe$_2$– group between the branching points resulted in a certain increase in the density and refractive index of the samples. Apparently, in this case a combination of the higher M of the sparse dendrimer compared to the 'dense' analogue and its compact packing ability due to the flexibility of the incorporated dimethylsiloxane spacer plays some role. DSC data show that the branched structure of macromolecules results in the expected lack of crystallization (see Online Supplementary Materials, Figure S6) that is characteristic of classical polydimethylsiloxane. Incorporation of a linear rarefying unit into the structure did not change the T_g. In the case of **4** and **10**, they are the same, $T_g = -123$ °C (Figure 1), and are typical of polydimethylsiloxanes. In the case of **5**, the $T_g = -134$ °C (see Figure S6) is lower, in agreement with the published data for low molecular linear PDMS.[36]

To conclude, the developed protocol employing difunctional sodium ethoxy(dimethyl)silanolate at the certain stage of the construction of the dendritic structure by the divergent method allows one to access sparse methylsilsesquioxane dendrimers. In future we plan to obtain similar compounds of higher generations for a more comprehensive study of the effect of the density and mobility of the dendrimer skeleton on their properties.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.05.037.

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