SYNTHESIS AND PROPERTIES OF HYBRID CARBOSILANE DENDRIMERS WITH CYCLOSILOXANE EXTERNAL SHELLS

Cite this: INEOS OPEN, 2020, 3 (6), 219–225
DOI: 10.32931/io2026a

Received 29 November 2020, Accepted 14 January 2021
http://inesopen.org

Abstract

The hydrosilylation of polyallylcarbosilane dendrimers with hydride-containing six- and eight-membered dimethylcyclosiloxanes affords a series of hybrid carbosilane–siloxane dendrimers featuring different densities of the surface cyclosiloxane layers, while retaining all other molecular parameters. The main physicochemical constants of the resulting dendrimers are defined. The possibility of functionalization of these dendrimers by the opening of cyclosiloxane structural moieties in the external shell is demonstrated by the example of the zero-generation dendrimer bearing heptamethylcyclotetrasiloxane terminal groups.

Key words: carbosilane dendrimers, siloxane dendrimers, cyclosiloxanes, NMR spectroscopy, hydrosilylation, intrinsic viscosity.

Introduction

The carbosilane dendrimers occupy a special place among numerous dendrimer systems described in the literature over the last 30 years [1–4]. The stability of a molecular backbone and high reactivity of functional groups during synthesis made these objects popular models for the investigation of dendrimers [5–9]. The last decade has witnessed a multitude of reports on the synthesis of carbosilane dendrimers with different external shells. In order to define the relationships between the properties of dendrimers and their structures, the homologous series of dendrimers featuring ethylene oxide external layers [10], 2-phenylethyl terminal [11] and perfluorinated groups [12] in the external shell were explored. The sulfur-containing carbosilane dendrimers [13] and stars based on carbosilane dendrimers [14] were synthesized. It was established that the structure of an external dendrimer shell has a determining impact on its physical properties, for example, glass-transition point, which changes depending on the nature of the external shell [8]. Particular attention is drawn to the thermodynamic properties of dendrimers of various compositions and structures [15, 16]. The values of standard thermodynamic characteristics allow for evaluating the behavior of macromolecules featuring different structures and densities of external shells.

The chemical nature of the derivatives of organosilicon dendrimers is extremely diverse. The dendrimers with nonfunctional siloxane external shells [17], siloxane dendrimers up to the fourth generation [18], boron-substituted carborane–carbosilane dendrimers [19], and carborane–siloxanes of various structures [20] are known today that can be used as branching centers for hybrid dendrimers. The synthesis and antiviral activity of carbosilane dendrimers with sulfonate terminal groups were reported [21]. The low-toxic derivatives with phosphonium terminal groups and their potential application in medicine were also described [22]. Liegertová et al. [23] synthesized the carbosilane dendrimers modified with glucose. Rasines et al. [24] obtained the anionic carbosilane dendrimers with carboxylate and sulfonate terminal groups.

All these evidence that the carbosilane dendrimers are of high importance in a variety of fields and the methods for their modification are constantly evolving. A literature survey has revealed that the properties of dendrimers, especially those of higher generations, are often explored by the examples of nonfunctional derivatives, whereas further development implies sequential functionalization of a system. In a seminal work of the research group of the full member of the Russian Academy of Sciences A. M. Muzafarov [25], this problem was solved by the parallel synthesis of functional derivatives and their nonfunctional analogs as the research objects for investigation of their properties, which eventually afforded a wealth of knowledge that demonstrates the unique features of dendrimers [26, 27].

Herein, we report on the synthesis of hybrid carbosilane–siloxane systems bearing cyclosiloxane units in the external shell which do not contain functional groups and, therefore, are stable and applicable for a long-term study. At the same time, unlike, the analogs described, for example, in Ref. [17], they can be further transformed by ring-opening, which demonstrates the potential for their application in the production of complex spatial architectures, such as polymer networks [28].

Based on the previous results obtained for the homologous series of nonfunctional carbosilane dendrimers, we have chosen...
a minimal set of generations as models that can provide objective information on the whole family of homologs. The initial dendrimers were those of the zero, third, and sixth generations that combine the properties of the simplest (zero), common (medium) and higher generations. The zero generation, obtained using tetraallylsilane as a branching center, was used to conduct a model reaction of the opening of the cyclosiloxane groups in the external shell.

**Results and discussion**

The goal of this work was to synthesize two modifications of hybrid carbosilane–siloxane dendrimers having cyclic nature of the external shells: with strained pentamethylcyclotrisiloxane and heptamethylcycloctetrasiloxane groups.

The following compounds were used as the modifying agents for the dendrimer external shell: 1,3,3,5,5-pentamethylcyclotrisiloxane, obtained from tetramethyldisiloxane by the published procedure [29], and 1,3,3,5,5,7,7-heptamethylcycloctetrasiloxane, obtained from α,ω-disodiumoxyhexamethyltrisiloxane by the conversion to hexamethyltrisiloxane and its further cyclization (Scheme 1). The conditions for selective formation of α,ω-disodiumoxyhexamethyltrisiloxane were described in Ref. [30].

**Scheme 1.** Synthesis of 1,3,3,5,5,7,7-heptamethylcycloctetrasiloxane.

The target hybrid carbosilane–cyclosiloxane dendrimers were obtained by the hydrosilylation in the presence of a platinum catalyst according to Scheme 2.

**Scheme 2.** Synthesis of hybrid carbosilane–cyclosiloxane dendrimers.

Polyallylfuctional carbosilane dendrimers of the third and sixth generations, synthesized according to the published procedure [31], were used as a basis. The reaction conversion was controlled by ¹H NMR spectroscopy. Figure 1 depicts the ¹H NMR spectra of the initial dendrimer and the reaction product. The absence of allyl proton signals in the range of 4.8–5.0 and 5.6–5.9 ppm in the product spectrum testifies the complete conversion.

The resulting dendrimers were purified by preparative GPC. Figure 2 shows the GPC curves of the third-generation carbosilane–cyclosiloxane dendrimer before and after purification.

**Figure 1.** ¹H NMR spectra of the polyallylcarbosilane (a) and carbosilane–cyclosiloxane (b) dendrimers.

**Figure 2.** GPC curves of the carbosilane–cyclosiloxane dendrimer of the third generation before (a) and after (b) purification on a preparative chromatograph.

**Figure 3.** Molecular structure of the hybrid carbosilane–cyclosiloxane dendrimer of the sixth generation [Si₁₂₅₃₂₅₆₂₅₆₃(Si₃-cycle)].

The identities of the resulting hybrid dendrimers were confirmed by the GPC, ¹H and ²⁹Si NMR spectroscopic data.

**Figure 4.** ²⁹Si NMR spectra of the dendrimers of the third (a) and sixth (b) generations bearing heptamethylcycloctetrasiloxane units.
The spectra of the [\text{Si}^{25}_{12} \text{(Si-cyclo)]} and [\text{Si}^{28}_{25} \text{(Si-cyclo)]} dendrimers show two sets of signals: (a) the downfield signal corresponds to the silicon atoms in the external carbosilane shell bound through a propylene bridge with the terminal cyclosiloxane groups; (b) the resonances of all silicon atoms of the internal moiety of the carbosilane dendrimer independent of the generation layer. The siloxane patterns are identical for all the samples explored. Of note is only the slight upfield shift of the signals with an increase in the generation number. The ratio of the integral intensities is in good agreement with the calculated value. In general, the spectrum confirms the expected structure.

Figure 5 depicts the $^{29}\text{Si NMR}$ spectra of the dendrimers of the sixth generation bearing pentamethylocyclotrisiloxane and heptamethylocyclotetrasiloxane groups in the external shell. The signals in the range of $-9.0…-10.0$ ppm correspond to the silicon atoms of pentamethylocyclotrisiloxane groups and those in the range of $-19.5…-20.5$ ppm refer to the silicon atoms of the heptamethylocyclotetrasiloxane groups.

![Figure 5. $^{29}\text{Si NMR}$ spectra of the dendrimers of the sixth generation with the pentamethylocyclotrisiloxane (a) and heptamethylocyclotetrasiloxane (b) external shells.](image)

To describe the behavior of the resulting dendrimers in solution, their intrinsic viscosities were measured. The resulting data are summarized in Table 1. The values of intrinsic viscosity [$\eta$] of the obtained hybrid systems in toluene are low, which is characteristic of dendrimers [32].

### Table 1. Characteristics of the G-n(Si3cycle/Si4cycle) dendrimers and elemental compositions of the sixth-generation dendrimers bearing pentamethylocyclotrisiloxane and heptamethylocyclotetrasiloxane external shells

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>$\text{MM}<em>{\text{calc.}}$/\text{MM}</em>{\text{LS}}</th>
<th>$T_g$, °C</th>
<th>$[\eta]_{0.5}$, dL/g</th>
<th>$\text{Si}$, %</th>
<th>$\text{C}$, %</th>
<th>$\text{H}$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Si}_1^4$ (Si3-cycle)]</td>
<td>1026/</td>
<td>-52</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Si}<em>{12}^4\text{C}</em>{2}^4\text{H}<em>{2}^2\text{O}</em>{2}^2$</td>
<td>10398/</td>
<td>-44</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Si}<em>{12}^4\text{C}</em>{2}^4\text{H}<em>{2}^2\text{O}</em>{2}^2$</td>
<td>10435</td>
<td>-44</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Si}<em>{12}^4\text{C}</em>{2}^4\text{H}<em>{2}^2\text{O}</em>{2}^2$</td>
<td>8537/</td>
<td>-42</td>
<td>0.03</td>
<td>32.58</td>
<td>43.27</td>
<td>8.99</td>
</tr>
<tr>
<td>$\text{Si}<em>{12}^4\text{C}</em>{2}^4\text{H}<em>{2}^2\text{O}</em>{2}^2$</td>
<td>79807</td>
<td>-42</td>
<td>0.03</td>
<td>33.59</td>
<td>42.99</td>
<td>9.02</td>
</tr>
<tr>
<td>$\text{Si}<em>{12}^4\text{C}</em>{2}^4\text{H}<em>{2}^2\text{O}</em>{2}^2$</td>
<td>1328/</td>
<td>-75</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Si}<em>{12}^4\text{C}</em>{2}^4\text{H}<em>{2}^2\text{O}</em>{2}^2$</td>
<td>1593</td>
<td>-75</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Si}<em>{12}^4\text{C}</em>{2}^4\text{H}<em>{2}^2\text{O}</em>{2}^2$</td>
<td>12771/</td>
<td>-62</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Si}<em>{12}^4\text{C}</em>{2}^4\text{H}<em>{2}^2\text{O}</em>{2}^2$</td>
<td>13693</td>
<td>-62</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Si}<em>{12}^4\text{C}</em>{2}^4\text{H}<em>{2}^2\text{O}</em>{2}^2$</td>
<td>104357/</td>
<td>-60</td>
<td>0.02</td>
<td>33.18</td>
<td>42.10</td>
<td>9.06</td>
</tr>
<tr>
<td>$\text{Si}<em>{12}^4\text{C}</em>{2}^4\text{H}<em>{2}^2\text{O}</em>{2}^2$</td>
<td>94653</td>
<td>-60</td>
<td>0.02</td>
<td>34.37</td>
<td>41.06</td>
<td>8.87</td>
</tr>
</tbody>
</table>

The available literature data suggest the constancy of the intrinsic viscosity in a homologous series or an extremal character of the viscosity curve depending on the generation number [25, 32, 33]. In our case, the viscosity constancy typical for carbosilane dendrimers is manifested [25].

The DSC studies allowed us to reveal the glass-transition points $T_g$ of the resulting dendrimers, which are listed in Table 1. It is obvious that an increase in the ring size leads to a reduction in the glass-transition point, which reflects the high mobility in the unstrained eight-membered cyclosiloxane units compared to the rigid six-membered ones. The dependence on the generation number in both cases is minimal. It should be noted that, in the case of a linear siloxane moiety, the value of $T_g$ in the surface layer was considerably lower than $-106$ °C [17], and investigation of the rheological properties of these systems confirms the presence of a specific intermolecular interaction of terminal siloxane groups and the formation of dendrimer crosslinks which produce an effect analogous to a mesh network for classical linear systems [34]. The mechanism of formation of these crosslinks has not been explained yet either by the results of X-ray scattering [27] or computer modeling [35]. In this particular case, we would like only to state that both of the dendrimers of the higher generations feature clear yield points; consequently, this phenomenon requires further detailed investigation by a complex of physical methods, starting from rheological studies analogously to those published in Ref. [26].

The molar masses defined by light scattering were in good agreement with the calculated ones. This means that the resulting systems fully justify their model nature. In particular, their solutions were studied by means of small-angle x-ray scattering, which afforded the linear sizes of the dendrimers in solution [36]. This allowed us to turn to the functionalization problem.

To evaluate the possibility of repeated functionalization of the dendrimers, we attempted to open the cyclosiloxane terminal groups of the model compound [\text{Si}^{1}_{4} \text{(Si4-cycle)]} using trifluoromethanesulfonic acid as a catalyst and hexamethyldisiloxane (HMDS) as a blocking agent. The reaction products were analyzed by GPC, $^1\text{H}$ and $^{29}\text{Si NMR}$ spectroscopy.

The model compound [\text{Si}^{1}_{4} \text{(Si4-cycle)]} was obtained according to Scheme 3 in the presence of a platinum catalyst, 1,3,5,7,5,7-Heptamethylocyclotetrasiloxane was used as a modifying agent.

![Scheme 3. Synthesis of the model compound [\text{Si}^{1}_{4} \text{(Si4-cycle)]} by the hydrolysis of tetrallylsilane.](image)

The identity of the isolated product was confirmed by the GPC, $^1\text{H}$ and $^{29}\text{Si NMR}$ spectroscopic data. Figure 6 depicts the GPC curves of the dendrimers with heptamethylocyclotetrasiloxane groups in the external shell after purification on a preparative chromatograph; the curve G-D corresponds to the model compound synthesized according to Scheme 3.
The ring-opening of the cyclosiloxane terminal groups in the presence of trifluoromethanesulfonic acid (Scheme 4) followed by blocking with HMDS and separation of the resulting mixture on a preparative chromatograph afforded compound 1.

Scheme 4. Opening of the peripheral cyclosiloxane groups by the example of the reaction with the model compound [Si₄( Si₄-cycle)].

Figure 7 shows the GPC curve of the reaction mixture where peak 1 corresponds to product 1 and peak 2 corresponds to excess HMDS and the curve of product 1 after isolation.

Figure 8. ¹H NMR spectra of product 1 (green) and the initial dendrimer [Si₄( Si₄-cycle)] (blue).

According to the ¹H NMR spectroscopic data (Fig. 8), the ratio of the integral intensities of protons of certain methyl groups in the product corresponded to the calculated values.

The ²⁹Si NMR spectrum (Fig. 9) of product 1 lacks the signal of the silicon atom with two methyl groups Me₃SiO at about −21 ppm and shows the signals in the range of 6–7 ppm corresponding to Me₃SiO, which evidences the opening of the cyclosiloxane terminal structural units, elimination of dimethylsiloxyl units, and blocking of the resulting derivative by trimethylsilyl groups.

Experimental

The ¹H NMR spectra were recorded on a Bruker WP-250 SY spectrometer; the ²⁹Si NMR spectra were registered on a Bruker Avance II 300 spectrometer with the operating frequency of 300 MHz. The chemical shifts in the proton spectra were defined relative to deuterochloroform (δ = 7.25 ppm) and those in the ²⁹Si NMR spectra—relative to tetramethylsilane (δ = 0.00 ppm). The spectra were processed with the ACD/Labs software package.

The analysis of volatile compounds by GLC was carried out on a Khromatek Analitik 5000 chromatograph (Russia) equipped with a kathometer detector, columns with the sizes of 2 m × 3 mm, and the immobile phase SE-30 (5%) applied to Chromatone-H-AW using helium as a mobile phase. The registration and calculation of the data were carried out with the Khromatek Analitik software (Russia).

The analytic GPC experiments were performed with a chromatographic system consisting of a Stayer 2 high-pressure pump (Akvilon, Russia), a RIDK 102 refractometer detector (Czech Republic), a JETSTREAM 2 PLUS column thermostat (KNAUER, Germany), columns with the length of 300 mm and the diameter of 7.8 mm filled with a Phenogel sorbent (Phenomenex, USA) with the particle sizes of 5 mm and pore sizes of 10⁵ and 10⁴ Å (with the separation range up to 75000 and 500000 D, respectively). THF was used as an eluent with the consumption rate of 1.0 mL/min. The registration and calculation of the data were carried out using the UniChrom 4.7 software (Belarus) with the definition of molar masses relative to polystyrene standards.

The direct definition of the weight-average molar masses of the dendrimers was performed on a Shimadzu chromatograph (Japan) consisting of a RID-10A refractometer, a Visocotek 270 LS double light-scattering detector equipped with a direct-angle (90°) and small-angle (7°) detectors (RALS and LALS), and Phenomenex columns (USA) with the sizes of 7.8 × 300 mm filled with a Phenogel sorbent with the pore sizes of 500, 10³, or 10⁴ Å. THF was used as an eluent. The data were analyzed with the Omnisec 4.5 software.
The column chromatography was carried out using silica gel 60 (0.063–0.100 mm, Merck) and toluene as an eluent.

The resulting dendrimers were purified using a preparative GPC chromatographic system consisting of a high-pressure pump (Akivlon), a RIDK 102 detector. Phenomenex preparative columns (USA: sizes 300 x 21.2 mm) filled with a Phenogel sorbent with the pore sizes of 500 or 105 Å, and 10 μm. THF was used as an eluent.

The intrinsic viscosity was measured on an Ubbelohde viscometer with the capillary diameter of 0.36 mm and the concentrations of working solutions within 0.5–2.7%. Toluene was used as a solvent. The measurements were carried out at 298 K with the accuracy of thermal regulation of 0.1 K.

All the reactions were conducted under an inert atmosphere using dry solvents. A xylene solution of platinum(0) (1,3-divinyl-1,1,3,3-tetramethyldisiloxane (2.1–2.4 % Pt) (PC-O72, Aldrich) was used as a catalyst.

The initial tetaallylsilane Si4(All) and carbosilane dendrimers of the third (Si323(All)) and sixth (Si655(All)) generations (the lower index corresponds to the number of silicon atoms, the upper index—to the number of functional groups, the bracketed value indicates the type of the functional silicon atoms, the upper index

The synthesis of the carbosilane–cyclotrisiloxane dendrimer of the sixth generation Si655(All) (Si6-cycle). Analogously to the synthesis of the new carbosilane–cyclotrisiloxane dendrimer of the third generation, the reaction of the polyallylsilane dendrimer of the sixth generation Si655(All) (0.42 g, 1.3–6 mol) and 1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane (1.18 g, 4.0·10−3 mol) afforded after evaporation 1.12 g of the crude product which was purified by preparative chromatography to give 0.77 g of Si655(All) (Si6-cycle) as a colorless waxy product. Yield: 69%.

Synthesis of the carbosilane–cyclotrisiloxane dendrimer of the zero generation Si1 (Si3-cycle). A solution of PC-O72 catalyst (12 μL) was added to a stirred solution of tetaallylsilane Si1(All) (0.36 g, 1.9·10−3 mol) in hexane (5 mL) under an argon atmosphere. Then, a solution of 1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane (2.63 g, 9.3·10−3 mol) was added dropwise. The reaction mixture was stirred at room temperature for 4 h. The low-boiling products and the solvent were removed under the reduced pressure (2 mm Hg). The resulting product was purified from the catalyst traces by passing its 5% toluene solution through a silica gel column. The solvent was removed under vacuum (2 mm Hg) to give 2.69 g of the crude product.

The synthesis of the carbosilane–cyclotrisiloxane dendrimer of the third generation Si323(All) (Si3-cycle). A solution of Parked’s catalyst (2 μL) was added to a mixture of the allylcarbosilane dendrimer of the third generation G-3(All) (0.17 g, 4.6·10−3 mol) and 1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane (0.5 g, 1.7·10−3 mol) in dry hexane (0.8 mL). The reaction mixture was stirred for 4 h at 25–40 °C. The excess of 1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane and the solvent were evaporated at 2 mm Hg to afford 0.60 g of a transparent viscous residue. The crude reaction product was purified by preparative chromatography (Phenogel 75K column, THF) to give 0.41 g of Si323(All) (Si3-cycle) as a colorless viscous product. Si157C143H1116O12S, mol. mass (calc.): 12770 g/mol. 1H NMR (CDCl3): δ = 0.08 (s, 84H, -(CH2)(3)Si(CH3)), 0.04 (s, 96H, -(CH2)(3)Si(3)O2), 0.06 (s, 576H, Si(CH3)3) in the ring), 0.55 (m, 120H, Si-CH2-CH2-CH2-Si), 1.30 (m, 240H, Si-CH2-CH2-CH2-Si) ppm. 29Si NMR (CDCl3): δ = 0.73 (s, 13Si, -(CH2)Si2(CH3)1), 1.06 (s, 16Si, -(CH2)Si3(CH3)2), –19.24 (s, 32Si, -(CH2)(3)Si(3)O2), –19.50 (s, 64Si, Si(CH3)2) in the ring), –20.32 (s, 32Si, Si(CH3)2) in the ring) ppm.
Synthesis of the carboisilane–cyclosiloxane dendrimer of the third generation Si_{25}^{3+} (Si3-cycle). A solution of PC-072 platinum catalyst (8 μL) was added to a stirred solution of the polyallylcarbosilane dendrimer Si_{25}^{3+} (All) (0.61 g, 0.17·10^{-3} mol) in hexane (5 mL) under an argon atmosphere. Then, a solution of 1,3,3,5,5-pentamethylocyclosiloxane (1.32 g, 6.32·10^{-3} mol) in hexane (3 mL) was added dropwise. The reaction mixture was stirred at room temperature for 4 h. The excess of 1,3,3,5,5-pentamethylocyclosiloxane and the solvent were removed under the reduced pressure (2 mm Hg). The resulting product was purified by the catalyst traces by passing its 5% toluene solution through a silica gel column. The solvent was removed under the reduced pressure to give 1.72 g of the crude product which was purified by preparative chromatography to give 1.35 g of the target dendrimer. Yield: 78%. Si:30C=H2=O, mol. mass (calc.) 10398 g/mol. 1H NMR (CDCl₃): δ 0.07 (s, 84H, -(CH₂)(CH₃)CH₂Si), 0.13 (s, 96H, -(CH₂)(CH₂)(Si)(O)₂), 0.16 (s, 384H, Si(CH₃)₂ in the ring), 0.60 (m, 240H, Si(CH₂)₃CH₂Si), 1.40 (m, 120H, Si(CH₂)₃CH₂Si) ppm. 29Si NMR (CDCl₃): δ 0.81 (s, 13Si, -(CH₂)₆Si(H)(CH₃)), 1.17 (s, 16Si, -(CH₂)₆Si(H)(CH₃)), −9.68 (s, 32Si, -(CH₂)(CH₃)₂Si(O)), −8.63 (s, 64Si, Si(CH₃)₂ in the ring) ppm. The product purity was controlled by GPC.

Synthesis of the carboisilane–cyclosiloxane dendrimer of the sixth generation Si_{256}^{2+} (Si3-cycle). The synthesis of the target dendrimer was carried out analogously to that of Si_{25}^{3+} (Si3-cycle) starting from the polyallylcarbosilane dendrimer of the sixth generation Si_{256}^{2+} (All) (1.30 g, 4.1·10^{-6} mol), 1,3,3,5,5-pentamethylocyclosiloxane (3.1 g, 1.5·10^{-7} mol) dissolved in hexane (14 mL), and PC-072 platinum catalyst (14 μL). The reaction mixture was treated analogously to the synthesis of Si_{25}^{3+} (Si3-cycle). The yield of the crude product was 3.45 g. The yield of the product after purification by preparative chromatography was 1.74 g (50%). Si_{102}C=H_{296}O_{1166}, mol. mass (calc.) 85374 g/mol.

Anal. Calc.: C, 41.06; H, 8.87; Si, 34.37. Found: C, 42.10; H, 9.06; Si, 33.18. 1H NMR spectrum (CDCl₃): δ 0.07 (s, 756H, -(CH₂)(CH₃)Si), 0.12 (s, 768H, -(CH₂)(CH₂)(Si)(O)₂), 0.15 (s, 3072H, Si(CH₃)₂ in the ring), 0.60 (m, 1520H, Si(CH₂)₃CH₂Si), 0.60 (s, 512H, -(CH₂CH₂CH₂Si)(O)₂), 1.35 (m, 1016H, Si(CH₂)₃CH₂Si) ppm. 29Si NMR (CDCl₃): δ 0.72 (s, 125Si, -(CH₂)₆Si(H)(CH₃)), 1.11 (s, 128Si, -(CH₂)₆Si(H)(CH₃)), −9.97 (s, 256Si, -(CH₂)(CH₂)(Si)(O)₂), −8.88 (s, 512Si, Si(CH₃)₂ in the ring) ppm.

Ring-opening of the cyclosiloxane groups in the dendrimer Si_{2}^{4+} (Si4-cycle). Trifluoromethanesulfonic acid (4.5 μL) was added to a mixture of dendrimer I, Si_{2}^{4+} (Si4-cycle), (0.28 g, 0.21·10^{-3} mol) and hexamethyldisiloxane (5.5 mL) under an argon atmosphere. The resulting mixture was stirred at 80 °C for 12 h. Then, sodium carbonate was added to the cooled reaction mixture to neutralize trifluoromethanesulfonic acid. The product was purified by preparative chromatography. Yield after purification was 0.063 g (23%). Si:30C=H₂=O, mol. mass (calc.) 1082 g/mol. 1H NMR (CDCl₃): δ −0.02 (s, 12H, -(CH₂)(CH₃)Si), −0.07 (s, 72H, -(CH₂)(CH₃), 0.51 (m, 8H, -(CH₂)₃CH₂CH₂CH₂Si), 1.32 (m, 16H, -(CH₂)(CH₂CH₂CH₂Si) ppm. 29Si NMR (CDCl₃): δ 1.00 (s, 1Si, -(CH₂)(Si)O), 6.89 (s, 4Si, O(Si)(CH₃)), −21.65 (s, 4Si, -(CH₂)(CH₂)(Si)(O)) ppm.

Conclusions

This work was supported by the Russian Foundation for Basic Research, project no. 20-33-70228. The molecular-weight distribution studies and registration of the NMR spectra were performed with the financial support from the Ministry of Science and Higher Education of the Russian Federation (no. 0086-2019-0005) using the equipment of the Collaborative Access Center “Center for Polymer Research” of ISPAM RAS.

Corresponding author

E-mail: elena.katarzhnova@ispam.ru. Tel: +7(495)332-5853495 (E. Yu. Katarzhnova)

References

10.1016/j.eurpolymj.2019.07.034
M. Malý, M. A. Muñoz
C. E. Gutierrez
10.1016/j.reactfunctpolym.2020.10.04746


E. Yu. Kazarzhnova et al., INEOS OPEN, 2020, 3 (6), 219–225