



SILICON-CONTAINING DENDRIMER WITH LONG SPACERS BETWEEN BRANCHING POINTS

Cite this: *INEOS OPEN*, 2024, 7 (1–3), 30–32
DOI: 10.32931/io2414a

Received 30 April 2024,
Accepted 1 June 2024

<http://ineosopen.org>

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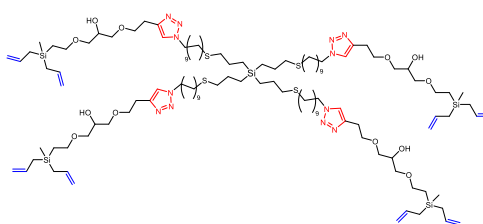
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Abstract

Dendrimers are macromolecules with a highly ordered, hyperbranched globular structure, which is ideal for a number of high-tech applications owing to the monodispersity, well-defined functionality, and combinatorial potential. In this communication, the synthesis of the first-generation silicon-containing dendrimer with long spacers between branching points using a combination of polyaddition reactions is presented.

Key words: dendrimers, giant dendrimers, long spacers, click chemistry, azide–alkyne cycloaddition.



Introduction

Dendrimers are macromolecules with a highly ordered, hyperbranched globular structure, which is ideal for a number of high-tech applications owing to its monodispersity, well-defined functionality, and combinatorial potential [1–5].

It is believed that dendrimers may have drawbacks associated with the limitations in the sizes and number of functional groups on their surface. This is explained by the limitation theory, which arose in early studies of de Gennes and is connected with an increase in the packing density of a dendrimer shell [6]. As is known, the limit of the de Gennes dense packing applies to theoretically pure dendrimers and, when the steric saturation of the outer shell is reached, it becomes insoluble. However, subsequent investigations [7–9] showed that dendrimer branches in some cases can unfold and bend inward, filling internal cavities, which leads to an increase in the density near the core. Using computational methods, Naidoo *et al.* [9] showed that more flexible and not bulky terminal spacers can be folded inward also for higher generations. As a result, the proportion of the terminal spacers folded inward in a dendrimer should increase sharply with the increasing generation number. Elongation of the internal spacers increases the dendrimer sizes, mass, and flexibility, which allows one to overcome the limitations associated with the de Gennes dense packing.

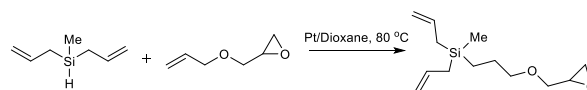
In this work, we present the synthesis of the first-generation silicon-containing dendrimer with long spacers between branching points by a combination of polyaddition reactions using a branching block.

Results and discussion

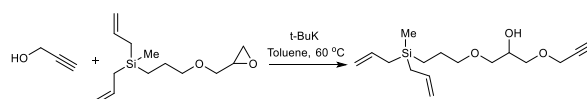
Compound **1** was obtained by the hydrosilylation of allyl glycidyl ether with diallyl(methyl)silane in the presence of a

Karstedt's platinum catalyst in dioxane at 80 °C (Scheme 1). The yield of **1** was 89%.

Compound **2** was obtained by the esterification with opening of an epoxide ring. The synthesis was carried out between compound **1** and propargyl alcohol in the presence of potassium *tert*-butoxide in toluene at 60 °C (Scheme 2). The yield of the resulting ester was 91%.

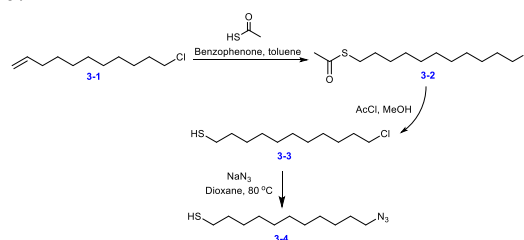


Scheme 1. Synthesis of compound **1**.



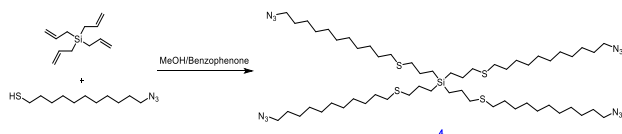
Scheme 2. Synthesis of compound **2**.

11-Chloro-1-undecene was synthesized by the earlier described method [12]. Its thiolation with thioacetic acid was performed under UV radiation in the presence of benzophenone as a catalyst (Scheme 3). The protective group in the product was removed in methanol in the presence of a catalytic amount of acetyl chloride. The conversion to an azide was carried out in the presence of dioxane at 80 °C. The yield of compound **3–4** was 67%.



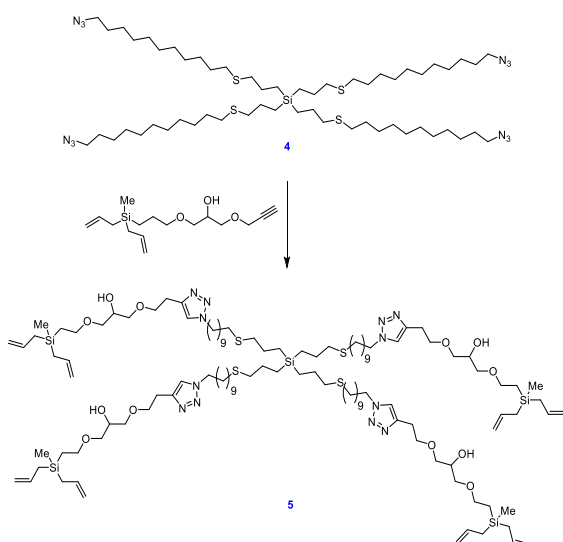
Scheme 3. Synthesis of compound **3–4**.

Then the branching center was synthesized by the thiol–ene addition reaction between compound **3-4** and tetraallylsilane in the presence of benzophenone in methanol under UV radiation (Scheme 4). The yield of compound **4** was 93%.



Scheme 4. Synthesis of the branching center.

At the final step, the first-generation dendrimer was obtained by the azide–alkyne cycloaddition reaction according to the previously developed method (Scheme 5) [13]. All the presented compounds were analyzed by ^1H NMR spectroscopy and gel permeation chromatography (GPC). The results obtained confirmed the occurrence of the reactions.



Scheme 5. Synthesis of the first-generation dendrimer with long spacers between branching points.

The resulting dendrimer was analyzed by ^1H NMR spectroscopy (see Fig. 1 and the Electronic supplementary information (ESI)). Its spectrum does not contain the signals at 2.60 and 3.24 ppm, corresponding to the acetylene and CH_2 protons of the azide group. At the same time, it reveals a new signal at 7.53 ppm, which corresponds to the proton in the triazole ring.

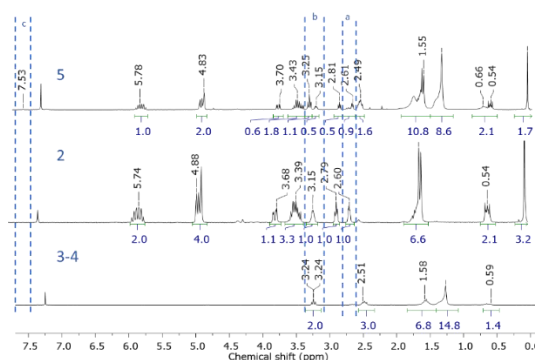


Figure 1. Comparison of the ^1H NMR spectra of the resulting compounds and the first-generation dendrimer.

Experimental section

General remarks

The work was concerned with pyridine (reagent grade, Spektrkhim) and organic solvents such as toluene, methanol and dioxane. All the reagents were preliminarily processed according to the standard methods [14]. The organic solvents and pyridine were dried over CaH_2 and then distilled under argon. Undecenol (98%, ABCR, Germany), allyl glycidyl ether (97%, Alfa Aesar, Germany), sodium azide (99% Ruskhim, Russia), propargyl alcohol (98%, ABCR, Germany), and thioacetic acid (98%, Acros Organics, Belgium) were purchased from commercial sources and used without further purification.

Analysis and general methodology

The ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer in CDCl_3 . The chemical shifts were referenced internally relative to the residual solvent signal (7.26 ppm, ^1H).

The GPC analysis was performed on a Shimadzu chromatograph (Japan, Germany) equipped with a RID 20 Å refractometer detector, using Phenogel 5u 10000 Å column (300×7.8 mm), polystyrene standards, and THF as an eluent at the temperature of 40°C with the flow rate of 1 mL/s.

Syntheses

Synthesis of the first-generation dendrimer with long spacers between branching points. Compounds **2** and **3-4**, ethyl acetate, and 3 mol % of CuBr used as a catalyst were loaded into a single-neck round-bottom flask equipped with a backflow condenser under an argon atmosphere. The reaction mixture was heated at 80°C for 5 h. The resulting first-generation dendrimer was purified by column chromatography using a hexane/dichloromethane mixture as an eluent. The solvent was removed under reduced pressure (oil pump, 1 Torr).

^1H NMR (CDCl_3): δ 7.52 (s, 1H, CH of the triazole ring), 5.84–5.66 (m, 2H, $\text{CH}_2=\text{CH}$), 4.87–4.80 (m, 4H, $\text{CH}_2=\text{CH}$), 4.34–4.19 (m, 2H, CH_2), 3.73–3.32 (m, 6H, CH_2), 2.58–2.44 (m, 2H, CH_2), 1.97–1.76 (m, 2H, CH_2), 1.55–1.52 (m, 8H, CH_2), 1.29–1.24 (m, 8H, CH_2), 0.61–0.47 (m, 2H, CH_2Si), 0.05–0.02 (m, 12H, CH_3) ppm.

Conclusions

The synthetic approach to the multifunctional branching block was developed that can be used for the production of dendrimers with long spacers between branching points using polyaddition reactions. The silicon-containing dendrimer with long spacers between branching points was synthesized and analyzed by ^1H NMR spectroscopy. The synthesis was carried out using click reactions. The total time for obtaining the first-generation dendrimer composed 24 h. Hence, the rapid synthesis of the first-generation dendrimer using commercially available reagents was demonstrated, which included only one purification step during the dendrimer isolation.

Acknowledgements

The synthesis of the first-generation dendrimer and

branching block was performed with financial support from the Russian Science Foundation (project no. 22-13-00459).

The syntheses of compounds **1** and **2** were carried out with financial support from the Government of the Tula Region (Decree no. 899 of December 30, 2021) within Agreement no. 11 of September 7, 2022.

The molecular-weight distribution and NMR spectroscopic studies were performed with financial support from the Ministry of Science and Higher Education of the Russian Federation (FFSM-2024-0001) using the equipment of the Collaborative Access Center "Center for Polymer Research" of ISPM RAS.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the structures, ¹H NMR spectra, and GPC curves of the compounds obtained. For ESI, see DOI: 10.32931/io2414a.

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