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Mendeleev Commun., 2016, **26**, 121–123

Mendeleev Communications

Acyclic polyphenylsilsesquioxane: synthesis and properties

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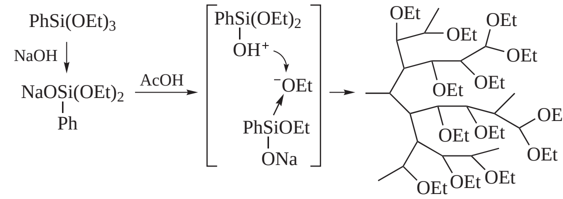
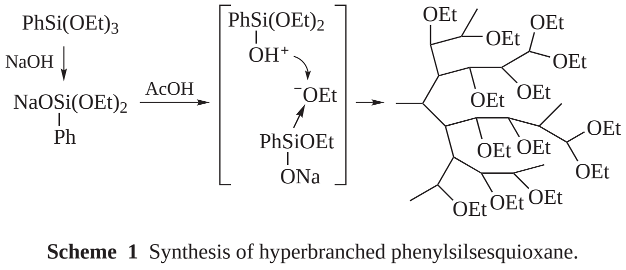
DOI: 10.1016/j.mencom.2016.03.012

New highly functionalized acyclic hyperbranched polyphenylsilsesquioxanes were obtained and transformed into acyclic nonfunctional or cross-linked nanogel particles with specified outer shell.



Polyphenylsilsesquioxanes are widely used as resins, varnishes, paints, compounds of various purposes as well as in electronics.[1,2] Introducing phenyl substituents into the composition of organosilicon polymers enables high thermal and radiation stability and high refractive index and improvement of their mechanical properties.[3] Rigidity and brittleness resulting from the high thermodynamic probability of cyclic structure formation while obtaining phenylsiloxanes limit their applications. Phenylsilsesquioxanes synthesized by the hydrolysis of trifunctional phenyl-containing silane possess a rigid polycyclic structure[4] incorporating ladder fragments or even, under specified conditions, cage-like polyhedral ones.[5,6] It is also possible to prepare a ladder polyphenylsilsesquioxane containing different stereoisomeric units in the main chain by the polycondensation of corresponding cyclic tetrafunctional monomers.[7,8] Literature analysis revealed that acyclic phenylsilsesquioxanes have not been obtained so far.

Herein, we synthesized acyclic hyperbranched polyphenylsilsesquioxanes and nanoparticles based on them.[9] Instead of commonly employed trichlorophenylsilane, commercially available triethoxyphenylsilane was used as a starting material, which made it possible to develop a modern ecofriendly chlorine-free method. As known, acyclic hyperbranched compounds[10] are formed *via* polycondensation of AB_2-type monomers with functional groups of different nature, when heterofunctional condensation of the groups occurs[11] excluding homofunctional one. In compliance with this, the intermediate sodium diethoxyphenylsilanolate $PhSi(ONa)(OEt)_2$, whose structure met the Flory criteria, was obtained from $PhSi(OEt)_3$. Afterwards, it was neutralized and heterofunctionally condensed to form an acyclic hyperbranched polyfunctional oligomer (Scheme 1). The entire process can be conducted in one-pot mode starting from the very triethoxyphenylsilane, which is obviously the main advantage of the procedure.



Scheme 1 Synthesis of hyperbranched phenylsilsesquioxane.

Synthesis of the sodium salt was carried out as previously described.[12] Then it was neutralized with an equivalent quantity of dry acetic acid. This protocol enables further condensation to give diethoxyhydroxyphenylsilane and, accordingly, the formation of hyperbranched polymer.†

GPC data (Figure 1) show that the obtained polymeric product possesses sufficiently narrow molecular-weight distribution, and

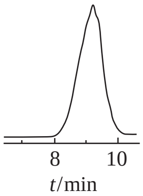


Figure 1 GPC curve of obtained polyphenylethoxysiloxane (MM = 1000, linear polystyrene standards, pores size 1000 Å).

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† All reagents were pre-treated in accordance with common methods.[15] Organoalkoxysilanes were distilled prior to use. Toluene was dried by boiling and distillation over calcium hydride. Acetic acid was dried by distillation over phosphorus oxide(V).

^{1}H NMR spectra were recorded on a Bruker AC-250 (250.13 MHz) spectrometer. Chemical shifts are referenced to residual nondeuterated solvent frequencies (δ =7.25 ppm for $CHCl_3$). Spectra were processed on a computer using the program ACDLABS. ^{29}Si NMR spectra were obtained with a Bruker Avance II-300 (59.6 MHz) instrument with the addition of the accelerating paramagnetic relaxation agent chromium(III) acetylacetonate. Chemical shifts are referenced to the internal standard tetramethylsilane. Spectra were processed on a computer using the program MestReNova.

Gel permeation chromatography (GPC) was conducted with a chromatographic system consisting of a high-pressure pump (Stayer series II, Aquilon), a refractive index detector (Smartline RI 2300, Knauer) and a column oven (Jetstream 2 Plus, Knauer). Thermostatically controlled temperature was 40 °C (±0.1 °C). The eluent was THF, and the flow rate was 1.0 ml min^{-1}. A column of 300×7.8 mm was filled with Phenogel

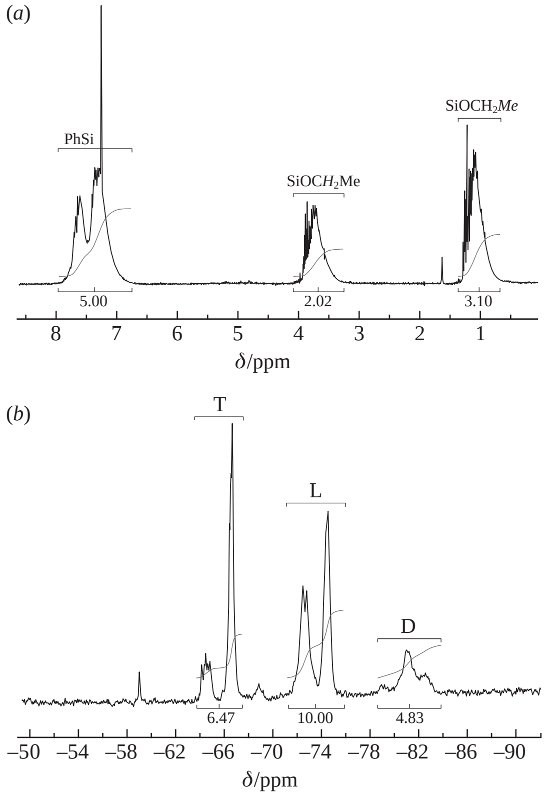

Figure 2 (*a*) ^{1}H and (*b*) ^{29}Si NMR spectra of obtained polyphenylethoxysiloxanes. D (dendritic) – tri-substituted silicon, L (linear) – di-substituted silicon, T (terminal) – mono-substituted silicon.

its molecular weight is rather moderate (about 1000). According to ^{1}H NMR spectra (Figure 2), the polymer structure corresponds to –PhSi(OEt)– unit, which corroborates that the monomer condensation mechanism is purely heterofunctional and indicates the formation of a hyperbranched polymer. ^{29}Si NMR spectra reveal that the product has three types of silicon atoms (L – linear) –[PhSi(OEt)–O]–, (T – terminal) [PhSi–O]$_{1.5}$– and (D – dendritic) [PhSi(OEt)$_2$–O]. The ratio of their content, *i.e.* degree of branching (DB) of polymer, is an important characteristic of product, which determines glass-transition temperature, mechanical strength, viscosity of solutions and melts, ability to incapsulation of monomer compounds. DB = 1 for precise structure of dendrimer, and DB for more defective polymers is usually no higher than 0.5.[13] Based on ^{29}Si NMR data, the synthesized polymers have DB value as 0.47. Thus, the obtained hyperbranched structure has minimal possible deficiency.

Functional groups were blocked with hexaorganodisiloxane or triorganoethoxysilanes with various organic substitutes to obtain stable non-functional polymers.[‡] In all cases the reaction was carried out in water-free acetic acid, *i.e.* in an active medium.[14] According to its mechanism, hydrolytic heterofunctional condensation can occur in the presence of water which can result from the esterification of acetic acid with alcohol released as a result of acetoxylation. Under the above conditions, the full conversion of alkoxy groups was achieved irrespective of their chemical nature and whether they were located on the surface of hyperbranched macromolecule or within its inner sphere. The structure of polymer backbone was not disturbed throughout blocking in all cases. The type of blocking groups was varied, and it was found out that it significantly influences the properties of polymer, for instance, thermal stability (Table 1).

As the condensation time of hyperbranched polyphenylsilsesquioxane in acetic acid (until the blocking agent is added) increases, intramolecular condensation of the functional groups starts to proceed. It results in the formation of cross-linked polycyclic structures with an external functional layer which can be blocked with monofunctional reagents. Simultaneous

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sorbent (Phenomenex) with a particle size of 5 μm, and a pore size of 10^3 Å. Data were detected and processed using the Mul'tiKhrom 1.6 GPKh program packages (Ampesand). The calibration of the GPC data was conducted using a Polystyrene Standard Calibration Kit for Lipophilic GPC (Merck).

Samples were examined using DSC (DSC_822e, Mettler Toledo) at a heating rate of 10 K min^{-1}. TGA was performed with a Derivatograth-C (MOM) in air and in argon atmosphere at a heating rate of 5 K min^{-1} for samples weighing 15 mg.

Monomer, sodium diethoxyphenylsilanolate. The synthesis was performed according to the previously described procedure.[12] Sodium hydroxide (1.0 g, 0.025 mol) was added to phenyltriethoxysilane (18.03 g, 0.075 mol). Stirring was carried out at room temperature until complete dissolution of the sodium hydroxide. Volatiles were removed *in vacuo* (1 mbar, 170 °C). The obtained sodium diethoxymethylsilanolate (5.52 g, 92% yield, calculated relative to NaOH) was dissolved in dry toluene (30.0 ml).

Hyperbranched polyphenylethoxysiloxane. Anhydrous acetic acid (1.28 g, 0.0213 mol) was added to the solution of sodium diethoxyphenylsilanolate (0.5 g, 0.0213 mol) in toluene. After 24 h, the solution was filtered and dried. Volatiles were removed *in vacuo* (1 mbar). Hyberbranched polyphenylethoxysiloxane was obtained in 97% yield. GPC: MM = 1100. ^{1}H NMR (CDCl$_3$) δ: 0.95–1.35 [m, 3H, (*Me*CH$_2$O)Si], 3.60–4.00 [m, 2H, (MeC*H*$_2$O)Si], 7.10–7.85 (m, 5H, PhSi). ^{29}Si NMR (CDCl$_3$) δ: –(83.5–80.0) (m, PhSiO$_{1,5}$), –(75.0–71.5) [m, PhSiO(OEt)], –(67.0–64.0) [m, PhSiO$_{0.5}$(OEt)$_2$].

[‡] *Synthesis of polyphenylsilsesquioxane with trimethylsiloxy terminal groups in active medium*. Hyperbranched polyphenylethoxysiloxane (0.5 g, 0.003 mol), hexamethyldisiloxane (1.47 g, 0.009 mol) and acetyl chloride (0.022 g, 0.0003 mol) were added to an excess of acetic acid (6.87 g, 0.12 mol). The mixture was refluxed for 24 h. The product was extracted with toluene and dried over Na$_2$SO$_4$. The volatiles were removed *in vacuo*. GPC: MM = 1000. T_g = –58 °C. ^{1}H NMR (CDCl$_3$) δ: 0.10 (m, 3H, SiMe), 7.10–7.85 (m, 5H, PhSi).

Synthesis of polyphenylsilsesquioxane with diphenylmethylsiloxy terminal groups in active medium. Hyperbranched polyphenylethoxysiloxane (0.5 g, 0.003 mol), diphenyltetramethyldisiloxane (2.58 g, 0.009 mol) and acetyl chloride (0.034 g, 0.00043 mol) were added to an excess of acetic acid (10.79 g, 0.18 mol). The mixture was refluxed for 24 h. The product was extracted with toluene and dried over Na$_2$SO$_4$. The volatiles were removed *in vacuo*. GPC: MM = 1100. T_g = 2.5 °C. ^{1}H NMR (CDCl$_3$) δ: 0.10 (m, 3H, SiMe), 7.10–7.85 (m, 5H, PhSi).

Synthesis of polyphenylsilsesquioxane with dimethylvinylsiloxy terminal groups in active medium. Hyperbranched polyphenylethoxysiloxane (0.5 g, 0.003 mol), divinyltetramethyldisiloxane (1.68 g, 0.009 mol) and acetyl chloride (0.024 g, 0.00031 mol) were added to an excess of acetic acid (7.63 g, 0.127 mol). The mixture was refluxed for 24 h. The product was extracted with toluene and dried over Na$_2$SO$_4$. The volatiles were removed *in vacuo*. GPC: MM = 1000. T_g = –49 °C. ^{1}H NMR (CDCl$_3$) δ: 0.10 (m, 3H, SiMe), 5.79–6.12 (m, 3H, Si–C*H*=C*H*$_2$), 7.10–7.85 (m, 5H, PhSi).

Synthesis of polyphenylsesquioxane nanogel (block agent was added after 2 h). A solution of hyperbranched polyphenylethoxysiloxane (0.5 g, 0.003 mol) in an excess of acetic acid (7.63 g, 0.127 mol) was refluxed for 2 h. Afterwards, divinyltetramethyldisiloxane (1.68 g, 0.009 mol) and acetyl chloride (0.024 g, 0.00031 mol) were added. The mixture was refluxed for 24 h. The product was extracted with toluene and dried over Na$_2$SO$_4$. The volatiles were removed *in vacuo*. GPC: MM = 10000–1000. ^{1}H NMR (CDCl$_3$) δ: 0.10 (m, 3H, SiMe), 5.79–6.12 (m, 3H, Si–C*H*=C*H*$_2$), 7.10–7.85 (m, 5H, PhSi).

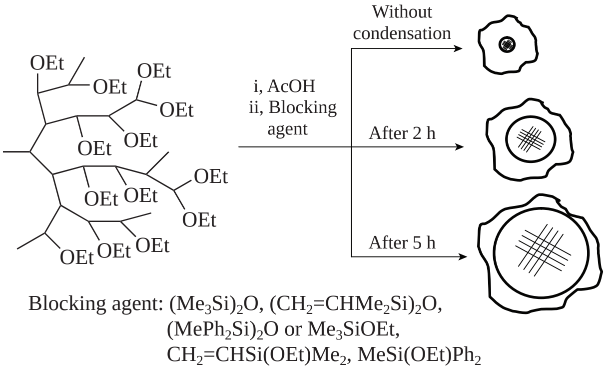
Synthesis of polyphenylsesquioxane nanogel (block agent was added after 5 h). A solution of hyperbranched polyphenylethoxysiloxane (0.5 g, 0.003 mol) in an excess of acetic acid (7.63 g, 0.127 mol) was refluxed for 5 h. Afterwards, divinyltetramethyldisiloxane (1.68 g, 0.009 mol) and acetyl chloride (0.024 g, 0.00031 mol) were added. The mixture was refluxed for 24 h. The product was extracted with toluene and dried over Na$_2$SO$_4$. The volatiles were removed *in vacuo*. GPC: MM = 32000–1000. ^{1}H NMR (CDCl$_3$) δ: 0.10 (m, 3H, SiMe), 5.79–6.12 (m, 3H, Si–C*H*=C*H*$_2$), 7.10–7.85 (m, 5H, PhSi).

Table 1 Thermal characteristics of the blocked hyperbranched phenylethoxysiloxanes.

Terminal group	MM[a]	T_g/°C	T_{dec}/°C (5% loss)	
			under argon	under air
Me_3SiO	1100	–58.0	240	220
$CH_2{=}CHSi(Me)_2O$	1000	–49.0	250	250
$MeSi(Ph)_2O$	1000	2.5	375	375

[a] MM was determined at the maximum of the peaks using polystyrene standards.

proceeding of the blocking and polycyclization makes it possible to control the product structure in a wide range. On raising the blocking agent concentration one may obtain an absolutely acyclic structure; whereas if it is added after the polycyclization has been proceeded for some time, products with a more dense core and higher molecular weight can be formed as a result of intermolecular interactions of the functional cores (Scheme 2).



Scheme 2 Synthesis of nanogel particles based on acyclic phenylethoxysiloxanes.

In accordance with GPC and ^{1}H NMR data, the ratio between the core (C_6H_5-Si signals) and surface layer ($CH_2{=}CH$–Si signals) sizes is determined by the condensation duration (Figures 3 and 4).

In conclusion, a procedure for obtaining a new acyclic hyperbranched polyphenylethoxysiloxane has been developed and realized as well as the factors affecting its formation have been determined. The high-functional structure can be transformed to nonfunctional one accompanied with either preservation of the acyclic framework or formation of cross-linked nanogel particles with external shell. The blocking triorganosilyl agent used significantly affects the properties of macromolecule and can be easily varied depending on requirements to material. The nanosized polymer systems obtained in a nonfunctional form seem to be very promising as components for lubrication composites and their functional precursors as cross-linking and modifying agents for polymer composites of different types.

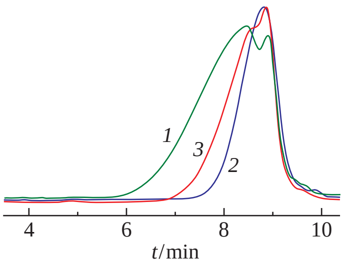


Figure 3 GPC curves of polyphenylethoxysiloxane blocked by dimethylvinylsiloxy groups: (*1*) without preliminary condensation (MM = 1000) and after (*2*) 2 h (MM = 10000–1000) and (*3*) 5 h (MM = 32000–1000) of condensation. Linear polystyrene standards, pores size 1000 Å.

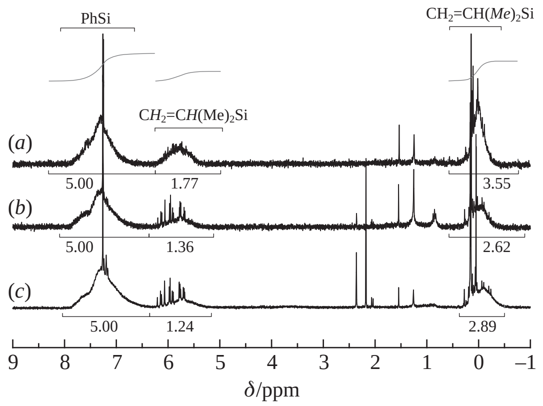


Figure 4 ^{1}H NMR spectrum of polyphenylethoxysiloxanes blocked with divinyltetramethyldisiloxane: (*a*) without preliminary condensation and after (*b*) 2 h and (*c*) 5 h of condensation.

This work was supported by the Russian Foundation for Basic Research (project no. 13-03-12239 ofi_m). Professor A. M. Muzafarov appreciates the Russian Science Foundation for financial support (project no. 14-23-00231).

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Received: 28th July 2015; Com. 15/4694