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Synthesis and rheological properties of star-shaped polydimethylsiloxanes based on carbosilane dendrimers

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Materials & Equipment

The following reagents and accessory compounds were used in this study: a 1st generation carbosilane dendrimer with allyl functional groups in the shell obtained previously by a reported procedure[S1]; dichloromethylsilane 97% from ABCR distilled with a reflux condenser; allyl chloride 98% from Acros, distilled; hexane 97.76% from OJSC “Ruskhim.ru” dried with calcium hydride and 3Å molecular sieves; toluene of “pure for analysis” grade from OJSC “Khimpromtorg” dried with sodium with benzophenone and 3Å molecular sieves; platinum(0)-1,3-divinyl, 1,1,3,3-tetramethyldisiloxane complex – 2% solution in xylene (Karstedt’s catalyst); 1-bromododecane 98% from Acros; magnesium chips 99% from Fluka; hexamethylcyclotrisiloxane (D_3) 95% from ABCR, dried and distilled over calcium hydride; butyllithium (1.6 *M* solution in hexanes) from Acros; light petroleum from OJSC “Ruskhim.ru” distilled in a rotary evaporator; silica gel from Khimmed 0.040-0.063 mm; anhydrous sodium sulfate from OJSC “Komponent-reaktiv”; saturated ammonium chloride solution from MCD.

GPC analysis was performed on a chromatographic system consisting of a “STAIER” s. 2” high-pressure pump (“Akvilon”, Russia), a Smartline RI 2300 refractometer and a “JETSTREAM 2 PLUS” thermostat (“KNAUER”, Germany). The temperature in the thermostat was 40°C (± 0.1°C). THF and toluene + 2% THF were used as the eluents; the flow rate was 1.0 ml min^{-1}, 300x7.8 mm columns and Phenogel sorbent (“Phenomenex”, USA), 5 μm, pores from 10^3 to 10^5 Å, were used.

^{1}H NMR spectra were recorded on a Bruker WP250 SY or Bruker Avance AV300 spectrometer using $CDCl_3$ or *n*-hexane as the solvent, and tetramethylsilane as the external standard. The spectra were processed on a computer using the “ACD LABS” program.

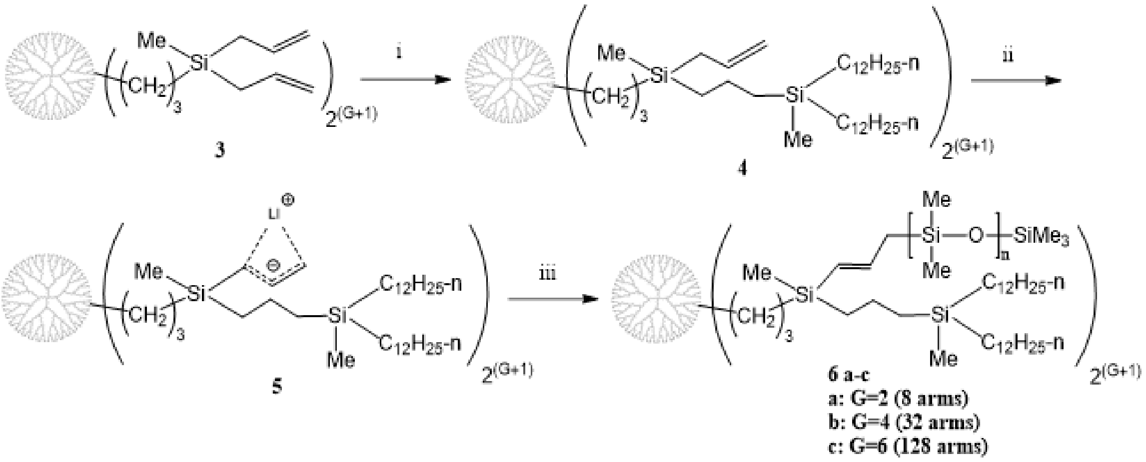
The rheological characteristics were measured on an Anton Paar - MCR 302 rheometer (Austria) in the constant shear rate mode using a plane-plane measuring unit (d = 50 mm).

Experimental

Carbosilane dendrimers of the 2nd, 4th, and 6th generations with a functional shell of allyl and didodecylmethylsilyl groups were synthesized as reported[S2, S3].

The polylithium derivatives of the 2nd, 4th, and 6th generations carbosilane dendrimers thus obtained were synthesized by lithiation of allyl groups by the reported procedure[S4].

The star-shaped polydimethylsiloxanes were obtained by anionic polymerization of hexamethylcyclotrisiloxane using the polylithium initiators synthesized previously. Hexamethylcyclotrisiloxane in 10% hexane solution and a lithium macroinitiator in an amount corresponding to a given arm length were stirred for 8 hours in inert atmosphere. After that, THF was added to activate the polymerization. The polymerization time was 14 hours in all the cases. After that, the reactive chain ends were terminated with trimethylsilyl groups. Lithium chloride was washed away with water and the solution was dried with sodium sulfate, then the solvents were removed in vacuo. The polymer was purified by re-precipitation of a solution in hexane with methanol. The number of arms was determined by generation of the initial dendrimer and, accordingly, by the number of active lithium centers in the structure. The arm length was determined by the “active center/initial monomer” ratio in the reaction system based on ^{1}H NMR data.



Scheme S1 *Reagents and conditions:* i, (n-$C_{12}H_{25}$)$_2$Si(Me)H, [Pt] (the Karstedt’s catalyst), toluene; ii, BuLi, TMEDA, hexane; iii: *cyclo*-($OSiMe_2$)$_3$, THF, then $ClSiMe_3$.

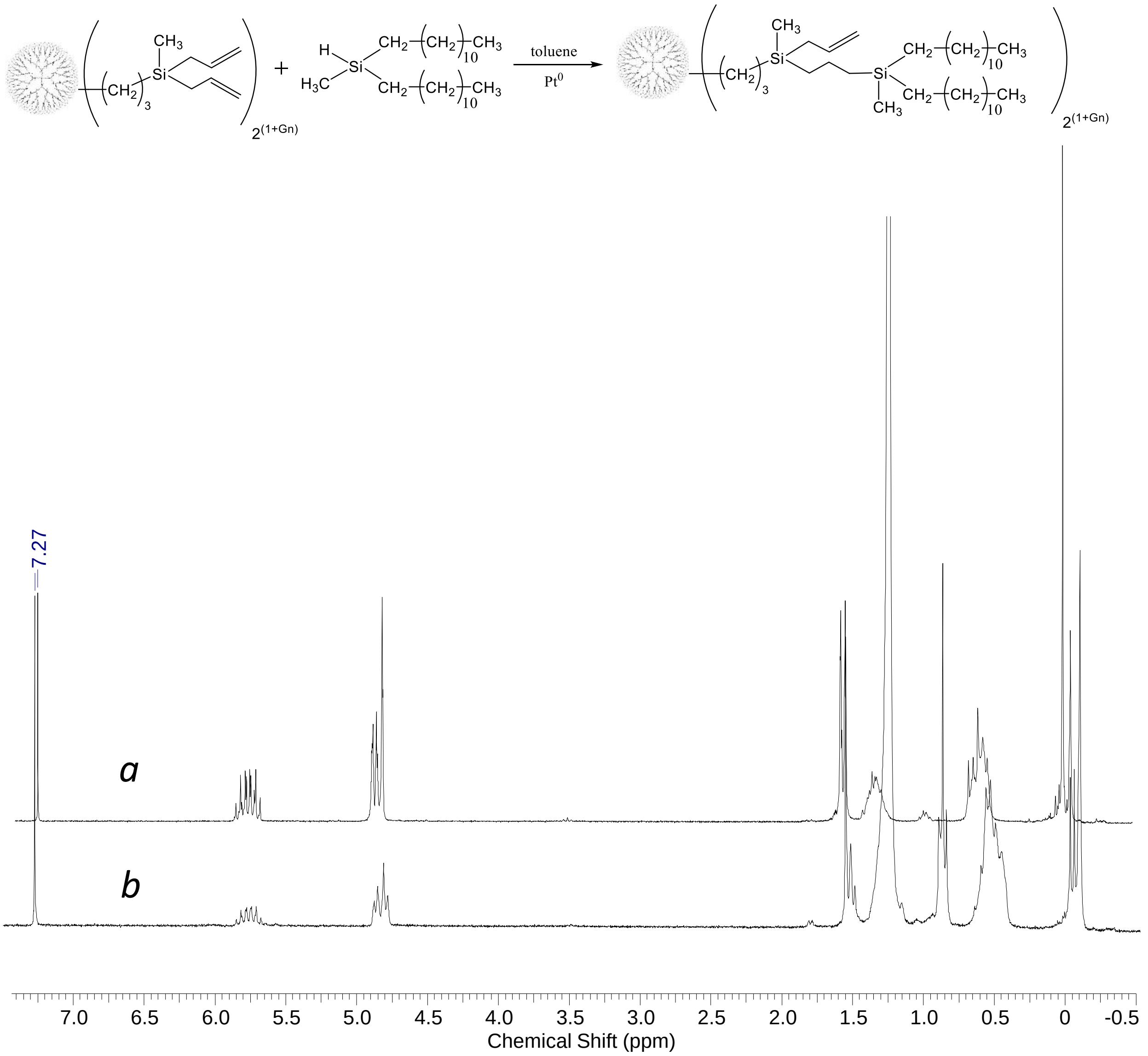


Figure S1. ^{1}H NMR monitoring of hydrosilylation of compound **3** (see Scheme S1, step i). Spectra of the starting 4th generation carbosilane dendrimer **3** (*a*) and its didodecylmethylsilyl derivative **4** (*b*).

Part *a*, dendrimer **3**, ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.76 (ddt, ^3J 16.4, 10.3, 8.2 Hz, 16H), 4.89 – 4.79 (m, 32H), 1.53 (dt, ^3J 8.2, ^4J 1.3 Hz, 32H), 1.39 – 1.20 (m, 30H), 0.64 – 0.47 (m, 60H), Σ -0.03 and -0.08 (s, 45H).

Part *b*, dendrimer **4**, ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.75 (dq, J = 16.8, 10.3, 8.0 Hz, 8H), 4.92 – 4.71 (m, 16H), 1.53 (dt, J = 8.1, 1.2 Hz, 32H), 1.25 (s, 350H), 0.93 – 0.82 (m, 48H), 0.66 – 0.33 (m, 92H), Σ -0.01, -0.04 and -0.08 (s, 69H).

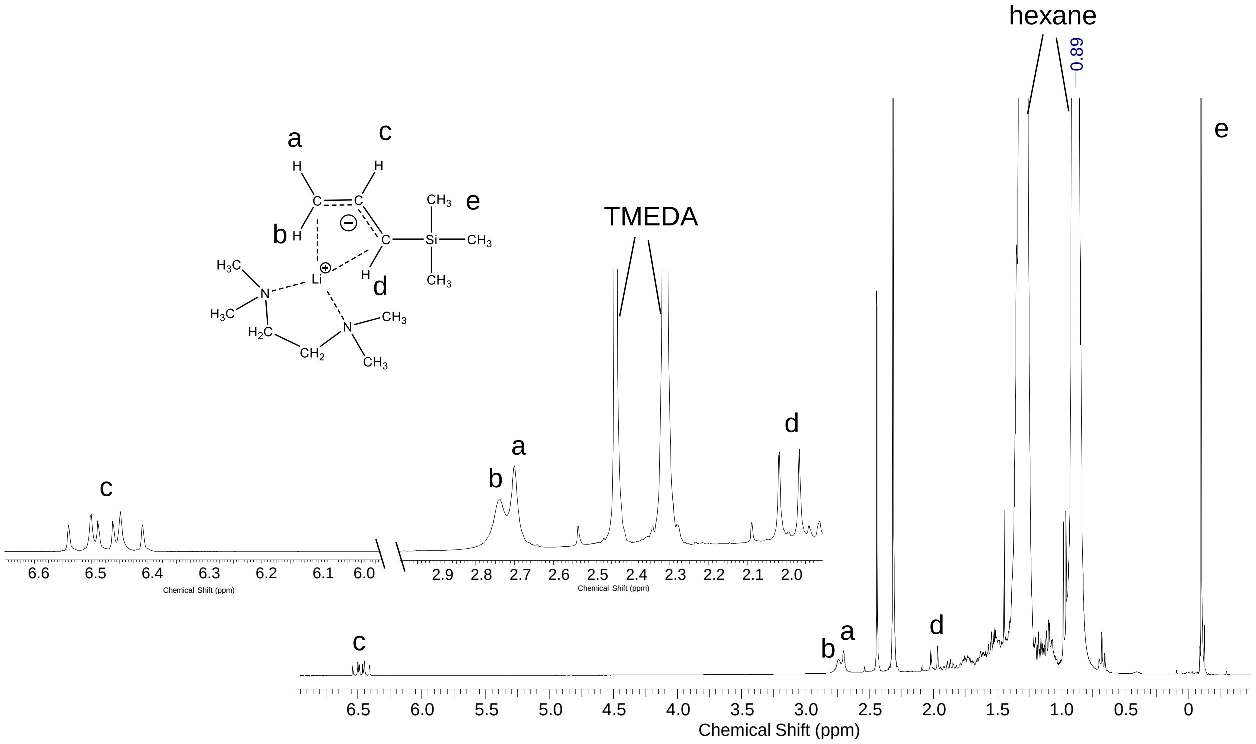


Figure S2. ^{1}H NMR spectrum of the lithiation product of trimethylallylsilane with *n*-butyllithium in the presence of TMEDA. ^{1}H NMR (300 MHz, hexane) δ 6.46 (dt, $^{3}J = 15.6$, 11.8 Hz, 1H), 2.80 – 2.65 (m, 2H), 1.99(d, $^{3}J = 15.6$ Hz, 1H), -0.10 (s, 9H).

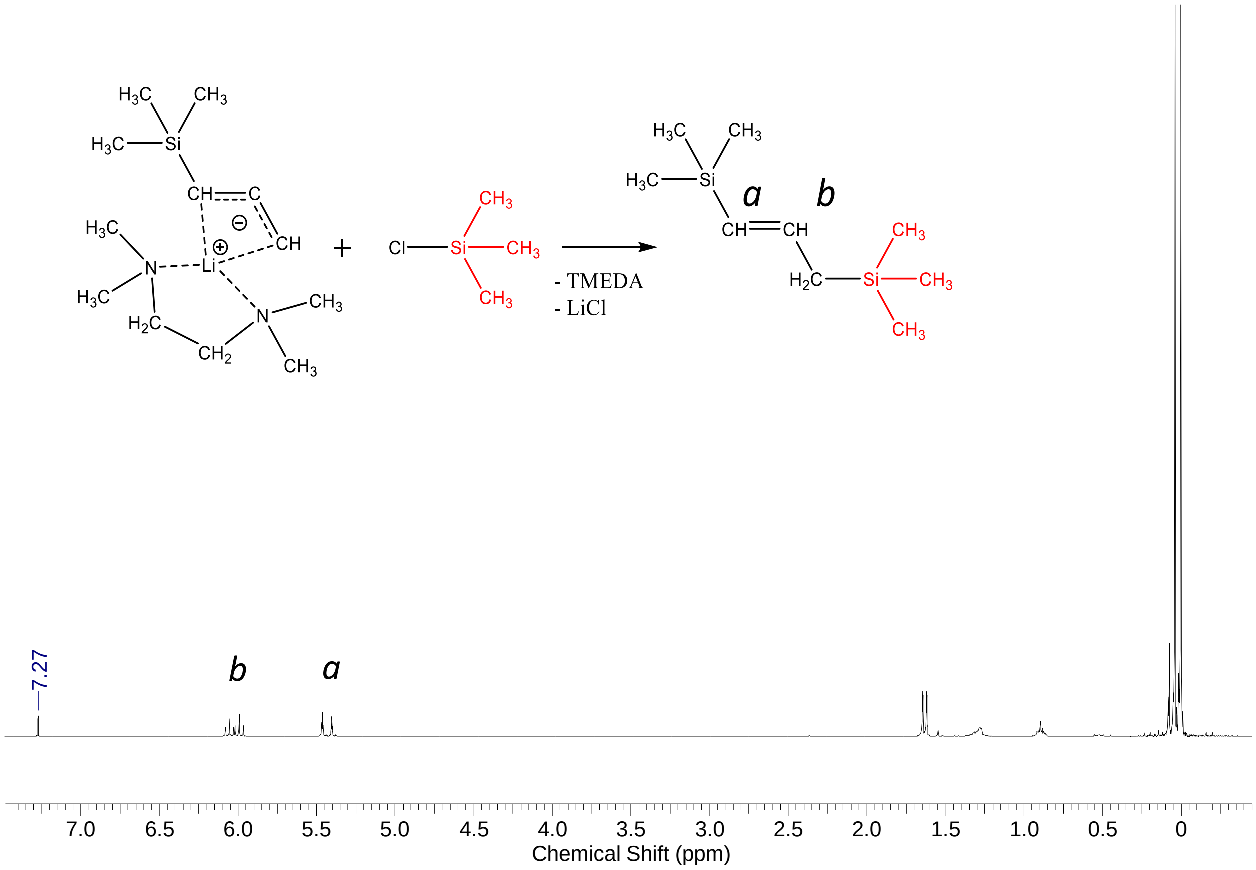


Figure S3. ^{1}H NMR monitoring of ClSiMe$_3$-blocking of lithiated allyl(trimethyl)silane derivative. ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.03 (dt, $^{3}J = 18.3$, 7.8 Hz, 1H), 5.44 (d, $^{3}J = 18.4$, 1.3 Hz, 1H), 1.63 (d, $J = 7.8$, 1.3 Hz, 2H), 0.04 (s, 9H), 0.01 (s, 9H).

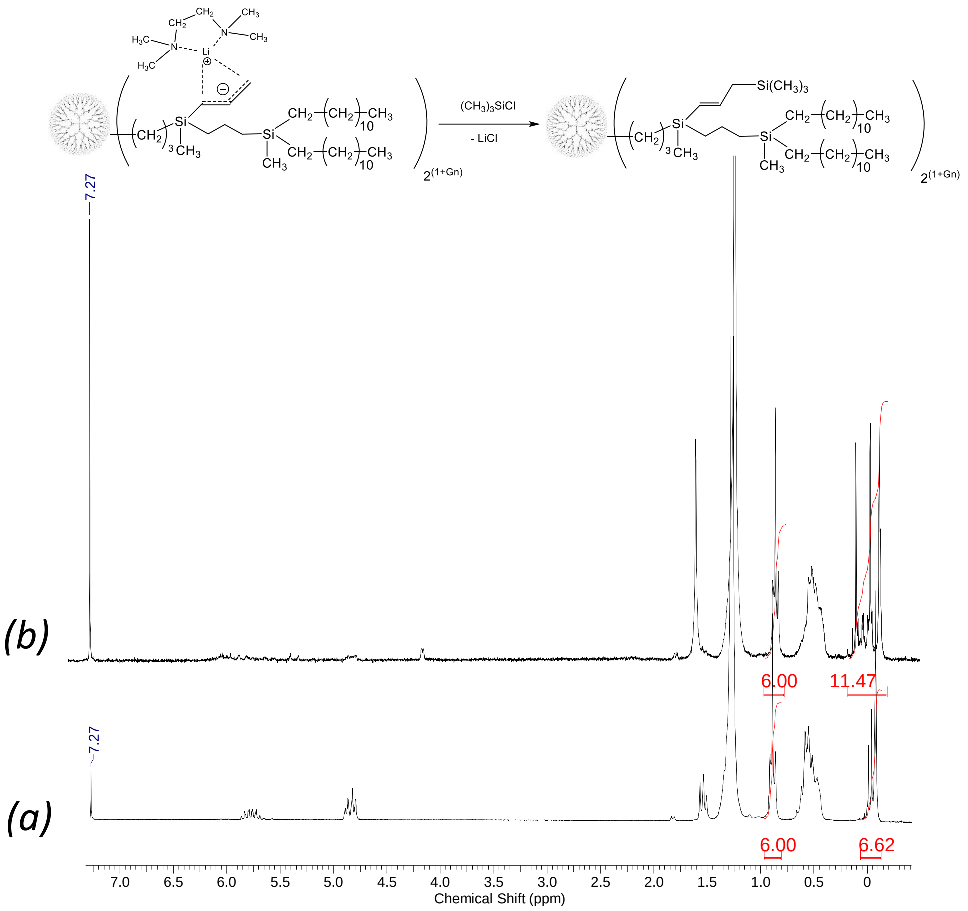


Figure S4. ^{1}H NMR monitoring of $ClSiMe_3$-termination of lithium macroinitiators. (*a*) Initial DDMS-derivative of carbosilane dendrimer 2nd generation **4** and (*b*) blocked with $ClSiMe_3$ lithium macroinitiator **5**, compound **6a** (see Scheme S1, steps ii and iii). The signals necessary for calculations (0 ppm $–Si\text{-}C\underline{H}_3$ and 0.9 ppm $–CH_2\text{-}C\underline{H}_3$) are integrated.

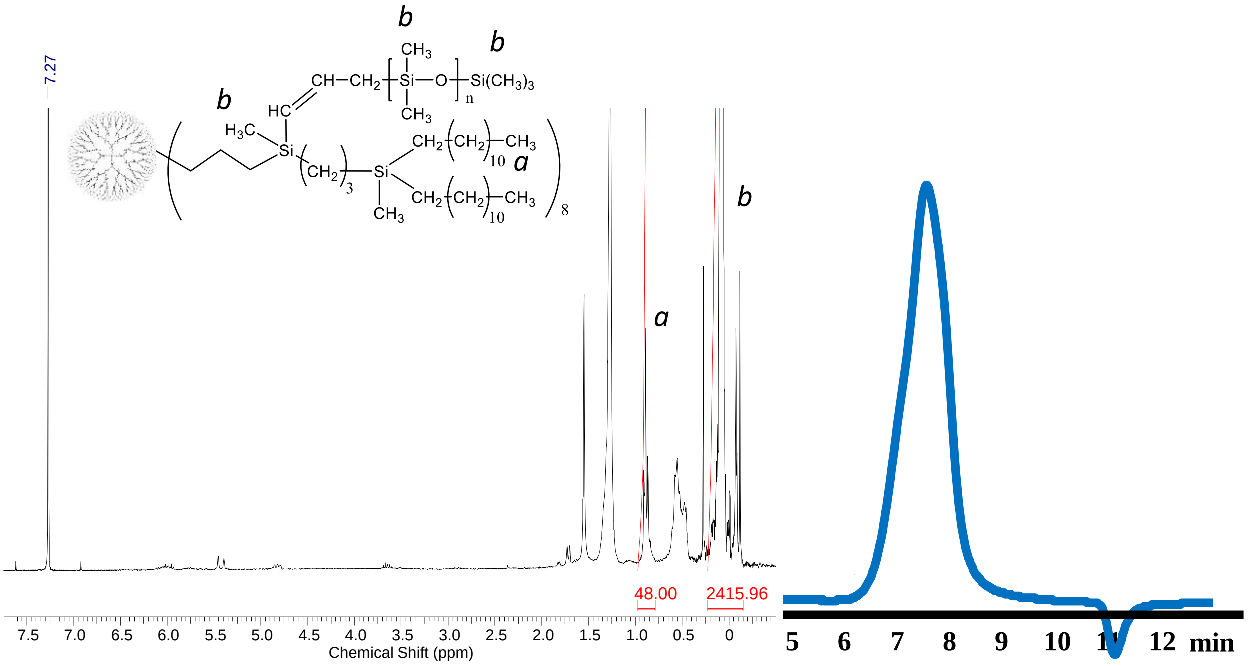


Figure S5. ^{1}H NMR spectrum and GPC curve of star-shaped PDMS with 8-arms **6a**. The signals necessary for calculations (0 ppm $–Si\text{-}C\underline{H}_3$ and 0.9 ppm $–CH_2\text{-}C\underline{H}_3$) are integrated.

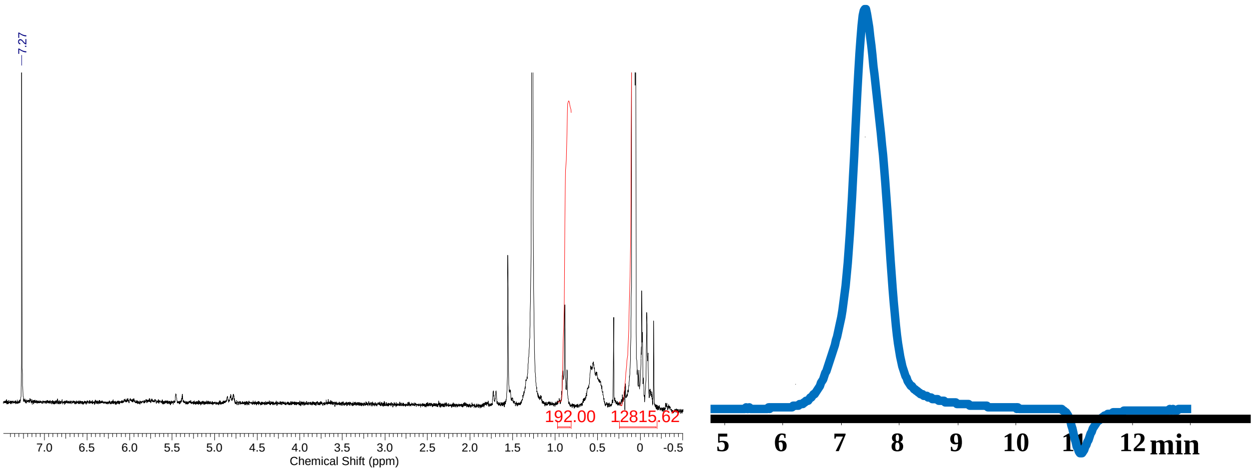


Figure SM-6. ^{1}H NMR spectrum and GPC curve of star-shaped PDMS with 32 arms **6b**. The signals necessary for calculations (0 ppm –Si-C$\underline{H}_3$ and 0.9 ppm –CH$_2$-C$\underline{H}_3$) are integrated.

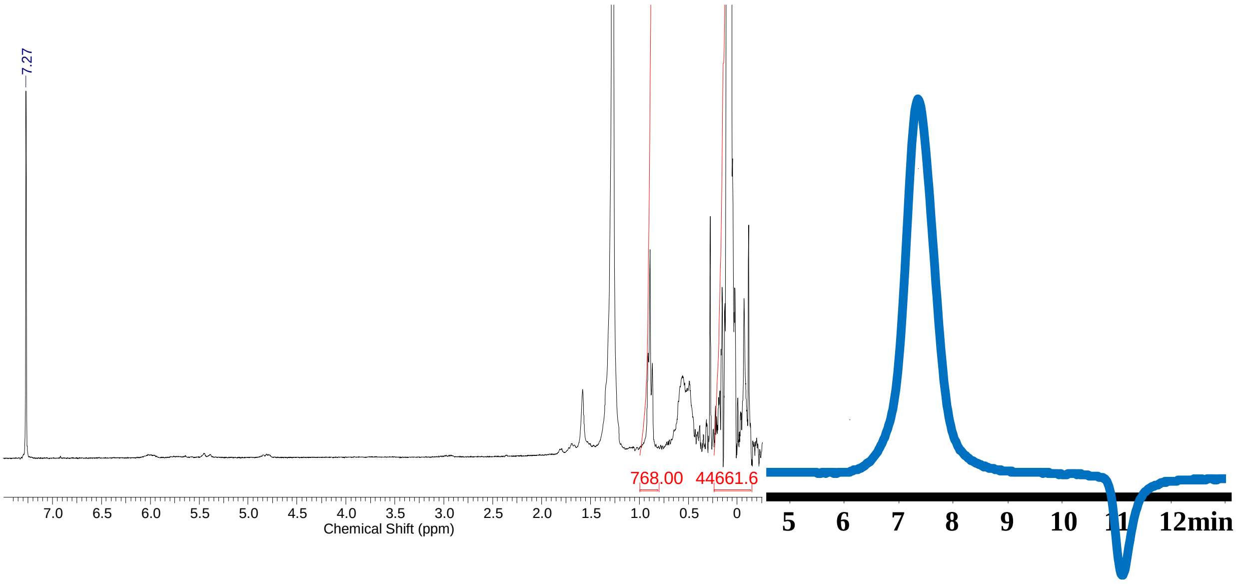


Figure S7. ^{1}H NMR spectrum and GPC curve of star-shaped PDMS with 128 arms **6c**. The signals necessary for calculations (0 ppm –Si-C$\underline{H}_3$ and 0.9 ppm –CH$_2$-C$\underline{H}_3$) are integrated.

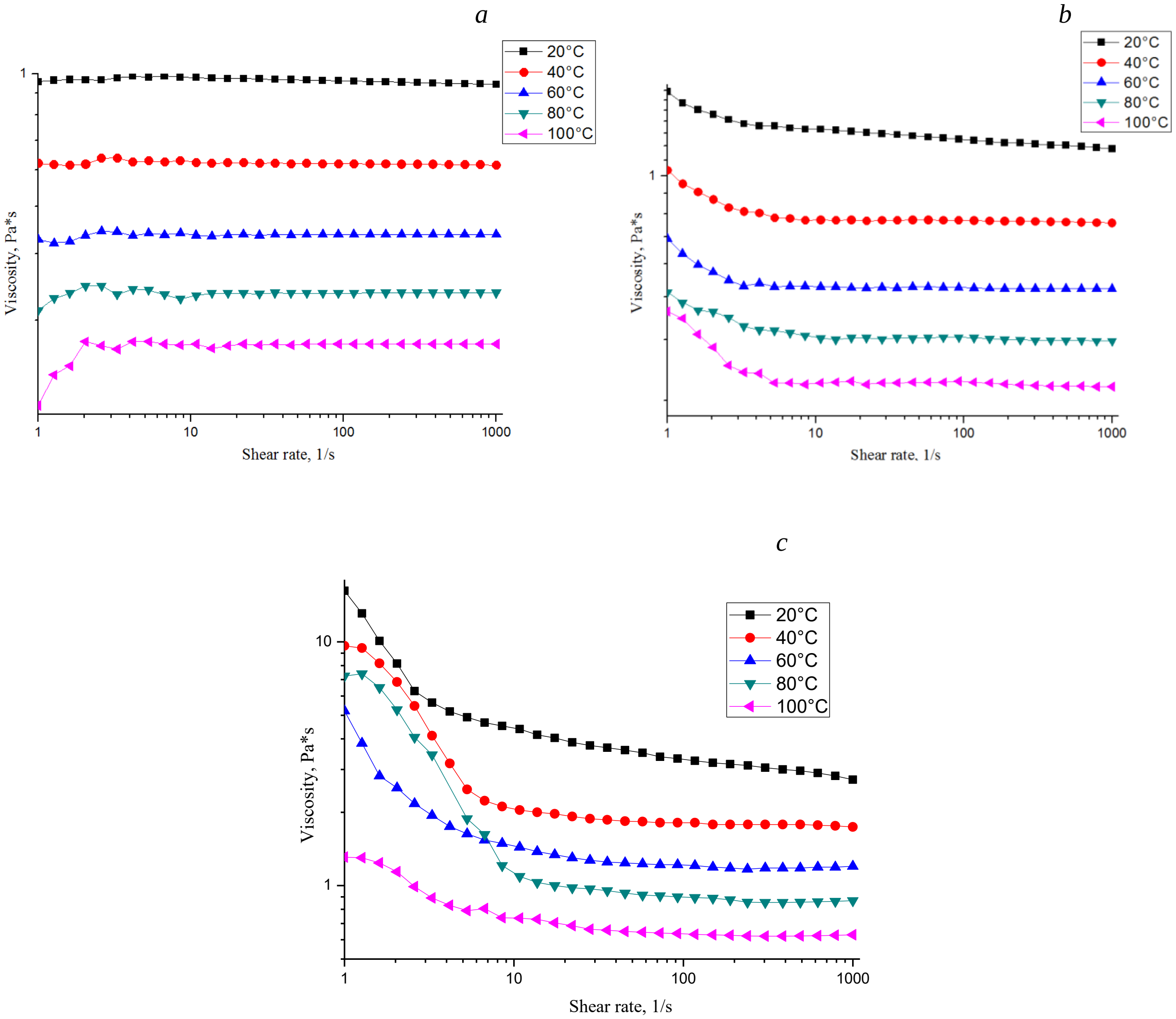


Figure S8. Flow curves of star-shaped PDMS with 8 **6a** (*a*), 32 **6b** (*b*) and 128 **6c** (*c*) arms at 20, 40, 60, 80 and 100 °C.

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