

SUPPORTING INFORMATION

A Novel Functionalized Stereoregular Macrocyclic Oligomeric Silsesquioxane: Synthesis and Its Fast Self-crosslinking *via* Thiol-ene Radical Addition Polymerization

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EXPERIMENTAL

Materials

Organic silanes such as vinyltrimethoxysilane, dimethylchlorosilane and trimethylchlorosilane and allyl bromide were purchased from Shanghai Reagent Co., Shanghai, China. 3-Bromopropyldimethylchlorosilane was prepared *via* the hydrosilylation reaction of dimethylchlorosilane with allyl bromide in this lab in the presence of Karstedt catalyst. The ¹H NMR spectroscopy showed that this compound was composed of 85 % of α-addition and 15 % of β-addition structures in the as-prepared product. Anhydrous copper (II) chloride (CuCl₂) was obtained from Ruanshi Chemical Co., Jiangsu, China. Silver nitrate (AgNO₃), sodium hydroxide (NaOH), pyridine and solvents such as ethanol and toluene were also purchased from Shanghai Reagent Co., China. Before use, toluene and pyridine were distilled over calcium hydride (CaH₂) and then stored in a sealed vessel in the presence of the molecular sieve of 4 Å.

Synthesis of Coordinate of Copper and Sodium with Vinylsiloxanolate

[Na₄[vinylSi(O)O]₁₂(Cu)₄](C₂H₅OH)(H₂O)₅]

The coordinate of copper and sodium with vinylsiloxanolate [Na₄[vinylSi(O)O]₁₂(Cu)₄](C₂H₅OH)(H₂O)₅] was prepared by the method of literature reported by Shchegolikhina *et al* [1-7]. Typically, to a flask, vinyltrimethoxysilane (15.520 g, 104.68 mmol), sodium hydroxide (4.200 g, 104.68 mmol), deionized water (12.960 g) and anhydrous ethanol (240 mL) were charged with vigorous stirring. The mixture was maintained at room temperature with vigorous stirring for 2 hours and then the solution of CuCl₂ (4.680 g, 34.88 mmol) dissolved in 48 mL of anhydrous ethanol was added. The reaction was performed at room temperature for one hour. The insoluble components were removed *via* filtration and then deionized water (4.000 g) was added to the filtrate. The mixture was further refluxed for 60 min and cooled to room temperature. The solution was stored at -5 °C for 72 hours to afford blue crystals. The resulting products were obtained *via* recrystallization and the coordinate of copper and sodium with vinylsiloxanolate (9.110 g) was obtained with the yield of 91.2%.

Synthesis of Dodecavinyl dodeca(trimethyl)cyclododecasilsesquioxane

[MOSS(CH=CH₂)₁₂] [Si(CH₃)₁₂]

The coordinate of copper and sodium with vinylsiloxanolate, *i.e.*, Na₄[vinylSi(O)O]₁₂(Cu)₄}(C₂H₅OH)(H₂O)₅ (3.500 g, 2.29 mmol) was added to the mixture composed of toluene (48 mL), trimethylchlorosilane (20.100 g, 184.39 mmol), and pyridine (11.900 g, 147.50 mmol) at room temperature with vigorous stirring. The reaction was performed at 35 °C for 24 hours. After cooling to room temperature, the reacted mixture was filtered to remove the solids, and the remaining solution was washed with deionized water until no chlorine ions were detected with aqueous silver nitrate (AgNO₃). After drying with anhydrous MgSO₄, all the solvents were eliminated with rotary evaporation to afford a light yellow liquid (3.790 g) with the yield of 94.5%. ¹H NMR (400 MHz, CDCl₃): 6.04 ~ 5.80 (*m*, 3H, O₃SiCH=CH₂), 0.096 [*s*, 9H, Si(CH₃)₃]; ²⁹Si NMR(ppm, CDCl₃): 8.72 (*cis-cis*-OSiMe₃), 8.56 (*cis-trans*-OSiMe₃), -81.84 (*cis-tran*-O₃SiVi), -81.89 (*cis-cis*-O₃SiVi). MALD-TOF-MS: *M* = 1923.4 Da (*i.e.*, 1946.4-23 for sodium or 1962.4-39 for potassium) (Calculated: *M* = 1923 Da).

Synthesis of Dodecavinyl dodeca(3-bromopropyl dimethyl)cyclododecasilsesquioxane

(MOSS[CH=CH₂]₁₂[Si(CH₃)₂CH₂CH₂CH₂Br]₁₂)

The above coordinate of copper and sodium vinylsiloxanolate, {Na₄[vinylSi(O)O]₁₂(Cu)₄}(C₂H₅OH)(H₂O)₅ (3.500 g, 2.29 mmol) was added to the mixture composed of toluene (48 mL), 3-bromopropylchlorodimethylsilane [*viz.* BrC₂H₅(CH₃)₂SiCl] (58.800 g, 274.8 mmol) and pyridine (17.900 g, 226.58 mmol) at room temperature. The silylation reaction was performed at 35 °C for 24 hours with vigorous stirring. After cooling to room temperature, the system was filtered to isolate the precipitates, and the solution was washed with deionized water until no chlorine ions were detected with aqueous silver nitrate (AgNO₃). After drying with anhydrous MgSO₄, all the solvents were eliminated with rotary evaporation to afford the light yellow liquid (6.810 g) with the yield of 91.5%. ¹H NMR (400 MHz, CDCl₃): 5.93 (*s*, 3H, O_{3/2}SiCH=CH₂), 3.42 (*t*, 2H, CH₂CH₂CH₂Br), 1.81 (*m*, 2H, CH₂CH₂CH₂Br), 0.97 (*m*, 2H, SiCH₂), 0.02 ~ 0.12 [*m*, 6H, Si(CH₃)₂]. ²⁹Si NMR (ppm, CDCl₃): -81.81 (*d*, SiO_{3/2}), 9.23 [*d*, Si(CH₃)₂CH₂CH₂CH₂Br]

***Synthesis of Dodecaethoxyldithiocarbonatedodecavinylcyclododecasilsesquioxane
[MOSS[CH=CH₂]₁₂[Si(CH₃)₂CH₂CH₂CH₂SSCOCH₂CH₃]₁₂]***

To a flask equipped with a magnetic stirrer, potassium ethyl xanthate (8.100 g, 50.58 mmol) and acetone (60 mL) were charged with vigorous stirring. Thereafter, MOSS[CH=CH₂]₁₂[Si(CH₃)₂CH₂CH₂CH₂Br]₁₂ (2.700 g, 0.843 mmol) dissolved in 10 mL of acetone was added dropwise at room temperature within 30 min. This reaction was performed at room temperature for 24 hours. The excess potassium ethyl xanthate was removed by filtration. The solvents and other volatile were removed *via* rotary evaporation to afford a yellow liquid (3.060 g). The crude product was dissolved in 200 mL of dichloromethane and the solution washed with deionized water three times. The organic layer was dried over anhydrous sulfate magnesium. After the solvent was removed *via* rotary evaporation, the product (2.820 g) was obtained with the yield of 90 %. ¹H NMR (400 MHz, CDCl₃): 5.93 (*s*, 3H, O_{3/2}SiCH=CH₂), 1.74 (*m*, 2H, CH₂CHSiO_{3/2}), 3.14 (*m*, 2H, CH₂CH₂CH₂SSC), 4.66 (*m*, 2H, OCH₂CH₃), 1.41 (*t*, 3H, OCH₂CH₃), 0.07-0.15 [*m*, 6H, Si(CH₃)₂]. ²⁹Si NMR (ppm, CDCl₃): -81.81 (*d*, SiO_{3/2}), 9.23 [*d*, Si(CH₃)₂CH₂CH₂CH₂].

***Synthesis of Dodecathiolpropyldodecavinylcyclododecasilsesquioxane
[MOSS[CH=CH₂]₁₂[Si(CH₃)₂CH₂CH₂CH₂SH]₁₂]***

Typically, to a flask equipped with a magnetic stirrer, the above MOSS[CH=CH₂]₁₂[Si(CH₃)₂CH₂CH₂CH₂SSCOCH₂CH₃]₁₂ (1.720 g, 0.465 mmol) and tetrahydrofuran (30 mL) were charged with vigorous stirring. Thereafter, butylamine (1.020 g, 14.2 mmol) were added to the solution. The aminolysis reaction was performed at room temperature for 8 hours. After eliminating the solvent *via* rotary evaporation, a light yellow liquid was obtained. The crude product was dissolved in 200 mL of dichloromethane and the solution washed with deionized water three times. The organic layer was dried over anhydrous sulfate magnesium. After the solvent was removed *via* rotary evaporation, the product (1.100 g) was obtained with the yield of 89%. ¹H NMR (ppm, CDCl₃): 5.93 (*s*, 3H, O₃SiCH=CH₂), 0.92 (*q*, 2H, CH₂CH₂SiO), 1.66 ~ 1.82 [*d*, 2H, Si(CH₃)₂CH₂CH₂CH₂SH], 2.67 (*t*, 2H, Si(CH₃)₂CH₂CH₂CH₂SH), 0.07 ~ 0.15 [*m*, 6H, Si(CH₃)₂]. ²⁹Si NMR (ppm, CDCl₃): -81.81 (*d*, SiO_{3/2}), 9.23 [*d*, Si(CH₃)₂CH₂CH₂CH₂SH].

Polymerization via Thiol-ene Radical Addition Reaction

To a flask equipped with a magnetic stirrer, MOSS[CH=CH₂]₁₂[Si(CH₃)₃CH₂CH₂CH₂SH]₁₂ (1.000 g) was charged and then AIBN (18 mg) was added to the flask with vigorous stirring. The reaction was carried at 70 °C. It was observed that within 15 min, the reactive system was gelled. The reaction was maintained at this temperature for one hour.

Measurements and Techniques

Nuclear Magnetic Resonance (NMR) Spectroscopy

The ¹H NMR measurements were performed on a Varian Mercury Plus 400 MHz NMR spectrometer at 25 °C and the ²⁹Si NMR spectra were obtained on a Bruker Avance III 400 MHz NMR spectrometer. The samples were dissolved with deuterium chloroform (CDCl₃) and the solutions were measured with tetramethylsilane (TMS) as an external reference.

MALDI-TOF-Mass Spectroscopy

The MALDI-TOF-Mass spectroscopy was carried out on an IonSpecHiRes MALDI mass spectrometer equipped with a pulsed nitrogen laser (l-337 nm; pulse with 3 ns). This instrument operated at an accelerating potential of 20 kV in reflector mode. Both sodium (Na) and potassium (K) are simultaneously used as the cationizing agents and all the data shown are for positive ions. Gentisic acid (2,5-dihydroxybenzoic acid, DHB) was used as the matrix with dichloromethane as the solvent.

Size-exclusion Chromatography (SEC)

The molecular weights were measured on a Waters 717 Plus autosampler size-exclusion chromatography apparatus equipped with Waters RH columns and a RI detector and the measurements were carried out at 25 °C with tetrahydrofuran (THF) as the eluent at the rate of 1.0 mL/min.

Dynamic Mechanical Thermal Analysis (DMTA)

The dynamic mechanical tests were carried out on a TA Instruments Q800 dynamic mechanical thermal analyzer (DMTA) in a single cantilever mode and this apparatus was equipped with a liquid nitrogen accessory. The frequency used is 1.0 Hz and the heating rate 3.0 °C/min. The specimen dimension was 25 × 5.0 × 2.0 mm³. The experiments were carried out from -120 °C to 180 °C.

Thermal Gravimetric Analysis (TGA)

The TGA measurements were carried out on a TA Instruments Q5000 thermal gravimetric analyzer. The experiment was conducted in nitrogen atmosphere from ambient temperature to 800 °C at a heating rate of 20 °C/min. The temperature of initial degradation (T_d) was taken as the onset temperature at which 5 wt % of weight loss occurred.

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Table S1 Molecular weights of MOSS macromers with SEC

Entry	M_{Theo} (Da)	$M_{n, \text{SEC}}$ (Da)	M_w/M_n
a	1920	1928	1.14
b	2640	2710	1.23
c	3204	3198	1.19
d	3696	3700	1.21

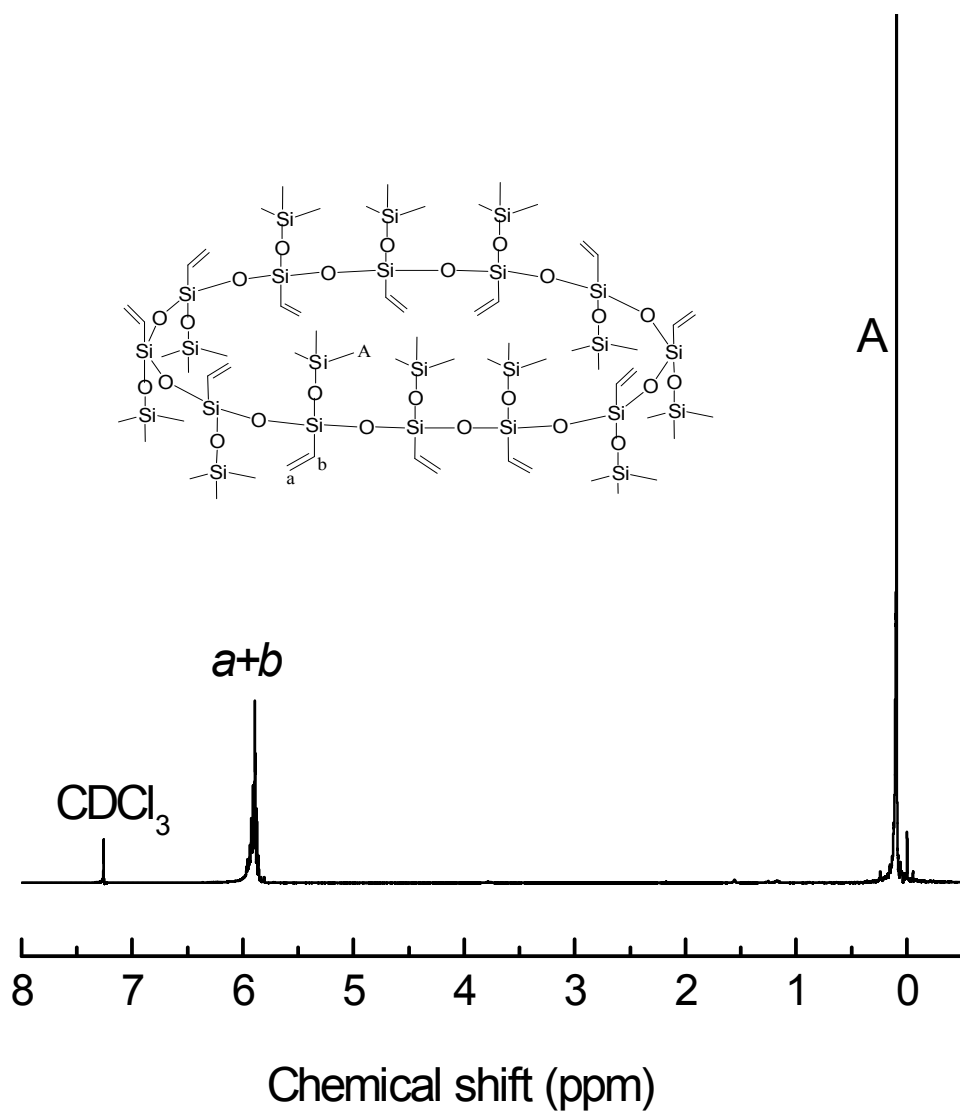


Figure S1 ^1H NMR spectrum of dodecavinyl dodeca(trimethyl) cyclododecasilsesquioxane (*viz.* $\text{MOSS}[\text{CH}=\text{CH}_2]_{12}[\text{Si}(\text{CH}_3)_3]_{12}$);

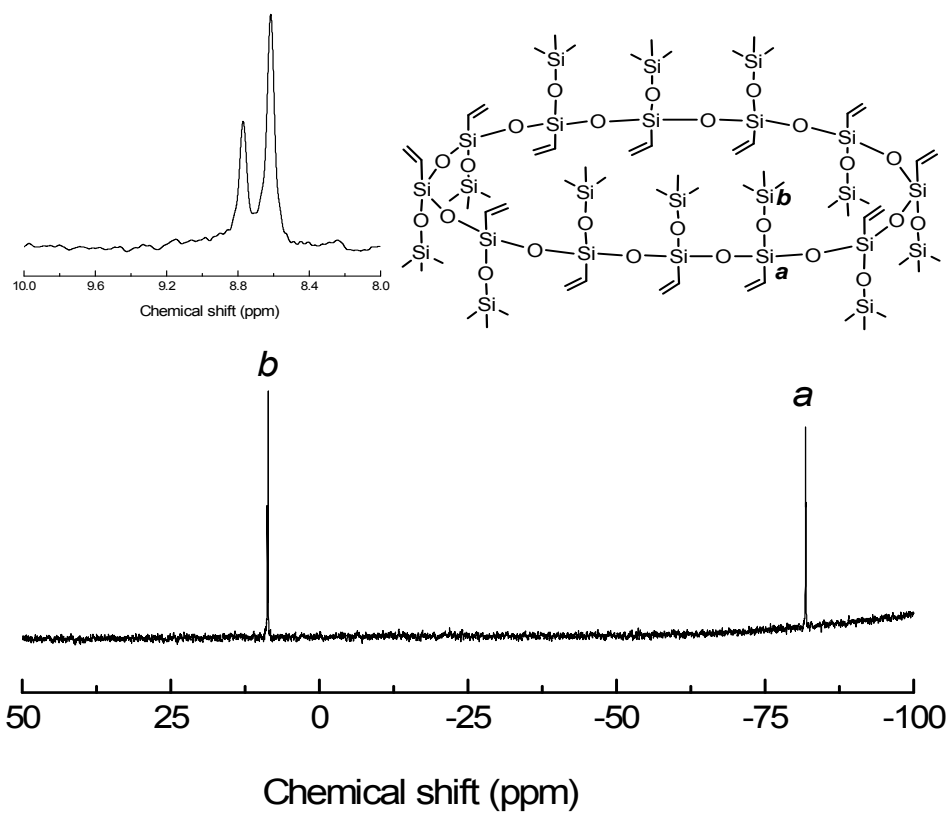


Figure S2 ^{29}Si NMR spectrum of dodecavinyl-dodeca(trimethyl)silyloxy cyclododecasilsesquioxane (*viz.* $\text{MOSS}[\text{CH}=\text{CH}_2]_{12}[\text{Si}(\text{CH}_3)_3]_{12}$);

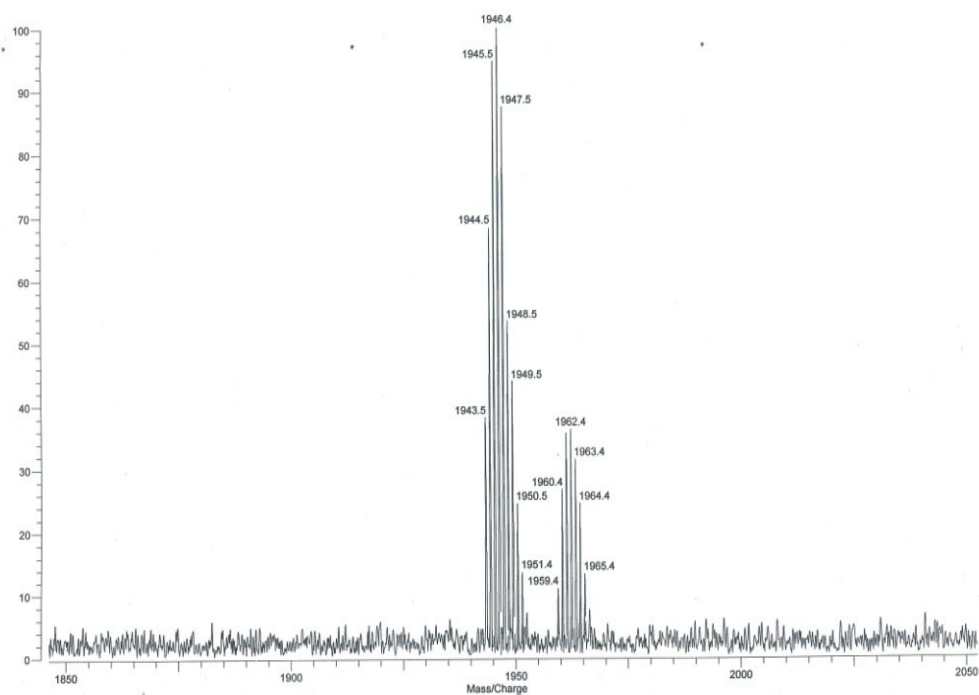


Figure S3 MALDI-TOF mass spectrum of dodecavinyl dodeca(trimethyl) cyclododecasilsesquioxane [viz. $\text{MOSS}[\text{CH}=\text{CH}_2]_{12}[\text{Si}(\text{CH}_3)_3]_{12}$];

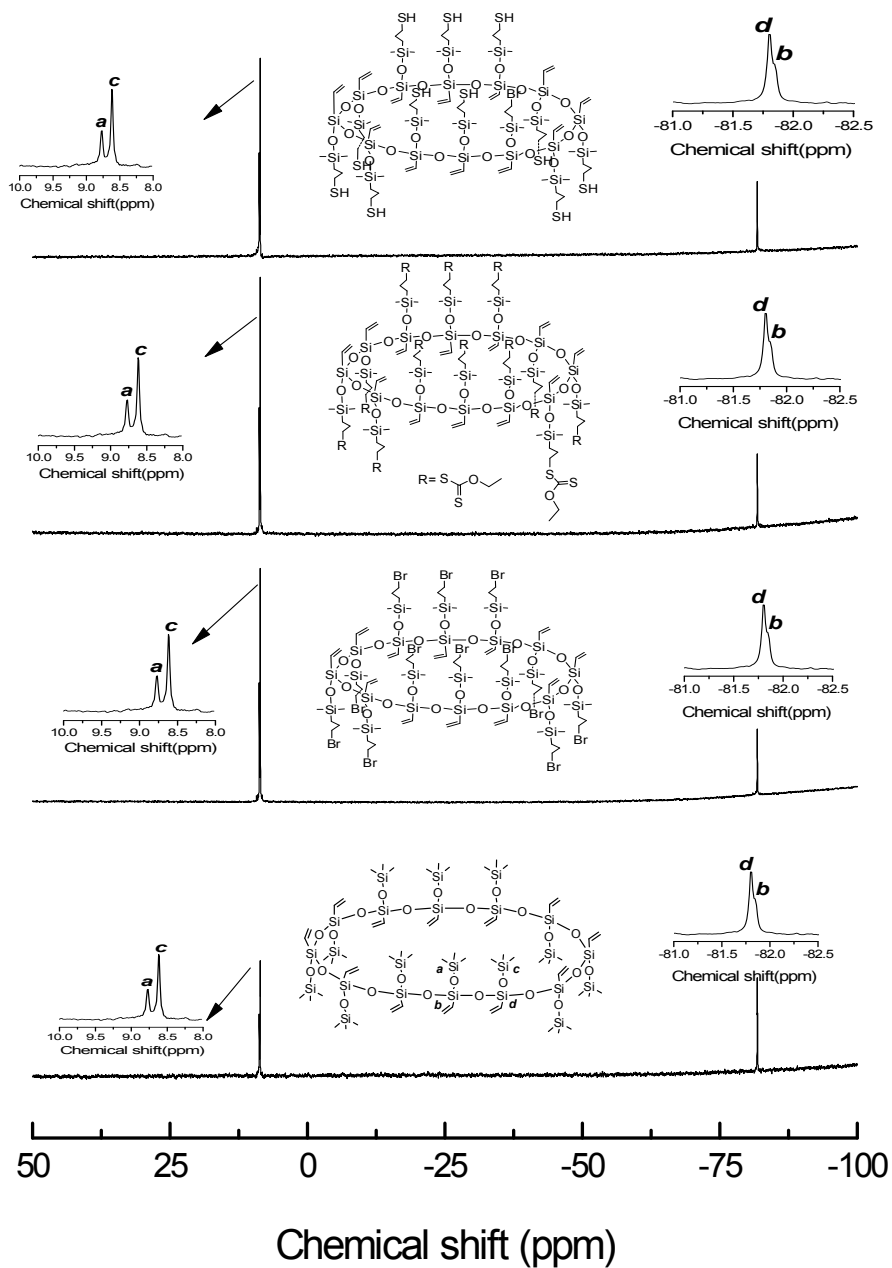


Figure S4 ^{29}Si NMR spectra of MOSS[CH=CH₂]₁₂[Si(CH₃)]₁₂, MOSS[CH=CH₂]₁₂[Si(CH₃)₂CH₂CH₂CH₂Br]₁₂, MOSS[CH=CH₂]₁₂[Si(CH₃)₂CH₂CH₂CH₂SSCOCH₂CH₃]₁₂ and MOSS[CH=CH₂]₁₂[Si(CH₃)₂CH₂CH₂CH₂SH]₁₂;

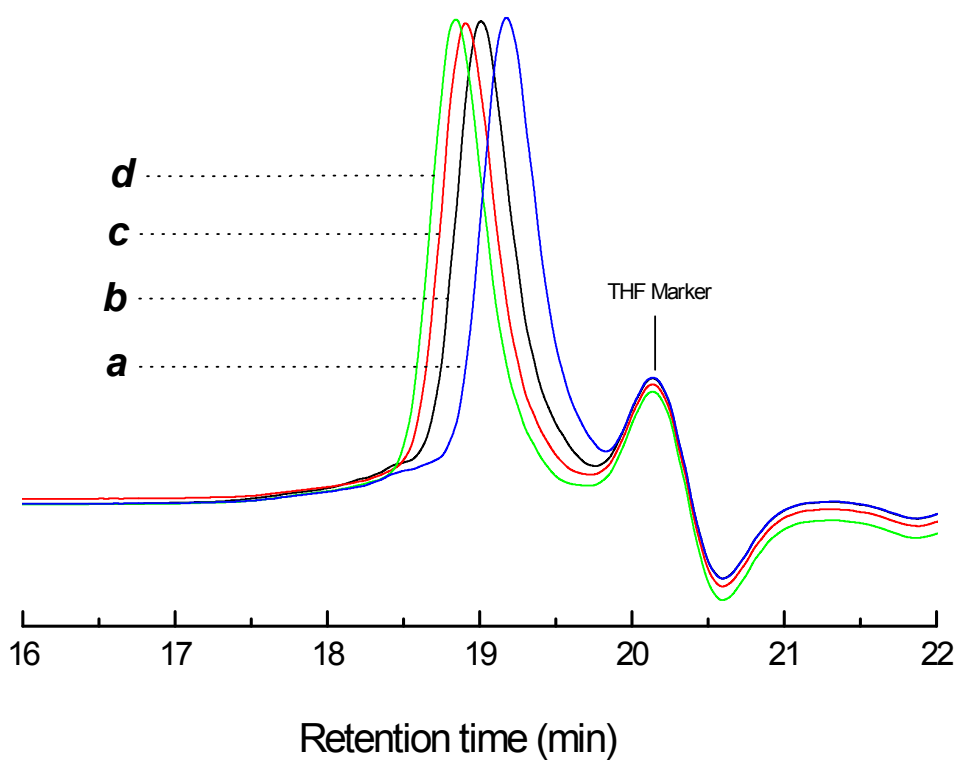


Figure S5 SEC profiles of MOSS macromers: a) $\text{MOSS}[\text{CH}=\text{CH}_2]_{12}[\text{Si}(\text{CH}_3)_3]_{12}$; b) $\text{MOSS}[\text{CH}=\text{CH}_2]_{12}[\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}]_{12}$; c) $\text{MOSS}[\text{CH}=\text{CH}_2]_{12}[\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}]_{12}$; d) $\text{MOSS}[\text{CH}=\text{CH}_2]_{12}[\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SSCOCH}_2\text{CH}_3]_{12}$