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 $^1$H NMR spectroscopy showed that this compound was composed of 85 % of $\alpha$-addition and 15 % of $\beta$-addition structures in the as-prepared product. Anhydrous copper (II) chloride (CuCl$_2$) was obtained from Ruanshi Chemical Co., Jiangsu, China. Silver nitrate (AgNO$_3$), 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 (CaH$_2$) 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

$[\text{Na}_4\text{vinylSi(O)O}]_{12}\text{(Cu)}_4(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})_3$]

The coordinate of copper and sodium with vinylsiloxanolate $[\text{Na}_4\text{vinylSi(O)O}]_{12}\text{(Cu)}_4(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})_3$] 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 CuCl$_2$ (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 Dodecavinyldodeca(trimethyl)cyclododecasilsesquioxane

$[\text{MOSS(}CH=CH_2\text{)}_{12}] [\text{Si(}CH_3\text{)}_{12}$]

The coordinate of copper and sodium with vinylsiloxanolate, *i.e.*, $\text{Na}_4[\text{vinylSi(O)}]_{12}(\text{Cu})_4(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})_5$ (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, $\text{O}_3\text{SiC}_2\text{H}_2$), 0.096 [s, 9H, $\text{Si(CH}_3\text{)}_3$]; ²⁹Si NMR(ppm, CDCl₃): 8.72 (cis-cis-$\text{OSiMe}_3$), 8.56 (cis-trans-$\text{OSiMe}_3$), -81.84 (cis-trans-$\text{O}_3\text{SiVi}$), -81.89 (cis-cis-$\text{O}_3\text{SiVi}$). 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 Dodecavinyldodeca(3-bromopropyl)dimethyl)cyclododecasilsesquioxane

$(\text{MOSS}[\text{CH}=\text{CH}_2\text{)}_{12}[\text{Si(}CH_3\text{)}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}]_{12}$)

The above coordinate of copper and sodium vinylsiloxanolate, $\text{Na}_4[\text{vinylSi(O)}]_{12}(\text{Cu})_4(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})_5$ (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, $\text{O}_3\text{SiC}_2\text{H}_2$), 3.42 (t, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$), 1.81 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$), 0.97 (m, 2H, $\text{SiCH}_3$), 0.02 ~ 0.12 [m, 6H, $\text{Si(CH}_3\text{)}_2$]. ²⁹Si NMR (ppm, CDCl₃): -81.81 ($d, \text{SiO}_3\text{Si}$), 9.23 [$d, \text{Si(CH}_3\text{)}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$]
Synthesis of Dodecaethoxydithiocarbonate dodecavinylcyclododecasilsesquioxane

\[ \text{MOSS}[\text{CH}=\text{CH}_2]_{12}[\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SSCOCH}_2\text{CH}_3]_{12} \]

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%.

$^1$H NMR (400 MHz, CDCl3): 5.93 (s, 3H, O$_3$SiC=CH$_2$), 1.74 (m, 2H, CH$_2$CHSilO), 3.14 (m, 2H, CH$_2$CH$_2$CH$_2$SSC), 4.66 (m, 2H, OCH$_2$CH$_3$), 1.41 (t, 3H, OCH$_2$CH$_3$), 0.07-0.15 [m, 6H, Si(CH$_3$)$_2$]. $^{29}$Si NMR (ppm, CDCl$_3$): -81.81 (d, SiO$_3$/2), 9.23 [d, Si(CH$_3$)$_2$CH$_2$CH$_2$CH$_3$].

Synthesis of Dodecatiolpropyldodecavinylcyclododecasilsesquioxane

\[ \text{MOSS}[\text{CH}=\text{CH}_2]_{12}[\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SH}]_{12} \]

Typically, to a flask equipped with a magnetic stirrer, the above MOSS[CH=CH$_2$]$_{12}$[Si(CH$_3$)$_2$CH$_2$CH$_2$SSCOCH$_2$CH$_3$]$_{12}$ (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%. $^1$H NMR (ppm, CDCl$_3$): 5.93 (s, 3H, O$_3$SiCH=CH$_2$), 0.92 (q, 2H, CH$_2$CH$_2$SilO), 1.66 ~ 1.82 [d, 2H, Si(CH$_3$)$_2$CH$_2$CH$_2$SH], 2.67 (t, 2H, Si(CH$_3$)$_2$CH$_2$CH$_2$SH), 0.07 ~ 0.15 [m, 6H, Si(CH$_3$)$_2$]. $^{29}$Si NMR (ppm, CDCl$_3$): -81.81 (d, SiO$_3$/2), 9.23 [d, Si(CH$_3$)$_2$CH$_2$CH$_2$SH].
**Polymerization via Thiol-ene Radical Addition Reaction**

To a flask equipped with a magnetic stirrer, MOSS[CH=CH\(_2\)]\(_{12}\)[Si(CH\(_3\)_3CH\(_2\)CH\(_2\)CH\(_2\)SH]\(_{12}\) (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 \(^1\)H NMR measurements were performed on a Varian Mercury Plus 400 MHz NMR spectrometer at 25 °C and the \(^{29}\)Si NMR spectra were obtained on a Bruker Avance III 400 MHz NMR spectrometer. The samples were dissolved with deuterium chloroform (CDCl\(_3\)) 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 (λ-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.

REFERENCES

### Table S1 Molecular weights of MOSS macromers with SEC

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Figure S1 $^1$H NMR spectrum of dodecavinyldodeca(trimethyl) cyclododesilsesquioxane (viz. MOSS[CH=CH$_2$]$_{12}$[Si(CH$_3$)$_3$]$_{12}$);
Figure S2 $^{29}$Si NMR spectrum of dodecavinyldodeca(trimethyl) cyclododecasilsesquioxane (viz. MOSS[CH=CH$_2$]$_{12}$[Si(CH$_3$)$_3$]$_{12}$);
Figure S3 MALDI-TOF mass spectrum of dodecavinyldodeca(trimethyl) cyclododecasilsesquioxane [viz. MOSS[CH=CH$_2$]$_{12}$[Si(CH$_3$)$_3$]$_{12}$];
Figure S4 $^{29}$Si NMR spectra of MOSS[CH=CH$_2$]$_{12}$[Si(CH$_3$)$_3$]$_{12}$, MOSS[CH=CH$_2$]$_{12}$ [Si(CH$_3$)$_2$CH$_2$CH$_2$CH$_2$Br]$_{12}$, MOSS[CH=CH$_2$]$_{12}$[Si(CH$_3$)$_2$CH$_2$CH$_2$CH$_2$], SSCOCH$_2$CH$_3$]$_{12}$ and MOSS[CH=CH$_2$]$_{12}$[Si(CH$_3$)$_2$CH$_2$CH$_2$CH$_2$SH]$_{12}$;
**Figure S5** SEC profiles of MOSS macromers: a) MOSS[CH=CH\textsubscript{2}]\textsubscript{12}[Si(CH\textsubscript{3})\textsubscript{3}]\textsubscript{12}; b) MOSS[CH=CH\textsubscript{2}]\textsubscript{12}[Si(CH\textsubscript{3})\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}SH]\textsubscript{12}; c) MOSS[CH=CH\textsubscript{2}]\textsubscript{12}[Si(CH\textsubscript{3})\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}Br]\textsubscript{12}; d) MOSS[CH=CH\textsubscript{2}]\textsubscript{12}[Si(CH\textsubscript{3})\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}SSCOCH\textsubscript{2}CH\textsubscript{3}]\textsubscript{12}