Synthesis of Poly(tetramethyl-*m*-silphenylenesiloxane), an Elastomer of Enhanced High-Temperature Stability

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Introduction

There have been numerous demands for high-temperature elastomers for applications in technological areas such as advanced aerospace, defense, and computer applications.[1] A good candidate polymer should have long-term thermal, thermooxidative, and hydrolytic stability at and above 300−350 °C, while at the same time possess excellent flexibility to very low temperatures. The polysiloxanes are one of the most important class of such elastomers due to their thermal stabilities, low glass transition temperatures, unusual surface properties, some dielectric properties, excellent gas permeability, and frequently also liquid-crystal behavior.[2] Their already good properties could presumably be greatly improved by the incorporation of more thermally stable aromatic groups into the polysiloxane backbone.[1]

In the first attempt of this type, Merker *et al.*[3] reported the synthesis of poly(tetramethyl-*p*-silphenylenesiloxane), which is a crystalline polymer and thus would exhibit rubberlike elasticity only at elevated temperatures. The possibility of introducing elastomeric behavior at lower temperatures by preparing *p*-silphenylene-siloxane as a *copolymer* has indeed been satisfactory.[1,4−7] However, a more elegant solution, which has long been suggested, is preparation of a *homopolymer* containing *m*- instead of *p*-silphenylene groups. The *m*-silphenylene groups should be less stiff than the *p* groups, and thus they should produce an elastomeric rather than crystalline polymer, without much loss in thermal stability.[8] Hence, poly(tetramethyl-*m*-silphenylenesiloxane) will contain the maximum number of aromatic groups in the polymer backbone in comparison to the silphenylenesiloxane *copolymers* without severely impairing the low-temperature elasticity.

This polymer has in fact been mentioned by Lee *et al.*,[9,10] but no detailed synthesis, characterization, or physical properties have been documented. In this note, we therefore report the total synthesis and partial characterization of poly(tetramethyl-*m*-silphenylenesiloxane), molecule **5** in Scheme 1.

Results and Discussion

The synthetic route for the preparation of polymer **5**, which is analogous to Merker's, [3] is outlined in Scheme 1.

The preparation of monomers of sufficiently high purity is pivotal to obtaining high molecular weight silarylenesiloxane polymers because the polymers must be made by condensation, or step-growth polymerization reactions. The synthesis of *m*-bis(dimethylhydroxysilyl)benzene has been reported by Beck,[11] Elliott,[12] and Rosenberg.[13] In our study each chemical reaction used was investigated and modified in order to obtain a product with maximum purity.

Disilane **3** was generated by a Grignard reaction, and the modification of Beck's method[11] was adopted in this laboratory. Due to the slow reactivity of the aryl halides and because it was found that 1-chloro-3-(dimethylsilyl)-benzene and disilane **3** cannot be separated by distillation, magnesium turnings were pulverized for 1 h before the reaction and were used in a large excess amount (4 equiv). The yield for the Grignard reaction was *ca.* 66% when starting from 1,3-dibromobenzene and *ca.* 24% from 1,3-dichlorobenzene.

The conversion of disilane **3** to disilanol **4** was a modified Merker−Scott-type hydrolysis. White cottony crystals of disilanol **4** were obtained in about 80% yield.

The condensation polymerization was carried out in benzene in the presence of 1 wt % (based on disilanol **4**) *n*-hexylamine-2-ethylhexoate.[14] The water was removed azeotropically using a Dean−Stark trap. After 24 h of reflux and removal of the solvent by distillation, a slightly opaque tacky polymer was obtained. It had a number-average molecular weight M_n of 3100 and a polydispersity index M_w/M_n of 1.39, as measured by gel permeation chromatography. After the prepolymer was kept in a vacuum oven for 2 days at 60 °C, a high molecular weight polymer was obtained, with M_n = 126 000; its polydispersity index $M_w/M_n = 2.06$ is very close to the theoretical value of 2.0 for the limit of large extents of reaction. The yield of the polymerization (including cyclic oligomers) is about 90% based on disilanol **4,** and the overall yield of polymer **5** starting with 1,3-dibromobenzene is *ca.* 42%. The polymer was purified by the fractional precipitation method using toluene as the good solvent and methanol as the nonsolvent. The polymer finally obtained was elastomeric and totally transparent. Unlike most of the siloxane polymers, the cyclic dimer of monomer **4** was one of the major constituents of the byproducts. The combined yield of all the cyclic oligomers was about 12%.

The surface properties of polymer **5** were determined by measuring contact angles. The contact angle with deionized water was 110°, and with methylene iodide it was 69°. Using the geometric mean method, the surface energy was calculated to be 24.4 dyn/cm, with a dispersion force component of 24.4 dyn/cm and a polar component of 0 dyn/cm. These results are very similar to those for poly(dimethylsiloxane).[2] The thermal behavior was monitored by DSC (differential scanning calorimetry) and STA (simultaneous thermal analysis, i.e., DSC and thermogravimetric analysis, TGA). The DSC experiments were run under a nitrogen atmosphere with a heating rate of 5 K/min. According to the DSC thermogram, the glass transition temperature was −52 °C and no crystalline melting peak was observed. For the STA analyses, shown in Figures 1 and 2, our attention was focused on the TGA results because TGA is usually more reliable than DSC at very high temperature. The TGA revealed that polymer **5** underwent a one-step degradation process under a nitrogen atmosphere, at a heating rate of 10 K/min. The onset temperature for the process was about 415 °C, and the weight loss was 67%. After 613 °C, no further significant weight loss was observed. The residue after 900 °C was about 33% in comparison to that of poly(dimethylsiloxane), specifically 0%. When the sample was run in air with a heating rate of 10 K/min, only a 1% weight loss was observed from 361 to 495 °C.

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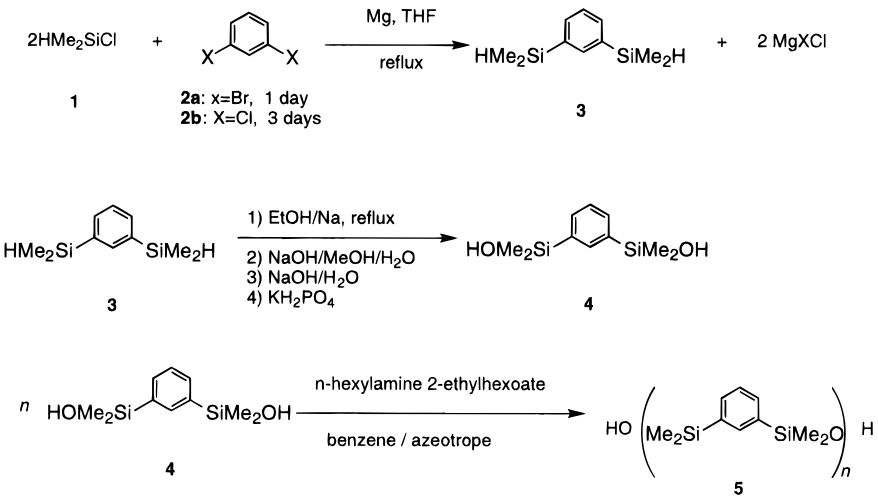
Scheme 1



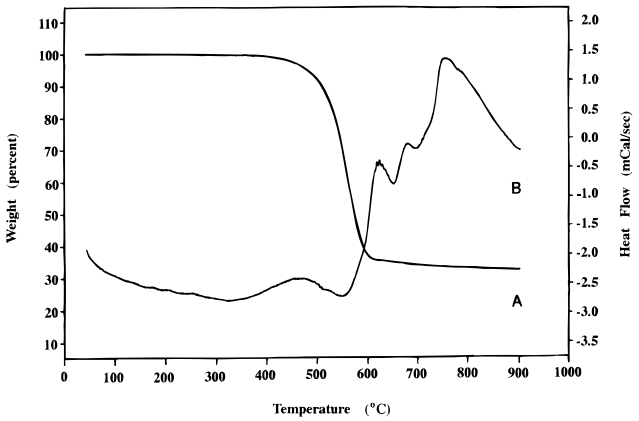


Figure 1. STA for polymer **5** under a nitrogen atmosphere at 10 K/min: (A) TGA curve; (B) DSC curve.

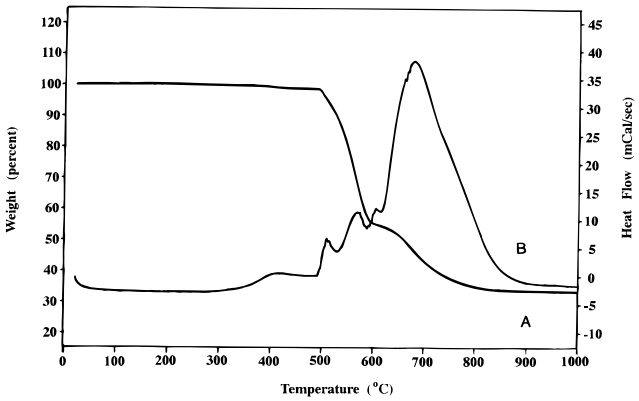


Figure 2. STA for polymer **5** under an air atmosphere at 10 K/min: (A) TGA curve; (B) DSC curve.

Subsequently a two-step process occurred with onset temperatures of 495 and 634 °C, respectively, with weight losses for these steps being 45% and 21%, respectively. No further degradation occurred after 800 °C, and the residue after 900 °C was 33%. This polymer thus shows great promise as a high-temperature siloxane elastomer.

Conclusions

Poly(tetramethyl-*m*-silphenylenesiloxane) has been successfully synthesized in a step-growth polymerization. It was found that a final high-vacuum finishing process is crucial for obtaining high molecular weight polymer. The molecular weights of the polymer were M_n = 126 000 and M_w/M_n = 2.06, and its glass transition temperature was −52 °C. No melting temperature was detected by DSC. The surface properties of this polymer are very similar to those for poly(dimethylsiloxane). TGA measurements revealed very good high temperature properties under a nitrogen or an air atmosphere.

Experimental Section

Chemicals and Measurements. 1,3-Dichlorobenzene, 1,3-dibromobenzene, *n*-hexylamine, and 2-ethylhexanoic acid (Aldrich) and dimethylchlorosilane (United Chemical Technologies) were used without further purification. The remainder of the chemicals were purchased from Fisher Scientific. Tetrahydrofuran (THF) and benzene were distilled from potassium prior to use. Petroleum ether was distilled from molecular sieves. All infrared spectra were recorded on a Perkin-Elmer Model 1600 series FTIR spectrophotometer using KBr cells or pellets. ^{1}H NMR (250 MHz) and ^{13}C NMR (62.9 MHz) spectra were recorded on a Bruker 250 MHz spectrometer with ^{1}H NMR referenced to tetramethylsilane at 0.00 ppm and ^{13}C NMR referenced to the center chloroform-*d* peak at 77.0 ppm. The gel permeation chromatography (GPC) was performed on a Waters gel permeation chromatography unit with a differential refractometer and three in-line columns having pore sizes of 500, 10^3, and 10^4 Å in toluene at 40 °C. The eluent flow rate was set at 1 mL/min, and the molecular weights were determined using polystyrene standards. The surface property characterization was carried out using a Video contact angle system and VCA2000 instrument. Thermal data were obtained with a Rheometric Scientific PL-DSC (differential scanning calorimeter) and a Rheometric Scientific PL-STA (simultaneous thermal analysis, i.e., DSC and thermogravimetric analysis, TGA).

Preparation of *m*-Bis(dimethylsilyl)benzene. The procedures for the preparation of disilane **3** are as follows. (1) First, 38.89 g of magnesium in a 500-mL three-neck flask equipped with an addition funnel with 22.8 mL of 1,3-dichlorobenzene in 40 mL of THF under an argon atmosphere was pulverized under mechanical stirring for 1 h. The flask was then charged with 49.1 mL of dimethylchlorosilane in 160 mL of THF. 1,3-Dichlorobenzene was added dropwise, and I_2 was added to initiate the reaction. After 3 days at reflux, the slurry was washed with petroleum ether and filtered. The filtrate was washed with water and dried with anhy-

drous sodium sulfate. The disilane **3** was obtained by vacuum distillation at 43−45 °C (under full vacuum). The yield was about 24%. (2) Second, 20.60 g of magnesium (in a 500-mL three-necked flask equipped with an addition funnel) with 25.00 g of 1,3-dibromobenzene in 20 mL of THF under an argon atmosphere was pulverized for 1 h. The flask was then charged with 26.0 mL of dimethylchlorosilane in 80 mL of THF. 1,3-Dibromobenzene was added dropwise. After 1 day at reflux, the raw products were washed with petroleum ether and filtered. The filtrate was washed with water and dried with anhydrous sodium sulfate. Disilane **3** was obtained after vacuum distillation at 43−45 °C (under full vacuum). The yield was about 66%. Spectroscopic data for disilane **3** are as follows. IR (THF): 3075 (m), 3037 (m), 3016 (m), 2962 (s), 2898 (m), 2122 (s), 1582 (m), 1432 (m), 1373 (s), 1256 (s), 1106 (s), 881 (s), 839 (s), 764 (s), 732 (s) cm^{-1}. ^1H NMR (250 MHz) ($CDCl_3$), δ: 7.58 (s, 1H), 7.40 (d, J = 7.50 Hz, 2H), 7.18 (t, J = 7.25 Hz, 1H), 4.32−4.27 (m, 2H), 0.20 (d, J = 3.75 Hz, 12H). ^{13}C NMR (62.9 MHz) ($CDCl_3$), δ: 139.7, 136.8, 134.9, 127.3, −3.7. Mass spectrum: m/z (relative intensity): 196 (1, isotope peak), 195 (4, isotope peak), 194 (M^+, $C_{10}H_{18}Si_2$, 17), 180 (7), 179 (35), 163 (4), 136 (15), 135 (100), 121 (5), 105 (7), 93 (5), 79 (2), 73 (8), 59 (12). HRMS m/z (M^+, $C_{10}H_{18}Si_2$): calcd, 194.0947; obsd, 194.0956.

Preparation of *m*-Bis(dimethylhydroxysilyl)-benzene. A 100-mL three-neck flask (equipped with a magnetic stirring bar and an addition funnel) with 9.70 g of disilane **3** under an argon atmosphere was charged with 15 mL of absolute ethanol and a small piece of sodium metal. The disilane **3** was added dropwise under refluxing with ethanol. Upon completion of the addition and 1 h after the evolution of hydrogen had stopped, this mixture was added dropwise with constant stirring into a mixture of 6 g of NaOH, 21 mL of MeOH, and 2.4 mL of H_2O. To this was added a solution of 6 g of NaOH in 24 mL of H_2O. After it was allowed to stand for half an hour, the mixture was added with constant stirring to a solution of 53.3 g of KH_2PO_4 in an ice-water bath. The precipitate formed was separated by filtration, dissolved in benzene, and washed with water. Upon removal of the solvent, the crude products were recrystallized from a mixture of benzene and petroleum ether (1:1 ratio by volume). The yield was approximately 80%, and disilanol **4** had a melting point of 85.6 °C. Spectroscopic data for disilanol **4** are as follows. IR (neat): 3356 (br, s), 3042 (w), 3020 (w), 2990 (w), 2960 (s), 2902 (w), 1895 (w), 1576 (m), 1403 (m), 1363 (m), 1254 (s), 1108 (m), 1063 (s) cm^{-1}. ^1H NMR (250 MHz) ($CDCl_3$), δ: 7.84 (s, 1H), 7.60 (d, J = 7.50 Hz, 2H), 7.38 (t, J = 7.25 Hz, 1H), 2.59 (s, 2H), 0.39 (s, 12H). ^{13}C NMR (62.9 MHz) ($CDCl_3$), δ: 138.4, 137.6, 134.3, 127.3, 0.04. Mass spectrum: m/z (relative intensity): 228 (0.7, isotope peak), 227 (2, isotope peak), 226 (M^+, $C_{10}H_{18}O_2Si_2$, 7), 213 (10), 212 (22), 211 (100), 193 (9), 98 (10), 75 (18). HRMS m/z (M^+, $C_{10}H_{18}O_2Si_2$): calcd, 226.0845; obsd, 226.0850.

Polymerization. A 25-mL one-neck flask, equipped with a magnetic stirring bar and a Dean−Stark trap under an argon atmosphere, was charged with 2.00 g of disilanol **4**, 5.0 mL of benzene, and 0.02 g of *n*-hexylamine-2-ethylhexoate. The mixture was refluxed for 24 h, and then the benzene was removed by distillation. The prepolymer was immediately moved into a vacuum oven at 60 °C and kept under full vacuum for 2 days. The polymerization yield was about 90%. Spectroscopic data for polymer **5** are as follows. IR (neat): 3064 (m), 3034 (m), 3018 (sh, m), 2954 (s), 2898 (m), 1952 (w), 1898 (w), 1605 (m), 1577 (s), 1496 (m), 1468 (m), 1440 (m), 1408 (m), 1364 (s), 1253 (s), 1178 (m), 1150 (sh,s), 1052 (br, s) cm^{-1}. ^1H NMR (250 MHz) ($CDCl_3$), δ: 7.75 (s,1H), 7.55 (d, J = 7.24 Hz, 2H), 7.31 (t, J = 7.21 Hz, 1H), 0.31 (s, 12H). ^{13}C NMR (62.9 MHz) ($CDCl_3$), δ: 138.8, 137.5, 134.0, 127.0, 1.0.

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