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Synthesis of terminal Si–H irregular tetra-branched star polysiloxanes. Pt-catalyzed hydrosilylation with unsaturated epoxides. Polysiloxane films by photo-acid catalyzed crosslinking

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Abstract

Acid catalyzed insertion of octamethylcyclotetrasiloxane (D_4) into the Si–O bonds of tetrakis(dimethylsiloxy)silane leads to irregular tetra-branched star polymers—tetrakis(ω-dimethylsiloxy)poly(dimethylsiloxy)silane (**I**). The terminal Si–H bonds of **I** have been modified by Pt-catalyzed hydrosilylation with 4-vinylcyclohexane-1,2-epoxide to yield a tetra-branched star polydimethylsiloxanes (PDMS) with terminal 2′-ethyl-4-cyclohexanyl-1,2-epoxide groups (II). Solutions of this material and a catalytic amounts of diaryl iodonium hexafluoroantimonate, a photo-acid catalyst, were cast onto glass slides and subsequently irradiated. This results in formation of crosslinked PDMS films (**V**). The soluble tetra-branched PDMS stars have been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR as well as by IR spectroscopy. Their molecular weight distributions have been determined by gel permeation chromatography (GPC), multi-angle laser light scattering (MALLS), and end groups analysis. Their viscosities were measured with a Brookfield viscometer. The thermal stability of the polymers and the crosslinked films were determined by TGA. The glass transition temperatures (T_g)s of the polymers were determined by DSC. The loss (G'') and storage (G') shear moduli of the films were determined by DMTA. Surface properties of the films were determined by measurement of static contact angles.

Similar star polymers, tetrakis(dimethylsiloxy)poly[3′,3′,3′-trifluoropropylmethylsiloxyl]silanes (**III**) were prepared by acid catalyzed equilibration of tetrakis(dimethylsiloxy)silane with 1,3,5-trimethyl-1,3,5-tris(3′,3′,3′-trifluoropropyl)cyclotrisiloxanes (D_3^F). These were, likewise, modified by Pt-catalyzed hydrosilylation with 4-vinylcyclohexane-1,2-epoxide. Films (**VI**) of this material were similarly prepared by photo-acid catalyzed crosslinking.

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1. Introduction

Siloxane materials have a number of properties which make them useful. Among these are low temperature flexibility, high thermal stability, biocompatibility, significant gas permeability, hydrophobicity, and oxidative resistance [1]. There is considerable interest in α,ω-difunctional linear polymers. Such materials are often called macromers or telechelic materials. The functional groups of such macromers can often be coupled to yield higher molecular weight polymers. In this sense, macromers are analogous to difunctional monomers. The terminal functional groups of such telechelic materials may also facilitate chemical modification [2]. α,ω-Difunctional PDMS is often prepared by acid or base catalyzed equilibration of a suitable difunctional tetramethyldisiloxane with a cyclic siloxane such as D_4 [3,4]. For example, α,ω-bis(Si–H)PDMS with a most probable molecular weight distribution ($M_w/M_n = 2$) is prepared industrially by acid catalyzed equilibration of tetramethyldisiloxane with D_4 [5,6].

α,ω-bis(Si–H) polysiloxanes have been converted to α,ω-bis(epoxy) polysiloxanes by use of Pt-catalyzed hydrosilylation addition reaction of the Si–H bonds across the C–C double bonds of unsaturated epoxides. There is considerable interest in chemical modification of polymers [7,8]. These epoxide groups can undergo ring opening polymerization and crosslinking on treatment with acid. Crosslinking is extremely important in converting low

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viscosity liquid PDMS into useful materials [9]. This is often accomplished by a peroxide catalyzed cure, by condensation of silanol terminated polysiloxanes or by Pt-catalyzed hydrosilylation reactions between Si–H and Si-vinyl terminated siloxanes. The photo-acid catalyzed ring opening cure of epoxides, used herein, has the advantage that it is perhaps the fastest known method of crosslinking [10–12].

There is considerable interested in branched polymers due to the fact that these may have properties which are distinct from the analogous linear materials. Among these are dendrimers, star, and hyperbranched materials. Star polymers have a single focal point from which branching originates. On the other hand, dendrimers, have a well-defined architecture and regular pattern of branching. These are generally prepared by a multi-step sequential synthetic process [13–15]. Dendrimers and star polymers have been prepared by both convergent and divergent synthetic approaches. By comparison to dendrimers, hyperbranched materials have an irregular pattern of branching. They may be prepared in a single-step by the direct polymerization of a monomer which has two mutually reactive functional groups, A and B, whose stoichiometry can be described as AB_x where x is greater than or equal to 2 [16]. There is considerable interest in highly branched silicon based materials [17–21].

2. Experimental

2.1. Spectroscopy

^1H, ^{29}Si, ^{19}F and ^{13}C NMR were obtained on Bruker AMX-500 spectrometer. Five percent w/v $CDCl_3$ solutions were used to obtain ^1H, ^{13}C and ^{19}F NMR spectra. Fifty percent w/v $CDCl_3$ solutions were used to obtain ^{29}Si spectra. ^{13}C NMR spectra were obtained with broadband proton decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a 60 s delay was used to acquire ^{29}Si NMR spectra. Residual $CHCl_3$ was used as an internal standard for ^1H and ^{13}C NMR. ^{29}Si NMR spectra were referenced to internal TMS. ^{19}F spectra were referenced to internal $CFCl_3$. Poly(methyl-3′,3′,3′-trifluoropropylsiloxane)s were not soluble in $CDCl_3$. Their NMR spectra were obtained on samples of neat liquid polymer to which was added a capillary of acetone-d_6 as a lock signal. IR spectra of neat films on NaCl plates were recorded using a Perkin–Elmer Spectrum 2000 FT-IR spectrometer.

2.2. Molecular weight analysis

GPC analysis of M_w/M_n was done on a Waters system equipped with a 501 RI detector. Two 7.8 mm × 300 mm Styragel HT 6E and HMW 6E columns in series were used with toluene or THF at a flow rate of 0.8 ml/min. The retention times were calibrated against polystyrene standards: 891,000; 212,400; 29,300; 3680, 770 g/mol. Multi Angle Laser Light Scattering (MALLS) was performed using a Wyatt-DSP detector, placed in line with the GPC system. A flow rate of 1.0 ml/min of THF or toluene was used. M_w/M_n was determined from laser light scattering measurements using the RI detector calibration constant and dn/dc values of -0.095 for PDMS [22] and -0.0202 for poly(methyl-3′,3′,3′-trifluoropropylsiloxane)s [23]. GPC and MALLS analysis of **I** and **II** were done with toluene, whereas **III** and **IV** were done with THF.

2.3. Differential scanning calorimetry

T_gs, $T_{cryst.}$s, and T_ms of the polymers were determined on a Shimadzu DSC-50. The DSC's were calibrated from the heat of transition (-87.06 °C), and the mp of cyclohexane (6.54 °C), [24] as well as the T_g of PDMS (-125 °C) [25]. After equilibration at -150 °C, the temperature was increased from -150 to 50 °C at 10 °C/min.

2.4. Thermal gravimetric analysis

TGA was performed on a Shimadzu TGA-50 instrument at a flow rate of 40 ml of nitrogen or air per min. The temperature was increased 4 °C/min from 25 to 800 °C. Viscosity measurements were obtained with a Brookfield Model DV-II Viscometer at a shear rate 3 s^{-1} at 24 °C.

2.5. Static contact angle measurements

Static contact angle (DCA) measurements were performed with a First Ten Ångstroms 4000 optical contact angle system (FTÅ) equipped with a video camera. Approximately, 10 μl of distilled/deionized water was placed on the film surface at room temperature and the contact angle calculated using the FTÅ drop shape analysis software. DCA measurements were made at the air/film interface.

2.6. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) of the films in a shear sandwich mode at frequencies of 1, 5, and 10 Hz and at a amplitude 4 μm were determined using TA Instruments Q800 Dynamic Mechanical Analyzer. After equilibration at -130 °C for 5 min, the temperature was increased at 2 °C/min to 20 °C.

2.7. Materials

Bis(4-dodecylphenyl)iodonium hexafluoroantimonate (GE UV 9380c), a photo-catalyst, was obtained from GE Silicones. D_4, tetrakis(dimethylsiloxy)silane, hexamethyldisilazane and D_3^F were purchased from Gelest. 1,3-Divinyltetramethyldisiloxane Pt complex (Karstedt catalyst) in xylene (2% Pt) was acquired from United Chemical

Technologies, Inc. Triflic acid was obtained from the 3 M Corp. Triethylamine, CH_2Cl_2, $MgCO_3$ and 4-vinylcyclohexane-1,2-epoxide were purchased from Aldrich.

2.8. Synthetic procedures

2.8.1. Tetrakis[ω-(dimethylsiloxy)polydimethylsiloxy]silane (*I*)

D_4 (30 g, 0.1 mol) and tetrakis(dimethylsiloxy)silane (0.5 g, 1.5 mmol) were placed in a 50 ml round bottom (rb) flask that was equipped with a Teflon-covered magnetic stir bar and sealed with a rubber septum. Triflic acid (15 μl) was added. The reaction was stirred for 1 h at 90 °C. The mixture was allowed to cool to room temperature and 0.5 g $MgCO_3$ and CH_2Cl_2 (20 ml) were added. The mixture was stirred for 2 h and then filtered through a pad of Celite. The volatiles were removed by evaporation under reduced pressure at 70 °C. A clear colorless liquid, 27 g, 88% yield, viscosity 267 centipoise, $T_g = -124.8$ °C, $T_{crys} = -93.0$ °C, $T_m = -50.0$ °C was obtained. Its molecular weight was determined by GPC, $M_w/M_n = 17{,}940/8630$, and by MALLS, $M_w/M_n = 29{,}200/12{,}200$. It had the following spectral properties. ^{1}H NMR δ: 0.12 (s, 1620H), 0.23 (d, 24H, $J = 3.0$ Hz), 4.76 (septet, 4H, $J = 3.0$ Hz). ^{13}C NMR δ: 1.07. ^{29}Si NMR δ: −6.89 (m, 4Si), −21.92 (s, 223Si). A value of $M_n = 20{,}000$ was found by ^{1}H NMR end group analysis based on integration of Si–H versus Si–CH_3 signals, while ^{29}Si NMR end group analysis based on integration of the Si–H versus Si–CH_3, gives $M_n = 16{,}800$.*IR* ν: 2964, 2906, 2796, 2128 (Si–H), 1447, 1413, 1260, 1095, 1013, 914, 864, 798, 701 cm^{-1}.

2.8.2. Low molecular weight *I*

In a separate experiment, D_4 (5 g, 16.9 mmol), tetrakis(dimethylsiloxy)silane (73 mg, 0.22 mmol) and triflic acid (10 μl) were reacted at 22 °C for 12 h. Hexamethyldisilazane was added to neutralize the mixture. The polymeric product was dissolved in toluene and was precipitated into methanol. In this way, 2.5 g of **I**, 53% yield, $M_w/M_n = 12{,}300/5400$ by GPC was obtained. ^{1}H NMR δ: 0.11 (s, 880H), 0.23 (d, 24H, $J = 3$ Hz), 4.78 (m, 4H). ^{13}C NMR δ: 1.09. ^{29}Si NMR δ: −6.9 (s, 4Si), −21.8 (s, 98Si), −109.1 (s, 1Si). End group analysis by ^{1}H NMR integration of the Si–H to the Si–CH_3 signals gives $M_n = 10{,}800$, while ^{29}Si NMR integration of the Si–H and Si Q signals gives $M_n = 7300$. The low molecular weight of this sample of **I**, permits observation of the ^{29}Si NMR signal (−109 ppm) due to the core Q silicate unit.

2.8.3. Tetrakis[ω-[2′-(4-cyclohexanyl-1,2-epoxide)ethyl] polydimethylsiloxy]silane (*II*)

I (20 g, $M_w/M_n = 17{,}940/8630$ by GPC), triethylamine (15 μl), CH_2Cl_2 (4 ml) and 4-vinylcyclohexane-1,2-epoxide (1.27 ml, 9.7 mmol) were placed in a 50 ml rb flask that was equipped with a Teflon-covered magnetic stir bar and sealed with a rubber septum. Karstedt catalyst (10 μl) was added. The solution was stirred at room temperature overnight. Volatiles were removed by evaporation under reduced pressure. The residue was purified by flash column chromatography on silica gel with hexanes/$CH_2Cl_2 = 4/1$ as the eluant. In this way, 19 g of **II**, 95% yield, viscosity 402 centipoise, $T_g = -122.8$ °C, $T_{crys} = -93.3$ °C, and $T_m = -52.7$ °C was obtained. Its molecular weight was found by GPC to be $M_w/M_n = 22{,}290/11{,}430$, and by MALLS, $M_w/M_n = 29{,}100/12{,}000$. ^{1}H NMR δ: 0.12 (s, 1820H), 0.53–0.56 (m, 8H), 0.88–0.96 (m, 2H), 1.10–1.19 (m, 2H), 1.21–1.26 (m, 8H), 1.31–1.36 (m, 2H), 1.38–1.47 (br m, 8H), 1.53–1.58 (br m, 2H), 1.71–1.77 (m, 2H), 1.83–1.90 (m, 2H), 2.06 (m, 4H), 2.21 (m, 4H), 3.17 (m, 8H). End group analysis, based on integration of ^{1}H NMR of the Si–CH_3 versus cyclohexanylethyl signals, gives $M_n = 22{,}450$. ^{13}C NMR δ: 0.98, 8.79, 14.97, 15.10, 23.58, 24.05, 25.40, 26.74, 29.54, 30.11, 30.43, 31.56, 32.27, 35.43, 51.88, 51.92, 52.65, 53.18. ^{29}Si NMR δ: 7.73, −21.92. IR ν: 2964, 2909, 1410, 1262, 1092, 1025, 864, 803, 697 cm^{-1}.

2.8.4. Tetrakis[ω-(dimethylsiloxy)poly(3′,3′,3′-trifluoropropyl)methylsiloxy]silane (*III*)

D_3^F (30 g, 64 mmol) and tetrakis(dimethylsiloxy)silane (0.68 g, 2.1 mmol) were placed in a 50 ml rb flask that was equipped with a Teflon-covered magnetic stir bar and sealed with a rubber septum. Triflic acid (10 μl) was added. The reaction was stirred for 3 h at 50 °C. The mixture was allowed to cool to room temperature and 0.5 g $MgCO_3$ and CH_2Cl_2 (20 ml) were added. The mixture was stirred for 3 h and then filtered through a pad of Celite. The volatiles were removed by evaporation under reduced pressure at 100 °C. A clear colorless fluid, 26 g, 87% yield, viscosity 1800 centipoise, $M_w/M_n = 10{,}150/7240$ by GPC, $M_w/M_n = 23{,}640/13{,}720$ by MALLS, and $T_g = -75$ °C was obtained. ^{1}H NMR δ: 0.28 (320H), 0.90 (210H), 2.17 (210H), 4.87 (4H). ^{13}C NMR δ: −1.67, −1.42, 9.17, 9.36, 28.20 (q, $J = 30$ Hz), 129.58 (q, $J_{C-F} = 276$ Hz). ^{19}F NMR δ: −69.46. ^{29}Si NMR δ: −5.55 (4Si), −23.09 (m, 155Si). The end group analysis, based on integration of ^{1}H NMR of Si–H and Si–CH_3 groups, gives $M_n = 16{,}640$. Similar end group analysis, based on ^{29}Si NMR integration, gives $M_n = 24{,}200$. IR ν: 2966, 2910, 2796, 2131 (Si–H), 1448, 1424, 1370, 1316, 1268, 1211, 1127, 1069, 1018, 898, 838, 805, 768 cm^{-1}.

2.8.5. Tetrakis[ω-[2′-(4-cyclohexanyl-1,2-epoxide)ethyl] poly(methyl-3′,3′,3′-trifluoropropyl siloxy)]silane (*IV*)

III (20 g), triethylamine (15 μl), CH_2Cl_2 (4 ml) and 4-vinylcyclohexane-1,2-epoxide (1 ml, 7.6 mmol) were placed in a 50 ml rb flask that was equipped with a Teflon-covered magnetic stir bar and sealed with a rubber septum. Karstedt catalyst (10 μl) was added. The solution was stirred at room temperature overnight. The volatiles were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with hexanes/$CH_2Cl_2 = 3/1$ as the eluant. In this way, 19 g, 95% yield of **IV**, viscosity 2100 centipoise, $M_w/M_n = 11{,}480/8360$ by GPC, $M_w/M_n = 21{,}750/12{,}380$ by MALLS, and $T_g = -69.7\,°C$ was obtained. ^{1}H NMR δ: 0.10 (3H), 0.72 (2H), 1.99 (2H). ^{13}C NMR δ: -0.90, 9.86, 15.47, 15.61, 24.53, 24.94, 26.33, 27.61, 28.71 (q, $J_{C-F} = 30$ Hz), 30.41, 30.72, 30.87, 31.00, 31.02, 31.17, 31.33, 31.36, 32.50, 33.32, 36.46, 51.98, 52.03, 52.76, 53.32, 128.59 (q, $J = 275$ Hz). ^{19}F NMR δ: -69.40. ^{29}Si NMR δ: 9.11 (4Si), -23.17 (169Si). The end group analysis, based on ^{29}Si NMR integration, gives $M_n = 26{,}400$. IR ν: 2966, 2911, 1446, 1421, 1370, 1315, 1268, 1212, 1129, 1071, 1020, 899, 840, 805, 768, 743 cm^{-1}.

*2.8.6. Preparation of films **V** and **VI***

To 10.0 g of **II** was added 65 mg (0.65 wt%) of the photo-acid catalyst [bis(4-dodecyl-phenyl)iodonium hexafluoroantimonate]. The mixture was stirred for 0.5 h under vacuum to remove adsorbed gas. Glass microscope slides were sequentially cleaned with acetone and CH_2Cl_2. With a pipet, ~0.5 ml of the mixture was spread on a flame-dried clean glass microscope slide (25 × 75 × 1 mm). Care was taken to ensure each slide was completely coated. These were placed on a level table for at least for 25 min before exposure for 15 min to UV radiation from a 450 W medium pressure Hanovia mercury lamp. The films (**V**) thus produced were removed from the glass slides using a clean single edge razor blade. These were used for DMTA, TGA, DSC and SCA measurements.

VI was prepared using a solution of 10 g of **IV** and 85 mg (0.85 wt%) of photo-catalyst as above.

*2.8.7. Removal of oligomers from **VI** and characterization of oligomers*

Leachable oligomers were extracted from **VI**, 430 mg, with CH_2Cl_2 using a soxhlet apparatus overnight. The residual film was dried by vacuum. A weight loss of 158 mg, ~36%, was observed. The residual crosslinked film weighed 272 mg. The leachate had the following characteristics: $M_w/M_n = 1080/1060$, ^{1}H NMR δ: 0.17 (s, 3H), 0.77 (m, 2H), 2.04 (m, 2H). ^{13}C NMR δ: -1.06, -1.01, -0.96, 9.17, 28.02 (q, $J = 30$ Hz), 127.46 (q, $J_{C-F} = 270$ Hz). ^{19}F NMR δ: -69.32 (m). ^{29}Si NMR δ: -22.90 (m). IR ν: 2966, 2910, 1448, 1369, 1315, 1269, 1211, 1129, 1071, 1029, 899, 838, 804 cm^{-1}.

3. Results and discussion

Regular siloxane dendrimers with terminal Si–H bonds have been prepared by a multi-step synthetic route [17,26]. Hyperbranched poly(carbosilane/siloxanes) with reactive terminal Si–H bonds have also been reported [27–29]. Herein, we report a one-step divergent synthesis of irregular telechelic tetra-branched PDMS stars in which each branch is terminated by a reactive Si–H functional group. This has been achieved by the acid catalyzed equilibration of tetrakis(dimethylsiloxy)silane with D_4. In this reaction, tetrakis(dimethylsiloxy)silane functions in a manner similar to tetramethyldisiloxane in the acid catalyzed equilibration with D_4 to yield α,ω-bis(Si-H)PDMS discussed above. The focal point of these tetra-branched PDMS stars is a silicate silicon atom. The ^{29}Si NMR signal due to the Q-unit silicate silicon could not be observed in high molecular weight **I** but has been observed at -109 ppm in a lower molecular weight sample of **I**.

Virtually all of the PDMS branches are terminated with reactive Si–H groups. This conclusion is based on the approximate agreement of the molecular weights determined by MALLS and end group analysis based on ^{1}H NMR integration. It is difficult to get reasonable GPC values for **I** and **II** using the refractive index detector, due to the similarity of the refractive indices of PDMS and THF. This also complicates accurate determination of dn/dc values for calculation of M_w/M_n values from MALLS data for **I** and **II**. For this reason, MALLS measurements of **I** and **II** were run with toluene as the eluant. On the other hand, **III** and **IV** are both virtually insoluble in toluene. It was thus necessary to use THF as solvent to determine M_w/M_n for **III** and **IV** by both GPC and MALLS.

The molecular weight determined by GPC, based on comparison to linear polystyrene standards, is lower than that determined by MALLS or end group analysis. It is well known that branched polymer have smaller hydrodynamic radii than the corresponding linear polymers of comparable molecular weight. For this reason, they often give lower values for molecular weight by GPC.

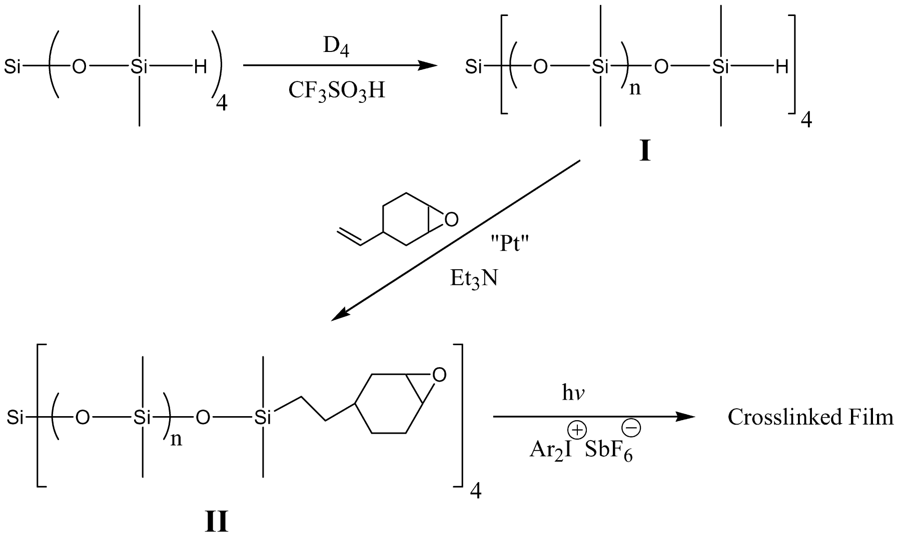
We have chemically modified the reactive Si–H bonds of our irregular tetra-branched PDMS by a Pt-catalyzed (Karstedt's catalyst) hydrosilylation reaction with 4-vinylcyclohexane-1,2-epoxide [12,30]. To achieve success, this reaction must be carried out with a small amount of triethylamine to prevent the ring opening of the epoxide rings by traces of acid. Tetra-branched telechelic PDMS stars with terminal epoxy groups have thus been prepared (Scheme 1).

The thermal properties: T_g, $T_{cryst.}$ and T_m of both **I** and **II** determined by DSC are very similar to that of linear PDMS (see Table 1) [31].

A similar reaction sequence was used to prepare telechelic tetrakis[ω-(dimethylsiloxy)poly(methyl-3′,3′,3′-trifluoropropylsiloxy)]silane (**III**) by acid catalyzed reaction

Table 1
Thermal properties of **I**, **II**, **III** and **IV**

	T_g (°C)	T_{cryst} (°C)	T_m (°C)
I	−124.8	−93	−50
II	−122.8	−93.3	−52.7
PDMS [34]	−125	−93	−50 to −40
III	−75	–	–
IV	−69.7	–	–
PFMS [35]	−70	–	–



Scheme 1. Synthesis of **I**, **II** and **V**.

of D_3^F. **III** was, likewise, converted into a epoxy terminated tetra-branched telechelic **IV** by Pt-catalyzed hydrosilylation reaction with 4-vinylcyclohexane-1,2-epoxide. The thermal properties of **III** and **IV**, determined by DSC, are very similar to that of linear poly(methyl-3′,3′,3′-trifluoropropyl)siloxane. (See Table 1) [32].

The thermal stability of the low molecular weight tetra-branched telechelic poly(siloxane)s (**I**–**IV**) has been determined by TGA. In nitrogen, they undergo catastrophic decomposition. For both **III** and **IV**, this occurs in two-stages. Almost 25% of the initial sample weight of both **III** and **IV** is lost by 200 °C. Further decomposition of **III** and **IV** begins at about 400 °C. By 500 °C no residue remains. On the other hand, thermal decomposition of **I** begins at ~100 °C. Approximately 10% of its initial sample weight is lost. The second stage of thermal decomposition of **I** begins at about 400 °C. The major decomposition of **II** begins at 400 °C. Both **I** and **II** leave virtually no residue above 660 °C (see Fig. 1).

The thermal decompositions of **I**–**IV** in air are similar, except that above 500 °C, both **I** and **II** leave residues which amount to ~35–40% of their initial sample weights. By comparison, above ~400 °C, **III** leaves a residue of ~30% while **IV** leaves a residue of ~15% (Fig. 2).

Solutions of both **II** and **IV** with the diaryl iodonium hexafluoroantimonate photo-acid catalyst (0.5 wt%) were prepared. These were each coated on clean glass slides and subjected to irradiation with a medium pressure 450 W Hanovia mercury lamp. $H^{+-}SbF_6$ generated by decomposition of the diaryl iodonium salt causes ring opening and polymerization of the terminal epoxide groups [10–12]. This resulted in formation of films **V** and **VI**, respectively.

The SCA of VI at the film air interface was 112.7°. The thermal decomposition of **VI** occurs in two stages. **VI** is stable until 200 °C. Between 200 and 250 °C, slightly more than 30% of the initial sample weight is lost. No further weight loss occurs until 400 °C. Above this temperature, catastrophic decomposition occurs. By 500 °C, virtually no

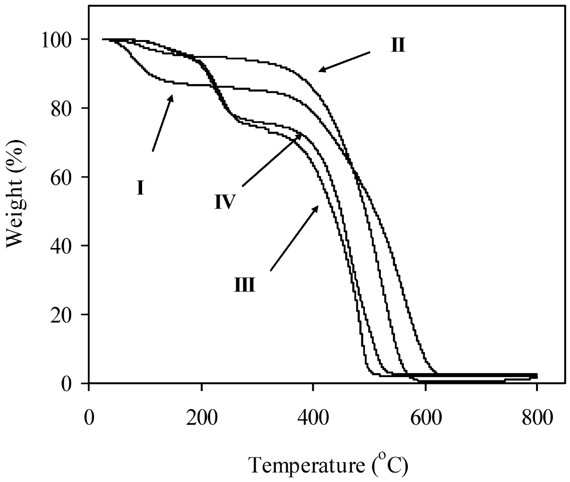


Fig. 1. TGA of **I**–**IV** in N$_2$.

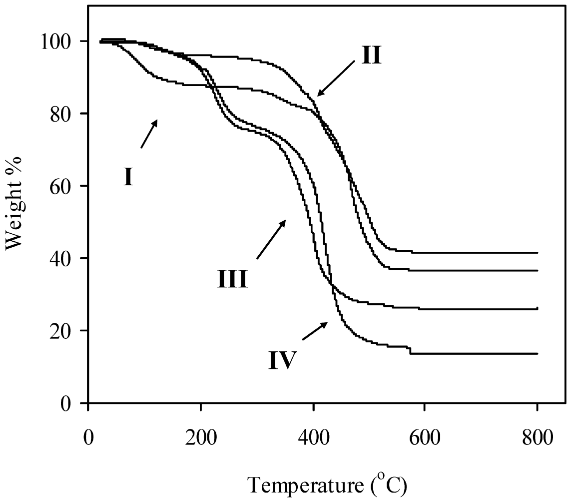


Fig. 2. TGA of **I**–**IV** in air.

residue remains (Fig. 3). The initial stage of thermal decomposition of **VI** may be to vaporization of ~35% of methyl-3′,3′,3′-trifluoropropylsiloxane oligomers, consistent with the weight loss of **VI** by soxhlet extraction with CH_2Cl_2. Apparently, when tetrakis(dimethylsiloxy)silane and D_3^F were equilibrated, cyclic oligomers of methyl-3′,3′,3′-trifluoropropylsiloxanes were formed in addition to **III**. Analysis by NMR of this material was consistent with cyclic methyl-3′,3′,3′-trifluoropropylsiloxane oligomers since no end groups were observed. This material had a narrow molecular weight distribution by GPC, M_w/M_n = 1080/1060. This value would be consistent with a cyclic heptamer. While possible, we suggest that a cyclic dimer of D_3^F is more likely which may be a major contaminant in both **III** and **IV**.

The presence of oligomers in siloxane materials is well known. Low molecular weight silicone oils are sometimes incorporated into siloxane materials in significant amounts. In fact, such silicone oils have been used to improve the biofoul release properties of marine silicone coatings [33–35].

The TGA of **VI** after extraction with CH_2Cl_2 showed a single catastrophic weight loss process which began at ~400 °C (see Fig. 3).

Contamination of **V** with cyclic PDMS oligomers is apparently not a problem based on the TGA of **V**. The TGA of film **V** shows only a small (~5%) weight loss between 200 and 400 °C. Above 430 °C, catastrophic decomposition occurs. By 550 °C, virtually no residue remains. The SCA of **V** at the film air interface was 109.7°.

The shear storage (G') and shear loss (G'') moduli of PDMS networks prepared by Pt-catalyzed hydrosilylation crosslinking of α,ω-bis(divinyl)PDMS and tetrakis(dimethylsiloxy)silane have been reported [35]. G' and G'' for **V** were measured at frequencies of 1, 5, and 10 Hz (Figs. 4 and 5).

Log G' of **V** has a value of ~6.7 Pa below −120 °C. A shallow minimum in the log G' which depends on the frequency is observed between −120 and −90 °C. The value of log G' is constant with a value of 6.5 Pa between −90 and −50 °C. Between −50 and −40 °C the value of log G' decreases to 4.2 Pa. Between −40 and 30 °C its value is fairly stable between 4.2 and 4.4 Pa.

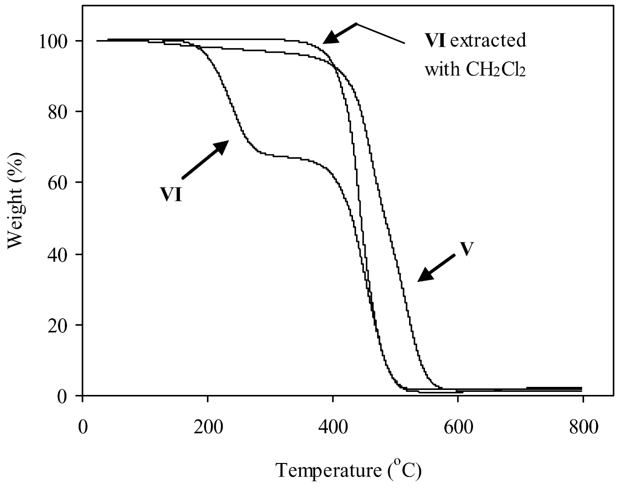


Fig. 3. TGA of **V** and **VI** in N_2 before and after extraction of oligomers.

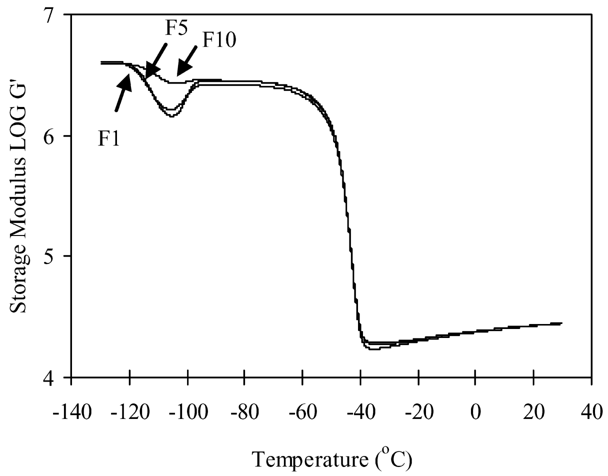


Fig. 4. Storage modulus (G') of **V** by DMTA.

On the other hand, log G'' of **V** has a value of 4.5 Pa at −130 °C. Its value increases between −130 to −110 °C to ~5.8 Pa. Between −110 and −95 °C, its value decreases to ~5.0 Pa. Between −95 and −50 °C, log G'' is essentially constant with a value of ~5.0 Pa. Between −50 and −40 °C, its value rapidly decreases. By 40 °C, log G'' observed at 1 Hz is only ~2.8 Pa. Between −40 and 30 °C, log G'' continues to decreases in value but at a slower rate. By 30 °C, it is only 2.2 Pa. The value of log G'' is dependent on the frequency in both the range of −120 to −110 °C and −40 to 30 °C.

The storage and loss moduli for **VI** were also measured at frequencies of 1, 5 and 10 Hz both before and after extraction to remove cyclic oligomers (Fig. 6). Log G' before extraction is stable between −130 and −100 °C with a value of ~6.8 Pa. Between −100 and −80 °C its value decreases to ~6.3 Pa. It maintains this value to −40 °C.

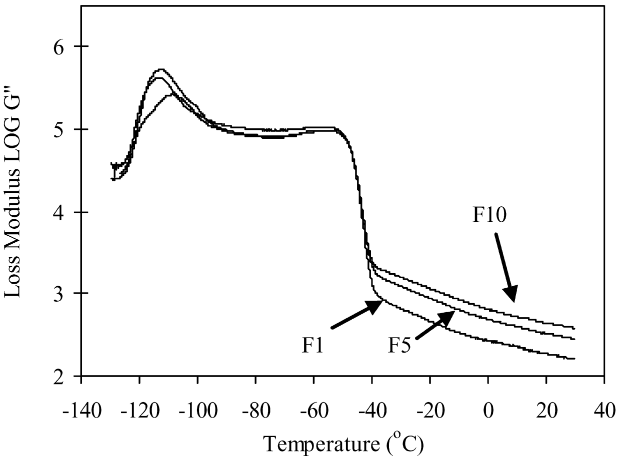


Fig. 5. Loss modulus (G'') of **V** by DMTA.

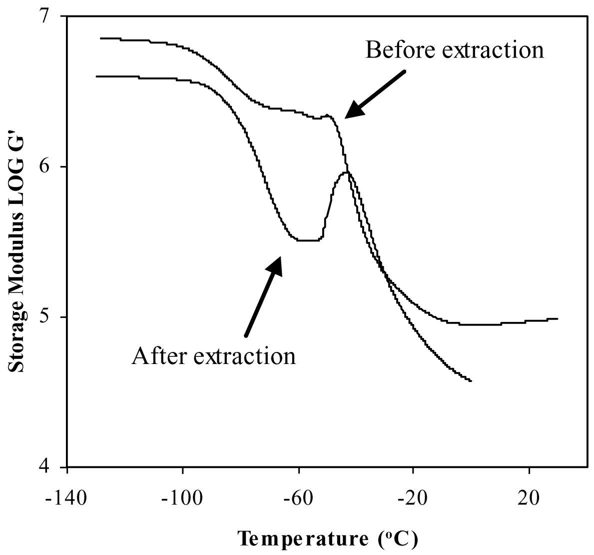


Fig. 6. Storage modulus (G') of **VI** before and after extraction ($\nu = 1$ Hz).

Between -40 and -10 °C, a rapid decrease in the value of log G' is observed. By -10 °C, its value is 5.0 Pa. The values of log G' observed depend on the frequency applied. This may indicate that these networks have unattached chains [35].

After extraction, log G' of **VI** has a value of 6.6 Pa between -130 and -90 °C. Between -90 and -70 °C, a rapid decrease in the value of log G' is observed. By -70 °C its value is ~5.5 Pa at a frequency of 5 Hz. Between -70 and -50 °C the value of log G' is stable but dependent on the frequency applied. Above -50 °C its value increases to a maximum of 6 Pa between -40 and -35 °C. Above this temperature log G' continuously decreases. By 0 °C, its value is ~4.5 Pa.

The effect of the cyclic oligomers on the loss modulus of **VI** is even more pronounced (Fig. 7). Log G'' shows a β peak at -90 °C and a T_g at -50 °C before extraction. Clearly, the beta transitions are more distinctive in **VI** than in **V**. Beta transitions are often associated with side chain or pendant group movements [36]. This is consistent with the structural difference between **V** and **VI**. **VI** possesses the larger 3′,3′,3′-trifluoropropyl pendant groups compared to the smaller methyl groups in **V**. After extraction of **VI**, these transitions occur at -80 °C and ~ -38 °C, respectively. These values obtained from the log G'' curves are dependent on the applied frequency. Clearly, the oligomers are effectively acting as a plasticizer which increases the interchain distance and reduces secondary intermolecular bonding [37].

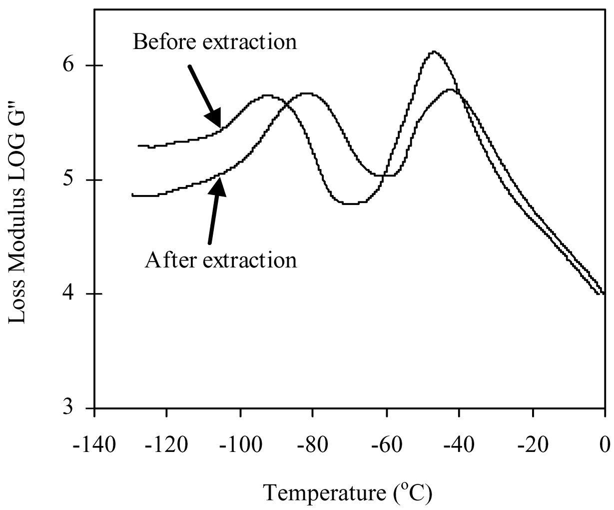


Fig. 7. Loss modulus (G'') of **VI** before and after extraction ($\nu = 1$ Hz).

4. Conclusion

Irregular tetra-branched telechelic siloxanes with PDMS or poly(methyl-3′,3′,3′-trifluoropropylsiloxy) branches and Si–H or epoxy terminal groups have been efficiently prepared. Acid catalyzed equilibration of tetrakis(dimethylsiloxy)silane with D_4 or D_3^F yields the Si–H terminated tetrabranched siloxanes (**I** and **III**). These have been converted to tetra-branched telechelic siloxanes with terminal epoxy groups (**II** and **IV**) by Pt-catalyzed hydrosilylation reactions with 4-vinylcyclohexane-1,2-epoxide. Photo-acid catalyzed crosslinking of the epoxy groups yields PDMS or poly(methyl-3′,3′,3′-trifluoropropylsiloxane) films **V** and **VI** respectively. All materials have been characterized. Removal of low molecular weight oligomers from **VI** has a marked effect on its storage and loss shear moduli.

Acknowledgements

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