Synthesis of Polymethyl(trimethylsiloxy)siloxane by Anionic Ring-Opening Polymerization of 1,3,5-Trimethyl-1,3,5-tris(trimethylsiloxy)cyclotrisiloxane

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ABSTRACT: Polymethyl(trimethylsiloxy)siloxane, the first linear polysiloxane in which each silicon atom of the polymer backbone is a trifunctional $RSiO_{3/2}$ (T) unit, has been prepared by anionic ring-opening polymerization of 1,3,5-trimethyl-1,3,5-tris(trimethylsiloxy)cyclotrisiloxane (**I**).

Introduction

Soluble linear polysiloxanes are commercially the most important type of inorganic/organic polymeric material. The backbone of these is generally made up of difunctional $R_2SiO_{2/2}$ (D) units in which R is typically methyl, phenyl, 3,3,3-trifluoropropyl, 3-cyanopropyl, or H.[1] Polydisperse high molecular weight linear polysiloxanes are often prepared by acid-catalyzed ring-opening polymerization of cyclotetrasiloxanes such as octamethylcyclotetrasiloxane (D_4).[2,3] Small amounts of a disiloxane, such as hexamethyldisiloxane (MM) which can serve as an end-capping unit, permit control of the molecular weight of the polymer. [2] Trifunctional $RSiO_{3/2}$ (T) units are found at branch points or cross-links.

Linear polysiloxane in which T units serve as the polymer backbone have not been previously reported. Living anionic ring-opening polymerization of cyclotrisiloxane has been used to prepare narrow molecular weight distribution polysiloxanes.[4,5] This is possible because ring opening is generally faster than equilibration or redistribution reactions. Regiospecific anionic ring-opening polymerization of monosubstituted cyclotrisiloxanes has been used to prepare highly regular polysiloxanes.[6,7]

Results

Polymethyl(trimethylsiloxy)siloxane, a linear polymer in which each siloxane unit of the polymer chain is a T unit, has been prepared by anionic ring-opening polymerization of **I** initiated by dilithiodiphenylsilanediolate (Figure 1).[4]

I was previously prepared in very low yield by hydrolytic polycondensation of methyltrichlorosilane with sodium metasilicate followed by trimethylsilylation with trimethylchlorosilane.[8] We have prepared **I** by reaction of 1,1-dichlorotetramethyldisiloxane (**II**)[9,10] with DMSO.[11−14] Alternatively, **I** has been prepared by reaction of **II** with 1,3-dihydroxy-1,3-dimethyl-1,3-bis(trimethylsiloxy)disiloxane (**III**)[15] in the presence of triethylamine. **III** was prepared by a palladium-on-carbon catalyzed oxidation of 1,3-dihydrido-1,3-dimethyl-1,3-bis(trimethylsiloxy)disiloxane with water.[16] **III** is expected to be inherently unstable since silanols are well-known to undergo facile condensation to siloxanes. For this reason, **III** was reacted with **II** promptly after its preparation.

Both methods to prepare **I** require **II**, which is not commercially available. We have prepared **II** by the ferric chloride/HCl superacid ($HFeCl_4$) catalyzed equilibration of hexamethyldisiloxane and methyltrichlorosilane.[17] In this reaction, trimethylchlorosilane is lost. In addition to **II**, a small amount of methylbis(trimethylsiloxy)chlorosilane is formed. **II** has previously been prepared by equilibration of methyltrichlorosilane and hexamethyldisiloxane in the presence of cyclic $(PNCl_2)_n$ (Figure 2).[9]

Although **I**, **II**, and **III** have been previously reported, they have not been fully characterized by modern spectroscopic methods. For this reason, we have included full experimental details and spectral characterization.

Experimental Section

^1H, ^{13}C, and ^{29}Si NMR spectra were obtained on a Bruker AMX-500 MHz spectrometer. ^{13}C NMR spectra were obtained with broad-band proton decoupling. Spectra of monomers were run in acetone-d_6. Because of its limited solubility in acetone, spectra of polymethyl(trimethylsiloxy)siloxane were run in benzene-d_6. ^1H and ^{13}C NMR spectra were internally referenced to residual acetone. A heteronuclear gated decoupling pulse sequence (NONOE) with a 60 s delay (for monomers) and a 30 s delay (for polymers) was used to acquire the ^{29}Si NMR spectra. These were referenced to an external TMS standard. IR spectra of neat films on NaCl plates for liquids were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer.

GPC analysis of the molecular weight distribution of the polymers was performed at 22 °C on a Waters system equipped with a R401 refractive index detector. Two 7.8 mm × 300 mm Styragel columns packed with <5 μm divinylbenzene cross-linked polystyrene: HR3 (pore size 1000 Å) and HR4 (pore size 10 000 Å) in series were used for the analysis. THF was used as the eluant at a flow rate of 0.6 mL/min. The retention times of the polymers were calibrated against those of known polystyrene standards whose $M_w/M_n < 1.09$.

Thermogravimetric analysis of the polymers was carried out on a Shimadzu TGA-50 instrument with a flow rate of 40 cm^3 of nitrogen or air per minute. The temperature was increased at 4 °C/min from 25 to 800 °C.

The glass transition temperature (T_g) of the polymer was determined by DSC on a Perkin-Elmer DSC-7. The DSC was

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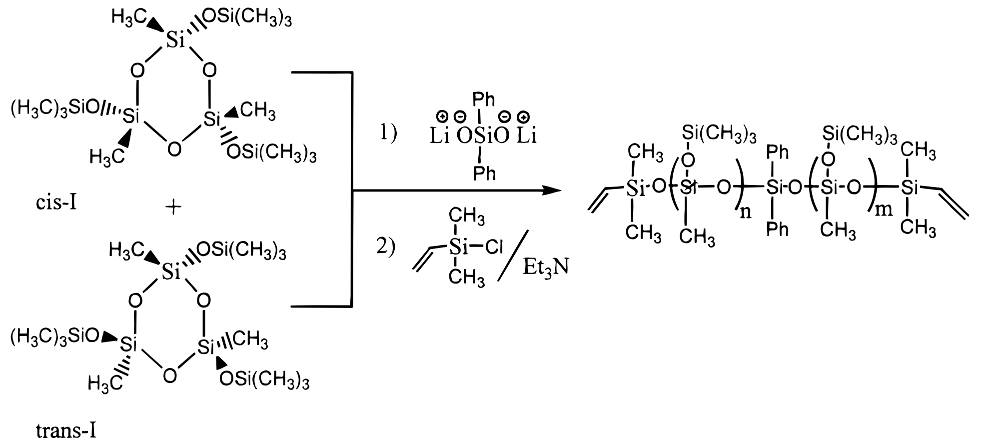

Figure 1. Anionic ring-opening polymerization of *cis*- and *trans*-1,3,5-trimethyl-1,3,5-tris(trimethylsiloxy)cyclotrisiloxane (**I**).

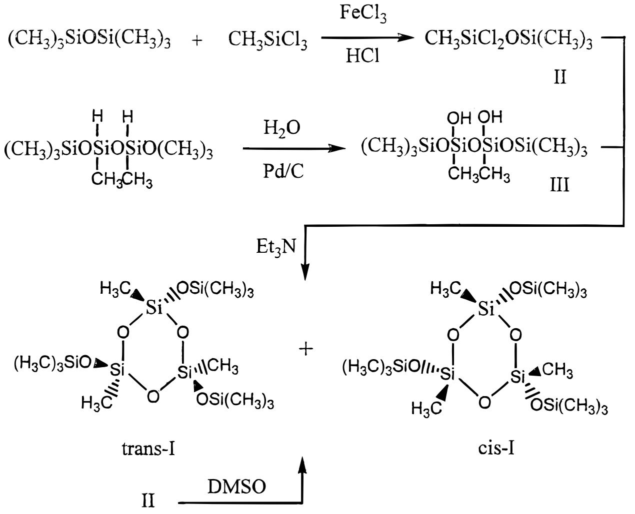

Figure 2. Synthesis of *cis*- and *trans*-1,3,5-trimethyl-1,3,5-tris(trimethylsiloxy)cyclotrisiloxane (**I**).

calibrated against the heat of transition (−87.06 °C) and the melting point of cyclohexane (6.54 °C),[18] as well as by determination of the T_g of poly(dimethylsiloxane) (−123 °C).[19] The temperature program for the analysis was begun at −150 °C and was increased at 10 °C/min to 50 °C.

Methyltrichlorosilane (99%), hexamethyldisiloxane (99%), and 1,3-dihydrido-1,3-dimethyl-1,3-bis(trimethylsiloxy)disiloxane (95%) were obtained from Gelest. Palladium on carbon (10%), ferric chloride hydrate, *p*-dioxane, and triethylamine were purchased from Aldrich. Reagents were used as obtained without purification. All reactions were run under nitrogen.

High-resolution mass spectra were run at the University of California, Riverside, Mass Spectroscopy Facility on a BG-7070 EHF instrument. Exact masses were determined by peak matching against known masses of perfluorokerosene. Ammonia was employed as the chemical ionization agent.

Elemental analysis was performed by Oneida Research Services Inc., Whitesboro, NY.

1,3-Dihydroxy-1,3-dimethyl-1,3-bis(trimethylsiloxy)disiloxane (III).[15] *p*-Dioxane (100 mL), distilled water (15 mL), and palladium on carbon (0.5 g, 10%) were placed in a 250 mL three-neck round-bottom flask equipped with a Teflon-covered magnetic stir bar. One neck was equipped with a pressure-equalizing addition funnel and the second with a reflux condenser, and the third was sealed with a rubber septum. 1,3-Dihydrido-1,3-dimethyl-1,3-bis(trimethylsiloxy)disiloxane (9.5 g, 34 mmol) was placed in the addition funnel and was added dropwise over 0.5 h at 20 °C. The solution was stirred overnight. It was then filtered to remove the catalyst. *p*-Dioxane and water were removed by evaporation under reduced pressure. The residue was purified by distillation through a 10 cm Vigreux column. A fraction bp 85−86 °C/2.5 mm, 8.0 g, 76% yield was obtained. It had the following spectral properties. ^{1}H NMR δ: 5.39 (s, 2H), 0.11 (s, 18H), 0.05 (s, 6H). ^{13}C NMR: 1.76 [$(C\mathrm{H_3})_3$SiO], −2.55 [$C\mathrm{H_3SiOH{-}O_{2/2}}$]. ^{29}Si NMR: 7.56 [$(\mathrm{CH_3})_3Si$O], −56.70 [$\mathrm{CH_3}Si\mathrm{OH{-}O_{2/2}}$]. IR ν: 3339 (Si−OH, br), 2961, 2903, 1269, 1254, 1056, 907, 843, 790, 756, 734 cm^{-1}.

1,1-Dichlorotetramethyldisiloxane (II).[9,10] Methyltrichlorosilane (75 g, 0.5 mol), hexamethyldisiloxane (57 g, 0.35 mol), and $\mathrm{FeCl_3}$ hydrate (0.05 g, 0.18 mmol) were placed in a 250 mL round-bottom flask equipped with a Teflon-covered magnetic stir bar and sealed with a rubber septum. Dry HCl was bubbled into the solution at 20 °C for 2.5 h. The reaction mixture was then distilled through a 50 cm vacuum jacketed distillation column packed with stainless steel saddles. A fraction bp 126 °C/760 mm, 32 g, 45% yield was collected. It had the following spectral properties. ^{1}H NMR δ: 0.79 (s, 3H), 0.22 (s, 9H). ^{13}C NMR: 6.05 [$C\mathrm{H_3SiCl_2}$], 1.29 [$(C\mathrm{H_3})_3$Si]. ^{29}Si NMR: 16.63 [$(\mathrm{CH_3})_3Si$], −18.60 [$\mathrm{CH_3}Si\mathrm{Cl_2}$].

Preparation of 1,3,5-Trimethyl-1,3,5-tris(trimethylsiloxy)cyclotrisiloxane (I)[8,19] by Condensation of II and III. A solution of triethylamine (7.4 g, 73 mmol) in 150 mL of diethyl ether was placed in a 500 mL three-neck round-bottom flask equipped with two 50 mL pressure-equalizing addition funnel and a Tru-bore mechanical stirred fitted with a Teflon paddle. A solution of **II** (7.1 g, 35 mmol) in 20 mL of diethyl ether was placed in one addition funnel. A solution of **III** (11 g, 35 mmol) in 20 mL of diethyl ether was placed in the other. The two solutions were added simultaneously dropwise over 2 h with stirring. After 2 h, triethylammonium chloride was removed by filtration. The ether solution was washed with water to remove excess triethylamine. It was dried over anhydrous magnesium sulfate and filtered, and the volatile solvents were removed by evaporation under reduced pressure. The residue was purified by fractional distillation. A fraction bp 66−68 °C/0.25 mm, 10.6 g, 68% yield was obtained. A 20:80 mixture of *cis*-**I** and *trans*-**I** had the following NMR spectral properties. *cis*-**I** ^{1}H NMR δ: 0.112 (s, 9H), 0.091 (s, 3H).^{13}C NMR: 1.83 [$(C\mathrm{H_3})_3$Si], −2.66 [$C\mathrm{H_3SiO_{3/2}}$]. ^{29}Si NMR: 9.55 [$(\mathrm{CH_3})_3Si$O], −57.20 [$\mathrm{CH_3}Si\mathrm{O_{3/2}}$]. *trans*-**I** ^{1}H NMR: 0.152 (s, 6H) 0.140 (s, 18H), 0.128 (s, 3H), 0.126 (s, 9H). ^{13}C NMR: 1.74[$(C\mathrm{H_3})_3$Si], 1.70[$(C\mathrm{H_3})_3$Si], −2.74[$C\mathrm{H_3SiO_{3/2}}$]. −2.84[$C\mathrm{H_3SiO_{3/2}}$]. ^{29}Si NMR: 9.55 [$(\mathrm{CH_3})_3Si$O], 9.40 [$(\mathrm{CH_3})_3Si$O], −56.65 [$\mathrm{CH_3}Si\mathrm{O_{3/2}}$] −57.22 [$\mathrm{CH_3}Si\mathrm{O_{3/2}}$]. IR ν: 2962, 1410, 1269, 1255, 1088, 1028, 870, 843, 793, 756 cm^{-1}. Elemental Anal. Calcd for $\mathrm{C_{12}H_{36}O_6Si_6}$: C, 32.39; H, 8.16 Found: C, 31.98; H, 7.83. High-resolution chemical ionization mass spectra: [$\mathrm{C_{12}H_{36}O_6Si_6} + \mathrm{NH_4^+}$] Calcd: 462.147. Found: 462.145.

Synthesis of 1,3,5-Trimethyl-1,3,5-tris(trimethylsiloxy)cyclotrisiloxane (I) by Reaction of II with DMSO. A solution of **II** (7 g, 34.5 mmol) in 35 mL of $\mathrm{CHCl_3}$ was placed in a 100 mL three-neck round-bottom flask equipped with a pressure-equalizing addition funnel, a reflux condenser, and a Teflon-covered magnetic stir bar. A solution of DMSO (3 g, 38.5 mmol) in 15 mL of $\mathrm{CHCl_3}$ was placed in the addition

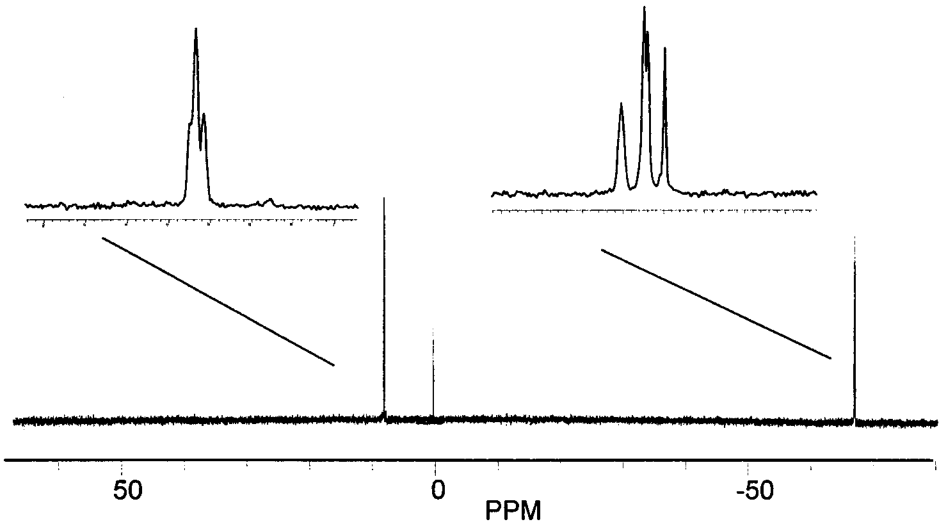

Figure 3. ^{29}Si NMR of polymethyl(trimethylsiloxy)siloxane.

funnel and was added dropwise over 1 h at room temperature. The solution was stirred for 2 h. The $CHCl_3$ solution was then washed with aqueous $NaHCO_3$ and then with water. It was dried over anhydrous magnesium sulfate and filtered, and the volatile solvents were removed by evaporation under reduced pressure. The residue was fractionally distilled, and a fraction bp 75−78 °C/0.5 mm, 2 g, 40% yield was obtained. This material was purified by column chromatography on silica gel using hexane as solvent. This permitted the separation of small amounts of 1,3-dimethyltetrakis(trimethylsiloxy)disiloxane,[20] which is formed by hydrolysis of the methylbis(trimethylsiloxy)chlorosilane impurity. The spectral properties of **I** were in complete agreement with those reported above.

1,3-Dimethyltetrakis(trimethylsiloxy)disiloxane. ^{1}H NMR δ: 0.13 (s, 36H), 0.055 (s, 6H). ^{13}C NMR: 1.86 [$(\mathit{C}H_3)_3$-Si], −1.88 [$\mathit{C}H_3SiO_{3/2}$]. ^{29}Si NMR: 7.87 [$(CH_3)_3\mathit{Si}$], −65.74 [$CH_3\mathit{Si}O_{3/2}$]. IR ν: 2960, 2902, 1415, 1252, 1058, 843, 794, 757 cm^{-1}. GC-MS m/e: 443 $(M - 15)^+$.

Polymethyl(trimethylsiloxy)siloxane. **I** (0.44 g, 1 mmol) was placed in a test tube equipped with a Teflon-covered magnetic stir bar and sealed with a rubber septum. The tube was purged three times with argon. THF (100 μL), HMPA (2 μL), and 10 μL of a THF solution of dilithiodiphenylsilanediolate (0.316 mol/L) initiator were added.[2] The reaction was stirred for 3 h at room temperature. Vinyldimethylchlorosilane (5 μL) and triethylamine (2.5 μL) were sequentially added to quench the polymerization reaction. The polymer was taken up in a minimum amount of diethyl ether and was precipitated into methanol. This procedure was repeated three times. The polymer was dried under vacuum. In this way, 0.38 g, 87% yield of material M_w/M_n = 24 950/16 260, T_g = −95 °C was obtained. ^{1}H NMR δ: 0.17 (s, 9H), 0.15 (s, 3H). ^{13}C NMR: 2.11 [$(\mathit{C}H_3)_3Si$], −1.59 [$\mathit{C}H_3SiO_{3/2}$]. ^{29}Si NMR: 8.49 [0.25 $(CH_3)_3\mathit{Si}$], 8.47 [0.5 $(CH_3)_3\mathit{Si}$], 8.43[0.25 $(CH_3)_3\mathit{Si}$], -66.59 (0.35[$CH_3SiO_{3/2}$]), −66.71 (0.24[$CH_3SiO_{3/2}$]), −66.72 (0.24[CH_3-$SiO_{3/2}$]), −66.81 (0.19[$CH_3SiO_{3/2}$]). IR ν: 2961, 2902, 1412, 1268, 1051, 873, 843, 790, 757 cm^{-1} (Figure 3).

In a separate experiment, lower molecular weight polymethyl(trimethylsiloxy)siloxane, M_w/M_n = 6340/5580, was prepared in 68% yield by reaction of **I** (1 g, 2.3 mmol) with 50 μL of a THF solution of dilithiodiphenylsilanediolate (0.316 mol/L) as above. This material had identical spectral properties, T_g, and TGA to those of the higher molecular weight material.

Discussion

Both methods used to prepare **I** lead to a mixture of *cis*-**I** and *trans*-**I**. *cis*-**I** should have three equivalent methyl groups and three equivalent trimethylsiloxy groups. This should give rise to two signals in each of the ^{1}H, ^{13}C, and ^{29}Si NMR. *trans*-**I**, on the other hand, has two different types of methyl groups in a 2:1 ratio and two different trimethylsiloxy groups in a 2:1 ratio. This should give rise to four peaks in each of the ^{1}H, ^{13}C, and ^{29}Si NMR spectra. As expected, the ^{1}H and ^{13}C NMR spectra of the mixture of *cis*- and *trans*-**I** each have six resonances. However, only five resonances are observed in the ^{29}Si NMR of the mixture. This may be due to fortuitous overlap of two signals in the ^{29}Si NMR. On the basis of their relative intensities, the peaks at 9.55 and −57.20 ppm in the ^{29}Si NMR are assigned to *cis*-**I** while those at 9.40, 9.55, −56.65, and −57.22 ppm have been assigned to *trans*-**I**. The cis/trans ratio is approximately 25/75.[19]

Saam has reviewed examples of stereoregular polysiloxanes obtained by anionic ring-opening polymerization of isomerically pure *cis*- or *trans*-cyclotrisiloxanes.[22] Unfortunately, we have not been able to separate *cis*-**I** and *trans*-**I**. For this reason, we have carried out the polymerization on the mixture. The reaction has been quenched by addition of vinyldimethylchlorosilane and triethylamine.

Living anionic polymerizations produce polymers with narrow molecular weight distributions ($M_w/M_n \sim 1$) because initiation is rapid and chain transfer is rare. In these reactions, the molecular weight (M_n) of the polymer should be equal to the molecular weight of the monomer multiplied by the concentration of monomer divided by the concentration of the initiator (M/I). To achieve such results, these reactions are typically conducted under conditions in which water and air are rigorously excluded in sealed glass apparatus. By comparison, our polymerization reactions have been carried out with rubber septum and syringe techniques. If our reaction were a living anionic ring-opening polymerization, the molecular weight of the high polymer would be ~140 000 while the molecular weight of the low polymer would be ~31 000. Note: dilithiodiphenylsilanoate is a difunctional initiator. For comparison, the molecular weight of the high polymer determined by GPC is 25 000/16 000 while that of the low molecular weight material is 6340/5580. It is frequently observed that the molecular weight distribution of lower molecular weight material is narrower than that of high molecular weight materials. The reasons for these results are not understood at this time.

End-group analysis of the low molecular weight polymer sample was carried out by ^{1}H NMR. The presence of Si−vinyl end groups and Si−phenyl groups from the initiator has been observed in the ^{1}H NMR of this material. Peaks due to Si−vinyl groups were observed at 5.81 (dd, 2H, $J = 20$, 3.5 Hz), 5.97 (dd, 2H, $J = 15$, 3.5 Hz), and 6.18 ppm (dd, 2H, $J = 20$, 15 Hz). Likewise, broad peaks due to Si−phenyl of the initiator were detected at 7.4 and 7.7 ppm. The intensity of these peaks was compared to those due to Si−CH_3 groups centered at 0.16 ppm. A ratio of 7.2 to 9 to 720 was found. The calculated ratio of Si−vinyl to Si−phenyl should be 6 to 10. Since it is quite difficult to accurately determine the intensity ratio of small peaks compared to very large ones, we assume that the integration is in fact 6:10:720. Since each methyl(trimethylsiloxy)siloxane unit has four Si−CH_3 groups, we calculate that the polymer has approximately 60 units and that M_n based on end-group analysis is ∼8800. While end-group analysis permits us to calibrate the molecular weight values determined by GPC, nevertheless the observed M_w/M_n are still lower than predicted.

Methyltrichlorosilane is a byproduct of the Rochow direct synthesis reaction between methyl chloride and activated silicon metal.[23,24] This reaction yields predominantly dimethyldichlorosilane, the monomer used to prepare poly(dimethylsiloxane)s. While methyltrichlorosilane can be used as a cross-linking agent, most of it is burned to produce fumed silica. We have utilized the acid-catalyzed equilibration of methyltrichlorosilane with hexamethyldisiloxane to convert this undesired material into a useful difunctional monomer **II**. Further, we have converted **II** into **I** by direct reaction with DMSO or by condensation with **III**. **II** undergoes anionic catalyzed ring-opening polymerization to yield a linear polymer polymethyl(trimethylsiloxy)siloxane. We hope that this new chemistry will increase the utility of methyltrichlorosilane.

Polymethyl(trimethylsiloxy)siloxane demonstrates that it is possible to prepare a linear polysiloxane in which the polymer backbone was made up of T units. We had hoped that the bulkier trimethylsiloxy groups compared to methyl groups would lead to a lower T_g than that of poly(dimethylsiloxane) (−123 °C)[19] while retaining high thermal stability. Thus, polydiethylsiloxane has a lower T_g (−139 °C)[25] than poly(dimethylsiloxane) but is thermally less stable, particularly in an oxidizing atmosphere. Our hypothesis was that replacement of a Si−methyl group by a larger trimethylsiloxy might lower the T_g of polymethyl(trimethylsiloxy)siloxane due to the greater free volume generated by motion of the larger trimethylsiloxy group while retaining thermal stability. In fact, the glass transition temperature of polymethyl(trimethylsiloxy)siloxane is −95 °C. While this is quite low, it is ∼30 °C higher than that of poly(dimethylsiloxane) (−123 °C).[19]

On the other hand, polymethyl(trimethylsiloxy)siloxane is thermally stable to 285 °C in both nitrogen and air. This is comparable to the thermal stability of polydimethylsiloxane. Above this temperature in a nitrogen atmosphere polymethyl(trimethylsiloxy)siloxane undergoes catastrophic decomposition. By 470 °C, there is no residue. For comparison, poly(dimethylsioxane) is well-known to undergo catastrophic decomposition to volatile cyclic siloxane monomers by the reversion reaction.[26] It is possible that the catastrophic thermal decomposition of polymethyl(trimethylsiloxy)siloxane in nitrogen proceeds in a similar manner. By comparison, in air by 425 °C only 65% of the initial sample weight of polymethyl(trimethylsiloxy)siloxane has been lost. No further weight loss occurs on heating to 800 °C. A stable char that amounts to 35% of the initial sample weight is formed (Figure 4).

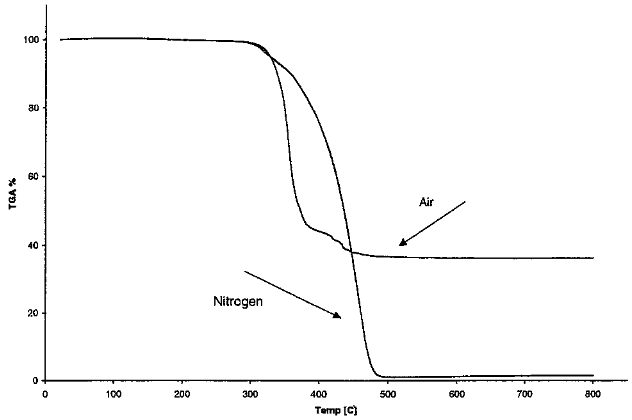

Figure 4. Thermogravimetric analysis of polymethyl(trimethylsiloxy)siloxane in N_2 and air.

Attempts to carry out acid-catalyzed polymerization of **I** with triflic acid were unsuccessful. Further studies on polymethyl(trimethylsiloxy)siloxane are in progress.

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