Synthesis of Poly(imidosiloxanes) via Disiloxane Equilibration Reactions

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ABSTRACT: An alternate polycondensation approach to poly(imidosiloxanes) is presented. Bis(pentamethyldisiloxanyl) bisimides were disproportionated in solution with an acid catalyst, resulting in the loss of hexamethyldisiloxane. High molecular weight polymers were prepared over a range of temperatures. An advantage of this method is that fully imidized polymers that are perfectly end-capped with trimethylsilyl groups and have a normal molecular weight distribution can be achieved. These polymers are often superior to those prepared via polyimidization with the same repeating unit. This method easily permitted the synthesis of a perfectly alternating copolyimide. Polymer modification by the insertion of dimethylsiloxane groups into the backbone via acid equilibration with octamethylcyclotetrasiloxane was also demonstrated.

Introduction

Poly(imidosiloxanes) have been extensively prepared over the past 30 years and have been formulated for use in a variety of applications.[1] In virtually all cases an α,ω-difunctionalized siloxane has been condensed with its complementary monomer. Usually this siloxane is a diamine or a dicarboxylic acid anhydride, and polyimidization[2] (Scheme I) or polytransimidization[3] is carried out to prepare the polymer. This approach often yields good results. However, relatively high temperatures are required for polymerization, and compete imidization is sometimes difficult to achieve. Polymerization at lower temperatures has been achieved by using the condensation of silanol end-capped imides with α,ω-dichlorosiloxanes or α,ω-dicarbamoylsiloxanes,[4] by the hydrosilation of bis(vinylsilyl) imides with α,ω-dihydrogenosiloxanes[5] and by Diels–Alder cycloaddition.[6] In some cases, particularly when a polydispersed macromonomer is used, stoichiometry of the complementary functionality is difficult to achieve.

Studies in this laboratory on the equilibration of siloxanes with the catalyst trifluoromethanesulfonic acid suggested that these reactions were sufficiently rapid and free of side reactions with imides[7] to permit the preparation of high molecular weight poly(imidosiloxanes) via siloxane equilibrations. These reactions are generally entropically driven with the equilibrium composition dependent on the amounts of the various silyl groups present. Siloxane equilibrations may be carried out over a broad range of temperatures. Therefore, we undertook the preparation of a poly(imidosiloxane) by the disproportionation of a bis(pentamethyldisiloxanyl) bisimide, with the removal of hexmethyldisiloxane driving the equilibrium to higher polymer.

We now report the successful preparation of thermoplastic poly(imidosiloxane) homopolymers via this technique (Scheme II). Additionally, we demonstrate the preparation of an alternating copolymer and the conversion of the thermoplastic homopolymer into an elastomeric silicone copolymer by the addition of octamethylcyclotetrasiloxane to the polymerization mixture without the isolation of the homopolymer.

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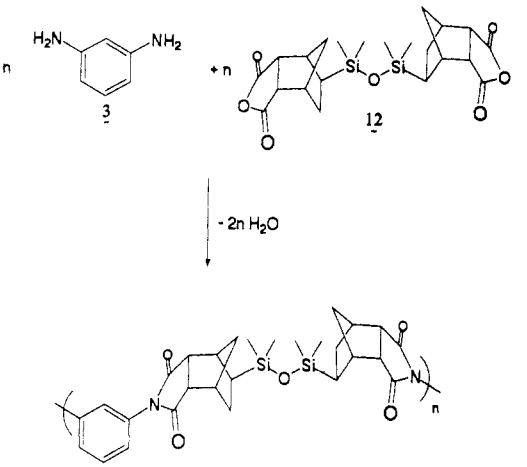
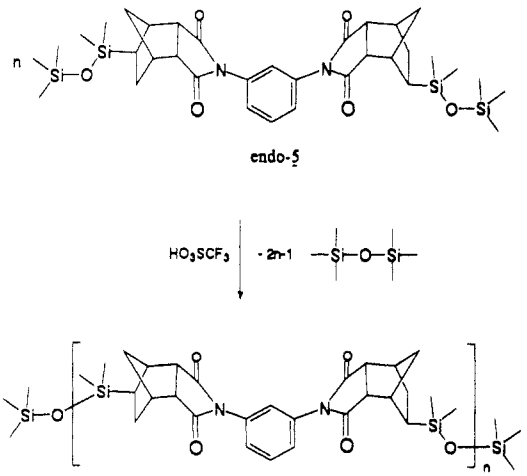
Scheme I
Polyimidization of 3 and 12



Scheme II
Polymerization of *endo*-5 via Siloxane Equilibration



Experimental Section

(1*R,2*S**,3*S**,4*R**,5*S**)-5-(Pentamethyldisiloxanyl)-2,3-norbornanedicarboxylic Anhydride (*endo*-2).** The synthesis of *endo*-2 from *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (*endo*-1) pentamethyldisiloxane is reported elsewhere.[8]

(1*R,2*R**,3*R**,4*R**,5*S**)-5-(Pentamethyldisiloxanyl)-2,3-norbornanedicarboxylic Anhydride (*exo*-2).** The synthesis of *exo*-2 was analogous to that of *endo*-2 using *exo*-1 and penta-

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methyldisiloxane. The thermal isomerization of *endo*-1[9] yielded a mixture from which *exo*-1 (mp 143–4 °C) was isolated by fractional crystallization from toluene. Distillation at 140 °C (0.4 mmHg) yielded pure *exo*-2 in a 98% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.2 (s, 3 H), 0.04 (s, 9 H), 0.07 (s, 3 H), 0.56 (AXYZ, 1.8, 7.4, and 9.1 Hz, 1 H), 1.18 (AX_2Y, 1.6 and 12.1 Hz, 1 H), 1.45 (AX_2Y, 1.5 and 12.1 Hz, 1 H), 1.47 (m, 1 H), 1.61 (m, 1 H), 2.78 (br s, 1 H), 2.83 (br d, 3.7 Hz, 1 H), 2.90 (br d, 1.6 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.87, −0.71, 1.74, 28.97, 29.10, 33.50, 41.47, 41.85, 48.65, 52.20, 172.73, 173.15. IR (film cast from $CDCl_3$): 2950 (s), 2860 (m), 1860 (m), 1780 (s), 1482 (w), 1460 (w), 1405 (w), 1320 (w), 1305 (w), 1255 (s), 1225 (s), 1215 (m), 1155 (w), 1130 (w), 1110 (w), 1060 (s), 1040 (m), 1000 (w), 975 (w), 930 (s), 905 (s), 845 (s), 802 (m), 780 (m), 770 (w), 755 (w), 690 (m) cm^{-1}.

N,N'-1,3-Phenylenebis[(1*R,2*S**,3*S**,4*R**,5*S**)-5-(pentamethyldisiloxanyl)-2,3-norbornanedicarboximide] (*endo*-5).** Two molar equivalents of *endo*-2 1.01 equiv of 1,3-diaminobenzene (3; Aldrich, distilled under 10 mmHg of N_2) and 0.25% by weight of 4-(*N*,*N*-dimethylamino)pyridine (4) were heated under N_2 with an oil bath. As the temperature rose to 160 °C from room temperature, the mixture melted, formed a solid salt, and liquified with the loss of water. When no more gas evolution was observed (15 min after the bath reached 160 °C), house vacuum (60 mmHg) was applied until degassing was complete. Analysis of GC indicated that a 95% yield of *endo*-5 was achieved. The reaction mixture was dissolved in hot isooctane and washed twice with dilute phosphoric acid and twice with water. The hydrocarbon layer was then dried over $CaCl_2$, heated, and filtered hot. The filtered solution was stored overnight. The finely divided white crystals that had formed were filtered and washed with cold hexane. A second crop of crystals formed from the solution, and the solution was again filtered. The combined crystals were dried under vacuum for 24 h. The crystals (85% isolated yield) were pure by GC and LC analysis and displayed a melting range of 144–52 °C, presumably due to the presence of both the meso and *d,l* stereoisomers. ^{1}H NMR (200 MHz, $CDCl_3$): δ −0.01 (s, 6 H), 0.01 (s, 24 H), 0.60 (AXY, 9 Hz, 7 Hz, 2 H), 1.62 (m, 8 H), 2.80 (m, 2 H), 2.84 (m, 2 H), 3.22 (m, 4 H), 7.30 (m, 3 H), 7.52 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.85, −0.74, 1.87, 25.65, 26.47, 39.98, 40.92, 41.31, 48.64, 51.19, 124.05, 125.86, 129.23, 132.40, 176.79, 177.02. IR (film cast from $CDCl_3$): 3462 (w), 2945 (s), 2865 (m), 1772 (m), 1705 (vs), 1604 (m), 1490 (s), 1453 (m), 1368 (vs), 1320 (m), 1309 (w), 1287 (w), 1280 (w), 1253 (vs), 1220 (w), 1175 (vs), 1055 (vs), 990 (w), 975 (w), 953 (w), 922 (w), 910 (m), 878 (w), 832 (vs), 800 (m), 780 (vs), 750 (s), 689 (s) cm^{-1}. UV (THF): λ_{max} = 218 nm, ε = 3.7 × 10^4 M^{-1} cm^{-1}.

N,N'-1,3-Phenylenebis[(1*R,2*R**,3*R**,4*R**,5*S**)-5-(pentamethyldisiloxanyl)-2,3-norbornanedicarboximide] (*exo*-5).** The synthsis was analogous to that of *endo*-5. The pure *exo*-5 was crystallized from a 2:1 hexane/CH_2Cl_2 mixture (mp 164 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.03 (s, 6 H), 0.05 (s, 18 H), 0.08 (s, 6 H), 0.63 (AXYZ, 9.0, 7.5, and 1.5 Hz, 2 H), 1.20 (br d, 10.9 Hz, 2 H), 1.39 (br d, 10.9 Hz, 2 H), 1.61 (m, 4 H), 2.78 (br s, 8 H), 7.31 (m, 3 H), 7.51 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.66, −0.54, 1.90, 29.87, 32.75, 41.01, 41.27, 43.39, 48.38, 52.06, 123.71, 125.86, 129.25, 132.52, 177.12, 177.63. IR (film cast from $CDCl_3$): 3460 (w), 2945 (s), 2865 (m), 1778 (m), 1710 (vs), 1605 (m), 1495 (s), 1455 (m), 1390 (m), 1370 (vs), 1310 (m), 1290 (w), 1280 (w), 1255 (vs), 1225 (w), 1180 (vs), 1140 (w), 1125 (w), 1110 (w), 1060 (vs), 1000 (w), 975 (w), 918 (m), 900 (w), 895 (w), 840 (vs), 810 (m), 780 (vs), 750 (m), 689 (m) cm^{-1}. UV (THF): λ_{max} = 219 nm, ε = 4.3 × 10^4 M^{-1} cm^{-1}.

1-Amino-3-[(1*R,2*S**,3*S**,4*R**,5*S**)-5-(pentamethyldisiloxanyl)-2,3-norbornanedicarboximido]benzene (6).** When an equimolar mixture of *endo*-2 and 3 was treated as in the preparation of *endo*-5, GC analysis indicated that a 65% yield of 6 resulted. The product mixture was dissolved in chloroform from which white crystals of 6 formed. After a recrystallization from chloroform and drying under vacuum, a 50% isolated yield was observed. The crystals were pure by GC and LC analysis (mp 156 °C). ^{1}H NMR (90 MHz, CD_2Cl_2): δ 0.10 (s, 15 H), 0.67 (br t, 9 Hz, 1 H), 1.65 (m, 4 H), 2.82 (br s, 2 H), 3.23 (m, 2 H), 3.83 (br s, 2 H), 6.65 (m, 3 H), 7.25 (t, 9 Hz, 1 H). IR (film cast from $CDCl_3$): 34.85 (m), 3392 (s), 32.35 (w), 2980 (vs), 2900 (m), 1778 (m), 1715 (vs), 1640 (m), 1620 (s), 1510 (s), 1492 (m), 1395 (s), 1322 (m), 1310 (w), 1300 (m), 1278 (vs), 1195 (vs), 1135 (w), 1072 (vs), 1016 (w), 1002 (w), 990 (w), 967 (w), 940 (w) 910 (m), 890 (w), 845 (vs), 822 (m), 800 (m), 757 (m), 705 (m) cm^{-1}. UV (THF): λ_{max} = 213 nm, ε = 2.2 × 10^4 M^{-1} cm^{-1}; λ_{max} = 242 nm, ε = 1.1 × 10^4 M^{-1} cm^{-1}; λ_{max} = 294 nm, ε = 3.5 × 10^3 M^{-1} cm^{-1}.

2,2-Bis[4-[[2-[3-[(1*R,2*S**,3*S**,4*R**,5*S*)-5-(pentamethyldisiloxanyl)-2,3-norbornanedicarboximido]phenyl]-1,3-dihydro-1,3-dioxo-2*H*-isoindol-6-yl]oxy]phenyl]propane (8).** Two equivalents of 6 were condensed with 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (7) in a fashion analogous to the preparation of *endo*-5. Attempts to crystallize 8 failed although IR and ^{1}H NMR spectra were consistent with the desired product. Preparative LC with a flow rate of 5 mL/min and a gradient elution from 100% hexane to 50% hexane/49.75% CH_2Cl_2/0.2% methanol/0.05% H_2O in 100 min gave a 96% yield of a slightly yellow glassy solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.01 (s, 6 H), 0.04 (s, 18 H), 0.05 (s, 6 H), 0.63 (AXY, 7.4 and 9.1 Hz, 2 H), 1.62 (m, 8 H), 1.74 (s, 6 H), 2.82 (m, 2 H), 2.86 (m, 2 H), 3.24 (m, 4 H), 7.02 (m, 4 H), 7.43 (m, 16 H), 7.87 (d, 8.5 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.84, −0.67, 1.93, 25.71, 26.59, 31.06, 40.05, 40.99, 41.19, 41.37, 42.56, 48.74, 51.30, 111.88, 120.04, 123.15, 123.92, 124.90, 125.46, 125.62, 125.82, 128.78, 129.17, 129.39, 132.37, 132.54, 134.13, 147.62, 152.67, 163.93, 166.17, 166.28, 177.02, 177.21. IR (film cast from $CDCl_3$): 2950 (s), 1775 (m), 1712 (vs), 1600 (m), 1500 (w), 1480 (m), 1360 (s), 1252 (s), 1170 (m), 1050 (s), 920 (w), 840 (s), 805 (w), 780 (m), 750 (m), 682 (w) cm^{-1}. UV (THF): λ_{max} = 225 nm, ε = 9.9 × 10^4 M^{-1} cm^{-1}; λ_{max} = 238 nm, ε = 9.9 × 10^4 M^{-1} cm^{-1}.

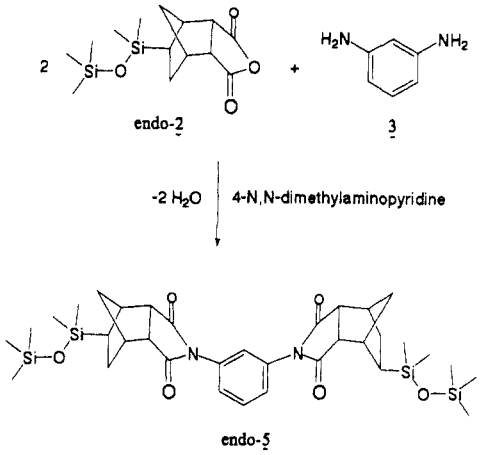
1-Amino-3-(pentamethyldisiloxanyl)propane (9). 1,3-Bis(3-aminopropyl)tetramethyldisiloxane (10) was equilibrated with a 10-fold molar excess of hexamethyldisiloxane at 70 °C catalyzed by 1 wt % of tetramethylammonium hydroxide. The base was quenched by the addition of a slight excess of phosphoric acid and the product 9 was distilled at 141 °C under nitrogen.

2,2-Bis[[4-[*N*-(3-pentamethyldisiloxanyl-1-propyl)-1,3-dihydro-1,3-dioxo-2*H*-isoindol-6-yl]oxy]phenyl]propane (11). Two equivalents of 9 and 1 equiv of 7 in dry toluene were condensed with 4 as a catalyst. When the theoretical amount of water was collected in a Barrett trap, the solution was reduced to a pale yellow residue. All attempts to crystallize the product failed. The ^{1}H NMR spectrum of the residue indicated that more than half of the expected methylsilyl groups were not present. A TLC analysis of the mixture indicated the formation of a series of homologues. Preparative LC effected the isolation of the desired product (11) from the higher homologues. Upon standing, white waxy crystals formed from the glass. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.02 (s, 10.6 H), 0.03 (s, 18 H), 0.06* (s, 1.4 H), 0.50 (m, 3.5 H), 0.85* (d, 8 Hz, 0.6 H), 1.18* (m, 0.2 H), 1.65 (m, 3.2 H), 1.71 (s, 6 H), 3.60 (t, 8 Hz, 4 H), 6.98 (m, 4 H), 7.27 (m, 8 H), 7.75 (d, 8 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −1.7*, −1.2*, 0.22, 1.95, 11.7*, 15.45, 22.63, 30.2*, 31.01, 40.5*, 40.95, 42.50, 111.51, 119.94, 122.41, 125.05, 125.58, 128.68, 134.63, 147.42, 152.78, 163.38, 167.96 (where an asterisk indicates signals that are assigned to the 1,2-propyl rather than the 1,3-propyl isomer). IR (film cast from $CDCl_3$): 2950 (s), 1770 (m), 1710 (vs), 1600 (m), 1500 (w), 1478 (m), 1445 (m), 1390 (s), 1360 (m), 1315 (w), 1255 (s), 1237 (s), 1175 (w), 1052 (s), 930 (w), 835 (s), 805 (w), 798 (w), 787 (w), 750 (m), 690, (w) cm^{-1}.

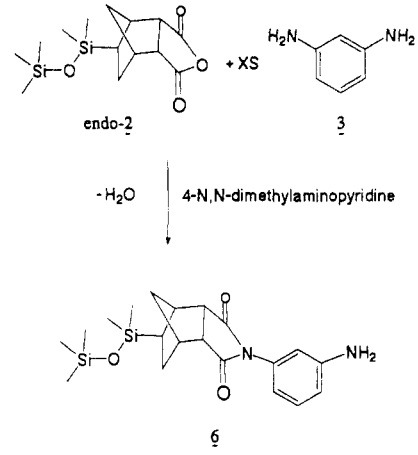
Polymerization was carried out in dry 1,2-dichlorobenzene at 70–80 °C (60 mmHg) or at room temperature (5 mmHg). Monomers were charged at 25–35 wt % with trifluoromethanesulfonic acid loadings of 0.1–0.2 wt %. Polymerization times were from 15 to 48 h. Hexamethyldisiloxane, some solvent, and traces of catalyst could be trapped as the reaction progressed.

The addition of octamethylcyclotetrasiloxane to a portion of the polymerized mixture from *endo*-5 prior to the quenching of the catalyst resulted in the precipitation of the polymer. Upon warming to 120 °C the mixture became homogeneous. The mixture was quenched after 4 h at room temperature. The filtered and stripped polymer could be cast into elastomeric films from chloroform. The incorporation of nine dimethylsiloxy units per phenylene residue was indicated by ^{1}H NMR analysis. Similar results were achieved by a slow dropwise addition of the cyclosiloxane at room temperature. Under these conditions no precipitation was observed.

Scheme III
Synthesis of *endo*-5

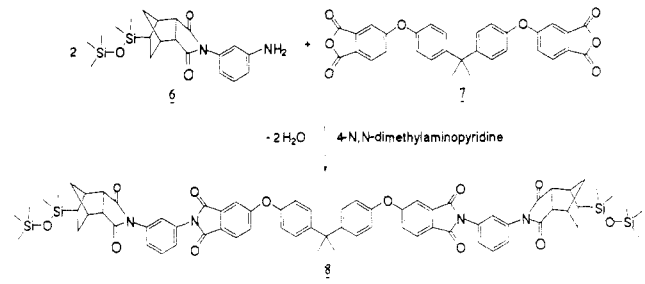


Scheme IV
Synthesis of 6

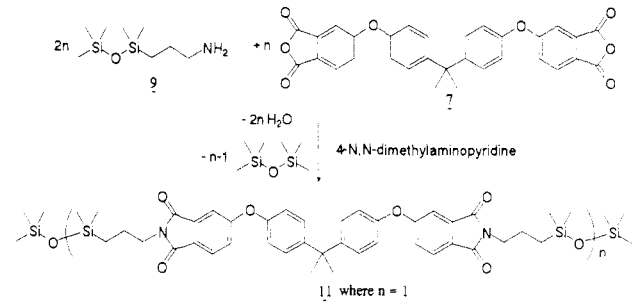


Gas chromatographic analysis was carried out with a Shimadzu GC-9A equipped with a 6 ft 3% OV-101 column from Altec. Liquid chroamtographic analysis and isolation was carried out with a Varian 5020. Analysis was carried out with a 4.6 mm × 50 cm LI-Si (5-μm) column. Preparative chromatography was carried out on a Lobar LiChroprep S 60 (40–63-μm) column with a flow rate of 5 mL/min and a gradient elution over 100 min from 100% hexane to 50% hexane/49.75% CH_2Cl_2/0.2% methanol/0.05% H_2O. Thin-layer chromatography was performed on 7.5 × 2.5 cm Baker-flex silica gel IB-F sheets with various proportions of hexane/acetone as the mobile phase. Proton nuclear magnetic resonance spectra were recorded on either a Varian EL-90 or XL-200. The ^{13}C and ^{29}Si NMR spectra were recorded on a Varian XL-300. Infrared spectral analysis was carried out on a Perkin-Elmer Model 598. Ultraviolet spectra were recorded on a Shimadzu UV-240. A Waters Model 244 was used for GPC analysis. Differential scanning calorimetry was carried out on a Perkin-Elmer DSC-2.

Scheme V
Synthesis of 8



Scheme VI
Synthesis of 11



Results and Discussion

Monomer Synthesis. The synthesis of **5** (Scheme III) was conveniently monitored by gas chromatography. The condensation reaction was reasonably rapid when the catalyst **4** was used. A small excess of **3** (1%) was used with the intent to convert all of **2** to **5** or **6** and subsequently remove **4** and **6** by an acid wash. Under these conditions conversion of *endo*-**2** was 97–8% by GC. The conversion did not improve appreciably with an increase of reaction time or temperature. Complete conversion of *exo*-**2** did occur under these conditions. With a 5% molar excess of **3** complete conversion of *endo*-**2** was achieved, but the yield of *endo*-**5** was much less. Three dilute phosphoric acid washings of the reaction mixture, dissolved in hot isooctane, did not remove all of the **6** present nor did it remove any of the unreacted *endo*-**2**. The flocculent white precipitate that formed from the solution upon cooling displayed no impurities by GC analysis. The broadness of the melting range is attributed to the presence of the meso and *d,l* stereoisomers although a single unresolved peak was observed in all GC and LC analysis of the product. Likewise, NMR analysis was unable to detect two isomers.

When **3** reacted with 1 equiv of *endo*-**2** (Scheme IV), the composition of the resulting mixutre was not significantly different than one would predict for equal reactivity of all amino functionality. In an attempt to prepare a sample for ^1H NMR spectroscopy, it was discovered that **6** could be selectively crystallized from the mixture in chloroform. An additional recrystallization resulted in pure **6** as indicated by GC and LC analysis. Upon condensation of **6** with **7**, a large yield of **8** (Scheme V) resulted by LC analysis. Preparative LC was required to isolate it in pure form.

The analogous synthesis of **11** (Scheme VI) did not result in a high yield of the desired bis(pentamethyldisiloxanyl)-bisimide. Due to the greater volatility of **9** and the high melting point of **7**, the reaction was carried out in solution. Although the imidization occurred to a large extent, the desired product was but one in a series of oligomers. This suggests that an intermediate in the condensation acted as a catalyst for the redistribution of siloxanes; however, neither **4**, **7**, nor **9** has been observed to redistribute under these conditions. Again preparative LC was necessary to isolate the desired product.

Polymerization. The conditions and results of the polymerizations of the various monomers are outlined in Table I. The progress of the polymerization, to a degree of condensation of 0.97, could easily be followed by the decrease in the relative area of the signals for the protons of the $Si-CH_3$ groups in the 90-MHz ^1H NMR spectroscopy. Generally it was observed that the reaction slowed significantly after 95% of the hexamethyldisiloxane was removed. Although loss of catalyst was observed in some runs, the decrease in polymerization rate was also

Table I
Polymers Prepared via Siloxane Condensation

monomer	wt % of monomer	wt % of acid[a]	reaction time[b]	M_n[c]	intrinsic viscosity	T_g[d]
endo-**5**	18	0.06	24	53 800	0.43	187
endo-**5**	15	0.06	30	47 100		181
3 + **12**	20		20	18 600	0.21	
exo-**5**	14	0.05	36	53 600	0.56	187
8	3	0.06	48	9 000		169
11	7	0.03	30	127 300		66

[a] Trifluoromethanesulfonic acid. [b] In hours. [c] Polymers were precipitated in hexane. The reported M_n is relative to polystyrene standards. The reported M_n's of *endo*-**5** and *exo*-**5** were for the linear portion of the polymers as it reflects the extent of reaction more than the cyclic linear mixture does. The cyclic portion in the case of *endo*-**5** is large (Figure 2), which is reflected in the significantly lower intrinsic viscosity of that polymer. [d] In degrees Celsius.

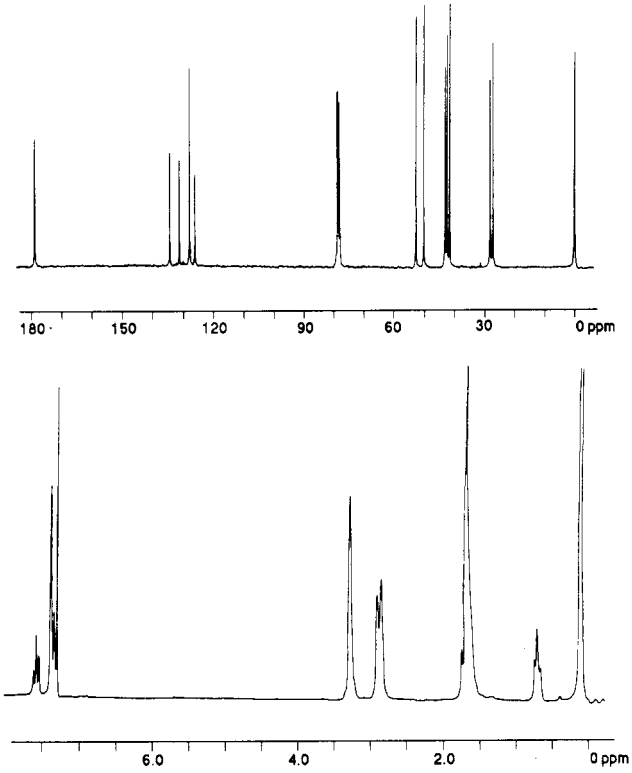


Figure 1. 200-MHz ^{1}H NMR and 75-MHz ^{13}C NMR spectra of poly(*endo*-**5**).

due to the difficulty in removing the vanishingly small amount of hexamethyldisiloxane from the increasingly viscous mixture. The NMR spectra, as seen in Figure 1 for the polymer from *endo*-**5**, indicated that the reaction proceeded cleanly. In the case of *endo*-**5**, molecular weight build was more easily attained than by polyimidization of **3** with (1*R**,2*S**,3*S**,4*R**,5*S**)-5,5′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(bicyclo[2.2.1]heptene-2,3-dicarboxylic anhydride) (**12**; Scheme I). The GPC analysis was consistent with linear polymers with a normal molecular weight distribution, which, in some cases, were in equilibrium with cyclic oligomers, as shown in Figure 2. The smallest cyclic resulting from *endo*-**5** was isolated and confirmed to be the cycic monomer.[10] As in the case of cyclosiloxanes, the concentration of monomer has a much greater effect on the final composition than does the temperature of polymerization.

The homopolymers from **5** differed significantly from those prepared via polyimidization of **3** and **12**. Those prepared by polyimidization of **3** and **12** always displayed peaks in their IR spectra for amine and anhydride. They were brown in color and films cast on glass adhered

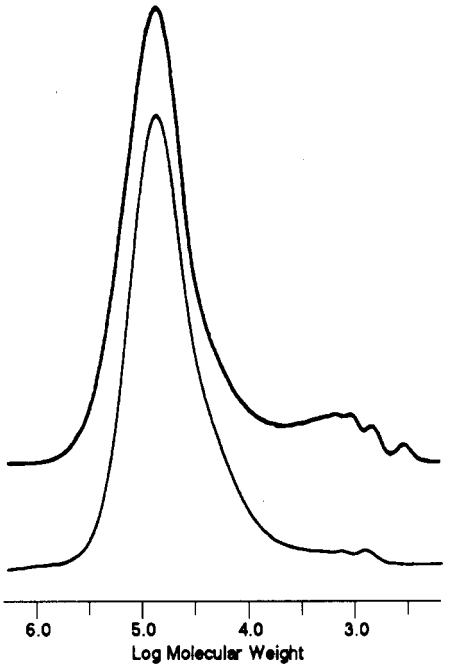


Figure 2. GPC traces of poly(*endo*-**5**), top, and poly(*exo*-**5**), bottom.

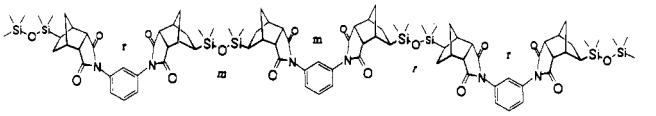
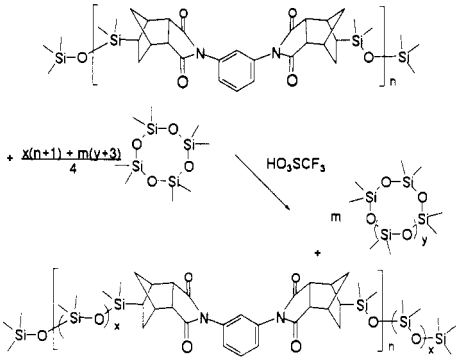


Figure 3. Trimer of *endo*-**5**, which contains meso and racemic configurations about the siloxane and the phenylene.

Scheme VII
Incorporation of Dimethylsiloxane into Poly(*endo*-5)



tenaciously. Those prepared via siloxane equilibration were nearly colorless and delaminated from glass after the evaporation of solvent from cast films. The IR spectra of these films showed no evidence of amine or anhydride. Although the polymers from **11** did not show a significant advantage to polycondensation of **7** and **10** in molecular weight build, they had much less color and were fully imidized. Again, films cast on glass delaminated upon the loss of solvent.

The polymers prepared from *endo*-**5**, *exo*-**5**, and **8** exhibited relative high glass transition temperatures and no melting transition. The polymer should be amorphous as there are both meso and racemic configurations possible about each phenylene ring and each disiloxane, as illustrated in Figure 3. The broad melting range of the crystalline monomers suggests that mixtures of the meso and racemic monomers are formed. As no transimidization is observed under the reaction conditions,[7] it would require a single diastereomer to have only meso or racemic configurations about the phenylene ring in the polymer.

Unfortunately, it is not clear from the spectra of the monomers that more than one diastereomer is present. By analogy to the preparation of **12** from *endo*-**5**,[7] the racemic and meso configurations about the disiloxane should form in equal prortions during polymerization. The NMR spectra of the polymers does not indicate the configurations present. This system has the potential for the preparation of more stereoregular polymers. The optically pure **5** would yield a stereoregular optically active polymer. Stereoregular polymers would not result from the polymerization of the resolved *meso*- or *d,l*-**5**, as both configurations about the disiloxane unit should form.

The T_g of the polymer resulting from *endo*-**5** was not the same for all batches. This would be expected if the proportions of the meso and racemic diastereomers that were isolated upon recrystallization differed from one crop of crystals to another, and this is presumably a factor. Additionally, the proportion of cyclic oligomers in the polymer would be expected to vary with the diastereomeric composition of the *endo*-**5** used. The polymer from **8** showed a lower T_g than some of the polymer from *endo*-**5**. This was not expected since the T_g of the poly(ether imide), Ultem, is almost 30 °C higher than the maximum observed for a polymer from *endo*-**5**. However, the average degree of polymerization of the polymer from **8** was not high, and the effect of molecular weight on the T_g may account for this result. The polymer from **8** was exhaustively end-capped with hexamethyldisiloxane[7] and reverted to **8**, confirming that transimidization did not occur during the polymerization.

Before quenching of the acid in the polymerization mixture of *endo*-**5**, the addition of octamethylcyclotetrasiloxane resulted in the preparation of a silicone copolymer (Scheme VII). The cyclosiloxane was added dropwise to avoid precipitation of the polymer rather than incorporation of dimethylsiloxy units. As the number of dimethylsiloxy units incorporated into the polymer increased, the miscibility of the polymer with the cyclosiloxane increased and the rate of cyclosiloxane addition was increased. The ^{1}H NMR spectrum of the copolymer after stripping of the residual cyclodimethylsiloxanes indicated that nine dimethylsiloxy units were incorporated. This was close to that predicted from the charged composition, considering each imide as a silicone chain end.[11] The resulting copolymer was a tough elastomer.

In summary, we have demonstrated a complementary method to the traditional condensation approach to polyimide siloxanes. The avantage of this method is that fully imidized and perfectly end-capped polymer can be prepared over a wide range of temperatures. The resulting polymer is considerably less colored, and often the molecular weight is superior to that prepared by polyimidization. The polymer can be subsequently modified to a silicone elastomer without an additional catalyst. Perfectly alternating copolymers may be prepared easily by this method. The synthetic strategy may be directed to the preparation of many siloxane polymers. Thus, many interesting functional units may be incorporated in a siloxane backbone in a controlled manner for the preparation of polymeric materials where a flexible backbone is desired.

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