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Preparation and Ring-Opening Polymerization of Cycloimidosiloxanes

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ABSTRACT: A mixture of cycloimidosiloxane oligomers was prepared via two routes. The first involved the trifluoromethanesulfonic acid catalyzed equilibration of *N,N'-m*-phenylenebis[(1*R**,2*S**,3*S**,4*R**,5*S**)-5-(pentamethyldisiloxanyl)-2,3-norbornanedicarboximide] (1) in a dilute solution in *o*-dichlorobenzene. Cyclic oligomers were also prepared by the acid-catalyzed depropagation of a high molecular weight homopolymer prepared from 1. Single-crystal X-ray analysis established that one of the major components was the cyclic monomer (±)-(2*R**,3*S**,3a*S**,12a*S**,13S*,14*R**,15a*R**,16*S**,20*S**,20a*R**)-2,3,3a,13,14,15,15a,16,17,19,20,20a-dodecahydro-17,17,19,19-tetramethyl-2,20:3,5:11,13:14,16-tetramethano-6,10-metheno-5*H*-dicyclopent-[*d,o*][1,7,13,2,18]oxadiazadisilacyclooctadecine-4,12,23,25(1*H*,12a*H*)-tetrone ((±)-2). The acid-catalyzed ring-opening polymerization of the mixed cyclics was demonstrated.

Introduction

The ring-opening polymerization of siloxanes has been well documented for more than three decades.[1] Although the equilibrium cyclic concentration is relatively large,[2] high polymer is easily achieved with basic or acidic initiators. A wide variety of cyclosiloxanes has been successfully polymerized, although most of these monomers are substituted with an alkyl or aryl pendent group and contain only silicon–oxygen bonds in the backbone of the cyclic and resulting polymer. Cyclosiloxanes containing atoms in the backbone other than silicon and oxygen are less common and are typically small rings of rather simple structure such as 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane.

In our studies of the preparation and modification of polyimides derived from α,ω-dianhydride-substituted siloxanes and diamines, we found that we could prepare superior polymers by the condensation of *N,N'-m*-phenylenebis[(1*R**,2*S**,3*S**,4*R**,5*S**)-5-(pentamethyldisiloxanyl)-2,3-norbornanedicarboximide] (1) with the elimination of hexamethyldisiloxane[3] (Scheme I) than we could by polyimidization of 5,5'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bisbicyclo[2.2.1]heptene-2,3-dicarboxylic anhydride (3) and 1,3-phenylenediamine with the elimination of water (Scheme II). The siloxane equilibration process involved is mechanistically similar to the ring-opening polymerization reaction of cyclic siloxanes. An ensemble of cycloimidosiloxane oligomers was observed to form along with linear polymer upon the condensation of 1 (Scheme I). The cyclic monomer (2) is a 16-member ring and can be isolated in a reasonably large amount.

This report outlines the preparation and isolation of cyclic oligomers, particularly the cyclic monomer, and describes the ring-opening polymerization of these cyclics to linear high polymer in concentrated solution. High molecular weight polymer is easily achieved at relatively low temperatures in closed systems. Thus, the method of ring-opening polymerization of siloxanes has been extended to the preparation of a polyimidosiloxane thermoplastic.

Experimental Section

Synthesis via Depropagation of Polymer. A 1 wt % solution of the polyimidosiloxane (2.5 g) in methylene chloride was dried over CaH_2 and filtered with a 5-μL Millipore filter. Trifluoromethanesulfonic acid was added such that the final mixture was 0.01 wt % in acid, and the mixture was stirred at room temperature for 3 days. After the reaction was terminated by the addition of an excess of MgO, the solution was filtered and concentrated on a rotary evaporator. Analysis by thin-layer chromatography indicated that most of the polymer had been converted to oligomers, with three oligomers predominating. A concentrated solution of the residue in acetone was prepared. A few large colorless cubic crystals and many smaller crystals were observed after 4 h. The filtered crystals (72% yield) were consistent with cyclic oligomers by NMR and IR spectroscopy. ^{1}H NMR (200 MHz, $CDCl_3$) of (±)-2 δ 0.01 (s, 6 H), 0.05 (s, 6 H), 0.67 (AXYZ, 2 H), 1.57 (m, 8 H), 2.71 (m, 2 H), 2.88 (m, 2 H), 3.23 (m, 4 H), 6.83 (m, 1 H), 7.34 (m, 2 H), 7.60 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) of (±)-2 δ −1.43, −0.43, 26.43, 26.93, 40.40, 41.11, 41.27, 48.39, 50.85, 126.19, 128.10, 130.32, 133.43, 177.09, 177.59; IR of a cyclic oligomer film from $CDCl_3$, 3465 (w), 2973 (s), 2950 (s), 2875 (s), 2862 (s), 1768 (m), 1710 (vs), 1600 (s), 1488 (s), 1440 (m), 1360 (vs), 1325 (m), 1312 (w), 1296 (w), 1280

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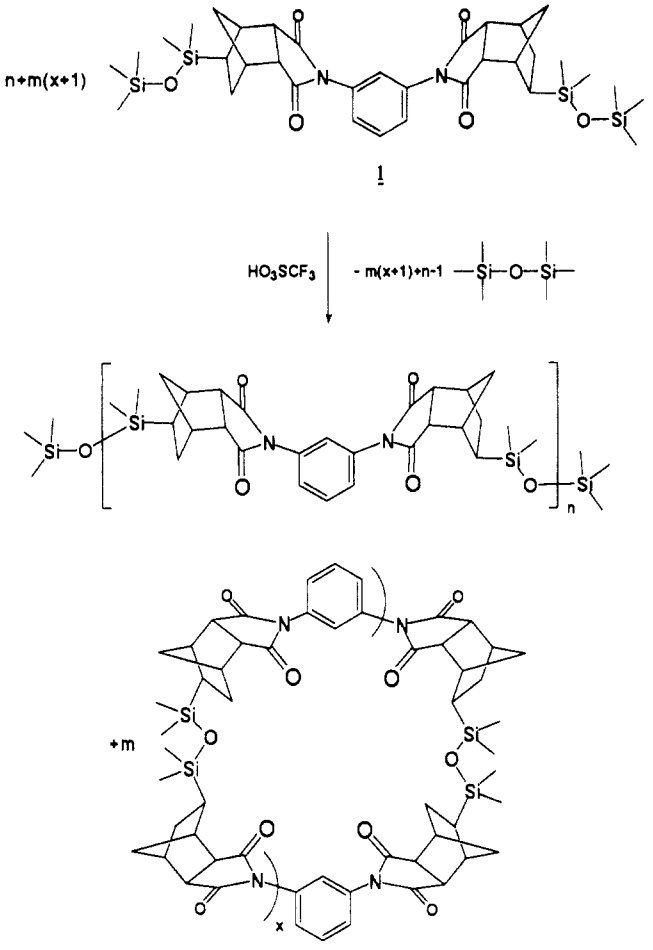
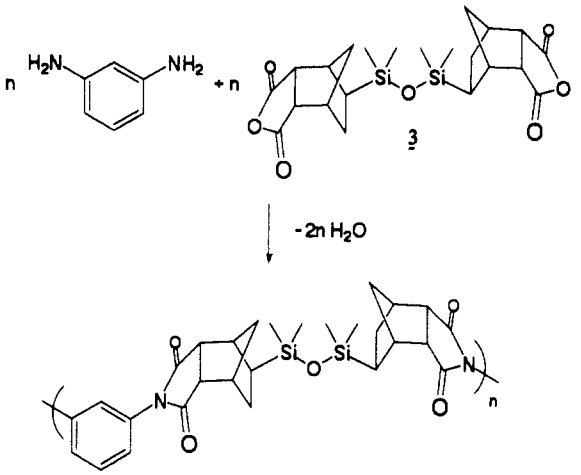
Scheme I
Siloxane Equilibration Polymerization of 1



Scheme II
Polyimidization of 1,3-Phenylenediamine and 3



(m), 1250 (vs), 1214 (w), 1178 (vs), 1159 (s), 1148 (s), 1120 (w), 1070 (vs), 1004 (w), 990 (w), 978 (w), 960 (m), 924 (s), 912 (w), 882 (m), 860 (w), 835 (vs), 805 (s), 785 (vs), 740 (vs), 715 (w), 705 (w), 692 (m), 662 (w), 623 (vs) cm^{-1}.

Cyclocondensation of 1. The acid equilibration of a 1 wt % solution of 1 (4.0 g) in 1,2-dichlorobenzene at 50 °C and 50 mmHg was carried out. After 24 h the catalyst was quenched and the solution filtered and concentrated. The thin-layer chromatography analysis of this residue indicated a large portion of the cyclic observed upon depropagation of the high polymer and much smaller amounts of other oligomers, including 1. Many large crystals formed from a concentrated acetone solution of the residue (41% isolated yield). Additional crystals were isolated from the mother liquor (23% yield). The ^1H NMR and IR spectra were consistent with those observed from the crystals of cyclic oligomers isolated from the depropagated polymer.

Ring-Opening Polymerization. The cyclic crystals (3.0 g) were dissolved in dichloromethane such that a 10 wt % solution resulted. The solution was dried over CaH_2 and then filtered and concentrated to a 40 wt % solution under dry nitrogen. Trifluoromethanesulfonic acid was added (0.05% by weight) and the solution sealed. Although the solution viscosity increased notably in 2 h, a large portion of the cyclics had crystallized out of solution. After standing overnight, most of the crystals had dissolved. The reaction vessel was then placed in a 50 °C bath, and the remaining crystals dissolved within 2 h, leaving an extremely viscous solution. After the catalyst was quenched with MgO, the solution was diluted with methylene chloride and filtered. A portion was precipitated in hexane. Another portion was concentrated to a nearly colorless film on a rotary evaporator. The two portions were analyzed by size exclusion chromatography. ^1H NMR (200 MHz, $CDCl_3$) δ 0.01 (s, 6 H), 0.03 (s, 6 H), 0.62 (m, 2 H), 1.59 (br d, 8 H), 2.77 (br s, 2 H), 2.83 (br s, 2 H), 3.21 (br s, 4 H), 7.30 (br d, 2 H), 7.32 (br s, 1 H), 7.53 (br t, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.73, 25.62, 26.60, 40.78, 41.42, 48.51, 50.84, 51.09, 124.09, 125.91, 129.31, 132.43, 176.73, 176.94; ^{29}Si NMR (60 MHz, $CDCl_3$) δ 7.0; IR polymer film from $CDCl_3$, 3370 (vw), 2960 (s), 2880 (m), 1781 (m), 1715 (vs), 1608 (m), 1494 (s), 1455 (m), 1360 (s), 1325 (w), 1312 (w), 1262 (vs), 1221 (vw), 1180 (s), 1075 (vs), 990 (w), 978 (w), 962 (m), 914 (s), 886 (w), 856 (w), 810 (vs), 782 (m), 752 (s), 692 (m), 662 (w) cm^{-1}.

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 a Varian XL-200. The ^{13}C NMR spectra were recorded on a Varian XL-300. Infrared spectral analysis was performed on a Perkin-Elmer Model 598. Size exclusion chromatography was performed on a Waters Model 244. Differential scanning calorimetry was performed on a Perkin-Elmer DSC-2.

Results and Discussion

The ^1H NMR was consistent with the product being cyclic oligomers as shown in Scheme I, as the ratio of methyl protons to aliphatic protons to aromatic protons was 3:4:5:1.[4] With the assumption that the lowest molecular weight cyclics and linears would be the most mobile, thin-layer chromatography plates indicated that the cyclics isolated from the cyclocondensation of 1 were similar on average than those isolated via polymer depropagation and had to be separated from linear oligomers, including the linear monomer 1.

A single-crystal X-ray analysis of a large colorless crystal, isolated via polymer depropagation, indicated that it was composed of the two racemic enantiomers of **2**.[5] The crystals were observed to melt at 303 °C with decomposition by DSC. Although the aromatic ring is conformationally frozen and the Si–O–Si bond angle is 20 larger than that observed for the parent anhydride[6] and expected for the polymer backbone, the ease and magnitude of its formation suggest that there is no appreciable strain energy. With the assumption that the cyclic monomer is essentially strainless and that the proportion of cyclic oligomer is as expected from Jacobson–Stockmayer theory,[7] the difference in the cyclic compositions for the two syntheses is easily rationalized by the difference in molecular weight of the linear portion at equilibrium.[8] Higher average molecular weight cyclics were formed via depropagation as they were in equilibrium with higher molecular weight linears.

The polymer prepared by ring-opening polymerization displayed no signals that could be assigned to end groups in the ^1H, ^{13}C, or ^{29}Si NMR spectra. This polymer was found to have a molecular weight higher than that of the polymer from which the cyclics were synthesized (intrinsic viscosity 0.56 vs 0.43). Size exclusion chromatography indicated that ca. 30% of the cyclics were fractionated from

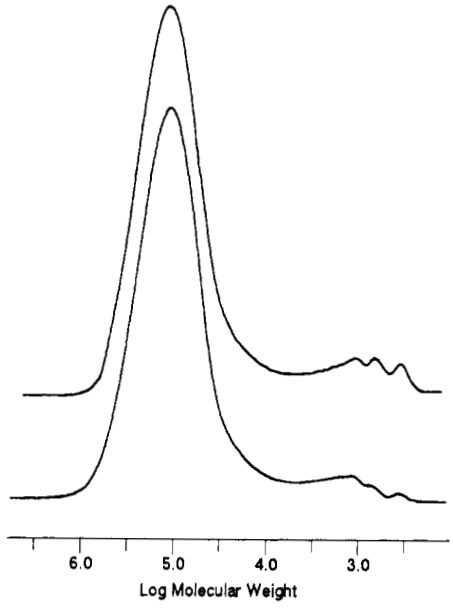


Figure 1. Size exclusion chromatography trace of the polymer before (top) and after (bottom) precipitation.

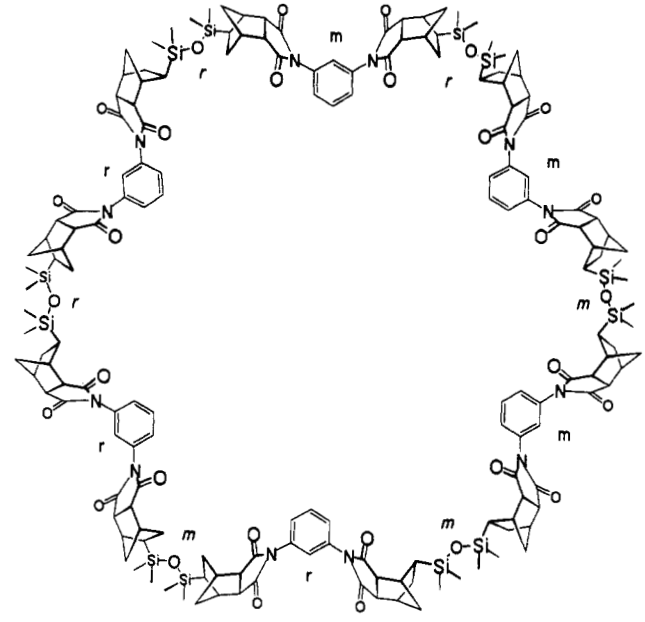


Figure 2. Hypothetical cyclic hexamer that shows all different relative configurations about the siloxane and the phenylene: rrr, rmr, rrm, rmm, mrm, and mmm.

the linear polymer by precipitation (Figure 1). The equilibrium cyclic fraction of ca. 9% by weight was estimated from the SEC trace assuming that the linear portion has a normal molecular weight distribution. Thus the equilibrium molar concentration of repeat units in cyclics should be ca. 0.08 M when high molecular weight polymer is formed.

As is typical of the ring-opening polymerization of cyclic siloxanes larger than the cyclic trimer, the polymerization would then be entropically driven. This permits the formation of high polymer over a wide range of temperatures, assuming the appropriate catalyst is chosen. As in the case with the condensation polymerization of **1**, there are a number of stereoisomeric placements centered about the aromatic ring and the siloxane oxygen that may be assumed by the cyclic oligomers as well as the polymer, as shown in Figure 2. A stereoregular polymer is not probable even in the case of the crystalline monomer (±)-**2**, as the placement of the two enantiomeric monomers is most likely random and both meso and racemic forms should result about the siloxane oxygen.[9] The NMR spectra did not distinguish the various stereoisomeric placements.

In summary, the synthesis and ring-opening polymerization of cycloimidosiloxane oligomers to a thermoplastic in solution were demonstrated. The resulting polymer was of higher molecular weight than that prepared by condensation polymerization. Ring-opening polymerization allows the preparation of high molecular weight polymer. It also permits the preparation of polyimides under conditions where condensation methods would be ineffective, such as within a closed system or at low temperatures.

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References and Notes

(1) (a) Noll, W. In *Chemistry and Technology of Silicones*; Academic Press: New York, 1968; pp 219–31. (b) Wright, P. V. In *Ring-Opening Polymerization*; Ivan, K. J., Saegusa, T., Eds.; Elsevier: New York, 1984; Vol. 2, Chapter 14.
(2) Semlyen, J. A.; Wright, P. V. *Polymer* **1969**, *10*, 543. Brown, J. F., Jr.; Slusarczuk, G. M. J. *J. Am. Chem. Soc.* **1965**, *87*, 931.
(3) Swint, S. A.; Buese, M. A. *Macromolecules*, in press.
(4) Since the polymer ends were trimethylsilyl groups, a linear oligomer of degree of polymerization of 15 would exhibit a methyl signal that would be 10% too high (3.3:4.5:1) relative to the other features of the spectrum. A degree of polymerization of more than 5 would be inconsistent with the chromatography data.
(5) Garbauskas, M.; Buese, M. A., submitted for publication.
(6) The Si–O–Si angle of the parent (±)-**3** was 141° rather than that of 160° for **2**.
(7) Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600.
(8) Buese, M. A. *Macromolecules* **1987**, *20*, 694. Carmichael, J. B.; Winger, R. *J. Polym. Sci., Part A* **1965**, *3*, 971. Carmichael, J. B.; Heffel, J. *J. Phys. Chem.* **1965**, *69*, 2218. Scott, D. W. *J. Am. Chem. Soc.* **1946**, *68*, 2294.
(9) A single enantiomer of **2** would ensure an optically active stereoregular polymer.