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Synthesis of Cyclic Siloxanes by the Thermal Depolymerization of Linear Poly(siloxanes)

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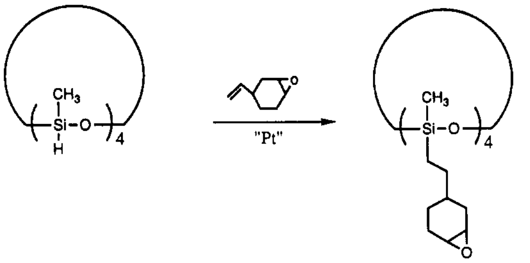
A novel method is described for the preparation of cyclic poly(siloxanes) by the thermal depolymerization ("cracking") of linear poly(siloxanes). With use of acidic Zeolite-type fixed bed catalysts at temperatures from 500 to 700 °C, it was shown possible to quantitatively convert linear polymers to a mixture of cyclics with ring sizes from 6 to 20. Mixed cyclics having differently substituted siloxy segmers incorporated in the ring could also be readily prepared by the cracking of the appropriate linear poly(siloxane) copolymers. The use of cyclic poly(siloxanes) for the preparation of highly reactive cyclic epoxysilicone monomers is also described.

Introduction

Recently, we have been engaged in the synthesis of novel cyclic epoxysilicone monomers that are of potential interest as substrates for UV-curable coatings because of their extraordinarily high rates of cationic ring-opening polymerization in the presence of onium salt photoinitiators.[1] Cyclic epoxysilicone monomers are colorless, low-viscosity mobile fluids that when cured give coatings with excellent chemical resistance and mechanical properties.

The starting materials for the synthesis of the above monomers are cyclic poly(siloxanes) bearing Si–H functional groups. These compounds are condensed with vinyl-containing epoxides in a platinum-catalyzed hydrosilylation reaction. For example, in eq 1 is depicted the reaction of 3-vinyl-7-oxabicyclo[4.1.0]heptane (4-vinylcyclohexene monooxide) with 2,4,6,8-tetramethylcyclotetrasiloxane (D^H_4) to give the tetrafunctional epoxy monomer shown. In this paper a shorthand nomenclature for siloxanes will be used, where D will denote a dimethylsiloxy moiety while D^H will indicate a methylsiloxy unit. The subscript gives the number of such units in the chain or ring. Having exhausted our in-house supply of D^H_4, we sought more of this compound from chemical supply houses only to discover that it was no longer available from these sources. It therefore became necessary to consider whether it might be possible to develop a new practical synthesis for these as well as other cyclic siloxanes.



(1)

Cyclic poly(siloxanes) are of strategic importance in the silicone industry and serve as the basis for the production of poly(dimethylsiloxanes) by a base-catalyzed ring-opening polymerization.[2] At the same time, hydrogen-functional poly(siloxanes) are of considerable interest for a variety of intermediates such as cross-linkers in the silicone rubber industry. Cyclic poly(dimethylsiloxanes) are conventionally produced by the hydrolysis of the corresponding disubstituted dichlorosilanes.[3] The hydrolytic method usually gives a mixture of cyclic poly(dimethylsiloxanes) and linear poly(dimethylsiloxanes). The proportion of the cyclics to linear oligomers has been optimized by careful choice of the solvent and conditions of the hydrolysis. While hydrolysis is the method of choice for the preparation of cyclic poly(dimethylsiloxanes), it is less satisfactory for the synthesis of cyclic poly(methylsiloxanes) due to the propensity of the Si–H bonds to undergo facile hydrolysis to give Si–OH groups. Some specialized hydrolysis conditions have, however, been developed for these latter materials.[4]

The thermolysis of poly(dimethylsiloxanes) in the presence of sodium hydroxide has been described by Hunter et al.[5] to give rise to cyclic poly(dimethylsiloxanes). Starting with a mixture of linear, high molecular weight poly(dimethylsiloxane) and sodium hydroxide, these workers found that it was possible to distill off the desired cyclic poly(dimethylsiloxanes) under reduced pressure. This reaction is limited in its scope only to poly(dialkylsiloxanes) since hydrogen functional siloxanes react with bases with the liberation of hydrogen and the formation of Si–O–Si bonds. Poly(dimethylsiloxanes) can also be redistributed to cyclics by using transition-metal complexes, especially those containing rhodium or iridium.[6]

A method for making cyclopolysiloxanes including those containing hydrogen functionality has been patented by Miller and Ryan[7] by the cracking of poly(siloxanes) over acid-treated clay or synthetic alumina silicate. This patent describes heating a mixture of the poly(siloxane) and one of the above catalysts together at such temperatures required to distill over the products. A serious drawback to this method is the explosion hazard posed by the presence of large amounts of hydrogen-functional poly(siloxane) at

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[1] Crivello, J. V.; Lee, J. L. *J. Polym. Sci., Polym. Chem. Ed.*, in press.

[2] Ivin, K. J.; Saegusa, T. *Ring-Opening Polymerization*; Elsevier: New York, 1984; p 1056.

[3] Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968; p 192.

[4] Curry, J. W. U.S. Patent 3,484,468, Dec 16, 1969 [*Chem. Abstr.* **1970**, *72*, 43844]; U.S. Patent 3,432,538, July 1, 1966 [*Chem. Abstr.* **1968**, *70*, 115319] both to Texas Instruments Co.

[5] Hunter, M. J.; Hyde, J. F.; Warrick, E. L.; Fletcher, H. J. *J. Am. Chem. Soc.* **1946**, *68*, 667. Hyde, J. F. German Patent 875046, July 6, 1949.

[6] Gustavson, W. A., Epstein, P. S.; Curtis, M. D. *J. Organomet. Chem.* **1982**, *238*, 87.

[7] Miller, C. J.; Ryan, W. P. U.S. Patent 3,714,213, Jan 30, 1973 [*Chem. Abstr.* **1973**, *78*, 136985] to General Electric Co.

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high temperatures. Because of this risk, commercial scale-up is precluded. Similarly, active white clays together with water have been used to give cyclic hydrogen-functional poly(siloxanes) from the corresponding linear polymers on heating.[8]

The synthesis of cyclic siloxanes containing a mixture of types of repeating segmers (copolymers) is problematic. Very recently, Buese[9] described a method whereby mixtures of poly(methylsiloxane) and D_4 are equilibrated in the presence of a strong acid catalyst such as trifluoromethanesulfonic acid to give a mixture of cyclic and linear poly(siloxanes) containing differently substituted siloxy groups. The difficulty of this method is that it requires high-dilution techniques and the use of large volumes of solvent. Last, cohydrolysis of dimethyldichlorosilanes and methyldichlorosilanes has been reported to give mixed cyclics although in low yields.[10]

Experimental Section

Materials and Characterization Methods. Poly(dimethylsiloxane) (SF 96; 50-cP fluid), poly(methylsiloxane) (SC 4300), and the Lamoreaux platinum catalyst[11] used in this work were obtained from the General Electric Silicone Products Business Division. This catalyst is prepared by heating a 1:7 mixture of chloroplatinic acid and *n*-octanol for 40 h at 70 °C. Copolymers containing various compositions of dimethylsiloxy and methylsiloxy segmer units were obtained from the Petrarch Chemical Co. Filtrol-20 was purchased from the Filtrol Corp. Type 5A molecular sieves were used as purchased from Aldrich Chemical Co. Zeolite molecular sieves LZM-8 and LZY-82 ($^1/_8$-in. extrudate pellets with a surface area of 625 m^2/g) were purchased from Alfa Chemical Co. and from the Union Carbide Corp. and were calcined for 5 h at 550 °C prior to use. Trifluoromethanesulfonic acid, 5-epoxy-1-hexene, and 7-epoxy-1-octene were obtained from the Aldrich Chemical Co. and purified by fractional distillation prior to use. 3-Vinyl-7-oxabicyclo[4.1.0]-heptane (VCHO) and *dl*-limonene monooxide were obtained respectively from the Union Carbide Corp. and SCM Corp. as a mixture of isomers (*dl* and meso) and distilled from CaH_2 prior to use.

Preliminary gas chromatographic analyses were made on a Hewlett Packard 5840A gas chromatograph equipped with flame ionization detector and 6 ft × $^1/_8$-in. OV 101 silicone columns. Further analyses were conducted with the aid of a VG analytical ZAF-2FGC mass spectrometer with attached Varian 6300 gas chromatograph equipped with 30-m DB1 poly(dimethylsiloxane) capillary columns and flame ionization detector.

Cracking of Poly(methylsiloxane) Using Filtrol-20. To a 250-mL three-necked round-bottom flask fitted with a magnetic stirrer, thermometer, capillary nitrogen inlet, pressure-equalizing addition funnel, distillation head, condenser, and receiver was placed 10 g of Filtrol-20. The flask was heated to 400–500 °C by using a mantle heater, and 20 mL of poly(methylsiloxane) (GE SC 4300) was added dropwise to the hot catalyst under approximately 40 mmHg pressure. There was observed rapid condensation of a liquid product in the condenser and receiver. Examination of the product using gas chromatography showed that the product consisted of four major products; D^{H}_{3}, D^{H}_{4}, D^{H}_{5}, and D^{H}_{6} in a ratio of 1:4:3:1 with smaller amounts of higher cyclics up to D^{H}_{10}.

Attempted Cocracking of Poly(dimethylsiloxane) and Poly(methylsiloxane). With use of the apparatus described in the previous experiment, a mixture of 14.8 g (0.2 mol segmer units) of poly(dimethylsiloxane) and 12 g (0.2 mol segmer units) of poly(methylsiloxane) was introduced dropwise onto the hot Filtrol-20 catalyst. GC analysis of the volatile product that was collected showed that the main product consisted chiefly of cyclic siloxanes derived from the poly(methylsiloxane) with just traces of cyclics from the poly(dimethylsiloxane) and mixed cyclics derived from both polymers.

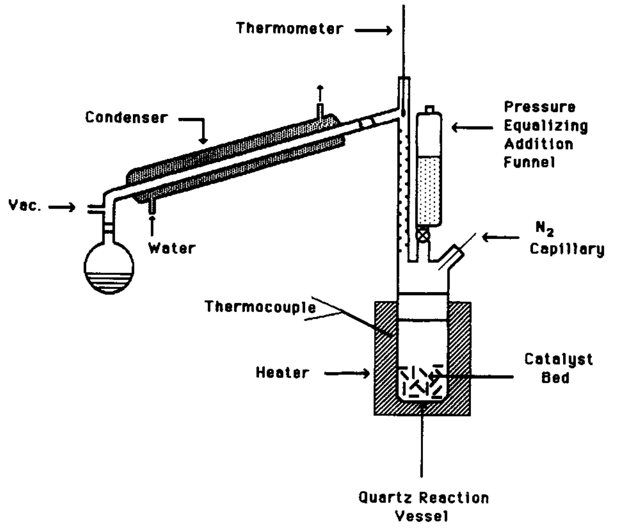

Figure 1. Apparatus for the preparation of cyclic siloxanes.

Preparation of Cyclic Poly(methylsiloxanes) over Acid-Treated Molecular Sieves. To 40 g of type 5A molecular sieves ($^1/_8$-in.-diameter pellets) obtained from Alfa-Ventron Co. was added 2 mL of concentrated sulfuric acid. The sieves were placed in a three-necked flask equipped with a distillation head, long condenser, receiver, flask, nitrogen capillary inlet, and pressure-equalizing addition funnel. After heating for 5 min at 400–500 °C during which water was removed from the catalyst, there was added dropwise by means of the addition funnel 56 g of a poly(methylsiloxane) fluid. Rapid distillation of the siloxane products occurred, and they were collected in the receiver. There were obtained 30.5 g of distillate consisting of a mixture of cyclic poly(methylsiloxanes) with major components D^{H}_{3}, D^{H}_{4}, D^{H}_{5}, and D^{H}_{6}. The ratio of the cyclics was approximately 1:2:2:1.

The apparatus was reassembled, and the same catalyst again heated to 400–500 °C. There was slowly added an additional 51 g of the poly(methylsiloxane) fluid. In the same manner, there was collected an additional 36 g of the above mixture of cyclics.

With use of the same apparatus, a mixture of 14.8 g (0.2 mol segmer units) of poly(dimethylsiloxane) and 12 g (0.2 mol segmer units) of poly(methylsiloxane) was introduced dropwise onto the hot acid treated molecular sieves. There was collected 15 g of distillate. GC analysis of the volatile product that was collected showed that the only products consisted of cyclic siloxanes derived from the poly(methylsiloxane) with no products from poly(dimethylsiloxane) and no mixed cyclics derived from both polymers. Examination of the reaction vessel showed that almost the entire amount of poly(dimethylsiloxane) remained as an unreacted oil in the cracking vessel.

Pure poly(dimethylsiloxane) (30 g) was added dropwise to 20 g of hot catalyst prepared as described above. The redistribution of this polymer took place very slowly, and only a trace of volatile product was obtained, which was shown to be almost pure D_4.

Preparation of Cyclic Poly(methylsiloxanes) by Equilibration over an Acidic Zeolite Catalyst. Linde LZY-82 molecular sieves were calcined at 550 °C for 3 h. Next, 20 g of the above calcined catalyst was placed in the apparatus as shown in Figure 1, and the reaction vessel heated to approximately 500–600 °C. To the hot catalyst under a vacuum of approximately 40 mmHg was added dropwise 41 g of GE SC 4300 poly(methylsiloxane) fluid. There was collected 29.5 g of distillate consisting of cyclics primarily in the range D^{H}_{3}–D^{H}_{8}.

The reaction vessel was reheated to 500–600 °C, and an additional 120.5 g of the poly(methylsiloxane) fluid was slowly added. There were collected an additional 103 g of the above mixture of cyclics. This experiment shows that the lifetime of the catalyst is long and suffers no degradation during the course of these studies.

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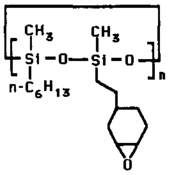
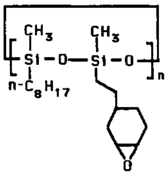
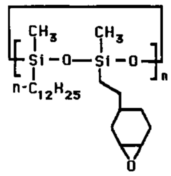
[8] Endo, I. Japan Kokai JP 52/69500, June 9, 1977 [*Chem. Abstr.* 1978, *87*(16), 118455b].

[9] Buese, M. A. *Macromolecules* 1987, *20*, 694.

[10] Heimberger, J.; Scheerschmidt, H.; Ruehlmann, K. *Plaste Kautsch.* 1978, *25*(7), 386.

[11] Lamoreaux, H. F. U.S. Patents 3,197,432 (1965), 3,197,433 (1965), and 3,220,972 (1965) [*Chem. Abstr.*, 1966, *64* 8237] to General Electric Co.

Table I. Characteristics of Cyclic Epoxysilicone Monomers

compound[a]	EEW[b]		elemental anal., % C	H	Si
	328	calcd	58.54	9.76	17.07
		found	57.80	9.82	16.48
	356	calcd	60.67	10.11	15.73
		found	59.29	9.51	15.58
	412	calcd	64.08	10.68	13.60
		found	63.24	10.27	13.52

[a] n = 1.5–5. [b] Epoxy equivalent weight.

Redistribution of Poly(dimethylsiloxane) over Acidic Molecular Sieves. With use of the same apparatus as described above and Linde LZY-82 molecular sieves, 25 g of poly(dimethylsiloxane) was added dropwise to the sieves heated to 400–500 °C under 40 mmHg. A product (14 g) consisting of primarily D_3 and D_4 in a ratio of 3:1 was obtained.

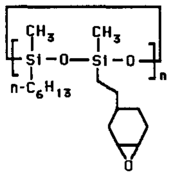
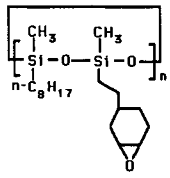
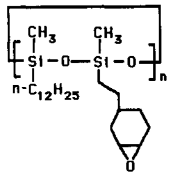
Redistribution of a Poly(dimethylsiloxane-*co*-methylsiloxane) Copolymer. To 20 g of calcined Linde LZY-82 molecular sieves heated to approximately 600 °C was added dropwise 42 g of (30–35%) methylsiloxane–(65–70%) dimethylsiloxane copolymer obtained from Petrarch Systems. Rapid distillation of a mixture of cyclic products occurred under 40 mmHg. There was collected 26.6 g of distillate. Examination of the products by gas chromatography showed that they consisted of a mixture of cyclics containing both dimethysiloxy and methylsiloxy units within the same rings with ring sizes from 6 to 20.

Equilibration and Cracking of Poly(dimethylsiloxane) and Poly(methylsiloxane). Combined together in a 250-mL Erlenmeyer flask were 44.4 g (0.6 mol segmer units) of poly(dimethylsiloxane) (GE SF 96, 50 cps) and 36 g (0.6 mol segmer units) of GE SC 4300 poly(methylsiloxane). To this mixture was added 1.5 g of trifluoromethanesulfonic acid, and the mixture stirred at 110–115 °C for 1.5 h. Thereafter, there was added 3 g of MgO, and the reaction mixture stirred for 15 min to neutralize the acid. The mixture was filtered under vacuum through a fritted funnel to obtain the equilibrated 50:50 copolymer as a colorless transparent oil.

Next, 62 g of the above copolymer containing randomly distributed dimethylsiloxy and methylsiloxy segmer units in the ratio of 1:1 was added to Linde LZ-Y82 molecular sieves at approximately 600 °C. Rapid distillation of the product took place, and there was obtained 58.1 g (94% yield) of a complex mixture of cyclic products. The product was examined first by gas chromatography and then by gas chromatography–mass spectroscopy. Positive identification could be made of the major peaks in the chromatogram as a mixture of cyclic poly(siloxanes) consisting mainly of six- and eight-membered rings and containing both D and D^H segmers.

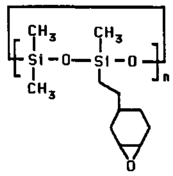
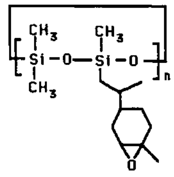
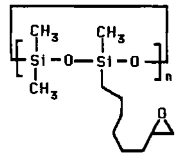
Preparation and UV Cure of Cyclic Silicone Epoxy Resins from a Mixture of Cyclic Hydrogen-Functional Poly(siloxanes). The following experiment is typical of those used in the preparation of cyclic epoxysilicone monomers shown in Tables I and III.

Table II. Properties of UV-Cured Cyclic Epoxysilicone Monomers

compound[c]	T_g[b] (5-s $h\nu$)	tack-free cure rate,[c] ft/min 2 lamps (300 W)	1 lamp (300 W)	1 lamp (200 W)	1 lamp (120 W)
	176	>500	>500	300	150
	167	>500	>500	300	150
	169	>500	350	200	100

[a] n = 1.5–5. [b] Measured at 20 °C/min on 6-mil films cured with a GE H3T7 Hg lamp by using 0.5 mol % photoinitiator [(4-$C_8H_{17}OC_6H_4)C_6H_5I^+SbF_6^-$]. [c] Determined on 1-mil films by using a RPC UV processor and 0.5 mol % photoinitiator.

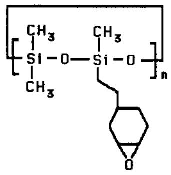
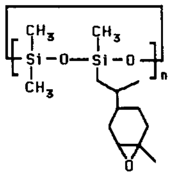
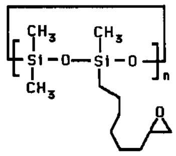
Table III. Characteristics of Cyclic Epoxysilicone Monomers

compound[a]	EEW[b]		elemental anal., % C	H	Si
	258	calcd	51.16	8.53	21.71
		found	49.94	8.50	22.10
	286	calcd	54.55	9.09	19.58
		found	52.65	9.07	18.87
	260	calcd	50.77	9.23	21.54
		found	49.40	8.91	21.88

[a] n = 1.5–5. [b] Epoxy equivalent weight.

To a 250-mL round-bottom flask equipped with a magnetic stirrer, reflux condenser, addition funnel, and nitrogen inlet were placed 13.4 g (0.1 equiv of Si–H groups) of the mixture of cyclic poly(siloxanes) containing a 1:1 ratio of dimethylsiloxy and methylsiloxy groups prepared as described above and 80 mL of toluene. To this mixture was added 2 drops of the Lamoreaux catalyst which contained 3.65% platinum by weight (resulting Pt concentration ~40 ppm), and the reaction mixture heated by using a water bath to 80 °C. Then, 13.6 g (0.11 mmol) of 3-vinyl-7-oxabicyclo[4.1.0]heptane (4-vinylcyclohexene monooxide) was added dropwise via the addition funnel at such a rate so as to maintain the temperature below 110 °C. After addition was complete, the reaction mixture was held at 90–95 °C for 3 h. After this time, the infrared spectrum showed no trace of the Si–H absorption at 2100 cm^{-1}. There was added 0.006 g of 2-mercaptobenzothiazole as a stabilizer, the reaction mixture cooled, and the bulk of the toluene removed on a rotary evaporator. Then, the remaining traces of solvent, unreacted epoxide, and traces of unreactive cyclodimethylsiloxanes were removed by heating for several hours at approximately 80 °C in a water bath under

Table IV. Properties of UV-Cured Epoxysilicone Monomers

compound[a]	T_g[b] (5-s $h\nu$)	tack-free cure rate,[c] ft/min 2 lamps (300 W)	1 lamp (300 W)	1 lamp (200 W)	1 lamp (120 W)
	196	>500	350	300	80
	195	>500	200	100	50
	163	80	30		

[a] n = 1.5–5. [b] Measured at 20 °C/min on 6-mil films cured with a GE H3T7 Hg lamp by using 0.5 mol % photoinitiator [(4-$C_8H_{17}OC_6H_4)C_6H_5I^+SbF_6^-$]. [c] Determined on 1-mil films by using a RPC UV processor and 0.5 mol % photoinitiator.

0.01 mmHg. There was obtained 39.5 g (93% yield) of a mixture of cyclic epoxysilicone monomers.

A 1% solution of (4-(octyloxy)phenyl)phenyliodonium hexafluoroantimonate in the above cyclic silicone epoxy monomer was spread as a 1-mil film onto a glass plate, and the film irradiated by using a GE H3T7 medium-pressure mercury arc lamp ballasted at 800 W located at a distance of 6 in. from the film. A clear, hard, tack-free film was obtained after an irradiation time of 1 s under these conditions.

Further UV polymerization studies were carried out as shown in Tables II and III by using a Model QC 1202 UV processor obtained from the RPC Equipment Co. This apparatus was equipped with two 12-in. medium-pressure mercury arc lamps mounted perpendicular to the direction of travel of the conveyor. The lamps could be operated together or independently at 380 V and 9.8 ± 0.8 A. The lamps could also be run at either high (300 W), medium (200 W), or low (120 W) power levels. The conveyor speed could be varied between 10 and 500 ft/min. Samples were coated as 1-mil films onto glass plates, passed through the curing chamber, and immediately tested for tack on exiting the chamber. Glass transition temperatures were measured by using a Perkin-Elmer DSC 2 differential scanning calorimeter at 20 °C/min.

Results and Discussion

Thermal Redistribution of Poly(methylsiloxane) and Poly(dimethylsiloxane). The most direct potential approach to the synthesis of hydrogen-functional cyclic siloxanes is by a thermally induced depolymerization or "cracking" reaction on poly(methylsiloxane) and/or its copolymers with poly(dimethylsiloxane). Since Si–H compounds undergo a variety of hydrolysis and condensation reactions in the presence of bases, it was decided to attempt to use acidic catalysts. In particular, a fixed bed heterogeneous acidic catalyst would be ideal in which linear polymers would be introduced into the bed at high temperatures while at the same time distilling off the desired cyclics.

Filtrol-20 (supplied by the Filtrol Co.) is a sulfuric acid treated bentonite clay commonly used as a catalyst in the commercial production of poly(dimethylsiloxanes). This catalyst was placed in a distillation apparatus and heated to 300–400 °C under partial vacuum with a slow stream of nitrogen. Then, a linear poly(methylsiloxane) fluid was added dropwise to the catalyst bed. A volatile product was collected as a distillate in the receiver flask that upon examination by gas–liquid chromatography proved to be a mixture of poly(methylsiloxane) cyclics with rings incorporating from 3 to 10 silicon–oxygen units. One complication associated with this catalyst was the observation that under the conditions of the cracking reaction, the very fine, light catalyst powder was carried over into the product by the nitrogen stream.

To overcome this difficulty, 5-Å molecular sieves (Linde Type 5A) were treated with concentrated sulfuric and then substituted for the Filtrol-20 in the above reaction. This catalyst performed very satisfactorily with respect to its ability to convert poly(methylsiloxane) fluids to cyclics. Further, because they are supplied as pellets, the acid-treated molecular sieves form stable fixed beds. However, this catalyst as well as Filtrol-20 suffers from the difficulty that byproducts are generated during their use that seriously contaminate the product. Both of these heterogeneous catalysts contain water that is collected along with the products. More seriously, under the reaction conditions, the absorbed sulfuric acid is reduced by the Si–H-containing substrates, and the product distillate contains hydrogen sulfide as well as other sulfur-containing compounds as contaminants. These byproducts are strong inhibitors for any subsequent transition-metal-catalyzed hydrosilylation reactions and are extremely difficult to remove completely from the products.

We next turned our attention to acidic Zeolite catalysts. Most of the above disadvantages of the sulfuric acid treated clays and molecular sieves are overcome by using such catalysts. In these materials, the acidic catalytic sites are attached to the three-dimensional open-cell matrix of the aluminosilicate. These Zeolite-type catalysts are the most reactive ones yet found and are easily capable of redistributing both poly(methylsiloxanes) and poly(dimethylsiloxanes) to their respective cyclics. Two catalysts were obtained from Linde Division of Union Carbide having code numbers LZM-8 and LZY-82. Both of these types of molecular sieves were active catalysts with the latter somewhat more reactive than the former. The catalysts are prepared for use by a preliminary calcining procedure at 500–550 °C for 3–5 h. This serves to convert the initially present ammonium salts to their acidic forms with the elimination of ammonia. Alternatively, the catalysts could be calcined in situ in the cracking apparatus by a brief thermal treatment at 600 °C for several minutes under vacuum. The cyclic poly(siloxane) products that are obtained by using these catalysts are pure and uncontaminated and are suitable directly for use in transition-metal-catalyzed hydrosilylation reactions.

In Figure 1 is shown a schematic drawing of the laboratory cracking apparatus used during the course of this work. It consists essentially of a quartz reaction vessel in which is placed a loosely packed bed of approximately 25–30 g of the desired zeolite catalyst. The reaction vessel is heated with a high heat capacity heater equipped with a thermocouple and gauge for temperature readout. Experiments were conducted under partial vacuum (~40 Torr) with a slow stream of nitrogen gas that was admitted by a fine capillary. As the products formed, they were passed through a fractionation column and then collected with the aid of a condenser and multiple-flask receiver. Preliminary experiments showed that the cracking reaction proceeded best at temperatures in the range 500–800 °C with the optimum being about 700 °C. At these temperatures, as the linear poly(siloxane) fluid is admitted

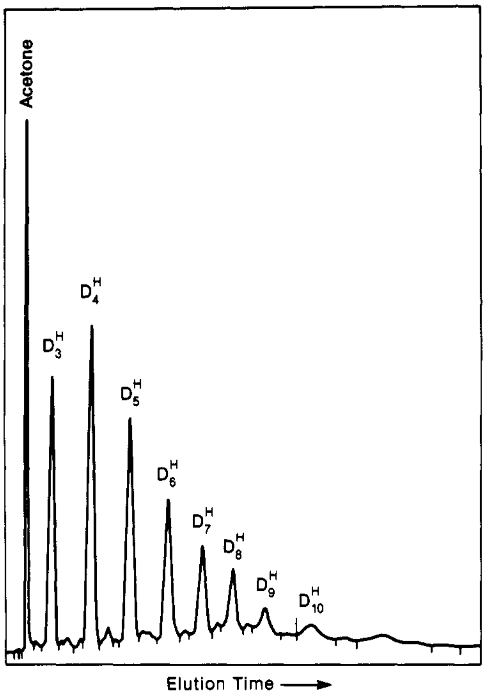
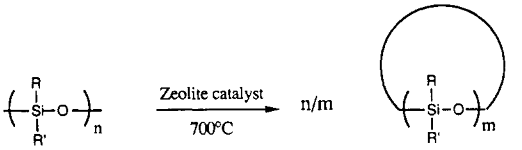


Figure 2. Gas chromatogram of the mixture of cyclics obtained from the zeolite-catalyzed cracking of poly(methylsiloxane) at 600 °C.

dropwise to the bed, the cyclic products flash off and are collected in the receiver. Examination of the catalyst bed after the cracking reaction showed it to be clean and free flowing with only a slight trace of carbonization. It has been found possible to reuse the catalyst bed in two subsequent cracking reactions without evidence of deterioration in its activity.

With pure poly(methylsiloxane) homopolymer, under the reaction conditions that have been outlined above, a distribution of cyclic poly(siloxanes) are obtained ranging from ring sizes of 6 to 20 (eq 2).

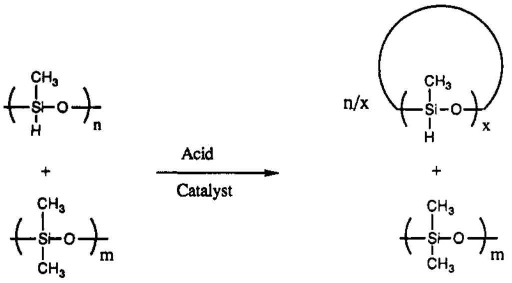


(2)

Figure 2 shows a gas chromatogram of the reaction products whose identities were positively verified by using gas chromatography–mass spectroscopy techniques. In the base line of the chromatogram are small peaks that consist of linear trimethylsilyl-terminated short-chain oligomers. These byproducts appear to arise as a consequence of the trimethylsilyl end groups present in the linear poly(methylsiloxane) fluid used as the starting material. The mixture of cyclic poly(methylsiloxanes) can be readily fractionated into their individual cyclic components through the use of a spinning-band distillation apparatus. Under normal conditions, the distribution of cyclics is such that it favors the most volatile and hence lowest molecular weight products. Depending on the specific catalyst and reaction conditions used, it has been observed that the above process conditions give mixtures enriched in the least thermodynamically stable products, i.e., cyclic trisiloxanes (six membered rings). This is in contrast to most of the other equilibrium-type methods cited above for the preparation of cyclic siloxanes, which always give distributions of the most thermodynamically stable products. The present kinetically controlled process can, therefore, advantageously be used for the specific preparation of certain difficult to obtain cyclic siloxanes, for example, $D^H{}_3$.

The thermal depolymerization of poly(dimethylsiloxane) over a LZY-82 zeolite catalyst was conducted under the same conditions as outlined above. Cyclic products with ring sizes from 6 to 12 were identified by using GLC–mass spectroscopy. However, the major products were the cyclic trimer, D_3 (40%), and the cyclic tetramer, D_4 (13%). As noted before for $D^H{}_3$, the presence of D_3 as the chief component in the cracking mixture points out that the reaction is under kinetic rather than thermodynamic control. As mentioned previously, D_3 is of considerable potential importance as a commercial intermediate in silicones technology. While the cyclic tetramer, D_4, is used industrially in the manufacture of silicones, because of its higher ring strain, D_3 ring-open polymerizes much more readily than D_4. D_3 is, therefore, the preferred monomer for silicone manufacture. However, there exists no satisfactory commercially viable synthesis for this monomer. Cracking poly(dimethylsiloxane) hydrolysate with recycle of the heavier cyclics could be an attractive high-yield method for its preparation. Parenthetically, when attempts were made to use either Filtrol-20 or sulfuric acid treated molecular sieves as catalysts for the thermal redistribution of linear poly(dimethysiloxanes) to cyclics, only very poor activity was noted. Again, acidic zeolite-type catalysts are the best yet found for this cracking reaction, although it was noted qualitatively that the cracking reaction for poly(dimethysiloxanes) is considerably less facile than the corresponding poly(methylsiloxanes) in the presence of these acidic catalysts.

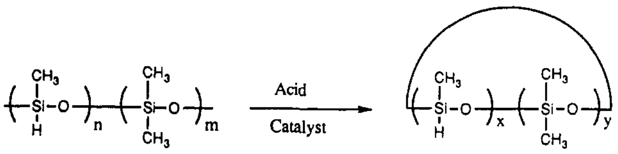
Synthesis of Cyclic Poly(siloxanes) Containing a Mixture of Siloxy Segmers. At the present time, there exists no simple, direct, and high-yield method for the synthesis of cyclic poly(siloxanes) containing a mixture of different substituted siloxy groups in the same ring. One goal of this research was to attempt to prepare such cyclic poly(siloxanes) by using the cracking reaction that we have just described. However, as mentioned, that while poly(methylsiloxanes) are rapidly and quantitatively redistributed to cyclics at temperatures from 400 to 500 °C, the corresponding poly(dimethylsiloxanes) require considerably more vigorous conditions and more reactive acidic catalysts. It was further observed that when a mixture of the above two silicone polymers were introduced into the apparatus shown in Figure 1 in an attempt to make mixed cyclics, the major cyclic products obtained were those from the poly(methylsiloxane) with only traces of cyclics derived from the poly(dimethylsiloxane) or mixed cyclics derived from both linear polymers. This is depicted in eq 3.



(3)

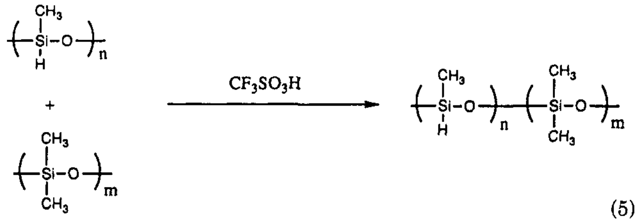
Clearly, the reactivity of the poly(methylsiloxane) is very much greater than that of poly(dimethylsiloxane) under these conditions.

It was, however, observed that it is possible to obtain mixed cyclic poly(siloxanes) by cracking linear copolymers containing both methylsiloxy and dimethylsiloxy segmer units (eq 4). Random copolymers of this type produced by the cohydrolysis of dimethyldichlorosilane and methyldichlorosilane are available from commercial sources,



$$\left(\underset{H}{\overset{CH_3}{\overset{|}{\underset{|}{Si}}}}-O\right)_n\left(\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{Si}}}}-O\right)_m \xrightarrow[\text{Catalyst}]{\text{Acid}} \left(\underset{H}{\overset{CH_3}{\overset{|}{\underset{|}{Si}}}}-O\right)_x\left(\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{Si}}}}-O\right)_y \quad (4)$$

namely, from the Petrarch Chemical Co. Subsequently, it was discovered that a mixture of the two respective homopolymers can be equilibrated by heating at 110–115 °C for 1.5 h in the presence of acidic catalysts such as trifluoromethanesulfonic acid to give the desired copolymers (eq 5).



$$\left(\underset{H}{\overset{CH_3}{\overset{|}{\underset{|}{Si}}}}-O\right)_n + \left(\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{Si}}}}-O\right)_m \xrightarrow{CF_3SO_3H} \left(\underset{H}{\overset{CH_3}{\overset{|}{\underset{|}{Si}}}}-O\right)_n\left(\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{Si}}}}-O\right)_m \quad (5)$$

The random copolymer containing a statistical distribution of the two segmer units can be readily and quantitatively converted to the desired mixed cyclics by using the above described process and the apparatus shown in Figure 1. Similarly, cyclic substrates having any degree of Si–H functionality can be prepared by cracking the appropriate poly(dimethylsiloxane-*co*-methylsiloxane) copolymer. Copolymers containing 85:15, 70:30, and 50:50 ratios of dimethylsiloxy to methylsiloxy units were cracked to the corresponding cyclics of the same composition. Figure 3 depicts the gas chromatogram of the cyclics derived from a statistical 1:1 poly(dimethylsiloxane-*co*-methylsiloxane) copolymer. As before, assignments of the individual peaks were made with the aid of gas chromatography–mass spectroscopy. It should be noted that rings containing from 3 to 10 siloxane bonds are present and that for every ring size every possible combination of the two different segmer units is represented. Further, for each ring size, those compounds that reflect the starting copolymer having a 1:1 methylsiloxy to dimethylsiloxy composition are the dominant products.[12]

It may be concluded that silicone polymers containing methylsiloxy segmers possess specific weak linkages that are major sites for attack by the solid redistribution catalysts. Cyclic poly(siloxanes) are formed whose composition reflects that originally present in the initial copolymer. Although the preparation of cyclic siloxanes incorporating only two different segmer types has already been demonstrated, it is in principle possible to similarly synthesize analogous cyclics in which three or more different segmer units are present by using the same methodology.

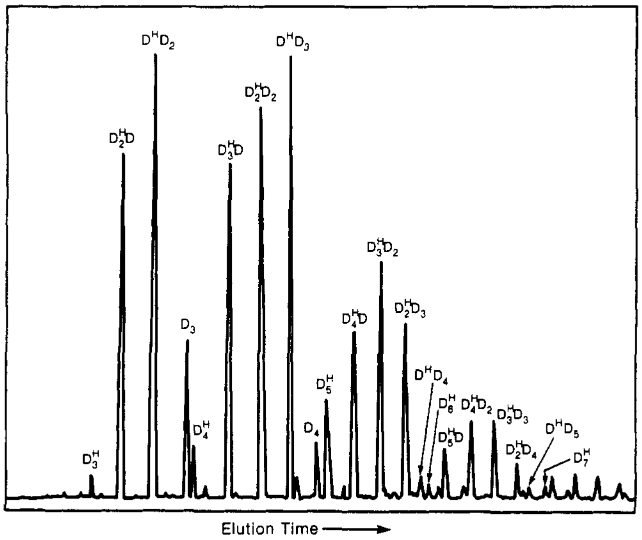
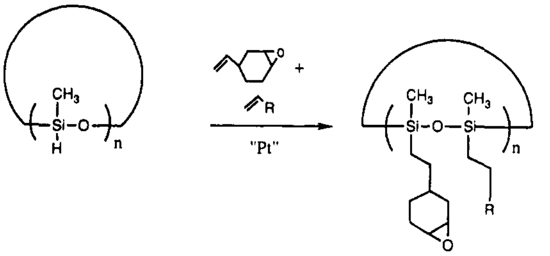


Figure 3. Capillary gas chromatogram of the mixture of cyclics obtained from the zeolite-catalyzed cracking of poly(methylsiloxane-*co*-dimethylsiloxane), 50:50 statistical copolymer, at 600 °C.

Synthesis of Epoxy-Functional Cyclic Poly(siloxanes). While hydrogen-functional cyclic poly(siloxanes) have numerous uses, only one will be described here, that of the preparation of epoxy-functional cyclic poly(siloxanes). The mixture of cyclic siloxanes D^H_3 through D^H_{10} obtained from the redistribution of poly(methylsiloxane) can be fractionated into their individual components by distillation. However, we elected to use the mixture of cyclics as obtained directly from the cracking reaction. A series of epoxysilicone monomers can be prepared by condensing the poly(methylsiloxane) cyclics with mixtures of alkenes and vinyl-containing epoxides in the presence of a platinum-containing catalyst (eq 6).



(6)

In Table I are depicted three different monomers that were synthesized by using a 1:1 stoichiometric mixture of α-olefins and 3-vinyl-7-oxabicyclo[4.1.0]heptane (4-vinylcyclohexene monooxide). In principle, with such mixtures of olefins and vinyl epoxides it is possible to prepare monomers with a range of desired epoxide functionalities and with a consequent variety of physical and chemical properties. The above epoxy-functional cyclic poly(siloxanes), which consist of a mixture not only of different ring sizes but also different stereo- and regioisomers, are reactive in photoinitiated cationic polymerization using onium salt photoinitiators.[1] In Table II are shown the cure speeds for the three monomers with (4-(octyloxy)phenyl)phenyliodonium hexafluoroantimonate as the photoinitiator. Table II shows a profile of the cure rates and T_g's for these monomers. Excellent, high T_g's were recorded along with high reactivities in cationic polymerization which are reflected in the UV cure rates noted in the table. Under these conditions, ring-opening or equilibration reactions involving the siloxane rings did not occur. Definitive evidence for this will be offered in subsequent papers.

Another approach to the preparation of cyclic epoxysiloxanes consists of carrying out the platinum-catalyzed hydrosilylation of cyclics containing mixed segmer units with vinyl-containing epoxides. Table III gives examples

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[12] A referee has correctly pointed out that the GC trace shown in Figure 3 is not one that one would expect from a depropagation of a fully random polymer where the ratio of D^H_3:D^H_2:D^HD_2:D_3 would be 1:3:3:1. This referee has noted and we have also observed that the deposition of SiO_2 on the detector of a flame ionization detector often causes difficulties in quantification due to an unstable response. We expect this may be one reason for observed product ratios rather than an incomplete equilibration of the starting copolymer or to kinetic factors during the depropagation reaction. Additionally, since some fractionation in the apparatus shown in Figure 1 would be expected to occur due to the presence of a distillation column, the product distribution would be expected to be skewed somewhat toward the more volatile products.

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of this approach in which cyclics containing equal numbers of dimethyl- and methylsiloxy groups were condensed with 3-vinyl-7-oxabicyclo[4.1.0]heptane and other epoxides. Table III also records the cure and T_g data obtained from the UV cure of these same monomers. Especially notable in this table are the high values obtained for those monomers containing cycloaliphatic epoxide groups after only 5 s of irradiation. In a similar manner, monomers having variable degrees of epoxide functionality can be prepared by using cyclic substrates derived by cracking the appropriate poly(dimethylsiloxane-*co*-methylsiloxane) copolymer and then carrying out the platinum-catalyzed hydrosilylation with a vinyl-substituted epoxide. As with the other cyclic epoxysilicone monomers prepared and described in Table I, the monomers reported above have excellent chemical resistance (very high gel contents) and hardness (pencil hardness *H* and above), which make them attractive for coatings applications.

Conclusions

In this paper we have described the development of a new method for the preparation of cyclic poly(siloxanes) from linear poly(siloxanes) by a nonequilibrium thermal depolymerization process. Zeolite fixed bed catalysts are preferred for this process, giving high yields of uncontaminated cyclic products. In addition, they are commercially available, inexpensive materials that are highly active, easy to use, and may be recycled without loss of activity. The depolymerization is carried out at temperatures from 400 to 800 °C, under which conditions the cyclic products flash away from the reaction zone, eliminating potential explosion and fire hazards. Last, the products of thermal cracking are eminently useful. Of particular interest are the cyclic epoxysilicone monomers which can be prepared directly from the cracking distillate. These monomers together with onium salt photoinitiators are exceptionally reactive substrates for UV curing applications because of their high rates of cure and excellent mechanical and chemical properties. Such rapidly curing systems are particularly useful for UV cured coatings, printing inks, and electronic encapsulations.

Acknowledgment. We acknowledge the generous gift of an analytical sample of mixed Si–H cyclics from D. Gross of the General Electric Silicone Products Business Division. We also thank W. Ligon and R. May for running the GC–MS characterization of the cyclic poly(siloxanes).

Electronic Structure of a New Ternary Chalcogenide: $NbNiTe_5$

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An attempt at analyzing the electronic structure and bonding in the metallic and paramagnetic compound $NbNiTe_5$ has been made, using extended Hückel tight-binding calculations. The metallic behavior of this compound originates primarily from Te 5p states. Rather anisotropic conductivity is expected. It is difficult to assign a definitive oxidation state to the elements in this compound, but we suggest that an oxidation formalism of $(Nb^{3+})(Ni^{2+})(Te)_5^{5-}$ may be appropriate. This accounts for the numerous Te–Te contacts and electronegativity considerations but not for the magnetic measurements. The bonding between tellurium and transition-metal atoms is highly covalent; the compound can be considered as an intermetallic phase. The title compound and its Ta and Pd derivatives are compared, as well as some layerlike rare-earth-metal tellurides.

The Structure

The interesting properties, metallic *and* paramagnetic, displayed by the recently characterized compound $NbNiTe_5$[1] prompted us to study its electronic structure. The D_{2h}^{17}-*Cmcm* structure of $NbNiTe_5$ forms a new layered structural type. Each layer is made of infinite chains of face-sharing bicapped trigonal $NbTe_8$ prisms running through the structure parallel to the *a* axis. The one-dimensional chains are brought together in an up and down fashion along the *c* axis, as for $ZrTe_5$.[2] But this time the structure is assembled so that the Te atoms of two adjacent chains form chains of octahedra where the Ni atoms are trapped. In other words, the one-dimensional chains of bicapped trigonal prisms (BCTP) are linked together via "intercalated" octahedral nickel atoms. This is depicted in Figure 1.

No close metal–metal contacts are observed in the crystal. The shortest Nb···Nb and Ni···Ni distances are

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(1) Liimatta, E. W.; Ibers, J. A. *J. Solid State Chem.* **1987**, *71*, 384.
(2) Furuseth, S.; Brattas, L.; Kjekshus, A. *Acta Chem. Scand.* **1973**, *27*, 2367.

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