Chem. Mater. **1993,** *5,* 983-988

Synthesis of Cyclooligomers via the Living Depropagation of Poly(dimethylsiloxane-*co*-methylhydrogensiloxane)

Pao-Sun Chang and Mark A. Buese*

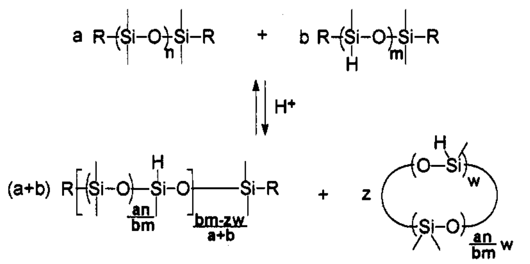
Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

Received February 25, 1993. Revised Manuscript Received April 27, 1993

The synthesis of cyclic cooligomers with dimethylsiloxy and methylhydrogensiloxy units was demonstrated using a small amount (<0.5 wt %) of trifluoromethanesulfonic acid as catalyst and no solvent. Cyclic oligomers were continuously stripped from the equilibrating poly(dimethylsiloxane-*co*-methylhydrogensiloxane) in a manner such that most bond redistribution occurred separately from the stripping of the cyclosiloxanes from the fluid. Using the residue of one synthesis as the source of catalyst for the next synthesis permitted nearly quantitative conversion of linear fluids into cyclics. Cyclics with ring sizes of three through eight were isolated. More than 50% of the mixture was cyclic tetramer and more than 95% of the cyclics had ring sizes of four, five, or six repeating units.

Introduction

A number of novel materials and processing techniques that require mono- or polyfunctionalized cyclosiloxanes as monomers have been reported in papers and patents.[1] The most common cyclosiloxane intermediates used to prepare these monomers were heptamethylcyclotetrasiloxane or mixed cyclic oligomers of dimethylsiloxane and methylhydrogensiloxane. The preparation of these Si–H-containing cyclics has been investigated by a number of research groups.[2] Most of the processes reported have been acid-catalyzed variations on the base catalyzed depropagation of poly(dimethylsiloxane) described by Hunter et al.[3] This approach takes advantage of the ability to undergo a ring-chain equilibrium which is displayed by many heterochain polymers as was originally modeled by Jacobson and Stockmayer.[4] Unlike the base-catalyzed depolymerization of poly(dimethylsiloxane), the syntheses of the mixed cyclo(dimethyl-*co*-methylhydrogensiloxane) (eq 1) have required large amounts of catalysts, have generally required high temperature and have often resulted in relatively poor yields, particularly with high proportions of Si–H. The distributions of isolated cyclics differed significantly from those of cyclosiloxanes in equilibrium with high polymer,[5] and the fractions of the two repeating units in the cyclics differed significantly from those in the original fluid in some cases.[6] Generally, the catalysts lose activity with time and conversion.



(1)

This laboratory has begun studies of siloxane networks and copolymers which are formed when the principal molecular weight building step is via siloxane redistribution.[7] A reliable synthesis of cyclosiloxanes containing Si–H functionality, particularly heptamethylcyclotetrasiloxane, was desired to prepare appropriate polyfunctional monomers.[8] It has been observed in kinetic studies of the acid-catalyzed redistribution of siloxanes that the rate of redistribution is dependent on acid orders that are greater than unity.[9] Water or a silanol appears to be required to permit redistribution at low temperatures, as dry silyl esters do not initiate the polymerization of cyclosiloxanes. This feature inherently leads to difficulties in the synthesis of these cyclics by stripping a redistributing fluid, since the boiling points of the products exceed 135 °C at atmospheric pressure and silanol condensation to siloxane and water is promoted by acid catalysts. Hence, dehydration is promoted under the appropriate conditions for stripping of the cyclics. This factor may account for the apparent loss of catalytic activity observed. Due to the very large amount of catalyst typically used, the loss of catalyst by stripping seems a less plausible explanation for the deactivation, though one would anticipate some acid loss during the stripping of cyclics in many systems. On the other hand, excess water can have a retarding effect upon the redistribution process.[8] Nevertheless, large quantities of water have been employed.[2b] The water and acid concentrations affect the amount of Si–H hydrolysis

---

[1] (a) Crivello, J. V.; Lee, J. *J. Polym. Sci., Polym. Chem.* **1990**, *28*, 497. (b) Buese, M. A. U.S. Patent 4,826,710, May 1989. (c) Tanaka, H.; Tarumi, Y.; Fujino, F. *Jpn. Kokai Tokyo* JP 6,273,250, Apr 1987.

[2] (a) Crivello, J. V.; Lee, J. *Chem. Mater.* **1989**, *1*, 445. (b) Endo, I. *Japan Kokai* JP 52/69500, June 1977. (c) Miller, C. J.; Ryan, W. P. U.S. Patent 3,714,213, Jan 1973.

[3] Hunter, M. J.; Hyde, J. F.; Warrick, E. L.; Fletcher, H. J. *J. Am. Chem. Soc.* **1946**, *68*, 667.

[4] Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600.

[5] (a) Semlyen, J. A.; Wright, P. V. *Polymer* **1969**, *10*, 543. (b) Carmichael, J. B.; Winger R. *Polym. Sci., Part A* **1965**, *3*, 971. (c) Brown, J. F.; Slusarczuk, G. M. J. *J. Am. Chem. Soc.* **1965**, *87*, 931.

[6] (a) Keohan, F. L.; Swint, S. A.; Buese, M. A. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 303. (b) Ziemelis, M. J.; Saam, J. C. *Macromolecules* **1989**, *22*, 2111.

[7] Chang, P.-S.; Buese, M. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33(2)*, 491.

[8] Chang, P.-S.; Hughes, T. S.; Zhang, Y.; Webster, Jr., G.R.; Poczynok, D.; Buese, M. A. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 891.

[9] (a) Gobin, C.; Masure, M.; Sauvet, G.; Sigwalt, P. *Makromol. Chem., Macromol. Symp.* **1986**, *6*, 237. (b) Wilczek, L.; Rubisztaijn, S.; Chojnowski, *J. Makromol. Chem.* **1986**, *187*, 39 and references therein.

0897-4756/93/2805-0983$04.00/0

which occurs simultaneously with the redistribution.[10] Subsequent condensation of the resulting silanols, or of the silanols with Si–H functionality, can ultimately lead to gelation. The rate of siloxane redistribution is quite high at room temperature when very strong acids are used. The quantity of cyclosiloxanes larger than the cyclic trimer in equilibrium with high molecular weight linear polymer is independent of temperature.[11] Therefore, except in the case where the cyclic trimer is the desired product, the yield cannot be improved by using high temperature, but the number of unwanted side reactions will increase. At sufficiently high temperatures radical formation can occur, giving rise to another set of undesired side reactions. For these reasons, an investigation of a relatively low-temperature process, employing low concentrations of acid and water, was undertaken. To study as general a process as possible, linear fluids rather than cyclosiloxanes were chosen as the primary source of comonomer units since there are inherently more limitations imposed on the process by the use of linear polymers.

This paper describes a process where linear copolymer was converted to mixed cyclic siloxanes in a high yield using a small amount of catalyst. It was found that by separating the process of cyclosiloxane removal from the redistribution process, a very high yield of cyclosiloxanes could be prepared by depropagation with very little catalyst in a manner that could be carried out continuously. The process was carried out in two ways. The first employed a single pot and imposed a temperature and pressure cycle on the equilibrating fluid. The second variation of the method permitted the removal of the cyclosiloxanes in a continuous fashion by using two chambers. One chamber was kept at room temperature and pressure for the primary redistribution of siloxane bonds, and the other was kept at an elevated temperature and a reduced pressure for the stripping of cyclics. The fluid was continuously exchanged between the two chambers. The conversion and product composition will be discussed. The use of 1,3-dioctyl-1,1,3,3-tetramethyldisiloxane to control the viscosity of the fluid and composition of the linear portion of the mixture will be presented. An example in which only a low molecular weight trimethylsilyl end-capped poly(methylhydrogensiloxane) was used showed that a significant improvement of the quality of the product cyclosiloxane composition could be obtained by successively depolymerizing the reagent fluid, polymerizing the impure cyclosiloxanes, and depolymerizing that polymer.

Experimental Section

A trimethylsilyl end-capped poly(dimethylsiloxane) fluid (Hüls CPs043) and octamethylcyclotetrasiloxane were used as received. A trimethylsilyl end-capped poly(methylhydrogensiloxane) fluid (Hüls PS-120) was washed twice with dilute sulfuric acid solution and three times with distilled water and dried over $CaCl_2$ prior to use. Trifluoromethanesulfonic acid was used as received from Aldrich or Parrish. Magnesium oxide (light powder) was purchased from Fisher and used as received. Tetramethyldisiloxane (Hüls), 1-octene (Aldrich), and a platinum–divinyltetramethyldisiloxane complex (Hüls PC075), the hydrosilation catalyst, were used as received in the preparation of 1,3-dioctyl-1,1,3,3-tetramethyldisiloxane.

Preparation of 1,3-Dioctyl-1,1,3,3-tetramethyldisiloxane. The relatively nonvolatile disiloxane, 1,3-dioctyl-1,1,3,3-tetramethyldisiloxane, was synthesized by the reaction of 20 g of 1,1,3,3-tetramethyldisiloxane, 17 g of 1-octene, and 0.02 mL of the hydrosilation catalyst (3.5% by weight Pt) to 70 °C for 2 h in a round-bottomed flask. Quantitative conversion was indicated by a gas chromatographic analysis. Approximately 0.2 g of MgO was added to the flask, and the product was distilled at 122–125 °C and 0.2 mmHg. ^1H NMR (300 MHz, $CDCl_3$) δ 0.08 (s, 12 H), 0.52 (t, 4 H), 0.92 (t, 6 H), 1.30 (m, 24 H); IR (NaCl plate) 2975 (s), 2900 (s), 2875 (m), 1900 (w), 1600 (w), 1460 (m), 1400 (w), 1375 (w), 1325 (w), 1250 (m), 1175 (w), 1075 (s), 850 (s), 800 (s), 450 (s) cm^{-1}.

One-Vessel Preparation of Cyclic Cosiloxanes. Into a 2-L round-bottomed flask were placed 150 g of poly(methylhydrogensiloxane), 750 g of octamethylcyclostetrasiloxane, and 150 g of poly(dimethylsiloxane) with octyldimethylsilyl end group. The latter was prepared by the redistribution of 1,3-dioctyl-1,1,3,3-tetramethyldisiloxane (10 g) and octamethylcyclotetrasiloxane (140 g) using trifluoromethanesulfonic acid (0.1 g) as catalyst.[12] The reaction mixture was stirred at room temperature, and a 2-g portion of trifluoromethanesulfonic acid was added to the flask. The reaction mixture was kept at room temperature for 2 h, during which time the cloudy mixture became viscous. The cyclic mixture was stripped from the reaction mixture using a rotary evaporator at a pressure of approximately 15 mmHg produced by a mechanical pump equipped with a trap cooled by liquid nitrogen. The water bath was maintained at 85 °C. The receiving flask contained MgO and was cooled with a dry ice/isopropyl alcohol bath. After 30 min, the removal of cyclics was noticeably slower and the fluid had clarified. The equilibration flask was disconnected from the rotary evaporator. Upon exposure to the air the fluid became cloudly as it had been before stripping. The flask was shaken, reconnected to the rotary evaporator, and the stripping repeated until it again slowed considerably. By multiple strippings, a total of 950 g (90.5% yield) of cyclic mixtures was obtained.

Two-Vessel Preparation of Cyclic Cosiloxanes. A 200-mL round-bottomed flask was charged with 112.5 g of polydimethylsiloxane and 37.5 g of poly(methylhydrogensiloxane) such that the ratio of dimethylsiloxy to methylhydrogensiloxyl units was 3:1. After trifluoromethanesulfonic acid (0.15 g) was added, the mixture was stirred for 1 h at room temperature. The formation of cyclosiloxanes was indicated by gas chromatography. The mixed cyclosiloxanes were separated from the equilibrated siloxane fluid using the apparatus shown in Figure 1, where the length of the column was 6.8 cm and the diameter was 2.0 cm. The siloxane fluid from the equilibrating flask was siphoned into the system and passed through the column, which was heated at 125 °C under vacuum (2 mmHg) with a constant stream of nitrogen bubbled through the fluid. The cyclosiloxanes were collected in a receiving flask which contained 0.8 g of MgO and cooled with a dry ice/isopropyl alcohol bath. The recovered linear portion was drained from the bottom of the column into another receiving flask. The linear fluid was then transferred back into the equilibrating flask and reintroduced into the stripping column. The quantity of fluid within the column was controlled by setting the inlet and outlet valves at the top and bottom of the column, respectively. The valves were set such that the rate at which the condensed cyclic mixture dropped into the receiving flask was perceived to be maximized. Periodically, the small contents of a trap between the condenser and the vacuum pump were returned to the equilibrating flask. The fluid was recycled until little cyclosiloxane could be isolated. This occurred when the quantity of fluid was not sufficient to maintain equilibrium in the column. A total of 133 g of cyclosiloxanes (89% yield) was obtained.

Continuous Preparation of Cyclic Cosiloxanes. An equilibrated fluid which contained 3000 g of polydimethylsiloxane, 1000 g of poly(methylhydrogensiloxane), and 2 mL of trifluoromethanesulfonic acid was stripped of cyclosiloxanes using a column of larger dimensions (106 cm in length and 3.5 cm in diameter). The fluid was passed through the column such that the cyclosiloxanes were collected at a rate of approximately 2 mL

---

[10] Noll, W. In *Chemistry and Technology of Silicones*; Academic Press: New York, 1968, Chapter 5.

[11] Wright, P. V. In *Ring-Opening Polymerization*; Ivan, K. J., Saegusa, T., Eds.; Elsevier: New York, 1984; Vol. 2.

[12] **Warning!** The substitution of a base for the acids used in this study can lead to the explosive formation of hydrogen gas.

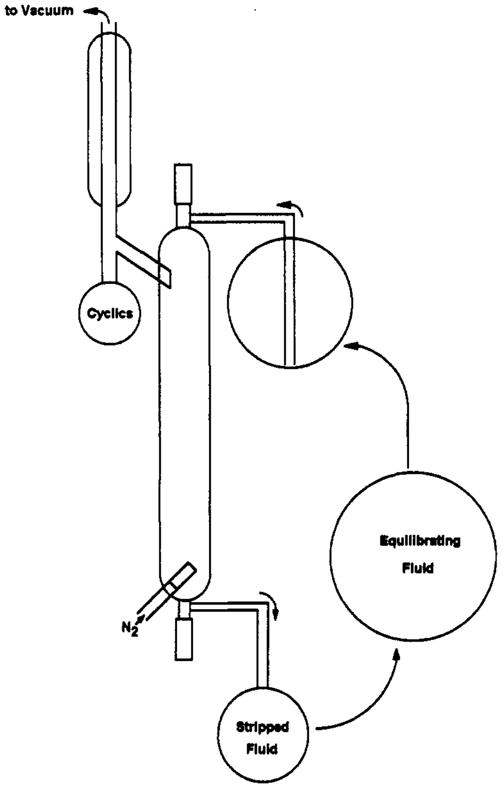


Figure 1. Apparatus for the continuous stripping of cyclosiloxanes.

min^{-1}. The stripping was carried out continuously until 3690 g (92% yield) of the original fluid was converted into mixed cyclosiloxanes. The equilibrating fluid was then charged with an additional 750 g of polydimethylsiloxane and 250 g of poly(methylhydrogensiloxane)s. An additional 1016 g of mixed cyclosiloxanes was recovered after the second charge (102% of the second charge).

Preparation of Cyclomethylhydrogensiloxanes. Cyclics were stripped from a 500-mL round-bottomed flask containing a mixture of 350 g of poly(methylhydrogensiloxane), 5.0 g of 1,3-dioctyl-1,1,3,3-tetramethyldisiloxane, and 1.0 g of trifluoromethanesulfonic acid using a rotary evaporator at a pressure of approximately 15 mmHg and a water bath temperature of 85 °C. The receiving flask contained 0.5 g of MgO and was cooled by a dry ice/isopropyl alcohol bath. After 150 g of volatile siloxanes was collected a gas chromatographic analysis of the fluid was performed which displayed a sizable portion of linears, and the stripping was stopped. The volatile siloxane fluid was centrifuged and the liquid decanted from the solid MgO, and 0.5 g of trifluoromethanesulfonic acid was added to the fluid. After the fluid became viscous, cyclics were stripped from the mixture as before. After 92 g of cyclics were collected a gas chromatographic analysis of the isolated fluid indicated that the mixture consisted almost exclusively of cyclosiloxanes.

Cyclocosiloxane mixtures were analyzed by gas chromatography using a Hewlett-Packard 5890A equipped with a 30-ft wide-bore capillary column (Restek Rx-X1) and a thermal conductivity detector employing a temperature gradient of 10 °C/min after 1 min at 45 °C and continued until the temperature reached 300 °C. A 6 ft × $^1/_8$ in. column packed with 3% OV-17 (Alltech) employing a gradient of 10 °C/min after 1 min at 60 °C and continued until the temperature reached 300 °C was used for the analysis of the stripped methylhydrogensiloxane oligomers. Integrations were carried out using a Hewlett-Packard 7890 recording integrator. Integrations of chromatography traces from mixtures of cyclics isolated by fractional distillation indicated that the relative areas of peaks were nearly proportional to mass. A GE GN300 nuclear magnetic resonance spectrometer was used to record ^{1}H NMR spectra. A Mattson 4020 FTIR was used to record the IR spectrum.

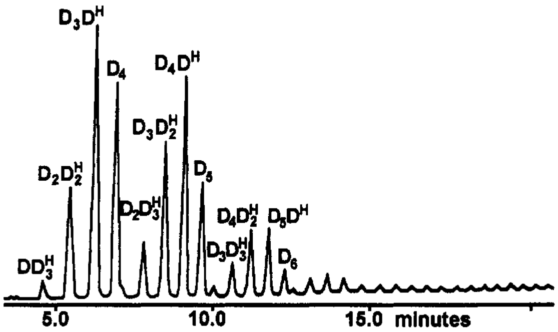


Figure 2. Gas chromatographic trace for the mixture of cyclosiloxanes in equilibrium with a copolymer with a 3:1 ratio of dimethylsiloxy (D) to methylhydrogensiloxy (D^H) units.

Table I. Distribution of Cyclic Tetramers and Pentamers in the Equilibrated Fluid

cyclic[a]	calculated[b]	determined[c]
D_4^H	0.004	
DD_3^H	0.049	0.04
$D_2D_2^H$	0.211	0.20
D_3D^H	0.422	0.44
D_4	0.316	0.32
D_5^H	0.001	
DD_4^H	0.015	
$D_2D_3^H$	0.088	0.10
$D_3D_2^H$	0.264	0.28
D_4D^H	0.396	0.40
D_5	0.237	0.22

[a] D and D^H refers to dimethylsiloxy and methylhydrogensiloxy unit respectively. [b] Determined by a binomial equation on the mole fraction of the two comonomer units.[6] [c] Calculated from the GC areas of like-sized rings.

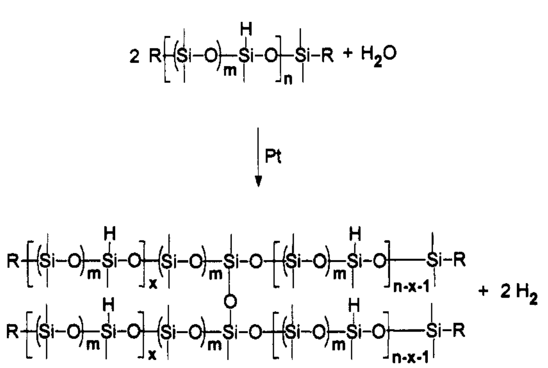
Results and Discussion

The redistribution of dimethylsiloxane gruops and methylhydrogensiloxane groups occurred rapidly by the addition of 0.2 wt % trifluoromethane sulfonic acid regardless of the source of the comonomer units. After 1 h, equilibrated fluids prepared from cyclic tetramers or from high molecular weight fluids were analyzed by gas chromatography (Figure 2). Cyclic compositions were observed which displayed a random distribution of comonomer units[6] (Table I) and produced quantities of cyclosiloxanes similar to those reported for cyclosiloxanes in equilibrium with high molecular weight poly(dimethylsiloxane).[5] Gas chromatographic analyses of this type are sensitive to the extent of reaction. Compositions of mixed cyclics which closely approximate the equilibrium compositions are not achieved until late in the redistribution reaction.

The initial reaction mixtures were prepared using 1,3-dioctyl-1,1,3,3-tetramethyldisiloxane. It was added to end-cap the mixture where the primary source of dimethylsiloxy units was octamethylcyclotetrasiloxane. This particular disiloxane was used for three reasons. The first reason was simply to control the viscosity of the resulting fluid by lowering the molecular weight of the resulting polymer. Second, small amounts of Si–H bond hydrolysis and subsequent condensation of the silanols have been observed under similar conditions, where pentaalkyldisiloxanes were disproportionated leading to the formation of trisiloxanes and higher oligomers.[13] If such reactions occur in this system, trifunctional units are formed (eq 2). The presence of monofunctional groups up to approxi-

---

(13) Swint, S. A.; Buese, M. A. *J. Organomet. Chem.* **1991**, *402*, 145.



(2)

mately 5 mol % of all functional groups will decrease the molecular weight of the linears while imposing little penalty in the quantity of cyclics which are formed.[14] The greater the concentration of monofunctional units in the system, the larger the amount of Si–H hydrolysis that the fluid can tolerate before the average functionality of the system exceeds two and gelation occurs. The third purpose for the disiloxane was to decrease the proportion of volatile linear siloxanes in the mixture. The molecular weight of the methylhydrogensiloxane fluid was 2270; therefore, the ratio of octyldimethylsilyl to trimethylsilyl end groups was 1:2. Since the two end-caps of a linear will be randomly chosen, only 44% ($0.67^2 \times 100\%$) of the linears have two trimethylsilyl end groups at the beginning of the stripping process. Since the asymmetric disiloxane, octylpentamethyldisiloxane, is less volatile than dodecamethylcyclohexasiloxane and does not distill under the stripping conditions, considerably less contamination of the stripped cyclics by small linears should be observed, even at relatively high degrees of depropagation, than in the absence of the added octyldimethylsiloxy groups.

Cyclic mixtures were isolated using a rotary evaporator. Cyclosiloxane collection was initially rapid. The cloudiness of the polysiloxane fluid which appeared upon addition of the acid dissipated within minutes after the initiation of the stripping process. The rate of cyclosiloxane removal dropped noticeably after the fluid clarified. When removed from the heating bath and opened to the atmosphere the cloudiness quickly returned, appearing first at the air surface and migrating slowly through the fluid. Rapid stirring restored the entire fluid to its original cloudy state. Aliquots of the clear stripped fluid taken immediately after removal from the rotary evaporator and mixed with MgO were nearly free of cyclosiloxanes, as indicated by gas chromatography. Once cloudy, the equilibrium cyclic composition was reestablished in the polysiloxane fluid within 5 min. The fluid was immediately placed back onto the rotary evaporator and the stripping process was repeated. Nearly identical observations were made with each repetition of the procedure.

Approximately 8% of the fluid was removed as cyclosiloxanes during every period of stripping. This is similar to the weight fraction of the stripped cyclics at equilibrium with linears in the presence of an active redistribution catalyst.[11] This implies that the catalyst deactivated soon after heating and vacuum were applied. Though litmus paper indicated the presence of acid[15] at the inlet to the receiving flask and MgO was required to prevent a slow polymerization of the collected cyclics, the majority of the catalyst appeared to remain in the polysiloxane fluid. The deactivation at high temperature and low pressure and activation upon exposure to the atmosphere was consistent with loss and absorption of water rather than a catastrophic loss of trifluoromethanesulfonate. Substituting a nonvolatile perfluorinated ion-exchange resin (nafion) at a 10-fold wt % level for trifluoromethanesulfonic acid gave similar behavior, although the rate at which the equilibrium cyclic concentration was reestablished was considerably slower.

The composition of the stripped cyclic mixture differed slightly from that which was in equilibrium with the fluid. It was nearly identical in the proportion of methylhydrogensiloxy units as the original equilibrated fluid but was slightly more enriched in smaller cyclics. This most likely resulted from the greater volatility of smaller cyclics. Cyclic tetramers were the largest porition of the mixture, although cyclics up to the nonamer were included. The stripped cyclics contained very little cyclic trimers. This is in contrast to the observations of Crivello[2a] using acid zeolites and considerably higher temperatures. The use of hot zeolites (>400 °C) resulted in depropagation within the stripping apparatus under conditions where the amount of liquid was kept low and where all cyclosiloxane products were gases. Under those conditions large amounts of cyclic trimers were formed, probably under almost exclusively kinetic control. In contrast, the equilibrium concentration of cyclosiloxanes was established prior to stripping, and the analysis of the stripped fluid indicates that the cyclosiloxanes were isolated in a similar composition. This difference suggests that most of the depropagation occurred prior to heating and evacuating the vessel to strip the cyclics from the fluid. Hence, one may consider this method as a complimentary, nearly thermodynamically controlled process to that of acid zeolite catalyzed depropagation.

The reaction was then carried out using the apparatus shown in Figure 1. By using a series of runs, a high proportion (89%) of the fluid was converted into cyclics. The process was stopped at that conversion since the amount of cyclics isolated in the last runs was becoming very small. Analysis of the fluid indicated that the cyclics were still present and the fluid was able to initiate the redistribution of fresh fluid. Approximately 7% of the fluid was stripped for each pass of the fluid through the stripping apparatus (Table II). Those passes immediately after the additions of the contents of the trap had slightly higher yields than other passes, suggesting that some redistribution was occurring within the apparatus. The composition of the cyclics isolated from the initial stripping was richer in Si–H groups than those from the last stripping (Table III). The ratio of dimethylsiloxy to methylhydrogensiloxy units in the fluid changed from 2.7:1 to 4:1 from the first to the last stripping as indicated by ^{1}H NMR spectra. The combined cyclics from all strippings had cyclic tetramers in nearly the same proportions as the initial equilibrated fluid. Likewise, the proportions of the different cyclic pentamers were similar to those of the initial fluid. In contrast, the proportion of the different ring sizes, for example total tetramer to total pentamer, was somewhat richer in the more volatile, smaller, ring. Though the fluid lost the more volatile methylhydrogensiloxy rich cyclic most readily, the proportion of cyclics in the remaining fluid became successively richer in dime-

---

(14) Buese, M. A. *Macromolecules* **1987**, *20*, 694.

(15) It is possible under these conditions that the volatile species is not trifluoromethanesulfonic acid but is rather a volatile silyl ester such as (trimethylsilyl)trifluoromethanesulfinate.

Table II. Yield of Cyclosiloxanes for Each Pass of Fluid through the Stripping Apparatus

no. of pass[a]	wt equilibrated fluid (g)	wt cyclics (g)	isolation yield[b] (wt %)
1	150.0	4.3	2.8
2	145.7	10.9	7.5
3	134.1	10.8	7.5
4	123.3	8.6	6.5
5	114.5	6.9	6.0
6*	107.6	9.3	8.6
7	98.3	6.8	6.9
8	91.5	5.1	5.5
9*	86.4	6.7	7.9
10	79.8	5.8	7.3
11	73.9	5.0	6.7
12*	67.2	5.4	8.1
13	61.7	4.2	7.9
14	57.2	4.0	7.0
15	53.2	4.2	7.9
16*	49.0	4.3	8.7
17	44.6	3.8	8.5
18	40.8	3.4	8.2
19	37.4	3.1	8.3
20	34.3	2.4	7.0
21	32.0	2.0	6.7
22	30.0	2.0	6.7
23*	28.0	2.2	8.1
24	25.8	2.1	7.9
25	23.8	1.6	6.6
26	22.2	1.5	6.7
27*	20.7	1.3	6.2
28	19.4	1.2	5.9
29	18.2	1.0	5.5

[a] The pass marked with asterisks were after the contents of the trap were returned to equilibrating fluid. [b] For each pass.

Table III. Change in the Cyclic Composition during the Stripping Process

	equilibrated fluid	stripped cyclic mixture		
		first strip	last strip	overall
DD_3^H	2.0	2.7	1.4	2.0
$D_2D_2^H$	10.4	14.8	9.4	11.9
D_3D^H	22.3	30.1	24.0	26.7
D_4	16.3	19.2	19.8	18.2
total 4mer	51.0	66.8	54.6	58.8
$D_2D_3^H$	3.5	3.9	3.7	3.9
$D_3D_2^H$	10.5	9.7	11.3	10.8
D_4D^H	14.0	10.5	14.5	12.9
D_5	6.7	3.9	6.2	5.3
total 5mer	34.7	28.0	35.7	32.9
$D_2D_4^H$	0.5	0.3	0.4	0.4
$D_3D_3^H$	1.9	1.0	1.6	1.4
$D_4D_2^H$	3.7	1.6	2.9	2.3
D_5D^H	3.4	1.1	2.3	1.9
D_6	1.3	0.3	0.8	0.6
total 6mer	10.8	4.3	8.0	6.6
$D_4D_3^H$	0.7	0.2	0.5	0.5
$D_5D_2^H$	1.0	0.4	0.6	0.6
D_6D^H	1.1	0.2	0.4	0.4
D_7	0.7	0.1	0.2	0.2
total 7mer	3.5	0.9	1.7	1.7

thylsiloxy units. Therefore by carrying the process to high conversion, the shift in the equilibrium composition to dimethylsiloxy-rich cyclics compensated for the differences in volatility of the cyclics, and the combined cyclic mixture was nearly the same as the comonomer composition of the original fluid.

Table IV. Yields of Cyclosiloxanes for Various Stripping Conditions

	rotary evaporator	stripping apparatus		
		batch	first charge	second charge
no. of strippings	40	29	continously	continously
yield (wt %)	90.5	88.5	92	102
g of cyclics/g of acid	9500	886	1845	2353[a]

[a] For combined charges of siloxanes.

Using a larger stripping column, a much greater rate of stripping was achieved. In virtually all respects the results were otherwise equivalent to those observed with the smaller column. This was anticipated since the siloxane redistribution reaction occurs without an accompanying exotherm.[11] The greater rate was most probably due solely to the increase in volume and surface area that could be achieved in the larger column. The process was carried out continuously. Three flasks were used in conjunction with the stripping column. One flask was for the introduction of fluid which had reached equilibrium. The other two flasks were used to collect the fluid sequentially. When one flask was filled from the outlet of the stripping column, the other was put in its place. The fluid that was removed was permitted to cool to room temperature, the flask was shaken, and the fluid was then returned to the flask from which fluid was introduced into the stripper. Between the top of the condenser and the vacuum pump were two liquid nitrogen traps in parallel. Periodically the path was switched between the traps and the acidic contents of the trap that was removed were returned to the equilibrating fluid.

Once a fluid was reduced to less than 10% of its original volume (92% yield of cyclics), fresh fluid was placed in the flask. No additional catalyst was needed. The resulting fluid was easily reduced to approximately the volume of the fluid which was present after the initial stripping. In this manner, essentially quantitative conversion of linear fluid to cyclics (102% yield based on solely the second charge of siloxane fluids) was achieved. The advantage of pursuing such a recycling approach is indicated in Table IV. Not only can cyclics be isolated more rapidly, but the effective yield and the effective catalyst turnover, grams of cyclosiloxane per gram of trifluoromethanesulfonic acid, can be increased significantly.

There are inherent limits to the process due to the molecular weight of the linears in equilibrium with the cyclics. Since the amount of cyclosiloxanes formed in this process is dependent on the molecular weight of the linears in equilibrium with the cyclics,[14,16] it is necessary to use fluids which exceed some minimal molecular weight. As the molecular weight of the linear fraction drops, the probability of stripping cyclics contaminated by small linears increases if the chain ends are volatile. Both of these limitations were encountered when attempting to isolate cyclic oligomers with only methylhydrogensiloxy groups. The poly(methylhydrogensiloxane) fluid that was used was capped with trimethylsilyl end groups and was reported to have a number average molecular weight of 2270, which is equivalent to 35 methylhydrogensiloxy groups per hexamethyldisiloxane residues per chain. By the addition of 1,3-dioctyl-1,1,3,3-tetramethyldisiloxane the proportion of chain ends was increased by 5.5%, which should decrease the weight of volatile linears by 7%[17] and

---

(16) (a) Carmichael, J. B.; Heffel J. *J. Phys. Chem.* **1965**, *69*, 2218. Scott, D. W. *J. Am. Chem. Soc.* **1946**, *68*, 2294.

(17) Calculated as the mole fraction of linears up to the 15mer (the largest observed by gas chromatography) assuming random placement of the two chain ends, a reduction in the degree of polymerization of the linear polymer to 33, and a normal molecular weight distribution.

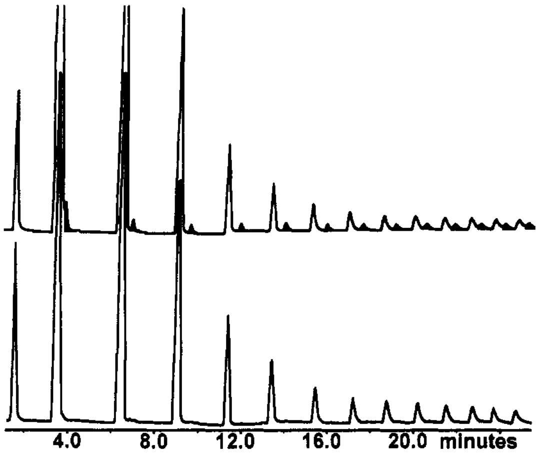


Figure 3. Gas chromatographic traces for the cyclomethylhydrogensiloxanes (open peaks) and trimethylsilyl-capped linears (filled peaks) stripped from a commercially available low molecular weight poly(methylhydrogensiloxoxane) with added 1,3-dioctyl-1,1,3,3-tetramethyldisiloxane (top) and those stripped from that cyclic mixture after its polymerization (bottom).

the weight of volatile cyclics by 1%.[18] More nonvolatile disiloxane was not added, since the decrease in the weight of volatile linears by increasing the nonvolatile proportion of a given sized linear is ultimately negated by the accompanying decrease in the molecular weight of the linears. This increases the fraction of small volatile linears. The fraction of volatile cyclics drops significantly after the degree of polymerization diminishes below approximately 20. After stripping 42% of the mass of the equilibrating flask, the rate of removal had slowed. The degree of polymerization of the linears in equilibrium with the cyclics was approximately 18 after that conversion. As seen in Figure 3, the cyclosiloxanes isolated by stripping were contaminated with linears that were approximately 4% by weight and had a number average degree of polymerization of approximately 5 as calculated from their area in the chromatographic trace. Stripping was stopped at that point, and the isolated siloxanes were redistributed by the addition of trifluoromethanesulfonic acid. The viscosity increase observed for the fluid was qualitatively consistent with the composition of approximately 180 methylhydrogensiloxy units to 1 hexamethyldisiloxane equivalent that was calculated from the areas under the chromatographic trace. The linear polymer at equilibrium would have an average degree of polymerization of approximately 165. As seen in Figure 3, the cyclosiloxanes stripped from that mixture were nearly free of linears. Hence, by recycling the stripped fluid, low molecular weight fluids could be converted into high molecular weight fluids and ultimately into pure cyclosiloxanes.

The composition of cyclo(methylhydrogensiloxane) oligomers of the final stripping was similar to that reported for cyclics in equilibrium with high molecular weight polymer with the exception of the cyclic trimer. Unlike the mixed cyclic oligo(dimethyl-*co*-methylhydrogensiloxane)s where the trimer was essentially absent, trimer constituted approximately 5% of the initially stripped mixture and 3% of the final cyclic mixture. This indicates that some redistribution probably occurred during stripping and suggests that the molecular weight of the linears and/or the viscosity of the equilibrating fluid affects the proportion of trimer stripped from the mixture. Nevertheless, the amount of trimer was much less than that observed at high temperatures over zeolites.[2a]

In summary, a continuous depropagation method for the preparation of mixed cyclosiloxanes has been developed. It results in very high yields using relatively low catalyst concentrations and temperatures. The degree of polymerization of the linears in the fluid from which the cyclics are isolated should be low enough that the fluid is not too viscous to be readily transferred into and from the stripping column but must be sufficiently high that volatile linears are not a significant portion of the stripped mixture. By the use of nonvolatile disiloxane and by recycling the stripped siloxanes or components of the stripped siloxanes after removal of a desired component, the quality of the equilibrating fluid can easily be maintained. The cyclics were formed in a ratio of comonomers virtually identical to that of the feed if the conversion was high. Little cyclic trimer was produced.

Acknowledgment. We gratefully acknowledge support for this research, which was partially funded by the Pennsylvania Commonwealth's Ben Franklin Partnership Program and partially funded by Dentsply International.

---

[18] Calculated as the sum of the cyclic 4mer through 15mer where their concentration was equal to [$x$mer] = $K_x p^x$ where $p = 1-1/33$ and the values of K_x were taken from: Semlyen, J. A.; Wright, P. V. *Polymer* **1970**, *11*, 462.