Polymerization of 1,3,5-Tri(1,3,5,7-tetra)-methyl-1,3,5-tri(1,3,5,7-tetra)-10-carbomethoxydecylctri(tetra)siloxane

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ABSTRACT

The cationic and anionic polymerization of 1,3,5-tri(1,3,5,7-tetra)methyl-1,3,5-tri(1,3,5,7-tetra)-10-carbomethoxydecyl-cyclotri(tetra)siloxane, catalyzed by sulfuric acid and alkali metal naphthalenes, respectively, was studied. With sulfuric acid the polymer yield increased with increasing catalyst concentration, while the molecular weights decreased. With potassium naphthalene the polymerization reaction was first order to monomer, and the molecular weights increased linearly with increasing the percent conversion in accordance with a "living" polymerization. In both cases the polymerization was an equilibrium reaction and the conversion was about 85%. Only low molecular weight polymers were obtained due to steric effects of the bulky long-chain substituents.

INTRODUCTION

The polymerization of cyclic siloxanes into higher molecular weight linear polymers is well known. This is usually accomplished by means of strong acids or bases [1-4] which are presumably capable of opening the ring by bond cleavage. Polysiloxanes such as polydimethylsiloxane possess unique properties of high water repellency, good electrical insulating properties, and low degree of variation of viscosity with temperature. While methyl silicones are by far the most commonly used, other alkyl silicones have particular properties which may lead to specialized uses. In general, as the size of the substituent on silicon is increased, the capability of forming stable high molecular weight polymers from the organocyclosiloxanes is decreased. Substituent size effect may be particularly illustrated by the case of diethylsubstituted organocyclosiloxanes. Under ordinary conditions these compounds are not converted to high polymers [5]. Another interesting case is that of di-t-butylsilane diol, which has never been converted to either a linear or cyclic poly(di-t-butylsiloxane) [6].

It was interesting to study the polymerization of 1,3,5-tri(1,3,5,7-tetra)-methyl-1,3,5-tri(1,3,5,7-tetra)-10-carbomethoxydecylcyclotri(tetra)siloxane. This mixture of approximately 1:1 of tri- and tetrasiloxanes was obtained by addition of dimethylchlorosilane to methyl undecenoate [7] and cyclization of the product [8, 9] to cyclic siloxane by controlled hydrolysis. These cyclosiloxanes have a bulky substituent which can, on the one hand, affect the ability of the monomer to polymerization, and on the other hand, the presence of the long-chain substituent may lend interesting physical properties to the polymer. These polymers may offer new possibilities for the utilization of vegetable oil derivatives.

EXPERIMENTAL

Materials

THF (Frutarom) was purified as previously described [10]. Sulfuric acid, analar (98%) (BDH), was used. 1,3,5-Tri(1,3,5,7-tetra)methyl-1,3,5-tri(1,3,5,7-tetra)-10-carbomethoxydecylcyclotri(tetra)siloxane, which is approximately a 1:1 mixture of tri- and tetracyclosiloxanes, was prepared and purified as previously described [8]. The alkali metal-naphthalene was prepared as before [10].

Acidic Polymerization of 1,3,5-Tri(1,3,5,7-tetra)methyl-1,3,5-tri(1,3,5,7-tetra)-10-carbomethoxydecylcyclotri(tetra)siloxane

Sulfuric acid (0.4×10^{-3} mole) was added at room temperature ($25°C$) to the cyclosiloxane (2×10^{-3} mole) in bulk without solvent. After 4 hr the polymerization system became immobile due to the viscosity increase. After completion of polymerization (overnight) (equilibrium reaction), the reaction mixture was diluted with CCl_4, washed with water, and dried over $CaCl_2$. The polymer (viscous oil) was precipitated by addition of petroleum-ether, and unreacted monomer was recovered on evaporation of solvents.

The conversion of monomer to linear polymer was about 82%.

Anionic Polymerization of 1,3,5-Tri(1,3,5,7-methyl-1,3,5,-tri(1,3,5,7-tetra)-10-carbomethoxydecylcyclotri(tetra)siloxane

The polymerization was carried out in a flask which was dried by flaming twice in vacuo, and filled with nitrogen. A typical experiment is given below. Potassium naphthalene (0.0625 mole/liter) was added at room temperature ($25°C$) to a 50% solution of the cyclosiloxane (3.75 moles/liter) in tetrahydrofuran under nitrogen. The characteristic green color of the reagent slowly changed to brown or reddish-brown, depending on catalyst concentration, and the viscosity of the solution increased markedly within 2 to 4 hr. The color of the solution persisted indefinitely until destroyed by the addition of an equivalent amount of HCl as terminating agent. The mixture was filtered and heated in vacuo on a boiling water bath to distill off the solvent and most of the naphthalene present. Petroleum ether was added to precipitate the linear polysiloxane and dissolve the unreacted monomer. The cyclosiloxane was found to have polymerized to an equilibrium conversion of about 86%.

Rate Measurements

The polymerizations were carried out as before. They were terminated after the required time by the addition of an equivalent amount of HCl. The polymerization mixture was evaporated to dryness and the degree of conversion was determined by precipitation of the polymer by petroleum ether. By this procedure the monomeric cyclosiloxane remains in solution, and it can be isolated by evaporation of the petroleum ether and purified using a column packed with activated aluminum oxide, neutral (20% water), and elution with ether-chloroform (1:1).

Number-Average Molecular Weights

The number-average molecular weights of polysiloxanes were determined by the cryoscopic method using CBr_4 [11] and calculated by

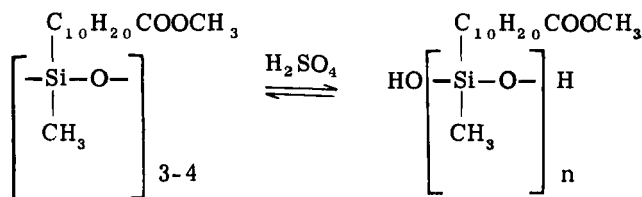$$\overline{M}_n = \frac{87,000m}{\Delta tm'}$$

where m is the weight of polymer, m' is the weight of CBr_4, and Δt is the decrease in melting point (°C).

The number-average molecular weights were also determined by vapor pressure osmometry.

RESULTS AND DISCUSSION

Acidic Polymerization

In the acidic polymerization, sulfuric acid was added at room temperature to the cyclic siloxane in bulk without solvent:

$$\begin{bmatrix} & C_{10}H_{20}COOCH_3 \\ & | \\ -Si-O- \\ & | \\ & CH_3 \end{bmatrix}_{3-4} \xrightarrow{\text{H}_2\text{SO}_4} \rightleftharpoons HO\begin{bmatrix} & C_{10}H_{20}COOCH_3 \\ & | \\ -Si-O- \\ & | \\ & CH_3 \end{bmatrix}_n H$$

In this case the final conversion of cyclic monomer to linear polysiloxane was about 82% (Fig. 1), and after 4 to 7 hr the polymerization system had become immobile due to the viscosity increase.

The polymer yield increased with increasing the H_2SO_4 concentration (Fig. 2, Table 1), and the molecular weights decreased.

Anionic Polymerization

Electron transfer complexes of alkali metals with polynuclear aromatics were found to be efficient as anionic polymerization initiators for cyclic siloxanes [12, 13].
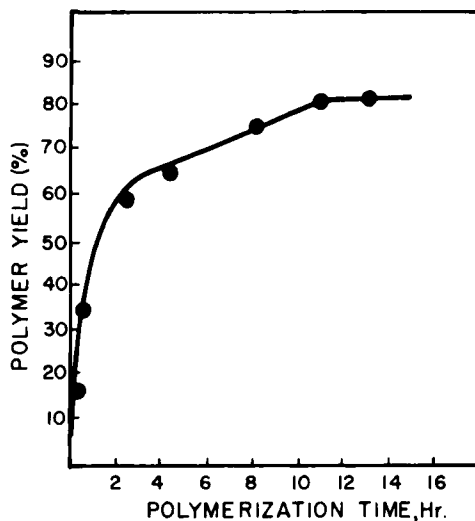
FIG. 1. H_2SO_4 catalyzed polymerization of 1,3,5-tri(1,3,5,7-tetra)methyl-1,3,5-tri(1,3,5,7-tetra)-10-carbomethoxydecyclcyclo-tri(tetra)siloxane (monomer, 2 mmole; catalyst, 0.7 mmole).
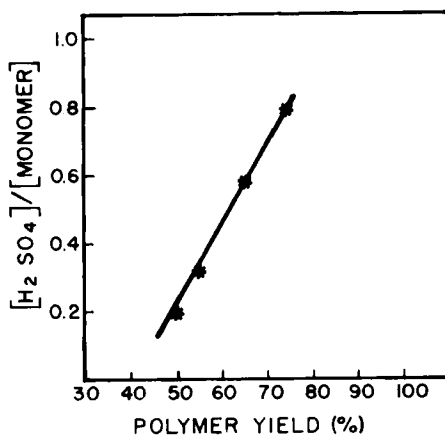
FIG. 2. Variation of polymer yield with the catalyst concentration (polymerization time, 4 hr; monomer amount, 2 mmole).

TABLE 1. Acidic Polymerization of 1,3,5-Tri(1,3,5,7-tetra(methyl-1,3,5-tri(1,3,5,7-tetra)-10-carbomethoxydecycyclotri(tetra)siloxane[a]

H_2SO_4 (mole)	Yield (%)	(η)[b](dl/g)	$\overline{M}_n$[c]
1.6×10^{-3}	74	0.08	1550
1.2×10^{-3}	65	0.15	2480
0.6×10^{-3}	58	0.24	3140
0.4×10^{-3}	52	0.30	3650

[a]Experimental conditions: concentration H_2SO_4 was added to the monomer (2×10^{-3} mole) at 25°C, polymerization time 4 hr.
[b]The intrinsic viscosity was determined in benzene at 25°C
[c]Determined by vapor pressure osmometry.

In the present polymerization we used potassium naphthalene as initiator. It was added at room temperature (25°C) to a 50% solution of the cyclic siloxane in THF. The viscosity of the mixture increased markedly within 2 to 4 hr, and the solution developed a brown color which persisted indefinitely until destroyed by the addition of methyl iodide or an equivalent of hydrochloric acid as terminating agent.

The polymerization was first order to monomer concentration as seen from the linear plots of log M_0/M_t (where M_0 is the initial monomer concentration and M_t is the concentration at time t) vs time (Fig. 3).

The molecular weights increased linearly with an increasing percent of conversion (Fig. 4) in accordance with a "living" polymerization [14]. The number-average molecular weights were determined by the cryoscopic method (in CBr_4), and it was found that the molecular weights obtained were not high (about 2000 to 4000) in contrast to the polymerization of hexamethylcyclotrisiloxane, perhaps due to the steric effect of the long-chain alkyl group attached to the silicon. This order of molecular weights shows that actually only 2 to 5 cyclic siloxane monomer units were added one to the other during the polymerization. All the polymers were viscous oils.

Lithium naphthalene was a much weaker catalyst than potassium naphthalene, and even after 1 week reaction time no significant polymerization was observed. This is similar to what was found in the respective polymerization with ethylene oxide [15, 16]. The inactivity of the Li-metal in epoxide polymerization has been explained as being due to extremely strong association of active centers [16].
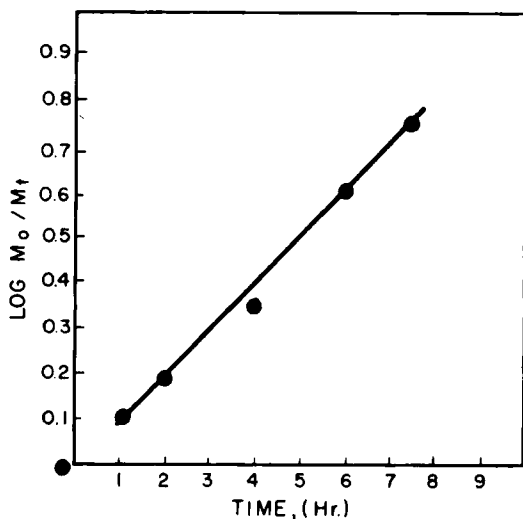
FIG. 3. Potassium naphthalene polymerization of 1,3,5-tri(1,3,5,7-tetra)methyl-1,3,5-tri(1,3,5,7-tetra)-10-carbomethoxydecylcyclo-tri(tetra)siloxane. Plot of log M_0/M_t vs time. [Potassium naphthalene], 0.625 mole/liter; [monomer], 3.750 moles/liter.
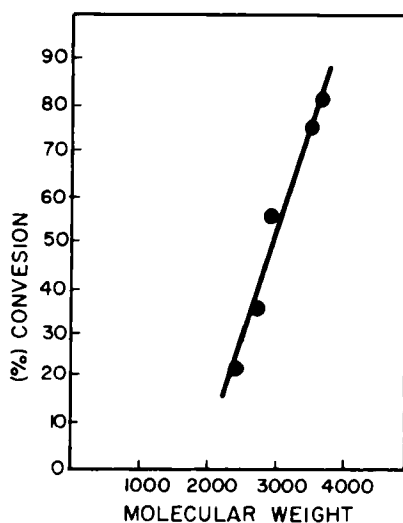
FIG. 4. Anionic polymerization of 1,3,5-tri(1,3,5,7-tetra)methyl-1,3,5-tri(1,3,5,7-tetra)-10-carbomethoxydecylcyclotri(tetra)siloxane. Plot of molecular weight vs percent conversion. [Monomer], 3.750 mole/liter; [potassium naphthalene], 0.0625 mole/liter.
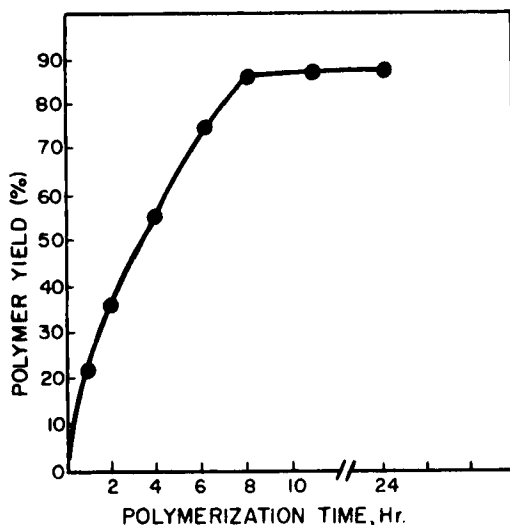
FIG. 5.   Potassium naphthalene polymerization of 1,3,5-tri(1,3,5,7-tetra)methyl-1,3,5-tri(1,3,5,7-tetra)-10-carbomethoxydecylcyclo-tri(tetra)cycloxanes in THF. [monomer], 3.750 mole/liter; [potassium naphthalene], 0.0625 mole/liter.

The cyclosiloxane was found to have polymerized to an equilibrium conversion of about 86% (Fig. 5). An equilibrium conversion of 84% was found on carrying out the potassium naphthalene-catalyzed polymerization at 0°C.

We also investigated the equilibrium depolymerization of the poly-methyl-10-(carbomethoxydecyl)cyclosiloxane. Potassium naphthalene was added to the pure polymer in THF solution (25°C). After 24 hr the polymer solution was neutralized with HCl, and cyclic monomer (about 10 to 18%) was found in the reaction mixture. The depolymeriza-tion was also investigated with H_2SO_4 (in ether) at room temperature (25°C). The amount of cyclic monomer in the equilibrium mixture was about 16%. It was possible to stabilize the polymer by blocking the active Si—OH groups by methylation. In the anionic polymerization this blocking was best carried out by adding methyl iodide for termina-tion at the end of the polymerization.

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