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Cationic Ring-Opening Polymerization of Cyclosiloxanes Initiated by Electron-Deficient Organosilicon Reagents[1a]

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ABSTRACT: The cationic ring-opening polymerization of octamethylcyclotetrasiloxane initiated by $R_3SiH-Ph_3C^+B(C_6F_5)_4^-$ (trityl TPFPB) in the absence of protic acids has been investigated. Mechanistic studies demonstrate that the polymerization proceeds by a single "long-lived" oxonium ion end. This novel polymerization is distinct from those initiated by protic acids. Cyclotrisiloxanes containing vinyl or trifluoropropyl groups could be polymerized in a similar manner, while the homopolymerization of trimethyltriphenylcyclotrisiloxane failed. The method has also been extended to the preparation of siloxane-containing diblock copolymers and comblike branched polysiloxanes.

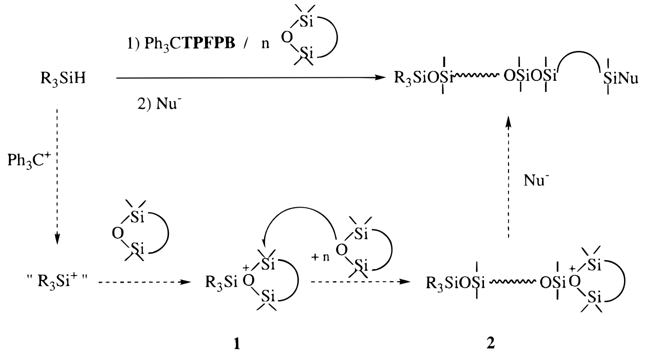
Introduction

In our recent studies of silyloxonium ions, we briefly stated that hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4) were polymerized in the presence of trisilyloxonium ions **1**, which were formed *in-situ* via Corey hydride transfer.[1b,2] We also proposed a mechanism for the novel polymerization reaction (see Scheme 1).

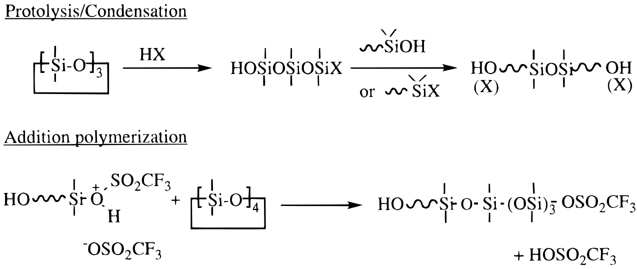
This novel polymerization, which appeared distinct from generally known cationic polymerizations of cyclosiloxanes, is of substantial interest from mechanistic and synthetic points of view. Although cationic ring-opening polymerization of cyclosiloxanes has been known for a long time, its mechanism has not been well established.[3] One of the reasons for this is that, in the acid-catalyzed polymerization, two active ends per chain are involved in polymer propagation, and both polycondensation and addition polymerization must be considered (see Scheme 2).

If the polymerization is initiated by an electrophilic trimethylsilyl type species, it will propagate only at one end as in the case of anionic polymerization of cyclosiloxanes, providing a simple model of addition polymerization. In other words such a polymerization could become a cationic approach to siloxane-containing diblock polymers, star polymers, or even graft polymers, which are difficult to obtain by conventional acid-catalyzed polymerization of cyclosiloxanes.[4] Although anionic ring-opening polymerization of cyclosiloxanes may lead to such polymers, it is generally performed under strictly anhydrous and inert experimental conditions, requiring high-purity chemicals, solvents, and monomers. Furthermore, monomers containing functional groups that are sensitive to nucleophiles cannot be applied. Consequently, a cationic polymerization allowing facile preparation of such polymers is of substantial interest. However, conventional electrophilc silylating agents, such as trimethylsilyl triflate (TMSOTf), do not initiate the ring-opening polymerization of cyclosiloxanes in the absence of protic acids.[3a] The results were interpreted as due to the lower nucleophilicity of siloxanes compared to ethers.[1b,3,5] The aim of our present work is not only to understand the mechanism of the polymerization of cyclosiloxanes in the presence of trisilyloxonium ions but also to develop a convenient synthetic methodology for polysiloxanes of various architectures. We now wish to report our studies on the novel polymerization of cyclosiloxanes initiated by trisilyloxonium ions in the absence of protic acids. The results of our studies support the proposed mechanism, and show the successful application of the method for the synthesis of siloxane-containing diblock copolymers and comblike graft copolymers.

Scheme 1



Scheme 2



Experimental Section

All NMR spectra were recorded on a Varian Unity-300 NMR spectrometer and the chemical shifts (^1H, ^{13}C, and ^{29}Si) referenced to tetramethylsilane. The size exclusion chromatography (SEC) of the polymers was performed on a Waters system with toluene as eluent and the molecular weight was calibrated with a poly(dimethylsiloxane) standard, except as otherwise indicated. Viscosities of polymers were measured in toluene using an Ubbelhode viscometer. The temperature was kept constant at 25 °C with the use of a water bath and a VWR 1120 thermostat. Intrinsic viscosities of the polymers were obtained by extrapolation of the reduced viscosity as a function of concentration (to zero concentration).

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Table 1. Conditions and Results of the Polymerization of D_3 and D_4 Initiated with Me_3SiH and (Trityl)TBFPB (Room Temperature, in CH_2Cl_2, $[M]_o = 1.5$ M)

run	monomer	M/Int	time (h)	yield[a] %	$M_w{}^b \times 10^{-4}$	$M_w/M_n{}^b$
1	D_3	50	2	74	0.8	1.9
2	D_3	100	3	73	1.2	2.0
3	$D_3 + D_3{}^c$	100 + 100	4 + 2	82	3.4	2.2
4	D_4	50	6	78	1.8	2.3
5	D_4	100	8	80	2.8	2.5
6	D_4	150	8	85	3.7	1.8
7	D_4	200	8	83	5.9	1.9
8	$D_4 + D_4{}^c$	150 + 150	10 + 12	83	7.0	1.8

[a] Isolated yields. [b] Measured by SEC, high polymers. [c] Resumption polymerization.

Table 2. Polymerization of D_4 by (Trityl)TPFPB and a Variety of Hydrosilanes (Room Temperature, in CH_2Cl_2, and $[M]_o = 1.5$ M)

run	hydrosilane	M/Int	time (h)	yield[a] %	$M_w{}^b \times 10^{-4}$	$M_w/M_n{}^b$
1	Me_3SiH	200	8	83	5.9	1.8
2	*i*-Pr_3SiH	200	8	64	5.0	1.8
3	*t*-Bu_3SiH	200	8	8	4.8	2.8
4	$PhMe_2SiH$	150	8	14	1.1	2.3
5	$(PhCH_2)_3SiH$	250	8	78	10.9	2.1
6	PS-$SiMe_2H^c$	200	8	81	5.7	2.0

[a] Isolated yields. [b] Measured by SEC, high polymers. [c] PS = polystyrene ($M_w = 1.5 \times 10^3$).

(Ph_3C)TPFPB was prepared according to modified literature methods.[6] Trivinyltrimethylcyclotrisiloxane (VMCS) and tris(trifluoropropyl)trimethylcyclotrisiloxane (TFMCS) were purchased from United Chemical Technologies. Poly(hydromethylsiloxane) (PHMS, $M_w = 1200$, Me_3Si-terminated) was obtained from Gelest. All other chemicals were purchased from Aldrich. All chemicals were kept under argon and used as received. Dichloromethane was distilled over calcium hydride before use.

^{29}Si NMR Studies of the Reaction Intermediates. (trityl)TPFPB (40 mg) and 0.4 mmol of D_3 were dissolved in 0.5 mL of dry CD_2Cl_2 in a 5 mm NMR tube under argon. The tube was cooled to −78 °C still under argon, and 2 mL (gas, at 20 °C) of trimethylsilane was introduced via a syringe to the mixture under rapid vortex stirring. The tube was then sealed and maintained at −78 °C till the yellow color disappeared. The NMR spectra of the samples were recorded at various temperatures.

Polymerization of the Cyclosiloxanes. (**1) Polymerization of D_4 Using Trimethylsilane and (Trityl)TPFPB (M/Int = 100): A Typical Procedure.** To a solution containing 10 mmol of D_4, 0.1 mmol of (trityl)TPFPB, and 4 mL of CH_2Cl_2 at 0 °C under argon was added 0.2 mmol of trimethylsilane via a syringe. The ice bath was removed after the addition of trimethylsilane and the reaction mixture was maintained at room temperature under magnetic stirring for 8 h. The reaction was followed by taking an aliquot of the reaction mixture at regular intervals and monitoring the conversion by ^1H NMR. After the reaction equilibrium was reached, MeOH was added to precipitate poly(dimethylsiloxane) and a white oily product was obtained. The resulting polymer was dissolved in pentane and washed with a small amount of MeOH. Upon removal of the solvent under vacuum, 2.4 g of poly(dimethylsiloxane) was obtained, yield 80%.

The M/Int ratios, reaction conditions, and yields for other experiments are given in Tables 1 and 2.

(2) Graft Polymerization of D_4 on PHMS in the Presence of (Trityl)TPFPB. The procedure was similar to the typical procedure (1), except that a reverse addition sequence was used. Thus a solution of (trityl)TPFPB (50 mg) in CH_2Cl_2 (1 mL) was added to a solution containing D_4 (2.3 g), PHMS (9 mg), and CH_2Cl_2 (4 mL) at 0 °C under argon. The resulting reaction mixture was worked up in a manner similar to that described in procedure 1. A colorless oily product (1.9 g) was obtained upon removal of solvent under vacuum, yield 82%. This procedure was also applied for the graft polymerization of D_4 on hydrodimethylsilyl-terminated polystyrene.

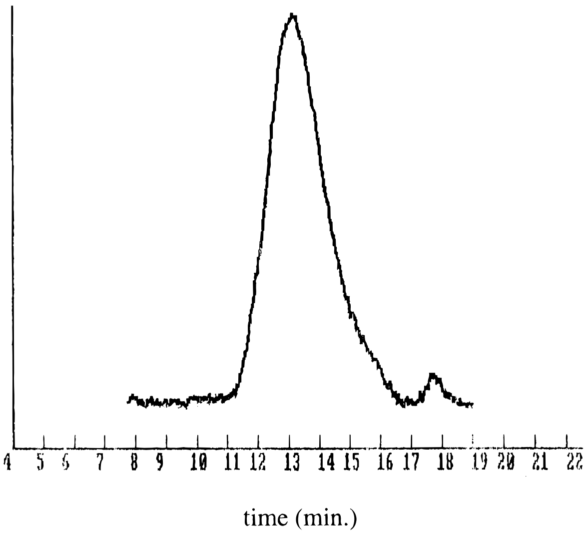


Figure 1. SEC chromatogram of the reaction mixture from D_4, Me_3SiH, and (trityl)TPFPB; $[M]_o = 1.5$ M, M/Int = 100, 20 °C, 15 h.

Results and Discussion

(1) Polymerization Studies of D_3 and D_4. Both D_3 and D_4 are readily polymerized at room temperature using (trityl)TPFPB and trimethylsilane as initiators. We carried out the polymerization of D_3 and D_4 at various monomer/initiator (M/Int) molar ratios and at different monomer concentrations. We found that, when the M/Int was higher than 50 and the monomer concentration ranged from 1 to 2 M, the polymerization proceeded well, giving a 70−90% yield of a high molecular weight linear polymer with polydispersity ranging from 1.8 to 2.5 (see Table 1). Cyclic oligomers were always present in the reaction mixtures. A typical SEC chromatogram of the resulting polymer from D_4 is shown in Figure 1.[7] A small shoulder of the oligomers and an even smaller monomer peak can be seen on this chromatogram. If the M/Int ratio or the concentration of the monomer was too low, the abstraction of halide or some other side reactions became predominant and gave quite complex results. Under similar conditions, the polymerizations of D_3 were found to be much faster than that of D_4. Such a differing behavior of D_3 and D_4 has been observed before.[3e]

The propagating chain end was monitored by ^{29}Si NMR spectroscopy at relatively low M/Int ratio and low monomer concentration and at a low temperature (-50 °C $< T < -20$ °C) in order to avoid side reactions. From the ^{29}Si NMR spectra recorded from a solution of D_3, (trityl)TPFPB, and trimethylsilane (M/Int = 10), it was noted that the polymerization took place even at −50 °C and, as the polymerization proceeded, the peak at 49 ppm associated with Me_3Si of the ion **1** disappeared while the peak at 10 ppm associated with the D silicon atoms of trisilyloxonium ions **1** or **2** survived (see Figure 2).[1] This indicates the presence of the oxonium ion **2** as the active propagating end (Scheme 1). Under similar conditions, D_4 was not polymerized even at −20 °C.

Resumption polymerization experiments were carried out at room temperature by addition of 1 equiv of D_3 or D_4 to an aliquot of a polymerization mixture of D_3 or D_4 initiated by trimethylsilane and (trityl)TPFPB. The molecular weights increased reasonably with no sub-

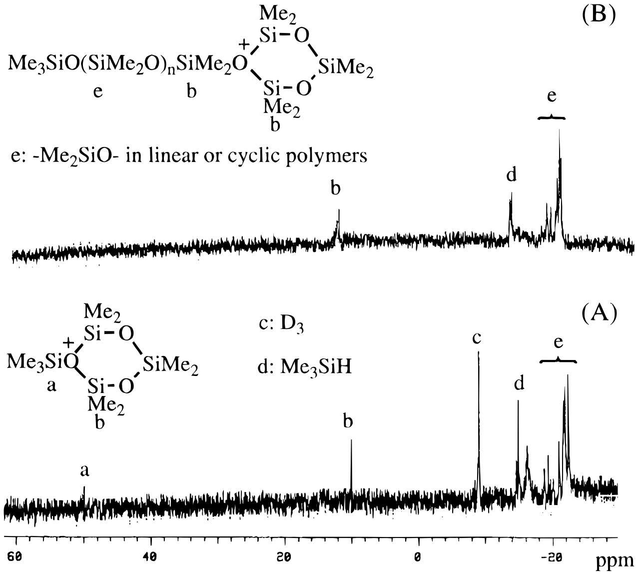


Figure 2. ^{29}Si NMR spectra of D_3, Me_3SiH, and (tritil)TPFPB in CD_2Cl_2 in 10:2.5:1 mol ratio: (A) at −50 °C; (B) at −30 °C. For peaks assignments, see ref 1.

stantial changes in polydispersity (see Table 1, runs 3 and 8). This indicates that the propagating silyloxonium ends are long-lived under the reaction conditions. However, back-biting under the reaction conditions results in relatively high polydispersity and cyclic oligomers in the reaction mixtures.

The polymerizations of D_4 using various hydrosilanes as initiator precursors are summarized in Table 2. With the use of triisopropylsilane or tribenzylsilane, the formation of the trisilyloxonium ions **1** seemed relatively slower than that with the use of trimethylsilane, as indicated by a slower disappearance of the color of the trityl cation. However, the polymerization using tribenzylsilane was as fast as those initiated with trimethylsilane, while the polymerization using triisopropylsilane was significantly slower (in all three cases, the formation of the trisilyloxonium ions **1** was much faster compared to the subsequent polymerization). In the case of tris(*tert*-butyl)silane, the color of the trityl cation did not significantly change over a period of 8 h, and less than 10% of the polysiloxane was obtained after quenching with methanol. The discoloration of the solution of (trityl)TPFPB/D_4 was spontaneous upon addition of dimethylphenylsilane. However, only 14% poly(dimethylsiloxane) was obtained after 8 h. The results indicate that the initiation rate of the polymerization depends not only on the formation of the trisilyloxonium ion but also on its reactivity toward cyclosiloxanes. The polymerization of D_4 using a macromolecular initiator was also performed to determine if a monosubstituted polysiloxane would be formed as expected. Such polymers are rarely obtained by cationic polymerization of cyclosiloxanes.[4] A polystyrene (M_w = 1500) terminated with a dimethylhydrosilyl group at one end was used in place of trimethylsilane as the precursor of the initiator. The polymerization was carried out under similar conditions with 200 parts of D_4. The yield, molecular weight, and polydispersity of the polymer were all quite similar to those obtained with trimethylsilane as the initiator (Table 2, runs 1 and 6). The molecular weights determined by SEC were quite close using either a UV or RI detector, indicating grafting of poly(dimethylsiloxane) onto the polystyrene. The results, together with those of the ^{29}Si NMR studies and the polymerization resumption experiments, demonstrate clearly that the polymer propagates by a single "long-lived" trisilyloxonium ion end as shown in Scheme 1. Moreover, the polymerization represents a successful approach to AB diblock copolymers and may be suitable for the synthesis of ABC-type multiblock copolymers. In contrast, acid-catalyzed ring-opening polymerizations of cyclosiloxanes are only suitable for the synthesis of ABA type copolymers.[4]

Table 3. Polymerization of a Variety of Cyclosiloxanes using Me_3SiH/(trityl)TPFPB (Room Temperature, in CH_2Cl_2, $[M]_0$ = 1.5 M)

run	monomer	M/Int	time (h)	yield[a] %	M_w[b] × 10^{-4}	M_w/M_n[b]
1	VMCS	100	8	76	2.4	3.3
2	D_4 + VMCS[c]	100 + 100	10 + 12	82	7.1	4.3
3	TFMCS	75	8	87	1.9[d]	1.7
4	PhMCS	100	15	*e*		
5	D_4 + PhMCS[f]	50 + 100	8	85[g]	2.3	2.0

[a] Isolated yields. [b] Measured by SEC, high polymer. [c] Resumption polymerization. [d] Measured in THF, calibrated using polystyrene standard. [e] >90% PhMCS recovered. [f] Copolymerization. [g] Based on D_4.

(2) Polymerization of Related Cyclosiloxanes. The electron-deficient organosilicon initiating systems were also used under similar conditions to polymerize other cyclosiloxanes, such as trivinyltrimethylcyclotrisiloxane (VMCS), tris(trifluoropropyl)trimethylcyclotrisiloxane (TFMCS), tetramethylcyclotetrasiloxane (HMCS), and trimethyltriphenylcyclotrisiloxane (PhMCS). The yields and M_w of polyVMCS and polyTFMCS were, as expected, comparable to those in the polymerization of D_4 under similar conditions (see Table 3). This implies that trisilyloxonium ions may survive in the presence of vinyl or trifluoromethyl groups under the experimental conditions. The polydispersity of polyVMCS was just slightly higher than that for the polymerization of D_4. The results obtained with VMCS can be considered as evidence against initiation by protic acids. Addition of VMCS to an aliquot of D_4, which was previously initiated by trimethylsilane/(trityl)TPFPB, yielded a copolymer, as expected (Table 3, run 2). The polymerization of HMCS may lead to a hyperbranched treelike polysiloxane. This very unique approach to hyperbranched polymers will be reported elsewhere. PhMCS could not be homopolymerized using our systems (see Table 3, run 4), indicating a dramatic effect of steric hindrance on the reactions. This result can be expected from the proposed reaction mechanism (Scheme 1), wherein the proximity of the two rings is prevented by steric hindrance of the phenyl groups. On the other hand, the random copolymerization of D_4 with PhMCS was successfully carried out with trimethylsilane/(trityl)TPFPB. The starting molar ratio of D_4/PhMCS was 0.5, and the ratio in the obtained polymer was 1.5. This indicates that the reaction between two D_4 or one PhMCS and one D_4 can occur, while the reaction between two PhMCS is prevented by steric hindrance.

Graft Polymerization of D_4 on PHMS. It is well-known that long chain branching can have dramatic effects on the mechanical properties of polymers. For polysiloxanes, branching is generally introduced by adding a small amount of tri- or tetrafunctional silanes. The branching sites in this case are not well controlled, and the branching density is not very high. As polysiloxanes can be grafted on the substrates having Si−H functional groups via the novel polymerization of cyclosiloxanes, the method may be extended for the synthesis of star- or comblike branched polymers. We

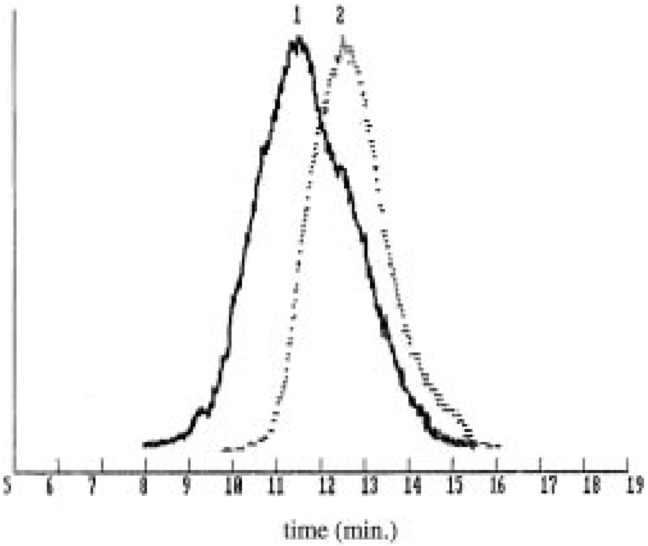
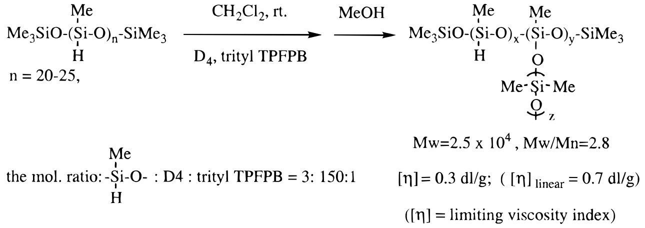


Figure 3. Size exclusion chromatograms: (1) graft polymer of D_4 on PHMS; (2) reference poly(dimethylsiloxane) from D_4, Me_3SiH, and (trityl)TPFPB.

Scheme 3



have synthesized a comblike branched poly(dimethylsiloxane), starting from poly(hydromethylsiloxane) (PHMS). The graft polymerization of D_4 was performed with PHMS (M_w = 1200, Me_3Si-ended) and (trityl)TPFPB under the described conditions (see Experimental Section). In a typical run, the reaction mixture was quenched with methanol 10 h after initiation and the polymer was separated. Neither precipitation nor gel formation was observed even if the reaction was maintained up to 30 h under argon, indicating a lack of cross-linking.

The resulting polymer has a M_w (by universal calibration)[8] 6-fold higher than that of the polysiloxane resulting from the polymerization of D_4, Me_3SiH, and (trityl)TPFPB (M/Int = 150/1) and it should be 7−8-fold according to calculations. The SEC chromatograms of the graft polymer and of the reference polymer are presented in Figure 3. The polydispersity of the graft polymer is not much higher than that of the reference polymer, indicating that the graft polymer was formed quite uniformly and cross-linking by chain transfer can be neglected. The result also supports the “single propagation” mechanism that we proposed (Scheme 1). Although the branching number could not be determined quantitatively, the intrinsic viscosity of the grafted polymer is significantly lower than that of the linear poly(dimethylsiloxane) having equal M_w, indicating a fairly branched polymer structure.[9] The isolated graft polymer is soluble in pentane and can be kept in air for weeks without gel formation. The reaction mixture, however, formed an insoluble elastomer upon exposure to moisture for 2 days. Thus this polymer may find application as self-curing silicone elastomers.

Conclusions

We have investigated a novel cationic ring-opening polymerization of cyclosiloxanes initiated by electron-deficient organosilicon reagents. We have demonstrated that the polymerization is distinguished in many respects from those initiated by protic acids or Lewis acids. This polymerization can be used as a model for the addition polymerization in mechanistic studies of the cationic ring-opening polymerization of cyclosiloxanes. It can also find wide synthetic applications based on its unique ability to provide tailored polymers. As examples, the novel system has been successfully applied to synthesize diblock copolymers, such as polystyrene-*co*-poly(dimethylsiloxane), and long chain branched comblike polysiloxanes. Moreover, as Si−H is a relatively stable functional group and readily available on polymers and organic compounds, this method can be easily extended to the synthesis of a wide range of siloxane-containing block copolymers. More extensive applications in developing polysiloxane materials and additional mechanistic studies are being pursued.

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