Macromolecules

Volume 29, Number 6 March 11, 1996

Silylcarboxonium and Silyloxonium Ion Intermediates of the Cationic Ring-Opening Polymerization of Lactones and Tetrahydrofuran Initiated by Electrophilic Trimethylsilylating Agents[1]

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Received August 29, 1995; Revised Manuscript Received January 2, 1996[⊗]

ABSTRACT: The initiation of the cationic ring-opening polymerization of lactones and tetrahydrofuran by electron-deficient organosilicon species has been investigated. The formation of the long-lived silylcarboxonium ion **1a** from γ-butyrolactone and the silyloxonium ion **2a** from THF has been evidenced by ^{1}H, ^{13}C, and ^{29}Si NMR. The structure and NMR chemical shifts of **2a** were also calculated using DFT/IGLO methods, and the results are in good agreement with experimental data. The nature of the ions is discussed in terms of the reactivity with respect to their methylated analogues. Polymerization of lactones initiated by *in situ* formed silylcarboxonium ions showed a much higher rate than that initiated by trimethylsilyl triflate, while polymerization of tetrahydrofuran in a similar manner failed. The mechanism of polymer initiation is discussed.

Introduction

The ring-opening polymerization of heterocyclic compounds initiated by silylating agents, i.e., trimethylsilyl triflate (TMSOTf), was first reported by Gong and Hall[2] and drew the interests of several research groups from the point of view of both the reaction mechanism and the potential application in synthesizing some graft copolymers.[3] However, in their studies it was found that TMSOTf is much less efficient than methyl triflate in initiating polymerization of some heterocyclic compounds, although TMSOTf was one of the most powerful silylating agents. The results were interpreted as due to either unfavorable thermodynamics for the formation of silylated onium ions or the lower reactivity of such silylated onium ions compared to their methylated analogues. The interpretation was not conclusive because of the lack of knowledge about the silylated onium ions.[3b,e] Previous studies also showed that TMSOTf is inactive in initiating the polymerization of cyclosiloxanes in the absence of protic acids.[4]

As a part of our studies on the structures, chemical properties, and potential applications of silylated carbocations and onium ions, we demonstrated that polymerization of cyclosiloxanes could be initiated by well-defined (trimethylsilyl)oxonium ions, generated *in situ* by a hydride transfer reaction (Scheme 1).[5,6] To our knowledge, this was the first report on the polymerization of cyclosiloxanes initiated by electron-deficient organosilicon species in the absence of any protic acids.

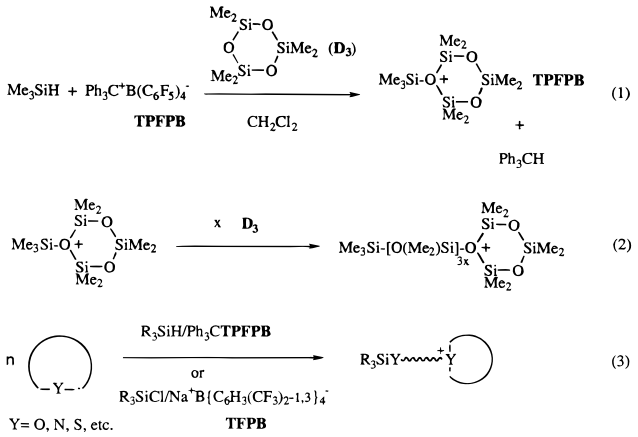
Recently, ketones and ethers were also reported to be silylated to form silylcarboxonium and silyloxonium ions in a similar manner as in eq 1 or by reacting a chlorosilane with the sodium salt of appropriate tetrakisaryl borates in the presence of an excess of ketone or ether.[7] This provided an approach to prepare and investigate directly the electron-deficient silylated species involved in the polymerization of heterocyclic monomers. During our systematic studies on silylated onium ions, we were interested in probing the roles of silylcarboxonium and silyloxonium ions in the ring-opening polymerization and the possibility of carrying out such polymerization of heterocyclic compounds with novel initiators (eq 3).

Herein we report our investigation of the polymerization of lactones and THF induced by silylated carboxonium and oxonium ions and compare the results with those initiated by TMSOTf or methyl triflate.

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

0024-9297/96/2229-1857$12.00/0

Scheme 1



Experimental Section

All NMR spectra were recorded on a Varian Unity-300 NMR spectrometer and the chemical shifts (^{1}H, ^{13}C, and ^{29}Si) referenced to tetramethylsilane. Gel permeation chromatography (GPC) of the polymers was performed on a Waters system with THF as eluent, and the molecular weight was calibrated with a polystyrene standard.

Na**TFPB**, Ph_3C**TFPB**, and Ph_3C**TPFPB** were prepared according to modified literature methods.[8,9] All other chemicals were purchased from Aldrich Chemical Co. Dichloromethane was distilled over calcium hydride before use.

Preparation and NMR Studies of (Trimethylsilyl)-carboxonium Ion 1a. Na**TFPB** (100 mg) and 0.1 mmol of γ-butyrolactone 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 0.1 mmol of chlorotrimethylsilane was introduced via a syringe to the mixture under rapid vortex stirring. The tube was then sealed and maintained at −78 °C till the completion of the reaction. The NMR spectra of the samples were recorded at various temperatures.

Preparation and NMR Studies of (Trimethylsilyl)-tetrahydrofuranium Ion 2a. The procedure was similar to that for ion **1**. Trimethylsilane (0.2 mmol) was introduced via a syringe to a mixture of 100 mg of trityl **TPFPB** and 0.1 mmol of THF in 0.5 mL of CD_2Cl_2 at −78 °C. The resulting mixture was maintained at this temperature for 2 h before the spectra were recorded.

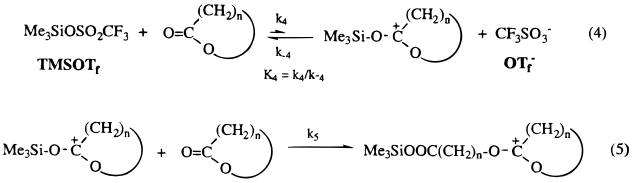
Polymerization of Lactones. To a solution containing 10 mmol of lactone, 0.1 mmol of Na**TPFB**, and 4 mL of CH_2Cl_2 was added 0.2 mmol of chlorotrimethylsilane via a syringe at 0 °C under N_2. The ice bath was removed after the addition of the chlorosilane, and the reaction mixture was maintained at the prescribed temperature under magnetic stirring for a set period (see Table 2 for details). The reaction was followed by taking small aliquots of the reaction mixture at regular intervals and monitoring the conversion ratio by ^{1}H NMR. Upon completion of the reaction, MeOH was added to precipitate the polymers. The polymers were washed with MeOH and dried under vacuum.

Structure and NMR Chemical Shift Calculations of 2a. Density functional theory (DFT) calculations of the structure of **2a** were carried out by using the GAUSSIAN-94[10] package of programs. Optimized geometries were obtained with DFT at the B3LYP/6-31G* level. IGLO calculations of NMR chemical shifts were performed according to the reported method[11] at the IGLO II′ level using B3LYP/6-31G* optimized geometries. Huzinaga[12] Gaussian lobes were used as follows. Basis II′: Si, 11s 7p 2d contracted to [51111111, 211111, 11], d exponent = 1.4 and 0.35; C, O: 9s 5p 1d contracted to [51111, 2111, 1], d exponent: 1.0, H, 3s contracted to [21].

Results and Discussion

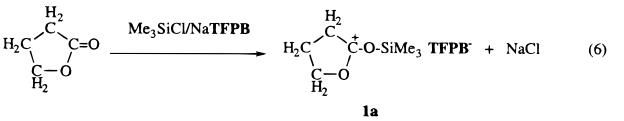
Studies of the Polymerization of Lactones. Ring-opening polymerizations of lactones initiated by TMSOTf are believed to proceed in a similar manner as methyl triflate, i.e., by a nucleophilic attack of the lactone on the (trimethylsilyl)carboxonium ion accompanied by the ring-opening (Scheme 2).[3b]

Scheme 2



As nucleophilic attack of lactones on the silicon atom is fast (*vide infra*), the initiation of the polymerization should be determined by the equilibrium constant K_4 and the rate constant k_5.[3b,e] In other words, the initiation rate depends on the concentration and the reactivity of the (trimethylsilyl)carboxonium ions. Consequently, the direct study of the (trimethylsilyl)carboxonium ions was of substantial interest as it may provide the clue for understanding the reactions and improving the efficiency of the initiation.

Since γ-butyrolactone does not polymerize at or below room temperature for thermodynamic reasons, its reaction with cationic initiators is often used to investigate the initiation reactions with no interference from propagation. As reported by Dunsing et al., no carboxonium ions could be detected by spectroscopic methods from the mixture of γ-butyrolactone and TMSOTf. They believed that the formation of the (trimethylsilyl)-carboxonium ions from lactones and TMSOTf is thermodynamically unfavorable. By using an approach reported by Kira and Sakurai,[7] we have been able to prepare and observe by means of NMR spectroscopy the long-lived (trimethylsilyl)carboxonium ion **1a** from γ-butyrolactone, with **TFPB** as a counteranion having a lower affinity toward the silicon atom.



The reaction (6) occurred even at −78 °C and was complete within minutes. Ion **1a** is surprisingly stable even at room temperature. Its ^{1}H, ^{13}C, and ^{29}Si NMR chemical shifts are listed in Table 1. Ion **1a** showed averaged signals with an excess of the lactone in the ^{1}H and ^{13}C NMR spectra even at −60 °C, indicating a fast exchange process. The ^{29}Si NMR spectrum of **1a** is relatively unaffected by the excess of lactone. The ^{1}H spectra of the mixtures of ion **1a** and γ-lactone in different ratios are shown in Figure 1. When trimethylchlorosilane (TMSCl) and Na**TFPB** are in excess over the lactone, no significant shifts in the ^{1}H NMR spectra were found compared to that of the TMSCl:Na**TFPB**:γ-lactone = 1:1:1 mixture. The speedy formation of ion **1a** and its fast exchange with the lactone at low temperature confirm that the attack of the lactone on silicon is a fast process.

The chemical shift of the γ-proton of ion **1a** is some 0.7 ppm more deshielded than that in the parent lactone and 0.3 ppm less than that in the methylcarboxonium ion **1b**. On the other hand, no significant changes in the ^{1}H spectrum of γ-lactone were observed after addition of 2 equiv of TMSOTf. Obviously, there is no significant amount of **1a** in the reaction mixture. In other words, K_4 in reaction 4 is very small. The ^{13}C

Table 1. NMR Chemical Shifts of Some Onium Ions and Their Precusors in CD_2Cl_2 at −40 °C

	^1H (J^3_{H-H}) [ppm (Hz)]				^{13}C (ppm)					
compound	$C_\alpha H_2$	$C_\beta H_2$	$C_\gamma H_2$	$SiCH_3$	C_α	C_β	C_γ	C=O	$SiCH_3$	^{29}Si (ppm)
γ-butyrolactone	2.5 (9)	2.3	4.3 (8)		27.8	22.2	68.7	178.0		
1a	3.1 (9)	2.5	5.0 (8)	0.54	32.1	21.3	80.6	192.3	−0.6	58
1b	3.4 (9)	2.7	5.3 (8)		32.6	21.6	85.8	197.0		
THF	3.58	1.73			62.5	25.8				
					65.1[a]	26.9[a]				
2a	4.54	2.35		0.61	79.6	25.5				63
					78.1[a]	26.1[a]				69[a]
2b	4.87	2.45			89.6	25.6				

[a] Calculated data by the IGLO method at IGLO II′//B3LYP/G-31G*.

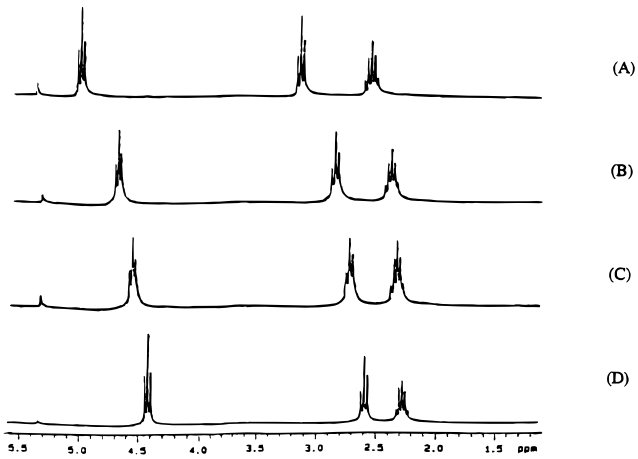


Figure 1. ^1H NMR of ion **1a** in the presence of excess γ-butyrolactone in CD_2Cl_2 at 0 °C. **1a**/γ-butyrolactone ratio: (A) no excess γ-butyrolactone; (B) 1:1; (C) 1:2; (D) 1:4.

Table 2. Polymerization of Some Lactones in Dichloromethane ([M]/[Int] = 100/1)

lactone	initiator	temp (°C)	time (h)	yield[a] (%)	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$
ϵ-caprolactone	TMSCl/ Na**TFPB**	20	20	94	21	14
ϵ-caprolactone	Me_3SiH/ Ph_3C**TFPB**	20	20	90	17	12
ϵ-caprolactone	MeOTf	20	24	87	11	7.6
ϵ-caprolactone	MeOTf/ Na**TFPB**	20	20	88	147	7.2
ϵ-caprolactone	TMSOTf	40	24	70	22	13
δ-valerolactone	TMSCl/ Na**TFPB**	20	4	88	19	12
δ-valerolactone	MeOTf	20	4	81	13	8.2
δ-valerolactone	TMSOTf	20	4	52	15	11
β-propiolactone	TMSCl/ Na**TFPB**	40	24	73	7.2	4.4

[a] Isolated yield.

NMR chemical shift of the γ-carbon in **1a** is 5 ppm less deshielded than that in **1b.** This indicates that the electrophilicity of the γ-carbon of **1a** might be lower than that of **1b**.

We carried out the polymerization of β-propiolactone, δ-valerolactone, and ϵ-caprolactone according to eq 3, using TMSCl and Na**TFPB** to generate *in situ* the corresponding silylcarboxonium ions as the actual initiators. The polymerization conditions and the results are listed in Table 2. We found that the polymerization of lactones using TMSCl/Na**TFPB** is in general much faster than that initiated by TMSOTf. The NMR spectra of the reaction mixture showed an immediate disappearance of the silylcarboxonium ions at 20 °C, which indicates the high initiation efficiency of the silylcarboxonium ions. Further rate studies revealed that the polymerization of ϵ-caprolactone using TMSCl/ Na**TFPB** is even faster than that initiated by methyl triflate (Figure 2). Considering the effect of the anion on the polymerization, we added 1 equiv of Na**TFPB** in the methyl triflate initiated polymerization of ϵ-caprolactone and found that the rate of the polymerization increased and became similar to that of the reaction initiated by TMSCl/Na**TFPB**. The effect of **TFPB** on the formation of **1b** was investigated by ^1H NMR spectroscopy. The NMR studies revealed that addition of Na**TFPB** resulted in faster and more extensive formation of **1b** (Figure 3). The higher rate of poly-

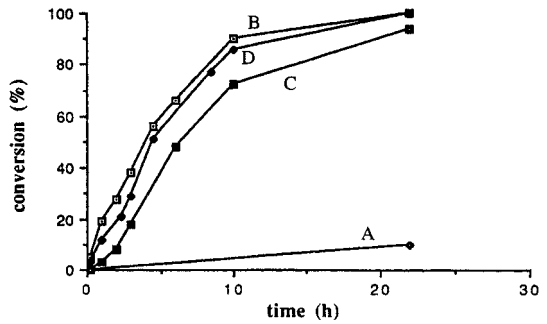


Figure 2. Polymer conversion of ϵ-caprolactone in dichloromethane initiated by (A) Me_3SiOTf, (B) Me_3SiCl/Na**TFPB**, (C) MeOTf, and (D) MeOTf/Na**TFPB** (determined by means of ^1H NMR). [M]/[Int] = 100; $[M_0]$ = 3 M; 20 °C.

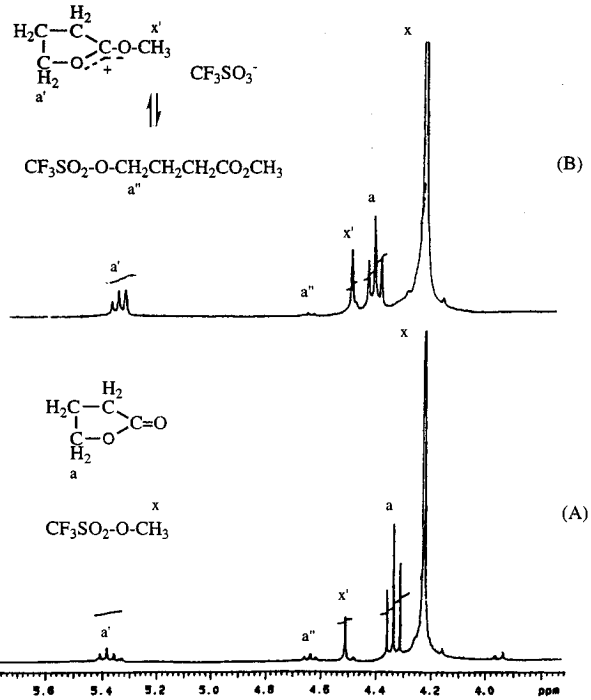


Figure 3. ^1H NMR spectra of γ-butyrolactone/MeOTf (1:2) mixture in CD_2Cl_2 at 20 °C: (A) after 24 h; (B) immediately after addition of Na**TFPB**.

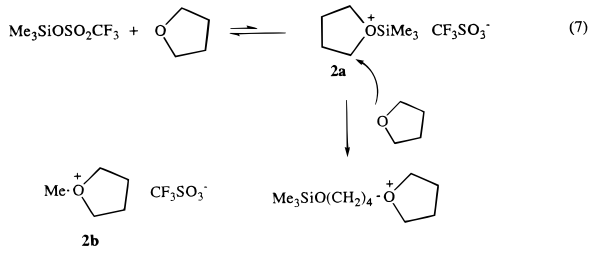
merization using TMSCl/Na**TFPB** may result from initiation or propagation or both. However, by comparing curve A with B and C with D in Figure 2, we can see, qualitatively at least, more efficient initiation by TMSCl/Na**TFPB** than TMSOTf. This can also be deduced from eqs 4 and 5, as the concentration of the (trimethylsilyl)carboxonium ion becomes higher by using TMSCl/Na**TFPB**.

Polymerization of δ-valerolactone and ϵ-caprolactone can also be initiated effectively by trimethylhydrosilane combined with trityl **TFPB** or trityl **TPFPB**, which generate *in situ* (trimethylsilyl)carboxonium ions. The results are similar to that obtained with TMSCl/Na**TFPB**. In contrast, ϵ-caprolactone cannot be polymerized under similar conditions by TMSCl/$NaBPh_4$. Upon addition of TMSCl into the solution of $NaBPh_4$ and the lactone in CD_2Cl_2, NaCl precipitated out. However, no (trimethylsilyl)carboxonium ion was found even at low temperatures as it reacts with BPh_4^-.[13]

We may conclude from the experimental results that low initiation efficiency of TMSOTf for the polymerization of lactones is due to both the lower content and the lower reactivity of the (trimethylsilyl)carboxonium ions compared to their methylcarboxonium ion analogues generated from methyl triflate and lactones. The silylation of lactones by TMSOTf is more likely to be thermodynamically unfavorable. Much more efficient initiation of the polymerization of lactones has been achieved by using novel approaches to generate silylcarboxonium ions. Since Si−H and Si−Cl are easily available functional groups in organosilanes or silicon-based polymers, the polymerization methods developed in our studies may have potential applications in synthesizing block copolymers from organosilanes and lactones.

Studies on the Initiation of THF Polymerization. Ring-opening polymerization of THF initiated by TMSOTf was first reported by Gong and Hall and further investigated extensively by Matyjaszewski et al. for both mechanistic and preparative purpose.[3c−e] Matyjaszewski et al. demonstrated that TMSOTf is again less efficient in initiating ring-opening polymerization of THF compared to methyl triflate. They attributed the slow initiation by TMSOTf in major part to the lower electrophilicity of the α-carbon in the silyloxonium ion **2a** compared to that in the methyloxonium ion **2b** rather than to unfavorable thermodynamics for the formation of the onium ion **2a** from TMSOTf and THF (Scheme 3). Their conclusion was drawn on the basis of some kinetic data and MNDO calculations without direct observation of the ion **2a**.[3e]

Scheme 3



Kira et al.[7a] have reported the generation of (trimethylsilyl)diethyloxonium ions by using Me_3SiH/trityl **TFPB** or Me_3SiCl/Na**TFPB** in the presence of a large excess of diethyl ether. Because the large excess of diethyl ether undergoes very fast exchange with the silyloxonium ion, the ^1H or ^{13}C NMR spectra of the

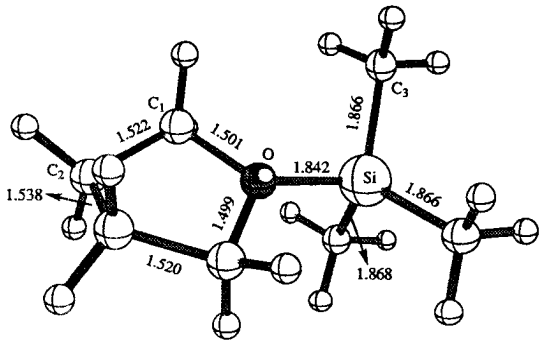


Figure 4. Calculated structure of the trimethylsilylated tetrahydrfofuran ion **2a** at the B3LYP/6-31G* level.

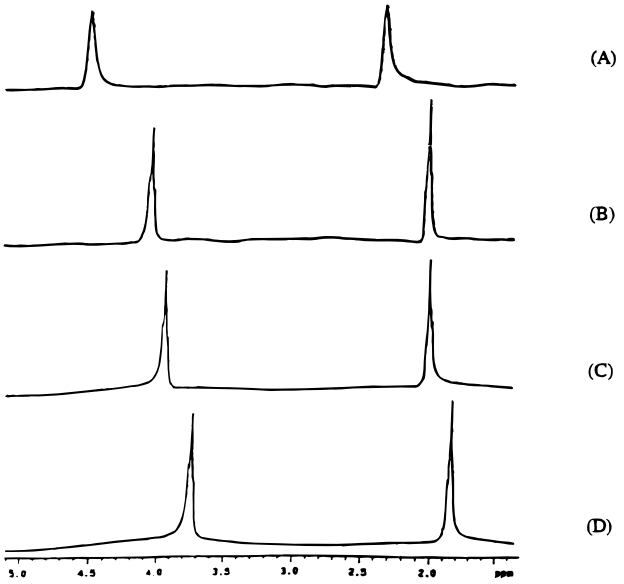
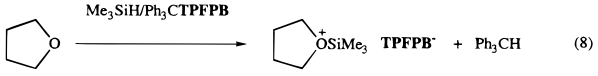


Figure 5. ^1H NMR of ion **2a** in the presence of excess THF in CD_2Cl_2 at −50 °C. **2a**/THF ratio: (A) no excess THF; (B) 1:1; (C) 1:2; (D) 1:4.

mixture displayed no detectable shifts from those of diethyl ether. We were unsuccessful in the preparation of ion **2a** using either Me_3SiH/trityl **TFPB** or Me_3SiCl/Na**TFPB** in the presence of 1 equiv of THF. However, we have been able to prepare ion **2a** by using trityl **TPFPB** instead of trityl **TFPB** (eq 8).



The ^1H, ^{13}C, and ^{29}Si NMR spectra of **2a** were recorded at −40 °C and their chemical shifts are listed in Table 1. In contrast to **1a**, **2a** is only stable below −20 °C. The structure and the NMR chemical shifts of **2a** were also calculated by DFT and IGLO methods (see Figure 4 and Table 1). The calculated NMR chemical shifts of **2a** are in good agreement with experimentally observed data. Figure 5 shows the effect of excess THF on the ^1H NMR spectrum of ion **2a**, and a fast exchange process is evident. The maximum ^1H NMR downfield shifts for the α- and β-methylene protons are δ 0.96 and 0.62, respectively, compared to those in THF, while the changes for ion **2b** are δ 1.29 and 0.72. The ^{13}C NMR of the α-methylene carbon of **2a** is 17.1 ppm more deshielded than that in THF, while the change for **2b** is 27.1 ppm. From these NMR data, we may expect a lower electrophilicity of the α-carbon atom in **2a** than in **2b**. On the other hand, these data also indicate that

the concentration of the ion **2a** formed from TMSOTf and THF is extremely low, since the THF signals have very small shifts upon addition of TMSOTf.[3e] The unfavorable thermodynamics for the formation of **2a** from TMSOTf and THF could be one of the reasons for slow initiation of THF polymerization, as shown in the polymerization of lactones. Employing our silyloxonium ion **2a** with **TPFPB** anion, we were not able to polymerize THF. The reason may be that the **TPFPB** anion either reacts with ion **2a** or the alkyloxonium ions formed in propagation steps under the polymerization conditions.

Conclusions

We have prepared and investigated the (trimethylsilyl)carboxonium ion **1a** and (trimethylsilyl)tetrafuranium ion **2a**. Our results show that TMSOTf is inefficient in forming silyloxonium ions from *O*-heterocyclic compounds, such as lactones, THF, and cyclosiloxanes.[5] This is one of the reasons for the slow initiation in the polymerization of heterocyclic monomers by TMSOTf. The NMR data also indicate that electrophilicity of the corresponding carbon atoms in the silyloxonium ions may be lower than that of the carbon atoms in their methylated analogues. The polymerizations of lactones were, however, effectively initiated by silylcarboxonium ions, which were formed *in situ* by our novel approaches using **TFPB** or **TPFPB** as counterions (eq 3). Although we were able to prepare silyloxonium ion **2a**, which is long-lived below −20 °C, it was unstable at room temperature and failed to initiate THF polymerization.

Acknowledgment. Support of our work by the Loker Hydrocarbon Research Institute is gratefully acknowledged.

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(1) Considered as Onium Ions 43; for Part 42, see ref 5a.
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