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POLYMERS OF CARBONIC ACID. 15. POLYMERIZATION OF CYCLOTRIMETHYLENE CARBONATE WITH TiCl_4 OR SbCl_5 AS INITIATOR

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ABSTRACT

Bulk polymerization of cyclotrimethylene carbonate (TMC) was conducted with either TiCl_4 or SbCl_5 as initiator. Reaction time, temperature, and monomer/initiator (M/I) ratio were varied. High yields ($> 90\%$) were obtained with both initiators, but the weight-average molecular weights (M_w) never exceeded 75,000. In contrast to SbCl_5 , TiCl_4 does not cause decarboxylation at temperatures below 150°C so that polycarbonates free of ether groups were formed. However, both initiators yield polycarbonates with more CH_2Cl than CH_2OH endgroups. In contrast to the sluggish TiCl_4 , SbCl_5 is reactive enough to initiate the polymerization of TMC in CHCl_3 at 25°C . Both TiCl_4 and SbCl_5 form complexes with the monomer via the carbonyl group. In the case of TiCl_4 , a solid 1:2 complex was isolated and characterized by IR- and ^{13}C -NMR CP/MAS spectroscopy. Furthermore, a crystalline 1:2 complex was synthesized with neopentenediol carbonate (NPC). In the case of SbCl_5 , no well-defined complex was obtained with TMC but a crystalline 1:1 complex was obtained with NPC. These NPC complexes proved to be useful as initiators of bulk polymerizations of TMC.

INTRODUCTION

Whereas aromatic polycarbonates have been intensively studied and commercialized over a period of four decades, relatively little work has been done on aliphatic polycarbonates. However, this class of polyesters has recently attracted more interest. In contrast to aromatic polycarbonates, the aliphatic polycarbonates are usually prepared by the ring-opening polymerization of cyclocarbonates. This situation raises the question of which catalyst or group of catalysts is best suited for the homopolymerization of cyclocarbonates, on the one hand, and for copolymerizations (including other heterocycles), on the other hand. Previous work of several research groups has mainly concentrated on anionic polymerization [1-8]. However, recent studies have shown [9-16] that Lewis acids such as BF_3 , SnCl_4 , SnBr_4 , SnI_4 , BuSnCl_3 , or Bu_2SnCl_2 allow the polymerization of cyclotrimethylenecarbonate (TMC) with high yields and high molecular weights. However, depending on the initiator and the reaction conditions, the chain growth process may involve more or less decarboxylation, so that the resulting polycarbonates contain ether groups. Furthermore, the polymerization mechanisms are not well understood, in particular when chlorine- or bromine-containing Lewis acids serve as initiators. The present work was aimed at studying and comparing TiCl_4 - and SbCl_5 -initiated polymerizations of TMC.

EXPERIMENTAL

Materials

TiCl_4 and SbCl_5 were purchased from Aldrich Co. (Milwaukee, Wisconsin, USA). TiCl_4 was distilled under dry nitrogen whereas SbCl_5 was used as supplied. TMC was a gift of Boehringer KG (Ingelheim, Germany). It was purified by recrystallization from CCl_4 and ligroin (mp 39-41 °C).

Polymerizations

TMC (50 mmol) was weighed into a 25-mL Erlenmeyer flask pretreated with dichlorodimethylsilane. The initiator was injected in form of a 1-M solution in dry chloroform. The reaction vessel (closed with a glass stopper and a steel spring) was completely immersed in a thermostated oil bath to prevent a temperature gradient. When the reaction time was over (see Tables 1-6), the reaction product was dissolved in 50 mL CH_2Cl_2 and precipitated into cold methanol. The reaction mixtures were prepared under an atmosphere of dry nitrogen.

Formation of the $\text{TiCl}_4 \cdot 2$ TMC Complex

A 1-M solution of TiCl_4 in dry chloroform was added dropwise with stirring to a 2-M solution of TMC in dry chloroform until equal volumes were mixed. The reaction mixture was cooled with ice for 1 hour and finally filtered under an atmosphere of dry nitrogen. After washing with a small amount of cold CHCl_3 , the isolated product was dried over P_4O_{10} in vacuo. Yield 83%.

TABLE 1. TiCl_4 -Initiated Polymerizations of TMC in Bulk at 60°C with $M/I = 200$ and Variation of the Reaction Time

Polymer	Time, hours	Yield, %	η_{inh}^a , dL/g	$\frac{\text{CH}_2\text{Cl}^b}{\text{monomer}}$	M_w^c
1	8	Oligomers	Oligomers	—	—
2	24	42.0	0.18	1/45	13,000
3	48	90.5	0.28	—	25,000
4	72	90.0	0.31	1/65	—
5	96	91.0	0.34	—	30,000
6	144	93.5	0.36	—	—
7	192	95.0	0.37	1/75	32,000

^aMeasured at 25°C with $c = 2$ g/L in CH_2Cl_2 .

^bMolar ratio of CH_2Cl endgroups/monomer units.

^cCalculated from the Mark-Houwink equation $[\eta] = 0.041 \times M_w^{0.62}$.

Analyses calculated for $\text{C}_8\text{H}_{12}\text{Cl}_4\text{O}_6\text{Ti}$ (393.9): C 24.39, H 3.07, Cl 36.00; found C 22.55, H 3.35, Cl 37.41%. Calculated for a 1:1 complex: $\text{C}_4\text{H}_6\text{Cl}_4\text{O}_3\text{Ti}$ (291.8): C 16.46, H 2.07, Cl 48.60%.

For spectroscopic data see Table 7.

The $\text{TiCl}_4 \cdot 2$ NPC complex was prepared analogously. Yield 85%.

Analyses calculated for $\text{C}_{12}\text{H}_{20}\text{Cl}_4\text{O}_6\text{Ti}$ (450.0): C 32.03, H 4.48, Cl 31.51; found C 30.06, H 4.38, Cl 31.58%.

For NMR spectroscopic data see Table 8.

Synthesis of the $\text{SbCl}_5 \cdot \text{NPC}$ Complex

A 1-M solution of SbCl_5 in CDCl_3 was added dropwise with stirring to a 1-M solution of NPC in CDCl_3 . After mixing equal volumes, the reaction mixture was cooled and worked up as described above. Yield 74%.

TABLE 2. TiCl_4 -Initiated Polymerizations of TMC with Variation of the Reaction Temperature (192 hours, $M/I = 200$)

Polymer	Temperature, $^\circ\text{C}$	Yield, %	η_{inh}^a , dL/g	Ether, ^b mol%	$\frac{\text{CH}_2\text{Cl}^c}{\text{monomer}}$
1	60	88.0	0.36	0	1/79
2	90	86.0	0.34	0	—
3	120	85.5	0.31	0	1/50
4	150	86.0	0.23	0.4	—
5	180	12.0	0.12	0.9	1/25

^aMeasured at 25°C with $c = 2$ g/L in CH_2Cl_2 .

^bMolar fraction of ether groups relative to the sum of ether and carbonate groups.

^cMolar ratio of CH_2Cl endgroups/monomer units.

TABLE 3. TiCl_4 -Initiated Polymerizations of TMC in Bulk at 60°C with Variation of the M/I Ratio

Polymer	Monomer initiator	Time, hours	Yield, %	η_{inh}^a , dL/g	CH_2Cl^b monomer	M_n^c g/mol	M_w^d	M_v^e	M_v^f
1	50	48	37.0	0.12	1/20	2,700	5,000	6,500	—
2	50	192	64.0	0.15	1/22	3,100	7,500	9,000	25,000
3	100	192	85.5	0.19	—	—	13,000	13,000	—
4	150	192	86.5	0.29	—	—	28,000	25,000	75,000
5	200	192	86.5	0.37	1/75	10,000	—	31,000	—
6	300	192	86.5	0.39	—	—	—	34,000	110,000
7	500	192	87.5	0.56	1/145	20,000	58,000	50,000	150,000
8	500	480	85.0	0.60	—	—	63,000	55,000	180,000

^aMeasured at 25°C with $c = 2$ g/L in CH_2Cl_2 .

^bMolar ratio of CH_2Cl endgroups/monomers units.

^cCalculated from the sum of CH_2OH and CH_2Cl endgroups.

^dDetermined by GPC in tetrahydrofuran using the universal calibration method.

^eCalculated from the Mark-Houwink equation $[\eta] = 0.041 \times M_w^{0.62}$.

^fCalculated from the Mark-Houwink equation $[\eta] = 2.77 \times 10^{-4} \times M_w^{0.677}$.

TABLE 4. SbCl_5 -Initiated Polymerizations of TMC with Variation of the Reaction Time (60°C, $M/I = 200$)

Polymer	Temperature, hours	Yield, %	η_{inh}^a , dL/g	Ether, ^b %	$\frac{\text{CH}_2\text{Cl}^c}{\text{monomer}}$
1	8	94.0	0.52	0.80	1/160
2	24	89.0	0.43	—	—
3	48	88.5	0.41	1.80	1/90
4	72	90.5	0.38	—	—
5	96	89.5	0.37	3.25	1/70

^aMeasured at 25°C with $c = 2$ g/L in CH_2Cl_2 .

^bPercentage of ether groups relative to the sum of ether and carbonate groups.

^cMolar ratio of CH_2Cl endgroups/monomer units.

Analyses calculated for $\text{C}_6\text{H}_{10}\text{Cl}_5\text{O}_3\text{Sb}$ (429.5): C 16.79, H 2.35, Cl 41.31; found C 16.86, H 2.55, Cl 41.01%. For NMR spectroscopic data see Table 8.

Measurements

The inherent viscosities were measured in CH_2Cl_2 with an automated Ubbelohde viscometer, thermostated at 25°C.

The IR spectra were recorded with a Nicolet SXB 20 FT-IR-spectrometer. Suspensions of TMC or NPC complexes in paraffin were used for this purpose.

The 100-MHz ^1H -NMR spectra were obtained on a Bruker AC-100 FT-NMR spectrometer in 5 mm o.d. sample tubes.

The 360-MHz ^1H -NMR spectra were recorded with a Bruker AM-360 FT-NMR spectrometer in 5 mm o.d. sample tubes.

TABLE 5. SbCl_5 -Initiated Polymerizations of TMC with Variation of the Temperature ($M/I = 200$, time = 8 hours)

Polymer	Temperature, hours	Yield, %	η_{inh}^a , dL/g	Ether, ^b %	$\frac{\text{CH}_2\text{Cl}^c}{\text{monomer}}$	M_w^d
1	60	88.0	0.54	0.9	1/170	—
2	90	92.0	0.37	3.0	—	—
3	120	90.5	0.31	3.5	1/60	35,000
4	150	90.0	0.27	3.6	—	—
5	180	75.0	0.21	3.7	1/40	20,000

^aMeasured at 25°C with $c = 2$ g/L in CH_2Cl_2 .

^bPercentage of ether groups relative to the sum of ether and carbonate groups.

^cMolar ratio of the CH_2Cl endgroups/monomer units.

^dDetermined by GPC in tetrahydrofuran using the universal calibration method.

TABLE 6. SbCl₅-Initiated Polymerizations of TMC in Bulk at 60°C with Variation of the M/I Ratio

Polymer	Monomer initiator	Time, hours	Yield, %	η_{inh}^a , dL/g	Ether, ^b mol%	CH ₂ Cl ^c monomer	M_w^d	M_v^e	M_v^f	$\frac{M_w^d}{M_n}$
1	50	2	87.0	0.13	—	—	—	—	—	—
2	50	8	89.0	0.15	2.3	1/40	11,000	12,000	16,000	1.7
3	100	8	92.0	0.22	1.4	1/70	—	—	40,000	2.0
4	150	8	93.5	0.38	—	—	34,000	31,000	85,000	2.2
5	200	8	93.0	0.50	0.6	1/180	50,000	42,000	—	2.0
6	300	8	93.0	0.53	—	—	—	—	—	—
7	500	8	93.0	0.76	0.6	1/220	75,000	65,000	190,000	1.5
8	500	24	91.0	0.74	—	—	70,000	60,000	170,000	1.6

^aMeasured at 25°C with $c = 2$ g/L in CH₂Cl₂.

^bMolar fraction of ether groups relative to the sum of ether and carbonate groups.

^cMolar ratio of CH₂Cl endgroups/monomer units.

^dDetermined by GPC measurements in THF using polystyrene standards in combination with the universal calibration method.

^eCalculated from the Mark-Houwink equation $[\eta] = 0.041 \times M_w^{0.62}$.

^fCalculated from the Mark-Houwink equation $[\eta] = 2.77 \times 10^{-4} \times M_w^{0.677}$.

TABLE 7. ^1H - and ^{13}C -NMR Chemical Shifts (δ) of TMC, Its TiCl_4 and SbCl_5 Complexes, and of Poly(TMC)

Nucleus	Compound	Solvent	Chemical shifts δ , ppm ^a		
			CO	C_α	C_β
^1H	TMC	CDCl_3	—	4.47	2.16
		$\text{C}_6\text{D}_5\text{NO}_2$	—	4.57	2.22
	Poly(TMC)	CDCl_3	—	4.24	2.06
		$\text{C}_6\text{D}_5\text{NO}_2$	—	4.33	2.14
^{13}C	$\text{TMC} \cdot \text{SbCl}_5$	CDCl_3	—	4.91	2.52
	TMC	CDCl_3	148.2	67.7	21.1
		$\text{C}_6\text{D}_5\text{NO}_2$	149.0	68.9	22.4
		— ^b	152.1	71.8	23.2
	Poly(TMC)	CDCl_3	154.9	64.3	28.1
		$\text{C}_6\text{D}_5\text{NO}_2$	155.7	65.2	28.8
		— ^b	157.1	66.7	29.9
	$\text{TiCl}_4 \cdot 2\text{TMC}$	— ^b	156.6	72.3	21.2
$\text{SbCl}_5 \cdot \text{TMC}$	CDCl_3	155.8	71.6	20.7	

^aRelative to internal TMS.^bSolid-state CP/MAS measurements.

TMS served as the internal standard for all solution measurements.

The 75.4-MHz ^{13}C -NMR CP/MAS spectra were recorded with a Bruker MSL-300 FT-NMR spectrometer using ZrO_2 double-bearing rotors. A spinning rate of 4 kHz, a contact time of 1 ms, and a repetition time of 4 seconds were used for all measurements.

RESULTS AND DISCUSSION

Polymerizations with TiCl_4

In order to obtain the highest possible molecular weight and in analogy to previous studies of TMC, all polymerizations were conducted in bulk. In the first series of polymerizations the temperature was maintained at 60°C , the M/I ratio was fixed at 200, and the reaction time was varied between 8 and 192 hours. The results, summarized in Table 1, show that the highest yield and the highest viscosity were obtained at the longest reaction time. This means the polymerization is relatively slow and continues over a period of 8 days. Another conspicuous result was revealed by ^1H -NMR spectroscopy; the absence of ether groups. In other words, perfect polycarbonates were obtained whereas BF_3 , SnCl_4 , SnBr_4 , and Bu_3SnCl cause partial decarboxylation under the same reaction conditions [13–16].

When the temperature is raised at a fixed reaction time of 8 days (192 hours) both yields and viscosities decrease continuously (Table 2). The GPC measurements of the reaction mixtures display a broad molecular weight distribution (MWD) with

TABLE 8. ^1H - and ^{13}C -NMR Chemical Shifts (δ) of NPC and Its TiCl_4 or SbCl_5 Complexes

Nucleus	Compound	Solvent	Chemical shifts δ , ppm ^a			
			CO	C_α	C_β	C_γ
^1H	NPC	CDCl_3	—	4.09	—	1.13
		$\text{C}_6\text{D}_5\text{NO}_2$	—	4.20	—	1.10
	$\text{SbCl}_5 \cdot 2\text{NPC}$ Poly(NPC)	CDCl_3	—	4.39	—	1.22
		CDCl_3	—	3.97	—	1.00
		$\text{C}_6\text{D}_5\text{NO}_2$	—	4.11	—	1.03
^{13}C	NPC	CDCl_3	147.9	77.2	28.1	20.7
		$\text{C}_6\text{D}_5\text{NO}_2$	148.5	78.0	28.7	20.8
		— ^b	151.2	78.7	30.4	22.7
	$\text{TiCl}_4 \cdot 2\text{NPC}$	— ^b	159.0	82.4	30.8	23.8
		— ^b	(160) ^c	83.9	31.1	23.4
	Poly(NPC)	CDCl_3	155.3	72.4	35.2	21.4
		$\text{C}_6\text{D}_5\text{NO}_2$	155.9	73.2	35.8	21.6

^aRelative to internal TMS.^b75.4 MHz ^{13}C -NMR CP/MAS spectra.^cBroad signal.

a tail to low molecular weight compounds. Backbiting degradation obviously occurs at higher temperatures and produces cyclic oligomers. The precipitated material shows a narrower MWD and seems to consist mainly of linear oligomers as evidenced by a high content of CH_2OH and CH_2Cl endgroups (Fig. 1). Furthermore, small amounts of ether groups were detected at the highest reaction temperatures (150 and 180°C, Table 2).

These endgroups and the $\text{CH}_2\text{—O—CH}_2$ structure were assigned in the following way. First, their chemical shifts and coupling constants were compared with those of 3-chloropropanol-1 and bis-*n*-propyl ether. Second, trifluoroacetic anhydride was added to the poly(TMC) solutions in CDCl_3 . The rapid esterification of the CH_2OH endgroups generates $\text{CH}_2\text{—O—COCF}_3$ endgroups with a chemical shift 0.5 ppm downfield of the CH_2OH groups. In contrast, the signal of the CH_2Cl group remains unchanged upon addition of trifluoroacetic anhydride. The signal of the $\text{—CH}_2\text{—O—CH}_2\text{—}$ groups shifts 0.1–0.2 ppm downfield due to H-bonds of the liberated trifluoroacetic acid.

Finally, a third series of polymerizations was conducted with variation of the M/I ratio (Table 3). Both inherent viscosities and GPC measurements indicate that the molecular weights increase with the M/I ratio. However, several observations agree in that these polymerizations do not obey the pattern of "living polymerizations." First, all samples possess a relatively high content of chloride endgroups, and the molar fraction of chloride endgroups exceeds that of OH endgroups (Fig. 1). Second, the number-average molecular weights (M_n) calculated from these end-

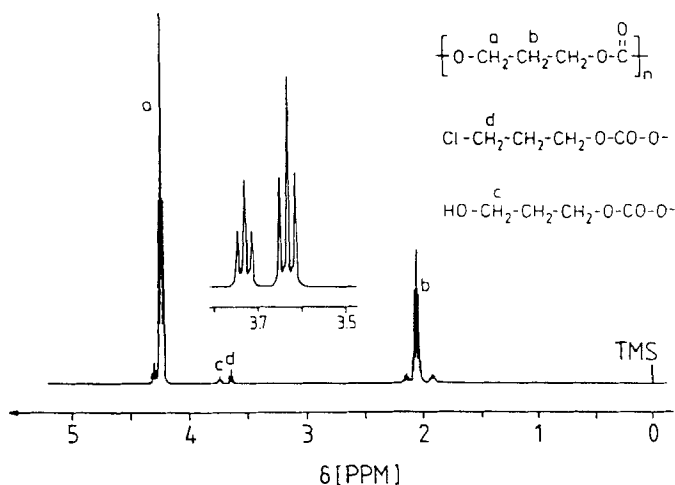


FIG. 1. 360 MHz $^1\text{H-NMR}$ spectrum of poly(TMC) prepared with TiCl_4 at 60°C ($M/I = 50$, No. 1, Table 3).

groups are considerably lower than the M/I ratios. Third, the M_w/M_n ratios obtained from GPC measurements are all above 1.8.

Polymerizations with SbCl_5

Three series of SbCl_5 -initiated polymerizations were conducted in bulk in analogy to those initiated with TiCl_4 . The variation of the reaction time at 60°C revealed several differences compared to the TiCl_4 -initiated polymerizations listed in Table 4. First, the SbCl_5 -initiated polymerizations were considerably faster and were complete after 8 hours. Longer reaction times result in a significant decrease of the molecular weight. Second, the isolated polycarbonates possess less CH_2Cl end-groups when compared at shorter reaction times. Third, the polycarbonates contain ether groups (Fig. 2). The fact that the polymerizations were complete in less than 8 hours whereas the number of chloride and ether groups increases with time indicates that side reactions take place which involve the polycarbonate backbone. In other words, these side reactions are not restricted to the chain growth process in contrast to BF_3 and SnCl_4 [13] where the polycarbonate backbone was stable at 60°C .

The high reactivity of SbCl_5 toward TMC is also documented by the finding that it can initiate the polymerization even at 20°C in solution (Fig. 3) in contrast to TiCl_4 . For the initial slope of the time/conversion curve (0–5%), a rate constant (k_p) of 2.8×10^{-4} L/mol·s was found, and a k_p of 1.05×10^{-3} L/mol·s was found for the maximum slope between 40 and 50% conversion. Unfortunately, the high reactivity of SbCl_5 prevented comparative kinetic studies in more polar solvents such as dimethylformamide, acetonitrile, nitromethane, or nitrobenzene because all these solvents react with SbCl_5 .

Variation of the reaction temperature (Table 5) yielded, as expected, polycarbonates with a higher content of ether groups. However, it is remarkable that the fraction of ether groups did not exceed 4% whereas under identical conditions

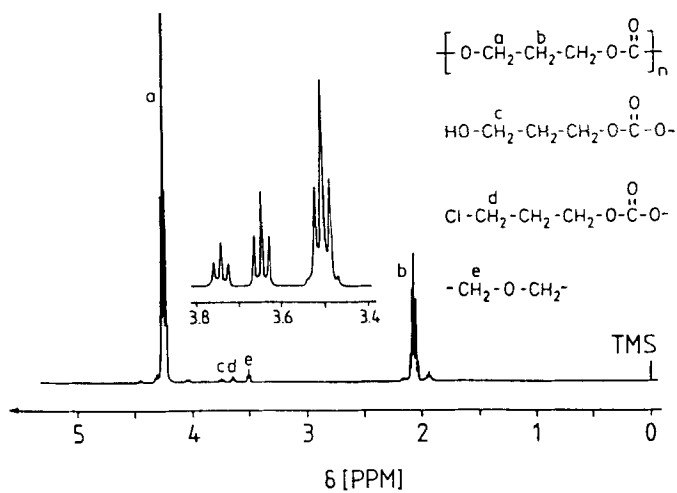


FIG. 2. 60 MHz ^1H -NMR spectrum of poly(TMC) prepared with SbCl_5 at 180°C ($M/I = 200$, No. 5, Table 5).

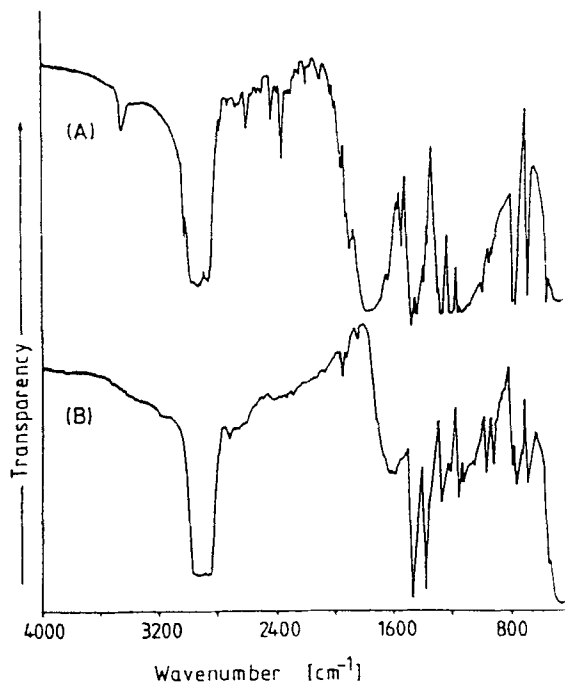


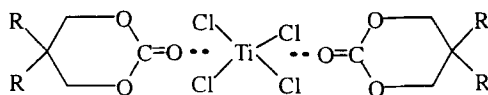
FIG. 3. IR spectra (suspensions in paraffin) of (A) neat TMC, (B) $\text{TiCl}_4 \cdot 2\text{TMC}$ complex.

percentages of 15–20 mol% were obtained when BF_3 , SnCl_4 , or SnBr_4 were used as initiators. From this point of view, SbCl_5 is in-between the extremes TiCl_4 and SnCl_4 (or SnBr_4). Taken together, the polymerizations summarized in Tables 1–6 reveal significant differences between TiCl_4 and SbCl_5 .

Complexation of TMC

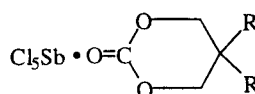
In order to gather more information on the polymerization mechanisms of TMC, it is useful to study the elementary steps of the initiation reaction. As reported previously [12–14], Lewis acids may form well-defined crystalline complexes when combined with aliphatic cyclocarbonates in chloroform. A solid 1:2 complex with the hypothetical structure **1** was also obtained when solutions of TiCl_4 and TMC in chloroform were mixed. However, addition of TiCl_4 to nitrobenzene or $\text{C}_6\text{D}_5\text{NO}_2$ yielded a yellow precipitate even in the absence of TMC, and thus, reactions of TiCl_4 with TMC were not studied in this polar solvent. Hence, the spectroscopic properties of this complex could not be determined in solution. The IR spectrum (Fig. 3) of the complex **1a** confirms the complexation of the carbonyl oxygen, which is the most basic and nucleophilic atom of the cyclocarbonates. Comparison with neat TMC reveals a considerable bathochromic shift of the $\text{C}=\text{O}$ stretch vibration. The ^{13}C -NMR CP/MAS spectrum displays a downfield shift of all carbon signals, with the most pronounced shift effect for the CO group (Fig. 4). The sharp signals and the identical chemical shifts of both $\text{O}-\text{CH}_2$ carbons support the symmetrical structure of the complex as outlined in formula **1**. Similar results were obtained when TiCl_4 was reacted with the double molar amount of neopentylene carbonate (NPC) in chloroform. The spectroscopic features of the complex **1b** were analogous to those of **1a**. The spectroscopy data of both complexes are listed in Tables 7 and 8.

The reaction of SbCl_5 with TMC in chloroform gave a gel-like precipitate, and all attempts to isolate a pure complex failed. The reaction of SbCl_5 and equimolar amounts of NPC in chloroform proved more successful. A well-defined 1:1 complex (**2b**) was isolated. The “CO band” of its IR spectrum exhibits a bathochromic shift



1a, b

a : R = H, b : R = CH_3



2a, b

a : R = H, b : R = CH_3

which is even stronger than that of the TiCl_4 complexes. An interesting observation was made when a double molar amount of NPC was added to a solution of SbCl_5 in CDCl_3 . The initially precipitated 1:1 complex (**2b**) went into solution and the ^1H -NMR spectrum revealed broad signals with a distinct downfield shift relative to neat NPC (Fig. 5). Obviously, the SbCl_5 forms a rapid dynamic equilibrium with all NPC molecules in solution. The same observation was made for BF_3 and TMC complexes [13].

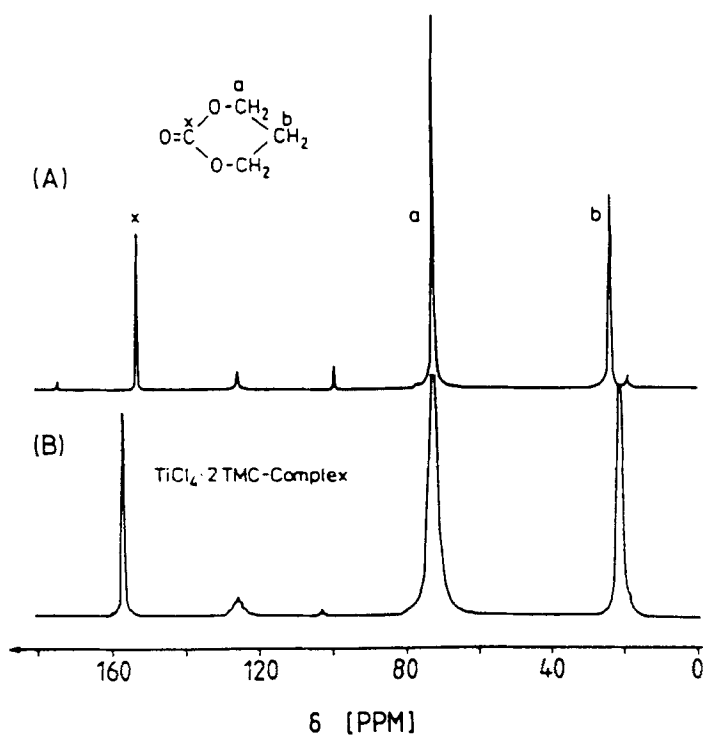
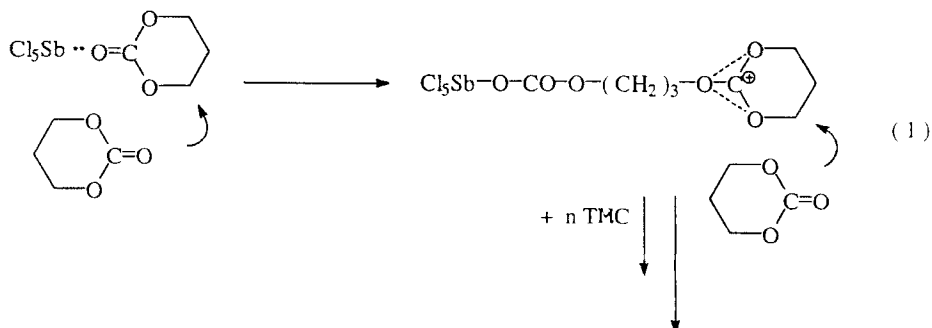
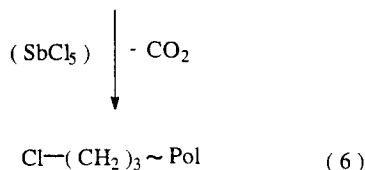
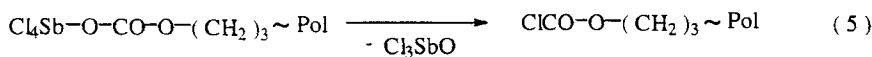
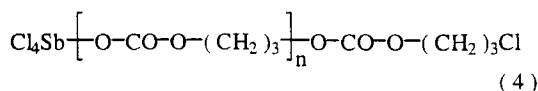
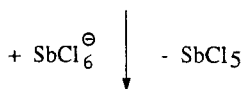
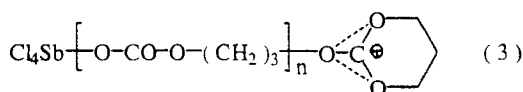
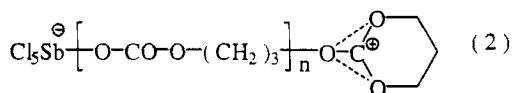


FIG. 4. 75.4 MHz ^{13}C -NMR CP/MAS spectrum of (A) neat TMC, (B) $\text{TiCl}_4 \cdot 2\text{TMC}$ complex.

When SbCl_5 was mixed with TMC in a 1:4 molar ratio, a clear solution was obtained in CDCl_3 . After 2 hours sharp ^1H -NMR signals of the growing polymer chains are observable, whereas the signals of the monomer are broad due to complexation equilibria (Fig. 6). However, it is not clear at this time why two pairs of broad signals are observable in contrast to the SbCl_5/NPC case. After 3 days the signals of the monomers have vanished, in agreement with the rapid conversion illustrated by Fig. 7. In addition to the signals of the polymer backbone, weak signals of ether and CH_2Cl endgroups are detectable (Fig. 7). The most interesting finding is a weak triplet at 5.3 ppm ("u" in Fig. 7). This signal was also observed in methyltriflate and BF_3 -initiated polymerizations of TMC [5] and may be attributed to the cationic endgroup (Eqs. 1-3).





Unfortunately, no kinetic studies were feasible with TiCl_4 in solution because a turbidity or a precipitate was formed under all circumstances. Yet, when the complexes **1a** or **2b** were added to molten TMC at 60°C , they reacted as initiators and produced poly(TMC) in high yields (Table 9). Therefore, it is obvious that the first step of the reactions between TMC (or NPC) and TiCl_4 or SbCl_5 is the formation of a complex such as **1a**, **b** or **2a**, **b**. The reaction of such a complex with an excess of TMC then initiates the chain growth process. A hypothetical scheme of a cationic polymerization process is outlined in Eqs. (1)-(6). Equations (4)-(6) provide hypothetical explanations for the formation of an excess of CH_2Cl endgroups relative to CH_2OH endgroups.

CONCLUSION

Both TiCl_4 and SbCl_5 initiate the polymerization of TMC in bulk and give high yields of poly(TMC). Due to side reactions such as the formation of CH_2Cl endgroups, only moderate molecular weights were obtained. From this point of

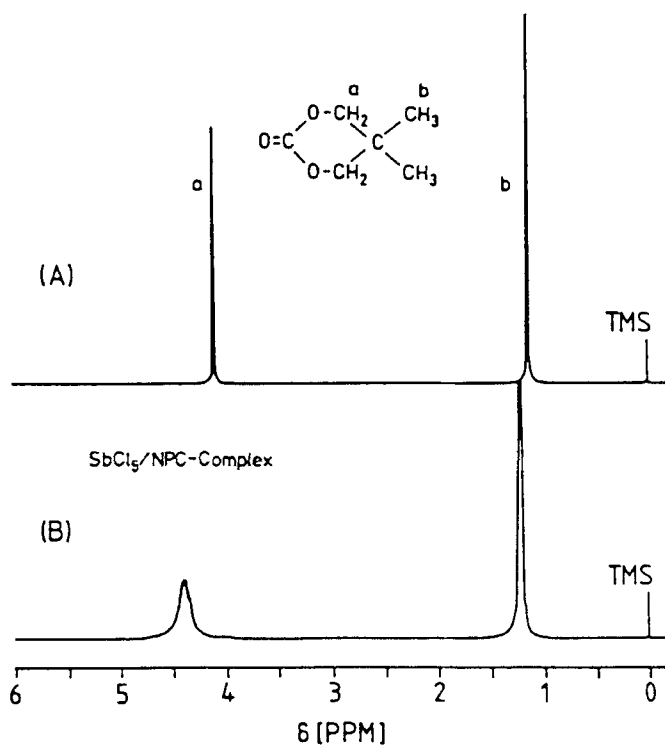


FIG. 5. 75.4 MHz ^{13}C -NMR CP/MAS spectra of (A) neat NPC, (B) $\text{SbCl}_5 \cdot \text{NPC}$ complex.

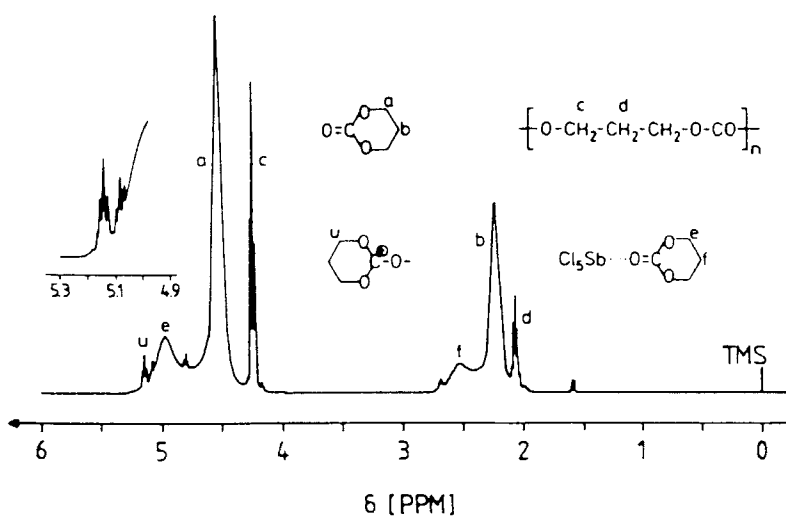


FIG. 6. 360 MHz ^1H -NMR spectrum of a SbCl_5/TMC mixture (molar ratio 1:4) in CDCl_3 at 20°C after 2 hours.

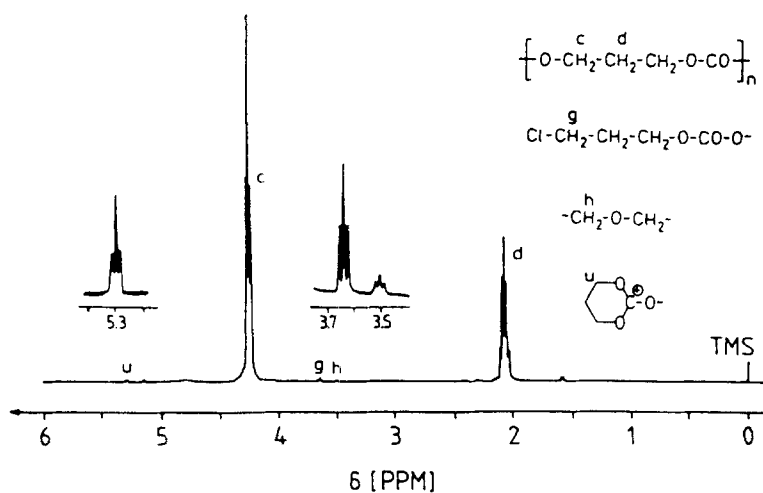


FIG. 7. 360 MHz $^1\text{H-NMR}$ spectrum of a SbCl_5/TMC mixture (molar ratio 1:4) in CDCl_3 at 20°C after 3 days.

TABLE 9. Polymerization of TMC in Bulk at 60°C Initiated with $\text{TiCl}_4 \cdot 2\text{NPC}$ or $\text{SbCl}_5 \cdot \text{NPC}$ Complexes ($M/I = 200$)

Polymer	Initiator	Time, hours	Yield, %	η_{inh}^a , dL/g	Ether, ^b groups	CH_2Cl^c endgroups
1	1b	8	0	—	0	
2	1b	24	Oligomers	—	0	
3	1b	48	94.0	0.35	0	1/90
4	1b	72	94.0	0.35	0	
5	1b	96	94.5	0.36	0	1/85
6	1b	144	95.0	0.35	0	—
7	1b	192	96.0	0.35	0	1/80
8	2b	8	94.0	0.4	1.0	1/140
9	2b	24	94.0	0.4	—	—
10	2b	48	94.0	0.50	3.0	1/110
11	2b	76	94.5	0.42	—	—
12	2b	96	94.5	0.37	4.3	1/65

^aMeasured at 25°C with $c = 2 \text{ g/L}$ in CH_2Cl_2 .

^bMol% of ether groups.

^cMolar ratio of CH_2Cl endgroups/monomer units.

view, BuSnCl_3 is the more efficient and attractive initiator [15]. From the preparative point of view, TiCl_4 is superior to the more reactive SbCl_5 because the resulting polycarbonates are free of ether groups. The well-known high Lewis acidity of SbCl_5 [17–19], the formation of ether groups, and the detection of signal “u” in reaction mixtures with TMC (Figs. 6 and 7) suggest that SbCl_5 -initiated polymerizations of TMC follow a cationic mechanism. In the case of TiCl_4 , no interpretation of the polymerization mechanism is offered at this time.

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