BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 26, pp. 4997–5003, 1995

0032-3861/95/$10.00+0.00

Polymers of carbonic acid: 13. Polymerization of cyclotrimethylenecarbonate with tin tetrahalides

Hans R. Kricheldorf* and Bettina Weegen-Schulz
Institut für Technische und Makromolekulare Chemie der Universität, Bundesstrasse 45, D-20146 Hamburg, Germany
(Received 31 October 1994; revised 20 February 1995)

Polymerizations of cyclotrimethylenecarbonate (TMC) with $SnCl_4$, $SnBr_4$ and SnI_4 were conducted in bulk. The reaction time, the temperature and the monomer/initiator (M/I) ratio were varied, and the influence of these parameters on yields and molecular weights was investigated. Yields above 90% were obtained with all these initiators, but the highest molecular weights ($M_w \approx 1.5 \times 10^5$) resulted from SnI_4-initiated polymerizations. SnI_4 has the additional advantage that the polycarbonates were free of ether groups when prepared at moderate temperatures (e.g. 60°C). In contrast, $SnCl_4$ and $SnBr_4$ cause partial decarboxylation even at 60°C, and at higher temperatures up to 20 mol% of the carbonate groups may be replaced by ether linkages. Furthermore, mechanistic studies were conducted. $SnCl_4$ and $SnBr_4$ form solid 1:2 complexes with TMC at 20–25°C. Infra-red, ^1H and ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopies indicate complexation at the carbonyl oxygen. Kinetic measurements of polymerizations in solvents of different polarity suggest cationic polymerization mechanisms. In addition to CH_2–OH, CH_2Cl and CH_2Br endgroups were detected by ^1H n.m.r. spectroscopy. The endgroup analyses of reaction mixtures and isolated poly(TMC) support the assumption of a cationic polymerization mechanism.

(Keywords: polymerization; cyclotrimethylenecarbonate; spectroscopy)

INTRODUCTION

Aliphatic polycarbonates attract increasing interest as hydrolytically and thermally degradable polymers. Numerous authors have used anionic initiators for the synthesis of homo- and copolymers by ring-opening polymerization of cyclocarbonates[1–7].

In contrast, relatively little information is available on the mechanistic and preparative aspects of cationic and insertion polymerizations of aliphatic cyclocarbonates. Endo and co-workers [8,9] and Albertsson and co-workers[10] have reported on cationic polymerizations of aliphatic cyclocarbonates. The present work is part of a broader study of Lewis acid-initiated polymerizations of lactones[11,12] and cyclocarbonates[13–17]. Lewis acids are of interest for both mechanistic and preparative aspects. It is not clear, a priori, that all Lewis acids initiate cationic polymerizations. Depending on their structure and that of the monomer, individual Lewis acids may also initiate insertion mechanisms. Different polymerization mechanisms do not only influence molecular weights, molecular weight distributions and endgroups, but also have a strong influence on the reactivities of comonomers in copolymerizations. According to our previous studies[13,17], Lewis acids offer a better chance of obtaining high molecular weights than do protic acids or carbenium ion donors. Whereas a previous paper describes stoichiometric reactions and polymerizations of cyclotrimethylenecarbonate (TMC) with various boron halogenides[17], the present work concentrates on tin tetrahalogenides as potential initiators. Both preparative and mechanistic aspects of SnX_4-initiated polymerizations were studied.

EXPERIMENTAL

Materials

Cyclotrimethylenecarbonate (TMC) was a gift of Boehringer KG (Ingelheim, Germany). It was recrystallized from ethyl acetate (m.p. 45–46°C) and stored over P_4O_{10}. $SnCl_4$, $SnBr_4$ and SnI_4 were purchased from Aldrich Co. (Milwaukee, WI, USA). $SnCl_4$ was distilled *in vacuo* prior to use. $CDCl_4$ and $C_6D_5NO_2$ were dried by storage over P_4O_{10}.

Polymerizations

TMC (50 mmol) was weighed into a 25 ml Erlenmeyer flask pretreated with dichlorodimethylsilane. After melting of the monomer at 50°C, the initiator was added by a syringe in the form of a 1 M solution in chloroform. The reaction vessel was closed with glass-stopper and steel spring and completely immersed into the thermostatically controlled oil bath. When the reaction time was over, the reaction product was

---

* To whom correspondence should be addressed

dissolved in 50 ml of CH_2Cl_2 precipitated into cold methanol and dried at 40°C *in vacuo*.

The reaction mixture was prepared in a glove box under dry nitrogen. SnI_4 was added as a neat solid material.

Formation of complexes

A solution of $SnCl_4$ (or $SnBr_4$) in dry chloroform (25 ml, 1 M) and a solution of TMC in chloroform (50 ml, 1 M) were mixed and cooled with ice. After 30 min the precipitate was filtered off under dry nitrogen, washed with dry CCl_4 and dried *in vacuo*.

$SnCl_4 \cdot 2$ TMC: yield 68%. Analyses calculated for $C_8H_{12}Cl_4O_6Sn$: C 20.68, H 2.60, Cl 30.52; found: C 20.15, H 3.08, Cl 30.16%.

$SnBr_4 \cdot 2$ TMC: yield 64%. Analyses calculated for $C_8H_{12}Br_4O_6Sn$: C 14.96, H 1.88, Br 49.75; found C 14.91, H 2.11, Br 50.04%.

Measurements

The inherent viscosities were measured with an automated Ubbelohde viscometer maintained thermostatically at 25°C.

The 75.4 MHz ^{13}C nuclear magnetic resonance (n.m.r.) cross polarization/magic angle spinning (CP/MAS) spectra were measured with a Bruker MLS 300 FT NMR spectrometer in double-bearing rotors made of ZrO_2. A pulse interval of 4 s and a contact time of 1 ms were used.

The 100 MHz ^1H n.m.r. spectra were recorded with a Bruker AC-100 FT NMR spectrometer in 5 mm o.d. sample tubes. For the kinetic measurements of *Figures 8* and *9*, 2.5 M solutions of TMC in $CDCl_3$ or $C_6D_5NO_2$ were used, and the initiator (monomer/initiator ratio (M/I) = 200) was injected in the form of a 1 M solution.

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

The gel permeation chromatography (g.p.c.) measurements were conducted with a Kontron HPLC (Md 420) equipped with a Waters differential diffractometer (Md 410) and four PSS-SDV columns (Polymer Standard Service GmbH, Germany) with pore sizes of 10^2, 10^3, 10^4 and 10^5 nm. Tetrahydrofuran (THF) served as solvent at 25°C with a flow rate of $1\ ml\ min^{-1}$.

The Mark–Houwink equation was determined by g.p.c. measurements of nine poly(TMC) samples in THF at 25°C. Unfractionated samples with M_w/M_n ratios in the range of 1.3–2.2 were used with M_w values in the range of 25×10^3. The measurements were conducted with a home-made g.p.c. apparatus of Bayer AG (Leverkusen, Germany) directly combined with a differential refractometer and an automatic Ubbelohde viscometer. The g.p.c. apparatus was equipped with five Styragel^R columns having pore sizes of around 10^2, 10^3, 10^4, 10^5 and 10^6 nm. Commercial polystyrene standards served for calibration.

RESULTS AND DISCUSSION

Optimization of reaction time and temperature

Preliminary experiments with $SnCl_4$ or $SnBr_4$ and TMC in chloroform and nitrobenzene have shown that polymerizations in solution at 20°C are slow. Therefore all polymerizations designed to elucidate the preparative usefulness of tin halogenide-initiated polymerizations were conducted in bulk. For variations of reaction time and M/I a minimum temperature of 60°C was selected, because this temperature is higher than the melting point of TMC (m.p. = 46–47°C) and allows a comparison with previous studies based on initiation with BF_3.

When the reaction time was varied at 60°C, $SnCl_4$-initiated (*Table 1*, nos 1–5) and $SnBr_4$-initiated polymerizations (*Table 2*, nos 1–5) show analogous results. The yields stay almost constant, whereas the viscosities decrease continuously with longer reaction times. In other words, the shortest time gave the best results. However, a further shortening of the time did not seem to be advisable, because yields obtained at 8 h are the lowest in both series. Thus it seems that a time of 8 h is close to the preparative optimum.

As reported previously[16], both $SnCl_4$ and $SnBr_4$ can form crystalline 1:2 complexes with TMC and other cyclocarbonates (e.g. form 1). In order to elucidate whether these complexes are active initiators and potential reaction intermediates in the SnX_4-initiated polymerizations of TMC, two parallel series of polymerizations were conducted with varying reaction times (nos 6–10 in *Tables 1* and *2*). Interestingly, the trends found in both series agree with each other and with those discussed for the SnX_4-initiated series (nos 1–5 in *Tables 1* and *2*). Whereas the yields are rather constant, the viscosities drop significantly with increasing time. For

Table 1 Polymerization of TMC in bulk at 60°C (M/I = 200) with $SnCl_4$ (nos 1–5) or $SnCl_4 \cdot 2$ TMC as initiators (nos 6–10)

No.	Time (h)	Yield (%)	η_{inh}[a] ($dl\ g^{-1}$)	Ether[b] (%)	CH_2Cl/M[c]
1	8	76.5	0.72	1.0	1/380
2	24	85.0	0.66	–	–
3	48	88.5	0.62	1.5	1/280
4	72	87.5	0.59	–	–
5	96	88.5	0.57	1.6	1/270
6	8	82.5	0.86	1.0	1/400
7	24	90.0	0.65	–	–
8	48	93.5	0.50	1.3	1/200
9	72	95.0	0.48	–	–
10	96	88.0	0.47	1.4	1/150

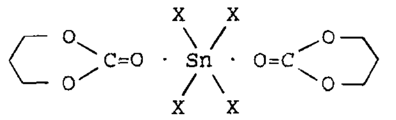
[a] Measured at 25°C with $c = 2\ g\ l^{-1}$ in CH_2Cl_2
[b] Molar percentage of ether groups relative to the sum of ether and carbonate groups
[c] Molar ratio of CH_2Cl endgroups to monomer units

Table 2 Polymerization of TMC in bulk at 60°C (M/I = 200) with $SnBr_4$ (nos 1–5) or $SnBr_4 \cdot 2$ TMC (nos 6–10) as initiators

No.	Time (h)	Yield (%)	η_{inh}[a] ($dl\ g^{-1}$)	Ether[b] (%)	CH_2Br/M[c]
1	8	87.0	0.57	1.7	1/250
2	24	90.0	0.55		
3	48	90.0	0.52	2.2	1/180
4	72	89.0	0.49	–	–
5	96	89.0	0.46	2.7	1/150
6	8	88.0	0.61	1.2	1/260
7	24	88.0	0.52		
8	48	88.0	0.47	1.5	1/180
9	72	88.5	0.42	–	–
10	96	88.0	0.39	1.4	1/140

[a] Measured at 25°C with $c = 2\ g\ l^{-1}$ in CH_2Cl_2
[b] Molar percentage of ether groups relative to the sum of ether and carbonate groups
[c] Molar ratio of CH_2Br endgroups to monomer units

both $SnCl_4$ and $SnBr_4$, the tendency of decreasing viscosities is even more pronounced when the complexes **1a** and **1b** were used as initiators. The reason for this difference is unclear as yet. However, these results demonstrate that the reactivity of both complexes is comparable with that of free $SnCl_4$ or $SnBr_4$.



1 a: X = Cl
b: X = Br

The four series listed in *Tables 1* and *2* also have in common that the polycarbonates isolated by precipitation into methanol possess ether groups in their backbones. The percentage of ether groups increases with time, and the same tendency was found for the CH_2–Cl or CH_2Br endgroups which were also detected in the ^1H n.m.r. spectra (*Figures 1* and *2*). These results suggest that the active chain end can attack its own backbone so that formation of cyclic oligomers by 'back-biting' degradation takes place. In agreement with this interpretation, g.p.c. measurements revealed that increasing reaction time results in broadening of the molecular weight distribution along with a shift to lower molecular weights. Unfortunately, peaks of individual cyclic oligomers were not detectable in the elution curves.

Variation of the reaction temperature (*Table 3*) revealed the following trends. The yields decrease slightly and the viscosities decrease more strongly. The percentage of ether and halogenide (end)groups rises sharply. The increasing molar fraction of ether linkages with higher temperatures is illustrated by *Figure 3* for $SnCl_4$. All these trends are particularly pronounced for SnI_4-initiated polymerizations (nos 11–15, *Table 3*). However, SnI_4 differs from $SnCl_4$ and $SnBr_4$ in two important

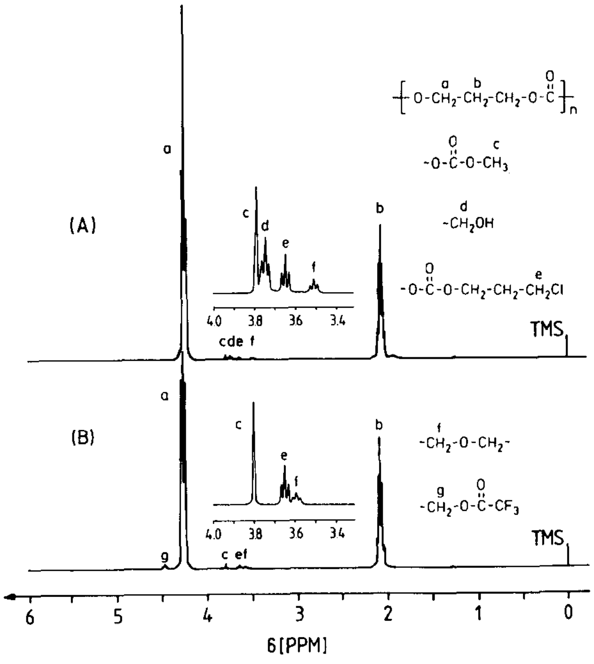


Figure 1 ^1H n.m.r. spectrum (360 MHz) of poly(TMC) initiated with $SnCl_4$ at 60°C

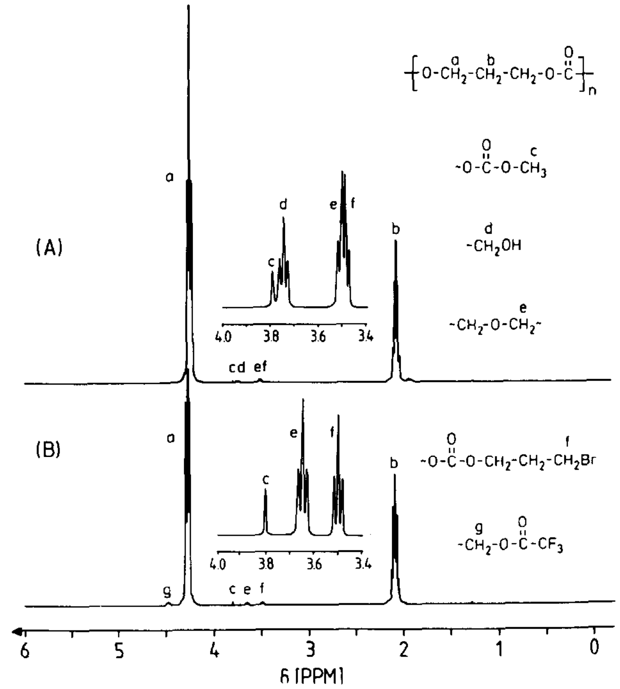


Figure 2 ^1H n.m.r. spectrum (360 MHz) of poly(TMC) initiated with $SnBr_4$ at 60°C

Table 3 $SnCl_4$, $SnBr_4$ and SnI_4-initiated polymerization of TMC in bulk (M/I = 200) with varying temperature

No.	Catalyst[a]	Temp. (°C)	Yield (%)	η_{inh}[b] ($dl\,g^{-1}$)	Ether[c] (mol %)	CH_2X/M[d]
1	$SnCl_4$	60	80.0	0.75	0.8	1/400
2		90	88.0	0.42	3.0	–
3		120	88.0	0.37	6.5	1/100
4		150	84.5	0.29	13.0	–
5		180	72.5	0.24	13.5	1/70
6	$SnBr_4$	60	92.5	0.65	1.5	1/300
7		90	90.0	0.39	3.0	–
8		120	88.0	0.36	8.0	1/100
9		150	82.0	0.25	20.0	–
10		180	82.0	0.25	20.0	1/80
11	SnI_4	60	88.5	1.12	0	1/600
12		90	87.5	0.91	0.5	–
13		120	87.0	0.47	2.5	1/190
14		150	55.0	0.17	15.5	1/70
15		180	Black oil	Black oil	–	–

[a] Reaction time: 8 h for $SnCl_4$ and $SnBr_4$, 48 h for SnI_4
[b] Measured at 25°C with $c = 2\,g\,l^{-1}$ in CH_2Cl_2
[c] Molar percentage of ether groups relative to the sum of ether and carbonate groups
[d] Molar ratio of halogenide endgroups to monomer units

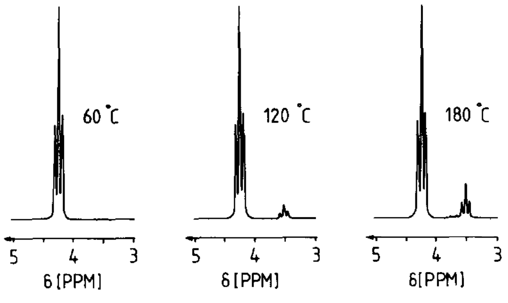


Figure 3 ^1H n.m.r. spectra (100 MHz) of poly(TMC) prepared by $SnCl_4$-initiated polymerizations (M/I = 200/1) illustrating the formation of ether groups (δ = 3.5 ppm)

aspects (summarized in *Table 6*). First, the polycarbonates prepared at 60°C do not contain ether groups in a concentration >0.5%. In other words, SnI_4 is in this work the only catalyst that allows the preparation of a nearly perfect polycarbonate backbone. Secondly, the SnI_4-initiated polymerizations are considerably slower, so that optimum yields and molecular weights require at least 48 h at 60°C and M/I = 200.

Finally, the identification of ether and endgroups should be commented upon. On the one hand, their assignments are based on comparisons with 3-chloro- or 3-bromo-1-propanol and with bis-n-butyl ether. On the other hand, they are based on the addition of trifluoroacetic anhydride to solutions of poly(TMC) in $CDCl_3$. This anhydride reacts rapidly with the OH endgroups, and the signal of the resulting $CH_2O{-}COCF_3$ endgroups shows a 0.5 ppm downfield shift relative to CH_2OH. A downfield shift of 0.1–0.15 ppm is observable for the ether signal after addition of trifluoracetic anhydride. It may be attributed to the influence of H-bonds between the ether oxygen and the liberated trifluoracetic acid. In agreement with this interpretation, the downfield shift increases with higher concentration of trifluoracetic acid. In contrast, the signals of the CH_2X endgroups remain almost unchanged (*Figures 1, 2*).

Influence of the monomer/initiator ratio

Three series of polymerizations were conducted in bulk at 60°C with variation of M/I (*Tables 4–6*). The influence of M/I on the molecular weights and the frequency of side reactions should be elucidated. The results of all three series show similar tendencies. The molecular weights increase with M/I, but they do not parallel it. Whereas the M/I values were increased by a factor of 10, the molecular weights varied by a factor of 4. This result means that the SX_4-initiated polymerizations do not obey the classical 'living pattern' of anionic polymerizations of vinyl monomers. This point needs to be emphasized because the data of *Tables 1* and *2* indicate that an active species is present, even long after complete conversion of the monomers. The deviation from the classical pattern of a living polymerization is confirmed by broad molecular weight distributions revealed by g.p.c. All samples examined had M_w/M_n values in the range of 1.4–2.2. Values of $M_w/M_n \geq 1.4$ agree with the obvious complexity of the polymerization mechanism (see below). The initiation involves the complexation of the monomer (**1a, 1b**), but this complexation is an equilibrium, which is unfavourable for a rapid, simultaneous initiation step. Furthermore, numerous side reactions take place which include scission of the main chain, such as formation of halogenide endgroups and back-biting degradation. The positive aspects of higher M/I are twofold: the frequency of side reaction is lower, and the molecular weights are higher. In the case of SnI_4 (*Table 6*), a maximum weight average molecular weight (M_w) of 150×10^3 was obtained.

A brief discussion of the molecular weight measurements is required. The M_w values obtained from g.p.c. measurements in THF using commercial polystyrene standards and the universal calibration method are approximately 20% higher than those obtained from the Mark–Houwink equation (1). This equation was also determined by g.p.c. measurements in THF at 25°C using nine unfractionated poly(TMC) samples prepared in previous work[17], but another g.p.c. apparatus with a different set of g.p.c. columns was used (see Experimental section). However, it should be kept in mind that viscosity average molecular weights (M_v) calculated in this way are necessarily somewhat lower than the true M_w values, and thus the agreement between both series of molecular weight measurements is acceptable. This point needs to be emphasized because another Mark–Houwink equation (2), was recently published for

Table 4 Polymerization of TMC with $SnCl_4$ in bulk at 60 C with variation of the initial monomer/initiator ratio

No.	M/I	Time (h)	Yield (%)	η_{inh}[a] ($dl\,g^{-1}$)	M_w[b]	M_v[c]	M_v[d]
1	50	2	67.5	0.35	40 000	30 000	24 000
2	50	8	83.0	0.35	44 000	32 000	
3	100	8	82.5	0.47	50 000	45 000	34 000
4	150	8	82.0	0.65	75 000	64 000	45 000
5	200	8	83.0	0.78	90 000	76 000	
6	300	8	82.5	0.82	95 000	85 000	60 000
7	500	8	78.0	1.11	125 000	110 000	80 000
8	500	20	86.5	1.06	120 000	100 000	

[a] Measured at 25 C with $c = 2\,g\,l^{-1}$ in CH_2Cl_2

[b] Determined by g.p.c. in THF at 25 C using commercial polystyrene standards along with the universal calibration method

[c] Calculated from the Mark–Houwink equation (1)

[d] Calculated from the Mark–Houwink equation (2)

Table 5 Polymerization of TMC with $SnBr_4$ in bulk at 60°C with variation of the initial monomer/initiator ratio

No.	M/I	Time (h)	Yield (%)	η_{inh}[a] ($dl\,g^{-1}$)	M_w[b]	M_v[c]	M_v[d]
1	50	2	80.0	0.27	30 000	25 000	–
2	50	8	92.0	0.28	31 000	26 000	20 000
3	100	8	91.5	0.33	36 000	33 000	–
4	150	8	89.0	0.53	55 000	50 000	–
5	200	8	89.0	0.64	74 000	64 000	45 000
6	300	8	90.0	0.67	77 000	67 000	–
7	500	8	89.5	0.92	110 000	96 000	67 000
8	500	20	92.5	0.83	97 000	88 000	–

[a] Measured at 25°C with $c = 2\,g\,l^{-1}$ in CH_2Cl_2

[b] Determined by g.p.c. in THF at 25°C using commercial polystyrene standards and the universal calibration method

[c] Calculated from the Mark–Houwink equation (1)

[d] Calculated from the Mark–Houwink equation (2)

Table 6 Polymerization of TMC with SnI_4 in bulk at 60°C with variation of time and initial monomer/initiator ratio

No.	M/I	Time (h)	Yield (%)	η_{inh}[a] ($dl\,g^{-1}$)	CH_2J/M[b]	M_w[c]	M_v[d]	M_v[e]
1	50	8	64.0	0.69		–		–
2	50	48	96.0	0.90	1/600	105 000	90 000	63 000
3	100	48	95.0	1.08				–
4	150	48	95.5	1.09		120 000	100 000	–
5	200	8	57.0	0.86		–	–	
6	200	24	86.5	0.98		115 000	95 000	68 000
7	200	48	95.0	1.10	1/800	–	–	–
8	300	48	93.5	1.27	–	150 000	125 000	88 000
9	500	48	90.0	1.22	1/900	135 000	115 000	–
10	500	144	94.0	1.14	1/700	125 000	105 000	75 000

[a] Measured at 25°C with $c = 2\,g\,l^{-1}$ in CH_2Cl_2

[b] Molar ratio of CH_2J endgroups to monomer units

[c] Determined by g.p.c. in THF at 25°C using commercial polystyrene standards and the universal calibration method

[d] Calculated from the Mark–Houwink equation (1)

[e] Calculated from the Mark–Houwink equation (2)

poly(TMC) by another research group[18]. When the M_w values were determined on the basis of equation (2) they were lower by approximately 30% (*Tables 4–6*). For reasons that will be discussed in a subsequent paper, the authors of the present work distrust the lower M_w values resulting from equation (2).

$$[\eta] = 4.10 \times 10^{-2} M_w^{0.62} \quad (25°C \text{ in THF}) \qquad (1)$$

$$[\eta] = 2.77 \times 10^{-4} M_w^{0.677} \quad (30°C \text{ in THF}) \qquad (2)$$

Mechanistic aspects

As reported previously[16], both $SnCl_4$ and $SnBr_4$ form crystalline 1:2 complexes with TMC when mixed in concentrated $CHCl_3$ solution. SnI_4 is almost insoluble in chloroform and most other inert organic solvents with the exception of CS_2. However, when concentrations of SnI_4 were used, preventing the precipitation of neat SnI_4, no solid complex was formed. Even the $SnCl_4$ and $SnBr_4$ complexes dissolve in nitrobenzene, and ^1H and ^{13}C n.m.r. spectra were measurable in solution (*Figure 4*). The chemical shifts of these solution spectra and those of the solid-state ^{13}C n.m.r. spectra (*Figure 5* and *Table 7*) support the structure outlined in formulas **1a** and **1b**. Infra-red spectra agree with this structure, exhibiting a significant bathochromic shift of the CO stretching vibration (*Figure 6*). The catalytic activity of **1a** and **1b**, documented in *Tables 1* and *2*, suggests that they play a key role in the initiation process.

The main mechanistic problem which needs to be solved is whether the SnX_4-initiated polymerizations follow an insertion mechanism, such as that outlined in equations (3)–(6), or obey the cationic mechanism illustrated by equations (7)–(11). One approach that allows discrimination between the mechanisms may be kinetic measurements conducted in solvents of different polarity. The polar solvent favours the dissociation of cationic chain end and anion, and thus improves the

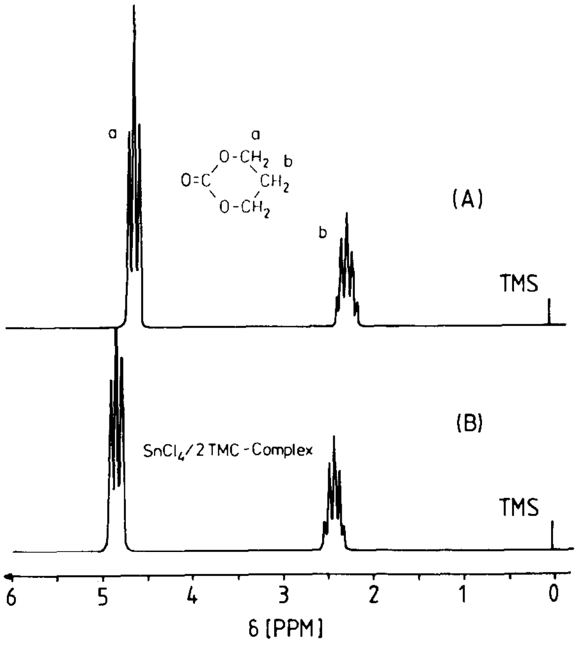


Figure 4 ^1H n.m.r. spectra (100 MHz, in $C_6D_5NO_2$) of (A) neat TMC, (B) $SnCl_4 \cdot 2$ TMC complex

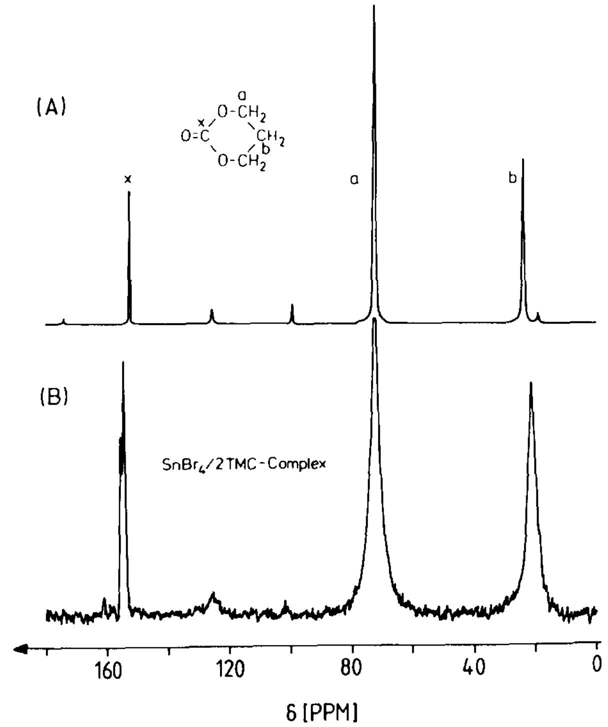
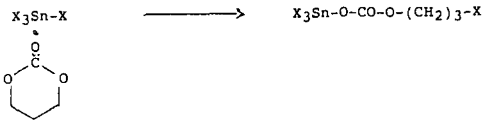


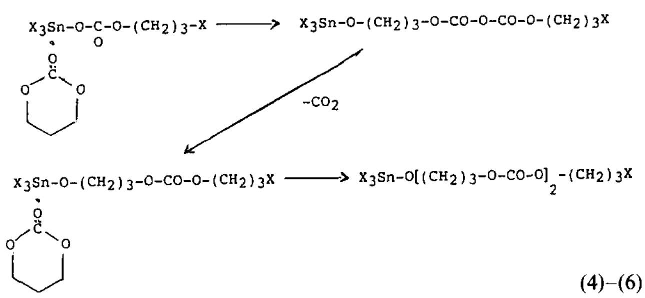
Figure 5 ^{13}C n.m.r. CP/MAS spectra (75.4 MHz) of (A) neat TMC, (B) $SnBr_4 \cdot 2$ TMC complex

Table 7 ^1H and ^{13}C n.m.r. chemical shifts of $SnCl_4$/TMC and $SnBr_4$/TMC complexes

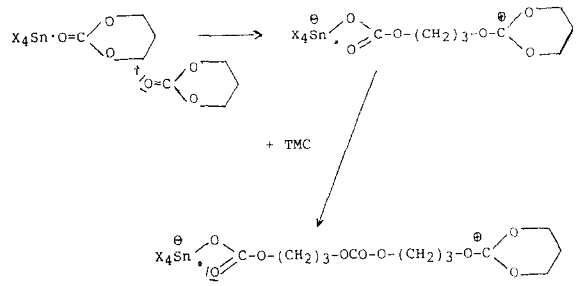
			Chemical shifts, δ (ppm)		
Nucleus	Compound	Solvent	CO	C_α	C_β
^1H	TMC	$CDCl_3$	–	4.47	2.17
		$C_6D_5NO_2$	–	4.57	2.22
	Poly(TMC)	$CDCl_3$	–	4.24	2.05
		$C_6D_5NO_2$	–	4.33	2.15
	$SnCl_4 \cdot 2TMC$	$C_6D_5NO_2$	–	4.85	2.44
	$SnBr_4 \cdot 2TMC$	$C_6D_5NO_2$	–	4.72	2.35
13C	TMC	$CDCl_3$	148.2	67.7	21.1
		$C_6D_5NO_2$	149.0	68.9	22.4
		solid	152.1	71.8	23.2
	Poly(TMC)	$CDCl_3$	154.9	64.3	28.1
		$C_6D_5NO_2$	155.7	65.2	28.8
		solid	157.1	66.7	29.9
	$SnCl_4 \cdot 2TMC$	$C_6D_5NO_2$	–	71.0	21.9
		solid	155.9/155.1	72.3	21.0
	$SnBr_4 \cdot 2TMC$	$C_6D_5NO_2$	152.0	70.0	22.1
		solid	155.2/154.3	72.1	21.0



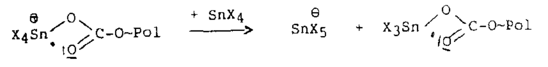
(3)



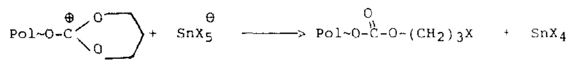
(4)–(6)



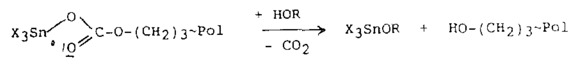
(7)–(8)



(9)



(10)



(11)

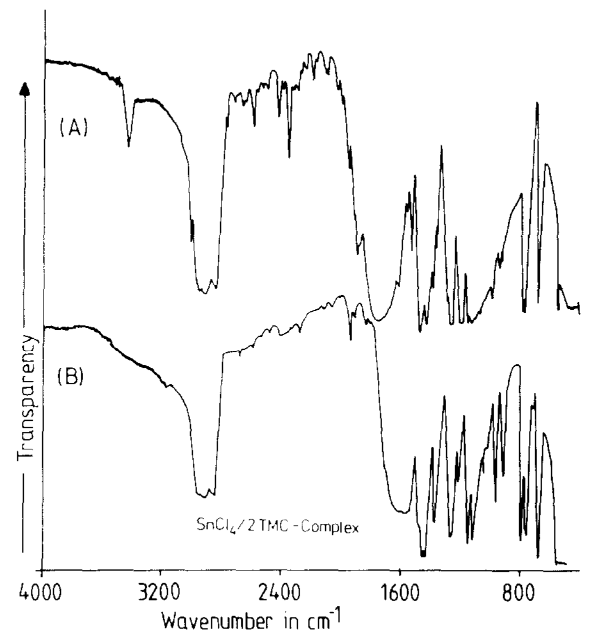


Figure 6 I.r. spectra (suspension in paraffin) of (A) neat TMC, (B) $SnCl_4 \cdot 2$ TMC complex

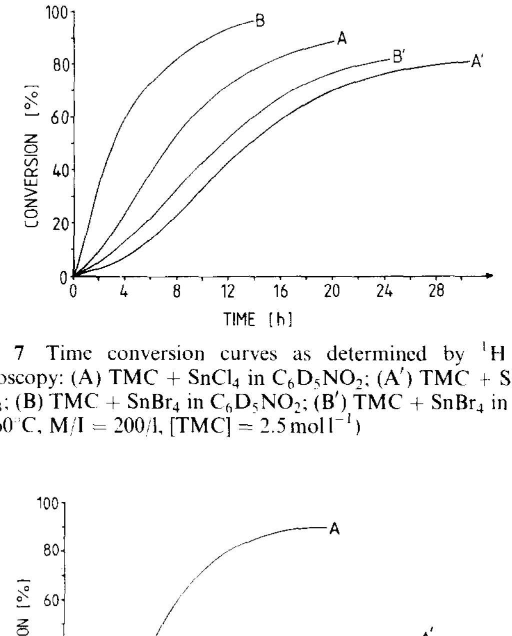


Figure 7 Time conversion curves as determined by ^1H n.m.r. spectroscopy: (A) TMC + $SnCl_4$ in $C_6D_5NO_2$; (A′) TMC + $SnCl_4$ in $CDCl_3$; (B) TMC + $SnBr_4$ in $C_6D_5NO_2$; (B′) TMC + $SnBr_4$ in $CDCl_3$ ($T = 60°C$, M/I = 200/1, [TMC] = $2.5\,\mathrm{mol\,l^{-1}}$)

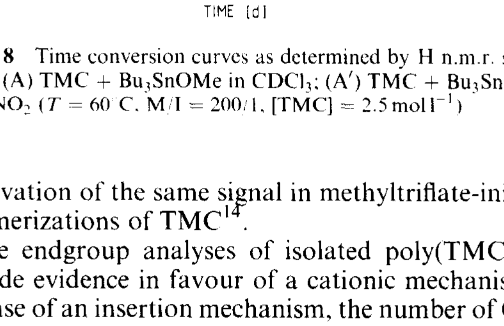


Figure 8 Time conversion curves as determined by H n.m.r. spectroscopy: (A) TMC + Bu_3SnOMe in $CDCl_3$; (A′) TMC + Bu_3SnOMe in $C_6D_5NO_2$ ($T = 60°C$, M/I = 200/1, [TMC] = $2.5\,\mathrm{mol\,l^{-1}}$)

access of monomers to the active chain end in the case of a cationic mechanism. In contrast, the polar solvent competes with monomers for coordination at the active endgroup (i.e. Sn atom) in the case of an insertion mechanism. Therefore, higher rates of polymerization in the polar solvent may be taken as evidence for a cationic mechanism. When $SnCl_4$- and $SnBr_4$-initiated polymerizations were conducted in $CDCl_3$ (dielectric constant 4.7) and in C_6D_5-NO_2 (dielectric constant 34.8), faster polymerizations were found in the more polar nitrobenzene (*Figure 7*).

From the almost linear slopes between 20 and 40% conversion, the following rate constants were determined: $k_p = 1.08 \times 10^{-3}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ in $CDCl_3$ and $k_p = 1.69 \times 10^{-3}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ in $C_6D_5NO_2$ for $SnCl_4$ as catalyst, or $k_p = 1.65 \times 10^{-3}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ in $CDCl_3$ and $k_p = 3.86 \times 10^{-3}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ in $C_6D_5NO_2$ for $SnBr_4$. These data suggest a cationic mechanism, and this kinetic argument is particularly strong because quite analogous results were obtained from methyltriflate-initiated polymerizations of TMC[14]. Furthermore, Bu_3Sn–OMe-initiated polymerizations were conducted at 60°C in $CDCl_3$ and $C_6D_5NO_2$ with M/I = 200. As illustrated by *Figure 8*, the kinetic results are opposite to those found for $SnCl_4$ or $SnBr_4$. The polymerization in $CDCl_3$ is more rapid by a factor of 8.4 than in nitrobenzene-d_5. Since Bu_3Sn–OMe is a typical insertion catalyst, its inverse kinetic pattern lends strong support to the assumption of a cationic mechanism in the case of $SnCl_4$ and $SnBr_4$.

Another argument in favour of a cationic mechanism results from ^1H n.m.r. measurements of reaction mixtures prepared with $SnCl_4$ (*Figure 9*). At higher conversions a signal (u) appears at 5.5 ppm which may be assigned to the O–CH_2 protons of a trioxocarbenium endgroup. This assignment is based on the downfield shift of 0.6 ppm relative to the neat monomer, and on the observation of the same signal in methyltriflate-initiated polymerizations of TMC[14].

The endgroup analyses of isolated poly(TMC) also provide evidence in favour of a cationic mechanism. In the case of an insertion mechanism, the number of CH_2X endgroups needs to match that of CH_2–OH endgroups or it may be higher, when side reaction such as (12) or

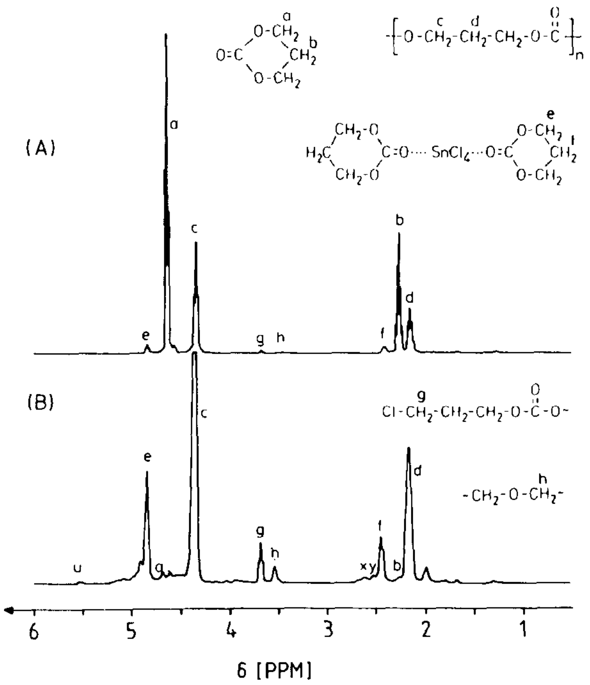
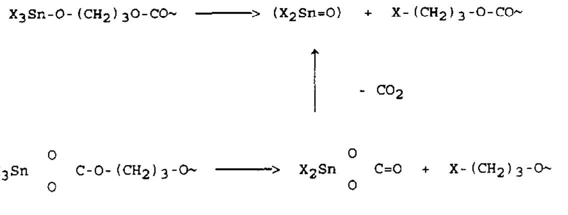


Figure 9 ^{1}H n.m.r. spectra (360 MHz) of the reaction mixture obtained from TMC and $SnCl_4 \cdot 2$ TMC (molar ratio 4:1) in $C_6D_5NO_2$ at 60°C: (A) after 4 h, (B) after 34 h

(13) take place. However, in the case of a cationic mechanism the number of CH_2X endgroups may be lower.

Finally, the formation of ether groups deserves a short discussion. The decarboxylation may be a side reaction of the growing steps or a side reaction between catalyst and polycarbonate backbone. In the latter case, the decarboxylation is not related to the polymerization mechanism. When a poly(TMC) free of ether groups was combined with $SnCl_4$ or $SnBr_4$ in $CDCl_3$ at 60°C, no ether groups were detectable even after 96 h. This negative result (also found for BF_3[17]) indicates that the decarboxylation is a side reaction of the chain growth process. The cationic nature of this decarboxylation process is supported by the following findings. First, heating of diethylcarbonate with methyltriflate causes decarboxylation and formation of diethylether along with methyl ethyl ether[14]. Secondly, $Bu_3Sn{-}OMe$-initiated polymerizations of TMC at 60°C yield a polycarbonate free of ether groups. A speculative mechanism explaining the decarboxylation has been discussed previously in connection with BF_3-initiated polymerizations[17].



(12)–(13)

CONCLUSION

$SnCl_4$, $SnBr_4$ and SnI_4 all enable the preparation of high molecular weight poly(TMC). In the case of $SnCl_4$ and $SnBr_4$, these polymerizations involve the formation of ether groups even at 60°C. All experimental evidence available at this time suggests that both catalysts initiate a cationic polymerization mechanism which is responsible for side reactions such as formation of CH_2X endgroups and ether groups. Unfortunately, the low solubility of SnI_4 in all common solvents prevented mechanistic studies. However, this catalyst is of particular interest because it yields the highest molecular weights and because the poly(TMC) prepared at 60°C is almost free of ether groups. In other words, SnI_4 is an attractive catalyst for preparative purposes.

ACKNOWLEDGEMENT

We thank Dr Kremer-Lukas (Bayer AG, Leverkusen) for determining the Mark–Houwink equation (1), and Dr Amecke (Boehringer GmbH, Ingelheim, Germany) for a gift of trimethylenecarbonate.

REFERENCES

1 Carothers, W. H. and Van Natta, F. J. *J. Am. Chem. Soc.* 1930, **52**, 314
2 Hostettler, F. and Cox, E. F. Ger. Offen 1545116 u. 1545117 (1964) to Union Carbide
3 Mues, P., Buysch, H. J., Brassat, B. and Heine, H. Ger. Offen DE 3.501.246 (1986) to Bayer AG; *Chem. Abs.* 1986, **105**, 191791c
4 Eichenauer, H., Leitz, E. and Ott, K. H. Ger. Offen DE 3.700.193 (1987) to Bayer AG; *Chem. Abs.* 1988, **109**, 191117v
5 Krimm, H., Buysch, H. J. and Botta, A. Eur. Pat. EP 50.111 (1982) to Bayer AG; *Chem. Abs.* 1982, **97**, 93020x
6 Kühling, S., Keul, H. and Höcker, H. *Makromol. Chem. Suppl.* 1989, **15**, 9
7 Kühling, S., Keul, H. and Höcker, H. *Makromol. Chem.* 1990, **191**, 1611
8 Ariga, T., Takata, T. and Endo, T. *J. Polym. Sci. Part A, Polym. Chem.* 1993, **31**, 581
9 Ariga, T., Takata, T. and Endo, T. *Macromolecules* 1993, **26**, 7106
10 Albertsson, A.-C. and Sjoling, M. *JMS–Pure Appl. Chem.* 1992, **A29**, 43
11 Kricheldorf, H. R., Jonté, J. M. and Dunsing, R. *Makromol. Chem.* 1986, **187**, 771
12 Kricheldorf, H. R. and Dunsing, R. *Makromol. Chem.* 1986, **187**, 1611
13 Kricheldorf, H. R., Dunsing, R. and Serra i Albet, A. Makromol. Chem. 1987, **188**, 2453
14 Kricheldorf, H. R. and Jenssen, J. *J. Macromol. Sci., Chem.* 1989, **A26**, 631
15 Kricheldorf, H. R., Weegen-Schulz, B. and Jenssen, J. *Makromol. Chem., Macromol. Symp.* 1992, **60**, 119
16 Kricheldorf, H. R. and Weegen-Schulz, B. *Makromol. Chem. Rapid Commun.* 1993, **14**, 405
17 Kricheldorf, H. R. and Weegen-Schulz, B. *Macromolecules* 1993, **26**, 5991
18 Zhu, K. J., Hendren, R. W. and Pitt, C. G. *Macromolecules* 1991, **24**, 1736