*Macromolecules* **1993,** *26,* 5991-5998 **5991**

# Polymers of Carbonic Acid. 11. Reactions and Polymerizations of Aliphatic Cyclocarbonates with Boron Halogenides

**Hans R. Kricheldorf* and Bettina Weegen-Schulz**

*Institut für Technische und Makromolekulare Chemie, Universität Hamburg,*
*Bundesstrasse 45, 20146 Hamburg, Germany*

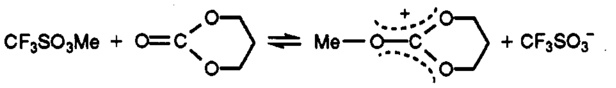
*Received June 24, 1992; Revised Manuscript Received July 26, 1993*[•]

ABSTRACT: Neopentylene carbonate (NPC) and trimethylene carbonate (TMC) were reacted with $BF_3{\cdot}OEt_2$, $BCl_3$, and $BBr_3$ under various conditions. When the cyclocarbonates and boron halogenides were combined in equimolar amounts at 20 °C in chloroform, crystalline complexes were formed in the cases of TMC–$BF_3$, NPC–$BCl_3$, and NPC–$BBr_3$. Depending on the reaction conditions, $BCl_3$ and $BBr_3$ react with both cyclocarbonates by ring opening and halogen transfer without initiating polymerization. In contrast, $BF_3{\cdot}OEt_2$ and its TMC complex are effective initiators, and polymerizations in bulk may yield polycarbonates in yield >95% and with high molecular weights ($M_w > 10^5$). However, all polycarbonates contain ether groups, and the molar fraction of ether groups increases with the temperature. This observation and the acceleration of the polymerization in polar solvents suggest a cationic mechanism.

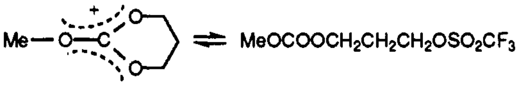
## Introduction

Aliphatic polycarbonates and copolymers of cyclocarbonates and lactones find increasing interest as biodegradable materials for pharmaceutical or medical purposes.[1-4] Furthermore, they may be of interest as oligomeric or polymeric additives with plastifying or thickening properties for a variety of applications.[5-7]

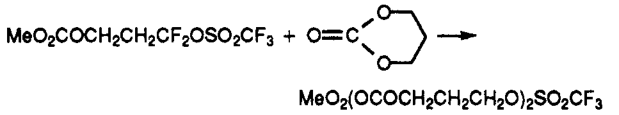
The present work is part of a broader study of the cationic polymerization of lactones and cyclocarbonates.[8,9] In two previous papers we have reported on polymerizations of neopentylene carbonate (NPC) and trimethylene carbonate (TMC) with methyl triflate or triflic acid as initiators. The results suggest the (simplified) polymerization mechanism outlined in eqs 1–3 in close analogy to the cationic polymerization of lactones.[10-12] Further studies will deal with reactions and polymerizations of aliphatic cyclocarbonates and various Lewis acids. The usefulness of $BF_3$ as initiator for the polymerization of aliphatic cyclocarbonates has been shortly demonstrated in two previous papers.[8,13] Furthermore, Albertsson and Sjöling have shown[14] that BF-initiated polymerizations of trimethylene carbonate (1,3-dioxanone-2) may yield high molecular weight polycarbonates, but these polycarbonates contained ether linkages. The present work was aimed at studying the elementary steps of boron halogenide initiated polymerizations of six-membered cyclocarbonates in more detail.



(1)



(2)



(3)

## Experimental Section

**Materials.** Neopentylene carbonate (NPC), a gift of Bayer AG (4150 Krefeld, FRG), was recrystallized from a mixture of $CCl_4$ and ligroin. Trimethylene carbonate (TMC), a gift of Boehringer Ingelheim (6507 Ingelheim, FRG), was recrystallized from $CCl_4$ and dried over $P_4O_{10}$ in vacuo. $BF_3OEt_2$, $BCl_3$ (1 M in hexane), and $BBr_3$ were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. $CCl_4$, $CHCl_3$, $CDCl_3$, $C_6H_5NO_2$, and $C_6D_5NO_2$ were dried over $P_4O_{10}$ and distilled.

**Synthesis of 1:1 Complexes.** The whole procedure was conducted in a glovebox under nitrogen dried over $P_4O_{10}$. A 20% (by weight) solution of a boron halogenide in dry chloroform (or a 1 M solution of $BCl_3$ in hexane) was added portionwise to a 20% (by weight) solution of a cyclocarbonate in dry chloroform until an equimolar mixture was obtained. After 10 min the resulting precipitate was isolated by filtration through a glass frit washed with a small amount of dry chloroform and dried in vacuo over $P_4O_{10}$.

**Hydrolytic Workup of Reaction Mixtures.** An equimolar mixture of boron halogenide and cyclocarbonate (50 mmol) in chloroform was prepared as described above. After storage for 1 h at 20 °C, the reaction mixture was diluted with chloroform (ca. 100 mL) and washed twice with 0.1 M aqueous hydrochloric acid. Finally, the reaction mixture was dried over $Na_2SO_4$ at 0 °C, filtered, and concentrated in vacuo. This procedure was applied to all six possible combinations of $BX_3$ and cyclocarbonates, regardless of whether solid complex was formed or not.

**Polymerizations in Solution (Table V).** All reaction mixtures were prepared in a glovebox under dry nitrogen. Trimethylene carbonate (50 mmol) was dissolved in 25 mL of dry $CHCl_3$ or nitrobenzene in a 50-mL Erlenmeyer flask with silanized glass walls (pretreatment with dimethyldichlorosilane). A total of 0.25 mL of a 1 M initiator solution in $CHCl_3$ (or $C_6H_5NO_2$) was added with a syringe. The reaction vessel was closed with a glass stopper and a steel spring and immersed in a thermostated oil bath. Finally, the reaction mixture was diluted with 25 mL of $CH_2Cl_2$ and precipitated into cold methanol (500 mL). The isolated polycarbonate was dried over $P_4O_{10}$ at 20 °C in vacuo. The polycarbonates prepared in $C_6H_5NO_2$ were reprecipitated from $CH_2Cl_2$/methanol.

**Polymerizations in Bulk (Tables VI–VIII).** Trimethylene carbonate (50 mmol) was molten in a 25-mL Erlenmeyer flask with silanized glass walls, and 0.25 mL of a 1 M initiator solution was injected with a syringe. The reaction vessel was closed with a glass stopper and a steel spring and thermostated. Finally, the reaction product was dissolved in 40 mL of dry $CH_2Cl_2$ and precipitated into cold methanol.

**Measurements.** The inherent and intrinsic viscosities were measured with an automated Ubbelohde viscometer thermostated at 25 °C. The $^1H$ NMR spectra were recorded with a Bruker AC-100 or AM-360 FT NMR spectrometer in 5-mm-o.d. sample tubes. Reaction mixtures in $CDCl_3$ or $C_6D_5NO_2$ were freshly prepared in a glovebox under dry nitrogen, transferred to the

---

[•] Abstract published in *Advance ACS Abstracts,* October 1, 1993.

0024-9297/93/2226-5991$04.00/0

NMR tubes, and doped with a trace of TMS for shift referencing.

The 25.4-MHz $^{13}C$ NMR spectra in solution were recorded with a Bruker AC-100 FT-NMR spectrometer in 10-mm-o.d. sample tubes with TMS as internal standard.

The 75.4-MHz $^{13}C$ NMR CP/MAS spectra were measured on a Bruker MSL-300 FT NMR spectrometer in $ZrO_2$ rotors at a spinning rate of 4 kHz. A contact time of 1 ms and a relaxation delay of 4 s were used in all cases. Approximately 1000–1500 transients were accumulated.

The GPC measurements were conducted on two instruments in two different laboratories. The $M_{max}$ values of Table VI were determined in tetrahydrofuran on a Kontron HPLC apparatus equipped with a Waters differential refractometer Md 410. A combination of four Ultrastyragel columns was used with pore sizes of $10^2$, $10^3$, $10^4$, and $10^5$ Å. The maxima of the elution curves were evaluated on the basis of the universal calibration method.

The $M_n$ and $M_w$ values of Table VI were determined with a homemade GPC apparatus of Bayer AG (Leverkusen, Germany) in tetrahydrofuran and in dichloromethane. A combination of nine columns with pore sizes in the range of $10^3$–$10^7$ Å was used, and a differential refractometer and an automated viscometer served as detectors. Again the universal calibration was applied.

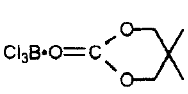
The IR spectra of suspensions in paraffin were measured with a Nicolet SXB-20 FT IR spectrometer.

## Results and Discussion

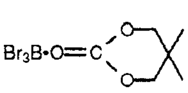
**Characterization of Complexes.** In order to elucidate the elementary steps of the reactions between boron halogenides and cyclocarbonates, all three boron halogenides were reacted with equimolar or double molar amounts of NPC and TMC. The reactions were conducted in chloroform and nitrobenzene at 20–25 °C. These solvents were selected because they differ largely in polarity (dielectric constant of $CHCl_3$ = 4.7 and of $C_6H_5NO_2$ = 34.8 at 25 °C) and because they are available in deuterated form, so that NMR studies of reaction mixtures prepared in NMR tubes are feasible. In addition to experiments conducted in NMR tubes (NMR data in Tables I and II), "preparative experiments" were conducted with 50-mmol quantities of monomers. These preparative experiments were exclusively conducted in chloroform (Tables III and IV) for two reasons. First, $BBr_3$ undergoes rapid redox reactions with nitrobenzene as indicated by the evolution of $Br_2$. Second, the moisture-sensitive or volatile reaction products are difficult to purify from nitrobenzene.

When NPC was reacted with $BF_3 \cdot OEt_2$, a clear solution was obtained in chloroform and in nitrobenzene. A shift of the $CH_2$ signal in the $^1H$ NMR spectra indicated the formation of a HPC–$BF_3$ complex. However, the chemical shifts of diethyl ether in this reaction mixture are slightly downfield of those of pure diethyl ether in chloroform. This result suggests the existence of equilibria between $BF_3$ and NPC, on the one hand, and $BF_3$ and $Et_2O$, on the other hand. Washing of the reaction mixture with cold water gave a yield of slightly contaminated NPC (Table III), indicating that the complexation of NPC was indeed the main reaction.

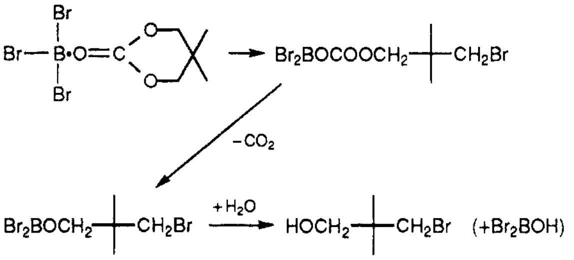
When $BCl_3$ was combined with NPC, a crystalline precipitate was formed regardless of the stoichiometry. Again washing of the reaction mixture yielded unreacted NPC. Whereas the Cl elemental analysis of the 1:2 reaction product is not satisfactory, the C and H analyses of both precipitates agree with each other and come close to the values calculated for a 1:1 complex (Table III). The IR spectra indicate the complexation of the carbonyl group (Figure 1), and the $^{13}C$ NMR CP/MAS confirm this point by a significant downfield shift of the CO signal (Table II and Figure 2) in agreement with formula 1. With $BBr_3$ only a 1:1 mixture yielded a crystalline precipitate. In this case the elemental analysis shows a satisfactory agreement with the values calculated for a 1:1 complex (2). The IR and $^{13}C$ NMR CP/MAS spectra are nearly identical with those of the $BCl_3$ complex. When the suspension of **2** in $CHCl_3$ is heated or when $BBr_3$ is reacted with a double molar amount of NPC, evolution of $CO_2$ occurs. IR spectra of the reaction mixtures taken at the end of the $CO_2$ evolution proved the absence of CO groups. The hydrolytic workup of the 1:2 reaction mixture yielded a rather pure 3-bromoneopentanol (Table III). This finding indicates that $BBr_3$ easily cleaves the NPC (and TMC) ring at the O–$CH_2$ bond (eqs 4–6). A similar cleavage of ethylene carbonate with bromotrimethylsilane (eq 7) has been reported previously.[15] It is also known that both $BBr_3$ and $Me_3SiBr$ cleave lactones with formation of ω-bromoalkanoic acids.[6,7,15,16]



1



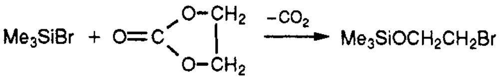
2



(4)

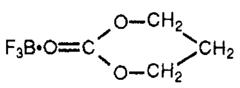
(5)

(6)



$$Me_3SiBr + O{=}C\begin{matrix} O{-}CH_2 \\ | \\ O{-}CH_2 \end{matrix} \xrightarrow{-CO_2} Me_3SiOCH_2CH_2Br \qquad (7)$$

When TMC was reacted with boron halogenides in the same way as NPC, analogous reactions were observed. However, in contrast to NPC, TMC yielded a crystalline, extremely hydroscopic $BF_3$ complex (Table IV). Again shifts in the IR, $^1H$ NMR (Figure 3), and $^{13}C$ NMR CP/MAS spectra (Figure 4) are consistent with a complexation of the carbonyl group. The C and H elemental analyses of the complexes isolated from 1:1 and 1:2 reaction mixtures indicate that again 1:1 complexes were formed. However, the F elemental analyses which were difficult to obtain (three different analytical laboratories reported problems) do not show an acceptable agreement. Since boron in $BX_3$ compounds only possesses one free p orbital suited for complexation, it is obvious that the TMC–$BF_3$ complex has a 1:1 composition. A detailed X-ray analysis of the complexes 1–3 is in progress.



$$F_3B \cdot O{=}C\begin{matrix} O{-}CH_2 \\ \\ O{-}CH_2 \end{matrix}\!\!>CH_2$$

3

The reaction of TMC with $BCl_3$ or $BBr_3$ never yielded a crystalline complex. 3-Chloropropanol (in combination with oligocarbonates) or 3-bromopropanol was the main reaction product (Table IV). These results demonstrate that a ring cleavage according to eqs 4–6 took place. Furthermore, these results indicate that TMC is more sensitive to such a ring cleavage than NPC in agreement with a higher polymerizability and higher ceiling temperature. Finally, all results together prove that the reactivity of boron halogenides with regard to ring cleavage increases in the following order: $BF_3 < BCl_3 < BBr_3$. Halotrimethylsilanes show an analogous order of reactivity in reactions with cyclocarbonates and lactones.[6,8,15,17] This order clearly parallels the nucleophilicity of halogens and

**Table I. $^1H$ NMR Chemical Shifts δ (ppm Relative to Internal TMS) of Neopentylene Carbonate (NPC), Trimethylene Carbonate (TMC), and Related Compounds**

| | | chemical shifts | | |
|---|---|---|---|---|
| compound | solvent | α-C | β-C | γ-C |
| NPC | CDCl | 4.09 | | 1.13 |
| | $C_6D_5NO_2$ | 4.20 | | 1.10 |
| NPC–$BCl_3$ | $C_6D_5NO_2$ | insol | | |
| poly-NPC | $CDCl_3$ | 3.97 | | 1.00 |
| | $C_6D_5NO_2$ | 4.11 | | 1.03 |
| 3-bromo-2,2-dimethylpropanol | | 3.39 | | |
| TMC | CDCl | 4.47 | 2.16 | |
| | $C_6D_5NO_2$ | 4.57 | 2.22 | |
| TMC–$BF_3$ | $C_6D_5NO_2$ | 5.06 | 2.63 | |
| poly-TMC | CDCl | 4.24 | 2.05 | |
| | $C_6D_5NO_2$ | 4.33 | 2.14 | |
| 3-chloro-1-propanol | $CDCl_3$ | 3.72<br>3.62 | 1.92 | |

**Table II. $^{13}C$ NMR Chemical Shifts δ (ppm Relative to Internal TMS) of Neopentylene Carbonate (NPC), Trimethylene Carbonate (TMC), and Related Compounds**

| | | | chemical shifts | | |
|---|---|---|---|---|---|
| compound | solvent | CO | α-C | β-C | γ-C |
| NPC | CDCl | 147.9 | 77.2 | 28.1 | 20.7 |
| | $C_6D_5NO_2$ | 148.5 | 78.0 | 28.7 | 20.8 |
| | [a] | 151.2 | 78.7 | 30.4 | 22.7 |
| NPC–$BCl_3$ | $C_6D_5NO_2$ | insol | | | |
| | [a] | 159.9 | 84.1 | 31.0 | 23.4 |
| NPC–$BBr_3$ | [a] | 160.0 | 84.0 | 31.5 | 24.2 |
| poly-NPC | CDCl | 155.3 | 72.4 | 35.2 | 21.4 |
| | $C_6D_5NO_2$ | 155.9 | 73.2 | 35.8 | 21.6 |
| | [a] | 156.9 | 73.5 | 35.8 | 24.2 |
| TMC | CDCl | 148.2 | 67.7 | 21.1 | |
| | $C_6D_5NO_2$ | 149.0 | 68.9 | 22.4 | |
| | [a] | 152.1 | 71.8 | 23.2 | |
| TMC–$BF_3$ | $C_6D_5NO_2$ | 158.0 | 72.4 | 21.3 | |
| | [a] | 160.4 | 75.2 | 21.5 | |
| poly-TMC | $CDCl_3$ | 154.9 | 64.3 | 28.1 | |
| | $C_6D_5NO_2$ | 155.7 | 65.2 | 28.8 | |
| | [a] | 157.1 | 66.7 | 29.9 | |

[a] CP/MAS spectra of solid products.

suggests that the complexation is followed by a nucleophilic attack of a halogen onto the O–$CH_2$ bond of the cyclocarbonate.

**Polymerizations with $BF_3$·$OEt_2$. Preparative Aspects.** All polymerizations described in this work were conducted with TMC, because the ceiling temperature of NPC is relatively low,[8,18,19] and the results obtained from NPC at temperatures above 50 °C may be affected by the thermodynamical instability of the corresponding polycarbonate. Some preliminary experiments (not listed in Tables V–VIII) conducted in bulk or nitrobenzene at 60 or 90 °C had shown that neither $BCl_3$ nor $BBr_3$ yields poly-TMC at M/I ratios of 200/1. Obviously, the formation of 3-chloro- and 3-bromopropanol (eqs 4–6) hinders a cationic chain growth. Therefore, $BF_3$·$OEt_2$ was used for most polymerizations studied in this work.

In a first series of polymerizations the reaction medium and the reaction time were varied, whereas the M/I ratio and the temperature were maintained. The results listed in Table V allow the following conclusions. The highest yields and inherent viscosities were obtained from polymerizations in bulk. Chloroform proved to be inferior to nitrobenzene for production of high yields and high molecular weight polymer. In chloroform both yields and viscosities increase slowly with the reaction time. A relatively slow polymerization was confirmed by kinetic measurements (see below). In the case of nitrobenzene or polymerizations in bulk the yields pass through a flat maximum and the viscosities drop slightly with increasing reaction time. Such results are typical for a relatively rapid polymerization followed by slow "backbiting" degradation.

In a second series of polymerizations the M/I ratio was varied, whereas the temperature and in most cases the time were kept constant (Table VI). When the polymerizations conducted at constant time (8 h) are compared (nos. 2–7), a continuous increase of the inherent viscosity with increasing M/I ratio is detectable. This result suggests that $BF_3$·$OEt_2$ reacts as a true initiator and not as a transesterification catalyst. Initiator means in this connection that the $BF_3$ is fixed to an individual chain either in the form of a dead end group or in the form of a counterion (see below). Variation of the reaction time (nos. 1 and 8, Table VI) indicates that the polymerizations are rapid enough to be complete within 2 h at a M/I ratio of 50/1 or within 8 h at a M/I ratio of 500/1.

GPC measurements were conducted in two different laboratories on two different instruments and evaluated by the universal calibration method. Furthermore, two different solvents, tetrahydrofuran and dichloromethane, were compared. The results agree in that inherent viscosities around 1.0 or higher can be correlated with weight-average molecular weights above 100 000 (Table VI). Two samples were also subjected to light scattering measurements in chloroform. Unfortunately the $M_w$ values obtained in this way are not highly accurate because of the low refractive increment. Nonetheless the light-scattering measurements confirm that the order of magnitude of $M_w$ values determined by GPC measurements is correct.

A short series of polymerizations was conducted at variable temperatures between 60 and 180 °C (Table VII). At constant time and M/I ratio, a significant decrease of the inherent viscosities was found at increasing temperatures. This result is partially due to backbiting degradation as discussed below. In addition to backbiting degradation, further side reactions take place, the most conspicuous one being the formation of ether groups. As demonstrated by the $^1H$ NMR spectra of Figure 5, all polycarbonates prepared by means of $BF_3$·$OEt_2$ contain ether groups, and the percentage of ether groups increases strongly with higher reaction temperatures. The formation of ether groups has already been reported for methyl triflate initiated polymerizations of NPC[8] and TMC[9] and seems to be characteristic for a cationic mechanism, since anionic initiators[9,18–20] and catalysts initiating insertion mechanisms[21] yield aliphatic polycarbonates bare of ether groups.

Finally, a series of polymerizations was conducted with the purpose of elucidating the reactivity of the $BF_3$–TMC complex 3 as initiator. The results listed in Table VIII suggest that this complex is as reactive or even more reactive than $BF_3$·$OEt_2$ and the highest molecular weights of this work were obtained with this complex as initiator. However, both complex 3 and $BF_3$·$OEt_2$ have in common that the resulting polycarbonates contain ether groups. The molar fraction of ether groups was rather independent of the initiator.

**Polymerizations with $BF_3$. Mechanistic Aspects.** Concerning the mechanistic aspects of $BF_3$·$OEt_2$ initiated Polymerizations of TMC, three points should be discussed in the present work: (I) the cationic nature of the polymerization mechanism, (II) the formation of ether groups, and (III) the role of degradation by backbiting. $BF_3$ is usually considered to be a cationic initiator, but in most papers dealing with $BF_3$·$OEt_2$ initiated polymeriza-

**Table III. Stoichiometric Reactions of Neopentanediol Carbonate (NPC) with Boron Halogenides at 20–25 °C in Chloroform**

| | $BX_3$/NPC | observation | yield[a] (%) | elem formula (form. wt) | elem anal. | | | | hydrolytic workup of the reaction mixture[d] |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | Cl/Br | |
| $BF_3$·$OEt_2$ | 1:1 | clear solution | | | | | | | 76% NPC (+ oligomers) |
| $BF_3$·$OEt_2$ | 1:2 | clear solution | | | | | | | 81% NPC (+ oligomers) |
| $BCl_3$ | 1:1 | crystalline precipitate | 52 | $C_6H_{10}O_3B_1Cl_3$ (247.31) | calcd[b] | 29.14 | 4.08 | 28.18 | 58% NPC |
| | | | | | found | 30.56 | 4.27 | 27.49 | |
| $BCl_3$ | 1:2 | crystalline precipitate | 32 | $C_{12}H_{20}O_6B_1Cl_3$ (377.46) | calcd[c] | 38.19 | 5.34 | 28.18 | 69% NPC |
| | | | | | found | 30.70 | 4.50 | 34.70 | |
| $BBr_3$ | 1:1 | crystalline precipitate | 51 | $C_6H_{10}O_3B_1Br_3$ (380.65) | calcd[b] | 18.93 | 2.65 | 62.97 | 81% NPC |
| | | | | | found | 19.12 | 2.78 | 61.12 | |
| $BBr_3$ | 1:2 | clear solution | | | | | | | 101% bromoneopentanol (contam) |

[a] Referred to NPC. [b] Calculated for a 1:1 complex. [c] Calculated for a 1:2 complex. [d] A second, parallel series of experiments was washed with cold water, and the content of the $CHCl_3$ phase was isolated.

**Table IV. Stoichiometric Reactions of Trimethylene Carbonate (TMC) with Boron Halogenides at 20–25 °C in Chloroform**

| | $BX_3$/TMC | observation | yield[a] (%) | elem formula (form. wt) | elem. anal.[d] | | | hydrolytic workup of the reaction mixture[e] |
|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | |
| $BF_3$·$OEt_2$ | 1:1 | crystalline precipitate | 79 | $C_4H_6O_3B_1F_3$ (169.89) | calcd[b] | 28.28 | 3.56 | 25% TMC |
| | | | | | found | 27.20 | 4.00 | |
| $BF_3$·$OEt_2$ | 1:2 | crystalline precipitate | 45 | $C_8H_{12}O_6B_1F_3$ (271.98) | calcd[c] | 35.33 | 4.45 | 24% TMC |
| | | | | | found | 28.30 | 3.80 | |
| $BCl_3$ | 1:1 | sirupous precipitate | | | calcd | | | 47% oligomers + 3-chloropropanol |
| | | | | | found | | | |
| $BCl_3$ | 1:2 | sirupous precipitate | | | calcd | | | 50% oligomers + 3-chloropropanol |
| | | | | | found | | | |
| $BBr_3$ | 1:1 | clear solution | | | calcd | | | 37.5% 3-bromopropanol |
| | | | | | found | | | |
| $BBr_3$ | 1:2 | clear solution | | | calcd | | | 23% 3-bromopropanol |
| | | | | | found | | | |

[a] Referred to TMC. [b] Calculated for a 1:1 complex. [c] Calculated for a 1:2 complex. [d] Three different analytical laboratories reported that reproducible F analyses were not feasible. [e] A second, parallel series of experiments was washed with cold water, and the content of the $CHCl_3$ phase was isolated.

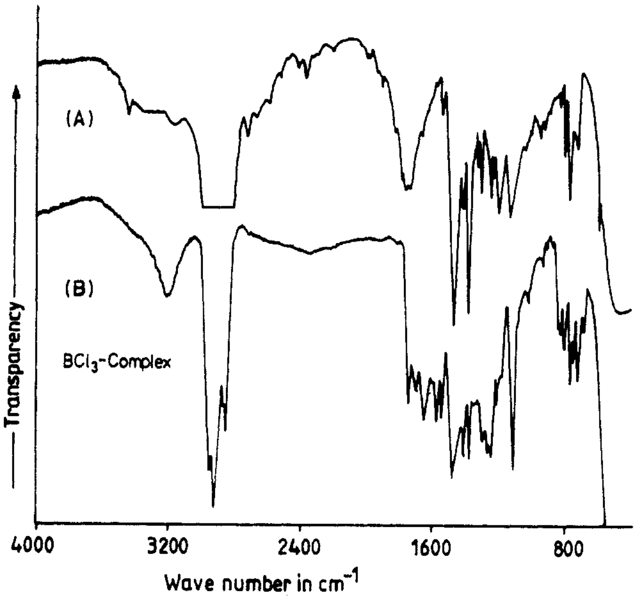


**Figure 1.** IR spectra of suspensions in paraffin: (A) pure NCP; (B) NPC–$BCl_3$ complex isolated from an equimolar reaction mixture in $CHCl_3$.

tions of heterocycles clearcut evidence for a cationic mechanism is lacking. Furthermore, it has been demonstrated[22,23] that $SnCl_4$ and $SnBr_4$ which were also considered to be cationic initiators do not in fact initiate a cationic polymerization of lactide and lactones, but an insertion mechanism. Moreover, the isolation of 1 and 2 and the failure of $BCl_3$ and $BBr_3$ to initiate the polymerization of TMC demonstrate that the formation of strong Lewis acid–monomer complexes should not be considered as reliable evidence for a cationic nature of the polymerization mechanism.

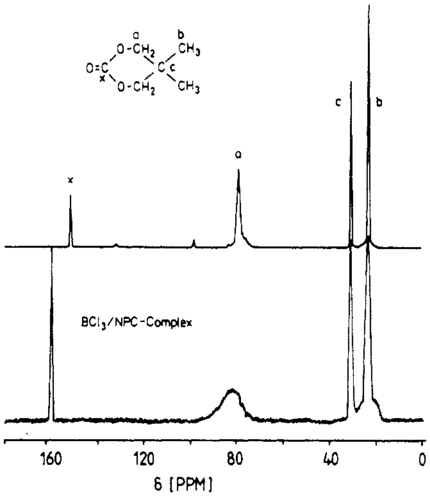


**Figure 2.** 75.4-MHz $^{13}C$ NMR CP/MAS spectra of (A) pure NPC and (B) a NPC–$BCl_3$ complex isolated from an equimolar reaction mixture in $CHCl_3$.

$BF_3$·$OEt_2$ may contain or may form under the given reaction conditions triethyloxonium ions (eq 8). Therefore, two initiation steps must be taken into account: (a) the alkylation step (eq 9) and (b) the complexation (eq 10). Taking into account the results obtained with methyl triflate,[9] both types of initiation should be followed by the chain growth outlined in eq 11.

The initiation with triethyloxonium ions is expected to yield polycarbonates with ethyl carbonate end groups. Therefore, several samples obtained by the polymerizations summarized in Tables V–VII were examined by $^1H$ NMR spectroscopy. However, the spectra measured with a sufficient signal-to-noise ratio never revealed the existence of ethyl carbonate end groups. In order to avoid

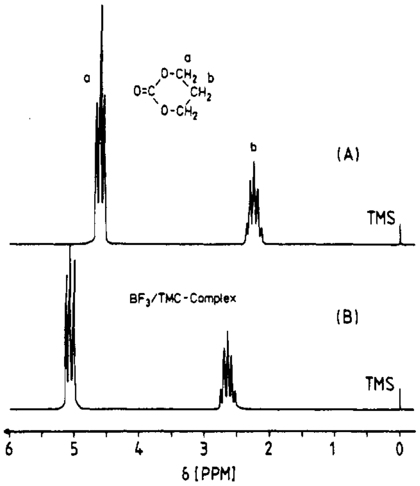


**Figure 3.** 100-MHz $^1H$ NMR spectra measured in $C_6D_5NO_2$: (A) pure TMC; (B) TMC–$BF_3$.

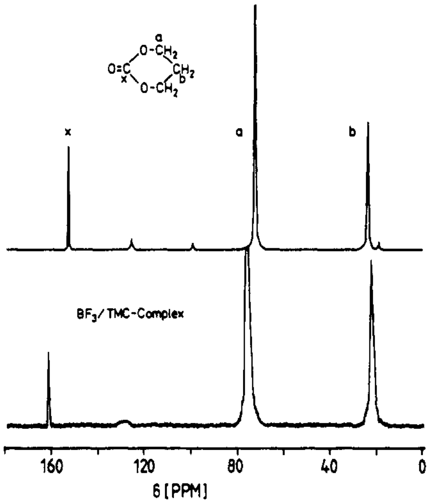


**Figure 4.** 75.4-MHz $^{13}C$ NMR CP/MAS spectra of (A) pure TMC and (B) a TMC–$BF_3$ complex in the solid state.

**Table V. $BF_3$·$OEt_2$ Initiated Polymerizations of Trimethylene Carbonate at 60 °C (M/I = 200/1[a])**

| no. | solvent | time (h) | yield (%) | $\eta_{inh}$[b] (dL/g) |
|---|---|---|---|---|
| 1 | $CHCl_3$ | 8 | 0 | |
| 2 | $CHCl_3$ | 24 | 51.9 | 0.2 |
| 3 | $CHCl_3$ | 48 | 57.2 | 0.3 |
| 4 | $CHCl_3$ | 72 | 78.8 | 0.4 |
| 5 | $CHCl_3$ | 96 | 78.6 | 0.4 |
| 6 | $C_6H_5NO_2$ | 8 | 82.1 | 0.9 |
| 7 | $C_6H_5NO_2$ | 24 | 84.6 | 0.7 |
| 8 | $C_6H_5NO_2$ | 48 | 81.7 | 0.7 |
| 9 | $C_6H_5NO_2$ | 72 | 74.8 | 0.8 |
| 10 | $C_6H_5NO_2$ | 96 | 77.0 | 0.7 |
| 11 | bulk | 8 | 91.3 | 1.0 |
| 12 | bulk | 24 | 94.6 | 1.0 |
| 13 | bulk | 48 | 95.8 | 0.8 |
| 14 | bulk | 72 | 96.2 | 0.9 |
| 15 | bulk | 96 | 94.8 | 0.8 |

[a] Initial molar monomer/initiator ratio. [b] Measured at 25 °C with $c$ = 2 g/L in $CH_2Cl_2$.

problems with overlapping $^1H$ NMR signals, polycarbonates prepared by $BF_3$·$OEt_2$ initiated polymerizations of NPC[8] were included in this study, but ethyl carbonate end groups were never found. This negative result and the high reactivity of the $BF_3$–TMC complex (Table VIII) suggest at first glance the conclusion that the polymerization process involves the reactions outlined in eqs 10–14.

Taking into account the numerous results published on reactions of $BF_3$ and other Lewis acids with dialkyl ethers or tetrahydrofuran,[24-28] the ion pair formed according to eq 12 (or less likely via eqs 13 and 14) is the active species in the propagation process. A detailed study of these mechanistic aspects was not intended in the present work but will be published in a future part of this series. The present work was aimed at proving (or disproving) the cationic nature of the entire polymerization process.

Regardless of the initiation step, two experimental results support a cationic chain growth. First, time/conversion curves recorded by $^1H$ NMR spectroscopy (Figure 6) show that the chain growth in nitrobenzene proceeds by a factor around 3 faster than that in the less polar chloroform. This factor was calculated from the apparent rate constants $1.7 \times 10^{-4}$ L/mol·s in $CDCl_3$ and $4.9 \times 10^{-4}$ L/mol·s in $C_6D_5NO_2$ determined for the first 20% conversion. The difference between the rate constants is small, but it is even smaller for the cationic initiator methyl triflate (rate constant: $9.5 \times 10^{-4}$ L/mol·s in $CDCl_3$ and $15 \times 10^{-4}$ L/mol·s in $C_6D_3NO_2$). Furthermore, when the weak Lewis acid $Bu_3Sn$–OMe is used which initiates a nonionic insertion mechanism,[10] an inverse kinetic pattern is found: the chain growth proceeds faster in chloroform (published in a future part of this series).

The second argument in favor of a cationic mechanism is the decarboxylation and formation of ether bonds. Albeit the details of the decarboxylation mechanism are still obscure, an alkylation step of a $CH_2$-bound oxygen must take place. In this connection the following basic question arises. Is the decarboxylation a direct side reaction of the propagation step or an independent reaction between $BF_3$ and the polymer backbone? Three observations prove that the former hypothesis is true. First, when a poly-TMC free of ether groups (prepared by means of $Bu_3SnOMe$[21]) was combined with $BF_3$·$OEt_2$ at a M/I ratio of 200/1 in nitrobenzene, ether groups were not formed at 20 °C within a period of 7 days in contrast to the polymerization of TMC (Figure 5). Second, analogous results were obtained with methyl triflate.[2] Third, a pure polycarbonate combined with $BF_3$·$OEt_2$ in bulk and heated to 60 °C does not form ether groups in contrast to the polymerization of TMC under the same conditions. In other words, the decarboxylation seems to be a characteristic side reaction of the cationic propagation step, but a detailed mechanism cannot be forwarded at the current stage of the research.

Further support for a cationic polymerization according to eqs 1–3 or 10–14 comes from GPC and $^1H$ NMR spectroscopic studies of reaction mixtures prepared at 20 °C in $C_6D_5NO_2$ from TMC and TMC–$BF_3$ with low M/I ratios (M/I = 2, 4, and 8). The course of these polymerizations was monitored until complete conversion was obtained. In addition to the $^1H$ NMR signals of monomer and polymer, six weak triplets were detectable, denoted u–z in Figure 7. Most interesting is signal u which shows the largest downfield shift (5.4–5.5 ppm) and most likely represents the active chain end, i.e., the trioxocarbenium ion. The same signal appears in the methyl triflate initiated reaction mixture (Figure 8) even more intensively.

Another interesting observation is the appearance of the TMC–$BF_3$ signals at the end of the polymerization (Figure 7B). When TMC and its $BF_3$ complex are mixed in $C_6D_5NO_2$, only one set of signals shows up with chemical shifts in between those of pure TMC and those of pure TMC–$BF_3$ (Figure 3). Furthermore, the triplet pattern coalesces into a broad signal (Figure 7A). These observations clearly indicate a rapid exchange reaction (equilibration) between $BF_3$ and all TMC molecules of the mixture. The appearance of the TMC–$BF_3$ signals at the

**Table VI. Bulk Polymerizations of TMC Initiated with $BF_3{\cdot}OEt_2$ at 60 °C with Variation of the M/I Ratio**

| no. | TMC/$BF_3{\cdot}OEt_2$ | time (h) | yield (%) | $\eta_{inh}$[a] (dL/g) | $M_{max}$[b] × $10^3$ | [$\eta$][c] (mL/g) | $M_n$[d] × $10^3$ | $M_w$[e] × $10^3$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 50:1 | 2 | 95.5 | 0.36 | 35 | | | | |
| 2[f] | 50:1 | 8 | 92.5 | 0.40 | 40 | 24 (THF) | 10 | 26 | 2.7 |
| | | | | | | 34 ($CH_2Cl_2$) | 8 | 27 | 3.3 |
| 3 | 100:1 | 8 | 92.5 | 0.72 | 75 | | | | |
| 4[g] | 150:1 | 8 | 92.0 | 0.83 | 85 | 48 (THF) | 35 | 93 | 2.6 |
| | | | | | | 89 ($CH_2Cl_2$) | 34 | 93 | 2.8 |
| 5 | 200:1 | 8 | 91.0 | 0.95 | 95 | 54 (THF) | 52 | 126 | 2.4 |
| | | | | | | 100 ($CH_2Cl_2$) | 52 | 121 | 2.3 |
| 6 | 300:1 | 8 | 89.0 | 1.05 | 110 | | | | |
| 7 | 500:1 | 8 | 88.0 | 1.15 | 130 | 62 (THF) | 60 | 130 | 2.2 |
| | | | | | | 128 ($CH_2Cl_2$) | 58 | 125 | 2.2 |
| 8 | 500:1 | 20 | 85.0 | 1.00 | 105 | | | | |

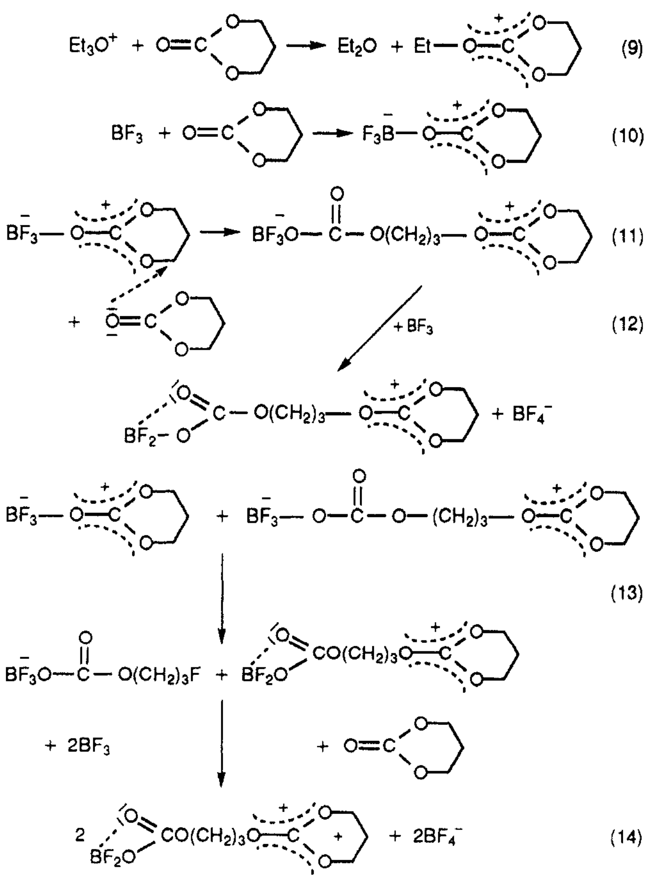
[a] Inherent viscosity measured at 25 °C with $c$ = 2 g/L in $CH_2Cl_2$. [b] Molecular weights determined by GPC (in THF) from the maxima of the elution curves. [c] Staudinger indices determined in tetrahydrofuran (THF) or in $CH_2Cl_2$. [d] Number-average molecular weights as determined by GPC in tetrahydrofuran (THF) or $CH_2Cl_2$. [e] Weight-average molecular weights as determined by GPC in tetrahydrofuran (THF) or $CH_2Cl_2$. [f] $M_w$ = (35 ± 10 × $10^3$ by light scattering in $CHCl_3$. [g] $M_w$ = (75 ± 20 × $10^3$ by light scattering in $CHCl_3$.

**Table VII. Bulk Polymerizations of TMC Initiated with $BF_3{\cdot}OEt_2$ under Variation of the Reaction Temperature (Time = 8 h, M/I = 200/1)**

| no. | temp (°C) | yield (%) | $\eta_{inh}$[a] (dL/g) | content of[b] ether groups |
|---|---|---|---|---|
| 1 | 60 | 92.0 | 0.9 | 2.0 |
| 2 | 90 | 96.5 | 0.8 | 3.0 |
| 3 | 120 | 94.0 | 0.7 | 6.0 |
| 4 | 150 | 87.0 | 0.5 | 15.0 |
| 5 | 180 | 84.0 | 0.4 | 18.0 |

[a] Inherent viscosity measured at 25 °C with $c$ = 2 g/L in $CH_2Cl_2$. [b] mol % of ether groups relative to the sum of ether and carbonate groups.

$$2BF_3{\cdot}OEt_2 \rightleftharpoons BF_3{\cdot}OEt^{0} + Et_3O^{+} \qquad (8)$$



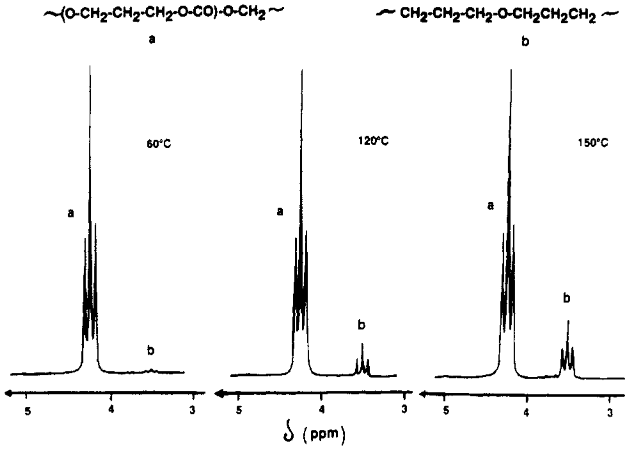
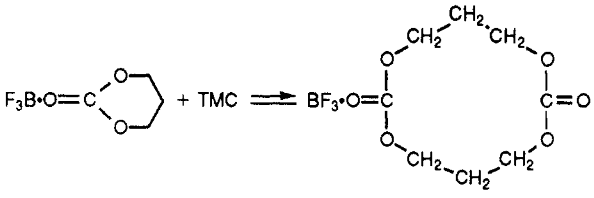


**Figure 5.** 100-MHz $^1H$ NMR spectra of a poly-TMC sample prepared in bulk with $BF_3{\cdot}OEt_2$ (M/I = 200/1) at three different temperatures (Table VII).

end of the polymerization demonstrates that most $BF_3$ molecules did not form a counterion of the cationic chain end. However, it cannot be excluded that $BF_3$ catalyzes an equilibration between monomer and dimer (eq 15) by intramolecular cyclization, of the zwitterion formed according to eq 11. The signals w and z in Figure 7 might originate from free and complexed dimer. Nonetheless,



it should be emphasized that the true polymerization process does not consist of an equilibration of cyclic species because the results of Table VI and the GPC measurements of the above reaction mixtures agree in that the DP (or $M_n$) increases with higher M/I ratios. The minimum elution times found after 7 days at 20 °C for M/I = 4, 8, and 16 were 30, 29, and 28 min. In other words, at least a small fraction of the $BF_3$ molecules react as true initiators (e.g., via eqs 10–12). In this connection the $M_w/M_n$ ratios listed in Table VI should mentioned. The broad molecular weight distributions clearly indicate that the $BF_3{\cdot}OEt_2$ initiated polymerizations do not follow the "living pattern". This finding agrees well with the complex initiation mechanism discussed above and with the existence of side reactions.

Finally the role of backbiting degradation needs a short discussion. The GPC curves of reaction mixtures obtained at 180 °C in bulk (Figure 9) as well as those obtained from polymerizations conducted a 20 °C in $C_6D_5NO_2$ agree in that the rapid chain growth is followed by a slow broadening of the molecular weight distribution and by

**Table VIII. $BF_3$-TMC Initiated Polymerizations of Trimethylene Carbonate (TMC) in Bulk at 60 °C (M/I = 200/1[a])**

| no. | time (h) | yield (%) | $\eta_{inh}$[b] (dL/g) | content of[c] ether groups |
|---|---|---|---|---|
| 1 | 8 | 96.0 | 1.34 | 1.1 |
| 2 | 24 | 94.5 | 1.28 | |
| 3 | 48 | 93.0 | 1.30 | 1.5 |
| 4 | 72 | 92.5 | 1.25 | |
| 5 | 96 | 92.0 | 1.25 | 1.9 |

[a] Initial molar monomer/initiator ratio. [b] Measured at 25 °C with $c$ = 2 g/L in $CH_2Cl_2$. [c] mol % of ether groups relative to the sum of ether and carbonate groups.

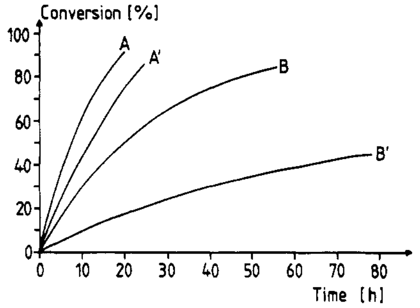


**Figure 6.** Polymerizations of TMC ($c$ = 2.5 mol/L) initiated with (A) methyl triflate in $C_6D_5NO_2$, (A') methyl triflate in $CDCl_3$, (B) $BF_3$·$OEt_2$ in $C_6D_5NO_2$, and (B') $BF_3$·$OEt_2$ in $CDCl_3$.

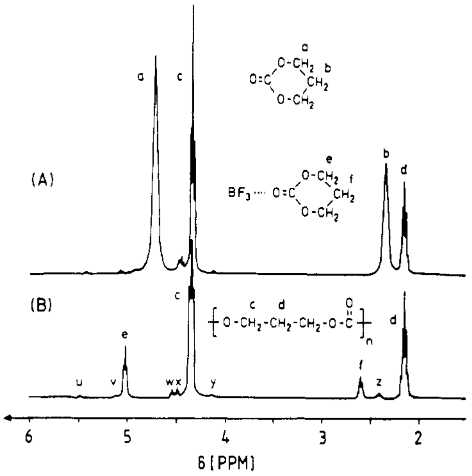


**Figure 7.** Reaction mixtures of TMC and TMC–$BF_3$ in $C_6D_5NO_2$ (mole ratio 4/1): (A) after 1 day; (B) after 4 days at 20 °C.

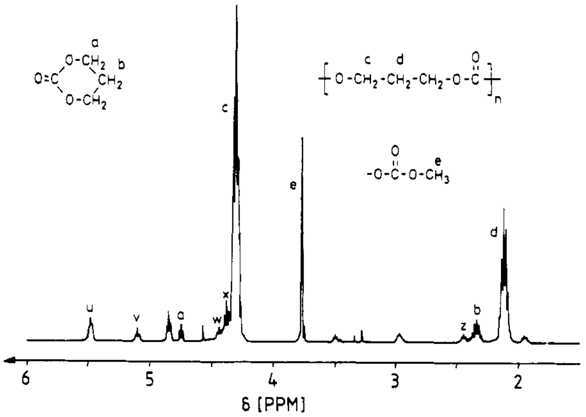


**Figure 8.** Reaction mixture of TMC and methyl triflate (mole ratio 5/1) in $C_6D_5NO_2$ after 1 day at 20 °C.

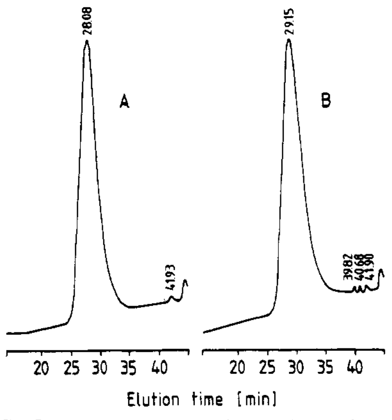


**Figure 9.** GPC measurements of reaction mixtures obtained from TMC and $BF_3OEt_2$ in bulk at 180 °C: (A) after 1 h; (B) after 24 h.

a shift to lower average molecular weights. In the case of methyl triflate initiated polymerizations, backbiting is rapid and prevents the formation of high molecular weights.[2] Thus the question arises as to why backbiting is slow and enables high molecular weights in $BF_3$ initiated polymerizations of TMC. A partial explanation results from the finding that only a fraction of the $BF_3$ molecules contributes to the formation of active chain ends. The concentration of active chain ends is, thus, considerably lower than expected from the M/I ratio. Second, an active covalent triflate end group is formed in a methyl triflate initiated polymerization (eq 2). Since methyl triflate is as reactive or even more reactive than the cyclic trioxocarbenium ion (for reasons of steric hindrance and solvation), the covalent triflate end group might be reactive and certainly flexible enough to participate in the backbiting degradation. Such a mechanism does not exist in $BF_3$ initiated polymerizations.

In this connection a study of Matyjaszewski et al.[29] concerning methyl triflate initiated polymerizations of tetrahydrofuran needs to be mentioned. Those authors demonstrated that the alkyl triflate end groups are dormant, so that the polymerization almost exclusively proceeds through the oxonium ion. However, it is premature to extrapolate these results to polymerizations of cyclocarbonates because the trioxocarbenium ions are several orders of magnitude more stable and less reactive than oxonium ions of THF. Therefore, an active role of covalent triflate end groups in polymerizations of cyclocarbonates should not be excluded until detailed kinetic measurements prove their dormant character. Regardless of these mechanistic details, the experimental facts clearly prove that the backbiting degradation is considerably more efficient in the case of methyl triflate initiated polymerizations with the consequence that $BF_3$·$OEt_2$ is the more attractive initiator from the preparative point of view.

## Conclusions

Boron halogenides may form crystalline complexes with NPC or TMC, but only the complexes of $BF_3$ are active as initiators. $BF_3$ initiated polymerizations give high yields and molecular weights, but the resulting polycarbonates contain ether groups. This finding, kinetic data, and $^1H$ NMR spectroscopic end-group analyses suggest a cationic polymerization mechanism involving cyclic trioxocarbenium ions in analogy to methyl triflate initiated polymerizations of cyclocarbonates. However, backbiting degradation is much more efficient in the case of the methyl triflate initiated polymerizations presumably due to the reactivity of a covalent triflate end group.

**Acknowledgment.** We thank Dr. Amecke (Boehringer Ingelheim KG) for a gift of trimethylene carbonate and Dr. Krämer-Lucas (Bayer AG, Leverkusen) for the GPC and light-scattering measurements.

## References and Notes

(1) Katz, A. R.; Mukherjee, D. P.; Kaganov, A. L.; Gordon, S. *Surg. Gynecol. Obstet.* **1985**, *161*, 213.

(2) Rodeheaver, G. T.; Powell, T. A.; Thacker, J. G.; Edlich, R. F. *Am. J. Surg.* **1987**, *154*, 544.

(3) Kawaguchi, T.; Nakano, M.; Juni, K.; Inoue, S.; Yoshida, Y. *Chem. Pharm. Bull.* **1983**, *31*, 1400, 4157.

(4) Kojima, T.; Nakano, M.; Juni, K.; Inoue, S.; Yoshida, Y. *Chem. Pharm. Bull.* **1984**, *32*, 2795.

(5) Hostettler, F.; Cox, E. F. (Union Carbide Corp.). German Offen 116 1 545, 1970; *Chem. Abstr.* **1965**, *63*, 11730d.

(6) Hostettler, F.; Cox, E. F. (Union Carbide Corp.). German Offen 117 1 545, 1969; *Chem. Abstr.* **1965**, *63*, 8589a.

(7) Hostettler, F.; Cox, E. F. (Union Carbide Corp.). German Offen 118 1 545, 1969; *Chem. Abstr.* **1965**, *63*, 11730b.

(8) Kricheldorf, H. R.; Dunsing, R.; Serra i. Albet, A. *Makromol. Chem.* **1987**, *188*, 2453.

(9) Kricheldorf, H. R.; Jenssen, J. *J. Macromol. Sci., Chem.* **1989**, *A26*, 631.

(10) Kricheldorf, H. R.; Jonté, M.; Dunsing, R. *Makromol. Chem.* **1986**, *787*, 771.

(11) Kricheldorf, H. R.; Dunsing, R.; Serra i Albet, A. *Macromolecules* **1987**, *20*, 2050.

(12) Hofmann, A.; Szymanski, R.; Slomkowski, S.; Penczek, S. *Makromol. Chem.* **1984**, *185*, 655.

(13) Kricheldorf, H. R.; Weegen-Schulz, B.; Jenssen, J. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 119.

(14) Albertsson, A.-C.; Sjöling, M. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, *A29*, 43.

(15) Kricheldorf, H. R. *Angew. Chem.* **1979**, *91*, 749; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 689.

(16) Olah, C. A.; Karpeles, R.; Narang, S. C. *Synthesis* **1982**, 963.

(17) Olah, C. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247.

(18) Keul, H.; Höcker, H.; Leitz, E.; Ott, K.-H.; Morbitzer, L. *Makromol. Chem.* **1988**, *189*, 2303.

(19) Keul, H.; Bacher, R.; Höcker, H. *Makromol. Chem.* **1986**, *187*, 2579.

(20) Kuhling, S.; Keul, H.; Höcker, H. *Makromol. Suppl.* **1989**, *15*, 9.

(21) Kricheldorf, H. R.; Jenssen, J.; Kreiser-Saunders, I. *Makromol. Chem.* **1991**, *192*, 2391.

(22) Kricheldorf, H. R.; Sumbél, M. *Makromol. Chem.* **1988**, *189*, 317.

(23) Kricheldorf, H. R.; Sumbél, M. *Eur. Polym. J.* **1989**, *25*, 585.

(24) Meerwein, H.; Battenberg, E.; Gold, H.; Pfeil, E.; Willfang, G. *J. Prakt. Chem.* **1939**, *154*, 83.

(25) Meerwein, H.; Delfs, D.; Morschel, H. *Angew. Chem.* **1960**, *72*, 927.

(26) Sims, D. *Makromol. Chem.* **1966**, *98*, 245.

(27) Goodrich, R. A.; Triechel, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 3509.

(28) Hoene, R.; Reichert, K.-H. W. *Makromol. Chem.* **1976**, *177*, 3545.

(29) Matyjaszewski, K.; Diem, T.; Penczek, S. *Makromol. Chem.* **1979**, *810*, 1817.