Polylactones. 16. Cationic Polymerization of Trimethylene Carbonate and Other Cyclic Carbonates

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POLYLACTONES. 16. CATIONIC POLYMERIZATION OF TRIMETHYLENE CARBONATE AND OTHER CYCLIC CARBONATES

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ABSTRACT

1,3-Dioxanone-2 (trimethylene carbonate) was polymerized by use of methyl triflate or triethyloxonium fluoborate under various reaction conditions. Chloroform, 1,2-dichloroethane, and nitrobenzene were used as solvents; the temperature was varied between 25 and 50°C; and the monomer/initiator ratio between 50 and 400. However, inherent viscosities above 0.29 dL/g ($\bar{M}_n > 6000$) were never obtained, owing to side reactions such as backbiting and formation of ether groups. IR and ^{1}H-NMR spectroscopy revealed that the polymerization mechanism agrees with that of the cationic polymerization of lactones in that propagation involves cleavage of the alkyl-oxygen bond. The active cationic chain end and the dead methylcarbonate end groups were identified by means of ^{1}H-NMR spectra. A reaction mechanism for the formation of ether groups is discussed. Furthermore, ^{1}H-NMR spectroscopy indicated that ethylene carbonate and biphenyl-2,2'-carbonate do not react with methyl triflate at 20, 60, or even 100°C.

INTRODUCTION

In a previous paper [1] we reported on the cationic polymerization of 5,5-dimethyl-1,3-dioxanone-2 (neopentanediole carbonate). It was found that the cationic polymerization of this monomer requires a temperature of at least 80°C, even when highly active initiators, such as methyl triflate, are used. At this relatively high temperature, side reactions and the low ceiling temperature prevent the formation of high molecular weight polycarbonates. In this connection the purpose of the present work was threefold. First, it should be determined whether cationic polymerization of the unsubstituted 1,3-dioxanone-2 yields high molecular weight polycarbonates. Second, the polymerization mechanism discussed for 5,5-dimethyl-1,3-dioxanone-2 should be confirmed for the unsubstituted cyclocarbonate. Third, the reactivity of five- and seven-membered carbonates toward methyl triflate should be elucidated.

EXPERIMENTAL

Materials

1,3-Dioxanone-2 (mp 45-47°C) was purchased from Aldrich (St. Louis, Missouri), recrystallized from 1,4-dioxane and ligroin, and stored over phosphorus pentoxide *in vacuo*. 1,3-Dioxolanone-2 (ethylene carbonate), 2,2'-dihydroxybiphenyl, as well as the deuterated solvents used for NMR spectroscopy, also purchased from Aldrich, were used without further purification. Chloroform, 1,2-dichloroethane, and nitrobenzene were distilled over phosphorus pentoxide.

4,5,6,7-Dibenzo-1,3-dioxanone-2 [4]

Approximately 0.7 mol phosgene was condensed and dissolved in 1 L dry tetrahydrofuran cooled with ice. Solutions of 0.5 mol 2,2'-dihydroxybiphenyl and 1.0 mol triethylamine in 200 mL dry tetrahydrofuran were added dropwise from two dropping funnels. After a reaction time of 1 h, carbon dioxide was introduced for 24 h to remove excess phosgene. Finally, the reaction mixture was filtered, treated with dry charcoal, and concentrated *in vacuo*. Complete crystallization of the product was achieved by portionwise addition of ligroin. The crude cyclocarbonate was recrystallized from ethyl acetate and ligroin. Yield: 64%, mp 100-101°C (101-102°C in Ref. 2).

Analysis. Calculated for $C_{13}H_8O_3$ (212.04): C, 73.58; H, 3.80%. Found: C, 73.45; H, 3.71%.

Polymerization of 1,3-Dioxanone-2

A 50-mL Erlenmeyer flask with ground-glass joints and silanized glass walls was used as the reaction vessel. 1,3-Dioxanone (4.0 g, 40 mmol) was dissolved in 25 mL of a dry solvent (see Table 2), and the initiator was added in the form of a 1 mol/L solution in the same solvent. The reaction vessel was closed with a flass stopper and steel spring. After the desired reaction time, the contents of the Erlenmeyer flask were poured into 400 mL cold methanol. The precipitated polycarbonate was isolated by filtration and dried at room temperature *in vacuo*. The reaction mixture was prepared in a glove box under dry nitrogen.

Decarboxylation of Diethyl Carbonate

Diethyl carbonate (40 mmol) and methyl triflate (2 mmol) were heated in a bath thermostated at 130°C. The evolution of carbon dioxide was qualitatively checked over a period of 2 h by passing the evolved gas into an aqueous solution of barium hydroxide or into a solution of benzylamine in diethyl ether. After 2 or 16 h the reaction mixture was cooled to 20°C. ^{1}H-NMR spectra of the mixture dissolved in $CDCl_3$ revealed the formation of diethyl ether, ethyl triflate, and methyl carbonate groups (Fig. 3).

Measurements

The inherent and intrinsic viscosities were measured with an automated Ubbelohde viscometer at 25°C. The IR spectra were obtained from KBr disks on a Perkin-Elmer Md 257 IR-spectrometer. The vapor pressure osmometry was conducted with a Hitachi-Perkin-Elmer Md 117 in chloroform solution. The ^{1}H-NMR spectra were recorded in 5 mm o.d. sample tubes either with a Bruker AC-100 FT-NMR spectrometer (Fig. 2) or with a Bruker AM 360 FT-NMR spectrometer (Fig. 1). TMS served as the internal standard for all measurements. The ^{1}H-NMR chemical shifts of 1,3-dioxanone-2 and its derivatives are summarized in Table 1.

RESULTS AND DISCUSSION

A. Polymerization of 1,3-Dioxanone-2

In previous studies of cationic polymerizations of lactones and 5,5-dimethyl-1,3-dioxanone-2, methyl triflate had proved to be one of the most effective initiators. This initiator was therefore also preferentially used in the present work. In a first series of polymerizations (Table 2) the solvent was varied from

TABLE 1. ^{1}H-NMR Chemical Shifts of 1,3-Dioxanone-2 and Its Derivatives in $CDCl_3$ [a]

Compound	δ (J)
1,3-Dioxanone-2	4.46 (t, 5.73); 2.15 (m, 5.73)
O-Methyl-1,3-dioxane	5.10 (t, 5.69); 2.56 (m, 5.69); 4.4 (s)[b]
1-Methyl carbonate 3-triflate of 1,3-propanediol	4.67 (t, 6.05); 4.25 (t, 6.05); 2.05 (m, 6.06); 3.78 (s)[c]
Poly(1,3-dioxanone2)	4.24 (t, 6.25); 2.02 (m, 6.25); 3.76(s)[d]

[a]Chemical shift δ in ppm relative to internal TMS, and coupling constants J in Hz.
[b]Methyl group of trioxocarbenium ion.
[c]Methyl carbonate group.
[d]Methyl carbonate end group.

TABLE 2. Methyl Triflate-Initiated Polymerizations of 1,3-Dioxanone-2 in Various Solvents[a]

No.	Solvent	Temperature, °C	Time, h	Yield, %	η_{inh},[b] dL/g	$\bar{M}_n$ [c]
1	Chloroform	25	24	0	—	—
2	ʼʼ	25	48	28	0.27	2700
3	ʼʼ	25	96	46	0.25	—
4	1,2-Dichloroethane	25	48	30	0.20	1800
5	ʼʼ	25	96	82	0.29	2700
6	ʼʼ	50	48	85	0.10	1000
7	ʼʼ	50	96	73	0.15	1100
8	Nitrobenzene	25	24	0	—	—
9	ʼʼ	25	48	81	0.28	—
10	ʼʼ	25	96	97	0.21	—

[a]Initial monomer/initiator ratio (M/I) = 100.
[b]Measured at C = 2 g/L in dichloromethane at 25°C.
[c]From vapor pressure osmometry in chloroform.

TABLE 3. Triethyloxonium Fluoroborate-Initiated Polymerizations of 1,3-Dioxanone-2

No.	Solvent	M/I^a	Temperature, °C	Time, h	Yield, %	η_{inh}, dL/g
1	1,2-Dichloroethane	50	25	96	8	0.13
2	,,	50	50	96	14	0.11
3	,,	100	25	48	79	0.11
4	Nitrobenzene	100	25	96	96	0.12
5	,,	100	25	192	98	0.12

[a]Initial monomer/initiator ratio.
[b]Measured at C = 2 g/L in dichloromethane at 25°C.

one of low (chloroform, 4.7), moderate (1,2-dichloroethane, 10.4), and high dielectric constant (nitrobenzene, 34). The yields obtained after 48 and 96 h at 25°C indicate that the rate of polymerization increases with increasing dielectric constant. In contrast, the molecular weights, as measured by the inherent viscosities, are quite independent of the reaction medium. Furthermore, the viscosities found for polymerizations in 1,2-dichloroethane (Table 2) suggest that the molecular weights decrease at higher temperatures due to back-biting degradation. Similar results were obtained for methyl triflate-initiated polymerizations of δ-valerolactone [3].

In a second series of polymerizations, triethyloxonium tetrafluoroborate was used as initiator (Table 3). As evidenced by both yields and viscosities, this initiator is less useful for preparative purposes than methyl triflate. Therefore, a third series of polymerizations was conducted, again with methyl triflate (Table 4). In this series the monomer/initiator ratio was varied in the two most promising reaction media. Yet, despite high M/I ratios, low reaction temperature, and long reaction times, high molecular weights were not obtained. The number-average molecular weights measured in chloroform are all in the range 1000-3000 (Tables 2 and 4). Even if one takes into account that $\bar{M}_n$ determined by VPO is highly sensitive to the presence of low molecular weight impurities, it is evident that the $\bar{M}_n$ values of the polycarbonates in Tables 2-4 are certainly lower than 5000. Similarly low $\bar{M}_n$ values were found for cationic polymerization of 5,5-dimethyl-1,3-dioxanone-2 [1]. Thus, the results in Tables 2-4 suggest the following conclusions. 1,3-Dioxanone-2 is more reactive than the substituted analog, and thus allows cationic polymeri-

TABLE 4. Methyl Triflate-Initiated Polymerizations of 1,3-Dioxanone-2 at 25°C with Various Monomer/Initiator Ratios

No.	Solvent	M/I^a	Time, h	Yield, %	$\eta_{inh},^b$ dL/g	$\bar{M}_n^c$
1	1,2-Dichloroethane	50	96	70	0.16	—
2	,,	100	96	82	0.29	3100
3	,,	150	192	89	0.22	2050
4	,,	200	192	90	0.23	2100
5	,,	300	192	88	0.23	2200
6	,,	400	192	86	0.26	2900
7	Nitrobenzene	50	96	63	0.12	—
8	,,	100	96	81	0.28	—
9	,,	150	96	88	0.29	—
10	,,	200	96	85	0.29	—
11	,,	300	96	82	0.26	—
12	,,	400	96	66	0.27	—

^{a}Initial monomer/initiator ratio.
^{b}Measured at $C = 2$ g/L in dichloromethane at 25°C.
^{c}From vapor pressure osmometry in chloroform.

zation to proceed at lower temperatures. Despite lower temperatures and a more favorable thermodynamic situation, significantly higher molecular weights were not obtained. This result and the finding that the measured viscosities are rather independent of the M/I ratio (for $M/I \geqslant 100$) suggests that chain growth is limited by side reactions causing termination.

B. Mechanistic Aspects

In a previous paper [1] it was demonstrated by IR and ^{1}H-NMR spectroscopy that methyl triflate initiation of 5,5-dimethyl-1,3-dioxanone-2 obeys the following mechanistic concept. The initiator alkylates the exocyclic oxygen, generating a trioxocarbenium ion (Eq. 1). Due to ring opening by the counter-

ion, an equilibrium with the covalent triflate is established (Eq. 2). The trioxocarbenium ion is attacked by another cyclocarbonate, so that the alkyl–oxygen bond is cleaved and the exocyclic oxygen of the nucleophile is alkylated (Eq. 3). An alternative propagation step is the reaction between the covalent triflate and monomer (Eq. 4). A clear-cut decision on which one of these alternative propagation steps is predominant could not be made.

In the present work, 1,3-dioxanone was combined with a twofold excess of methyl triflate in chloroform solution. In analogy to previous results, propagation could be suppressed by excess initiator, and ^{1}H-NMR spectroscopy revealed the signals of the trioxocarbenium ion (Eq. 1). Furthermore, the signals of the covalent triflate formed according to Eq. (2) were detected (Fig. 1). In other words, the ^{1}H-NMR spectra of methyl triflate/1,3-dioxanone-2 mixtures exactly confirm the reaction scheme of Eqs. (1)-(4) deduced from spectroscopic studies of the 5,5-dimethyl derivative. However, a result of particular interest is the observation that, even for the more reactive 1,3-dioxanone-
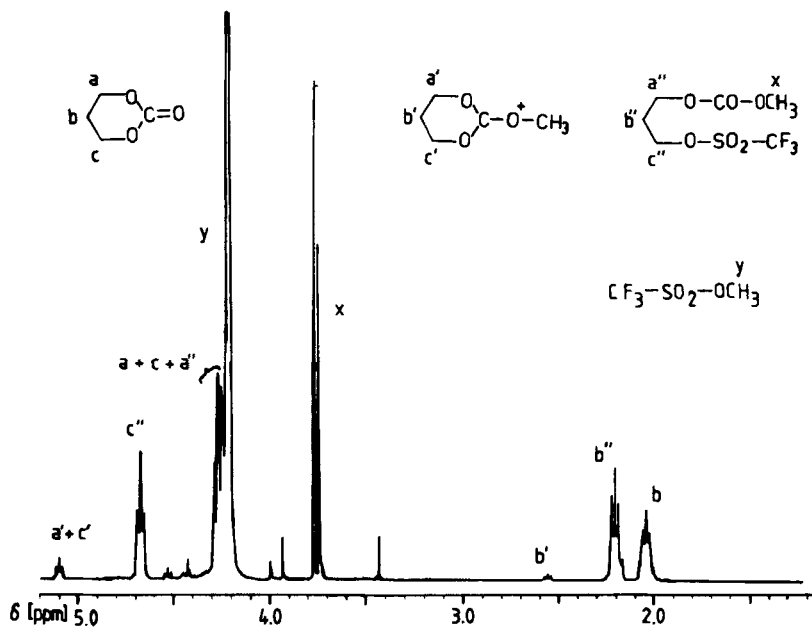

FIG. 1. 360 MHz ^{1}H-NMR spectrum of a reaction mixture prepared from methyl triflate and 1,3-dioxanone-2 (mole ratio 2:1) in CDCl$_3$ at 20°C, measured after 24 h.

2, a slight excess of initiator suffices to suppress propagation to a great extent. This finding indicates that the covalent initiator is slightly more reactive than the initially formed trioxocarbenium ion. An analogous result was obtained for methyl triflate-initiated polymerizations of δ-valerolactone [3].

For trioxocarbenium ions resulting from 5,5-dimethyl-1,3-dioxanone-2, the low reactivity with respect to further chain growth (i.e., nucleophilic attack of a monomer) may be explained by steric hindrance of the geminal methyl substituents. This steric argument is clearly not valid for 1,3-dioxanone-1 and δ-valerolactone. Yet even for unsubstituted heterocycles, the access of a monomer molecule to the electrophilic CH_2-group of a cyclic cationic chain end (Eq. 3) may be sterically more hindered than the reaction with the covalent end group (Eq. 4) for three reasons. First, the "substituent" of the electrophilic $O-CH_2$-group in a cyclic cation is branched in contrast to the covalent triflate end group; second, the neighboring counterion; and third, the greater stability of the solvation shell are additional obstacles in the case of the cyclic carbenium ions. In any case, the results obtained here with 1,3-dioxanone-2 confirm that for cationic polymerizations of heterocycles (in contrast to vinyl monomers), chain growth via covalent active end groups (Eq. 4) may well compete with propagation via ionic end groups (e.g., Eq. 3). Similar results were reported for cationic polymerizations of cyclic ethers [4].

$$R = H, CH_3 \tag{1}$$

$$CH_3-O-\overset{\overset{O}{\|}}{C}-O-CH_2CR_2CH_2OSO_2CF_3 \tag{2}$$
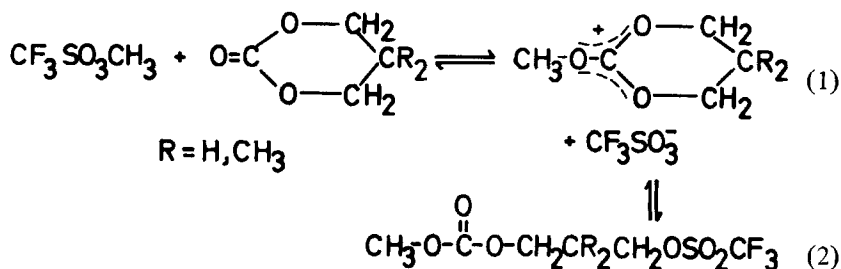
For poly(trimethylene carbonate) made by methyl triflate-initiated polymerization (see Table 1 or 3), the following ^{1}H-NMR spectroscopic features were found. In agreement with the polymerization mechanism of Eqs. (1)-(4), signals of methyl carbonate end groups are detected (Figs. 1 and 2). However, it is difficult to explain why, in all cases, signals appear at 3.75 and 3.80 ppm instead of just one signal. Still more conspicuous is a triplet at 3.4 ppm (signal y in Fig. 2). This chemical shift is characteristic of an ether group $(-CH_2-O-CH_2)$ or of an hydroxyl end group $(-CH_2-OH)$. Weak signals of ether groups have also been reported for cationic polymerizations of 5,5-dimethyl-1,3-dioxanone-2 [1].

$$CH_3O-\overset{O}{\underset{O}{C}} \cdots \overset{O-CH_2}{\underset{O-CH_2}{CR_2}} + O=C\overset{O-CH_2}{\underset{O-CH_2}{CR_2}} \quad (3)$$

$$CH_3O-\overset{O}{\overset{\parallel}{C}}-OCH_2CR_2CH_2\overset{O-C}{\underset{O-CH_2}{\overset{O-CH_2}{CR_2}}}$$

$$CH_3O-\overset{O}{\overset{\parallel}{C}}-OCH_2CR_2CH_2-OSO_2CF_3 + O=C\overset{O-CH_2}{\underset{O-CH_2}{CR_2}} \quad (4)$$

$$-[-O-\overset{a}{C}H_2-\overset{b}{C}H_2-\overset{a}{C}H_2-O-CO-]_n-O\overset{c}{C}H_3$$

$$\sim\sim\sim\overset{z}{C}H_2-O-CO-CF_3$$

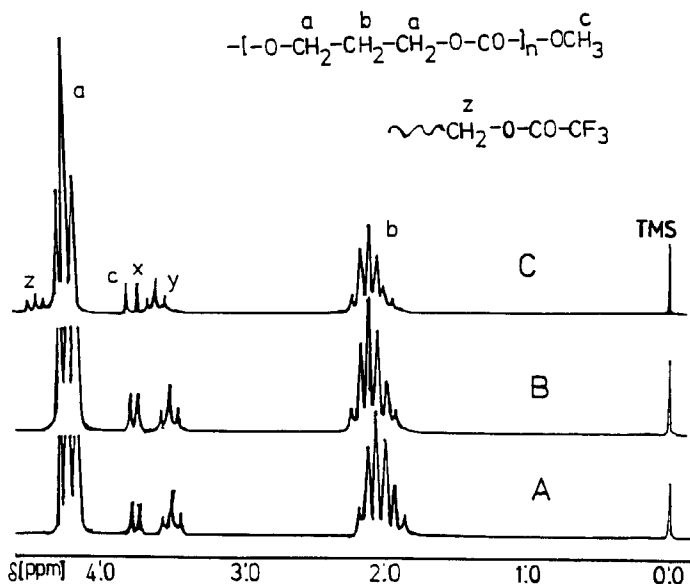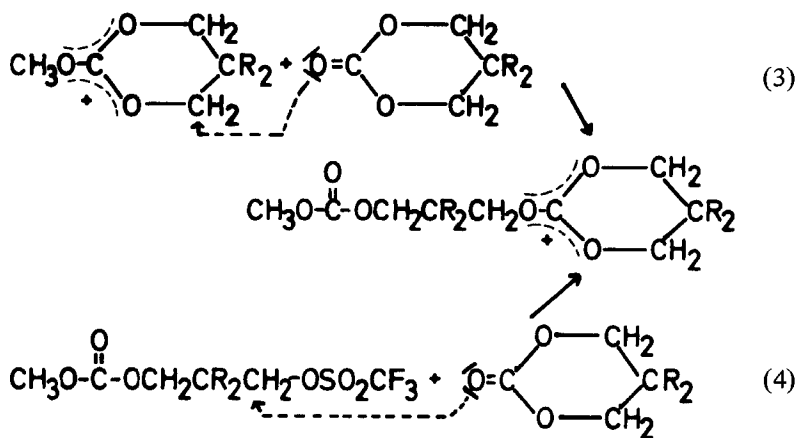FIG. 2. 100 MHz ^{1}H-NMR spectra measured at 20°C in CDCl$_3$. (A) Methyl triflate-initiated poly(1,3-dioxanone-2) after isolation from methanol; No. 3, Table 4. (B) The same sample 20 h after addition of phenylisocyanate. (C) The same sample 20 h after addition of trifluoroacetic anhydride.

In order to obtain clear-cut evidence in favor or against CH_2-OH end groups, samples of poly(1,3-dioxanone-2) isolated from methyl triflate-initiated polymerizations by precipitation with moist methanol were treated with phenyl isocyanate or trifluoroacetic anhydride. These reaction were conducted in $CDCl_3$ solutions in NMR tubes, and ^{1}H-NMR spectra were recorded after 4 and 20 h. In the case of phenylisocyanate, the spectra of the reaction mixture did not display a significant change (Fig. 2A and B). Yet, after precipitation, the isolated polycarbonate exhibited the signal of phenyl protons. Obviously, phenylisocyanate had reacted with a small fraction of $-CH_2OH$ end groups. This conclusion was confirmed by the reaction with trifluoroacetic anhydride. As demonstrated in Fig. 2C, a new triplet appears at 4.3 ppm (signal z in Fig. 2), which represents the methylene protons of a trifluoroacetate end group. This latter method was recently described by Duda et al. for the identification of CH_2ON end groups in poly(ϵ-caprolactone) [5]. Since the triplet at 3.4 ppm (y in Fig. 2) did not vanish, these studies clearly demonstrate that the methyl triflate-initiated polycarbonate samples possess both CH_2OH end groups and CH_2-O-CH_2 ether groups. In most samples the mole fraction of ether groups is in the range of 5-10% relative to carbonate groups.

The existence of two methyl end group signals, the formation of ether groups, and the relatively low molecular weights found for all polymerizations listed in Tables 1-3 indicate that cationic polymerizations of cyclocarbonates are accompanied by side reactions. At least one of those side reactions must be a transfer reaction because high conversions are obtainable despite low molecular weights. Since cationic polymerization of δ-valero- or ϵ-caprolactone [3, 6] may yield polyesters with $\bar{M}_w$ up to 70 000, it is clear that lactones and cyclocarbonates show quite different behavior with regard to side reactions and molecular weights.

Thus, the question arises how the different behavior of lactones and cyclocarbonates in cationic polymerizations may be explained. A polymerization mechanism involving oxonium ions according to the scheme reported in previous decades for lactones [7, 9] is outlined in Eqs. (5) and (6). Since the same mechanism may be formulated for lactones, it cannot explain the absence of ether groups in cationically synthesized polylactones. Therefore, the alternative reaction sequences of Eqs. (7)-(13) seem to be more likely. The key steps of this mechanistic scheme are the intramolecular migration of an alkyl group (Eqs. 8 and 11), which may also be considered as an intramolecular nucleophilic substitution. These equlibria are certainly shifted far to the left side due to the stabilization of the trioxocarbenium ion. Yet, following the reactions, the formation of oxonium ions (Eq. 9 or 11) ends up with the irreversible decarboxylation of Eq. (10). Because the initiator is re-

generated according to Eq. (10), the reaction pathways (7)-(10) and (1), (11), and (12) may be called cationically catalyzed decarboxylation of carbonates. With regard to the polymerization mechanism, it must be added that the reaction sequence of Eqs. (1), (11), and (12)—if it takes place at all—requires cationic copolymerization of the resulting oxetanes for its completion. Equations (13) and (14) explain the formation of methyl ether end groups without the growing step of Eq. (6).

In order to obtain better insight into the reactivity of aliphatic carbonates, a mixture of diethyl carbonate and 5 mol% methyl triflate was refluxed for 16 h. Slow evolution of carbon dioxide was detected along with the formation of diethyl ether. After reaction for 2 h, the conversion was 10%, and after 16 h it was 30% (Fig. 3). The ^{1}H-NMR spectra of the reaction mixture also revealed the formation of methyl carbonate groups and ethyl triflate (Fig. 3). Hence, the results clearly support the reaction sequence (7)-(10).
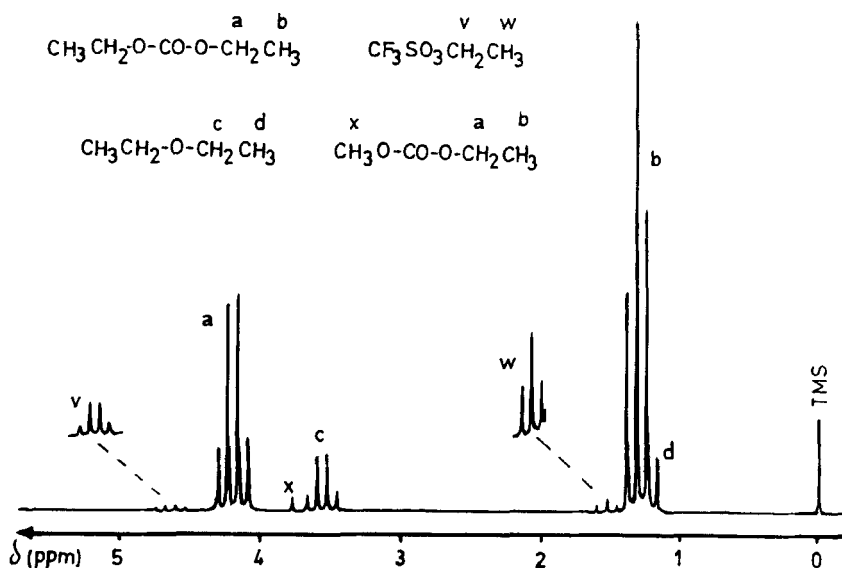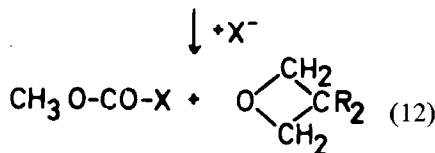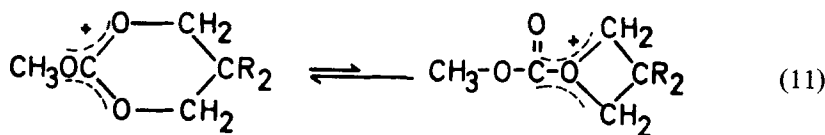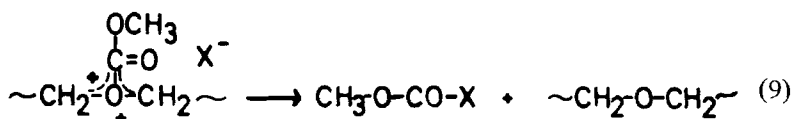
FIG. 3. 100 MHz ^{1}H-NMR spectrum of the reaction mixture obtained from pure diethyl carbonate and 5 mol% methyl triflate after 16 h at 120-130°C (measured in $CDCl_3$ with internal TMS reference).

$$R_2C\begin{matrix} CH_2-O \\ \\ CH_2-O \end{matrix}C{=}O \ + \ CH_3X \ \rightleftharpoons \ R_2C\begin{matrix} CH_2-\overset{+}{O}{-}CH_3 \\ \\ CH_2-O \end{matrix}C{=}O \quad X^- \tag{5}$$

$$R = H, CH_3$$

$$R_2C\begin{matrix} CH_2-O \\ \\ CH_2-O \end{matrix}C{=}O \ + \ O{=}C\begin{matrix} O-CH_2 \\ \\ O-CH_2 \end{matrix}CR_2 \ \rightleftharpoons \ O{=}C\begin{matrix} O-CH_2 \\ \\ \overset{+}{O}-CH_2 \end{matrix}CR_2 \tag{6}$$

$$CH_3O-CH_2CR_2CH_2O-C{\equiv}\overset{+}{O}$$

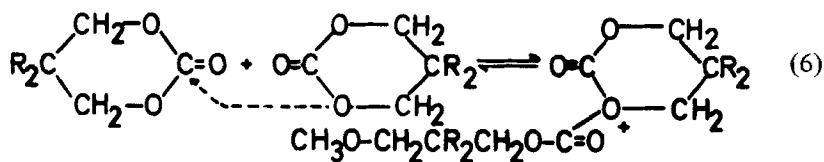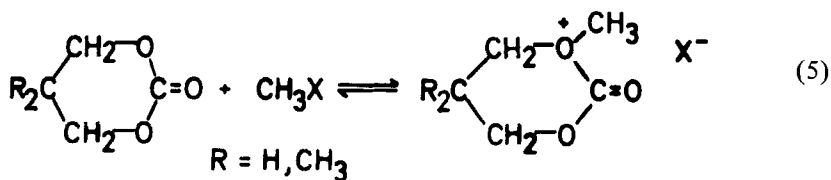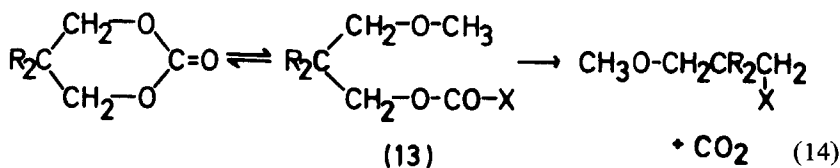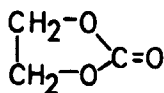$${\sim}CH_2-O-\overset{O}{\overset{\|}{C}}-O-CH_2{\sim} \ + \ CH_3{-}X \ \rightleftharpoons \ {\sim}CH_2-O{=}\overset{+}{\overset{O-CH_3}{C}}{-}O-CH_2{\sim} \quad X^- \tag{7}$$

$$X^- \ \overset{O-CH_3}{\underset{CH_2-O{=}\overset{+}{C}{-}O{-}CH_2}{}} \ \rightleftharpoons \ \overset{O-CH_3}{\underset{\overset{+}{C}H_2{-}\overset{+}{C}{-}CH_2}{C{=}O}} \quad X^- \tag{8}$$

$${\sim}CH_2{=}\overset{+}{\underset{+}{O}}{-}CH_2{\sim} \ \longrightarrow \ CH_3{-}O{-}CO{-}X \ + \ {\sim}CH_2{-}O{-}CH_2{\sim} \tag{9}$$

with $\overset{OCH_3}{\underset{}{C{=}O}} \quad X^-$ over the left structure.

$$CH_3{-}O{-}CO{-}X \ \longrightarrow \ CH_3X \ + \ CO_2 \tag{10}$$

$$CH_3\overset{+}{O}C\begin{matrix} O-CH_2 \\ \\ O-CH_2 \end{matrix}CR_2 \ \rightleftharpoons \ CH_3{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{+}{O}\begin{matrix} CH_2 \\ \\ CH_2 \end{matrix}CR_2 \tag{11}$$

$$\Big\downarrow {+}X^-$$

$$CH_3\,O{-}CO{-}X \ + \ O\begin{matrix} CH_2 \\ \\ CH_2 \end{matrix}CR_2 \tag{12}$$

$$R_2C \begin{array}{c} CH_2-O \\ \\ CH_2-O \end{array} C=O \rightleftharpoons R_2C \begin{array}{c} CH_2-O-CH_3 \\ \\ CH_2-O-CO-X \end{array} \longrightarrow CH_3O-CH_2CR_2CH_2 \\ \qquad\qquad\qquad X$$

$$\text{(13)} \qquad\qquad \bullet\, CO_2 \qquad \text{(14)}$$
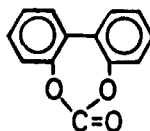
C. Five- and Seven-Membered Cyclocarbonates

3   4

In order to find out to what extent other cyclocarbonates are prone to cationic polymerization, the five- and seven-membered monomers 3 and 4 were treated with methyl triflate. In a first series of experiments, monomers 3 and 4 were mixed with equimolar amounts of methyl triflate in $CDCl_3$ and subjected to ^1H NMR at 25 or 60°C at increasing time intervals. Yet, even after 48 h no reaction was detectable. The same negative result was obtained when $CDCl_3$ was replaced by deuteronitrobenzene. However, when 3 was reacted with methyl triflate in CD_5NO_2 at 100°C, an unidentified reaction occurred. Several polymerizations of 3 with methyl triflate were therefore conducted in nitrobenzene at 100°C with M/I ratios of 50 and 100. The reaction time was varied from 8 to 48 h, but no polymer was found on precipitation with methanol or diethyl ether. From the reaction mechanisms of Eqs. (1)-(4) and (7)-(14), it is obvious that the aromatic monomer 4 is not suited for cationic polymerization because the aromatic carbons of the C–O bonds do not undergo alkylation. However, it is unclear why the dioxolanone-2 (3) does not polymerize.

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