

## Effect of Substituents on Cationic Polymerization of Six-Membered Spiro Orthocarbonates

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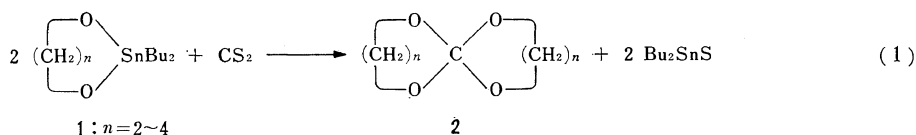
**ABSTRACT:** Six-membered spiro orthocarbonates with methyl substituents were prepared from cyclic dibutylstannyl glycolates and carbon disulfide, then polymerized using boron trifluoride etherate as the catalyst in 1,2-dichloroethane at 30°C. The methyl substituent caused a decrease in the polymer yield. The 2,8-dimethyl and 2,4,8,10-tetramethyl spiro monomers were polymerized by a 1,10-transfer reaction to bring about polyethercarbonates analogously to the unsubstituted spiro monomer. The spiro-monomer having 3,3,9,9-tetramethyl substituents underwent a 1,10-transfer polymerization at 30°C accompanied with the formation of polycarbonate segment which was partially depolymerized to the corresponding cyclic carbonate monomer at refluxing temperature of 1,2-dichloroethane. Contrary to the above, no polymer was obtained from the 2,2,4,8,8,10-hexamethyl spiro monomer.

**KEY WORDS** Spiro Orthocarbonate / Cationic Polymerization / Transfer Polymerization / Substituent Effect / Polyethercarbonate /

Transfer polymerization of vinyl or cyclic monomers<sup>1-5</sup> is a subject of considerable interest in polymer chemistry. The longest transfer reaction reported so far by other workers is the 1,8-transfer polymerization of spiro-

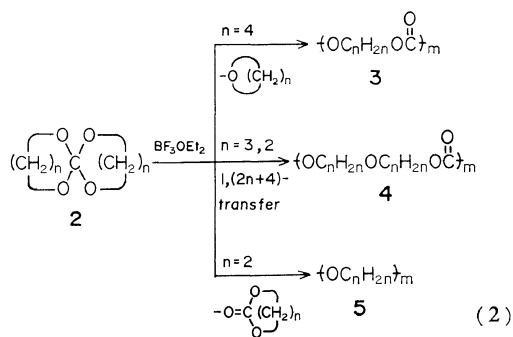
orthocarboxylate, 1,4,6-trioxaspiro[4.4]nonane, catalyzed by the Lewis acid.<sup>5</sup>

Recently new synthetic methods for making spiro orthocarbonates as new heterocyclic monomer types have been established by us using



organostannyl<sup>6,7</sup> or tellous<sup>8</sup> glycolate derivatives and carbon disulfide; a typical example for such a preparation is shown in eq 1.

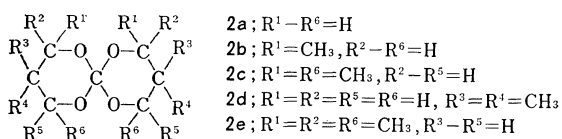
We reported already in our letter<sup>9</sup> that cationic polymerization of the unsubstituted five- to seven-membered spiro orthocarbonates (**2**) could be performed using boron trifluoride etherate (BF<sub>3</sub>OEt<sub>2</sub>) as the catalyst in 1,2-dichloroethane at 30°C, and that the ring size of the spiro monomer **2** strongly affected the mode of the polymerization reactions as indicated by eq 2. The seven-membered spiro monomer was



polymerized, eliminating the tetrahydrofuran to form polycarbonate **3** ( $n=4$ ), and the five-membered spiro monomer was polymerized with a 1,8-transfer reaction to form the polyethercarbonate **4** ( $n=2$ ), but this was accompanied by the elimination of ethylene carbonate to form the polyether **5** ( $n=2$ ). In contrast to these polymerizations involving elimination reactions of cyclic ether or carbonate, the unsubstituted six-membered spiro orthocarbonate (**2a**;  $n=3$ ) was polymerized with a 1,10-transfer reaction to afford polyethercarbonate **4a** ( $n=3$ ). Such a type of 1,10-transfer polymerization of **2a** is probably the longest transfer polymerization reported so far and a rare example of the homopolymerization of one kind of the monomer **2a** to give an alternating structure which corresponds to the 1:1 copolymer of six-membered cyclic carbonate with four-membered cyclic ether.

Separate from our study regarding the preparation and polymerization of spiro orthocarbonates, Endo and Bailey reported that spiro orthocarbonates were polymerized without shrinkage during this process and showed the desirable character in these physical properties.<sup>10-12</sup> However, our interest is directed to the reactivity and the mode of polymerization of **2**.

In this paper, we have reported on the preparation of methyl-substituted six-membered spiro orthocarbonate monomers (**2b**–**2e**), and studies on the influence of methyl substituents on the polymerizability and the mode of cationic ring-opening polymerization.



## EXPERIMENTAL

### General

No correction was made for any of the melting and boiling points. IR and NMR spectra were recorded with a JASCO IRA-1 and a Hitachi Perkin-Elmer R-24 spectrometer,

respectively.

Glycols, dibutylstannyl oxide, and  $BF_3OEt_2$  were commercially available and used without further purification. Carbon disulfide, 1,2-dichloroethane, toluene, and hexane were dried in the usual manner.

Dibutylstannyl glycolates (**1b**–**1c**) were prepared from corresponding glycols and dibutylstannyl oxide by azeotropic dehydration in refluxing toluene similar to the method reported previously,<sup>13</sup> and were carefully dried by heating at 120°C under vacuum. As an exception, the glycolate **1e** was prepared by reaction of 2-methyl-2,4-pentanediol with diethoxydibutylstannane at 100°C with removal of the ethanol formed in vacuum. The melting and boiling points are as follows: 4-methyl-2-dibutylstanna-1,3-dioxane (**1b**), mp (recrystallized from toluene) 97–100°C [lit.<sup>14</sup> bp 165°C (0.25 mm)]; 4,6-dimethyl-2-dibutylstanna-1,3-dioxane (**1c**), bp 138°C (0.3 mm); 5,5-dimethyl-2-dibutylstanna-1,3-dioxane (**1d**), mp (recrystallized from toluene) 108–111°C; 4,4,6-trimethyl-2-dibutylstanna-1,3-dioxane (**1e**), bp 139°C (1.5 mm) [lit.<sup>14</sup> 143°C (1.5 mm)].

The spiro-monomer, 1,4,6,10-tetraoxaspiro[4.5]decane (**10**), was prepared by the method appearing in the literature.<sup>6</sup>

### Preparation of 2,8-Dimethyl-1,5,7,11-tetraoxaspiro[5.5]undecane (**2b**)

The dibutylstannyl glycolate **1b** (32 g, 97 mmol), 1,2-dichloroethane (25 ml) and slight excess amount of carbon disulfide (10 ml) were introduced into a glass autoclave equipped with a mechanical stirrer under dry nitrogen, and the mixture was heated for 5 hr at 85°C. After evaporation of the excess carbon disulfide and the solvent, a large quantity of hexane was added to the reaction mixture to precipitate a small amount of yellow viscous liquid of the oligomeric material from **2b**. Following decantation to remove the liquid by-product and the subsequent evaporation of hexane from the mixture, 2.9 g (32%) of **2b** were obtained by distillation under reduced pressure: bp 82–86°C (1 mm); NMR ( $CHCl_3$ )  $\delta$  1.24 (d, 6,  $J=6.2$  Hz,  $CH_3$ ), 1.58 (m, 4,  $CH_2$ ), 3.98 (m, 4,  $OCH_2$ ), and 4.34 ppm (m, 2,  $OCH$ ); IR ( $CHCl_3$ ) 1130 and 1015  $cm^{-1}$  ( $\nu_{C-O}$ ).

*Preparation of 2,4,8,10-Tetramethyl-1,5,7,11-tetraoxaspiro[5.5]undecane (2c)*

Glycolate **1c** was allowed to react with carbon disulfide for 10 hr at 90°C, as in the case of **2b**. After evaporation of carbon disulfide and the solvent, a considerable amount of hexane was added to precipitate a white solid of **2c**: yield 27%; mp (CCl<sub>4</sub>) 153–155°C; NMR (CHCl<sub>3</sub>)  $\delta$  1.23 (d, 12,  $J=6.2$  Hz, CH<sub>3</sub>) 1.49 (m, 4, CH<sub>2</sub>), and 4.16 ppm (m, 4, CH); IR (CHCl<sub>3</sub>) 1100 and 1025 cm<sup>-1</sup> ( $\nu_{C-O}$ ).

*Preparation of 3,3,9,9-Tetramethyl-1,5,7,11-tetraoxaspiro[5.5]undecane (2d)*

The glycolate **1d** was allowed to react with carbon disulfide for 13 hr at 85°C, and the reaction mixture was worked-up as mentioned above to afford the white crystal **2d**: yield 56%; mp (CCl<sub>4</sub>) 138–140°C; NMR  $\delta$  0.99 (s, 12, CH<sub>3</sub>) and 3.65 ppm (s, 8, CH<sub>2</sub>); IR (CHCl<sub>3</sub>) 1115 and 1010 cm<sup>-1</sup> ( $\nu_{C-O}$ ).

*Preparation of 2,2,4,8,10-Hexamethyl-1,5,7,11-tetraoxaspiro[5.5]undecane (2e)*

The glycolate **1e** was allowed to react with carbon disulfide for 13 hr at 110°C. The reaction mixture was distilled giving a colorless liquid of **2e**: yield 52%; bp 102–104°C (5 mm); NMR (CHCl<sub>3</sub>)  $\delta$  1.21 (d, 6,  $J=5.6$  Hz, 4- and 10-CH<sub>3</sub>), 1.29 (s, 12, 2- and 8-CH<sub>3</sub>) 1.39 (d, 4,  $J=6.1$  Hz, CH<sub>2</sub>), and 4.20 ppm (m, 2, CH); IR (CHCl<sub>3</sub>) 1125 and 1025 cm<sup>-1</sup> ( $\nu_{C-O}$ ).

*Polymerization of Spiro Orthocarbonates*

Generally, the spiro monomer (3 mmol) and BF<sub>3</sub>OEt<sub>2</sub> (1–8 mol % based on **2**; mainly 4 mol %) in 1,2-dichloroethane (3 ml) were sealed in a glass tube under dry nitrogen and held at 30.0±0.1°C. After the polymerization reaction was stopped by adding a few drops of 10% diethylamine in 1,2-dichloroethane, the solvent and the unreacted monomer were evaporated under vacuum at 50–100°C to give the corresponding polymer as a colorless viscous material. The mean molecular weights measured by GPC were 5600 and 4800 for the polymers from **2a** and **2d**, respectively, and less than 4000 for that from **2b** or **2c**.

The monomer **2d** was also polymerized in refluxing 1,2-dichloroethane using BF<sub>3</sub>OEt<sub>2</sub> as catalyst. After the polymerization reaction was stopped by addition of diethylamine and the

solvent was evaporated, the tetramer and the polymer of 3,3-dimethyloxetane were extracted with hexane, and then the monomer **2d** and the cyclic carbonate, 5,5-dimethyl-1,3-dioxan-2-one (**9d**), were sublimed under vacuum at 50–100°C to give the polymer as a viscous material. The tetramer of 3,3-dimethyloxetane was sublimed under vacuum at 130°C from the soluble products in hexane and the residual material contained the polyether: tetramer; mp 153–156°C (lit.<sup>15</sup> 157°C); NMR (CHCl<sub>3</sub>)  $\delta$  0.83 (s, CH<sub>3</sub>) and 3.08 ppm (s, CH<sub>2</sub>); IR (CHCl<sub>3</sub>) 1139 cm<sup>-1</sup> ( $\nu_{C-O}$ ): polyether; NMR (CHCl<sub>3</sub>)  $\delta$  0.87 (s, CH<sub>3</sub>) and 3.11 ppm (s, CH<sub>2</sub>); IR (CHCl<sub>3</sub>) 1131 cm<sup>-1</sup> ( $\nu_{C-O}$ ). The NMR and IR spectra of the carbonate **9d** were coincident with those of an authentic sample.

*Hydrolysis of the Polymer Obtained from 2b*

To a solution of the polymer **4b** (0.20 g) in aqueous 20% ethanol (5 ml) was added sodium hydroxide (0.5 g). The homogeneous solution was refluxed for 2 hr. After neutralization of the solution with diluted hydrochloric acid, the hydrolyzed product was extracted repeatedly with chloroform. The extract was washed with a small amount of water and dried with anhydrous sodium sulfate. Evaporation of chloroform gave the glycol HOCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>OCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>OH (**6**; 0.14 g) which was determined as not involving any other glycol by GLC; IR (CHCl<sub>3</sub>) 1080 ( $\nu_{C-O}$ ) and 3460 cm<sup>-1</sup> ( $\nu_{OH}$ ).

The glycol **6** was acetylated by refluxing acetic anhydride in pyridine to form the diacetate CH<sub>3</sub>COOCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>OCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>OCOCH<sub>3</sub>; NMR (CHCl<sub>3</sub>)  $\delta$  1.13 (d, 3,  $J=6.0$  Hz, CH<sub>3</sub>C—O), 1.23 (d, 3,  $J=6.0$  Hz, CH<sub>3</sub>C—OCO), 1.74 (m, 4, CH<sub>2</sub>—C), 2.00 (s, 6, CH<sub>3</sub>COO), 3.38 (t, 2,  $J=6.4$  Hz, CH<sub>2</sub>—O), 3.5 (m, 1, CH—O), 4.11 (t, 2,  $J=6.6$  Hz, CH<sub>2</sub>—OCO), and 4.97 ppm (m, 1, CH—OCO); IR (CHCl<sub>3</sub>) 1735 cm<sup>-1</sup> ( $\nu_{C=O}$ ).

*Solid-State Polymerization of Unsubstituted Monomer 2a*

Solid-state polymerization of crystalline monomer **2a** (0.2 g) was carried out in hexane (2 ml) at -10–30°C using BF<sub>3</sub>OEt<sub>2</sub> (0.023 mol/l) as the catalyst. A viscous polymer was obtained after working-up the polymerization mixture in

the manner mentioned above.

Polymerization of crystalline monomer **2a** was also examined with  $\gamma$ -ray irradiation in a sealed tube under dry nitrogen at room temperature. No polymer was obtained at a total dose of  $10^4$ – $10^6$  r.

## RESULTS AND DISCUSSION

### Preparation of Spiro Monomers

Six-membered spiro orthocarbonates (**2b**–**2e**) substituted by methyl groups were successfully prepared by the reaction of dibutylstannyl glycolates (**1b**–**1e**) with carbon disulfide analogously to the preparation of the unsubstituted monomer **2a**<sup>2</sup> (eq 1), and the results are shown in Table I.

The yields and reaction conditions described in Table I indicate that the reaction for the preparation of **2** was affected by the methyl substituent. Symmetric spiro orthocarbonates, **2a**, **2c**, and **2d**, were obtained as solids, but the unsymmetric **2b** and **2e** were liquids. Al-

though orthocarbonate is known to be an organic dehydrating agent, 3,3,9,9-tetramethyl-substituted monomer **2d** was exceptionally stable in the moisture of the air.

### Polymerizability of the Substituted Spiro Orthocarbonates

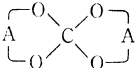
The cationic polymerization of the substituted spiro-monomers was carried out in 1,2-dichloroethane using  $\text{BF}_3\text{OEt}_2$  as the catalyst. Yields of polymers and the polymerization conditions are summarized in Table II.

Methyl substituents in the monomer caused the polymerizability to decrease, so that the apparent rates of polymerization have the following order: **2a** > **2b** > **2c**, **2d** > **2e**. The most bulky monomer **2e** did not allow formation of a polymer even within the long period of the polymerization time.

### Characterization of the Polymers Formed and Modes of Polymerizations

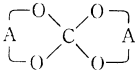
The polymer obtained from 2,8-dimethyl-

Table I. Preparation of six-membered spiro orthocarbonates

A in 	Condition		Yield, %	mp, °C (bp, °C/mm)
	Temp, °C	Time, hr		
–CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> – ( <b>2a</b> ) <sup>a</sup>	105	10	92	132–133
–CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> – ( <b>2b</b> )	85	5	32	(82–86/1)
–CH(CH <sub>3</sub> )CH <sub>2</sub> CH(CH <sub>3</sub> )– ( <b>2c</b> )	90	10	27	153–155
–CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> – ( <b>2d</b> )	85	13	56	138–140
–C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )– ( <b>2e</b> )	110	13	52	(102–104/5)

<sup>a</sup> Data from ref 7.

Table II. Polymerization of six-membered spiro orthocarbonates

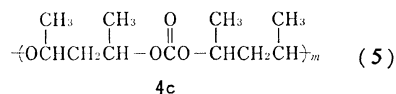
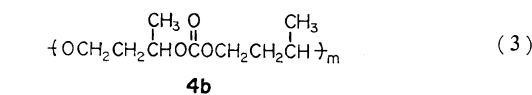
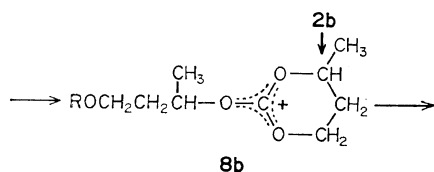
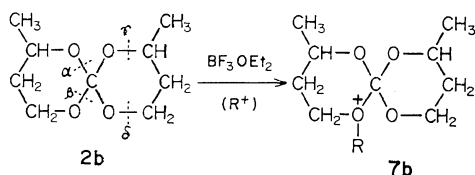
A in 	( <b>2a</b> ) <sup>a</sup>	$\text{BF}_3\text{OEt}_2$ , mol %	Temp, °C	Time, hr	Polymer yield, wt %
–CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> – ( <b>2a</b> ) <sup>b</sup>		1	30	16	91
–CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> – ( <b>2b</b> )		4	30	24	50
		4	30	148	75
–CH(CH <sub>3</sub> )CH <sub>2</sub> CH(CH <sub>3</sub> )– ( <b>2c</b> )		4	30	240	9
		4	30	720	42
–CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> – ( <b>2d</b> )		4	30	168	13
		8	reflux	0.5	45
–C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )– ( <b>2e</b> )		4	30	240	0

<sup>a</sup> 1.0 mol/l of 1,2-dichloroethane.

<sup>b</sup> Data from ref 9.

substituted monomer **2b** had the characteristic bands of a carbonate structure at  $1740\text{ cm}^{-1}$  and ether band at  $1125\text{ cm}^{-1}$ . The NMR spectrum showed three pairs of signals whose areas were nearly the same. The signal observed at a higher field are reasonably assigned to the methyl, methylene, and methine protons related to the ether linkage:  $\delta$  1.15 (d, 3,  $J=6.2\text{ Hz}$ ,  $\text{CH}_3\text{—C—O—C}$ ), 3.43 (t, 2,  $J=6.1\text{ Hz}$ ,  $\text{CH}_2\text{—O—C}$ ), and 3.6 ppm (m, 1,  $\text{CH—O—C}$ ). Those at a lower field are assignable to the groups related to the carbonate linkage:  $\delta$  1.30 (d, 3,  $J=6.2\text{ Hz}$ ,  $\text{CH}_3\text{—C—OCOO}$ ), 4.18 (t, 2,  $J=6.3\text{ Hz}$ ,  $\text{CH}_2\text{—OCOO}$ ), and 4.86 ppm (m, 1,  $\text{CH—OCOO}$ ). The 3- and 9-methylene protons appeared at  $\delta$  1.78 ppm (m, 4,  $\text{C—CH}_2\text{—C}$ ). From these spectroscopic data, it is demonstrated that the monomer **2b** gives the polyethercarbonate **4b** in the cationic polymerization. Additional evidence for this structure **4b** was provided by alkaline hydrolysis of the polymer. The hydrolyzed product was only the glycol **6** whose structure was confirmed by the NMR spectrum as to its diacetate.

Thus the cationic polymerization of **2b** is represented by the 1,10-transfer reaction analogous to the polymerization of the unsubstituted monomer **2a**, as formulated in eq 3.



Generally, it has been observed that cationic ring-opening reactions of  $\alpha$ -methyl-substituted cyclic ether, such as propylene oxide, undergo two comparable fissions of the methyl-substituted and unsubstituted carbon—oxygen bonds.<sup>16,17</sup> In the cationic 1,10-transfer polymerization of the monomer **2b**, four modes of the ring opening may be possible according to the two positions of attack by an active species and those of the bond fissions;  $\alpha$ - $\gamma$ ,  $\alpha$ - $\delta$ ,  $\beta$ - $\gamma$ , and  $\beta$ - $\delta$  fissions in **2b**.

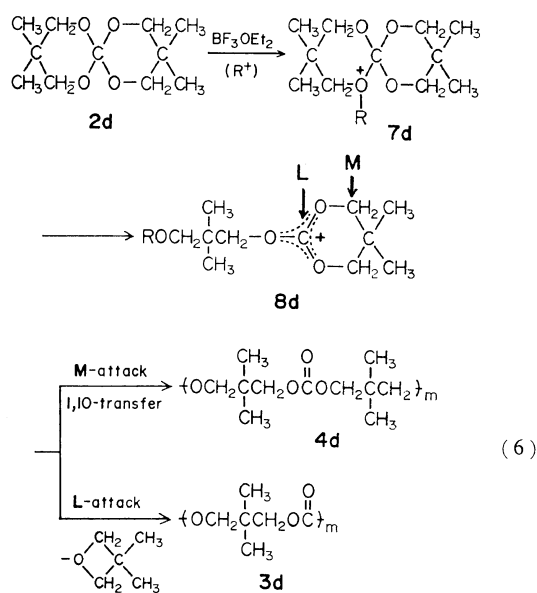
From the structure **4b** of the polymer obtained,  $\alpha$ - $\gamma$  and  $\beta$ - $\delta$  fissions are excluded, and ring-opening mode of  $\alpha$ - $\delta$  or of  $\beta$ - $\gamma$  fission is considered to be predominant. It is reasonably postulated that the monomer **2b** may be attacked with an electrophile (catalyst) at the oxygen of 5-position to cause the  $\beta$ -fission because of the smaller steric hindrance. And, a nucleophilic attack by the monomer may easily occur on the methyl-substituted carbon at 8-position in **8b** to cause the  $\gamma$ -fission because of increasing carbonium-ion character at the methyl-substituted carbon atom in the trioxocarbonium ion **8b**. A similar mode of attack of a monomer on the methyl-substituted carbon of a dioxocarbonium ion intermediate was reported in the case of the cationic ring-opening polymerization of 4-methyl-2-vinyl-1,3-dioxolane.<sup>18</sup>

The IR spectrum of the polymer obtained from 2,4,8,10-tetramethyl-substituted monomer **2c** showed the bands at  $1740\text{ cm}^{-1}$  ( $\nu_{\text{C=O}}$ ) and  $1125\text{ cm}^{-1}$  ( $\nu_{\text{C-O}}$ ). The NMR spectrum also showed two pairs of signals related to the ether and carbonate structures:  $\delta$  1.23 (d,  $J=6.0\text{ Hz}$ ,  $\text{CH}_3\text{—C—O—C}$ ), 3.66 (m, 2,  $\text{CH—O—C}$ ), 1.32 (d,  $J=7.0\text{ Hz}$ ,  $\text{CH}_3\text{—C—OCOO}$ ), and 4.93 ppm (m, 2,  $\text{CH—OCOO}$ ). The 3- and 9-methylene protons appeared at  $\delta$  1.54 ppm. It is supposed

that the monomer **2c** is also polymerized with 1,10-transfer reaction to give the polyethercarbonate having the structure **4c**, as shown in eq 5.

The monomer having four methyl groups at 3,3,9 and 9-positions was found to be polymerized in a complicated way, using  $\text{BF}_3\text{OEt}_2$  in 1,2-dichloroethane at  $30^\circ\text{C}$ . The colorless viscous polymer was obtained and it showed  $\nu_{\text{C}=\text{O}}$  ( $1745\text{ cm}^{-1}$ ) and  $\nu_{\text{C}-\text{O}}$  ( $1130\text{ cm}^{-1}$ ) bands in the IR spectrum, and two singlets of methylenes at  $\delta$  3.15 ( $\text{CH}_2-\text{O}-\text{C}$ ) and 3.98 ppm ( $\text{CH}_2-\text{OCOO}$ ) in the NMR spectrum. The area of the former peak was smaller than that of the latter in the NMR spectrum. It has been suggested that the polyethercarbonate structure **4d** was formed with the formation of the polycarbonate structure **3d**. Moreover, two singlets observed at  $\delta$  0.99 and 0.93 ppm were assignable to methyl protons in **3d** and in **4d**, respectively. Therefore, the polymerization mode of the monomer **2d** is shown by eq 6, which is concerned with the 1,10-transfer reaction to form **4d** and with the elimination reaction of 3,3-dimethyloxetane to form **3d**. It has been known that 3,3-dimethyloxetane easily polymerizes in the presence of a cationic catalyst to give a mixture of the tetramer and the polyether.<sup>15</sup> These products were also obtained in the polymerization of **2d** to support the elimination of 3,3-dimethyloxetane.

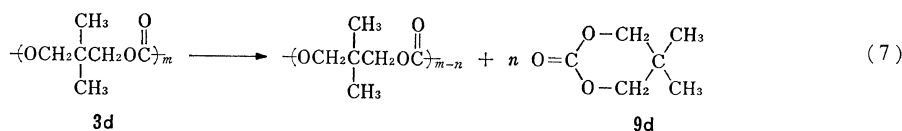
The 1,10-transfer polymerization of **2d** may require the more sterically hindered **M**-attack by the ether-oxygen atom in the monomer **2d** to the propagating terminal in **8d** in eq 6, because the electron pair of oxygen atom at nucleophilically attacking point in the monomer **2d** is located at the 1,3-diaxial position against the 3- or 9- dimethyl group, and the electrophilic point **M** is located adjacently to the tertiary carbon in **8d**. On the other hand, the **L**-attack of **2d** to the trioxocarbonium ion **8d** should be favored to form the segment of **3d**,

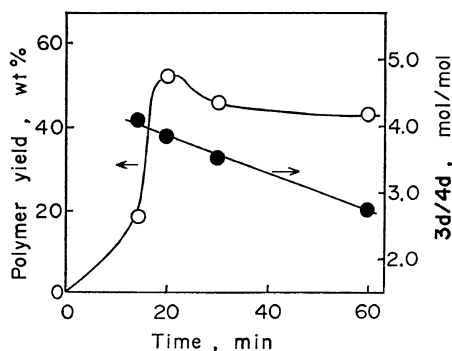


because the **L**-attack is probably unaffected by steric hindrance through elimination of the oxetane.

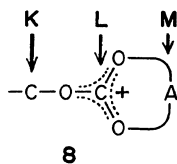
The monomer **2d** was also polymerized in refluxing 1,2-dichloroethane using  $\text{BF}_3\text{OEt}_2$  as catalyst. The polymer showed similar NMR and IR spectra mentioned above. The yield and composition of the polymer are plotted against the polymerization time in Figure 1. The yield reached a maximum value after the polymerization for 20 min, and then gradually decreased. The content of the polycarbonate unit **3d** also decreased. It has been known that the polycarbonate **3d** is depolymerized by heating to afford the cyclic carbonate **9d**.<sup>19</sup> So, the decrease in the polymer yield is reasonably explained by the depolymerization of **3d**-type sequence formed in the early stage of the polymerization (eq 7). The carbonate **9d** was isolated *in vacuo*.

The monomer **2e** having six methyl substituents





**Figure 1.** Polymerization of 3,3,9,9-tetramethyl-substituted six-membered spiro orthocarbonate (**2d**) catalyzed by  $\text{BF}_3\text{OEt}_2$  in refluxing 1,2-dichloroethane: monomer, 1.0 mol/l;  $\text{BF}_3\text{OEt}_2$ , 8 mol % based on **2d**.



at the 2,2,4,8,8, and 10-positions could not be polymerized due to the large steric hindrance.

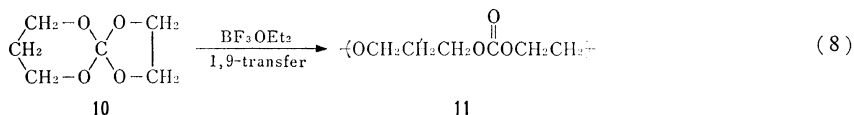
A variety of cationic polymerization reactions

of spiro orthocarbonates are represented in terms of the ambident nature of the heterocyclic trioxocarbonium ion **8**. The monomer is able to react at the positions **K**, **L**, and **M**.

Methyl substituents of the spiro monomers affect the reactivities and the modes of polymerization. Methyl substituents in the  $\alpha$ -position from the oxygen atom decreased the polymerizability of six-membered spiro orthocarbonates, but did not affect the mode of polymerization. Therefore, the 1,10-transfer polymerization occurred in the case of  $\alpha$ -substituted spiro monomers. Contrary to this, methyl substituents in the  $\beta$ -position decreased the polymerizability of the monomer **2d** and strongly affected the mode of polymerization.

#### Other Related Polymerizations

The unsymmetric spiro orthocarbonate **10** consisting of six- and five-membered rings was also polymerized using  $\text{BF}_3\text{OEt}_2$  as the catalyst in 1,2-dichloroethane for 4 hr at  $30^\circ\text{C}$  to afford colorless viscous material in 76-% yield. The IR spectrum of the polymer showed bands of  $\nu_{\text{C=O}}$  ( $1753\text{ cm}^{-1}$ ) and  $\nu_{\text{C-O}}$  ( $1124$  and  $1049\text{ cm}^{-1}$ ). The NMR spectrum showed signals at  $\delta$  1.94 (m, 2,  $\text{C-CH}_2\text{-C}$ ), 3.51, 3.58 (two t, 4,  $\text{CH}_2\text{O}$ ) and 4.25 ppm (t, 4,  $\text{CH}_2\text{-OCOO}$ ). These data are in agreement with the polyethercarbonate structure **11** formed by a 1,9-transfer polymerization of **10**, as shown in eq 8.



The polymerization of the monomer **2a** was examined in the solid state. In hexane, the crystalline monomer **2a** was polymerized using  $\text{BF}_3\text{OEt}_2$  as catalyst at  $-10$ – $30^\circ\text{C}$  to give the polyethercarbonate **4a** as a viscous liquid. This result could not be distinguished from that of the homogeneous polymerization in solution. The crystalline monomer **2a** was irradiated with  $\gamma$ -ray in dry nitrogen at a total dose of  $10^4$ – $10^6$  r; however, no reaction was observed.

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