

Cationic Copolymerization of 1,3-Dioxolane with Tetrahydrofuran Initiated with Methyl Fluorosulfate

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ABSTRACT: Cationic copolymerization of 1,3-dioxolane (DOL) with tetrahydrofuran (THF) was carried out in chloroform at 0°C with methyl fluorosulfate ($\text{CH}_3\text{OSO}_2\text{F}$) and triethyloxonium tetrafluoroborate (Et_3OBF_4) as initiators. The gas chromatographic determination of the residual monomers during the copolymerization revealed that both DOL and THF were consumed concurrently from the initial stage of the polymerization with $\text{CH}_3\text{OSO}_2\text{F}$. With Et_3OBF_4 , on the other hand, only THF was consumed at first, followed by the rapid consumption of DOL after an induction period. The fractionation of the reaction products and the microstructural analysis by ^1H and ^{13}C NMR spectroscopy showed that the products obtained with $\text{CH}_3\text{OSO}_2\text{F}$ were real copolymers containing an appreciable amount of cross-over diads, while those with Et_3OBF_4 were block copolymers and/or mixtures of homopolymers. The structures and reactivities of the growing species in these two copolymerization systems are discussed on the basis of these findings.

KEY WORDS 1,3-Dioxolane / Tetrahydrofuran / Copolymerization / NMR / Random Copolymer / Block Copolymer / Ionic Species / Ester Species / Methyl Fluorosulfate /

In a previous paper,¹ we reported kinetic studies on the cationic polymerization of 1,3-dioxolane (DOL) initiated with methyl fluorosulfate ($\text{CH}_3\text{OSO}_2\text{F}$) in deuteriochloroform, and concluded that the polymerization proceeded through an ester growing species, although the coexistence of an undetectable amount of oxonium ionic growing species can not be ruled out. This conclusion was drawn on the basis of a large negative value of the activation entropy [$\Delta S_p^\ddagger = -42 \text{ cal mol}^{-1} \text{ deg}^{-1}$ ($-176 \text{ J k}^{-1} \text{ mol}^{-1}$)], which is characteristic of dipole-dipole $\text{S}_{\text{N}}2$ reactions producing ionic species, e.g., the Menschutkin reaction, together with ^1H and ^{13}C NMR spectral data of the reaction system. This paper describes the cationic copolymerization of DOL with THF which was undertaken in chloroform using two different initiators, $\text{CH}_3\text{OSO}_2\text{F}$ and Et_3OBF_4 , in order to make clear the reactivity of the ester growing species in the polymerization of DOL.

The cationic copolymerization of DOL with THF using stable oxonium salts as initiators has been attempted by two research groups.^{2,3} Yamashita *et al.*² confirmed by the gas chromatographic de-

termination of the unreacted monomers during the copolymerization initiated with Et_3OBF_4 that preferential polymerization of THF occurred in the initial stage of the copolymerization, and that once DOL began to polymerize after an induction period, the polymerization of THF slowed down gradually and eventually ceased. However, it was resumed, although very slowly, after the polymerization of DOL reached the equilibrium conversion. Lyudvig *et al.*³ studied the same copolymerization with $\text{Et}_3\text{OSbCl}_6$ as an initiator and they concluded that the propagating species of DOL, which are supposedly solvated by THF monomers, grow only by the addition of DOL monomers, in agreement with the results of Yamashita *et al.*²

It seems strange at first glance that DOL cannot copolymerize with THF, because both DOL^{4,5} and THF^{6,7} copolymerize with 3,3-bis(chloromethyl)oxacyclobutane (BCMO), and both growing species of DOL and THF grow essentially by the $\text{S}_{\text{N}}2$ mechanism, although the former has an oxycarbenium ionic character⁸⁻¹¹ and the latter is a tertiary oxonium ion.¹² One of the possible reasons for the reluctant cross-over propagations in the DOL-THF

copolymerization system is the preferential occurrence of an oxonium ion exchange reaction at the growing chain end with DOL and THF units as the penultimate and terminal units, respectively.² Therefore, it would be expected that if the copolymerization is carried out under the conditions where propagations proceed through ester species, instead of ionic species, by using a superacid derivative as an initiator, a random copolymer might be formed from DOL and THF. Conversely, if a random copolymer is actually obtained, it would be taken as a strong support for the presence of an ester species in the polymerization of DOL initiated with a superacid derivative. In this paper, we report the results of the cationic copolymerization of DOL with THF initiated with $\text{CH}_3\text{OSO}_2\text{F}$ and Et_3OBF_4 , and discuss the structures and reactivities of the growing species.

EXPERIMENTAL

Materials

1,3-Dioxolane (DOL) was prepared according to the procedure described by Astle *et al.*,¹³ dried over metallic sodium, and fractionally distilled from calcium hydride. bp 75–76°C. Tetrahydrofuran (THF) was dried over, and distilled from, metallic sodium, bp 66°C. Commercial methyl fluorosulfate ($\text{CH}_3\text{OSO}_2\text{F}$) was purified by distillation. bp 92–94°C. Triethyloxonium tetrafluoroborate (Et_3OBF_4) was prepared by the method of Meerwein *et al.*¹⁴ Chloroform was washed with sulfuric acid, dilute aqueous sodium carbonate, and water successively, and dried over anhydrous sodium sulfate; distillation followed. bp 61°C.

Copolymerization

Prescribed amounts of monomers, chloroform, and a chloroform solution containing the initiator were introduced in this order into a glass ampule under a nitrogen atmosphere. The ampule was then cooled at liquid nitrogen temperature, sealed off, and kept at 0°C for a desired time. The copolymerization was terminated by the addition of a few ml of a methanol-trimethylamine (volume ratio, 4:1) solution. The mixture was poured into a large amount of methanol. The precipitate was purified by reprecipitation from its chloroform solution into methanol (methanol-insoluble polymer). The methanol solution was concentrated under reduced pressure. The residue was dissolved in 50 ml of chloroform,

and the solution was washed with 10 ml of water three times. The solvent was evaporated and the residue was dried under vacuum to a constant weight (methanol-soluble polymer).

Characterization of Copolymers

¹H and ¹³C NMR spectra were taken in deuteriochloroform, using tetramethylsilane as an internal standard at room temperature. The former were recorded on a JNM MH-100 spectrometer working at 100 MHz, and the latter on a JNM FX-100 Fourier transform spectrometer at 25 MHz. The number average molecular weight of the copolymers was determined by a Hewlett Packard vapor pressure osmometer Model 302 on solutions in benzene at 37°C.

Fractionation of Copolymer

A sample of copolymer (0.30 g) was dissolved in a few ml of chloroform. To this solution was added a large volume of hexane to precipitate the insoluble polymer (insoluble fraction 1). The supernatant solution was separated by decantation, and the solvent was evaporated under reduced pressure to recover the hexane-soluble polymer (soluble fraction 1). The hexane-insoluble fraction was dissolved again in chloroform, and the above procedure was repeated to give soluble fraction 2 and insoluble fraction 2. This cycle was repeated two more times to obtain soluble fractions 3 and 4 and insoluble fraction 4.

Syntheses of Model Compounds

3,6,8,11-Tetraoxatetradecane. Paraformaldehyde (3.74 g, 0.12₄ mol), ethylene glycol monoethyl ether (22.6 g, 0.25₁ mol), 50 ml of benzene, and a small amount of *p*-toluenesulfonic acid were introduced into a flask with a water separating apparatus. The mixture was refluxed for about three hours until a predetermined amount of water was distilled off. Then the solution was neutralized with sodium carbonate and distilled. bp 87–88°C [10 mmHg (1.33 kPa)]; yield, 62.8%; ¹H NMR δ 1.22 (CH_3 -, 6H), *ca.* 3.6 ($-\text{OCH}_2$ -, 12H), and 4.74 ($-\text{OCH}_2\text{O}$ -, 2H) ppm; ¹³C NMR δ 15.2 (CH_3 -), 66.5, 66.9, and 69.7 ($-\text{OCH}_2$ -), and 95.1 ($-\text{OCH}_2\text{O}$ -) ppm.

3,6,8-Trioxadodecane. 3,6,8,11-Tetraoxatetradecane (5.05 g, 26.2 mmol), butyl alcohol (3.00 g, 40.5 mmol), and a small amount of *p*-toluenesulfonic acid were placed into a flask, and the

mixture was refluxed for one hour. Then the solution was neutralized with sodium carbonate and distilled. bp 79–80°C [24 mmHg(3.20kPa)]; yield, 18.6%; ^1H NMR δ 0.94 (CH_3 -, 3H), 1.23 (CH_3 -, 3H), 1.54 ($-\text{CH}_2$ -, 4H), ca. 3.6 ($-\text{OCH}_2$ -, 8H), and 4.77 ($-\text{OCH}_2\text{O}$ -, 2H) ppm; ^{13}C NMR δ 13.8 and 15.1 (CH_3 -), 19.4 ($-\text{CH}_2$ -), 31.8 ($-\text{CH}_2$ -), 66.6, 66.8, 67.6, and 69.8 ($-\text{OCH}_2$ -), and 95.3 ($-\text{OCH}_2\text{O}$ -) ppm.

RESULTS

Cationic Copolymerization of DOL with THF

The cationic copolymerizations of DOL with THF initiated with $\text{CH}_3\text{OSO}_2\text{F}$ and Et_3OBF_4 were carried out in chloroform. The conversions and the mole fractions of DOL and THF units in the products were calculated by the gas chromatographic determination of the residual monomers during the copolymerizations. Figure 1 shows the time-conversion curves in the copolymerization of DOL with THF initiated with $\text{CH}_3\text{OSO}_2\text{F}$ and Et_3OBF_4 . The apparent rate of propagation in the copolymerization initiated with $\text{CH}_3\text{OSO}_2\text{F}$ is lower than that initiated with Et_3OBF_4 . The difference in the copolymerization behavior between the two initiator series is emphasized in the plots of mole fraction of DOL unit in the products and the conversion (Figure 2).

In the copolymerization initiated with Et_3OBF_4 , only THF is consumed at the initial stage of the copolymerization, and DOL is consumed rapidly after an induction period. This phenomenon is essentially the same as that reported previously.² On the other hand, when $\text{CH}_3\text{OSO}_2\text{F}$ is used as initiator, DOL is consumed more rapidly than THF from the initial stage of the copolymerization after a prolonged induction period (Figures 1 and 2). Such a polymerization behavior suggests that the reactivities of the growing species of DOL and THF in the latter copolymerization system are different from those in the former system.

The results of the copolymerization of DOL with THF are summarized in Table I. The yields were calculated from the weight of the isolated polymers. The copolymers obtained with $\text{CH}_3\text{OSO}_2\text{F}$ (Runs 2–5) were highly viscous or waxy materials, and their average molecular weights were appreciably lower than those of the homopolymers obtained with the same initiator (Runs 1 and 6) and the copolymer prepared with Et_3OBF_4 (Run 7).

Figure 3 shows a typical ^1H NMR spectrum of the

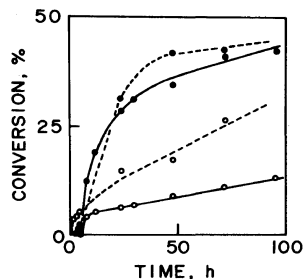


Figure 1. Time-conversion curves in copolymerization of DOL with THF: Total monomers, 10 mol dm^{-3} ; solvent, CHCl_3 ; temp, 0°C ; mole fraction of DOL in feed, 0.50; initiator, (—), $\text{CH}_3\text{OSO}_2\text{F}$ and (---) Et_3OBF_4 ; monomer, ●, DOL and ○, THF.

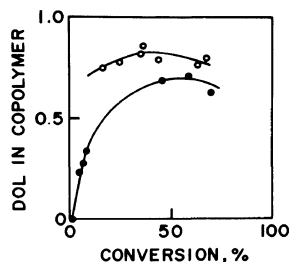


Figure 2. Mole fraction of DOL in copolymer vs. conversion (based on mol %) in copolymerization of DOL with THF: temp, 0°C ; solvent, CHCl_3 ; mole fraction of DOL in feed, 0.50; ○, $\text{CH}_3\text{OSO}_2\text{F}$; ●, Et_3OBF_4 .

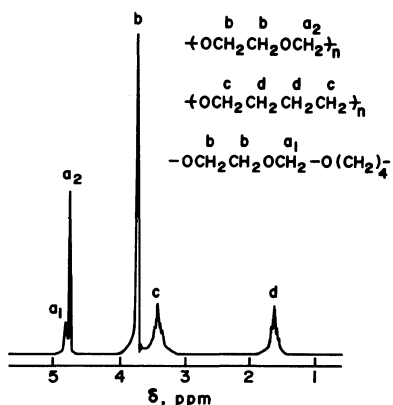


Figure 3. ^1H NMR spectrum of DOL-THF copolymer: mole fraction of DOL in copolymer, 0.60; CDCl_3 ; ca. 10%; room temp.

copolymer. From the ^1H NMR spectra of the homopolymers of DOL and THF, the peaks a₂, b, c, and d are assigned as follows.

Table I. Copolymerization of DOL with THF^a

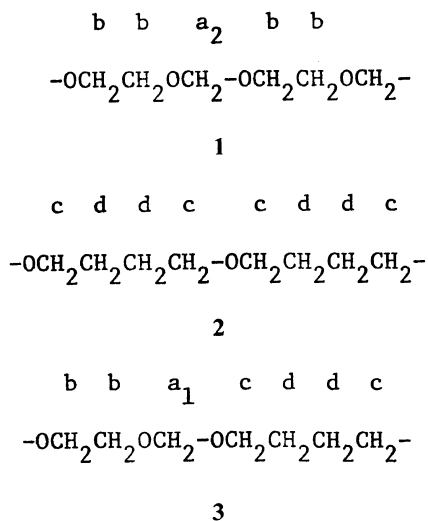
Sample No.	Mole fraction of DOL in feed	Time h	Fraction No. ^b	Yield		MW ^c
				%		
1	0.00	48	I	50.6	—	5700
			II	—	—	—
2	0.20	96	I	9.2	—	2300
			II	15.6	—	2000
3	0.50	48	I	10.1	—	1400
			II	4.8	—	900
4	0.50	96	I	19.3	—	1400
			II	9.0	—	900
5	0.80	96	I	34.3	—	2200
			II	9.3	—	1000
6	1.00	48	I	21.2	—	6500
			II	1.4	—	9000
7 ^d	0.50	48	I	24.5	—	7400
			II	7.4	—	1300

^a Concn. of total monomers, 0.10 mol; temp, 0°C; solvent, CHCl₃; initiator, CH₃OSO₂F, 1 mol % to monomers.

^b I, methanol-insoluble fraction; II, methanol-soluble fraction.

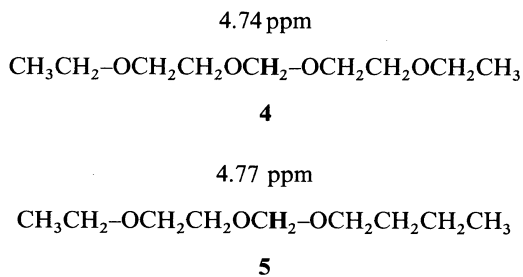
^c VPO, benzene, 37°C.

^d Initiator, Et₃OBF₄.



The peak a₁ at δ 4.77 is assignable to the acetal protons adjacent to THF monomer unit. The assignments of the peaks a₁ and a₂ are confirmed by model

compounds: 3,6,8,11-tetraoxatetradecane **4** and 3,6,8-trioxadodecane **5** show their acetal proton signals at δ 4.74 and 4.77 ppm, respectively, which correspond to the peaks a₂ and a₁ in the ¹H NMR spectrum in Figure 3. However, the acetal proton signals are more properly assigned in terms of the triad sequences to be suggested later.



In the ¹H NMR spectra of the copolymers prepared with Et₃OBF₄, no signal corresponding to signal a₁ in Figure 3 is observed. Therefore, it is very

Table II. Fractionation of DOL-THF copolymers

Sample No. ^a	Initiator	[DOL] MW ^c	Hexane-sol fraction				Hexane-insol fraction	Total	
			1	2	3	4	4		
2	CH ₃ OSO ₂ F	0.28 ₉ 2300	wt fraction, %	31.2	11.8	9.8	20.6	14.5	87.9
			[DOL]	0.06 ₇	0.13 ₅	0.23 ₂	0.22 ₂	0.61 ₂	—
			MW ^c	1400	1400	1000	2600	2500	—
4	CH ₃ OSO ₂ F	0.83 ₄ 1400	wt fraction, %	6.0	3.5	4.1	2.5	77.0	93.1
			[DOL]	0.44 ₈	0.56 ₅	0.64 ₉	0.73 ₇	0.95 ₅	—
			MW ^c	1000	1100	1100	1400	1400	—
7	Et ₃ OBF ₄	0.82 ₈ 7400	wt fraction, %	0	3.0	3.5	0.4	93.2	100.1
			[DOL]	—	0.45 ₁	0.63 ₄	0.60 ₆	0.83 ₈	—
			MW ^c	—	2000	3700	—	7700	—
8 ^b	—	0.49 ₃ —	wt fraction, %	9.0	32.5	9.7	—	50.7	101.9
			[DOL]	0.02 ₃	0.01 ₇	0.06 ₂	—	0.96 ₃	—

^a Sample numbers correspond to those in Table I (methanol-insoluble fraction).

^b A mixture of poly(DOL) ($M_n = 2300$) and poly(THF) ($M_n = 3400$).

^c VPO, benzene, 37°C.

likely that a mixture of homopolymers and/or block copolymers of DOL and THF are formed in the cationic copolymerization initiated with Et₃OBF₄.

The ¹³C NMR spectra of the copolymers prepared with CH₃OSO₂F show two acetal carbon signals at δ 95.6 and 96.0 ppm, while those of the polymers prepared with Et₃OBF₄ show a single acetal carbon signal at δ 95.6 ppm, which corresponds to the acetal carbon of the DOL homopolymer.

The observed differences in the ¹H and ¹³C NMR spectra of these copolymers strongly suggest that the mechanisms of the copolymerizations are different in these two initiator systems.

Fractionation of Copolymers

Some copolymers and a mixture of DOL- and THF-homopolymers were fractionated into hexane-soluble and -insoluble fractions as described in detail in the Experimental part. The results are listed in Table II. In the case of the homopolymer mixture (No. 8), DOL- and THF-homopolymers were separated almost completely into the hexane-insoluble and -soluble fractions, respectively. On the other hand, in the fractionations of the copolymers prepared with CH₃OSO₂F as an initiator (No. 2 and 4), the mole fraction of DOL in the hexane-soluble parts

are lower than those in the original copolymers, and those in the hexane-insoluble parts are higher than those in the original copolymers. The variation in the number-average molecular weight of each fraction

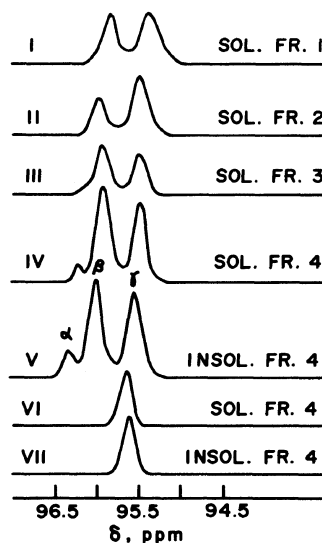
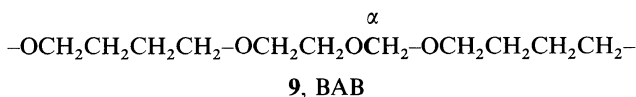
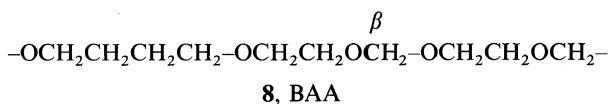
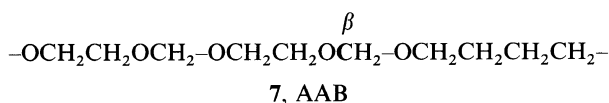
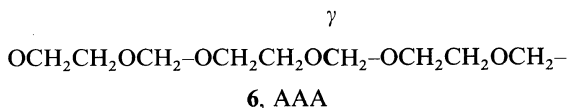


Figure 4. Expanded ¹³C NMR spectra of acetal carbons of fractionated DOL-THF copolymers: I-V, sample No. 2; VI and VII, sample No. 7.

seems to indicate that the fractionation is not only due to composition but also due to molecular weight. Taking the aforementioned NMR data into account, the fractionation data on the product obtained with Et_3OBF_4 (No. 7) suggest the formation of block copolymers.

Expanded ^{13}C NMR spectra of the acetal carbons of some fractionated polymers are shown in Figure 4. In spectra IV and V, three signals, α , β , and γ are

distinctly observed; these probably arise from triad sequences. The signal γ at δ 95.6 ppm corresponds to that of the acetal carbon in the DOL homopolymer, and is assigned to the acetal carbon in the triad AAA **6**. From the chemical shifts of the acetal carbon in **4** and **5** (δ 95.1 and 95.3 ppm, respectively) the signals β and α may be assignable to the acetal carbons in the triads (AAB **7**+BAA **8**) and BAB **9**, respectively, where A and B denote DOL and THF units.



As the relative peak area of the signal a_1 in Figure 3 is close to that of the signal α in Figure 4, the signal a_1 in Figure 3 can be assigned to the acetal protons in the triad BAB. Accordingly, the signal a_2 should be due to the acetal protons in the triads AAB, BAA, and AAA. The validity of these assignments is confirmed by the calculation of AB diad fractions based on the assignments of the three signals α , β , and γ , as will be described below. ^{13}C NMR spectra of the hexane-soluble and -insoluble parts of the copolymers prepared with Et_3OBF_4 show only one signal, assigned to the acetal carbon in the triad AAA (VI and VII in Figure 4); this indicates that very few AB diad, if any, are present in the copolymer chain.

Compositions and Diad Fractions

The mole fraction of DOL in copolymers can be calculated from the relative peak area of the proton signals a_1 , a_2 , and d in Figure 3.

$$[A] = 2(a_1 + a_2) / \{2(a_1 + a_2) + d\} \quad (1)$$

$$[B] = 1 - [A] \quad (2)$$

where $[A]$ and $[B]$ are the mole fractions of the corresponding units. As mentioned above, the signal a_1 in Figure 3 is assignable to the acetal protons in the BAB triad **9**, and the diad fraction $[AB]$ is calculated as follows.

$$[AB] = [A] \cdot P_{AB} \quad (3)$$

$$P_{BAB} = P_{AB}^2 = a_1 / (a_1 + a_2) \quad (4)$$

where P_{AB} and P_{BAB} define the probabilities of the diad AB and the triad BAB in a copolymer chain, respectively; that is, the former is the probability that an A unit has a neighboring B unit and the latter is the probability that an A unit has B units on both sides.

Combining eq 3 and 4, one obtains

$$[AB] = [A] \sqrt{\frac{a_1}{a_1 + a_2}} \quad (5)$$

The diad fractions [AA] and [BB] are given by eq 6 and 7.

$$[\text{AA}] = [\text{A}] - [\text{AB}] \quad (6)$$

$$[\text{BB}] = [\text{B}] - [\text{AB}] \quad (7)$$

In Table IV, the copolymer compositions and diad fractions of some of the samples are summarized, together with the average sequence lengths, \bar{l}_A and \bar{l}_B , and the run number R , which refers to the number of sequences per 100 monomer units in a copolymer chain.¹⁵

$$\bar{l}_A = [\text{A}]/[\text{AB}] \quad (8)$$

$$\bar{l}_B = [\text{B}]/[\text{AB}] \quad (9)$$

$$R = 200 [\text{AB}] \quad (10)$$

P_{BAB} , P_{AAB} , P_{BAA} , and P_{AAA} define the probabilities of the triads BAB, AAB, BAA, and AAA in a copolymer chain, respectively.

$$P_{\text{BAB}} + P_{\text{BAA}} + P_{\text{AAB}} + P_{\text{AAA}} = 1 \quad (11)$$

$$P_{\text{BAB}} = P_{\text{AB}}^2 = \left(\frac{[\text{AB}]_i}{[\text{A}]_i} \right)^2 = \frac{\alpha}{\alpha + \beta + \gamma} \quad (12)$$

$$\begin{aligned} P_{\text{BAA}} + P_{\text{AAB}} &= 2P_{\text{AA}}P_{\text{AB}} \\ &= 2 \left(\frac{[\text{A}]_i - [\text{AB}]_i}{[\text{A}]_i} \right) \left(\frac{[\text{AB}]_i}{[\text{A}]_i} \right) \\ &= \frac{\beta}{\alpha + \beta + \gamma} \end{aligned} \quad (13)$$

$$\begin{aligned} P_{\text{AAA}} = P_{\text{AA}}^2 &= \left(\frac{[\text{A}]_i - [\text{AB}]_i}{[\text{A}]_i} \right)^2 \\ &= \frac{\gamma}{\alpha + \beta + \gamma} \end{aligned} \quad (14)$$

where α , β , and γ mean the relative peak areas of the corresponding acetal carbon signals in Figure 4, $[\text{A}]_i$ is the mole fraction of DOL in fractionated copolymers, which is evaluated from the ^1H NMR spectra, and the subscript i is the fraction number. The $[\text{AB}]_i$ of each fraction can be determined from eq 12–14. The moles of DOL and THF units A_i and B_i , and the cross-over diad AB_i in each fraction are given by eq 15, 16, and 17, respectively.

$$A_i = W_i \left(\frac{74.08 [\text{A}]_i}{72.11 (1 - [\text{A}]_i) + 74.08 [\text{A}]_i} \right) \frac{1}{74.08} \quad (15)$$

$$= W_i \left(\frac{[\text{A}]_i}{72.11 + 1.97 [\text{A}]_i} \right)$$

$$B_i = A_i ([\text{B}]_i / [\text{A}]_i) \quad (16)$$

$$AB_i = A_i ([\text{AB}]_i / [\text{A}]_i) \quad (17)$$

where $[\text{A}]_i$ and $[\text{B}]_i$ are the mole fractions of DOL and THF units, respectively, in fraction i , and W_i is the weight of the corresponding fraction. The total $[\text{A}]_i$ and $[\text{AB}]_i$, which should be equal to those of the unfractionated copolymer if the assignments of the signals α , β , and γ in Figure 4 are correct, are calculated from eq 18 and 19, respectively.

$$[\text{A}]_t = \frac{\sum_{i=1}^n A_i}{\sum_{i=1}^n A_i + \sum_{i=1}^n B_i} \quad (18)$$

$$[\text{AB}]_t = \frac{\sum_{i=1}^n AB_i}{\sum_{i=1}^n B_i} \quad (19)$$

The diad fractions $[\text{AB}]_i$ and $[\text{AB}]_t$ were calculated from eq 12–14 and 19, respectively, for the fractionated copolymers (No. 2). The data given in Table III show that the $[\text{AB}]_i$ values calculated from the three signals α , β , and γ , respectively, in Figure 4 are equal within the experimental error and that the $[\text{AB}]_t$ diad fraction of the original copolymer, 0.09₄, which is determined from eq 5, is nearly equal to the $[\text{AB}]_t$ diad fraction 0.07₇, which is calculated from eq 19. These results indicate that the assignments of the peaks α , β , and γ in Figure 4 are correct.

The composition and diad fractions of the copolymers are summarized in Table IV. All fractions of the copolymers obtained with $\text{CH}_3\text{OSO}_2\text{F}$ (No. 2–5) contained the cross-over diad AB in varying amounts, indicating that these were real copolymers of DOL and THF. It must be noted, however, that there are noticeable differences in the copolymer composition and diad fractions between the hexane-soluble and -insoluble parts, and also between the methanol-soluble and -insoluble parts. Such broad

Table III. Diad fractions, $[AB]$, $[AB]_i$, and $[AB]_r$ in fractionated DOL-THF copolymer^a

Sample No.	Fraction No.	$[AB]_i^b$			A_v	$[AB]^c$
		α	β	γ		
	Original	—	—	—	—	0.09 ₄
2	Hexane-sol 1	—	0.02 ₂	0.01 ₉	0.02 ₀	—
	2	—	0.03 ₇	0.03 ₀	0.03 ₃	—
	3	—	0.11 ₆	0.07 ₃	0.09 ₅	—
	4	0.05 ₇	0.09 ₉	0.07 ₅	0.07 ₇	—
	Hexane-insol 4	0.24 ₂	0.21 ₃	0.23 ₀	0.22 ₈	—
	$[AB]_r^d$	—	—	—	—	0.07 ₇

^a Sample number corresponds to that in Table I (methanol-insoluble fraction).

^b Calculated from eq 12—14.

^c Calculated from eq 5.

^d Calculated from eq 19.

distributions of the copolymer composition and diad fractions may suggest that this copolymerization cannot be treated statistically by the conventional copolymerization theory. The product prepared with Et_3OBF_4 (No. 7) is probably a block copolymer and/or a mixture of the homopolymers, judging from the data given in Tables II and IV. The detectable limit of the cross-over diad AB by means of 1H and ^{13}C NMR spectroscopy seems to be at most 1% to the total diad fractions. Therefore, the fact that no signal due to the cross-over diad AB was observed in the 1H and ^{13}C NMR spectra implies that there is none or at most a very small amount of the cross-over diad in the copolymer obtained with Et_3OBF_4 .

DISCUSSION

As described in a previous section, the formation of real copolymers in the cationic copolymerization of DOL with THF initiated with CH_3OSO_2F was confirmed by means of 1H and ^{13}C NMR spectroscopy and the fractionation of the copolymers. On the other hand, block copolymers and/or mixtures of homopolymers were formed in the copolymerization with Et_3OBF_4 . In the cationic polymerization of cyclic ethers and acetals initiated with conventional cationic initiators such as Et_3OBF_4 and BF_3Et_2O , the propagation takes place through the oxonium ions¹² and the oxycarbenium ions,⁸⁻¹¹ respectively. Therefore, the cationic copolymerization of DOL with THF initiated with Et_3OBF_4 may proceed

through the oxonium ion for THF and the oxycarbenium ion for DOL.

The growing species of DOL **10** is attacked by DOL and THF monomers to form **12** and **13**, respectively. The ion **12** is attacked by other monomers to propagate further. The oxonium ion **13**, however, cannot propagate because of the occurrence of an oxonium-exchange reaction: The nucleophilic attack of DOL and THF occurs exclusively on the oxymethylene carbon of the penultimate DOL unit (arrow a) rather than on the α -methylene carbon of the THF ring (arrow b), because the positive charge on the former carbon should be higher than that on the latter one, on account of the electron-withdrawing effect of the adjacent oxygen; in addition, the five membered THF oxonium ring is relatively stable. Therefore the attack of THF on the oxonium ion **13** leads only to an exchange reaction involving the THF unit at the growing chain end. The attack of DOL on **13** generates the ion **12**, with its degree of polymerization increased by one compared with that of **10**. In other words, chain growth from the oxonium ion **13** takes place only by the attack of DOL through the formation of the ion **12**, and no AB diads can be formed in the polymer chain. However, the ion **10** is solvated by THF monomers so the reaction (20) is very slow at the initial stage of the copolymerization.

Copolymerization of Dioxolane with Tetrahydrofuran

Table IV. Compositions and diad fractions of DOL-THF copolymers

Sample No. ^a	Fraction No. ^a		[A]	[B]	[AB]	[AA] ^b	[BB] ^b	\bar{I}_A	\bar{I}_B	R	
2	I	Unfractionated ^c	0.28 ₉	0.71 ₁	0.09 ₄	0.19 ₅	0.61 ₇	3.1	7.6	19	
		Fractionated ^d									
		Hexane-sol 1	0.06 ₇	0.93 ₃	0.02 ₀	0.04 ₇	0.91 ₂	3.4	46.7	4	
		2	0.13 ₅	0.86 ₅	0.03 ₃	0.10 ₂	0.83 ₂	4.1	26.2	7	
		3	0.22 ₂	0.76 ₈	0.09 ₅	0.13 ₇	0.67 ₃	2.4	8.1	19	
		4	0.22 ₂	0.77 ₈	0.07 ₇	0.14 ₅	0.70 ₁	2.9	10.1	15	
		Hexane-insol 4	0.61 ₂	0.38 ₈	0.22 ₈	0.38 ₄	0.16 ₀	2.7	1.7	46	
		Σ^e	0.28 ₃	0.71 ₇	0.07 ₇	0.20 ₆	0.64 ₀	3.7	9.3	15	
		II	Unfractionated ^c	0.35 ₃	0.64 ₇	0.17 ₀	0.18 ₃	0.47 ₇	2.1	3.8	34
		3	I	Unfractionated ^c	0.93 ₀	0.07 ₀	0.07 ₀	0.86 ₀	0.00 ₀	13.3	1.0
II	Unfractionated ^c		0.60 ₀	0.40 ₀	0.21 ₂	0.38 ₈	0.18 ₈	2.8	1.9	42	
4	I	Unfractionated ^c	0.83 ₄	0.16 ₆	0.10 ₃	0.73 ₁	0.06 ₃	8.1	1.6	21	
		Fractionated ^d									
		Hexane-sol 1	0.44 ₈	0.55 ₂	0.05 ₇	0.39 ₁	0.49 ₅	7.9	9.7	11	
		2	0.56 ₅	0.43 ₅	0.09 ₉	0.46 ₆	0.33 ₆	5.7	4.4	20	
		3	0.64 ₉	0.35 ₁	0.09 ₁	0.55 ₈	0.26 ₀	7.1	3.9	18	
		4	0.73 ₇	0.26 ₃	0.08 ₄	0.65 ₃	0.17 ₉	8.8	3.1	17	
		Hexane-insol 4	0.95 ₆	0.04 ₄	0.07 ₃	0.91 ₂	0.00 ₀	21.7	1.0	9	
		Σ^e	0.84 ₈	0.15 ₂	0.08 ₈	0.76 ₀	0.06 ₄	9.6	1.7	18	
		II	Unfractionated ^c	0.62 ₈	0.37 ₂	0.17 ₉	0.44 ₉	0.19 ₃	3.1	2.1	36
		5	I	Unfractionated ^c	0.99 ₀	0.01 ₀	—	—	—	—	—
II	Unfractionated ^c		0.93 ₆	0.06 ₄	0.06 ₄	0.87 ₂	0.00 ₀	14.6	1.0	13	
7	I	Unfractionated ^c	0.82 ₈	0.17 ₂	0.00 ₀	—	—	—	—	—	
		Fractionated ^d									
		Hexane-sol 2	0.45 ₁	0.54 ₉	0.00 ₀	—	—	—	—	—	
		3	0.63 ₄	0.36 ₆	0.00 ₀	—	—	—	—	—	
		4	0.60 ₆	0.39 ₄	0.00 ₀	—	—	—	—	—	
		Hexane-insol 4	0.83 ₈	0.16 ₂	0.00 ₀	—	—	—	—	—	
		Σ^e	0.80 ₇	0.19 ₃	0.00 ₀	—	—	—	—	—	
II	Unfractionated ^c	0.50 ₅	0.49 ₅	0.00 ₀	—	—	—	—	—		

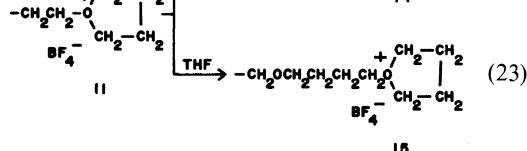
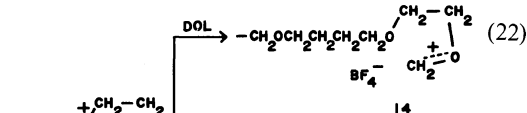
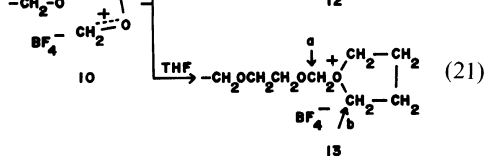
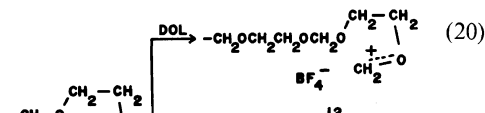
^a Sample numbers correspond to those in Table I.

^b [AA]=[A]-[AB] and [BB]=[B]-[AB].

^c Determined from ¹H NMR spectra.

^d Determined from ¹H NMR spectra for [A] and [B], and from ¹³C NMR spectra for [AB].

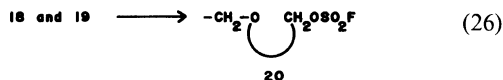
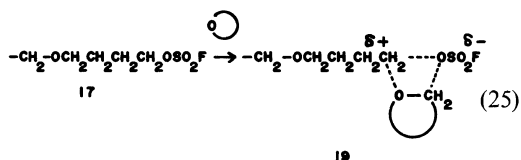
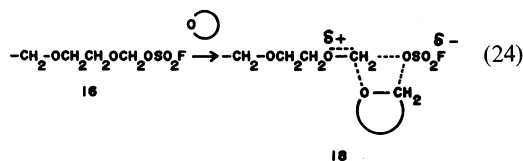
^e [A] and [AB] were calculated from eq 18 and 19, respectively.



On the contrary, the growing species of THF **11** with a penultimate THF unit is attacked by DOL and THF to form **14** and **15**, respectively. The former produces a BA diad, and the latter forms a BB diad in the copolymer chain. However, the oxonium ion **11** is relatively stable; it is thus very difficult to achieve ring-opening by the addition of DOL, because the basicity of DOL is lower than that of THF. Consequently, only a few BA diads are formed in the polymer chains. Since the growing species **13** does not propagate by the addition of THF and the reaction (23) precedes the reaction (22), mixtures of homopolymers and/or a block copolymer of THF sequence followed by DOL sequence will be formed.

On the other hand, the cationic polymerization of DOL with THF initiated with $\text{CH}_3\text{OSO}_2\text{F}$ produces real copolymers containing appreciable numbers of AB diads along the polymer chain. A possible explanation for the formation of the AB diads is the difference between the growing species of DOL and THF in these two initiator series. In the cationic polymerization of cyclic ethers initiated with superacids or their esters, the contributions of ester growing species have been confirmed by means of ^1H , ^{13}C , and ^{19}F NMR spectroscopy.¹⁷ Moreover, in the cationic polymerization of DOL in chloroform with $\text{CH}_3\text{OSO}_2\text{F}$, the propagation through the ester species $\text{---OCH}_2\text{OSO}_2\text{F}$ has been deduced from kinetic data as well as NMR spectral data.¹ From these

results, it seems likely that the ester species of DOL and THF contribute to the formation of the real copolymer described above. Thus, the cross-over diads of DOL-THF and THF-DOL would be formed by the addition of THF and DOL to the ester species **16** and **17**, respectively, presumably through the four-membered cyclic transition states **18** and **19** (eq 24-26).



Although there is no direct evidence for the proposed four-membered cyclic transition states, this mechanism seems to be preferable to the conventional $\text{S}_{\text{N}}2$ mechanism for the following reason. If the propagation proceeds by $\text{S}_{\text{N}}2$ mechanism, there would be formed, although transiently, an ionic species with a OSO_2F^- counter ion. For example, a THF oxonium ion with a penultimate DOL unit would be formed when THF attacks the ester species **16** by an $\text{S}_{\text{N}}2$ mechanism. Such an oxonium ion cannot propagate because of the oxonium exchange reaction on the oxymethylene carbon of the DOL unit, as described before (eq 21). For the cross-over propagation to occur, the THF oxonium ion must be rapidly transformed to its ester species by the nucleophilic addition of OSO_2F^- counter ion to the α -methylene carbon of the THF ring, not to the oxymethylene carbon of the DOL unit, before the oxonium-exchange reaction with DOL monomer takes place. Therefore, the mechanism involving the four-membered cyclic transition states through which ester species are directly formed is probably more reasonable than an $\text{S}_{\text{N}}2$ mechanism involving the intervention of ionic species.

In summary, DOL-THF copolymers containing

an appreciable amount of the cross-over diads were obtained in the copolymerization in chloroform with $\text{CH}_3\text{OSO}_2\text{F}$ as the initiator, while block copolymers and/or mixtures of homopolymers were formed with Et_3OBF_4 . The difference in the copolymerization behavior between these two systems suggests that the former system involves the ester growing species **16** and **17** which make the cross-over propagations feasible. However, in view of the finding that the distributions of the copolymer composition and diad fractions were rather broad, our results cannot exclude the possibility that ionic growing species may coexist, although in an undetectably low concentration, with the ester growing species in the $\text{CH}_3\text{OSO}_2\text{F}$ -chloroform system.

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