

Poly(alkylene oxide) Ionomers. II.* Solution Co- and Terpolymerization of Trioxane for the Preparation of Poly(oxymethylene) Ionomers

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ABSTRACT: Solution polymerization of trioxane (TO) with 1, 3-dioxolane (DO) gave copolymers of various comonomer compositions. TO was also copolymerized with ethyl glycidate (EG) and terpolymerized with DO and EG to polymers of low EG content. The copolymers were acetate-endcapped or base-treated to give stable co- and terpolymers. The treatment of EG containing poly(oxymethylene) (POM) copolymers with sodium hydroxide in methanol at elevated temperatures gave POM ionomers. The polymers were characterized by their infrared and PMR spectra for their general structure and co- and terpolymer composition. POM copolymers with only EG as comonomer showed low base stability but those which contained ethylene oxide (EO), either alone or in combination with EG, gave polymers of high base stability.

KEY WORDS Poly(oxymethylene) / Trioxane / 1, 3-Dioxolane / Ethyl Glycidate / Terpolymers / Ionomers / Acetate Endcapping / Base Stability /

Ionomers are copolymer of ethylene and 20—30-mol% methacrylic or acrylic acid completely or partially neutralized with sodium hydroxide,¹ or with phosphonate and sulfonate^{2,3} groups.

Ionomers based on the poly(oxymethylene) (POM) backbone chain have been described and some mechanical and spectroscopic properties have been measured.⁴⁻¹⁰ One method for the preparation of the copolymers of TO and EG⁵ was a copolymerization technique which consisted of mixing the monomers and the initiator in the gas phase^{4,5} above the ceiling temperature of polymerization of the comonomers and then cooling the initiated monomers¹¹ to cause polymerization. A high molecular weight copolymer of TO and EG was prepared which could be acetate-capped or base-treated to give directly the ionomer. The ionomer could be converted into the free acid with acetic acid or it could be transformed into other polymeric alkali salts with the corresponding metal chlorides in aqueous suspension.⁶

Other POM ionomers were prepared by the reac-

tion of epichlorohydrin—TO copolymers with thioglycolate.^{8,9} This method has advantages in that copolymers of TO and epichlorohydrin can be readily prepared at various comonomer compositions. On the other hand, the thioglycolate treatment is cumbersome and, as other polymer reactions, not always complete. Copolymers of styrene oxide—TO could undergo numerous substitution reactions on the benzene rings of styrene in spite of the acid sensitivity of the POM backbone chain.¹²

The advantage of the gas-phase copolymerization of TO and EG is that larger quantities of copolymers of relatively uniform molecular weight distribution and comonomer composition can be prepared. The base stability of this polymer is relatively low and the molecular weight of the base-stable polymer is low, indicating that the polymers were “blocky” and little transacetalization occurred and that EG was preferentially incorporated in the copolymer in the early part of the polymerization. The latter stage of the copolymerization was essentially a homopolymerization of the TO. Another advantage of polymerization by mixing in the vapor phase is that larger quantities of poly-

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mers are easily prepared and that both the change to various copolymer compositions and the change in initiator concentration are readily achieved.

Solution and bulk copolymerization of TO with suitable comonomers, studied extensively for epoxides and 1,3-dioxolane which have no functional groups, have advantages over polymerization technique from the gas phase. Comonomers and initiators of low volatility may be used and copolymers which are more "randomized" by transacetalization can be prepared.⁷ The uniformity and dependability of run to run variations of individual copolymer preparations are, low.

It was the objective of this work to prepare co- and terpolymers of TO, DO, and EG in solution or in the bulk in order to prepare copolymers and terpolymers which could then be characterized or hydrolyzed with sodium hydroxide to ionomers. In subsequent work the properties of the polymers will be measured by calorimetric, dynamic mechanical, and dielectric techniques.

EXPERIMENTAL PART

Materials

Monomers. Trioxane (Celanese Research Co.) (TO) was recrystallized from dichloromethane and distilled from sodium, in the presence of a small amount of benzophenone, immediately before use (Karl Fischer analysis: ~ 60 ppm H_2O). 1,3-Dioxolane (Eastman Organic Chemicals) (DO) was distilled from lithium aluminum hydride before use (Karl Fischer analysis: ~ 28 ppm H_2O).

Ethyl glycidate (EG) was prepared in 50–60% yield from ethyl acrylate by epoxidation with 90% H_2O_2 and trifluoroacetic acid anhydride.

Initiators. Gaseous boron trifluoride (Matheson Products) was used as supplied. Boron trifluoride–diethyl etherate (Aldrich Chemical Co.), antimony pentachloride (Ventron Alfa Products) (bp $86^\circ C$, 30 mm) and trifluoromethane sulfonic acid (Aldrich Chemical Co.) (bp $76^\circ C$, 30 mm) (TFS) were distilled through a Vigreux column and stored in the refrigerator, in tightly capped bottles, before use.

Reagents. Ethyl acrylate (Aldrich Chemical Co.), propionic anhydride (Aldrich Chemical Co.) (bp $68^\circ C$, 25 mm) and triethylamine (Eastman Kodak Co.) were distilled before use. Trifluoroacetic anhydride (Aldrich Chemical Co.), 90% hydrogen peroxide (FMC Corp.), glacial

acetic acid (Fisher Scientific Co.), *dl*- α -pinene (Aldrich Chemical Co.), and tributylamine (Aldrich Chemical Co.) were used without further purification.

All solid reagents, including the metal halides, bases, buffers, and drying agents, were obtained from the Fisher Scientific Company or from Ventron Alfa Products and used as supplied.

1,2-Dichloroethane (Aldrich Chemical Co.), dichloromethane (Fisher Scientific Co.), and 1,4-dioxane (Mallinckrodt Chemical Works) were distilled from lithium aluminum hydride before use [Karl Fischer analysis (1,2-dichloroethane): < 40 ppm H_2O]. When dry methanol and ethanol were required, these solvents were refluxed over calcium oxide for 48 h, distilled from sodium and stored over molecular sieves. Dimethylformamide (99% pure) and benzyl alcohol (Aldrich Chemical Co.) were used as supplied.

Polymer Solvents. *p*-Chlorophenol (mp 38 – $40^\circ C$) (Eastman Kodak Co.), was distilled at reduced pressure (bp $94^\circ C$, 8 mm). For viscosity measurements, two percent by weight of *dl*- α -pinene was added to the *p*-chlorophenol. Deuterated and undeuterated hexafluoro-2-propanol (Aldrich Chemical Co.), hexafluoroacetone sesquihydrate (Aldrich Chemical Co.), and octafluoro-1-pentanol (Pfaltz & Bauer Inc.) were used without further purification. Hexafluoroacetone sesquihydrate was buffered with triethylamine (one percent by weight) before use.

Measurements

Most infrared spectra were measured on a Perkin-Elmer 727 Spectrophotometer, and some polymer spectra on a Perkin-Elmer 283 Spectrophotometer. Solid samples were measured as thin films (~ 1 -mm thick) or as pressed pellets and liquid samples between sodium chloride plates. The peak assignments were made to the nearest 0.1 micron.

Gas chromatograms of liquid samples were recorded on a Varian 920 Aerograph with helium as the carrier gas.

The NMR spectra of low molecular weight compounds were measured on a 60-MHz R-24 Hitachi Perkin-Elmer Spectrometer, polymer spectra in deuterated hexafluoroacetone sesquihydrate on a 90-MHz R-32 Perkin-Elmer Spectrometer.

Solution Polymerizations

a. Trioxane–1,3-Dioxolane Copolymers. TO

(102.5 g, 1.4 mol) was distilled from sodium directly into a three-necked round-bottom flask equipped with a glass stopper and a stirring rod and shaft unit. At the end of the distillation, a rubber septum was quickly placed around the flask neck through which the TO had been introduced, the entire assembly was transferred to a dry box, and freshly distilled, dry 1,2-dichloroethane (240 ml) was added to the TO. The flask was shaken until all the TO had dissolved, 11.2 g (0.15 mol) of DO was added and the septum was quickly fitted into place.

For each run, the initiator solution was prepared freshly by syringing 0.1 ml (1.3×10^{-3} mol) of TFS through a rubber septum, into a vial containing 14 ml of 1,2-dichloroethane with dry nitrogen blanketing.

The polymerization flask, containing monomers and the solvent, was rapidly transferred from the dry box and immersed into an oil bath at 40°C. Rapid stirring was begun as a slow stream of dry nitrogen was passed through the flask. The initiator solution (9 ml) was added through the septum into the flask over a period of 1 min. After two additional minutes the reaction mixture became cloudy, the reaction was allowed to proceed for three hours during which time precipitation of polymer continued, the mixture was filtered, washed with a 5-% sodium bicarbonate solution, water and finally with methanol. It was dried at 65°C (30 mm) for 16 h to give 111 g (97-% yield) of polymer. (TD-A).

Crude copolymer (30 g) was allowed to react with 7.5 g of potassium hydroxide in 450 ml of benzyl alcohol at 160°C to remove the base-unstable portions. Nitrogen was slowly bubbled into the reaction mixture to minimize polymer oxidation during the one-hour reaction. A fine white solid (25 g, 83-% yield) was finally obtained.

Copolymers TD-B and TD-C, each incorporating increasingly higher levels of DO, were prepared and stabilized in the same manner. Thus, 90.0 g (1 mol) of TO and 18.5 g (0.25 mol) of DO, in

250 ml of dichloroethane, and 0.06 mol (8.5×10^{-5} mol) of TFS gave 104 g (96% yield) of TD-B (5-min induction period, 95-% base-stable copolymer).

TD-C was obtained in 67-% yield from 42.2 g (0.47 mol) of TO with 14.8 g (0.20 mol) of DO after 0.03 ml (4.6×10^{-4} mol) of TFS were added to the two monomers dissolved in 125 ml of 1,2-dichloroethane (15-min induction period, base stability 87%).

The intrinsic viscosities of the base-stable copolymers were measured at room temperature in a hexafluoroacetone—water mixed solvent (molar ratio, 1/1.5) (Table I).¹³

The NMR spectra of the 3 copolymers (deuterated hexafluoroacetone sesquihydrate, 35°C) showed δ : 4.8 to 5.2 (CH_2O , 2); 3.7 to 4.0 ($\text{CH}_2\text{CH}_2\text{O}$, 4). The mole percent of oxyethylene units determined from the integrated NMR signals, is also listed in Table I. The NMR peak assignments in the copolymers are confirmed by a comparison of the spectrum for TD-C (Figure 1a) with those for a "gas phase" TO homopolymer¹⁷ (Figure 1b) and a poly-DO prepared in bulk using antimony pentachloride as the cationic initiator (Figure 1c).

The ratio of the 7.8- μ absorbance (backbone ethylene torsion vibration) to the standard 4.3- μ absorbance, in the infrared, remained unchanged at 1.7 for samples TD-A and TD-B but increased to 2.0 for TD-C (Figure 2). A relatively weak hydroxyl absorption (2.7 μ —3.0 μ) was observed in all three cases.

b. Trioxane—Ethyl Glycidate Copolymers. An attempt was made to prepare a TO—EG copolymer in solution. Accordingly 1.5 g (1.7×10^{-2} mol) of TO and 0.25 g (2.1×10^{-3} mol) of EG were dissolved in 3.3 ml of 1,2-dichloroethane and reacted with 0.001 ml (1.5×10^{-5} mol, 0.09 mol%) of TFS for 3 h at 40°C. No polymer was recovered from the reaction mixture. The same amount of TO, dissolved in 3.3 ml of 1,2-dichloroethane at 40°C, gave an 80-% yield of homopolymer, 5 min after

Table I. Characterization of trioxane—1,3-dioxolane copolymers

Sample designation	TD-A	TD-B	TD-C
Intrinsic viscosity, dl/g	2.3	1.9	3.2
Weight-average molecular weight	9.8×10^4	7.2×10^4	1.6×10^5
$\text{CH}_2\text{CH}_2\text{O}$ units/100 CH_2O units based on PMR	2.2	3.2	4.2

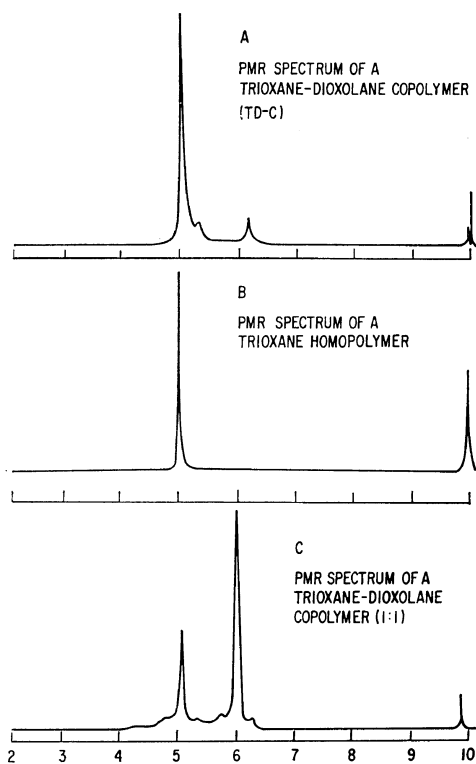


Figure 1. NMR spectra of trioxane—1, 3-dioxolane copolymers: A, copolymer of low DO content (TD-C); B, trioxane homopolymer; C, 1:1 copolymer.

the addition of 0.001 ml of the initiator.

High yields of copolymer could be obtained by adding less comonomer, more initiator and by adjusting the reaction temperature close to the melting point of TO. In a representative example, 11.4 g (1.3×10^{-1} mol) of TO, 0.75 g (6.5×10^{-3} mol, 5 mol%) of EG and 0.006 ml (9.3×10^{-5} mol, 0.07 mol%) of TFS were allowed to react in 25 ml of 1, 2-dichloroethane for three hours at 60°C to give a 93-% yield of copolymer with a 19-% base-stable fraction.

c. Trioxane—Ethyl Glycidate—1, 3-Dioxolane Terpolymers. In a series of experiments, ethylene oxide units were introduced randomly along the backbone of polymer chains containing methylene oxide units and 1-thoxycarbonyloxyethylene units. The purpose of these experiments was to obtain ionizable polymers, in moderate yields, that exhibited high base stabilities. All reactions, except one, were carried out in 25 ml of 1, 2-dichloroethane for three hours at 60°C. The results of

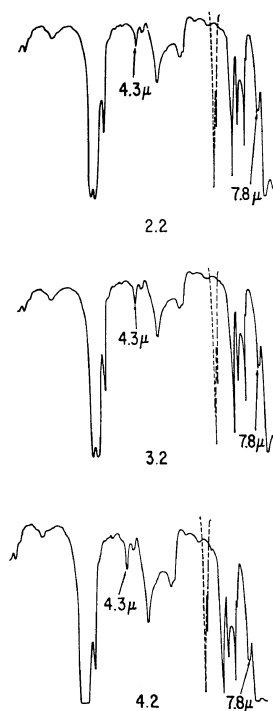


Figure 2. Infrared spectra of trioxane—1, 3-dioxolane copolymers.

these experiments are summarized in Table II.

In the course of three scale-up procedures, the amount of EG in the feed was varied from 5 to 15 mol percent while the amount of DO was maintained constant (10 mol%). The resulting terpolymers were labeled TED-A, TED-B, and TED-C, respectively. The TO and DO monomers, dissolved in 1, 2-dichloroethane, were stirred vigorously in a three-necked round-bottom flask, immersed in an oil bath at 65°C. The boron trifluoride diethyl etherate initiator was added as a solution in 1, 2-dichloroethane through a rubber septum directly into the reaction medium. After approximately 15 minutes, the solution in the polymerization flask became cloudy. At this point, the EG was rapidly added to the reaction mixture through an addition funnel. The reaction was allowed to proceed for a specified period of time after which stirring was discontinued and the flask was removed from the oil bath.

The workup and drying procedures were the same as those used for the recovery of copolymers TD-A, TD-B, and TD-C. The reaction conditions

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Table II. Solution polymerization of trioxane, ethyl glycidate, and 1, 3-dioxolane

Trioxane, mol %	Ethyl glycidate, mol %	1, 3-Dioxolane, mol %	Initiator, mol %	Yield, %	Base stability, ^a %
95	5	0	0.07 ^b	93	19.0
85	5	10	0.10 ^b	28	—
85	5	10	0.07 ^c	62	85.5
85	5	10	0.07 ^c	62	95.0
90	5	5	0.05 ^c	90	41.5
75	15	10	0.06 ^c	40 ^d	69.5
75	10	15	0.12 ^c	52	78.5

^a Polymer recovered after high temperature exposure to potassium hydroxide.^b Trifluoromethane—sulfonic acid.^c Boron trifluoride diethyl etherate.^d Thirty minutes at 60°C in 15 ml of 1, 2-dichloroethane.**Table III.** Synthesis of trioxane—ethyl glycidate—1, 3-dioxolane terpolymers

Sample designation	TED-A	TED-B	TED-C
Trioxane, g (mol)	184.0(2.04)	161.9(1.80)	178.5(1.98)
Ethyl glycidate, g (mol)	12.4(0.11)	26.1(0.23)	45.9(0.40)
1, 3-Dioxolane, g (mol)	16.8(0.23)	16.6(0.23)	19.5(0.26)
Initiator, ml (mol), Solvent, 400 ml	0.20(1.6 × 10 ⁻³)	0.18(1.5 × 10 ⁻³)	0.22(1.8 × 10 ⁻³)
Conditions	2.0 h at 65°C	2.5 h at 65°C	3.0 h at 65°C
Yield, in percent	63	63	50

and yields for these experiments are listed in Table III.

A Parr reactor was charged with 15 g of crude terpolymer (TED-A) and 300 ml of ethanol. The reactor was flushed with nitrogen and then pressurized with nitrogen to approximately 40 psi. The contents of the reactor were heated to 160°C and stirred at that temperature for 1 h. At the end of the reaction, the autoclave was lifted out of the variac heating unit and immersed in a bucket of ice—water, causing the thermally stabilized terpolymer to rapidly precipitate out of the solution. The solid was washed several times with methanol and dried at 60°C (30 mm) for 16 h. The procedure was repeated for TED-B and TED-C. The yields of heat treated TED-A, TED-B, and TED-C were 91, 96, and 95%, respectively.

d. Ionic Derivatives of the Terpolymers. Thirty g of crude TED-A terpolymer were allowed to react with 4.5 g (0.11 mol) of sodium hydroxide in a methanol—water mixture (400 ml/250 ml) for 1 h at 160°C. The reaction was carried out in a Parr reactor at approximately 240 psi. Before heating the reactants to 160°C, the reactor was pressurized with a slight positive nitrogen pressure. At the end of the reaction, the contents of the Parr reactor were rapidly cooled to room temperature by immersing the stainless steel reaction vessel into a bucket of ice—water. The solid precipitate was filtered, washed with water and with methanol and finally dried at 60°C (30 mm) for 15 h. The sodium salts of TED-B and TED-C were prepared in exactly the same way. The yields of the TED-A, TED-B, and TED-C sodium salts were 93, 83, and

Table IV. Characterization of the ionic derivatives of trioxane—ethyl glycidate—1, 3-dioxolane terpolymers

Sample designation	TED-A (Salt)	TED-B (Salt)	TED-C (Salt)
Intrinsic viscosity, dl/g	0.30	0.28	0.27
Weight-average molecular weight ^a	1.50 × 10 ⁴	1.40 × 10 ⁴	1.40 × 10 ⁴
Mol % -CH ₂ CH(COO ⁻ Na ⁺)O- based on Na analysis	0.9	1.7	2.0

^a Based on ref 14.

88%, respectively. Their intrinsic viscosities (at 110°C in octafluoropentanol) and respective weight-average molecular weights are given in Table IV. The amount of 1-sodium carboxylate oxyethylene units in the sodium salts (mole percent) are also shown in Table IV.

e. Acid Derivatives of the Terpolymers. Sodium salts of the three terpolymers (5 g) were stirred vigorously, in separate round-bottom flasks, each with 5 ml of glacial acetic acid, 45 ml of deionized water and 200 ml of dioxane, for 3 h, at room temperature, under nitrogen. The filtered solids were washed repeatedly with water, then with methanol and dried under vacuum for 16 h at 60°C. The yields of the corresponding polymeric acids were 90% or higher (taking into account the replacement of a sodium atom with a hydrogen atom during the reaction). The intrinsic viscosity (at 110°C in octafluoropentanol) was 0.3 dl/g for all three acids (unchanged from that of the three salt precursors).

Figure 3 shows the infrared spectra of the heat treated ester, the sodium salt and the acid derivatives of TED-A. Two new absorptions between

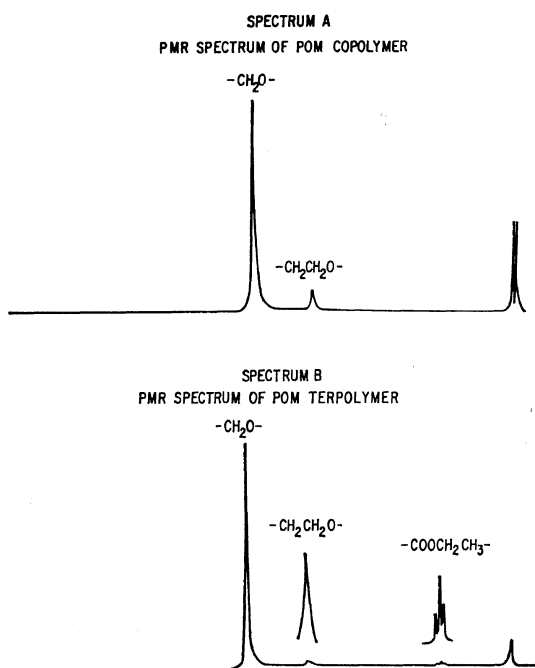


Figure 3. PMR spectra of POM co- and terpolymers: A, trioxane—1, 3-dioxolane copolymers; B, trioxane—1, 3-dioxolane—ethyl glycidate terpolymer.

6.2 and 6.3 μ and between 7.0 and 7.1 μ , due to the carboxylate anion in the salt, are seen to replace the 5.8- μ absorption due to the ester carbonyl. The spectrum of the polymeric acid shows a new absorption at 5.8 μ and a weak absorption at 6.2 μ , due possibly to the carboxylate anion of the salt precursor.

Table V shows the results of the sodium analyses of the salt and acid derivatives of TED-A, TED-B, and TED-C.

Table V. Sodium content in the derivatives of trioxane—ethyl glycidate—dioxolane terpolymers

Sample designation	TED-A	TED-B	TED-C
wt % Na in the salts	0.55	1.01	1.22
wt % Na in the acids	0.10	0.10	0.10

Bulk Polymerization

Bulk polymerizations to prepare TO—EG copolymers were also investigated. In one attempt, 1.5 g (1.7×10^{-3} mol) of TO, 0.25 g (2.1×10^{-3} mol) of EG and 0.001 ml (1.5×10^{-5} mol) of TFS (added as a solution in 0.1 ml of 1, 2-dichloroethane) were utilized, and the reaction was allowed to proceed for 2 h at 70°C. A 24-% yield of polymer was obtained. After high temperature exposure to potassium hydroxide, 11% of stable polymer was recovered.

Additional attempts to copolymerize EG with TO, in the presence of higher levels of TFS, gave low yields of products with low base stable fractions. When 1.5 g of TO was allowed to react with 0.001 ml of TFS (added as a solution in 0.1 ml of 1, 2-dichloroethane) at 70°C, gelation of the reaction mixture occurred within 3 min and an 85-% yield of homopolymer could be isolated. These results are summarized in Table VI.

Table VI. Bulk polymerization of trioxane and ethyl glycidate reaction conditions; 15 min at 70°C

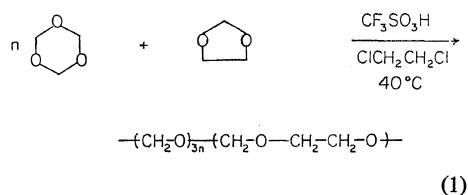
Trioxane, mol %	Ethyl glycidate, mol %	Initiator, mol %	Yield, %	Base stability, %
95	5	15.9	58	33
90	10	26.0	32	36
85	15	9.3	44	5

RESULTS AND DISCUSSION

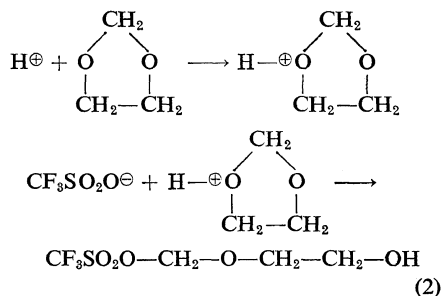
Copolymers of TO and DO, TO and EG and terpolymers of TO, DO, and EG were prepared in solution with BF_3 and TFS as initiators. While TFS was effective for TO—DO copolymerization, it was not very effective when EG was the co- or monomer. The polymers were heat-treated or base-degraded to stable POM polymers.

TO—DO copolymers of three different compositions, 7, 11, and 14 mol% of DO, were prepared with TFS as the initiator in yields in excess of 95%. The base stability of these materials was greater than 85% and the molecular weight as judged by the intrinsic viscosity was near or greater than 2 dl/g, which corresponds to a molecular weight of 100,000. The characteristics of these polymers are shown in Table I.

Penczek and coworkers¹⁵ have shown that the best results, *i. e.*, short induction periods, high polymerization rates, high degrees of polymerization and a low content of unstable fraction, comparable with other POM copolymers, have been obtained when TO was copolymerized with DO in the presence of the ester or anhydride derivatives of TFS. The excellent performance of these systems as cationic initiators was ascribed to the low nucleophilicity and stability of the $\text{CF}_3\text{SO}_2\text{O}^\ominus$ anion. The occurrence of transacetalization reactions in the solution polymerization of cyclic acetals initiated by cationic species from TFS is well established. In view of these facts, the TFS initiating system was selected in an attempt to prepare random copolymers in high yield exhibiting high molecular weights and base stabilities (eq 1). The results of the present work showed that these attempts proved successful. It has also been shown¹⁶



that in the copolymerization of TO with DO, initiated by cationic species, TO was more reluctant to participate in the initiation step. On the basis of this finding, the possible initiation step was the reaction of TFS with DO (eq 2).



Two phenomena were characteristic of cyclic acetal polymerizations initiated with the anhydride of TFS: shorter induction periods were observed at comparable conditions than with triphenyl methyl salts (AsF_6^\ominus or SbF_6^\ominus anions), and much lower concentrations of superacid anhydride were needed to achieve the same polymerization rates than with the triphenylmethyl cation.

Table VII shows a comparison of the results for the copolymerization of TO with DO in the presence of TFS, its anhydride or other types of cationic initiators. The copolymerizations¹⁵ were conducted at 60°C in cyclohexane as the solvent and in the presence of 2.0 weight percent (sum of

Table VII. Cationic ring-opening copolymerization of trioxane with 1, 3-dioxolane

Initiator	Initiator concn, mol/l	Comonomer concn (trioxane+DO), mol/l	Induction period, sec	Mol wt	% Yield	
					Stable fraction	Unstable fraction
$(\text{CF}_3\text{SO}_2)_2\text{O}^a$	8×10^{-4}	7.0+0.4	240	1.4×10^5 ^c	74	6
$(\text{CF}_2\text{SO}_2)_2\text{O}^a$	1×10^{-3}	7.0+0.4	120	1.4×10^5 ^c	82	7
$\text{CF}_3\text{SO}_2\text{OH}^b$	5×10^{-3}	4.6+0.6	120	9.8×10^4 ^d	81	16
$\text{CF}_3\text{SO}_2\text{OH}^b$	3×10^{-3}	4.0+1.0	300	7.2×10^4 ^d	91	5
$\text{CF}_3\text{SO}_2\text{OH}^b$	4×10^{-3}	4.0+1.6	900	1.6×10^5 ^d	58	9
$\text{BF}_3\text{O}(\text{C}_4\text{H}_9)_2^a$	4×10^{-2}	7.3+0.4	120	8.8×10^4 ^c	75	6
$(\text{C}_6\text{H}_5)_3\text{C}^\oplus \text{AsF}_6^\ominus^a$	6×10^{-3}	6.5+0.3	200	8.6×10^4 ^c	78	6

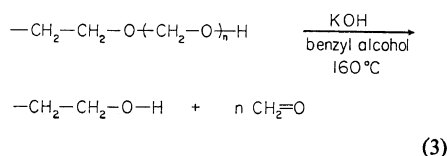
^a Reference 15.

^b This work.

^c \bar{M}_n .

^d \bar{M}_w .

monomers) of poly(ethylene oxide) with $\bar{M}_n = 40,000$. All copolymerizations listed in Table VII were carried out for three hours except for the one initiated with the triphenyl methylum salt (AsF_6^\ominus anion) which lasted for two and a half hours. The base stabilization of some copolymers was carried out in benzyl alcohol at 150°C in the presence of tri-*n*-butylamine for 30 min. The other copolymers were stabilized according to the procedure described earlier (eq 3).



The overall performance of the systems initiated with TFS or its anhydride is better than those initiated with other types of cationic initiators, both in terms of molecular weight of the final product and the amount of initiator needed to achieve the same polymerization rates, the same amount of base-unstable fraction and final yields. The induction period increased dramatically in the systems studied in the present work when the amount of DO in the feed was increased from 12 to 30 mol% (based on mol TO + mol DO) at approximately the same level of initiator. On the other hand, less initiator was needed to produce similar or better results. In the copolymerization of TO with relatively small amounts of DO systems using TFS or its anhydride, the molecular weights of resulting copolymers were higher than those with complex anions such as AsF_6^\ominus (see Table VII).

The moderate yield and high molecular weight obtained for the copolymer with 30 mol% of DO (based on mol TO + mol DO) in the feed (TD-C) may be due to the fact that the polymerization was stopped at a relatively low %-conversion (when copolymer rich in DO was still present). This DO-rich copolymer was still soluble in dichloroethane and may have been removed during the isolation of the insoluble copolymer.

Spectrum A in Figure 4 shows a PMR spectrum of a TO—DO copolymer (deuterated hexafluoroacetone sesquihydrate, 35°C). The major peak (δ 4.8 to 5.2) corresponds to the two oxymethylene protons and the secondary peak (δ , 3.7 to 4.0) corresponds to the four oxyethylene protons. Spectra

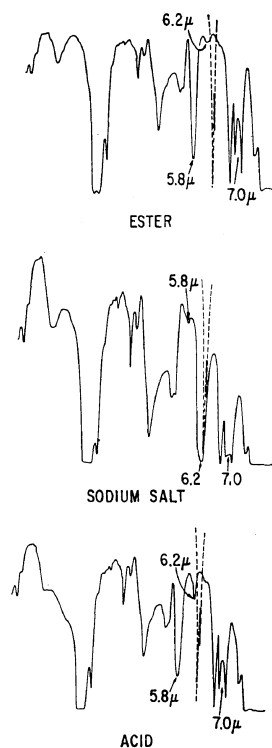


Figure 4. Infrared spectra of POM derivatives: A, ester; B, sodium salt; C, acid.

Table VIII. Correlation of molecular weight with endgroup analysis by infrared

Sample designation	Molecular weight, \bar{M}_w	2.9 μ /4.3 μ
TD-A	9.8×10^4	0.55
TD-B	7.2×10^4	0.60
TD-C	1.6×10^5	0.40

such as these were used to determine the compositions of copolymers TD-A, TD-B, and TD-C as well as the TO—DO copolymer prepared earlier (Part I).

Table VIII shows that the molecular weight of these copolymers was inversely proportional to the concentration of OH endgroups (Figure 2) [ratio of the OH absorption (at 2.9 μ) to the standard POM absorption at 4.3 μ]. The weak OH absorption was an indication of the high molecular weight of the copolymers (low hydroxyl endgroup content).

TO—EG Copolymers

Low yields, a high portion of a base-unstable

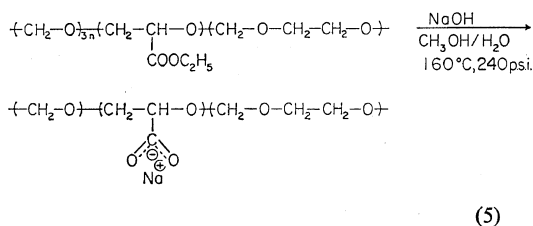
Table IX. Composition of trioxane—ethyl glycidate—1, 3-dioxolane terpolymers^a

Sample designation	TED-A	TED-B	TED-C
Mol % of 1-carboethoxy oxyethylene units (based on PMR of the ester)	1.0	1.8	2.0
Mol % of 1-carboethoxy oxyethylene units (based on Na analysis of the salt)	0.9	1.7	2.0
Mol % of oxyethylene units (based on PMR of the ester)	1.2	1.3	1.2
Mol % of oxyethylene units (based on PMR of the salt)	1.2	1.3	1.2
Mol % of oxyethylene units (based on PMR of the acid)	1.2	1.3	1.2

^a All compositions are based on 100 mol CH₂O.

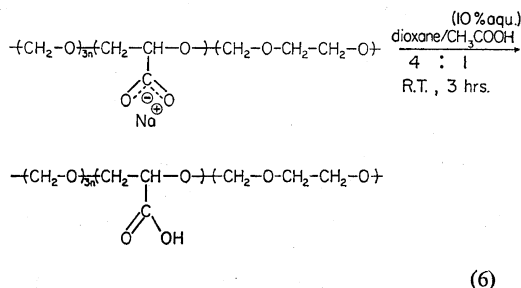
sis of the polymeric salts.

An improved base-hydrolysis technique was utilized in this work to convert the crude polymeric ester terpolymer to the corresponding polymeric salt. The advantage of this "solution" technique (eq 5) over the slurry technique¹⁷ is ap-



parent from infrared analysis of the product (Figure 4). Only 20% of the amount of sodium hydroxide, used in the slurry technique, was necessary to replace all of the ester carbonyl groups with the corresponding sodium carboxylate groups (in this case, the 5.8- μ absorption, due to the ester carbonyl, was almost completely absent).

The polymeric salt was converted to the free acid by treatment with 10-% CH₃COOH in dioxane at room temperature for 3 h (eq 6).



Infrared analysis were also carried out on thin films of the acid derivative of TED-A, prepared in a KBr pelletizer. After subjecting these films to a five-minute heat treatment at 160°C (in a Carver press) followed by fast cooling back to room temperature, a new peak at 5.6 μ was observed to grow in the infrared spectrum of this "heat-treated" acid (Figure 5). This peak is regarded

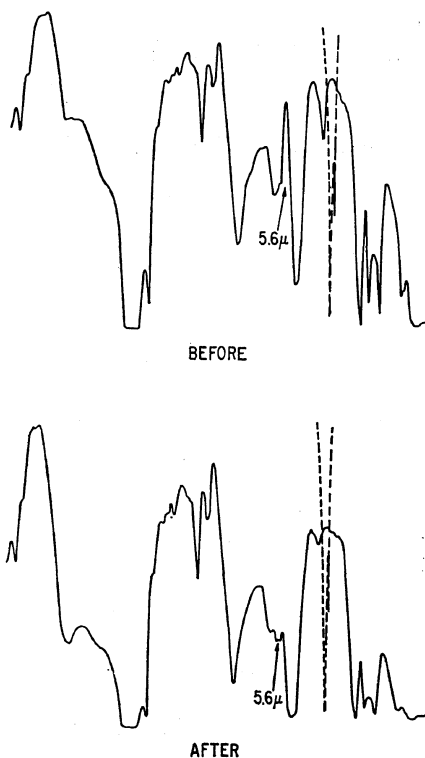


Figure 5. Infrared spectra of POM acids: A, before heat treatment; B, after heat treatment.

as evidence for the presence of anhydride in the sample. 0.02 g of the "heat-treated" acid were still soluble in 0.1 ml of hexafluoro-2-propanol, indicating that extensive crosslinking reactions had not occurred during the heat treatment. Similar results were also obtained for the acid derivatives of TED-B and TED-C terpolymers.

Various possible anhydride structures may be postulated for the polymeric anhydrides on the basis of these results. The formation of a seven-membered cyclic anhydride would suggest the presence of short blocks of substituted oxyethylene units along the chain, whereas, a linear anhydride could only result from mild crosslinking reactions or from chain extension reactions between substituents near an endgroup. No distinction could be made on the basis of our IR analysis of the anhydride peaks.

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