

Cationic Homo- and Co-polymerizations of Ethyl Glycidate

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ABSTRACT: Cationic homo- and co-polymerizations of ethyl glycidate (EG) have been studied with triethyloxonium tetrafluoroborate (TEOFB) and superacid ester catalysts. The homopolymerization of EG gave a paste-like material of low molecular weight with TEOFB catalyst. A superacid ester catalyst such as ethyl trifluoromethanesulfonate underwent only the initiation process with EG and the propagation was negligibly slow in this system. Copolymerization of EG with tetrahydrofuran (THF) gave a copolymer with TEOFB. When THF remained unreacted after the completion of copolymerization, the copolymer composition was in all cases EG : THF = 1 : 2. These results were understood in terms of the penultimate effect. The same copolymerization by a superacid ester catalyst, however, always yielded copolymers of the EG/THF = 1/2 composition. This result was explained in the same way as the TEOFB case, taking the EG polymerizability by a superacid ester into account.

KEY WORDS Ethyl Glycidate / Cationic Polymerization /
Copolymerization / Tetrahydrofuran / Oxonium Salt / Superacid Ester /
Penultimate Effect /

Cyclic ethers and particularly epoxides have been known for a long time to polymerize to polyethers even of very high molecular weight.^{1,2} While cyclic ethers polymerize primarily with classical cationic initiators and aluminum and zinc organic compounds by what is often referred to as coordinative anionic polymerization,³ epoxides undergo polymerization by classical cationic and anionic mechanisms and also by the above mentioned coordinative mechanism.^{1,2} Most of the work has been done on unsubstituted and methyl-substituted compounds, namely ethylene oxide and propylene oxide; substituent groups with higher polarity and the functionality have not been studied to any extent. The monomers with the most reactive groups were those with a chloromethyl substitution as, for example, in epichlorohydrin⁴ and 3,3-bis(chloromethyl)oxetane.⁵

Epoxides which have functional groups directly attached to the epoxide rings have been already known.⁶ Their synthesis is not particularly easy as it requires trifluoroacetic acid as the oxidizing

agent, which in turn must be prepared from 90 % H₂O₂ and trifluoroacetic acid. Glycidaldehyde,⁷ glycidyl esters,⁸ and glycidonitrile⁷ have been prepared; glycidaldehyde was polymerized *via* both the epoxide group and the aldehyde group, depending on the reaction conditions.⁹ These monomers have been copolymerized with trioxane¹⁰ and the properties of co- and ter-polymers with 1,3-dioxolane with a relatively low percentage of glycidate incorporated were investigated.¹¹ These polymers were then hydrolyzed to the corresponding poly(oxymethylene)ionomers and their free acids. The co- and ter-polymerizations were accomplished with classical cationic initiators, both in bulk solution¹¹ and by a process in which the monomers were mixed in the vapor phase.¹²

It was the purpose of this work to study the cationic homo- and co-polymerization of ethyl glycidate, especially the investigation of suitable initiators and conditions for the production of high-molecular-weight homopolymer and copolymer.

EXPERIMENTAL

Materials

EG was synthesized by epoxidation of ethyl acrylate with a mixture of trifluoroacetic anhydride and 90 % H_2O_2 .^{13,14} A yield of less than 50% was normally obtained. The other major side product was ethyl β -trifluoroacetoxy- α -hydroxypropionate: this product can be cyclized with NaH to the epoxide.

Tetrahydrofuran (THF) and CH_2Cl_2 were purified as previously reported.¹⁵

Triethyloxonium tetrafluoroborate (TEOFB) was synthesized according to Meerwein's method.¹⁶ Ethyl (EtOTf) and methyl trifluoromethanesulfonate (MeOTf) were synthesized according to a previously published procedure.^{17,18}

Measurements

NMR Measurements. ^1H NMR spectra were taken on a Varian HA-100 or Hitachi R-20B (60 MHz) instrument. ^{19}F NMR spectra were taken on a Hitachi R-20B (54 MHz) instrument.

Molecular Weight Determinations. The molecular weights of all polymers were measured by vapor pressure osmometry (Hitachi Perkin-Elmer Model 115) in CHCl_3 at 35°C.

The infrared spectra were recorded on a Hitachi Grating Infrared Spectrophotometer, Model EPI-G3.

Column chromatography to fractionate a sample of EG-THF copolymer was carried out on a silica gel column and CHCl_3 was used as the carrier solvent.

Preparations

Polymerization Procedures. All polymerizations were carried out under dry nitrogen. A carefully dried NMR tube (5 mm \times 150 mm) was closed with a three-way cock and placed into a dry ice-ethanol bath at -78°C . Solvent and initiator or initiator solutions were introduced into this tube with a microsyringe. The NMR tube was then sealed and shaken to prevent the contents from warming above the bath temperature. The tube was then gradually warmed to room temperature and was kept at 35°C to allow the polymerization to proceed. When desirable, the reaction was followed by monitoring the ^1H or ^{19}F NMR spectrum at 35°C. After the reaction was considered complete, the polymerization was stopped by opening the NMR tube and

adding an approximately 10 % solution of aqueous ammonia in methanol (0.1 ml). The mixture was then poured into a large excess of hexane (30–50 ml). The polymer precipitated under these conditions; it was isolated by decantation and dried *in vacuo* at 0.1 mm. If a soluble fraction was obtained, the mother liquid was evaporated to dryness under reduced pressure and the residue was identified.

Hydrolysis of EG-THF Copolymer. In a 50 ml Erlenmeyer flask, a copolymer of EG-THF 1:2 (0.273 g) was added to 7.0 ml of aqueous 0.2 N NaOH solution. The initially heterogeneous mixture was heated to 80°C under nitrogen, and the reaction allowed to proceed for 10 h, by which time it became homogeneous. The mixture was then cooled to room temperature and divided into two parts. From one part of the mixture (3 ml) the water was evaporated and the polymer extracted with chloroform. The chloroform solution was dried over sodium sulfate and evaporated under reduced pressure; it gave 0.103 g of the sodium salt of the copolymer.

To the other part of the aqueous solution (4.0 ml) was added 0.2 N HCl (2.5 ml); the water was evaporated and the polymer was extracted with chloroform. After the evaporation, 0.126 g of the free acid of the copolymer was obtained.

RESULTS AND DISCUSSION

Homopolymerization of EG and its copolymerization, primarily with THF and also with other cyclic ethers, to very low-molecular-weight polymers have been accomplished with oxonium salts and superacid esters. It was not surprising that triflic acid derivatives gave polymers of low molecular weight, in view of our earlier experience in the preparation of poly(ethylene oxide) from ethylene oxide.¹⁹ The other possible source of low molecular weight of our Poly-EG and copolymers is the cationic chain transfer possibility of the ester group, as described below.

Homopolymerization of EG

Triethyloxonium Tetrafluoroborate (TEOFB) as the Initiator. EG was polymerized with TEOFB at 35°C in CH_2Cl_2 . The monomer (EG) was completely consumed under these conditions and a polymer was obtained as a paste-like material, which was soluble in methanol, diethyl ether, acetone, CHCl_3 , and CH_2Cl_2 , but was only partially soluble in hexane.

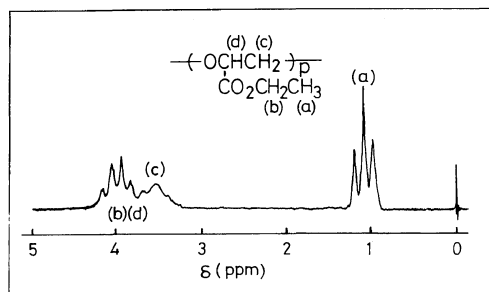
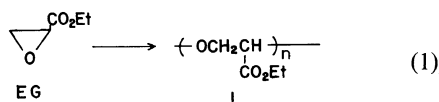


Figure 1. 100 MHz ^1H NMR spectrum of Poly-EG in CDCl_3 (chemical shift in δ (ppm) relative to TMS).

The molecular weight of the polymer was found to be low. The hexane soluble fraction was 68% in weight of the total polymer; the molecular weight of this fraction was 460. The hexane-insoluble part consisted of 32% of the total polymer; its molecular weight was 1200 as measured by VPO. The structure of the polymer is consistent with a carboxy substituted poly(ethylene oxide) (eq 1) of structure 1, whose ^1H NMR spectrum is shown in Figure 1. A triplet at 1.1 ppm indicates the methyl group and a quartet at 4.1 ppm the methylene group of the ethyl ester group. Broad overlapping bands between 3.5 and 4 ppm indicate the methylene and methine protons.

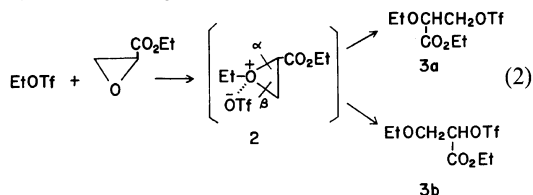


Superacid Esters as Initiators. At 35°C the polymerization of EG with methyl (MeOTf) and ethyl trifluoromethanesulfonate (EtOTf) proceeded very slowly; however, at 60°C a polymer of EG was obtained in a 28% yield after 5 days. 70% of EG was converted to an hexane-insoluble polymer when $[\text{EG}]_0 = 4.8 \text{ mol/l}$ and $[\text{MeOTf}]_0 = 4.7 \text{ mol}\%$ for $[\text{EG}]_0$ were used in CH_2Cl_2 .

The initiation step was examined by ^{19}F NMR spectroscopy. A mixture of 5.0 mmol of EG and 5.2 mmol EtOTf in 5 ml of chloroform was kept at 35°C for 30 days. A ^{19}F NMR spectrum developed and showed three peaks at -3.17 , -2.88 , and -2.73 ppm (relative to $\text{CF}_3\text{CO}_2\text{H}$) in a relative intensity ratio of 22, 10, and 68%, respectively. The resonance peak at -2.73 ppm was identified as unreacted EtOTf. It was found that 58% of the EG was consumed. The course of the reaction was confirmed by ^1H NMR spectroscopy, which indicated that the

main reaction consisted of an addition of EtOTf to EG and gave a 1:1-reaction product.

The main course of the reaction can be described by the following scheme.



The intermediate oxonium ion, 2, is unstable and evidently undergoes immediate further reaction because it was not detected. Two peaks (-3.17 ppm and -2.88 ppm) are the triflic esters 3a and 3b, 3a being the β -scission product of 2 and 3b being the α -scission product of 2. Other peak assignments, however, have not been established yet. Both α and β -scissions of the growing oxonium ion or oxonium end are probably involved also in the propagating stage. We have not made any attempts at this time to distinguish between α and β -scissions in the propagating step in further cationic polymerization work, as the NMR spectra are still too complicated to be fully analyzed. For simplicity, only the β -scission mode is indicated in this paper, although it should be emphasized that α and β -scissions are in principle possible in this polymerization, leading to H-H and H-T linkages.

When MeOTf was used as the initiator for the polymerization of EG, EtOTf was produced, in addition to oligomers which have both ethyl or methyl ester groups in the ester group. The formation of these species obviously occurred because of the very efficient ester exchange reaction indicated in eq 3. This exchange reaction between carboxylic esters and fluorosulfonate esters is not unknown and has been specifically noted in the reaction between methyl acetate and ethyl fluorosulfonate.¹⁸

Copolymerization of EG with THF

Triethyloxonium Tetrafluoroborate as Initiator. The copolymerization of EG with THF was carried out with various monomer concentrations at 35°C in CH_2Cl_2 . The THF concentration used was

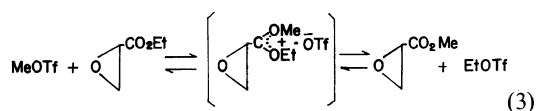


Table Ia. Reaction conditions of the cationic copolymerization of EG(M₁)-THF(M₂) with triethyloxonium tetrafluoroborate as initiator^a

Sample no.	Initial monomer concentration			Reaction time, h	[M ₂] _e , mol/l
	[M ₁] ₀ , mol/l	[M ₂] ₀ , mol/l	[M ₁] ₀ /([M ₁] ₀ + [M ₂] ₀), mol%		
1	3.82	0.99	79.5	12	0
2	2.28	1.18	66.0	6	0
3	3.63	3.66	49.8	8	0
4	1.37	2.65	34.1	14	0
5	1.10	2.95	27.1	11	0.68
6	0.96	3.70	20.5	12	1.42
7	0.48	3.70	11.5	12	1.92
8	0.16	3.24	4.8	12	2.98

^a [I]₀ = 1.8%; solvent, CH₂Cl₂; reaction temp, 35°C.**Table Ib.** Cationic copolymerization of EG(M₁)-THF(M₂) with triethyloxonium tetrafluoroborate as initiator; copolymer compositions

Sample no.	Insoluble part in hexane			Soluble part in hexane		
	Yield, ^a %	M ₁ /(M ₁ +M ₂), ^b %	M _w	Yield, %	M ₁ /(M ₁ +M ₂), ^b %	M _w
1	92.3	79.1	1180	5.4	81.8	410
2	81.6	66.4	1630	10.8	65.2	520
3	73.8	50.8	3860	15.6	50.5	320
4	80.6	35.2	3630	4.8	35.5	—
5	71.4	34.8	1480	5.5	33.2	360
6	60.3	33.3	1280	9.4	36.8	420
7	29.8	33.0	1220	5.2	32.5	390
8	10.6	32.8	1160	2.3	34.3	—

^a Based on the total amount of the initial feed of monomers.^b Determined by ¹H NMR spectroscopy.

lower than the equilibrium monomer concentration of THF homopolymerization (which is [M]_e = 4.2 mol/l at 35°C in CH₂Cl₂) (Table I). EG was consumed completely in all experiments. However, there was an equilibrium monomer concentration of THF which depended on the reaction conditions. It is clear however that the equilibrium monomer concentration of homopolymerization cannot normally be transferred to any copolymerizations, as it is quite possible to add two monomer units without infringing on the principle of equilibrium monomer concentration. This term should be understood here as the concentration of monomer which is not consumed anymore during copolymerization. The copolymer of EG and THF was paste-like, soluble in

Table II. Fractionation of oxonium salt initiated EG(M₁)-THF(M₂) copolymer by column chromatography^a

Fraction	Weight, g	Copolymer composition, M ₁ /(M ₁ +M ₂) ^b mol%
1	0.140	34.2
2	0.082	32.8
3	0.072	33.6
4	0.093	33.4

^a Copolymer sample no. 6 was used. Silica gel column was employed using CHCl₃ as carrier solvent.^b The composition was determined by ¹H NMR spectroscopy.

Table III. Cationic copolymerization of EG(M₁)-THF(M₂) with ethyl triflate initiator in CH₂Cl₂ at 35°C

Sample no.	Initial monomer concentration				Time, h	[M ₂] _e , mol/l	Yield, %	Copolymer	
	[M ₁] ₀ , mol/l	[M ₂] ₀ , mol/l	[M ₁] ₀ /([M ₁] ₀ + [M ₂] ₀), %	[I] ₀ , mol%				M ₁ /(M ₁ +M ₂), %	M _w
9	0.43	3.31	11.4	12.5	72	2.42	33.3	32.3	1050
10	0.58	2.78	17.3	12.0	15	1.72	48.1	35.0	1630
11	0.79	2.50	24.0	10.0	50	0.95	69.1	33.4	1280
12	2.58	2.66	49.7	7.5	25	0	74.6	33.5	1240
13	2.70	1.40	65.9	8.5	26	0	57.2	34.5	1060

^a Based on the total amount of initial feed.

^b Determined by ¹H NMR spectroscopy.

acetone, methanol, diethyl ether, CHCl₃, CH₂Cl₂, and CH₃CN, and partially soluble in hexane. The copolymer composition was essentially the same in the hexane-insoluble and hexane-soluble portions of the polymer (Table I).

In order to demonstrate that a true copolymer was obtained with a reasonably constant copolymer composition, a copolymer sample was fractionated by column chromatography (Table II). The copolymer composition in four fractions was within a narrow range, which indicates that an actual copolymer of EG and THF was obtained. Figure 2 shows the relationship between the initial amount of monomer-feed ratio and the final polymer composition and Figure 3 illustrates the ¹H NMR spectrum of the copolymer (EG:THF = 1:2 composition).

It should be noted that copolymers obtained in the systems above the equilibrium monomer concentration of THF ([M₂]_e > 0) showed in all cases a copolymer composition of M₁:M₂ = 1:2 (see Table I). These results may be explained by considering the penultimate effect in this polymerization as follows. The nucleophilic reactivity of THF is much higher than that of EG, and hence, THF attacks preferentially the propagating oxonium ion of EG. The EG homounit formation is not possible because of the low nucleophilicity of the ring oxygen atom of EG and the propagating end of **4** is produced. THF attacks **4** exclusively because, again, of the higher nucleophilic reactivity of THF and produces **5**, which does not depolymerize to give **4** due to the penultimate effect of the EG unit, probably reflected in the steric factor of EG. In the next addition step there is no more effect of the EG unit in **5** and the propagation of THF from **5** does not take place,

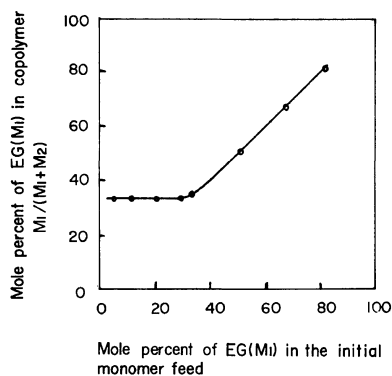


Figure 2. Curve of copolymer composition of EG(M₁)-THF(M₂) mixtures initiated with triethyl-oxonium tetrafluoroborate in CH₂Cl₂ at 35°C.

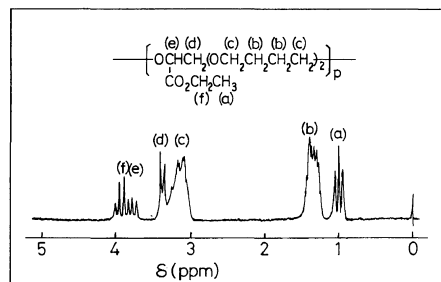
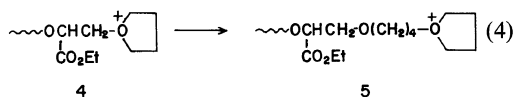


Figure 3. 100 MHz ¹H NMR spectrum of EG-THF copolymer in CDCl₃ (chemical shift in δ (ppm) relative to TMS).



because the monomer concentration of THF is lower than that of the equilibrium concentration. Further addition of THF would require a higher concentration than the equilibrium one of THF homopolymerization. The same type of penultimate effect has been observed in the copolymerization of THF with 3,3-bis(chloromethyl)oxetane.²⁰

The EG-THF polymer was hydrolyzed with 0.2*N* NaOH and the sodium salt of the polyether ionomer was isolated. The infrared spectrum of the ionomer is shown in Figure 4, which also shows the infrared spectrum of the starting copolymer and that of the free acid which was obtained by neutralization of the salt. As expected, the characteristic features of the infrared spectra were the changes of the absorption band of $\nu_{C=O}$. The $\nu_{C=O}$ of the ester is located at 1750 cm^{-1} (Figure 4a). The absorption band is shifted to 1610 cm^{-1} in the carboxylate form (Figure 4b) and the absorption band appears at 1710 cm^{-1} in the form of the free acid (Figure 4c). The copolymer

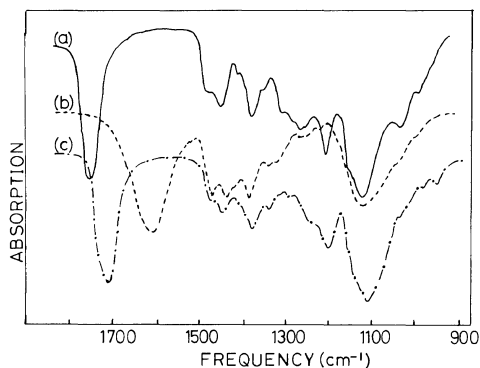


Figure 4. IR spectra of glycidate-THF copolymers: (a) EG-THF copolymer; (b) sodium glycidate-THF copolymer; (c) glycidic acid-THF copolymer.

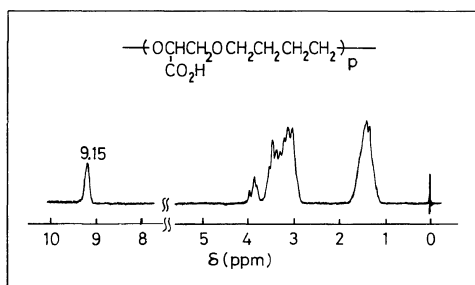


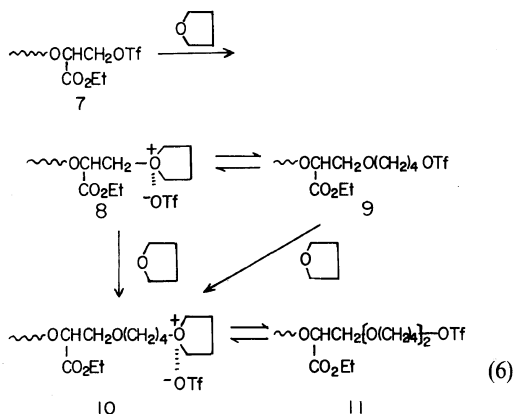
Figure 5. 60 MHz ^1H NMR spectrum of hydrolyzed copolymer in CDCl_3 (chemical shift in δ (ppm) relative to TMS).

structure of **6** is indicated by the infrared spectrum (4c) and also by the NMR spectrum which is free of the proton resonance of the ethyl group of the carboxylate (Figure 5) (eq 5).



6

Superacid Ester as Initiator. Copolymerization of EG and THF with triflate esters proceeded slowly. It is interesting to note that the composition of the EG/THF polymer is always in the ratio of EG/THF = 1/2, regardless of the initial monomer-feed ratio (Table III). When the feed ratio was $[\text{M}_2]_0 > 2[\text{M}_1]_0$, the equilibrium monomer concentration of THF was observed as in the case of the TEOFBI initiator. The reason why a 1:2-copolymer composition is obtained also in this case seems to be the same as in the case of the oxonium initiator system. When $[\text{M}_1]_0$ was higher than or approximately the same as $[\text{M}_2]_0$, THF was consumed completely by copolymerization, showing a $[\text{M}_2]_e = 0$, but the EG monomer remained still unreacted. This result is understandable because the homopolymerization of EG is a very slow reaction with EtOTf as the initiator. The mechanism of the EG/THF copolymerization is suggested as follows and involves the oxonium/macroester equilibrium, at least at the THF propagation end, a mechanism which has been described in detail previously.^{15,21} The EG species of the propagating ester **7** is attacked exclusively by THF because of the higher nucleophilic reactivity of THF and gives **8** which is in equilibrium with the ester species **9**. THF is again



(6)

