Poly(alkylene oxide) ionomers: 1. Copolymerization of trioxane by gas phase mixing of comonomers and initiator

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Uniform copolymers of trioxane with 1,3-dioxolane and ethyl glycidate of various comonomer compositions were prepared. A special reactor was used which allowed mixing of comonomers and initiator in the gas phase above the polymerization temperature of the mixture. Polymerization was accomplished by rapidly quenching the initiated mixture to dry ice temperature, giving polymer yields in excess of 80%. The polymers were either base treated or endcapped with propionic anhydride to obtain stable materials. The copolymers of trioxane and ethyl glycidate were treated with sodium hydroxide in aqueous dioxane at 85°C to give polyoxymethylene (POM) ionomers. The polymeric sodium salts could also be exchanged to other alkali salts of POM ionomers with various alkali chlorides while the polymers were either in suspension or in film form. Treatment of the sodium salts with acetic acid gave the free POM carboxylic acids. All polymers were characterized by their inherent viscosity, infra-red spectrum and p.m.r. spectrum.

INTRODUCTION

Oxymethylene polymers with ionic groups first attracted the attention of investigators some time ago[1], as a result of the interesting properties displayed by ionomers based on polyethylene[2].

Polymers of trioxane and various cyclic ethers have been studied extensively in the past, primarily those of ethylene oxide or 1,3-dioxolane, and have been found to have very attractive mechanical properties with enhanced resistance to auto-oxidation[3,4]. The stiffness of these copolymers, however, was approximately 20% lower than that of the POM homopolymer.

It was found that oxymethylene copolymers could be prepared[1,5], containing a variety of reactive groups as side chain branches from the main polymer chain, and in some cases as terminal groups on the polymer chain. Such reactive groups in these POM copolymers had also a potential as grafting sites in ionic polymerizations. Copolymers of trioxane with epoxides having –CN, –COOR, –OR side groups were prepared by a simple polymerization technique in a flow apparatus[5]. The comonomers were mixed together above the polymerization temperature of trioxane or the comonomer, which is between 130° and 140°C and gaseous BF_3 was added as the initiator[1,5]. This gas mixture was quenched causing polymerization, and the copolymer was isolated. Analysis of the copolymers showed that the ethyl glycidate, or glycidonitrile were indeed incorporated into the polymer. Although it was claimed that up to 20 mol % of these comonomers could be incorporated, in fact no more than 5% incorporation of comonomers was described. The copolymers, which were obtained in high yield and with an inherent viscosity of about 1, were generally acetate endcapped. Without endcapping the base stability of these polymers ranged from 15 to 50%. This is substantially lower than the normal ethylene oxide–trioxane copolymer which, even at 2 mol % incorporation, had a base stability in excess of 90%.

As expected, the modulus of these polymers was considerably higher than that of POM homopolymer even at low comonomer incorporations and the nitrile and carboxylate containing copolymers gave values of their flexural modulus 50 to 100% higher than that of the normal trioxane–ethylene oxide copolymer. It was found relatively difficult to incorporate a larger comonomer percentage of glycidate derivatives (which have the carboxylate group directly attached to the polymerizable epoxide group) into the POM chain.

Later workers have taken different approaches for the preparation of POM ionomers: a copolymer of trioxane with higher epichlorohydrin comonomer content could be readily prepared[6] and allowed to react with thioglycolate to give a POM ionomer which had a side group of the structure $-CH_2-SCH_2-COO^-$

Another type of ionomer was prepared by copolymerizing trioxane with styrene oxide[7,8] and subsequent substitution reactions on the phenyl ring of the styrene oxide which included diazotization reactions of amine derivatives.

The gas phase technique[1] for the preparation of several POM copolymers permitted the preparation of copolymers of trioxane with butadiene dioxide, glycidonitrile, ethyl glycidyl ether, ethyl glycidate, methyl glycidate, and also ethylene oxide and propylene oxide with an inherent viscosity as high as 1.6 dl/g. The base stability ranged from 15 to 50% depending on the type of comonomer. Comonomers with up to 2 mol % ethyl glycidate exhibited an inherent viscosity of 1.0 dl/g when endcapped but the uncapped product was only 30% base stable.

One of the attractive features of the gas phase process was that copolymers or terpolymer could be prepared under steady state conditions with copolymer homogeneity both in copolymer composition and molecular

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weight[11]. Homogeneous copolymer of trioxane and propylene oxide with a higher comonomer content and a markedly higher molecular weight was prepared without induction period at a higher rate than in bulk polymerization with BF_3 as the initiator, using the same batch of comonomers.

It was the purpose of this work to prepare trioxane–ethyl glycidate copolymers of low ethyl glycidate content by polymerization after gas phase mixing, to prepare ionomers by hydrolysis with sodium hydroxide and to characterize these copolymers by spectroscopic means.

EXPERIMENTAL

Materials

Monomers. Trioxane (Celanese Research Co.) 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) was distilled from lithium aluminium hydride before use (Karl Fischer analysis: <28 ppm H_2O).

Initiator. Gaseous boron trifluoride (Matheson Products) was used as supplied.

Reagents. Ethyl acrylate (Aldrich Chemical Co.), propionic anhydride (b.p. 68°C, 25 mmHg, Aldrich Chemical Co.) and triethylamine (Eastman Chemical 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 and drying agents, were obtained from the Fisher Scientific Company or Ventron Alfa Products and were used as supplied.

Solvents

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

Polymer solvents. p-Chlorophenol (m.p. 38°–40°C) (Eastman Chemical Co.) was distilled at reduced pressure (b.p. 94°C, 8 mmHg). For viscosity measurements, 2% by weight of dl-α-pinene was added to the *p*-chlorophenol. Deuterated and undeuterated hexafluoroisopropanol (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 (1% by wt) before use.

Polymer stabilizers. Cyanoguanidine (Aldrich Chemical Co.) and di-β-naphthyl-*p*-phenylene diamine antioxidant were used as supplied. These stabilizers were added to the polymer only for the 60°C inherent viscosity measurements.

Measurements

Most infra-red spectra were recorded on a Perkin–Elmer 727 spectrophotometer. Some polymer spectra were recorded on a Perkin–Elmer 283 spectrophotometer. Solid samples were measured as thin films (~1 mil thick) or as pressed pellets, and liquid samples were measured between sodium chloride plates. The peak assignments were made to the nearest 0.1 μm.

Gas chromatograms on liquid samples were recorded on a Varian 920 Aerograph. Helium was used as the carrier gas.

The p.m.r. spectra of low molecular weight compounds were measured on a 60 MHz R–24 Hitachi–Perkin–Elmer Spectrometer. Polymer spectra were recorded at room temperatures, in deuterated hexafluoroacetone sesquihydrate, on a 90 MHz R–32 Perkin–Elmer Spectrometer.

Synthesis of ethyl glycidate

A solution of peroxytrifluoroacetic acid was prepared by adding, with stirring over a 5 min period, trifluoroacetic anhydride (76.5 ml, 0.54 mol) to a 250 ml beaker containing a suspension of 90% hydrogen peroxide (12.5 ml, 0.45 mol) in ethylene dichloride (50 ml) cooled in an ice bath.

The resulting colourless solution was carefully transferred to an addition funnel fitted to a 1000 ml three necked round bottom flask which was also equipped with a reflux condenser and a motor stirring unit. The flask contained a mixture of 1,2-ethylene dichloride (250 ml), disodium hydrogen phosphate (204 g, 1.44 mol) and ethyl acrylate (22.9 g, 0.23 mol) maintained under a nitrogen blanket, with efficient stirring. The contents of the flask were refluxed by immersing the flask in an oil bath set at 100°C. The solution in the addition funnel was then added dropwise, over a 30 min period, to the boiling mixture. The resulting slurry was stirred vigorously, at reflux, for an additional 30 min.

The reaction was terminated first by removing the heat source and immersing the flask into an ice bath and then by adding approximately 500 ml of water, through the addition funnel, while the stirring and nitrogen flow were still being maintained. The water dissolved most of the salts. The contents of the flask were subsequently transferred to a 2 l beaker and stirred with an additional 500 ml of water to complete the dissolution of salts. The organic layer was separated and the aqueous layer was extracted with three 100 ml portions of methylene chloride. The combined organic extracts were washed with 100 ml of 5% sodium bicarbonate solution and dried over magnesium sulphate.

Most of the solvent was evaporated at reduced pressure at a temperature not exceeding 40°C. The residual liquid was then fractionated through a Vigreux column to yield 11.8 g (52%) of ethyl glycidate (b.p. 73°–77°C, 30 mmHg) (literature values: 88–90°C, 60 mmHg; 60°–64°C, 23 mmHg[9]).

The infra-red spectrum (liquid film) showed absorptions at 5.8 μm (C=O ester stretching), 8.0 μm (C=O ester) and 11.0–13.0 μm (deformation vibrations of the epoxy group) and no absorption at 6.0 to 6.1 μm (indicating the absence of C=C). The p.m.r. spectrum (CCl_4) showed δ values: 1.30 ($COOCH_2C\underline{H}_3$, 3); 2.88 ($>C\underline{H}_2$, 2); 3.35 ($>C\underline{H}-$, 1); 4.22 ($COOC\underline{H}_2CH_3$, 2) (*Figure 1*).

Polymerization after mixing in gas phase reactor

Trioxane–dioxolane copolymer. Trioxane (81.8 g, 0.91 mol) and 1,3-dioxolane (17.0 g, 0.23 mol) were in-

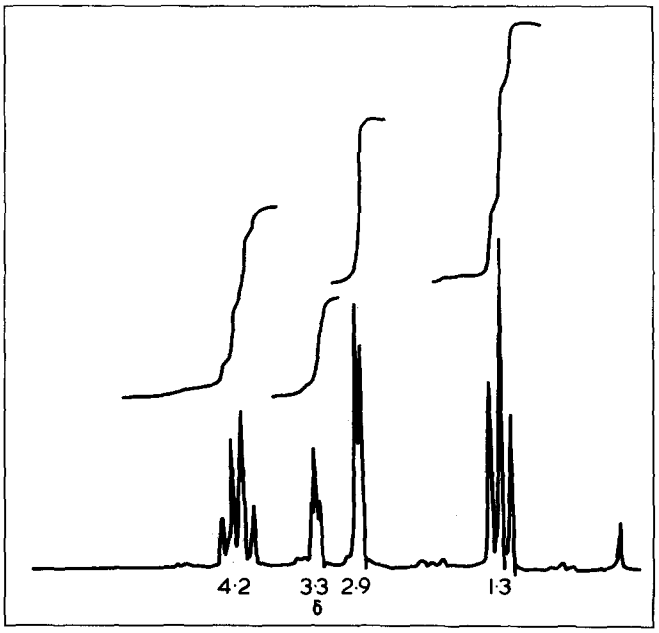


Figure 1 P.m.r. spectrum of ethyl glycidate

troduced in separate nitrogen gas streams into the top of a stainless steel cylindrical mixer[5] along with the boron trifluoride initiator, also in a nitrogen carrier. The reactor (*Figure 2*) had a diameter of approximately 3 in and a length of 12 in and was jacketed with a standard heating tape to control the temperature in the mixing device. (For details, see the literature[11,5]).

Immediately prior to polymerization, an amount slightly in excess of the indicated weight of trioxane was distilled from sodium directly into a three necked round bottom glass vaporizer. The heating tapes surrounding the flow lines for the trioxane and the 1,3-dioxolane and those surrounding the cylindrical mixer were then set to achieve a temperature of approximately 140°C in each of the lines and within the mixer. Two oil baths, one adjusted to 120°C and the other to 80°C, were utilized to heat the two monomers to approximately 5°C below their respective boiling points.

Nitrogen was passed through the trioxane and 1,3-dioxolane and, at approximately the same instant, a gaseous mixture of five volumes of nitrogen per volume of BF_3 was introduced in the upper area of the reactor at a rate of 5 ml/min. The mixed vapours from the upper stage of the reactor were quenched in the lower portion of a large filter flask which was immersed in a dry ice–isopropanol mixture. Nitrogen gas was bled off through an exhaust port in the neck of the collection vessel.

The polymerization reaction was allowed to proceed for 1 h. The amount of each monomer used up in the polymerization was determined by weighing each vaporizer flask before and after the run.

A chalky white solid was collected in the filter flask, washed successively with water, aqueous sodium bicarbonate, water and methanol and finally dried at 65°C (30 mmHg) for 16 h to give 85.3 g (87% yield) of polymer. The polymer was insoluble in most common organic solvents but swelled in water and in acetone.

Base unstable polymer and polymer segments were removed in the following way: 20 g of crude polymer was heated to 160°C for 1 h with a solution of 5.0 g of potassium hydroxide in 300 ml of benzyl alcohol under a nitrogen blanket. The solid which precipitated upon cooling was filtered, washed with water and methanol and dried at 80°C (30 mmHg) for 16 h to give 12.2 g (61% yield) of polymer.

The inherent viscosity of a 0.1% solution of the base stable copolymer in *p*-chlorophenol–α-pinene (98:2) at 60°C was 0.83 dl/g. The p.m.r. spectrum (deuterated hexafluoroacetone sesquihydrate, 35°C) showed δ values: 4.8 to 5.2 $(C\underline{H}_2O)$; 3.7 to 4.0 $(C\underline{H}_2C\underline{H}_2O)$. According to the p.m.r. analysis, the copolymer consisted of approximately 7 mol % of oxyethylene units, as judged by the relative integrated signal intensities of the oxyethylene protons and oxymethylene protons of the main chain repeat units.

Trioxane homopolymer and trioxane–ethyl glycidate copolymer. Trioxane (117.2 g, 1.30 mol) and boron trifluoride initiator were introduced in separate nitrogen gas streams into the top of the reactor, following the same procedure as described above. The comonomer flow line was temporarily shut off by means of a three-way Teflon stopcock. The same reaction conditions, described in the previous section, were maintained for this experiment.

During the 1 h reaction, a fluffy white solid was collected in the filter flask; afterwards, it was worked-up with water, aqueous sodium bicarbonate, water again and acetone and dried in a vacuum oven at 65°C for 16 h, and gave 99.2 g (85% yield) of polymer.

After 1 h the stopcock was opened to allow the mixture of ethyl glycidate (8.0 g, 0.07 mol) and nitrogen gas to flow into the top of the reactor together with the trioxane (117.2 g, 1.30 mol) and the boron trifluoride (temperature 130°–140°C), with nitrogen as carrier gas; the receiver was also changed. (The ethyl glycidate vapour was obtained by heating the liquid monomer with a silicone oil bath set at 190°C.) A chalky white solid was collected in the filter flask, during the next hour. After the run, the same work-up and drying procedures were followed and gave 105.1 g (85% yield) of polymer.

The flow rates of the trioxane–nitrogen mixture and of the boron trifluoride–nitrogen mixture were maintained constant for the entire duration of both reactions. The total amount of each monomer utilized in the combined runs was again determined by weighing each vaporizer flask before and after the two reactions. Approximately one

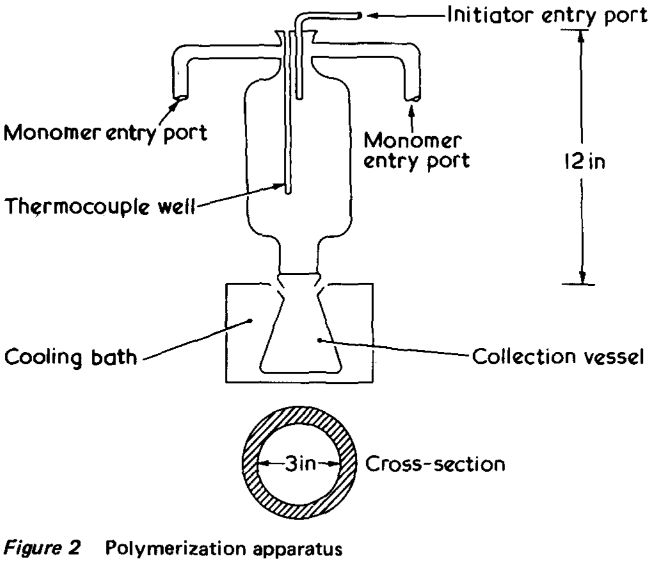


Figure 2 Polymerization apparatus

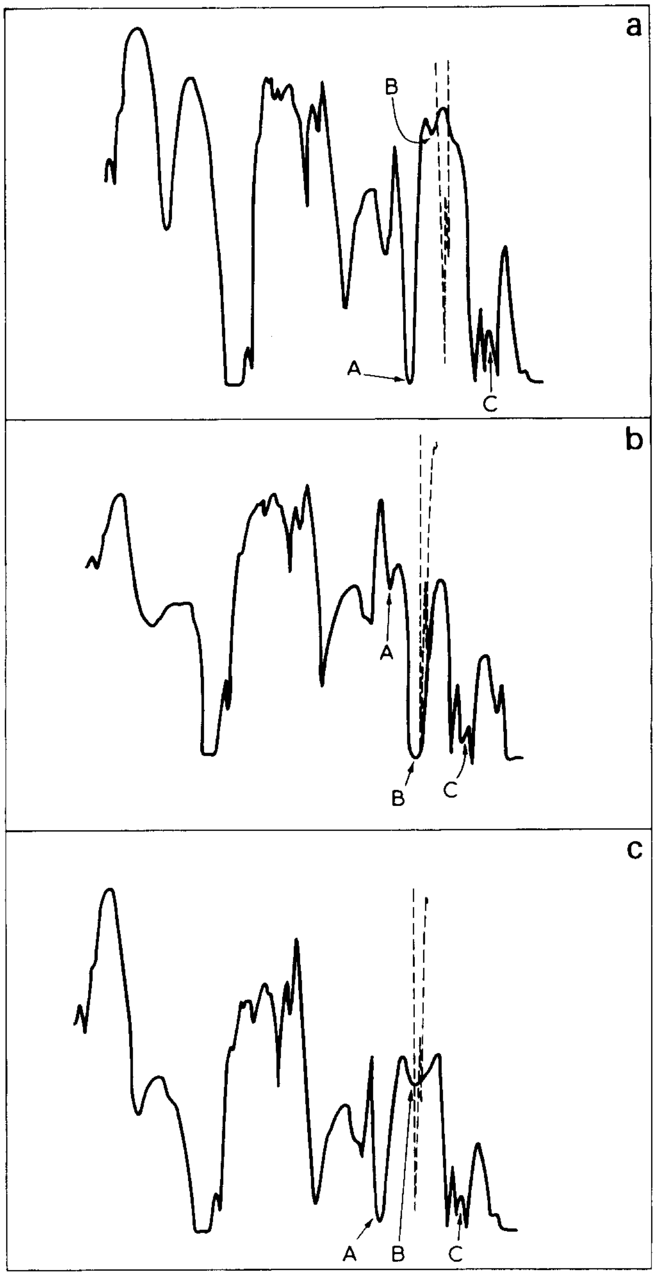


Figure 3 I.r. spectra of POM derivatives. (a) Ester; (b) sodium salt; (c) acid. A, 5.8 μm; B, 6.2 μm; C, 7.0 μm. – – –, 6.25 μm band of polystyrene

half of the total amount of trioxane was used up in the 1 h homopolymerization reaction and the other half was consumed during the 1 h copolymerization reaction.

Polymer stabilization was achieved as follows. The thermally unstable homopolymer was ester-endcapped by dissolving 10 g of the polymer in a mixture containing 1000 ml dimethylformamide, 400 ml pure propionic anhydride and 90 ml of tributylamine at 160°C, under nitrogen. After dissolution occurred, the mixture was stirred under reflux at 155°C for an additional 30 min. 9.4 g (94% yield) of the polymer, which precipitated upon cooling, were recovered after work-up. The presence of the propionate groups was verified by infra-red spectroscopy. A new absorption at approximately 5.8 μm, caused by the ester carbonyl group, replaced a broad absorption between 2.7 and 3.0 μm which was originally present and was caused by the hydroxyl endgroups.

The base stability of the trioxane–ethyl glycidate copolymer (i.e. the amount of polymer recovered after exposure of the copolymer to a potassium hydroxide–benzyl alcohol mixture at 160°C) was 35%. This treatment is a standard procedure for POM copolymer; in this case unstable polymer ends and the ester group are removed.

3.1 g (62% yield) of heat treated ester copolymer was obtained by heating 5.0 g of the crude trioxane–ethyl glycidate copolymer in 750 ml dimethylformamide to approximately 160°C until a clear light golden solution resulted. The gel which precipitated upon cooling was then washed with methanol and finally dried under vacuum.

The inherent viscosity of a 0.1% solution of the heat treated ester copolymer in *p*-chlorophenol–α-pinene (98:2) at 60°C was 0.35 dl/g while that of the endcapped homopolymer was 1.35 dl/g. The d.s.c. melting points of the same homopolymer and copolymer were 170° and 161°C, respectively. The copolymer exhibited a strong infra-red absorption at 5.8 μm due to the ethyl ester carbonyl on the side chains (*Figure 3*). The p.m.r. spectrum of the same copolymer (2 mol %) in deuterated hexafluoroacetone sesquihydrate showed δ values: 4.8 to 5.2 ($C\underline{H}_2O$); 1.2 to 1.4 ($COOCH_2C\underline{H}_3$).

Ionomers from trioxane–ethyl glycidate copolymer. 40 g of crude trioxane–ethyl glycidate copolymer was slurried with 30 g (0.75 mol) of sodium hydroxide in a dioxane–water mixture (1600 ml: 400 ml) for 1 h at 85°C, under nitrogen. The solid product, filtered from the mixture after the slurry was cooled to room temperature, was washed with methanol and dried under vacuum (30 mmHg) at 60°C for 16 h and gave 18.5 g (45% yield) of polymer.

The infra-red spectrum of this polymer (*Figure 3*) showed two new absorptions between 6.2 and 6.3 μm and between 7.0 and 7.1 μm due to the carboxylate anion but retained a weak shoulder at 5.8 μm due to the polymeric ester. The inherent viscosity of a 0.1% solution of the ionomer in *p*-chlorophenol–α-pinene (98:2) at 60°C was 0.33 dl/g. Sodium (1.1 mol %), found by analyzing the polymer for sodium, corresponded to approximately 1.4 mol % of all the comonomer units.

Two 100 ml round bottom flasks were each charged with 5 g of the sodium salt of the trioxane–ethyl glycidate copolymer, 35 ml deionized water and 1.9 g (0.05 mol) of lithium chloride or 3.8 g (0.02 mol) of caesium chloride, respectively. The flasks were then equipped with a magnetic stirring bar and fitted with a condenser. The reactants were stirred vigorously at room temperature, under nitrogen. The pH of the metal chloride aqueous solutions, during the lithium and caesium exchange reactions, changed from 6.1 to 6.6 and from 4.8 to 6.6, respectively. After 1 h, the solids were recovered by filtration, washed extensively first with deionized water to remove salt impurities, then with methanol and finally dried over phosphorus pentoxide, for 16 h at 60°C (30 mmHg). The polymer recovery from both reactions was nearly quantitative.

Analysis of the polymeric caesium salt for sodium (0.2% Na) indicated that approximately 0.3 mol % of the comonomer units in the polymer had not exchanged. The analyses of the polymeric lithium salt (Li, 0.3%; Na, 0.04%) showed that approximately 1.3 mol % of the comonomer units in the polymer had not exchanged. The inherent viscosities of 0.1% solutions of the polymeric salts in *p*-chlorophenol–α-pinene (98:2) at 60°C were 0.32 dl/g for the lithium salt and 0.34 dl/g for the caesium salt. Infra-red absorptions, due to the carboxylate anion in the lithium and caesium ionomers, were found at 6.2 and 7.0 μm, and at 6.3 and

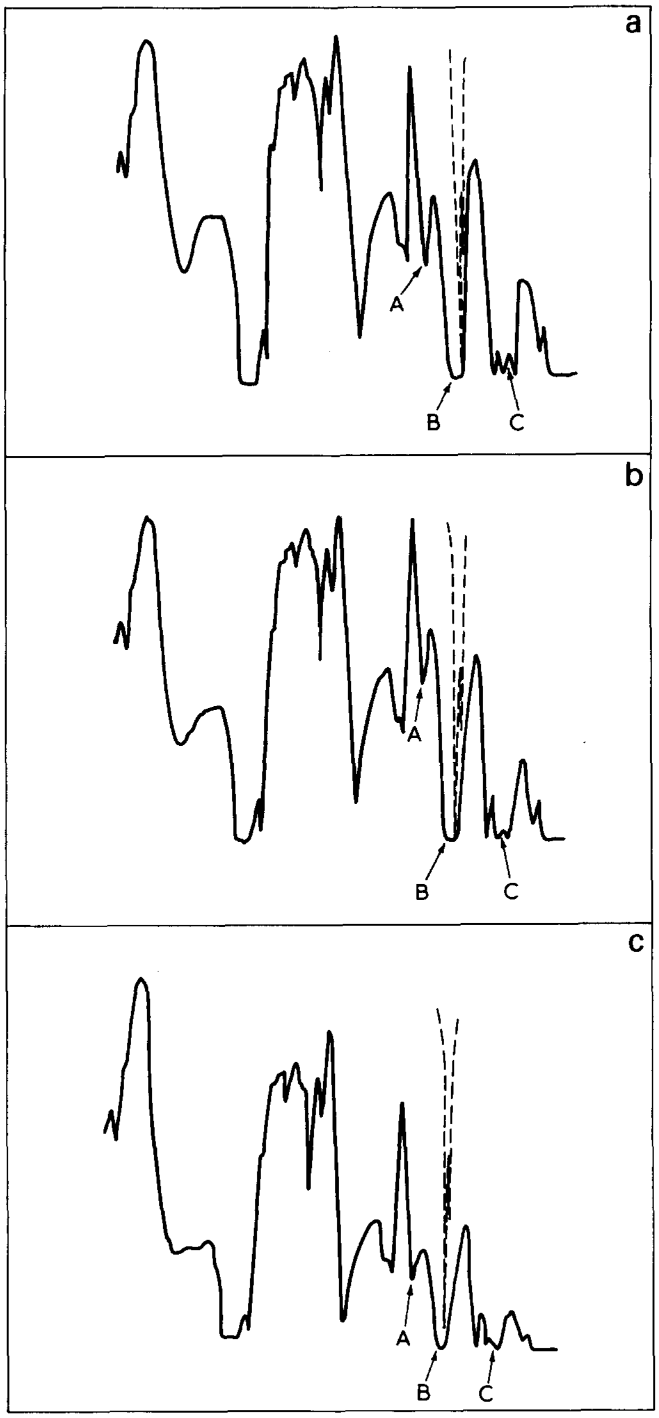


Figure 4 I.r. spectra of POM carboxylates. (a) Li; (b) Na. A, 5.8 μm; B, 6.2 μm; C, 7.0 μm (c) Cs: A, 5.8 μm; B, 6.2 μm; C, 7.1 μm

7.1 μm, respectively. In both cases, a small shoulder at 5.8 μm, due to a small percentage of residual ester carbonyl, was still present (*Figure 4*).

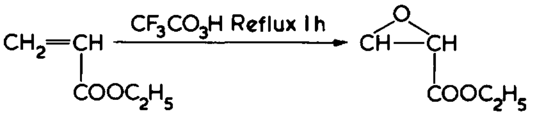
Acid derivative of trioxane–ethyl glycidate copolymer. The sodium salt of the trioxane–ethyl glycidate copolymer (5 g) and 5 ml of glacial acetic acid were stirred vigorously in 200 ml dioxane and 45 ml deionized water for 3 h at room temperature, under nitrogen. The filtered solid was washed repeatedly with water, then with methanol and finally dried under vacuum, at 60°C for 16 h, to give 4.2 g (84% yield) of polymer.

The infra-red spectrum of the polymeric acid exhibited the characteristic broad carboxylic acid carbonyl absorption at 5.8 μm (*Figure 3*); its inherent viscosity in a 0.1% solution in *p*-chlorophenol–α-pinene (98:2) at 60°C was 0.36 dl/g. The presence of less than 0.05% sodium in the polymer indicated that the hydrolysis reaction had essentially gone to completion.

RESULTS AND DISCUSSION

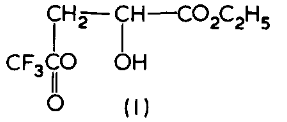
Ethyl glycidate (EG) was synthesized in good yield and used for the gas phase copolymerization of trioxane and EG. This copolymer was hydrolyzed to the ionomer of polyoxymethylene and the ionomer was transformed into other polymeric salts and also into the free polymeric acid.

Ethyl glycidate was prepared by epoxidation of ethyl acrylate with peroxytrifluoroacetic acid (equation 1) in 50–60% yield[9,10].



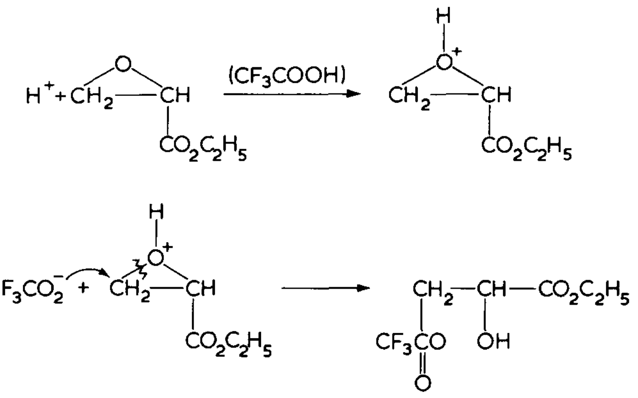
(1)

A major by-product was also obtained in nearly 40% yield which boiled at 95°–99°C. (40 mmHg) and was identified spectroscopically as ethyl(2-hydroxy-3-trifluoroacetoxy) propionate (I) with the following structure:



(I)

The substituted propionate (I) could be converted to ethyl glycidate by refluxing with sodium hydride in benzene; the total yield of ethyl glycidate was 84%. The formation of (I) sheds some light on the mechanism of ring opening of ethyl glycidate in the presence of cationic species. (I) is apparently formed by the reaction of the trifluoroacetic acid with already formed ethyl glycidate.



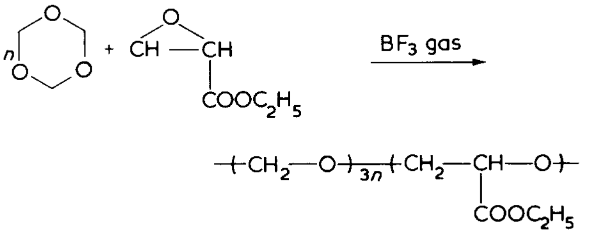
The above mechanism indicates that the major by-product, isolated according to the particular reaction conditions used in the synthesis of ethyl glycidate, resulted from the attack of the nucleophile on the unsubstituted carbon of the protonated epoxide.

Polymerizations from the gas phase

It was initially found desirable to study the copolymerization of trioxane and 1,3-dioxolane to test the capability of the apparatus for the copolymerization procedure and also to find out about the composition of the trioxane–1,3-dioxolane copolymer obtained by the gas phase polymerization technique. The copolymerization with a comonomer mixture of 80 mol % trioxane and 20 mol % 1,3-dioxolane was carried out for 1 h and the polymer was obtained in an overall yield of 87%. This polymer was base treated and 61% of base stable copolymer was obtained. This is a lower base stable fraction than would normally be obtained by a copolymerization of trioxane and 1,3-dioxolane in solution or in bulk and suggested that the randomization reaction (i.e. transacetalization which normally occurred in the bulk copolymerization of trioxane and ethylene oxide) apparently had not occurred extensively under these conditions or might have occurred at a lower rate than the chain propagation. Furthermore, 1,3-dioxolane was not incorporated into the polymer in the same ratio as supplied in the feed as only 7 mol % oxyethylene units were found in the polymer.

The gas phase mixing technique for polymerizations is a very flexible operation which was demonstrated in another type of experiment. Trioxane homopolymerization was carried out in the presence of boron trifluoride for approximately 1 h and an 85% yield of homopolymer was obtained. This homopolymer was then endcapped with propionic anhydride. The inherent viscosity of the endcapped homopolymer was 1.35 dl/g, indicating a molecular weight range typical for homopolymers and also copolymers which had been synthesized by a similar process. Since POM was obtained of this high inherent viscosity it indicated that the trioxane was very pure and contained only small amounts of chain transfer agents.

Polymerization was continued without turning the reactor off, but by opening the stopcock of the vessel containing the ethyl glycidate comonomer, copolymerization of trioxane and ethyl glycidate was performed (equation 2).



(2)

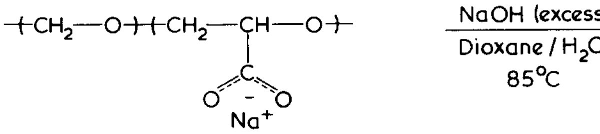
After 1 h of reaction an excellent yield (85%) of copolymer was obtained. The endcapping of this material was carried out in DMF and propionic anhydride, but the inherent viscosity of the capped material was somewhat lower than that of the homopolymer. During the process of dissolving the polymer in DMF a substantial amount of unstable polymer ends was degraded and only 60% of the trioxane–ethyl glycidate copolymer, which was now propionate endcapped, could be recovered.

The base stability of the uncapped trioxane–ethyl glycidate copolymer prepared in this work compares well with the base stability of trioxane–ethyl glycidate copolymers of roughly the same composition, prepared previously by the same process (*Table 1*). The reaction time and initiator flow rate for the preparation of the copolymers listed in *Table 1* were 60 min and 5 ± 1.5 ml/min, respectively.

The methyl glycidate copolymers exhibited slightly higher base stability values than the corresponding ethyl glycidate copolymers in the same composition range. The methyl esters also showed a tendency towards higher base stabilities when less comonomer was fed into the reactor.

In order to prepare a base stable ester of POM, the trioxane–ethyl glycidate copolymer was heat treated in DMF solution at approximately 160°C which degraded the uncapped end of the POM chain. A 62% yield of stable ester copolymer with a rather low viscosity of 0.35 dl/g was obtained. This copolymer was identified by its infra-red absorption, particularly the characteristic >C=O bands at approximately 5.8 μm as seen in *Figure 3*. According to the p.m.r. analysis, the copolymer consisted of approximately 2 mol % carboethoxy oxyethylene units, as judged by the relative integrated signal intensities of the ethyl ester methyl protons and those of the oxymethylene protons.

The copolymer of trioxane–ethyl glycidate was transformed into the sodium salt of the ionomer by slurrying the swollen polymer in a 0.5 M sodium hydroxide solution in dioxane–water at 85°C (equation 3).



$$-\!\!\!+CH_2-O+\!\!\!+CH_2-\underset{\underset{O^-\ Na^+}{\overset{|}{C(=O)}}}{CH}-O+ \quad \xrightarrow[\text{85°C}]{\text{NaOH (excess)}}_{\text{Dioxane}/H_2O}$$

(3)

Since the polymeric ester was only swollen in the dioxane–water–sodium hydroxide solution but did not dissolve completely, the reaction did not go to completion and a shoulder due to a residual ester group, as seen by the i.r. spectrum, always remained in ionomers prepared by this technique. A variety of reaction times and reaction temperatures, amounts of base and different relative volumes of dioxane to water were tried without removing the ester group completely from the final polymeric ionomer. Higher base ratios did not cause further hydrolysis but only caused colour formation in the final product. The inherent viscosity of the polymeric salt was essentially unchanged from that of its ester precursor.

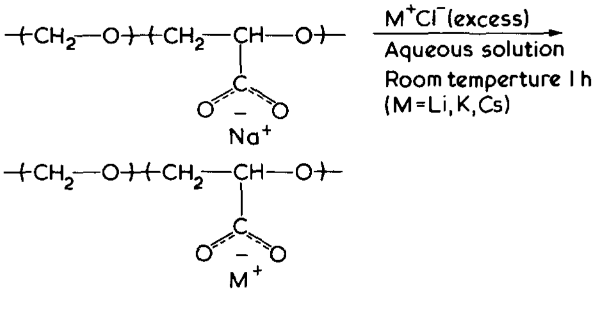
The –OH group absorption between 2.7 and 3.3 μm is very strong in all three derivatives of the oxymethylene copolymer but sharper in the case of the heat treated ester than in that of the polymeric salt or the polymeric acid (*Figure 3*). The absorption intensity indicates that the molecular weight of the polymer is relatively low and is in agreement with the viscosity values obtained for these polymers. The hydroxyl group absorption is broader in the salt and in the acid than in the case of the ester and is probably due to the presence of hydrogen-bonded carboxylic acid hydroxyl groups. It may also indicate the presence of bound water in the samples as the acid and salt derivatives of these polymers including those based on POM were expected to exhibit a higher affinity towards water, a phenomenon which has been observed in other ionomers. The sodium salt of the POM ionomer could be exchanged

Table 1 Base stability of trioxane–alkyl glycidate copolymers prepared in the gas phase

Alkyl glycidate: trioxane molar feed ratio	Base stability of the uncapped product (wt %)
1:27	44[a]
1:30	53[a]
1:50	57[a]
1:19	35[a,b]
1:40	34[c]
1:93	30[c]

[a]Methyl glycidate, ref 1; [b] ethyl glycidate; this work; [c] ethyl glycidate, ref 1

with other salts by treating the sodium salt of the polymer with alkali metal chloride salts in aqueous suspension (equation 4).

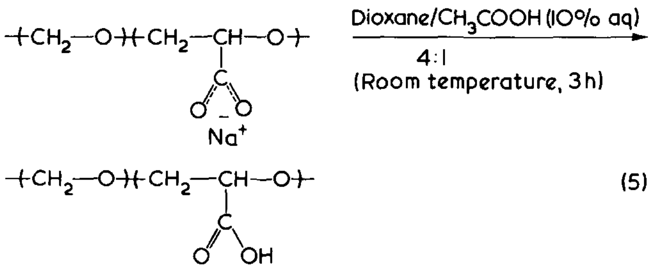


(4)

The exchange of metal ions by the method using various alkali metal salts has been described previously for the POM ionomer with $-CH_2-SCH_2COO^-$ side groups. A change in the pH of the metal chloride aqueous solution was also noticed and a final value of 6.6 was normally obtained although the initial lithium chloride solution had a pH of 4.8. The exchange reaction of alkali cations was highly effective but not quantitative and 1.3 mol % of the salt portions had not exchanged as judged by the analysis of the polymers for lithium and sodium.

A slight shift of the infra-red carbonyl absorptions of the carboxylate anions to higher wavelength (the asymmetrical stretching band moving from 6.2 to 6.3 μm and the symmetrical stretching band moving from 7.0 to 7.1 μm) was observed as the size of the cation increased from lithium to caesium (*Figure 4*). The carboxylate anion has two strongly coupled carbon to oxygen bonds with bond strengths intermediate between C=O and C–O. Apparently this bond strength shifted even further toward the C–O bond strength as the size of the cation increased. A similar effect was reported for other interactions of inorganic salts with polar polymers[12]. A slight but real shift of the ester carbonyl from 5.8 to 5.9 μm in going from a 1:1 'solution' of $Ca(NO_3)_2$ in poly(methyl acrylate) to one containing $Zn(NO_3)_2$ in the same proportions and finally to one in which cadmium replaced the zinc cation in the nitrate salt. Their observations were interpreted in terms of complex formation between the polymer and the salts in the solid state. The structure of this complex allowed for an analogous interaction between the cation in the salt and the carbonyl group of the polymer chain to what is observed in the ionic salts prepared in this work.

The polymeric sodium salt could be converted into the corresponding acid by treatment of the polymer under mild conditions with dioxane–acetic acid mixtures (equation 5).



(5)

This exchange reaction was also carried out in inhomogeneous systems but a complete replacement of the metal ion by the proton was achieved; the exchange had to be carried out under mild conditions in order to avoid the acid catalysed degradation of the polyoxymethylene backbone chain. The inherent viscosity of the acid polymer was found unchanged from its precursor, the ionomer. The conversion of the polymeric sodium salt to the polymeric acid was essentially complete within 3 h as indicated by analysis for sodium in the polymeric acid. A very small amount of sodium or a small amount of sodium acetate impurity which may not have been washed out and retained in the product was indicated by the presence of a shoulder in the i.r. spectrum at 6.2 μm which is normally characteristic of the carboxylate anion (*Figure 3*).

It has been demonstrated that polymerization from the gas phase is an effective way to prepare homo- and copolymers of trioxane especially copolymers that have carboxylate groups as functional groups. These groups can be hydrolyzed to polyoxymethylene ionomers and converted to poly(oxymethylene acids).

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REFERENCES

1 Martin, K. V. and Vogl, O. US Pat. 3 284 411 (1966)
2 Rees, R. W. Br. Pat. 1 011 981 (1966)
3 Walling, C., Brow, F. and Bartz, K. W. US Pat. 3 027 352 (1962)
4 Barker, S. J. and Price, M. B. 'Polyacetals', Elsevier, New York, 1974
5 Martin, K. V. US Pat. 3 316 218 (1968)
6 Wissbrun, K. F., Berardinelli, F. M. and Price, M. B. US Pat. 3 488 322 (1970)
7 Cherdron, H. 'Polymerization of Heterocyclics', (Eds. O. Vogl and J. Furukawa,) Marcel Dekker, New York, 1973
8 Weissermel, K., Fischer, E., Haefner, K. H. and Cherdron, H. *Angew. Makromol. Chem.* 1968, 415, 168
9 Aboul-Enein, H. Y. *Synth. Commun.* 1974, 4, 255
10 Payne, G. B. and Denning, P. H. US Pat. 3 053 856 (1962)
11 DeMejo, L. P. *PhD Thesis* University of Massachusetts (1977)
12 Wissbrun, K. F. and Hannon, M. J. *J. Polym. Sci. (Polym. Phys. Edn)* 1975, 13, 223