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POLY(ALKYLENE OXIDE) IONOMERS: SYNTHESIS AND BRIEF CHARACTERIZATIONS

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POLY(ALKYLENE OXIDE) IONOMERS: SYNTHESIS AND BRIEF CHARACTERIZATIONS

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ABSTRACT

Methyl 10,11-epoxyundecanoate was copolymerized with propane oxide and 1-butane oxide using a modified aluminumalkyl/water/acetylacetone (1:0.5:1) initiating system. Hydrolyses of the copolymers to a series of ionomers containing 10, 5, 2, and 1 mol.-% sodium carboxylate groups were accomplished.

Key Words: Poly(alkylene oxide) ionomers; Methyl 10,11-epoxyundecanoate; Alkylene oxide copolymers; Propane oxide; 1-Butane oxide.

INTRODUCTION

Polymers with salt of carboxylic acids have been introduced to the commercial polymers with the discovery of ionomers, carboxylates based on ethylene/methacrylic acid copolymers of approximately 10% of carboxylate units in the polymers (1–5).

Epoxides have been polymerized for many years not only with traditional cationic or anionic initiators (6–10), but also with modified alkyl metal initiating systems. Trialkylaluminum as well as zinc alkyls has been a desirable starting compound for many modifications that have created effective anionic coordination initiating systems. Acetylacetone (AcAc) modification (11,12) provided the first systems that also allowed the polymerization of functional epoxides.

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The first “functional” polyethers were based on copolymers of ethyl glycidate with trioxane (polyoxymethylenes) (13, 14) or epoxides (15).

The series of methyl ω-epoxyalkanoates, with 0–7 methylene spacer groups were homopolymerized (16–18) to high-molecular-weight polymers. The rate of polymerization was found to increase as the number of methylene groups between the polymerizable group and the carbomethoxy group increased and became constant when more than three methylene groups separated the polymerizable group from the carbomethoxy group.

Methyl ω-epoxyalkanoate homopolymers with longer methylene spacer groups were semicrystalline showing multiple melting peaks that were attributed to the partial crystallization of the paraffinic side chain (18). Methyl 10,11-epoxyundecanoate (MEU) (8 methylene groups) was also homopolymerized. The polymerizations were carried out on a small scale in vacuum-sealed polymerization tubes) with 5 mol.-% of the initiating mixture.

Copolymerizations of MEU (30 mol.-%) with epoxides (70 mol.-%) were also carried out (19–22). The copolymerization of MEU with EO gave copolymers with 15 and 4 mol.-% incorporation of MEU and a glass transition temperature (T_g) of approximately –58°C. Higher levels of MEU incorporation were obtained with the less reactive propane oxide (PO) (22 mol.-%) 1-butane oxide (BO) (25 mol.-%), epichlorohydrin (ECH) (17 mol.-%), 1-hexane oxide HO (25 mol.- and phenylglycidyl ether (PGE) (26 mol.-%). Copolymers of MEU with EO are semicrystalline elastomers because of the long sections of EO units, but all other copolymers of MEU were found to be amorphous.

It was the objective of this work to synthesize amorphous poly(alkylene oxide) ionomers of PO (homopolymer T_g = –63°C) or BO (homopolymer T_g = –62°C) (23) poly(alkylene oxide) ionomers based on 10 mol.-% ω-epoxyalkanoate comonomer. These copolymers were judged more desirable because the great difference in reactivities between MEU and EU would only give copolymers with long blocks of EU units that form crystallizable sections. Our other objective was to synthesize these poly(alkylene oxide) in large quantities, which required the development of a polymerization technique suitable for large-scale polymerization runs.

EXPERIMENTAL

Purification of Solvents and Reagents

10-Undecenoic acid was esterified to methyl 10-undecenoate, which was epoxidized to MEU with *m*-chloroperoxybenzoic acid.

PO was refluxed for 30 min over calcium hydride, then distilled (b.p., 34°C) and stored at 5°C. BO was heated to reflux for 12 h over calcium hydride, then distilled (b.p., 63°C).

AcAc was heated over phosphorous pentoxide, fractionally distilled (b.p., 139°C), and stored under nitrogen.

N,*N*-Dimethylacetamide (DMAc) was stirred over phosphorous pentoxide for 12 h and then fractionally distilled under reduced pressure (b.p., 58–58.5ºC/10 mm Hg). It was stored under purified nitrogen in a drying column filled with 4× Linde molcular sieves.

1,4-Dioxane was refluxed under nitrogen for 12 h over lithium aluminum hydride (LAH), then fractionally distilled from LAH (b.p., 100°C). Tetrahydrofurane (THF) was heated to reflux for 12 h over LAH and then fractionally distilled (b.p., 65°C).

All chemicals were obtained from Aldrich Chemical Company. Solvents and reagents were used as received.

Measurements

General Procedures and Methods

The infrared (IR) spectra were recorded on the Perkin-Elmer Model 727 spectrophotometer. Solid samples were measured as KBr pellets. The IR spectra of most of the polymers were measured as thin films cast directly onto a single NaCl plate from chloroform or from 1,4-dioxane solutions. The peak assignments were made to the nearest 5 cm^{-1}.

Inherent viscosity measurements were carried out at 30 or 60°C using Ubbelohde viscometers. The values reported are average values of three to five determinations. Solution concentrations were 0.1 or 0.5 g/dL in the appropriate solvent.

Determination of Residual Acid Groups in Polymers

One liter of a 25 wt.-% stock solution of sodium methoxide in methanol was prepared by the addition of sodium to methanol. This solution was placed in a 500-mL volumetric flask, which was capped with a rubber stopper and placed under nitrogen. A sodium methoxide solution (10.8 mL) was drawn from the container using a 20-mL syringe and transferred into the volumetric flask. To obtain a 0.1 *N* solution, the volumetric flask was filled up to the mark with purified DMAc, and the sodium methoxide solution was used immediately.

To a dry 125-mL Erlenmeyer flask was added a Teflon®-coated magnetic stirring bar and the flask was closed with a rubber cap and purged with nitrogen. The compound (250 mg) to be analyzed was placed into the Erlenmeyer flask and 50 mL of anhydrous DMAc was added to dissolve the sample.

The 0.1 *N* solution of sodium methoxide was placed in the 50-mL buret and the titrant was added dropwise to the stirred solution, which was maintained at 60°C. Thymol Blue was used as the indicator. At the end of the titration, the solution changed color from dark green to blue.

Determination of the Copolymer Composition

Poly(MEU-co-PO) and Poly(MEU-co-BO) by IR

Solutions of PMEU, in varying concentrations in chloroform, were prepared. An IR cell for liquid samples was assembled using a 0.5 mm-Teflon® spacer to guarantee a constant width of the cell for IR measurements. The absorbance of the carbonyl (C=O) peak at 1740 cm^{-1} was measured for each sample. From these measurements, calibration plots of absorbency (1740 cm^{-1}) versus moles of C=O in the sample were made. IR spectra for ester-substituted copolymer samples were measured in solutions (0.5 g/dL). The carbonyl (C=O) absorbency at 1740 cm^{-1} was measured and the moles C=O present in the samples were then determined from the calibration curve and the mole percent of MEU units incorporated in each copolymer was calculated.

Preparations

Preparation of the TEA/Water/AcAc Initiator Solution

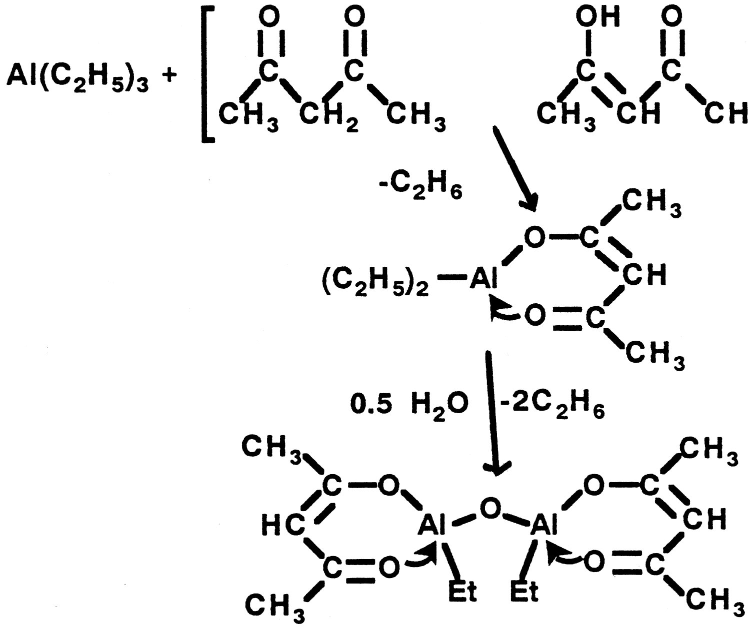
A one liter, one-neck, round-bottom flask, equipped with a vacuum adapter and a Teflon®-coated stirring bar was flamed out. After cooling to room temperature under nitrogen, under a flow of nitrogen, TEA (70 mL; 0.5 mol) was carefully transferred from a steel container to the reaction flask with a nitrogen-purged double-ended needle.

The reaction vessel was partially immersed in an ice/water bath, then fitted with a dry side-arm addition funnel. The addition funnel was charged with AcAc (53 mL) in anhydrous diethyl ether (400 mL). Over a period of 3 h the solution was added slowly to the stirred TEA. A slight positive pressure of nitrogen was maintained throughout the apparatus to sweep away the ethane formed during the reaction. After the addition was completed, the pale yellow solution was stirred for 1.5 h to allow completion of the reaction [see Eq. (1)].

Using a 10-mL syringe, distilled water (4.6 mL) was added dropwise to the ethereal solution over a 1-h period. The initiator solution was stirred for an additional 1.5 h, closed tightly with a rubber septum, and stored in a refrigerator. The initiator solution was aged for 1 week before it was used.

Copolymerizations of MEU with PO and BO

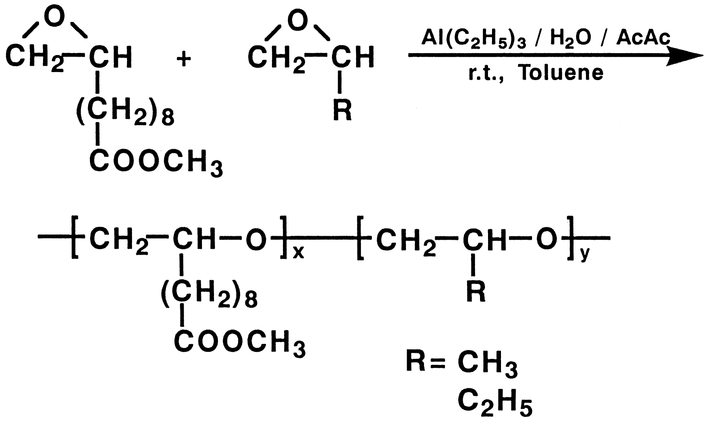
Copolymerizations of MEU with PO or BO were carried out in a resin kettle at room temperature in a toluene solution (16% w/v for the copolymerization of MEU with PO and 22% w/v for the copolymerization of MEU with BO with 4 mol.-% of the aluminumalkyl-type initiator). The comonomer feeds contained 13 mol.-% of MEU and 87 mol.-% of PO or 87 mol.-% 60. The same precautions as



Equation 1.

for large-scale homopolymerization of MEU were necessary. The copolymerizations were allowed to proceed for 6 weeks [see Eq. (2)].

In both copolymerization experiments, the mixture had formed a solid plug of polymer after 1 week. No specific study was made to determine when the maximum yield for these copolymers was achieved. The behavior of the comonomer mixture in the large-scale copolymerization was similar to that of the comonomer mixtures in small-scale copolymerizations that had previously been carried out in



Equation 2. Copolymerization of MEU with PO and BO.

sealed tubes (10). As the results in Table 1 indicate, MEU was found to copolymerize with PO or BO to high molcular weight polymers in the large-scale copolymerizations (carried out in a resin kettle). Copolymers were obtained in 75–80% yields. They were found to have approximately 10 mol.-% MEU incorporated. The P(MEU-*co*-BO) had an inherent viscosity of 0.7 dL/g (0.5% in 1,4-dioxane, 30°C). The gel permeation chromatography (GPC) average molcular weights (M_n = 74,000 and M_w = 150,000) calculated on the basis of previous measurements (10) were found for this copolymer. P(MEU-*co*-BO) had an inherent viscosity of 0.9 dL/g (0.5% in 1,4-dioxane, 30°C).

The IR spectra of the copolymers showed typical features of the MEU units in the polyether chain and showed absorptions assignable to the alkylene oxide comonomer units. The spectra of P(MEU-*co*-PO) and P(MEU-*co*-BO) exhibited bands centered at 1100 cm^{-1}, the characteristic stretching frequency for the polyether backbone, and a strong carbonyl (C=O) stretch at 1740 cm^{-1}. A strong carbonyl (C=O) stretch at 1740 cm^{-1} in the IR spectrum of MEU allowed for the convenient measurement of the absorbance for this peak and consequently for the calculation of the mol.-% of functional monomer incorporated in each copolymer.

P(MEU-*co*-PO)

Large-Scale Copolymerization of MEU with PO

A dried 2-L round-bottom flask fitted with a Teflon®-coated magnetic stirring bar, a rubber septum, and a vacuum adapter was filled with nitrogen and charged with toluene (680 mL) and MEU (63 mL; 57 g; 0.26 mol). The content of the flask was purged with nitrogen for 2 h and then PO was added (100 g, 120 mL, 1.7 mol). A TEA/H_2O/AcAc initiator solution (315 mL) was transferred into the polymerization vessel.

Polymerization was allowed to proceed for 6 weeks. Gelation was noticed the next day. The polymerization vessel was opened and the polymer was cut into small pieces with scissors. Acidified methanol/water mixture (1:1; 1.5 L, 3 mL of concentrated hydrochloric acid) was placed into an operating Waring blender and the polymer was added in pieces.

The precipitated copolymer was collected by filtration, the filter cake was washed with methanol/water (1:1); the final washing had a small amount of antioxidant added. The product was then dried for 12 h and stored under nitrogen.

Yield of the crude copolymer was 120 g (75%). The inherent viscosity of the copolymer (0.5% in chloroform, 30°C) was 1.5 dL/g. The polymer, had an average molcular weight of M_n = 160,000 and M_w = 320,000 (based on polystyrene calibration standards) as determined by GPC analysis of the copolymer in THF solution (0.15% w/v) (10). The IR spectrum (thin film) showed absorptions at 1740 cm^{-1} (C=O stretch, ester) and 1100 cm^{-1} (C—O—C stretch, ether). The relative composition of the copolymer was 10 ± 1 mol.-% MEU and 90 ± 1 mol.-% PO.

*100% Hydrolysis of P(MEU-*co*-PO*

Into a 1-neck 500-mL round-bottom flask was placed P(MEU-*co*-PO) (5 g) and 1,4-dioxane (200 mL) and the mixture was stirred in an oil bath at approximately 100°C. Aqueous sodium hydroxide solution (10 mL, 4 *N*) was then added and the copolymer solution stirred. The reaction mixture became increasingly turbid and in approximately 1 h and precipitation of P($EUA^{-}Na^{+}$-*co*-PO) started.

The reaction was stopped after 2.5 h. The solid was filtered, washed with 1,4-dioxane, and dried. The copolymer was placed into an Erlenmeyer flask with acetone (100 mL) and the mixture was stirred for 1 day. The solid was then isolated by filtration and dried under reduced pressure (0.01 mm Hg).

Yield of the polymer was 4 g (80%). The IR spectrum (thin film from methanol) showed absorptions at 1560 cm^{-1} (C=O stretch, carboxylate anion), and 1100 cm^{-1} (C—O—C stretch, ether). The relative composition of the copolymer was 10 ± 1 mol.-% EUA^{-} Na^{+} and 90 ± 1 mol.-% PO.

*50% Hydrolysis of P(MEU-*co*-PO)*

P(MEU-*co*-PO) (5 g) was dissolved in 1,4-dioxane (200 mL) heated to 100ºC and a 4 *N* aqueous sodium hydroxide solution (10 mL) was added. The reaction mixture became turbid in approximately 1 h and precipitation of a solid, P($EUA^{-}Na^{+}$-*co*-PO) began. The reaction was stopped after 1 h and 15 min. The solid was isolated by filtration, washed with 1,4-dioxane, and dried.

The terpolymer was placed in an Erlenmeyer flask with acetone (100 mL), the suspension was filtered, and the solid was dried. Yield of the polymer was 2.3 g (60%). According to the IR spectrum (thin film), the composition of the terpolymer was 5 ± 0.3 mol.-% MEU, 5 ± 0.3 mol.-% EUA^{-} Na^{+}, and 90 ± 0.1 mol.-% PO.

*20% Hydrolysis of P(MEU-*co*-PO)*

P(MEU-*co*-PO) (5 g) was dissolved in 1,4-dioxane (200 mL) heated to 100°C, and a 4 *N* aqueous sodium hydroxide solution (10 mL) was added. After 30 min, the reaction was stopped by pouring the solution into hexane-ether (1:1); a solid precipitated which was isolated by filtration, washed with hexane-ether (1:1), and dried. The terpolymer was stirred in acetone (100 mL) filtered, and the solid was dried.

Yield of the polymer was 2 g (50%). The IR spectrum (thin film) showed a composition of the terpolymer as 8 ± 0.8 mol.-% MEU, 2 ± 0.2 mol.-% EUA^{-} Na^{+}, and 90 ± 0.1 mol.-% PO.

*10% Hydrolysis of P(MEU-*co*-PO)*

P(MEU-*co*-PO) (5 g) was dissolved in 1,4-dioxane (200 mL), heated to 100°C and a 4 *N* aqueous sodium hydroxide solution (10 mL). After 15 min the reaction was stopped by pouring the solution into hexane–diethylether (1:1). The organic phase was dried and the solvent evaporated.

Yield of the polymer was 2.5 g (60%). The IR spectrum (thin film) stretch, ether) showed that the composition of the terpolymer was 9 ± 0.8 mol.-% MEU, 1 ± 0.1 mol.-% $EUA^- Na^+$, and 90 ± 1 mol.-% PO.

Poly(EUA-*co*-BO)

Large-Scale Copolymerization of MEU with BO

In a 2-L resin kettle, fitted with a Teflon®-coated magnetic stirring bar was charged under nitrogen toluene (600 mL) and MEU (58 g; 0.26 mol). Next, BO was added (125 g; 1.7 mol), the solution was purged with dry nitrogen, and the TEA/H_2O/AcAc initiator solution (260 mL) was added. The solution was left at room temperature under a slight nitrogen pressure. The polymerization was allowed to proceed for 6 weeks. Gelation was noticed within 1 h after the initiation.

After the polymerization was judged complete, the vessel was opened and the polymer was cut into small pieces with scissors. Acidified methanol (2 L) (3 mL of concentrated hydrochloric acid) was placed into a Waring blender; the blender was turned on to the appropriate speed and the polymer was added section by section. The copolymer was collected from the suspension by filtration and washed with methanol; the final washing had a small amount of antioxidant added. The polymer was dried and stored under nitrogen. Yield of the crude copolymer was 110 g (80%).

The crude P(MEU-*co*-BO) (35 g) was placed into a 2-L Erlenmeyer flask and a 1:1 mixture (1 L) of 1,4-dioxane and toluene was added together with 6 mL of acidified methanol; this mixture dissolved the polymer. The slightly turbid solution was filtered through a fritted filter, and concentrated on a rotary evaporator to 150 mL. Slow precipitation into 1.5 L of methanol yielded 25 g of white copolymer. The inherent viscosity (0.5% in chloroform, 30°C) was 1.5 dL/g. The IR spectrum (thin film) showed absorptions at 1740 cm^- (C=O stretch, ester); 1240, 1195, and 1170 cm^{-1} (C—O stretch, methyl ester) and 1100 cm^{-1} (C—O—C stretch, ether). The composition of the copolymer was 10 ± 1 mol.-% MEU and 90 ± 1 mol.-% BO.

*100% Hydrolysis of P(MEU-*co*-BO)*

P(MEU-*co*-BO) (5 g) was dissolved in 1,4-dioxane (200 mL) heated to 100°C and a 4 *N* aqueous sodium hydroxide solution (10 mL) was added. The reaction mixture became increasingly turbid over the period of 1 h, and then the precipitation of the solid started.

The reaction was stopped after 2 h 45 min. The solid was isolated by filtration, washed with 1,4-dioxane, and dried. The copolymer was slurried in acetone (100 mL) the solid was isolated by filtration and dried.

Yield of the polymer was 4 g (80%). The IR spectrum showed the composition of the copolymer to be 10 ± 0.5 mol.-% $EUA^- Na^+$ and 90 ± 1 mol.-% BO.

*50% Hydrolysis of P(MEU-*co*-BO)*

P(MEU-*co*-BO) (5 g) was dissolved in 1,4-dioxane (200 mL), heated to 100°C, and a 4 *N* aqueous sodium hydroxide solution (10 mL) was added. The reaction mixture became turbid and was stopped after 1 h and 20 min, then poured into a 1:1 mixture of *n*-hexane/diethyl ether. The terpolymer was isolated, washed with acetone, and dried.

Yield of the polymer was 3.5 g (70%). The IR spectrum (thin film) showed the composition of the terpolymer to be 5 ± 0.5 mol.-% MEU, 5 ± 0.5 mol.-% EUA^- Na+ and 90 ± 1 mol.-% BO.

*20% Hydrolysis of P(MEU-*co*-BO)*

P(MEU-*co*-BO) (5 g) was dissolved in 1,4-dioxane (200 mL), heated to 100°C, and a 4 *N* aqueous sodium hydroxide solution (10 mL) was added. After 30 min, the reaction was terminated by pouring the mixture into an diethyl ether/hexane (5:1). After a few hours, the terpolymer was isolated by filtration, washed, soaked in acetone for 1 day, and dried.

Yield of the polymer was 2.4 g (60%). The IR spectrum (thin film) showed the composition of the terpolymer to be 8 ± 0.8 mol.-% MEU, 2 ± 0.2 mol.-% $EUA^- Na^+$, and 90 ±1 mol.-% BO.

*10% Hydrolysis of P(MEU-*co*-BO)*

P(MEU-*co*-BO) (5 g) was dissolved in 1,4-dioxane (200 mL), heated to 100°C, and a 4 *N* aqueous sodium hydroxide solution (10 mL) was added. After 15 min reaction time, the mixture was poured into ether/hexane (5:1). The organic phase was isolated, dried, and the solvent was removed under reduced pressure. The polymer was washed with acetone and dried.

Yield of the polymer was 2 g (60%) The IR spectrum (thin film) showed the composition of the terpolymer to be 8 ± 0.9 mol.-% MEU, 1 ± 0.1 mol.-% EUA^- Na^+, and 90 ±1 mol.-% BO.

RESULTS AND DISCUSSION

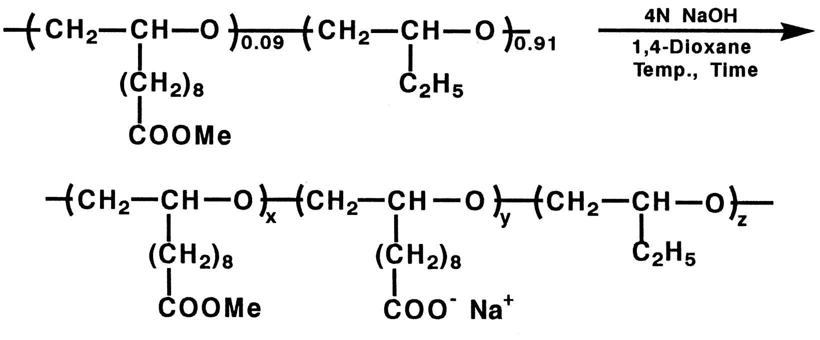
Preparation of Triethylaluminum/Water/Acetylacetone Initiator and Polymerizations and Copolymerizations of MEU with PO and BO

Preparation of Triethylaluminum/Water/Acetylacetone Initiator

The initiator solution was prepared according to a procedure that was outlined in general by Bansleben (22) and Muggee (23). TEA was transformed in two steps to an initiator, which showed high activity for the polymerization of MEU. TEA (1 mol) was first reacted with AcAc (1 mol in ether). The subsequent reaction with water (0.5 mol) gave a homogeneous, light yellow initiator. It is believed that the stoichiometry of the formation of the initiator follows a sequence as shown in Equation (3). From all previous information, these initiating systems function both as initiator and complexing agents for functional (ester) groups. It has been estimated that 2–3% of the initiating systems actually function as initiator.

The reverse sequence, where an etheral solution of TEA was first allowed to react with water, was tried but not pursued due to the formation of precipitates of aluminum compounds with only small amounts of initiator activity.

Relatively large quantities of the initiator were prepared and stored at 0–50°C in the glass container sealed with a rubber septum. Although it was not an objective of this investigation to establish the influence of temperature and time used in the preparation of the initiator on the initiator activity, the highest activity of the initiating mixture was found to be between 1 and 3 weeks of storage at



$$\left[\mathrm{CH_2{-}CH({(CH_2)_8COOMe}){-}O}\right]_{0.09}\left[\mathrm{CH_2{-}CH(C_2H_5){-}O}\right]_{0.91} \xrightarrow[\text{Temp., Time}]{\text{4N NaOH}}_{\text{1,4-Dioxane}}$$

$$\left[\mathrm{CH_2{-}CH({(CH_2)_8COOMe}){-}O}\right]_x\left[\mathrm{CH_2{-}CH({(CH_2)_8COO^- Na^+}){-}O}\right]_y\left[\mathrm{CH_2{-}CH(C_2H_5){-}O}\right]_z$$

1. $x = 0$, $y = 0.090$, $z = 0.910$
2. $x = 0.045$, $y = 0.045$, $z = 0.910$
3. $x = 0.072$, $y = 0.018$, $z = 0.910$
4. $x = 0.081$, $y = 0.009$, $z = 0.910$

Equation 3. Hydrolysis of P(MEU-*co*-BO).

50°C. Interestingly, good initiator activity was found to prevail over a much longer period of time than it was previously anticipated, but a minimum of 1 week of aging was essential for the activity [see Eq. (1)].

P(MEU-*co*-PO) and P(MEU-*co*-BO) were prepared in 100-g quantities in the proper copolymer composition of approximately 10% of MEU copolymer content in yields of 75–80% without difficulties [see Eq. (2), Tab. (1)].

Hydrolysis of P(MEU-*co*-PO) and P(MEU-*co*-BO)

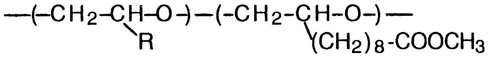
Hydrolysis of P(MEU-*co*-PO)

The copolymer of MEU and PO was converted to a series of poly(alkylene oxide) ionomers by hydrolyzing the pendant ester groups with a 4 *N* aqueous solution of sodium hydroxide. The copolymer used for the reaction had an inherent viscosity of 1.5 dL/g (0.5% in chloroform, 30°C) and contained approximately 9.5 mol.-% pendant ester groups. A 2.5% by weight solutions of the P(MEU-*co*-PO) in 1,4-dioxane were stirred with a 4 *N* aqueous sodium hydroxide solution (10 mL, 6 molar excess OH to ester groups) for 2.5 h, 1 h, and 15 min, 30 and 17 min at 100°C. Copolymers hydrolyzed for 2.5 h and 1 h 15 min precipitated from the reaction mixture [see Eq. (4)].

The copolymer hydrolyzed for 2.5 h (no. 1 in Tab. 2), was isolated in 90% yield, and its inherent viscosity was 0.72 dL/g (0.5% in water, 30ºC). Elemental analysis of this ionomer found 4.3% sodium, indicating quantitative conversion of the ester groups (10 mol.-%) to the sodium carboxylate form. The relative composition of the copolymer was 10 ± 1 mol.-% $EUA^- Na^+$ and 90 ± 1 mol.-% PO (10% hydrolyzed).

The copolymer hydrolyzed for 1 h 15 min (no. 2 in Tab. 2 was isolated in 60% yield and had an inherent viscosity of 0.80 dL/g, 0.5% in water, 30°C). The relative composition (by IR method) of the polymer was 5 ± 0.3 mol.-% EUA^- Na^+, 5 ± 0.3 mol.-% MEU, and 90 ± 1 mol.-% PO (50% hydrolyzed). Copolymers

Table 1. Copolymers of MEU with PO and BO



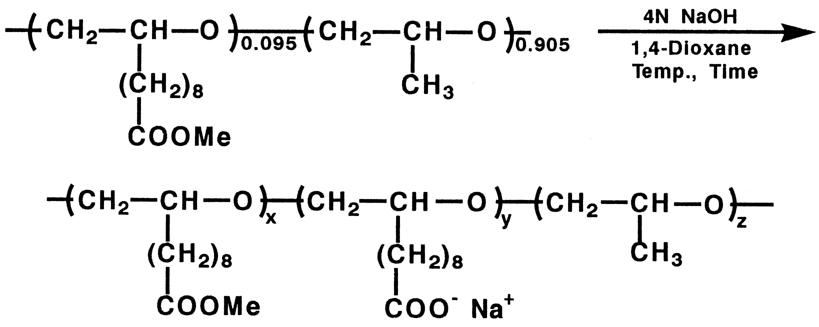
$$—(–CH_2–\underset{R}{CH}–O–)—(–CH_2–\underset{(CH_2)_8\text{-}COOCH_3}{CH}–O–)—$$

Comonomer	*R*	Amount of monomer	Solution concentrated (w/v%)	Yield %	$n_{inh}{}^a$ (dL/g)	Mole % MEU^b in copolymer
Propane Oxide	CH_3	100 g	16	75	0.70	9.5
1-Butane Oxide	CH_2CH_3	125 g	22	80	0.91	9.3

[a] Solvent: toluene.

[b] 0.5% in 1,4-dixane, 30ºC.

[c] Comonomer feed contained 13 mol.-% MEU.



1. $x = 0$, $y = 0.095$, $z = 0.905$

2. $x = 0.047$, $y = 0.047$, $z = 0.905$

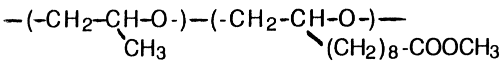
3. $x = 0.076$, $y = 0.019$, $z = 0.905$

4. $x = 0.086$, $y = 0.009$, $z = 0.905$

Equation 4. Hydrolysis of P(MEU-*co*-PO).

hydrolyzed for 32 min (no. 3 in Tab. 2) and 17 min (no. 4 in Tab. 2) did not precipitate from the reaction mixture. The copolymer no. 3 was precipitated from hexane-diethyl ether (1:1) mixture and purified by repeated soakings in acetone. The relative composition (by IR method) of the polymer isolated in 50% yield was 2 ± 0.2 mol.-% $EUA^- Na^+$, 8 ± 0.8 mol.-% MEU, and 90 ± 1 mol.-% PO (20% hydrolyzed). The copolymer no. 4 was isolated in 50% yield and the relative composition of this ionomer (by IR method) was 1 ± 0.1 mol.-% $EUA^- Na^+$, 9 ± 0.9 mol.-% MEU, and 90 (+/- 1) mol% PO (10% hydrolyzed).

Table 2. Hydrolysis of Poly(MEU-co-PO)a



$$-(-CH_2-\underset{CH_3}{CH}-O-)-(-CH_2-\underset{(CH_2)_8-COOCH_3}{CH}-O-)-$$

Copolymer	Time	Percent hydrolysis	n_{inh} (dL/g)	Yield (%)	Precipitation Reaction Mixture
1. $x = 0, y = 0.10,$ $z = 0.90$	2 h 30 min	100	0.72^b	90	+
2. $x = 0.05, y = 0.05,$ $z = 0.90$	1 h 15 min	50	0.80^b	60	+
3. $x = 0.08, y = 0.02,$ $z = 0.90$	32 min	20	—	50	–
4. $x = 0.09, y = 0.01,$ $z = 0.90$	17 min	10	—	50	–

[a] Reaction conditions: 1,4-dioxane, 100ºC, 10 mL of 4 *N* aqueous sodium hydroxide solution.
[b] 0.5% in water, 30ºC.

The IR spectra of all four ionomers showed the characteristic C—O stretching frequency for the poly(alkylene oxide) backbone near 1110 cm^{-1}. Differences in the frequency and intensity of the carbonyl stretch (C=O) could also be observed by comparing the spectra. The carbonyl stretching frequency of the starting P(MEU-*co*-PO) appeared at 1740 cm^{-1}. P(EUA^{-}Na^{+}-*co*-PO) (100% hydrolyzed), obtained by the hydrolysis of poly(MEU-*co*-PO), showed a strong carboxylate anion stretch at 1560 cm^{-1} P(EUA^{-}Na^{+}-*co*-MEU-*co*-PO) (50% hydrolyzed) showed the carbonyl stretching frequency at 1740 cm^{-1} and the carboxylate anion stretch at 1560 cm^{-1}, both of the same intensity. P(EUA^{-}Na^{+}-*co*-MEU-*co*-PO), 20 and 10% hydrolyzed showed, in addition to a strong carbonyl stretching frequency at 1740 cm^{-1}, a weak carboxylate anion stretch at 1560 cm^{-1}. Intensities of the carboxylate anion stretch were proportional to the percent of hydrolysis of copolymers.

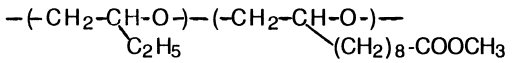
Hydrolysis of P(MEU-*co*-BO)

P(MEU-*co*-BO)

The copolymer of MEU and BO was converted to a series of the corresponding poly(alkylene oxide) ionomers by hydrolysis of the pendant ester groups with a 4 *N* aqueous solution of sodium hydroxide. The reaction, shown in Equation (4), was carried out in an analogous manner to the hydrolysis of P(MEU-*co*-PO). The copolymer used for the reaction had an inherent viscosity of 1.5 dL/g and contained approximately 10 mol.-% pendant ester groups. 2.5% by weight solutions of P(MEU-*co*-BO) in 1,4-dioxane were hydrolyzed with 4 *N* aqueous sodium hydroxide solution (10 mL, 6 molar excess OH^{-} to ester groups) for 2 h 45 min, 1 h 20 min, 30 min, and 15 min at 100°C. Copolymers, hydrolyzed for 2 h 45 min and 1 h 20 min, precipitated from the reaction mixture. The copolymer hydrolyzed for 2 h 45 min (no. 1 in Tab. 3) was isolated in 85% yield and had an inherent viscosity of 0.91 dL/g. Elemental analysis of this ionomer gave 4.0% of sodium, indicating an essentially quantitative conversion of the ester groups (10.0 mol.-%) to the sodium carboxylate form. The relative composition of the copolymer was 10 ± 1 mol.-% EUA^{-}Na^{+} and 90 ±1 mol.-% BO (100% hydrolyzed).

The copolymer hydrolyzed for 1 h 20 min (no. 2 in Tab. 3) was isolated in 60% yield; and its inherent viscosity was 0.80 dL/g. The relative composition of the polymer was 5 ± 0.5 mol.-% EUA^{-}Na^{+}, 5 ± 0.5 mol.-% MEU, and 90 ±1 mol.-% BO (50% hydrolyzed). Copolymers hydrolyzed for 30 min (no. 3 in Tab. 3) and 15 min (no. 4 in Tab. 3) did not precipitate from the reaction mixture. The copolymer no. 3 was precipitated from *n*-hexane/ether (1:1) mixture and purified by repeated soakings in acetone. The relative composition of the polymer isolated in 45% yield was 2 ± 0.2 mol.-% EUA^{-}Na^{+}, 8 ± 0.8 mol.-% MEU, and 90 ± 1 mol.-% BO (20% hydrolyzed). The copolymer no. 4 was isolated in 50% yield and the relative composition of this ionomer was found to be 1 ± 0.l mol.-% EUA^{-} Na^{+}, 9 ± 0.9 mol.-% MEU, and 90 ± 1 mol.-% BO (10% hydrolyzed).

Table 3. Hydrolysis of P(MEU-co-BO)[a]



$-(-CH_2-CH(C_2H_5)-O-)-(-CH_2-CH((CH_2)_8-COOCH_3)-O-)-$

Copolymer	Time	Percent hydrolysis	n_{inh} (dL/g)	Yield (%)	Precipitation Reaction Mixture
1. $x = 0, y = 0.090, z = 0.910$	2 h 45 min	100	0.91[b]	85	+
2. $x = 0.045, y = 0.045, z = 0.910$	1 h 20 min	50	0.80[b]	60	+
3. $x = 0.072, y = 0.018, z = 0.910$	32 min	20	—	50	–
4. $x = 0.081, y = 0.009, z = 0.910$	15 min	10	—	50	–

[a] Reaction conditions: 1,4-dioxane, 100ºC, 10 mL of 4 *N* aqueous sodium hydroxide solution.
[b] 0.5% in water, 30ºC.

The IR spectra of all four ionomers showed the characteristic C—O stretching frequency for the poly(alkylene oxide) backbone near 1110 cm^{-1}. Differences in the frequency and intensity of the carbonyl stretch (C=O) can also be observed by comparing the spectra. The carbonyl stretching frequency of the starting P(MEU-*co*-BO) appears at 1740 cm^{-1}. P(EUA$^-$Na$^+$-*co*-BO) (100% hydrolyzed), obtained by the hydrolysis of P(MEU-*co*-BO), showed a strong carboxylate anion stretch at 1560 cm^{-1}. Poly(EUA$^-$Na$^+$-*co*-MEU-*co*-BO) (50% hydrolyzed) showed the carbonyl stretching frequency at 1740 cm^{-1} and the carboxylate anion stretch at 1560 cm^{-1}, both of the same intensity. P(EUA$^-$Na$^+$-*co*-MEU-*co*-BO), 20 and 10% hydrolyzed showed, in addition to a strong carbonyl stretching frequency at 1740 cm^{-1}, a weak carboxylate anion stretch at 1560 cm^{-1}, intensities of the carboxylate anion stretch were proportional to the percentage of hydrolysis.

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