Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

POLY(10,11-EPOXYUNDECANOIC ACID), POLY(5,6-EPOXYHEXANOIC ACID), AND SOME OF THEIR DERIVATIVES

Otto Vogl[a][b]; Leszek B. Kiliman[a]
[a] Polytechnic University, 6 MetroTech Center, Brooklyn, NY, U.S.A. [b] Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA, U.S.A.

To cite this Article Vogl, Otto and Kiliman, Leszek B.(2001) 'POLY(10,11-EPOXYUNDECANOIC ACID), POLY(5,6-EPOXYHEXANOIC ACID), AND SOME OF THEIR DERIVATIVES', Journal of Macromolecular Science, Part A, 38: 2, 123 — 135

To link to this Article: DOI: 10.1081/MA-100103338

URL: http://dx.doi.org/10.1081/MA-100103338

J. MACROMOL. SCI.—PURE APPL. CHEM., A38(2), 123–135 (2001)

POLY(10,11-EPOXYUNDECANOIC ACID), POLY(5,6-EPOXYHEXANOIC ACID), AND SOME OF THEIR DERIVATIVES

Otto Vogl* and Leszek B. Kiliman

Polytechnic University, 6 MetroTech Center, Brooklyn, NY 11201

ABSTRACT

The two most accessible ω-undecanoates, 5-hexenoate and 10-undecenoate have been epoxidized to the corresponding 5,6-epoxyhexanoate and improved polymerization techniques have allowed a large-scale production of the polymers. Quantitative hydrolysis made the polymeric acids available for their transformation with diimidazolylcarbonyl to the highly reactive polymeric carboxylic acids imidazolids.

Key Words: Methyl 10,11-epoxyundecanoate; 2,6-Dimethylphenyl 5,6-epoxyhexanoate; Polymerization; Polymeric imidazolids; 10,11-Epoxyundecanoic acid; 5,6-Epoxyhexanoic acid; Polymer reactions.

INTRODUCTION

The discovery of modified metal alkyls, especially triethylaluminum (1–3) but also zinc alkyls (4,5) allowed the extensive studies of the polymerization of epoxides (6,7) and other cyclic ethers. Further improvements of the systems provided initiating systems that also allowed the polymerization of epoxides that also have additional functional groups in the molecule (8–16).

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*Corresponding author: Otto Vog, Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003-4350. E-mail: vogl@polysci.umass.edu

Prime candidates for investigations of reactions on polymers based on acid functions were polymers based on 5,6-epoxyhexanoic acid and 10,11-epoxundecanoic acid. It had been determined that a flexible side chain of at least three methylene groups was necessary to separate the effect of the polymerizable group, and ultimately, the polyoxyethylene backbone chain from the functional groups, the carboxylic acid esters. Of particular interest was the polymerization of ω-epoxyalkanoates, where the polymerizability of the epoxides was not only studied as a function of the number of methylene spacer groups separation of the epoxide from the carboxylic ester function (13,14,17). Copolymerizations of epoxides with ω-epoxyalkanoates were also studied with the objective of synthesizing poly(alkylene oxide) ionomers (17,18).

In the course of the work on copolymers of propane oxide and 1-butane oxide with methyl 10,11-epoxyundecanoate, the initiating system was perfected and at the same time large-scale polymerization techniques developed. This work led to the preparation of amorphous alkylene oxide based ionomers.

It was the objective of this work to prepare homopolymers of 5,6-hexanoic acid and 10,11-undecanoic acid. 5-Hexenoic acid was available from the pyrolysis of ω-caprolactone and 10-undecenoic acid was available commercially, obtained from castor oil. It was the further objective of this investigation to epoxidize the terminal olefinic group of the two esters and to polymerize them. The ultimate objective was to hydrolyze the polymeric esters to the acids and to convert them to the reactive polymeric acid imidazolids (19,20). These polymeric imidazolids were to be the basis for the synthesis of polymeric esters and amides with mesogenic groups, work that will be reported in a subsequent article.

EXPERIMENTAL

Reagents and Solvents

2,6-Dimethylphenyl hexenoate was prepared from 5-hexenoic acid and 2,6-dimethylphenol in the presence of trifluoroacetic anhydride (b.p. 85–95ºC).

10-Undecenoic acid was esterified to methyl 10-undecenoate, which was epoxidized to methyl 10,11-epoxyundecanoate (MEU) with *m*-chloroperoxybenzoic acid.

Diimidazolylcarbonyl (Im_2CO) (19) was obtained from PPG Industries and used as received. It is very sensitive against moisture and must be handled carefully.

Dichloromethane (DCM) was distilled (b.p. 40ºC) from calcium hydride 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 X 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, including *m*-chloroperbenzoic acid, were obtained from Aldrich Chemical Company. Solvents and reagents were used as received.

Measurements

General Procedures and Methods

The 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°C 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.

Microanalyses were carried out by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

Preparations

Poly(5,6-epoxyhexanoic Acid)

Synthesis of 2.6-dimethylphenyl 5.6-epoxyhexanoate (DMPEHx)

A dry 100-mL, one-neck round-bottom (under nitrogen) was charged with m-chloroperoxybenzoic acid (3.8 g; 22 mmols) and 70 mL of dichloromethane and then chilled to 5ºC. A solution of 2,6-dimethylphenyl 5-hexenoate (5 g; 22 mmol) in dichloromethane (10 mL) was added dropwise over a period of 1 h at a temperature of 0 to 5ºC. Shortly after the addition was completed, a white precipitate appeared. After stirring overnight, the precipitate (m-chlorobenzoic acid) was removed by filtration, the filtrate concentrated under reduced pressure. The residue was diluted with a diethyl ether.the solution washed successively with water, a 5% aqueous sodium bicarbonate solution, water, and dried over anhydrous magnesium sulfate. The solution was concentrated and the resulting crude DMPEHx was distilled at 0.05 mm Hg (b.p. 98–101ºC). Polymerization grade DMPEHx was obtained after two distillations (18 g, 44%). The IR spectrum (neat film) showed absorptions at 1740 cm^{-1} (C=O stretch, ester), 910, 830 cm^{-1} (epoxide ring-stretching modes).

Elem. Anal.: Calcd. for $C_{14}H_{18}O_3$: C, 71.79%; H, 7.69%. Found: C, 71.58%; H, 7.52%.

Polymerization of 2.6-dimethylphenyl 5,6-epoxyhexanoate [(Poly(DMPEHx)]

A 125 × 20-mm polymerization tube was charged at room temperature with DMPEHx (1.8 g, 7.7 mmol) and toluene (8 mL) and nitrogen blanketed. The $AI(C_2H_5)_3/H_2O$/AcAc initiator solution (1.3 mL, 0.42 mmol aluminum) was added with a syringe and the mixture left at room temperature. An increase in viscosity was noticed after 1 h; the tube content was gelled the next morning. Polymerization was allowed to proceed for 10 days at room temperature.

After the tube was opened, a mixture of 1,4-dioxane (30 mL) and methanol (3 mL) was added to a polymer gel and gave a highly viscous solution. Additional 70 mL of 1,4-dioxane was added and the mixture was stirred for 12 h, filtered and concentrated to ca. 50 mL. Poly(DMPEHx) was precipitated by a dropwise addition of the residue into acidified methanol (500 mL methanol, 2 mL conc. hydrochloric acid). The precipitate was collected by filtration, the solid was washed with methanol, and dried. The yield of a white, elastomeric Pply(DMPEHx) was 1.2 g (66%). The inherent viscosity of the polymer (0.5% in $CHCI_3$, 30ºC) was 1.5 dL/g. The average molcular weights M_n = 230,000 and M_w = 500,000 (based on polystyrene calibration standards) of poly(MEU) was determined bv gel permeation chromatography in THF solution (0.15 w/v%)(10).

The IR spectrum (thin film) showed absorptions centered at 1740 cm^{-1} (C=O stretch, ester); 1240 , 1198, and 1170 cm^{-1} C-O stretch, methyl ester); and 1105 cm^{-1} (C-O-C stretch, ether).

Elem. Anal.: Calcd. for -(-$C_{14}H_{18}Q_3$-)- C, 71.79%; H, 7.69%
Found: C, 71.47%; H, 7.79%.

Poly(5.6-epoxyhexanoic acid sodium salt)[Poly(EHxA$^{\cdot -}$ Na$^+$)]

A three-neck, 500-mL round-bottom flask with poly(DMPEHx) (9 g, 39 mmols) and was then purged with nitrogen. 1,4-Dioxane (220 mL) was added, and the flask was partially immersed in a 100ºC oil bath. Poly(DMPEHx) dissolved rapidly to a turbid solution. A 4 N aqueous sodium hydroxide solution (27 mL, 0.108 mol OH^-) was added, causing the formation of two phases. The mixture was stirred, the reaction mixture became very viscous, difficult to stir and a white solid began to precipitate. After 2 h, a white solid was collected by filtration and washed with methanol and the polymer was dried. Yield of the poly(EHxA$^-$ Na$^+$) was 5.5 g (92%). The IR spectrum showed absorptions centered at 1565 cm^{-1} (COO^- stretch, carboxylate anion) and 1100 cm^{-1} (C-O-C stretch, ether).

Poly(5,6-epoxyhexanoic acid) [Poly(EHxA]

A three-neck 1-L round-bottom flask was charged under nitrogen with P(EHxA$^-$Na$^+$) (5.5 g, 36 mmols). The polymer was dissolved in distilled water (200 mL) and gave a slightly turbid, viscous solution. Glacial acetic acid (30 mL, 0.53 mol) was added and precipitation of a solid occurred almost immediately. The mixture was stirred for several hours and filtered. the white solid filter cake was washed with water and dried. The yield of poly(EHxA) was 4.2 g (88%). The IR spectrum (thin film) displayed absorptions at 3540-2350 cm^{-1} (O-H stretch, carboxylic acid), 1710 cm^{-1} (C=O stretch, carboxylic acid), 1100 cm^{-1} (C-O-C stretch, ether).

Elem. Anal.: Calcd. for -(-$C_6H_{10}O_3$-)-: C, 55.38%; H, 7.69%
Found: C, 55.56%; H, 7.78%.

Poly(5.6-epoxyhexanoic acid imidazolide) [(PolyImEHxA)]

A 250-mL round-bottom flask under nitrogen was charged with poly(EHxA) (0.8 g, 6 mmol) and DMAc (40 mL) was added directly from the drying column into the reaction flask. After stirring at room temperature for some time, 1,1’-diimidazolyl carbonyl (lm_2CO) (1 g, 6 mmols) was added to the polymer solution. The solution was left at room temperature with stirring for 1–2 h. The imidazolid of poly(Ehx) (Poly(ImEHx) was not isolated and the solution was used for further reactions.

Poly(10,11-epoxyundecanoic Acid)

Polymerization of methyl 10,11-epoxyundecanoate [Poly(MEU)]

A 2-L resin kettle, fitted with a Teflon®-coated magnetic stirring bar, two rubber stoppers, a gas inlet, and an outlet was evacuated to 0.01 mm Hg and carefully flamed-out. After cooling to room temperature, the resin kettle was filled with nitrogen and the procedure was repeated three times. Under the flow of nitrogen, the vessel was charged with MEU (150 mL; 0.6 mol) and toluene (570 mL), and the mixture was purged with nitrogen. $AI(C_2H_5)_3/H_2O$/AcAc initiator solution (98 mL; 31.7 mmol) was then added. The polymerization was allowed to proceed for 3 weeks under a slight nitrogen pressure. Gelation was noticed after 1 day.

The resin kettle was opened, the rubbery material was taken out and cut into small pieces with a pair of scissors. Acidified methanol (1.5 L) (6 mL of conc. hydrochloric acid) was placed in a Waring blender, and the polymer was added piece by piece.

A suspension was obtained which was filtered and washed with methanol; for the last work up a small amount of antioxidant was added. The yield of the crude polymer was 113 g (83%). The inherent viscosity of the polymer (0-5% in $CHCl_3$, 30ºC) was 1.4 dL/g. This corresponds to average molcular weights of poly(MEU) M_n = 193,000 and M_w = 450,000 (based on polystyrene calibration standards) as determined by gel permeation chromatography in THF solution (0.15 w/v%) [10].

The IR spectrum (thin film) showed absorptions centered at 1740 cm^{-1} (C=O stretch, ester); 1240, 1198, and 1170 cm^{-1} (C-O stretch, methyl ester); and 1105 cm^{-1} (C-O-C stretch, ether).

Elem. Anal.: Calcd. for -(-$C_{12}H_{22}O_3$-)-: C, 67.29%; H, 10.28%
Found: C, 67.08%; H, 10.40%

Poly(10,11-epoxyundecanoic acid sodium salt [Poly(EUA^-Na^+)]

A three-neck, 500-mL round-bottom flask charged with poly(MEU) (5.0 g, 23 mmol), was then purged with nitrogen for 20 min. 1,4-Dioxane (120 mL) was added, and the flask was partially immersed in a 100ºC oil bath. Poly(MEU) dissolved rapidly and produced a slightly turbid solution. A 4N aqueous sodium hydroxide solution (15 mL, 0.060 mol OH^-) was added, causing the formation of two phases. After 10 min, the viscosity of the opaque reaction mixture started to increase rapidly, and a white solid began to precipitate. After 1 h, the precipitated polymer was collected by filtration and washed with methanol and dried. The white polymer was a free-flowing powder.

The yield of the poly(EUA^-Na^+) was 4.6 g (89%). The inherent viscosity of the polymer (0.5% in water, 30ºC) was 0.41 dL/g. The IR spectrum (KBr wafer) showed absorptions centered at 1565 cm^{-1} (COO stretch, carboxylate anion) and 1100 cm^{-1} (C-O-C stretch, ether).

Poly(10,11-epoxyundecanoic acid) [Poly(EUA)]

A three-neck 2-L, round-bottom flask was charged with poly(EUA^-Na^+) (40 g, 184 mmols carboxylate groups), flushed with nitrogen, and the polymer dissolved in distilled water (1.2 L); it gave a turbid solution. Glacial acetic acid (240 mL, 4.2 mol) was added which caused a precipitation to a highly swollen solid to occur almost immediately. The mixture was stirred for several hours, then filtered. The white granular solid was washed successively with water, acetone, and then air-dried. Final drying was carried out at 0.01 mm Hg over phosphorus pentoxide. The yield of wax-like poly(EUA) was 35 g (85%). The inherent viscosity of the polymer (0.5% in 1,4-dioxane, 30ºC) was 0. 5 d L/g. The IR spectrum (thin film) displayed absorptions at 3540–2350 cm^{-1} (O-H stretch, carboxylic acid), 1710 cm^{-1} (C=O stretch, carboxylic acid), 1110 cm^{-1} (C-O-C stretch, ether), and 925 cm^{-1} (O-H out-of-plane bending).

Elem. Anal.: Calcd. for -(-$C_{11}H_{20}O_3$-)-: C, 65.97%; H, 10.07%
Found: C, 66.10%; H, 9.92%.

Poly(10,11-Epoxyundecanoic Acid Imidazolid) [Poly(ImEUA)]

A 250-mL round-bottom flask was charged under nitrogen with poly(EUA) (2 g, 9.8 mmols), and DMAc (100 mL) was added directly from the drying column into the reaction flask. After stirring at room temperature until everything was dissolved, lm_2CO (15 mmol) was added (30% excess) to the polymer solution. The solution was left for 2 h at room temperature; The imidazolid of poly(10,11-epoxyundecanoic acid) [poly(lmEU)] was not isolated and the solution was used directly for further reactions.

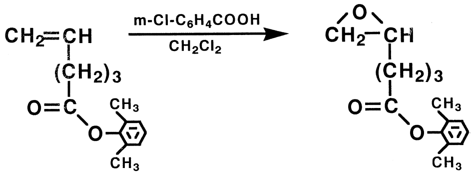
RESULTS AND DISCUSSION

2,6-Dimethylphenyl 5,6-epoxyhexanoate (with three methylene spacer groups between the functional and polymerizable group) and MEU with eight methylene spacer groups were synthesized in substantial quantities. DMPEH and DMPU were homopolymerized using a modified initiator system devised by Muggee and Bansleben. The large-scale polymerization was accomplished in a resin kettle.

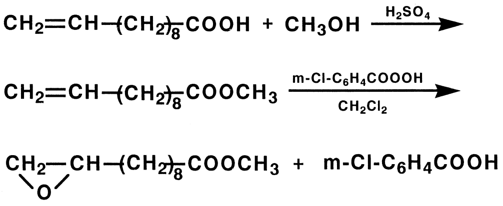
2,6-Dimethylphenyl 5,6-epoxyhexanoate (DMPEH) was prepared according to the reaction scheme presented in Equation 1. 5-Hexenoic acid had been synthesized by pyrolysis of ω-caprolactone at 610ºC (20) by S. Xie; a 30% yield was obtained (~400 g had been prepared). Bailey, in his initial work on the subject had demonstrated that the pyrolysis of caprolactone could produce as much as 50% yield of 5-hexenoic acid. In our hands, 30% yields could be obtained routinely

5-Hexenoic acid was then esterified with 2,6-dimethyiphenol using trifluoroacetic acid as the condensing agent. It had also been reported that the esterification of 5-hexenoic acid with 2,6-dimethylphenol could be successfully carried out through its imidazolyl derivative (20).

In this investigation, a modified procedure for the esterification of 5-hexenoic acid with 2,6-dimethylphenol was used. The reaction vessel was first charged with benzene as a solvent followed by 2,6-dimethylphenol and 5-hexenoic acid. The reaction mixture was cooled with ice/water bath to lower the possibility of the side reactions and trifluoroacetic anhydride was added dropwise from an addition funnel. This sequence of addition yielded (75%) 2,6-dimethylphenyl 5-hexenoate. In the final step of this synthesis, 2,6-dimethylphenyl 5-hexenoate



Equation 1. Synthesis of 2,6-dimethylphenyl 5,6-epoxyhexanoate.



$$CH_2{=}CH{-}(CH_2)_8{-}COOH + CH_3OH \xrightarrow{H_2SO_4}$$

$$CH_2{=}CH{-}(CH_2)_8{-}COOCH_3 \xrightarrow[CH_2Cl_2]{m\text{-}Cl\text{-}C_6H_4COOOH}$$

$$CH_2{-}CH{-}(CH_2)_8{-}COOCH_3 + m\text{-}Cl\text{-}C_6H_4COOH$$

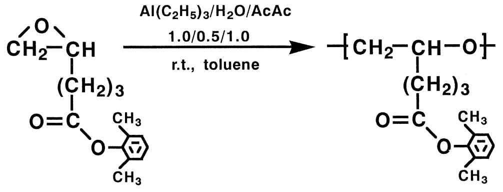
Equation 2. Synthesis of MEU.

was treated with m-chloroperoxybenzoic acid. The procedure used for this epoxidation was similar to the epoxidation of methyl 10-undecenoate described above. Purification and distillation under reduced pressure gave polymerization grade DMPEHX in 44% yield.

MEU was synthesized in two steps outlined in Equation 2. 10-Undecenoic acid (b.p. 137ºC/2 mm) is commercially available in a purity of over 95%. Direct preparation of the methyl ester by acid-catalyzed esterification in excess methanol yielded clear, colorless methyl 10-undecenoate (16) in over 90% yield. Although, of concern, no isomerization of the terminal double bond to an internal position was detected. MEU was obtained in yields exceeding 90%. Similar conditions for the epoxidation of a series of methyl alkenoates containing different numbers of methylene groups in the molecule have been previously reported (13) (Eq. 2).

The polymerization of 2.6-dimethylphenyl 5.6-epoxyhexanoate (DMPEHX) was accomplished in a toluene solution (20%) with 5 mol-% of the $AI(C_2H_5)_3/H_2O/AcAc$ (1.0/0.5/1.0) initiating system (Eq. 3). Polymerizations of methyl 5,6-epoxyhexanoate were reported in the past (14). They were carried out on a small scale in sealed tubes with benzene as a solvent and with $AI(C_2H_5)_3/H_2O/AcAc$ (1.0/0.5/1.0) as the initiating system. The highest yield of an isolated polymer (33%) was found for the polymerization conducted at 65ºC for 6 days. The inherent viscosity of poly(DMPEHx) was 0.37 dL/g (0.5% solution in 1,4-dioxane).

Polymerization of DMPEHx was carried out in a resin kettle with a similar initiating system that had been used for the polymerization of MEHx. A 66% yield of the white, elastomeric poly(DMPEHx) was obtained after 10 days with an inherent viscosity of 1.5 dL/g (0.5% solution in $CHCI_3$, 30ºC). Table 1 shows the results for our polymerizations of MEHx and DMPEHx.



Equation 3. Polymerization of DMPEHx.

Table 1. Polymerizations of MEU

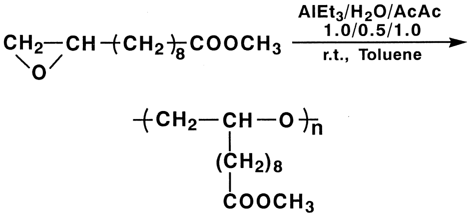
				$Al(C_2H_5)_3/H_2O/AcAc$[a] Initiator			Polymer	
Experiment	Charged monomer (g)	Solvent	Solution conc. (w/v %)	Aging time (days)	mL charged[b]	Polymer. (days)	yield (%)	η_{inh} (dL/g)
1. Seald tube	**14.5**	**Benzene**	**20**	**7**	**10**	**21**	**63**	**1.8**[c]
2. Resin kettle	**135**	**Benzene**	**21**	**7**	**98**	**21**	**83**	**2.4**[d]

[a] Initiator composition: 1 mol $Al(C_2H_5)_3$/0.5 mol H_2O/ 1 mol AcAc.

[b] 5 mole.-% initiator based on MEU.

[c] 0.5% solution in 1,4-dioxane, 30°C.

[d] 0.5% solution in THF, 30°C.



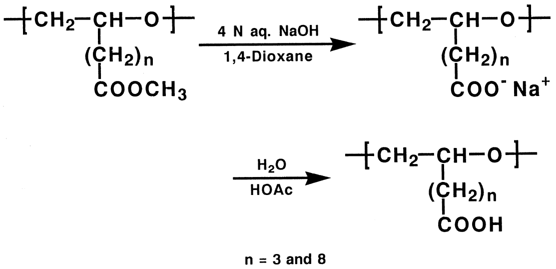
Equation 4. Polymerization of MEU.

MEU was polymerized in toluene solutions (20–25%) with 5 mol-% of the $Al(C_2H_5)_3/H_2O/AcAc$ (1.0/0.5/1.0) initiating system in a resin kettle according to Equation 4. Earlier polymerizations were carried out in sealed tubes, but the scale-up described in this provided quantities of polymers. A 63% yield of polymer was reported for polymerizations conducted in a sealed polymerization tubes. A 83% yield of polymer was obtained after the same period of time when the polymerization was carried out in a resin kettle. Both experiments yielded poly(MEU) with inherent viscosities 1.8 dL/g and 2.4 dL/g, respectively (Tab. 2).

A relative number-average (M_n) and weight-average (M_w) molcular weights were determined by comparing results of the polymerizations with previously established standards (10). Relative to polystyrene calibration standards, the calculated molecular weight averages were: 1) from a sealed tube polymerization the polymer had an inherent viscosity of 1.8 dL/g, a GPC molcular weight of M_n = 250,000 and M_w = 580,000 and the molcular weight distribution (MWD) was 2.32 close to the most probable MWD, and 2) from a resin kettle polymerization the polymer had an inherent viscosity 2.4 dL/g, M_n = 333,000, M_w = 770,000 and the MWD was 2.30.

Poly(5,6-epoxyhexanoic acid) and poly(10,11-epoxyundecanoic acid) were prepared by converting the pendant ester groups of poly(DMPEHx) and poly(MEU) to the sodium carboxylate form as shown in Equation 5.

A 1,4-dioxane solution of poly(DMPEHx) was treated with a 4 N aqueous sodium hydroxide solution (fourfold excess of OH^- to ester), for 2 h at 100ºC.



Equation 5. Synthesis of poly(10,11-epoxyundecanoic acid) (*n* = 8 and poly(5,6-epoxyhexanoic acid) (*n* = 3).

Table 2. Polymerizations of DMPEHx and MEHx

Experiment	Charged monomer (g)	Solvent	Solution conc. (w/v %)	$Al(C_2H_5)_3/H_2O/AcAc$ initiator[b] Aging (days)	$Al(C_2H_5)_3/H_2O/AcAc$ initiator[b] Volume in mL	Polymer. in days	Polymer Yield	n_{inh} (dL/g)
1. Seald tube[a]	**1.0**	**benzene**	**26**	**-**	**0.34**	**6[c]**	**33**	**0.37[d]**
2. Flask[f]	**16**	**toluene**	**20**	**7**	**13**	**28[e]**	**66**	**1.5[d]**

[a] Results for MEHx after refrence (1,4).

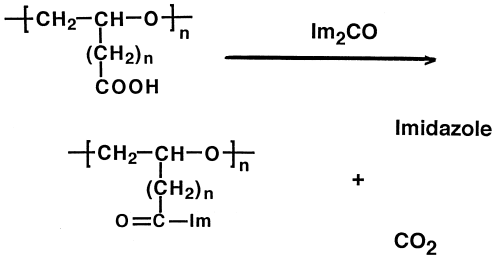
[b] Initiator composition: 1.0 mol.-% $Al(C_2H_5)_3$/0.5 mol.-% H_2O/1.0 mol.-% AcAc.

[c] At 65^{0}C.

[d] 0.5% in 1,4-dioxane, 30^{0}C.

[e] At room temperature.

[f] Results for DMPEHx, open system.



Equation 6. Synthesis of ω-epoxyalkanoic acid imidazolids.

Poly(EHxA$^-$Na$^+$), precipitated from the mixture and was easily recovered, and Poly(EHxA$^-$Na$^+$) was obtained in a yield of more than 90%. Poly(MEU) was also hydrolyzed and gave the sodium carboxylate form in nearly quantitative yield under similar hydrolysis conditions. The presence of metal carboxylate groups along the entire length of the polyether backbone (one carboxylate group/repeating unit) greatly influenced the properties of polymers. In contrast to the ester-substituted poly(alkylene oxide)s, poly(EHxA$^-$Na$^+$) and poly(EUA$^-$Na$^+$) were not elastomeric at room temperature. Poly(EHxA$^-$Na$^+$) is a hard solid and poly(EUA$^-$Na$^+$) is a free-flowing powder. The poly(alkylene oxide) carboxyiate salts were found to be insoluble in all organic solvents but soluble in water (Eq. 5).

Neutralization of the pendant carboxylate salt groups was accomplished with a two-fold excess of glacial acetic acid at room temperature in aqueoius solutions. The use of stronger inorganic or organic acids was not found desirable. Polycarboxylic acid salts and polyacids were characterized by IR spectroscopy.

Polymeric Imidazolids of poly(EHxA) and poly(EUA) were prepared by allowing to react about 10 mmol of poly(EHxA) or poly(EUA) under nitrogen in DMAc (200 mL) solutions with lm_2CO (15 mmol) (30% excess) for 2 h at room temperature (Eq. 6). The polymeric imidazolids of poly(ImEHxA) Poly(ImEUA) were used for further reactions without isolation. This work will be reported in a subsequent article.

ACKNOWLEDGMENTS

This work was supported by the Mark Chair of the Polytechnic University and the National Science Foundation. We are very grateful to Dr. Kania of PPG Industries for providing us with a generous supply of Im_2CO. We are also grateful to S. Xie for the synthesis of 400 g of 5-hexenoic acid. We would like to express our appreciation for the help we obtained from Lyn Roberts during the final preparation of the manuscript.

REFERENCES

1. Furukawa, J.; Saegusa, T. *Polymerization of Aldehydes and Oxides*; Wiley-Interscience: New York, 1963.
2. Vandenberg, E. J. J. Polym. Sci. **1960**, *47*, 486.
3. Vandenberg, E. J. Belg. Patent 579, 074, 1959, to Hercules Co.
4. Furukawa, J.; Tsuruta, T.; Sakata, R.; Saegusa, T.; Kawasaki, A. Makromol. Chem. **1959**, *32*, 90.
5. Furukawa, J.; Tsuruta, T.; Saegusa, T.; Sakata, R.; Kakogawa, G.; Kawasaki, A.; Harada, I. J. Chem. Soc. Ind. Chem. Sec. **1959**, *62*, 1 1269.
6. Gaylord, N. G.; *Polyethers, Part I;* Wiley-Interscience: New York, 1963.
7. *Polyethers,* Vandenburg, E.J., Ed.*;* ACS Symposium Series, No. 6, American Chemical Society: Washington, DC, 1975.
8. Vogl, O.; Muggee, J.; Bansleben, D. Polymer J. **1980**, *12(9)*, 677.
9. Bansleben, D.A.; Janovic, Z.; Vogl, O.J. Polym. Sci.-Polym. Chem. Ed. **1984**, *22*, 3263.
10. Bansleben, D.A.; Hersman, M.J.; Vogl, O.J. Polym. Sci.-Polym. Chem. Ed. **1984**, *22*, 2489.
11. Muggee J.; Vogl, O.J. Polym. Sci.-Chem. Ed. **1984**, *22*, 2501.
12. Bansleben, D.A; Vogl, O.J. Polym-Sci- Polym Chem. Ed**. 1985**, *23*, 673.
13. Muggee J.; Vogl, O.J. Polym. Sci.-Polym. Chem. Ed. **1985**, *23*, 649.
14. Muggee, J.; Vogl, O.J. Polym. Sci.-Polym.Chem. Ed. **1986**, *4*, 2327.
15. Bansleben, D.A. Ph.D. Thesis. University of Massachusetts: Amherst, MA, 1982.
16. Muggee, M. J. Ph.D. Thesis. University of Massachusetts: Amherst, MA, 1982.
17. Vogl, O.; Kiliman, L. B. J. Macromol. Sci.,—Pure & Appl. Chem. **2001**, A38(2).
18. Kiliman, L. B. Ph.D. Thesis. Polytechnic University: Brooklyn, NY, 1993.
19. Staab, H. A.; Wendel, K. Ber. **1960**, *93*, 2910.
20. Staab, H. A.; Lüking, M.; Dürr, F. H. Ber. **1962**, *95*, 1275.

Received August 30, 2000