Polymer Bulletin 7, 513-520 (1982)

Polymer Bulletin

Methyl 5-Epoxyacetylsalicylate

Preparation and Copolymerization

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SUMMARY

Methyl 5-epoxyacetylsalicylate was prepared by epoxidation of methyl 5-vinylacetylsalicylate with m-chloroperbenzoic acid in yields of 70 to 80%. The compound, m.p. 39°-40°C, is difficult to purify and is unstable. Methyl 5-epoxyacetylsalicylate was characterized and its polymerization was attempted. Although no homopolymer could be prepared, methyl 5-epoxyacetylsalicylate could be copolymerized with styrene oxide and propylene oxide with $Et_3Al/H_2O/AcAc$ (1/0.5/1) as the initiator; low yield of copolymer was obtained but good incorporation of methyl 5-epoxyacetylsalicylate was achieved. Polymerization and copolymerization attempts with other initiators, particularly Et_3Al/H_2O and $BF_3 \cdot O(C_2H_5)_2$ were unsuccessful.

INTRODUCTION

Oxirane rings are commonly introduced into organic molecules by epoxidation of a double bond. Such epoxidations, even in rather complicated molecules highly substituted with functional groups, proceed readily especially when the double bond is electron rich. The opening of such oxirane rings, particularly by nucleophiles, is a common reaction.

Polymerization of ethylene oxide (oxirane) and alkyl substituted (terminal) oxiranes, such as propylene oxide, butene-1 oxide and internal epoxides, such as butene-2 oxide has been extensively studied. Oxiranes substituted with more polar groups, such as chloromethyl groups (epichlorohydrin or 1,4-dichlorobutene-2 oxide) or glycidyl ethers have also been polymerized (FURUKAWA, SAEGUSA 1963). These monomers are readily polymerized with acids and bases, but high molecular weight was often achieved only with modified aluminum alkyl and zinc alkyl initiator systems (FURUKAWA, SAEGUSA 1963).

More recently, systematic investigations have been undertaken to prepare functionally substituted epoxides and to study their polymerization and copolymerization (VOGL et al. 1982) (MUGGEE 1982) (VOGL et al. 1980). It was found that glycidate esters could be copolymerized with trioxane (MARTIN, VOGL 1966) (DEMEJO et al. 1978) (DEMEJO et al. 1979) and with other cyclic

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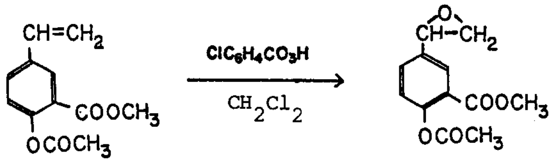
ethers (SAEGUSA et al. 1979) (TIRRELL et al. 1980). For homo- or copolymerization of functionally (carboxylate) substituted epoxide to occur effectively, a spacer group had to be introduced between the reactive epoxide and the carboxylate group. These methyl ω-epoxy alkanoates (terminal epoxides) were synthesized, polymerized and copolymerized (even with ethylene oxide) when a spacer of three methylene groups separated the epoxy and the carboxylate group (VOGL et al. 1982). Terminal epoxides with functional groups more complicated than a carboxylate group have not been prepared nor has their polymerization or copolymerization been studied.

In our studies of the polymerization of polymerizable ultraviolet absorbers, or polymerizable compounds with biologically active groups, we have studied extensively polymerizable vinylsalicylic acid derivatives. Three isomers of vinylsalicylic acid (3-vinyl-, 4-vinyl-, and 5-vinyl-) were prepared and their polymerization was investigated (IWASAKI et al. 1980) (TIRRELL, VOGL 1980) (BAILEY et al. 1976). Most intensively studied were the derivatives of 5-vinylsalicylic acid (BAILEY et al. 1976).

It was the objective of this work to prepare the epoxide of methyl 5-vinylacetylsalicylate (Equation 1), to characterize the compound and to attempt polymerization and copolymerization with other epoxides such as styrene oxide (StO) and propylene oxide (PO) and to characterize briefly these polymers.



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EXPERIMENTAL PART

Materials

All chemicals (reagent grade) were obtained from Aldrich Chemical Co.; they were used as received unless stated otherwise.

Benzene and dichloromethane were washed and then dried. Benzene was then heated to reflux over potassium-sodium alloy, dichloromethane over calcium hydride, and distilled before use. Diethyl ether and n-pentane were heated to reflux over metallic sodium, distilled and stored over molecular sieves. m-Chloroperbenzoic acid was used as received.

Propylene oxide (PO) was heated to reflux over calcium hydride for 3 hours and distilled just before use. Styrene oxide (SO) and acetylacetone (AcAc) were distilled at 20 mm immediately before use. Methyl 5-vinylacetylsalicylate (M5VAS) was prepared according to the literature (BAILEY et al. 1976).

Measurements

Infrared spectra were measured on a Perkin Elmer 727 spectrophotometer on polymer films cast on sodium chloride plates. Peak assignments were made to the nearest 5 cm^{-1}. ^{1}H NMR spectra were recorded on a 60 MHz A-60 Varian Spectrometer in $CDCl_3$.

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

Preparations

Methyl 5-Epoxyacetylsalicylate (MSO). In a 3-neck, round bottom flask, cooled in an ice bath and equipped with a thermometer, stirrer and drying tube, m-chloroperbenzoic acid (29 g, 0.17 mole) was dissolved in dichloromethane (400 ml). M5VAS (28 g, 0.13 mole) dissolved in 50 ml of dichloromethane was added dropwise with stirring over a period of 20 min. while the temperature of the reaction mixture was maintained between 3 and 5^{o}C. After 2 hours the ice bath was removed and the reaction was allowed to continue at room temperature for one day. The solution was decanted from the precipitate, washed successively with solutions of 5% of sodium bisulfite, 2% of sodium carbonate, and water until the reaction mixture was neutral; after drying the solution over magnesium sulfate, it was concentrated at room temperature (20 mm). After two days in the freezer (-20°C) the colorless residue solidified to give 26g (87%) of crude MSO, m.p. 36°-40°C.

Purification of Methyl 5-Epoxyacetylsalicylate. Crude MSO (26 g, 0.11 mole) was treated with 500 ml of anhydrous diethyl ether/n-pentane (1:1), the solution was decanted from a small amount (1.5 g) of an insoluble, colorless oil and transferred into a 3-neck flask which was fitted with a 3-way stopcock. The flask was purged with nitrogen and immersed in a dry ice/acetone bath whereby MSO precipitated as a white solid. After one hour the supernatant solution was removed with a syringe and the recrystallization repeated two more times. The residual crystalline solid was dried for 12 hours (0.03 mm, room temperature) and gave 9.2 g (35%) of pure MSO, m.p. 39°-40°C.

ANAL. CALC. for $C_{12}H_{12}O_5$: C, 61.02%; H, 5.12%. Found: C, 61.06%; H, 4.96%. The IR spectrum in CCl_4 showed absorption bands at 895 and 850 cm^{-1} (epoxide) and at 1775 and 1730 cm^{-1} (acetyl and ester carbonyl). The absorption bands at 1620 and 890 cm^{-1} (vinyl), present in M5VAS, had disappeared. The ^{1}H NMR spectra ($CDCl_3$) showed: $\delta = 2.35$ ppm ($\underline{CH_3}CO$, triplet); $\delta = 3.88$ ppm ($COO\underline{CH_3}$, triplet). Superimposed on these chemical shift peaks are $\delta = 2.50$-4.00 ppm (epoxy protons, triplet); $\delta = 6.90$-8.00 ppm (aromatic protons).

Polymerizations with $Et_3Al/H_2O/AcAc$ as Initiator: The system $Et_3Al/H_2O/AcAc$ (1/0.5/1) was used for initiation; the following general procedure was followed for the polymerization experiments: A polymerization tube was charged with a 10% solution of MSO (and/or StO, PO) in benzene and degassed by three freeze-thaw cycles. The ethereal solution of freshly prepared initiator was then added, and the polymerization tube sealed at 0.01 mm; after 2 weeks at room temperature the tube was opened and the contents worked up as described for each of the following experiments.

Attempted Homopolymerization of Methyl 5-Epoxyacetylsalicylate (MSO): A benzene (12 ml) solution of MSO (1.18 g, 5 mmole) and $Et_3Al/H_2O/AcAc$ initiator system (0.25 mmole in 0.26 ml, 5 mole %) were allowed to react for 2 weeks; the reaction mixture was diluted with 50 ml of benzene, washed successively with 0.02 N HCl and water and poured into 600 ml of methanol. Since no precipitation of polymer occured, the solvent was evaporated; unchanged starting material (MSO) was recovered.

Copolymerization of Methyl 5-Epoxysalicylate (MSO) with Styrene oxide (StO) [Poly(StO-co-MSO)]: StO (1.20 g, 10 mmole) and MSO (1.18 g, 5 mmole) in benzene (25 ml) were allowed to react in the presence of $Et_3Al/H_2O/AcAc$ (0.75 mmole, 0.77 ml, 5 mole %). After 2 weeks the contents of the polymerization tube were diluted with 50 ml of benzene and poured slowly into 800 ml of 0.01 N methanolic HCl. A white polymer precipitated and was isolated by filtration. After washing the product with methanol it was redissolved in benzene and reprecipitated in methanol to give 0.21 g (9% yield) of copolymer.

The inherent viscosity of the material in benzene (0.2%, 22°C) was 1.2 dL/g. The IR spectrum showed absorption bands at 1775 and 1730 cm^{-1} (carbonyl group) (Figure 1).

ANAL. CALC. for $-\!\!(C_8H_8O)\!\!-_{0.77}-\!\!(C_{12}H_{12}O_5)\!\!-_{0.23}$. C, 75.62; H, 6.39. Found: C, 75.65; H, 6.54.

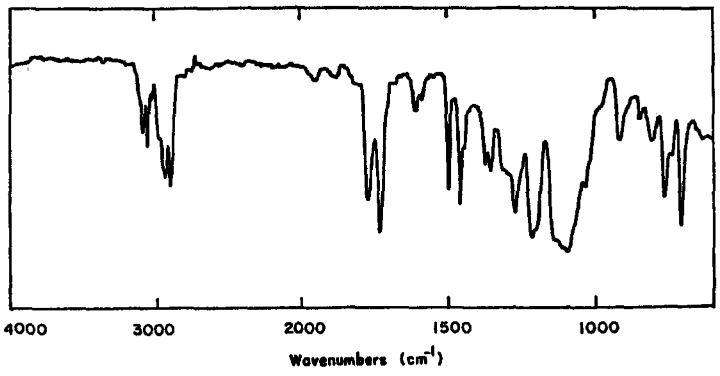


FIGURE 1: IR Spectrum of Poly(MSO-co-StO)

Copolymerization of Methyl 5-Epoxyacetylsalicylate (MSO) with Propylene Oxide (PO). [Poly(PO-co-MSO)]: PO (1.16 g, 20 mmole) and MSO (1.18 g, 5 mmole) in benzene (25 ml) were allowed to react in the presence of $Et_3Al/H_2O/AcAc$ (0.125 mmole, 1.29 ml, 5 mole %); after 2 weeks the reaction mixture had become viscous. The mixture was diluted with 50 ml of benzene, and the solution poured slowly and with stirring into 800 ml of 0.01 N methanolic HCl. A small amount of a white polymer precipitated; the mixture was filtered, the solid washed with methanol, redissolved in benzene and reprecipitated in methanol to give 0.12 g (5% yield) of copolymer A. The methanol solutions were concentrated and poured into water. Polymer B, a yellow, greasy appearing product, was isolated (0.38 g, 16%). The inherent viscosity of the polymers in benzene (0.2%, 22°C) was 2.1 dL/g for polymer A and 0.8 dL/g for polymer B. Elemental analysis confirmed that A was a copolymer of StO and MSO with 60 mole % of MSO incorporated.

ANAL. CALC. for $\text{-}\!\!(C_3H_6O)_{0.40}\text{-}\!\!(C_{12}H_2O_5)_{0.60}\text{-}$: C, 61.42; H, 7.24. Found: C, 61.31; H, 7.26.

IR spectra revealed that polymer B had a higher proportion of PO in the copolymer than A and that a significant amount of the MSO component had been deacetylated (Figure 2). Total yield of copolymers A and B was 0.50 g, 21%.

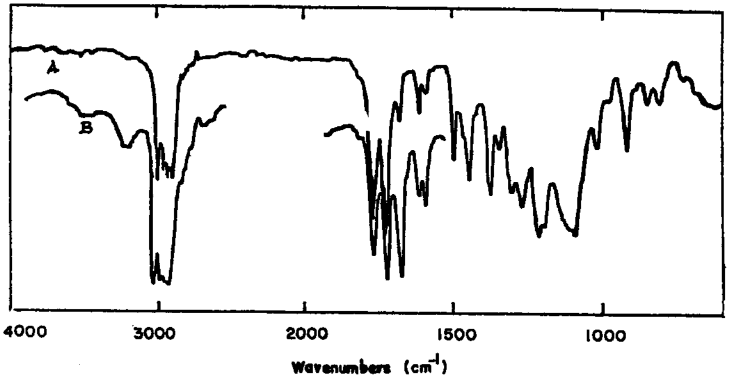


FIGURE 2: IR spectrum of Poly(MSO-co-PO)
(A) Fraction A; (B) Fraction B

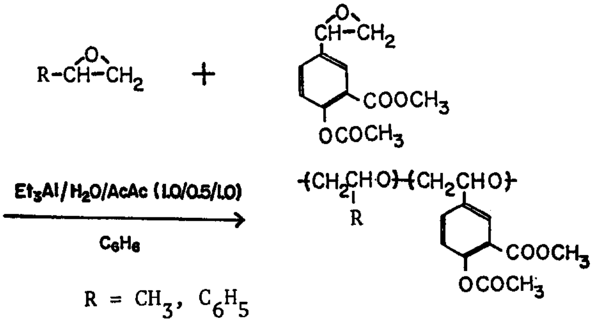
<u>Copolymerization of Styrene Oxide (StO) with Propylene Oxide (PO)</u>. <u>[Poly(StO-co-PO)]: StO (1.20 g, 10 mmole) and PO (1.16 g, 20 mmole)</u> in benzene (25 ml) were allowed to react in the presence of $Et_3Al/H_2O/AcAc$ (1.5 mmole, 1.55 ml, 5 mole %). After 2 weeks the reaction mixture was diluted with benzene and the solution poured into 800 ml of 0.01 N methanolic HCl. A white, solid precipitated and was isolated by filtration; the polymer was washed with methanol, redissolved in benzene and reprecipitated in methanol to give 1.47 g (62% yield) of poly(StO-co-PO). The inherent viscosity in benzene (0.2%, 22°C) was 1.5 dL/g and, based upon elemental analysis, had 50 mole % of StO incorporated.

ANAL. CALC. for $-(C_8H_8O)_{0.5}-(C_3H_6O)_{0.5}-$: C, 71.02; H, 8.59. Found: C, 71.38; H, 8.69.

RESULTS AND DISCUSSION

Methyl 5-epoxyacetylsalicylate (MSO) was synthesized in a yield of 70-80% by epoxidation of 5-vinylacetylsalicylate with m-chloroperbenzoic acid (Equation 1). Purification of the product by distillation was not successful yielding partially deacetylated material; however MSO (m.p. 39°-40°C) could be purified by dissolving it in diethyl ether/n-pentane and cooling the solution to -78°C. MSO is not very stable; even in pure, dry form and stored in the refrigerator it undergoes some decomposition and possibly oligomerizes as judged by the IR spectrum of MSO after storage. An odor of acetic acid was always noticeable on opening vials containing MSO which had been stored for a few days. Therefore, MSO was always freshly prepared from M5VAS prior to its use in polymerization experiments.

Attempts to homopolymerize MSO were not successful but it could be copolymerized with StO and PO with $Et_3Al/H_2O/AcAc$ (1.0/0.5/1.0) as initiator (Equation 2). With 33 mole % of MSO in the monomer feed and StO as the comonomer, a copolymer of MSO and StO with 23 mole % of MSO incorporated could be isolated in 9% yield. In an analogous reaction with PO and 20 mole % of MSO as the comonomer, two distinctly different fractions of poly(PO-co-MSO) were isolated in a combined yield of 21%. Fraction A was not soluble in methanol and had 60 mole % of MSO incorporated while Fraction B was soluble in methanol. The IR spectrum showed that at least part of the MSO-moiety had been deacetylated in Fraction B (Figure 4). Poly(StO-co-MSO) appears to be glassy but poly(PO-co-MSO) was quite flexible; both polymers were tough enough to form films by solvent casting. The inherent viscosities of these copolymers ranged from 1 to 2 dL/g.



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For comparison, the homopolymerizations of StO and PO and the copolymerization of StO with PO were investigated with the same initiator systems as used for the copolymerization of MSO with StO or PO; poly-StO was obtained in 46% yield and had an inherent

TABLE 1: Homo- and Copolymerizations Initiated with $Et_3A/H_2O/AcAc$ (1.0/0.5/1.0)

Solvent: Benzene; Reaction Time: Two Weeks; Reaction Temperature: 25°C

Polymer		Feed of Monomer, in g (mmole)			Initiator[a] in ml (mmole)	Benzene in ml	$[\eta]$, in dL/g[c]	Yield, in g (%)	Incorp. in mole %
		MSO	StO	PO					
Poly(MSO)		1.18(5.0)	--	--	0.26(0.25)	12	—	none	—
Poly(StO)		--	2.40(20.0)	--	1.02(1.0)	24	2.6	1.11 (46)	100 StO
Poly(PO)		--	--	2.32(40.0)	2.04(2.0)	23	8.2	2.32 (100)	100 PO
Poly(MSO-co-STO)		1.18(5.0)	1.20(10.0)	--	0.77(0.75)	22	1.2	0.21 (9)	23 MSO
Poly(MSO-co-PO)[b]	(A)	1.18(5.0)	--	1.16(20.0)	1.29(1.25)	24	2.1	0.12 (5)	60 MSO
	(B)						0.8	0.38 (16)	
Poly(StO-co-PO)		--	1.20(10.0)	1.16(20.0)	1.55(1.5)	24	1.5	1.47 (62)	50 StO

[a] 0.97 mmole/ml in diethyl ether

[b] (A) methanol - insoluble fraction
(B) methanol - soluble fraction

[c] 0.2% in benzene, 22°C

viscosity of 2.5 dL/g; poly-PO was obtained in quantiative yield with high inherent viscosity. The copolymer of StO with PO was obtained in 62% yield; with a monomer feed 33 mole % of StO, the sample of poly(StO-co-PO) had 50 mole % of StO incorporated. The inherent viscosity of poly(StO-co-PO) was 1.5 dL/g (Table 1).

Homopolymerization of MSO and its copolymerization with PO or StO in CH_2Cl_2 (room temperature) and with typical cationic initiator systems were also briefly investigated. The system Et_3Al/H_2O (1/0.5) did produce oligomers of MSO but no high polymers. $BF_3 \cdot O(C_2H_5)_2$ was not effective in initiating either oligomerization or homopolymerization of MSO. This cationic system also gave homopolymers of PO only in low yield (20%) and of low molecular weight but did not produce copolymers of PO with MSO.

Acknowledgements: This program was initiated when O.V. was a Senior Fellow and Visiting Professor at Kyoto University, Kyoto, Japan as recipient of the Senior Scientist Fellowship Award by the Japan Society for the Promotion of Science. The work was in part supported by the Unitika Chemical Company and the Materials Research Laboratory of the University of Massachusetts. T.K. would like to express his appreciation to the Unitika Company for granting him a leave of absence to work at the University of Massachusetts. We would like to express our appreciation to Paula Loeffler for her assistance in the preparation of this manuscript.

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Accepted May 28, 1982
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(Received at Springer June 18, 1982)