$\Delta H_3 = 0.97$ kcal/mole

polymer (solid) $\longrightarrow$ monomer (liquid)

$\Delta H_4 = \Delta H_2 - \Delta H_3 = 4.92$ kcal/mole

Volume Changes. For butyraldehyde d^{20}_4 is 0.802.[15] The density of a polymer film (cast from methylene dichloride) was determined as d^{20}_4 0.970 by noting its ability to sink or float in

known methanol–water mixtures whence $\Delta V_0 = -15.5$ cc/mole. Compressibilities were measured in a mercury-displacement pie-zometer similar to that of Newitt and Weale.[16] Butyraldehyde was measured directly, and the polymer by comparing the compressi-bility of methanol alone with that observed when a known weight of polymer film was placed in the piezometer, and the remainder filled with methanol. Observed molar volumes at 9000 atm were 72.4 and 64.0 cc/mole for monomer and polymer, respectively, whence $\Delta V = -8.4$ cc/mole.

(15) T. E. Smith and R. F. Bonner, Ind. Eng. Chem., 43, 1170 (1951). Several standard references give d^{20}_4 0.8170 apparently as reported by J. W. Bruhl, Ann., 203, 18 (1880).

(16) D. M. Newitt and K. E. Weale, J. Chem. Soc., 3092 (1951).

Preparation and Polymerization of cis- and trans-Dideuterioethylene Oxides

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Abstract: In order to provide further information on the mechanism and stereochemistry of epoxide polymeriza-tion, cis- and trans-dideuterioethylene oxides have been prepared and polymerized by cationic, anionic, and coordi-nation catalysts. The infrared spectra of crystalline films of the polymers showed distinct differences depending on the configuration of the monomer. It is concluded that all three polymerization mechanisms must proceed by in-version of configuration at the carbon atom undergoing ring-opening attack.

Vandenberg[1a] has proposed that polymerization of trans-2-butene oxide by a cationic catalyst (triethyl-aluminum–water at $-78°$) and of cis-2-butene oxide by a coordination catalyst (triethylaluminum–water–acetyl-acetone) each proceed with inversion of configuration at the carbon atom undergoing ring opening.[1b]

It seemed of significance to extend these observations to ethylene oxide, to establish whether a similar steric course holds at a primary carbon atom as at a secondary. Furthermore, since ethylene oxide (but not 2-butene oxides) may be readily polymerized by anionic cata-lysts, the stereochemistry of all three major mechanisms of epoxide ring opening polymerization could be cor-related for a single monomer.

This goal has been achieved by the preparation of cis- and trans-1,2-dideuterioethylene oxides from the corresponding ethylenes.[2] The latter were prepared by known reduction procedures from dideuterioacetylene.
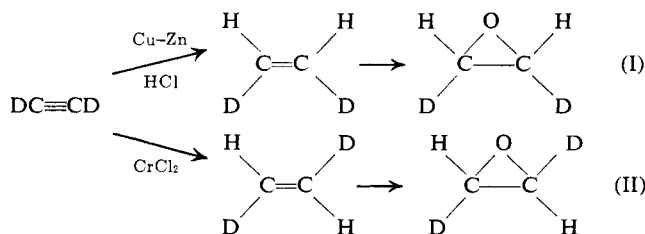
These two monomers were each polymerized by two typical coordination catalysts, ferric chloride–propylene

oxide[3] and diethylzinc–water,[4] by a cationic catalyst, triethylaluminum–water,[1,5] and by two anionic cata-lysts, solid potassium hydroxide[6] and potassium t-butoxide in dimethyl sulfoxide.[7] The results are summarized in Table I.

Table I. Bulk Polymerization of Deuterated Ethylene Oxides

Monomer	Catalyst	Yield, g	Intrinsic viscosity	Av mol wt[a]
cis-DEO	AlEt$_3$–H$_2$O	0.30	0.39	27,000
	ZnEt$_2$–H$_2$O	0.75	0.65	60,000
	FeCl$_3$–PO	0.33	0.65	60,000
trans-DEO	AlEt$_3$–H$_2$O	0.60	0.30	16,000
	ZnEt$_2$–H$_2$O	0.68	0.61	56,000
	FeCl$_3$–PO	0.60	1.34	214,000
	KOH	0.45	0.25	13,000
	K-t-BuO in DMSO	0.63	0.43	32,000

[a] $[\eta] = 9.8 \times 10^{-4} M^{0.59}$.

The stereochemistry of the monomer units in the polymers was revealed by their infrared spectra in their crystalline films. Polymers derived from the cis monomer all had essentially identical spectra, regardless of which catalyst system was used for their preparation. The same was true for all polymers derived from the trans monomer. The marked differences between the

(1) (a) E. J. Vandenberg, J. Am. Chem. Soc., 83, 3538 (1961); J. Polymer Sci., B2, 1085 (1964); (b) see E. J. Vandenberg, "The Organolithium Cleavage of Aliphatic Polyethers," Abstracts, IUPAC Polymer Symposium, Tokyo, 1966.

(2) (a) W. Traube, Ber., 49, 1962 (1916); (b) S. Ikeda, private com-munication; (c) R. L. Arnett and B. L. Crawford, J. Chem. Phys., 18, 118 (1950).

(3) M. E. Pruitt and J. B. Baggett, U. S. Patent 2,706,181 (April 12, 1955).

(4) J. Furukawa, T. Tsuruta, R. Sakata, T. Saegusa, and A. Kawasaki, Makromol. Chem., 32, 90 (1959); J. Polymer Sci., 36, 541 (1959).

(5) R. O. Colclough and K. Wilkinson, ibid., C1, 311 (1963).

(6) L. E. St. Pierre and C. C. Price, J. Am. Chem. Soc., 78, 3432 (1956).

(7) C. C. Price and D. Carmelite, ibid., 88, 4039 (1966).

**Table II.** Infrared Absorption Maxima of Deuterated Polyethylene Oxides

| Poly(cis-DEO)		Poly(trans-DEO)	
Cm⁻¹	Rel absorption	Cm⁻¹	Rel absorption
3550	Medium	3550	Medium
2920	Very strong	2920	Very strong
2380	Medium to strong	2380	Medium to strong
2150	Strong	2150	Strong
1400	Weak (shoulder)	1380	Medium
1370	Medium (shoulder)	1340	Strong
1330	Strong	1330	Strong (shoulder)
1300	Medium (shoulder)	1300	Medium
1275	Medium	1160 to 1100	Very strong
1180 to 1100	Very strong		
		1060	Strong
1010	Strong	990	Decreasing intensity
		975	
985	Strong	950	
935	Medium	890	Medium
860	Medium	860	Medium
795	Weak	800	Medium
740	Medium	745	Medium

two types of spectra can be seen from an examination of Table II.

Since the marked differences in spectra largely disappear in solution, it seems clear that they arise from a different disposition of hydrogen and deuterium in the crystalline arrangement. We conclude, therefore, that all polymers from cis monomer have the same configuration at the two asymmetric carbons, and that this is different from the configuration in all the polymers from trans monomer.

Since there is abundant evidence that base attack on epoxides is bimolecular and proceeds by an SN2 process involving inversion of configuration at the atom being attacked,[8] we assume that the same will be true for the base-catalyzed propagation step in anionic polymerization. Thus the cis (meso) monomer will give dl units in polymer and the trans (dl) monomer will give meso units.

cis(meso) → (dl)

trans (dl) → (meso)
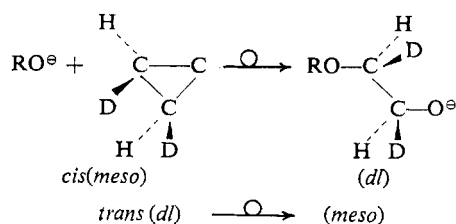
On the basis of this assumption, the cationic and coordination catalysts also proceed by inversion of configuration at the carbon atom undergoing attack, as had been previously proposed by Vandenberg[1] for 2-butene oxide polymerization by similar catalyst systems.
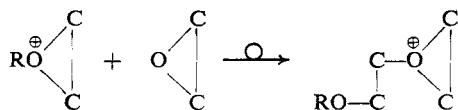
There has been some speculation in the literature that coordination propagation might occur at a single metal

(8) R. E. Parker and M. S. Isaacs, Chem. Rev., 59, 758 (1959).

atom center.[9] It would seem difficult to explain an inversion mechanism in such a system, although, if propagation indeed occurred by such an SNi-like process, retention of configuration might be expected. The fact that inversion is indeed the observed steric course seems to require that at least two separate metal sites are involved. A partial model for the transition state in propagation which appears to meet the presently known facts is represented below.
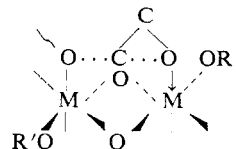
The presence of the hindered, asymmetric bornyl group at R′ could explain the optical selectivity of the diethylzinc–D-borneol catalyst reported by Tsuruta.[10]

Experimental Section

cis-Dideuterioethylene was prepared by reducing 5 l. of dideuterioacetylene with copper-activated zinc and hydrochloric acid by vigorous stirring for 3 days.[2a] The product, collected in a liquid nitrogen trap, amounted to 5–7 ml.

trans-Dideuterioethylene was prepared by reducing 5 l. of dideuterioacetylene with aqueous chromous chloride by stirring for 2 hr[2b] to give 5–6 ml (77–90%) of product.

Bromohydrin was prepared by slow simultaneous addition of liquid bromine and gaseous dideuterioethylene to a well-stirred aqueous solution. The reaction mixture was saturated with potassium chloride and extracted with ether; after drying, distillation gave 3–5 g (10–15%) of bromohydrin, bp 47–51° (15 mm).

Ethylene oxide was obtained by treatment of the bromohydrin with 25% aqueous alkali. The product, collected in a liquid nitrogen trap, amounted to ca. 1 g (60%). The infrared spectra are summarized in Table III.

Table III. Infrared Spectra of 1,2-Dideuterioethylene Oxides in Carbon Tetrachloride

trans		cis	
Cm⁻¹	% absorption	Cm⁻¹	% absorption
2980	80	3060	75
2700	85		
2220	40	2260	70
1710	20	1720	5
1600	10	1600	15
1470 (sh)	15		
1435	30		
1370	65	1385	40
1340	40	1340	10
1290	15		
1220	45	1235	70
1190 (sh)	60		
1120	90	1110	15
1070	40	1070	15
1040	25		
950	50	955 (sh)	60
915	10	940	70
880	80	870	75
835	55	850	80

Polymerization of Deuterated Ethylene Oxides. (1) ZnEt₂–H₂O **Catalyst.** A polymerization tube having a ℥ 10/30 joint was

(9) (a) J. Furukawa, "Polymerization of Aldehydes and Oxides," Interscience Publishers, Inc., New York, N. Y., 1963, pp 187–190; (b) C. C. Price and M. Osgan, J. Am. Chem. Soc., 78, 4787 (1956).

(10) S. Inoue, T. Tsuruta, and N. Yoshida, Makromol. Chem., 79, 34 (1964).

flushed with nitrogen several times using a serum cap and syringe needle. A solution of diethylzinc in heptane (225 µl) was added using a syringe with a needle as a vent, followed by 1 µl of water. The capped tube was placed in liquid nitrogen until the contents had frozen. The serum cap was then removed, and the tube was connected to a vacuum system, together with a graduated receiver containing ethylene oxide, still frozen in liquid nitrogen. The system was pumped out to less than 1 mm and degassed several times. The liquid nitrogen bath under the ethylene oxide was replaced with an equilibrium mixture of liquid and solid carbon tetrachloride ($-22°$). The ethylene oxide began to distil into the polymerization tube. It required about 0.5 hr to distil 1 ml (ca. 1 g) of monomer. At the end of this time, the stopcock on the ethylene oxide reservoir was closed, and the liquid nitrogen bath under the polymerization tube was replaced with Dry Ice to prevent condensation of liquid oxygen. The tube was sealed while under reduced pressure, allowed to warm to room temperature, and placed in a bath at $80 \pm 1°$. During a 3- to 4-day period, a white solid gradually formed in the tube. The tube was cooled in Dry Ice and opened using a torch. The white waxy solid was dissolved in hot benzene (10 ml) to which was added a small amount of 2,6-di-t-butyl-p-cresol as an antioxidant. The solution was filtered to remove the suspended catalyst, and the polymer was precipitated by pouring slowly into heptane (200 ml) with stirring. The fibrous polymer collected on the stirring rod. It was pressed dry using filter paper. The yields, intrinsic viscosities, and calculated molecular weights of the polymers appear in Table I.

(2) AlEt₃–H₂O Catalyst. The same procedure was used except that 225 µl of 1.45 M triethylaluminum in heptane and 6 µl of water was used as the catalyst. The polymer was worked up as described in the preceding section.

(3) FeCl₃–Propylene Oxide Complex Catalyst. In a 1-l. round-bottomed flask was placed 200 ml of anhydrous diethyl ether which was kept at 15–30° by intermittent cooling in an ice bath while 40 g (0.25 mole) of anhydrous ferric chloride was added in approximately 5-g increments with swirling to mix and dissolve. When all the solid had dissolved, the solution was filtered using a fritted funnel. A pinch clamp was put on the suction line and opened intermittently to avoid evaporation of the ether. The dark brown ether solution was transferred to a 2-l. three-necked flask fitted with a mechanical stirrer, thermometer, condenser, and separatory funnel. The system was then purged with nitrogen. In the separatory funnel was placed 58 g (1 mole) of propylene oxide, which had been recently dried and distilled from calcium hydride. A drying tube containing calcium chloride was inserted into the top of the funnel. Propylene oxide was added dropwise with stirring and cooling at 15–20° during the addition. The solution was digested for 15 min at room temperature. The volatile products were removed under reduced pressure using a water aspirator and rotary evaporator. When only a viscous dark brown syrup was

left, the temperature was raised to 40° using a water bath to complete removal of volatile material. The syrup was kept in a dry flask. The exact yield was not determined.

Two drops of the catalyst was added into a polymerization tube which had been flushed several times with dry nitrogen. The tube was then placed on the vacuum system, evacuated, and cooled using liquid nitrogen. Ethylene oxide (1 ml) was distilled in as previously described. The polymerization was carried out at 80° for 4 days.

(4) Polymerization of trans-Dideuterioethylene Oxide Using Potassium Hydroxide. Freshly fused potassium hydroxide (0.185 g, 3.3 mmoles) which had been ground under nitrogen was placed in a polymerization tube which was flushed with nitrogen, attached to the vacuum system, evacuated, and cooled in liquid nitrogen. trans-Dideuterioethylene oxide (1 g, 22 mmoles) was distilled in, and the tube was sealed under reduced pressure, allowed to warm to room temperature, and placed in a bath at 80 ± 1° for 48 hr. The tube was opened, and the solid contents were dissolved in 5 ml of benzene with heating. The solution was shaken with Amberlite acid ion-exchange resin until neutral to pH paper. The polymer was precipitated by pouring the filtered benzene solution into 200 ml of heptane with stirring.

(5) Polymerization of trans-Dideuterioethylene Oxide Using Potassium t-Butoxide in Dimethyl Sulfoxide. A solution of potassium t-butoxide (740 mg, 6.7 mmoles) in dimethyl sulfoxide (25 ml) was made up and 1.5 ml of this solution was added to a polymerization tube containing a stirring magnet. The contents of the tube were frozen in liquid nitrogen, and the tube was evacuated. trans-Dideuterioethylene oxide (1 g, 22 mmoles) was distilled in, and the tube was sealed under reduced pressure. The contents of the tube were stirred for 1 week at room temperature, with no evidence of polymerization. The tube was opened and 1.5 ml of catalyst solution was added. Polymerization occurred after 3 days at room temperature. The polymer was isolated as described for the potassium hydroxide catalyst.

Analytical Methods. All viscosity measurements were made at 25 ± 0.1° in benzene using an Ubbelohde dilution-type viscometer (flow time for benzene, 74.5 sec).

Infrared spectra of the monomers and polymers were obtained using a Perkin-Elmer "Infracord" spectrophotometer. One sample of each isomeric polymer was analyzed using a Perkin-Elmer Model 521 spectrophotometer to obtain accurate measurement of absorption maxima, in the region from 700 to 1500 cm⁻¹. These are tabulated in Table II.

The polymer samples were in the form of solid films obtained by dissolving a small amount of the polymer in benzene, placing a few drops of the solution on a sodium chloride disk, and allowing the solvent to evaporate.

The spectra of the monomers were run in carbon tetrachloride solution.