showing disappearance of any $-$OH peak at 3500 cm^{-1} in its infrared spectrum and appearance of a carbonyl group at 1720 cm^{-1}. Polymer stability was followed by molecular weight change in a vapor osmometer. The acetylated polymer showed no degradation in 30 min, conditions under which unacetylated polymer decomposed completely.

A simpler way of preparing stable polymer proved to be polymerization using TTBP catalyst in the presence of acetic anhydride. After 22 hr at 8000 atm polymer was isolated similar in infrared spectrum and stability to that resulting from the ketene treatment. Evidently in the presence of an effective catalyst polymerization proceeds quite rapidly to equilibrium, after which slow acetylation of the end groups takes place, effectively freezing the equilibrium even after pressure is released.

Experimental Section

Materials. "Pure" *n*-butyraldehyde was prepared by washing commercial material with bicarbonate, drying over magnesium sulfate, and fractionating through a packed column, bp 75.3–75.5°, and storing in a dark bottle over Drierite in a drybox. Before use it was "prepolymerized" at 8000 atm for 16–20 hr and unreacted aldehyde distilled on a vacuum line into sealable ampoules. These in turn were opened in a drybox under nitrogen immediately before filling reaction vessels. "Old" butyraldehyde was commercial material used without purification. Parabutyraldehyde was prepared by adding 2 ml of concentrated H_2SO_4 to 100 ml of butyraldehyde. The mixture was allowed to stand 24 hr, washed free of acid with water and bicarbonate solution, dried, and distilled, bp 114–115° (19 mm), n^{25}D 1.4258. Di-*t*-butyl peroxyoxalate was prepared as described by Bartlett[18] and stored as a 10% frozen solution in benzene at $-20°$. Galvinoxyl was prepared as described by Coppinger.[19] Other reagents were commercial materials, purified as necessary by conventional means and purity checked by melting point or other physical properties.

High-pressure techniques were essentially those described previously.[26] Large-scale (5–30 ml) experiments were run in collapsible Teflon vessels as in previous work. For some runs, notably survey experiments on phenol catalysis, smaller vessels were employed constructed of Teflon "spaghetti tube" approximately 36 mm long and 3 mm in internal diameter, the ends closed with Teflon plugs protected in turn from the hydraulic fluid by Neoprene serum caps. These had a capacity of 0.2 ml, and as many as 24 could be placed simultaneously in the pressure system.

Polymer Characterization. Polymer was precipitated with methanol, dissolved in chloroform, and reprecipitated as necessary followed by drying in a vacuum desiccator. It was obtained as a white powder, soluble in aromatic and chlorinated solvents. Infrared spectra were run in CCl_4 and molecular weights, when reported, were obtained in benzene or CCl_4 solution at approximately 50° using a commercial vapor pressure osmometer (Mechrolab, Inc., Mountain View, Calif.). In the experiments listed in Table I, total product was determined by evaporating a weighed aliquot of the reaction mixture to constant weight under vacuum in a rotary evaporator at room temperature. Polymer was determined as methanol-insoluble material, and it and parabutyraldehyde were confirmed by infrared spectra.

Acetylation of polymer with ketene was accomplished by passing ketene from a ketene generator into a stirred benzene solution of polymer at room temperature. Reaction was continued until samples showed complete disappearance of -OH absorption at 3500 cm^{-1}. Acetylation under pressure was achieved by carrying out normal TTBP-catalyzed polymerizations in the presence of a few per cent acetic anhydride.

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[26] C. Walling and J. Pellon, *J. Am. Chem. Soc.*, **79**, 4777, 4786 (1957).

Organic Reactions under High Pressure. XI. The Butyraldehyde–Polybutyraldehyde Equilibrium[1]

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Abstract: The equilibrium between *n*-butyraldehyde and its linear polyacetal has been investigated at 0–20° and pressures of 7000–10,000 atm, and results have been interpreted in terms of a ceiling temperature for the polymerization process. For the equilibrium, with 1 *M* monomer in hexane $\Delta S_p = -29.1 \pm 1$ cal/deg mole and $\Delta V_p = -8.0 \pm 1$ cc/mole in this pressure range. Direct measurement at atmospheric pressure at 20° gives $\Delta V = -15.5$ cc/mole and $\Delta H = -5.07$ kcal/mole. Extrapolation to atmospheric pressure indicates a ceiling temperature of $-75°$ for 1 *M* aldehyde in fair agreement with experiment. The importance of this low value on the polymerization properties of aldehydes and the stabilities of their polymers is discussed.

As shown in the preceding paper of this series,[2] the high-pressure polymerization of *n*-butyraldehyde to a linear polyacetal is a simple acid- (or base-) catalyzed process in which propagation occurs by successive addition of aldehyde to free hydroxyl end groups of a growing polymer chain. Accordingly, propagation steps are freely reversible, and this paper describes a study of the effect of pressure and temperature on the monomer–polymer equilibrium. Our treatment of the results is based upon the concept of ceiling temperature, developed by Dainton and Ivin,[3,4] which they express in the form

$$T_c = \frac{\Delta H_0}{\Delta S_0 + R \ln [M]/[M]_0} \qquad (1)$$

Equation 1 defines a ceiling temperature T_c at which propagation and depropagation of the growing chains in an addition polymerization occur at equal rates. Thermodynamic quantities refer to either the propagation process or the over-all polymerization reaction

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[1] Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

[2] C. Walling and T. A. Augurt, *J. Am. Chem. Soc.*, **88**, 4163 (1966).

[3] F. S. Dainton and K. J. Ivin, *Nature*, **162**, 705 (1948).

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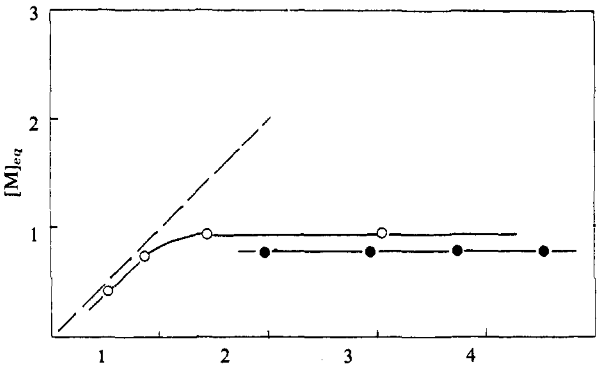

Figure 1. Determination of monomer–polymer equilibrium in butyraldehyde polymerization: ○, 8650 atm, 15°; ●, 9750 atm, 20°.

(equivalent for long chains). Subscript zeros refer to some standard state for the work discussed here taken as 1 M monomer at 1 atm pressure, and the variation with concentration implies ideal solution behavior for the monomer.

If pressure is applied to such a system, a new ceiling temperature is defined

$$T_{c(p)} = \frac{\Delta H_p}{\Delta S_p + R \ln [M]/[M]_0} \tag{2}$$

where subscript p's now refer to a new standard state—1 M monomer at pressure P.

The relation between (1) and (2) may be obtained by inserting the thermodynamic expressions for variation of ΔH with T and P.

$$\Delta H_p = \Delta H_0 + \int_1^P \Delta V \mathrm{d}P - T_p \int_1^P (\partial \Delta V/\partial T)_p \mathrm{d}P + \int_{T_0}^{T_P} \Delta C_p \mathrm{d}T \tag{3}$$

$$\Delta S_p = \Delta S_0 + \int_{T_0}^{T_P} (\Delta C_p/T)\mathrm{d}T - \int_1^P (\partial \Delta V/\partial T)_p \mathrm{d}P \tag{4}$$

Here integrations over temperature are to be performed at $P = 1$ atm, and over pressure at T_p. If these values for ΔH_p and ΔS_p are substituted into (2), terms containing $(\partial\Delta/\partial T)_p$ cancel and we obtain

$$T_{c(P)} = \frac{\Delta H_0 + \int_1^P \Delta V \mathrm{d}P + \int_{T_0}^{T_P} \Delta C_p \mathrm{d}T}{\Delta S_0 + R \ln [M]/[M]_0 + \int_{T_0}^{T_P} (\Delta C_p/T)\mathrm{d}T} \tag{5}$$

where ΔV represents the volume change accompanying polymerization (and is presumably a function of P), and ΔC_p is the difference in specific heat of polymer and monomer.[5]

Since ΔH_0, ΔS_0, ΔC_p, and ΔV are all negative quantities in most polymerizations (sulfur is an interesting exception), we can see from eq 5 that the ceiling temperature rises as either monomer concentration or pressure is increased. Further, as Dainton and Ivin pointed out originally, polymerization is observed only when $T < T_c$ for the particular conditions of pressure and monomer concentrations involved. This general form of the dependence of T_c on pressure and concentration has been already demonstrated for two reversible polymerizations: the anionic polymerization of α-methylstyrene by Kilroe and Weale,[6] and the base-catalyzed polymerization of chloral by Busfield and Whalley.[7]

Results and Discussion

Equilibrium Measurements. Investigation of ceiling temperature phenomena involves determination of monomer–polymer equilibria as a function of temperature and pressure. In spite of the easy reversibility of the polymerization process, quantitative measurements proved more difficult than expected. Experiments with undiluted n-butyraldehyde gave poor reproducibility and inaccurate results. Here polymer was essentially insoluble in monomer so that polymerization either ran to completion or, below the ceiling temperature, failed to occur at all. In addition, reaction (either polymerization or depolymerization) became slower and slower as ceiling conditions were approached. The apparent ceiling temperature was also found to drift owing to slower irreversible competing reactions which consumed and thus diluted monomer. In acid-catalyzed experiments formation of parabutyraldehyde was the complicating process.[2] In experiments catalyzed by triethylamine, formation of butyraldol produced similar difficulties.

In spite of these complications, the reversible nature of the polymerization and its dependence on pressure were plainly evident. Reactions can be followed qualitatively in our equipment by measurement of the slow drift in hydrostatic pressure with time (see Experimental Section). At pressures a few hundred atmospheres above ceiling conditions, pressure dropped slowly indicating polymerization. If the pressure was then dropped below ceiling conditions, depolymerization led to a slow pressure rise. Systems could be recycled repeatedly from polymerization to depolymerization, even though exact ceiling conditions could not be defined accurately for the reasons mentioned above.

Difficulties were effectively overcome by investigating the equilibria using solutions of n-butyraldehyde in an inert solvent (n-hexane) with small quantities of triethylamine as catalyst. In this system the polymer is largely insoluble and remains as a colloidal suspension. As polymerization proceeds, aldehyde concentration drops until it reaches its equilibrium value for the particular pressure and temperature involved as defined by eq 5. The treatment assumes reasonably ideal solution properties for the butyraldehyde–hexane system.

The expected relation between initial and final aldehyde concentrations is illustrated in Figure 1. For aldehyde concentrations below the equilibrium value no change in concentration should occur. With larger amounts concentrations should drop to a (constant) equilibrium value. Any slow irreversible formation of butyraldol might lower points corresponding to low initial aldehyde concentrations, but should yield the same equilibrium concentration if enough aldehyde were

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[5] Except for the assumption about ideality, the derivation given is rigorous; see, for example, K. Denbigh, "The Principles of Chemical Equilibrium," Cambridge University Press, Cambridge, England, 1964, p 96.

[6] J. G. Kilroe and K. E. Weale, *J. Chem. Soc.*, 3849 (1960).

[7] W. K. Busfield and E. Whalley, *Trans. Faraday Soc.*, **59**, 679 (1963).

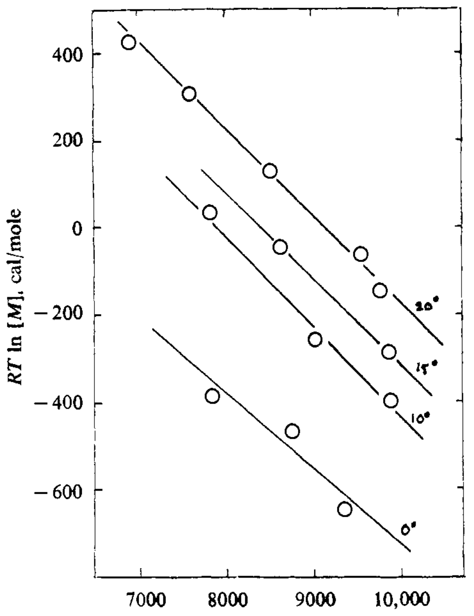

Figure 2. Variation of equilibrium concentration of butyraldehyde with pressure at constant T.

initially present. Experimental points for two typical sets of conditions show that these predictions are verified, and other experiments established that final aldehyde concentrations were independent of reaction times ranging from 50 to 150 hr and changes in catalyst concentrations from 0.18 to 0.36 *M*. This independence and the qualitative reversibility described above make us confident in our results, even though equilibria were approached from only one direction in this set of measurements.

All our results on equilibrium measurements, made in this manner over a temperature range of 0–20° and at pressures of 7000–10,000 atm, are summarized in Table I. As predicted by eq 5, equilibrium monomer concentrations decrease regularly with decreasing temperature and increasing pressure.

Table I. Equilibrium Concentrations of *n*-Butyraldehyde

P, atm	Temp, °C	$[M]_{eq}$, *M*
7810	0	0.49
8750	0	0.42
9370	0	0.30
7840	10	1.07
9020	10	0.63
9900	10	0.48
8650	15	0.92
9860	15	0.58
6910	20	2.09
7600	20	1.70
8520	20	1.25
9570	20	0.90
9750	20	0.78

In the course of the work some observations were also made on the rate of the polymerization process well short of equilibrium. Results fitted an empirical equation indicating a reaction first order in amine and third order in aldehyde, quite different from the autocatalytic nature of the phenol-catalyzed reaction.[2]

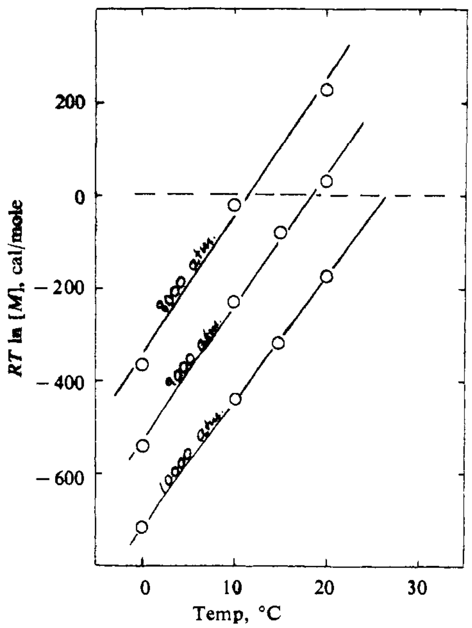

Figure 3. Variation of equilibrium concentration of butyraldehyde with temperature at constant pressure.

Evaluation of Thermodynamic Quantities. If eq 5 is rewritten in the form

$$RT \ln [M]/[M]_0 = \Delta H_0 + \int \Delta V \mathrm{d}P - T\Delta S_0 + \int \Delta C_p \mathrm{d}T - T\int (\Delta C_p/T)\mathrm{d}T \quad (6)$$

it is evident that ΔV may be evaluated by plotting $RT \ln [M]/[M]_0$ *vs.* P for experiments at a single temperature. Figure 2 shows such plots for the data of Table I. Within experimental error plots are linear with no significant temperature dependence and give an average value of $\Delta V = -8.0 \pm 1$ cc/mole (average deviation).

This value is quite different from ΔV_0, the volume change at atmospheric pressure, which may be obtained directly as $\Delta V_0 = -15.5$ cc/mole from density measurements on monomer and polymer. We have also determined compressibility of monomer and polymer. The polymer compressibility in particular is subject to some uncertainty, but the results give $\Delta V = -8.4$ cc/mole at 9000 atm. The good agreement with the slopes of the plots in Figure 2 supports the validity of our equilibrium measurements.

Similarly, from eq 2 ΔS_p may be obtained by plotting $RT \ln [M]/[M]_0$ *vs.* temperature at constant pressure. Data obtained from the smoothed curves of Figure 2 appear in Figure 3. Plots again appear linear and pressure independent, and their intersections with the dashed horizontal line indicate the ceiling temperature for polymerization of 1 *M* *n*-butyraldehyde at various pressures. The average slope corresponds to $\Delta S_p = -29.1 \pm 1$ cal/deg mole (average deviation).

Substitution of $\Delta S_p = -29.1$ cal/deg mole, $T = 291$ °K, $R \ln [M]/[M]_0 = 0$ (data at 9000 atm from Figure 3) into (2) gives $\Delta H_p = -8.5$ kcal/mole. We have also measured ΔH at atmospheric pressure and 293° directly from the heat absorbed on depolymerization of polybutyraldehyde, obtaining $\Delta H = -5.07$ kcal/mole for the conversion of 1 *M* monomer in hexane to polymer, or -4.92 kcal/mole for the conversion of liquid monomer to solid polymer.

Comparison of quantitites measured at atmospheric and high pressure and an estimate of ceiling temperature at atmospheric pressure may be made in several ways, and we proceed as follows. The ceiling temperature at atmospheric pressure may be calculated from an equation similar to (5) with subscript p's replaced by o's and the signs of integrals reversed. If we assume that ΔV varies linearly with pressure from -15.5 cc/mole at 1 atm to -8.0 cc/mole at 9000 atm, $\int \Delta V \mathrm{d}P$, as written in (5), has the value -2.6 kcal/mole. Typical noncrystalline polymers (*e.g.*, polymethyl methacrylate and polystyrene) have ΔC_p for polymerization approximately -0.1 cal/g deg; accordingly we take $\Delta C_p = -7$ cal/mole deg. Using these values, graphical solution of (5) gives $T_{c(0)} = 198$°K for 1 *M* monomer, and the integrals over T have the values $\int \Delta C_p \mathrm{d}T = -650$ cal/mole and $\int (\Delta C_p/T)\mathrm{d}T = -2.7$ cal/mole deg. Evidently they represent only small corrections, the chief change in T_c being due to $\int \Delta V \mathrm{d}P$.[8] ΔH_0 may be calculated *via* (3) from our room temperature value of -5.07 kcal/mole and $\int C_p \mathrm{d}T = -0.65$ kcal/mole as -4.42 kcal/mole. Combining this value with $T_c = 198$° gives $\Delta S_0 = -22.3$ cal/deg mole.

Our previous observation[2] that butyraldehyde is polymerized by hindered phenol catalysts at atmospheric pressure at -100° but not at -80° suggests tht $T_c \leq 193$°K. However, these results refer to pure aldehyde ($R \ln [\mathrm{M}]/[\mathrm{M}]_0 = 4.7$ cal/deg mole). Correcting to 1 *M* gives $T_{c(0)} \leq 164$°K. The 34° discrepancy from the calculated value amounts to a 17% error in $\Delta H_0/\Delta S_0$ as calculated or considerable departure from ideality in the butyraldehyde–polybutyraldehyde system.

The foregoing treatment has obviated any necessity for evaluating $(\partial \Delta V/\partial T)$ in eq 3 and 4. Actually its value is difficult to estimate since it must decrease rapidly with pressure. Substituting $\Delta H_p = -8.5$ kcal/mole, $\Delta H_0 = -5.07$ kcal/mole, and $\int \Delta V \mathrm{d}P = -2.6$ kcal/mole into (3) indicates an average value of 0.013 cc/mole deg at 1–9000 atm, but the estimate is subject to large uncertainty.

Our results and thermodynamic quantities seem consistent with other results in the literature. Polymerization of butyraldehyde with catalyst systems yielding stereoregular crystalline polymer has been reported by Natta[9] to take place at -78°. Since ΔH now includes a heat of fusion, a higher ceiling temperature would be anticipated. The ceiling temperature for undiluted acetaldehyde apparently lies above -40°,[10] but below -35°.[11] Busfield and Whalley[7] obtained $\Delta H = -8.0$ kcal/mole and $\Delta S = -28$ cal/deg mole for chloral polymerization (0.1 mole fraction in pyridine).

For formaldehyde (gaseous monomer at 1 atm pressure) $\Delta H = -12$ kcal/mole,[12] but different measurements[12,13] of ΔS give -30 to -42 kcal/deg mole. Evidently the considerable differences in ceiling temperature for different aldehydes come chiefly from differences in ΔH. The relative stability of formaldehyde polymers compared with those of higher aldehydes thus arises in large part from a more negative value of ΔH. The difference, in turn, has several causes: first, formaldehyde yields a crystalline polymer, so ΔH involves a heat of fusion; second, alkyl substitution increases the strength of the carbonyl π bond (as indicated by heats of hydrogenation). Finally, substitution may introduce some steric crowding along the chain of a noncrystalline polymer. If this last factor is important as is the case in vinyl polymers, ΔH for polyketal formation may actually be positive, and the so-far-unknown polymerization of simple ketones should be observable only at high pressures. Electron-withdrawing groups, on the other hand, destabilize the carbonyl π bond, as shown by the more favorable equilibria for hydration and other addition processes, so ΔH becomes more negative for chloral than for *n*-butyraldehyde.

Finally, it is worth pointing out that the large differences between carbonyl compounds and olefins in both their apparent ease of polymerization and the stabilities of the resulting polymers are as much a matter of polymerization thermodynamics as of reaction mechanism. Although ΔS's are similar,[2] ΔH for most olefin polymerizations lie in the range of -15 to -20 kcal/mole and ceiling temperatures are well above room temperature. Consequently, studies on both polymerization and polymer stability have usually been made under conditions where polymer was thermodynamically stable. However, application of the same conditions to aldehydes and their polymers places them *above* their ceiling temperatures in a region where polymerization cannot occur, and depolymerization becomes a facile acid- or base-catalyzed process.

Experimental Section

Preliminary measurements were made in a variety of Teflon vessels in our high-pressure apparatus, frequently following reaction by pressure change as described earlier.[14] As noted in the Discussion, polymerization was detected by a slow downward drift in pressure, while depolymerization was accompanied by a pressure rise. A large number of such measurements were made. While in qualitative agreement with those described below they are not reported here in detail.

Equilibrium measurements were carried out in our high-pressure apparatus in the small Teflon tubes as described in the preceding paper,[2] using purified aldehyde in *n*-hexane containing freshly distilled triethylamine as catalyst. Equilibrium concentrations were determined by quickly distilling hexane and aldehyde out of the reaction mixture into a cold trap under high vacuum at room temperature, and determining the aldehyde/hexane ratio by gas–liquid partition chromatography (Carbowax 20M column at 80°). The analysis was calibrated with known mixtures, and investigation using synthetic reaction mixtures showed that transfer was quantitative and that samples could be stored in liquid nitrogen until analysis without change in composition.

Heat of depolymerization was measured in a simple adiabatic calorimeter using acetic acid as catalyst and correcting for the heat capacity of the equipment and heat of mixing of acetic acid with hexane. The following quantities were measured.

$$\text{polymer (1 } M \text{ in hexane)} \longrightarrow \text{monomer (1 } M \text{ in hexane)}$$

$$\Delta H_1 = 5.07 \text{ kcal/mole}$$

$$\text{polymer (solid)} \longrightarrow \text{monomer (in hexane)}$$

$$\Delta H_2 = 5.89 \text{ kcal/mole}$$

$$\text{monomer (liquid)} \longrightarrow \text{monomer (in hexane)}$$

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(8) Since liquid compressibilities decrease markedly in the 1–9000-atm range, a plot of ΔV *vs.* P is actually probably concave upward, and in fact our own data (Figure 2) show no detectable change (certainly <2 cc/mole) in ΔV above 7000 atm. Similarly ΔC_p was estimated at room temperature and approaches zero at lower temperatures. Accordingly our estimates of all integrals are large and represent maximum values.

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(14) C. Walling and J. Pellon, *J. Am. Chem. Soc.*, **79**, 4782 (1957).

$$\Delta H_3 = 0.97 \text{ kcal/mole}$$

$$\text{polymer (solid)} \longrightarrow \text{monomer (liquid)}$$

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

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 piezometer similar to that of Newitt and Weale.[16] Butyraldehyde was measured directly, and the polymer by comparing the compressibility 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.

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Preparation and Polymerization of *cis*- and *trans*-Dideuterioethylene Oxides

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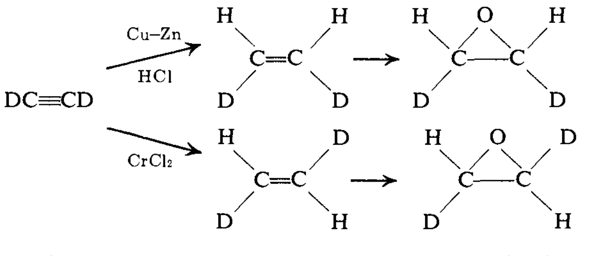
Contribution from the Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104. *Received April 18, 1966*

Abstract: In order to provide further information on the mechanism and stereochemistry of epoxide polymerization, *cis*- and *trans*-dideuterioethylene oxides have been prepared and polymerized by cationic, anionic, and coordination 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 inversion 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 (triethylaluminum–water at −78°) and of *cis*-2-butene oxide by a coordination catalyst (triethylaluminum–water–acetylacetone) 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 catalysts, the stereochemistry of all three major mechanisms of epoxide ring opening polymerization could be correlated 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.



(I)

(II)

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 catalysts, 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_2O	0.30	0.39	27,000
	$ZnEt_2$–H_2O	0.75	0.65	60,000
	$FeCl_3$–PO	0.33	0.65	60,000
trans-DEO	$AlEt_3$–H_2O	0.60	0.30	16,000
	$ZnEt_2$–H_2O	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

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(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.

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