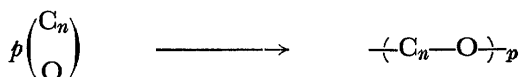


# HIGH POLYMERIZATION OF ALDEHYDES, ALKYLENE OXIDES AND DIKETENE

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The polyethers are polymers which are prepared by "ring-opening" polymerization of carbonyl compounds and cyclic ethers. Ignoring side-chains and hydrogen atoms, these processes may be represented by the general scheme:



When  $n = 1$ , the monomer is an aldehyde or a ketone, and polymerization proceeds by "opening" of the carbonyl group to give acetal or ketal linkages. The "opening" of a carbonyl group ( $n = 1$ ) is different from those of cyclic ethers ( $n \geq 2$ ) in electronic character: in the former case, the ring-opening takes place by the transformation of a  $\pi$ -bond into two  $\sigma$ -bonds, while in the latter case no such change occurs.

In "ring-opening" polymerization, the catalyst has a very important influence on the course of polymerization. With certain catalysts, only low molecular weight polymers are produced, whilst, with others, high molecular weight polymers can be prepared. With a few exceptions, catalysts for the ring-opening polymerization are ionic, and can be classified into three groups: cationic, anionic and co-ordinate anionic. The influence of these catalysts on the polymerization of cyclic ethers, including carbonyl compounds, is illustrated in *Table 1*.

*Table 1.* Activities of various catalysts for the polymerization of cyclic ethers; H indicates the formation of high molecular weight polymer, and M/L the formation of medium or low molecular weight polymer; I indicates that the catalyst is inactive

<i>n</i>	<i>Monomer</i>	<i>Catalyst</i>		
		<i>Cationic</i>	<i>Anionic</i>	<i>Co-ordinate anionic</i>
1	Aldehyde	M/L	M/L	H
2	Ethylene oxide	M/L	M/L	H
3	Cyclo-oxabutane	H	I	M/L(?)
4	Tetrahydrofuran	H	I	I

Both cationic and anionic catalysts induce the polymerization of formaldehyde. Acetaldehyde is polymerized by a cationic catalyst (Lewis acid), or by a co-ordinate anionic catalyst such as an organometallic compound or a metal alkoxide. They give amorphous (atactic) and crystalline (isotactic) polymers respectively. Alkylene oxides can be polymerized by all three

kinds of catalysts, but only co-ordinate anionic catalysts afford high molecular weight polymers. Cyclo-oxabutane and its derivatives, especially the 3,3-bis(chloromethyl)-derivative, are usually polymerized by a typical cationic catalyst. Polymerization of four-membered ring cyclic ethers by alkylmetal compounds and metal alkoxides has been reported recently; these catalysts are probably of the co-ordinate anionic type. Tetrahydrofuran can be polymerized only by a cationic catalyst.

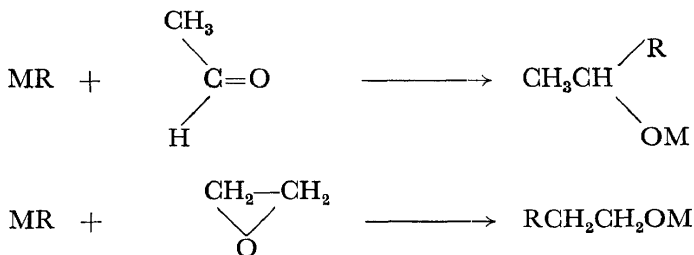
It is very interesting to note that many common catalysts are known for the polymerization of acetaldehyde and ethylene oxide (see *Table 2*).

*Table 2.* Common catalysts for the polymerization of acetaldehyde and ethylene oxide

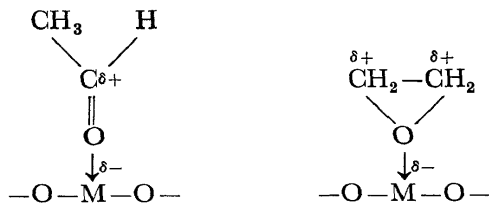
<i>Catalyst</i>	<i>Acetaldehyde</i>	<i>Ethylene oxide</i>
Lewis acid	Very active: atactic polymer	Very active: low mol. wt. polymer
Alumina	Active: atactic polymer	Active: low mol. wt. polymer
Alumina-alkylmetal	Stereo-block polymer	High mol. wt. polymer
Metal alkoxide-H <sub>2</sub> O	Stereo-block polymer	High mol. wt. polymer
Alkylmetal	Isotactic polymer	Less active
Metal alkoxide	Isotactic polymer	Less active

These catalysts, except for the Lewis acid catalysts, are believed to bring about "co-ordinate anionic polymerization", in which a metal-oxygen linkage is an essential feature of the active species.

An alkylmetal compound contains no metal-oxygen linkage, but it produces a metal alkoxide when it reacts with either acetaldehyde or ethylene oxide:

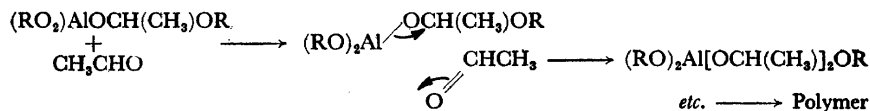


In co-ordinate polymerization, a lone pair of electrons on the oxygen atom of the monomer forms a co-ordinate link with the metal of the catalyst, *e.g.*:



As the result of this co-ordination, the carbon atom of the carbonyl group, or the carbon atoms of the epoxide ring, have a reduced electron density and thus become susceptible to attack by an anion. Propagation proceeds through the transfer of the anion at the end of the growing chain to the

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Similarly, for ethylene oxide:

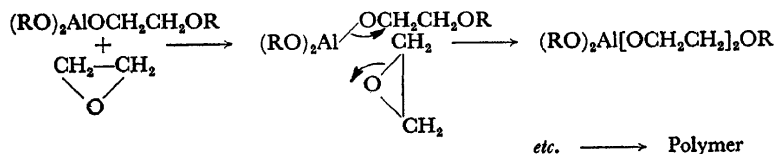
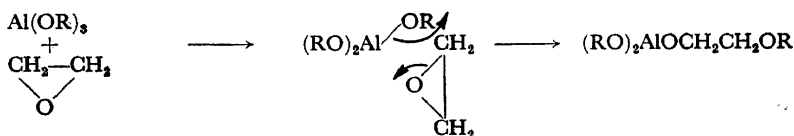


Table 3. Illustration of characteristics of co-ordinate catalysts in the polymerization of aldehyde and ethylene oxide

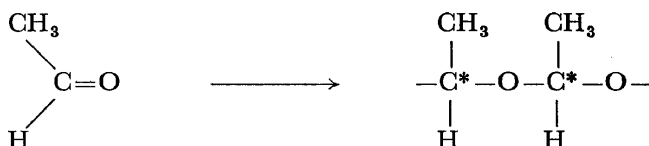
	<i>Acetaldehyde</i>	<i>Ref.</i>	<i>Ethylene oxide</i>	<i>Ref.</i>
(I) Alumina: $\begin{array}{c} \sim\text{O}-\text{Al}-\text{O}-\text{Al}-\text{O}-\text{Al}-\text{OH} \\   \quad   \quad   \\ \text{O} \quad \text{O} \quad \text{O} \\ \} \quad \} \quad \} \end{array}$	Active: atactic, high mol. wt. polymer	1	Active: low mol. wt. polymer	2
(II) Alumina + alkylmetal (diethyl-zinc): $\begin{array}{c} \sim\text{O}-\text{Al}-\text{O}-\text{Al}-\text{O}-\text{Al}-\text{OZnC}_2\text{H}_5 \\   \quad   \quad   \\ \text{O} \quad \text{O} \quad \text{O} \\ \} \quad \} \quad \} \end{array}$	Active: stereoblock, high mol. wt. polymer	3	Active: high mol. wt. polymer	4
(III) Metal alkoxide + H <sub>2</sub> O: $\begin{array}{c} \text{RO}-\text{Al}-\text{O}-\text{Al}-\text{O}-\text{Al}-\text{OR} \\   \quad   \quad   \\ \text{OR} \quad \text{OR} \quad \text{OR} \end{array}$	Active: stereoblock, high mol. wt. polymer	5	Very active: high mol. wt. polymer	6
(IV) Metal alkoxide: $\begin{array}{c} \text{RO}-\text{Al}-\text{OR} \\   \\ \text{OR} \end{array}$	Active: isotactic polymer	7, 8	Less active: less high mol. wt. polymer	9, 10
(V) Alkylmetal: $\begin{array}{c} \text{R}-\text{Al}-\text{R} \\   \\ \text{R} \end{array}$	Active: isotactic polymer	11	Less active: less high mol. wt. polymer	12-15

Although the activities of these catalysts may be ascribed to metal-oxygen linkages, they differ according to the group attached to the oxygen atom. The characteristics of these catalysts in the polymerization of acetaldehyde and ethylene oxide is roughly illustrated in *Table 3*, although the representation contains some oversimplification.

In this paper the co-ordinate polymerizations of acetaldehyde and alkylene oxides are discussed.

### POLYMERIZATION OF ACETALDEHYDE

The high polymerization of acetaldehyde was first reported independently by Travers<sup>16</sup> and by Letort<sup>17</sup>. They observed the polymerization accidentally when they froze the monomer in order to degas it under high vacuum. Several methods for the polymerization of acetaldehyde have been reported, and these are summarized in *Table 4*. As in the case of polypropylene, amorphous and crystalline polyacetaldehydes are possible according to the regularity of the configuration of the carbon atoms of the backbone chain:



Crystalline polymers of acetaldehyde have been found to possess an isotactic structure<sup>11</sup>.

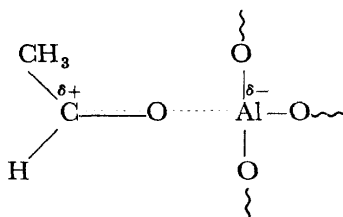
*Table 4.* Polymerization of acetaldehyde

<i>Method of polymerization</i>	<i>Type of polymer</i>	<i>Reference</i>
Freezing method	Rubbery, atactic	16-25
Adsorption method (alumina)	Rubbery, atactic	1
Lewis acid catalyst	Rubbery, atactic	26
Persulphate catalyst	Rubbery, atactic	27
Amine-polyphosphoric acid	Rubbery, atactic	28
Organometallic compound	Resinous, isotactic	7, 8, 11
Metal alkoxide	Resinous, isotactic	7, 8, 26, 29
Alumina-diethylzinc	Stereo-block	3
Aluminium alkoxide-H <sub>2</sub> O	Stereo-block	5

As mentioned before, the real active species of an organometallic compound catalyst can be assumed to be a metal alkoxide. A common characteristic of alumina and a metal alkoxide, *e.g.* an aluminium alkoxide, is that they are co-ordinated by the monomer in the initiation and propagation steps. Co-ordination of acetaldehyde on alumina was confirmed by infrared spectroscopy<sup>1</sup>. It was found that the normal carbonyl band of liquid acetaldehyde at 5.8  $\mu$  shifts to about 6.4  $\mu$  when acetaldehyde is adsorbed on alumina<sup>1</sup>. This shift may be attributed to the co-ordination of a lone pair of electrons on the carbonyl oxygen which brings about a reduction of

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the double-bond character of the carbonyl bond as a result of polarization of the following type:



The close relation between the catalytic activities and the adsorption powers of various alumina samples may be taken to indicate that the polymerization proceeds by the successive attack of the end of the growing chain on the monomer adsorbed on a neighbouring site.

The co-ordination of carbonyl oxygen to metal alkoxide is also well-illustrated by the "Meerwein complex"<sup>30, 31</sup>. The Meerwein complex plays an important rôle in several reactions involving a metal alkoxide and a carbonyl compound. In the complex (I), hydride ion transfer from the alkoxy group to the carbonyl group produces the complex (II); this reaction is the "Meerwein-Ponndorf-Verley Reduction"; the reverse reaction is the "Oppenauer Oxidation" (see *Scheme 1*).

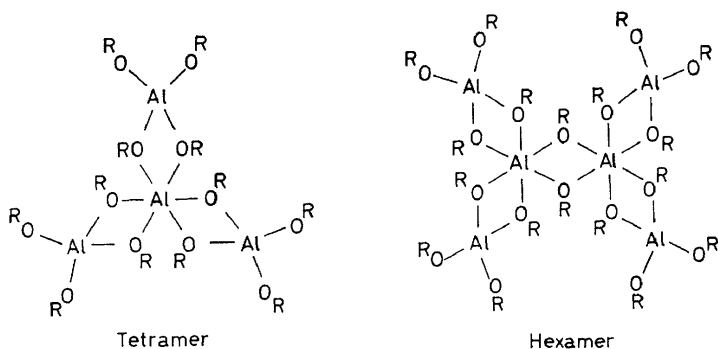
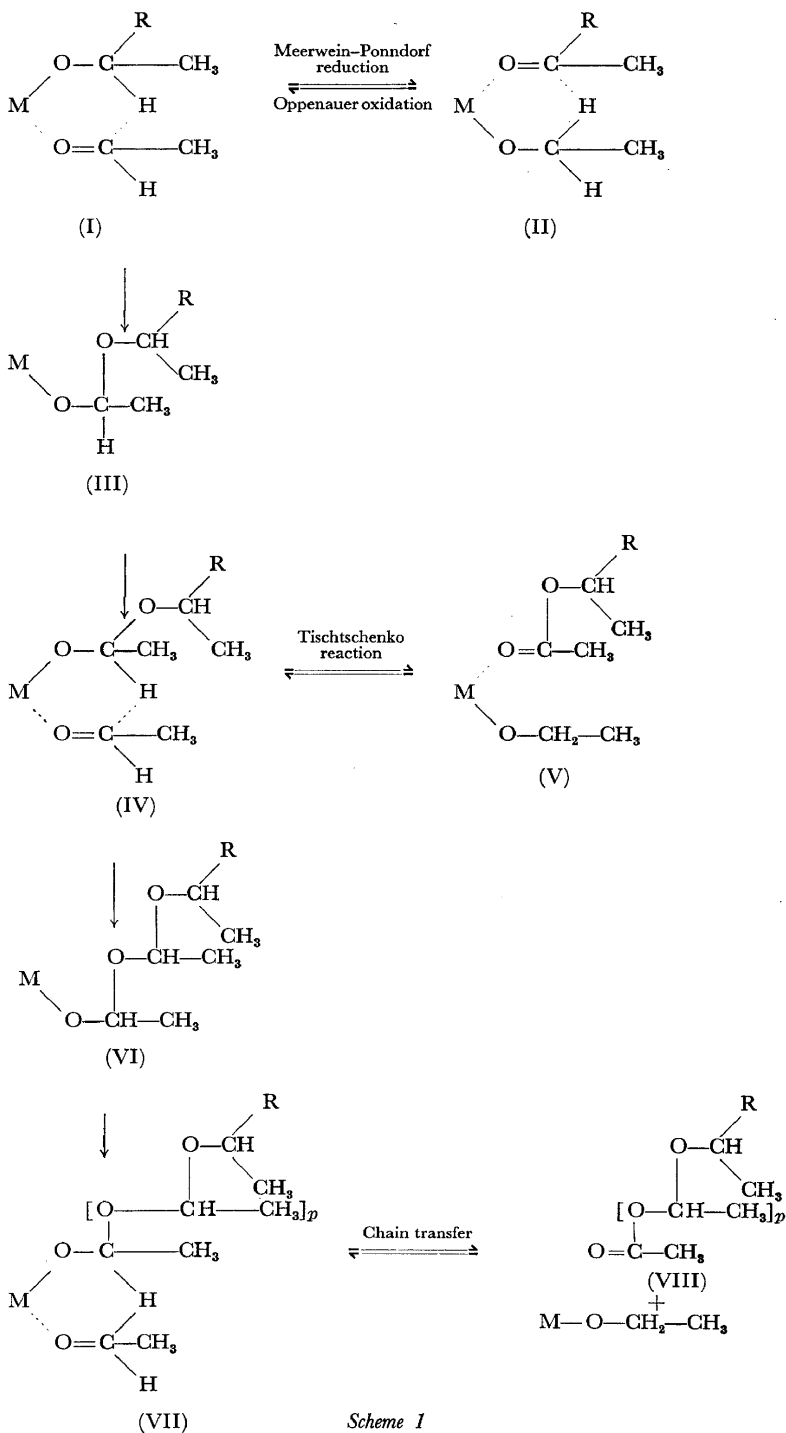


Figure 1. Aggregation of aluminium alkoxide

In the complex (I), the transfer of the alkoxy anion to the carbonyl-group of the co-ordinated aldehyde is also possible; this leads to a new metal alkoxide (III). Another monomer molecule can co-ordinate to the alkoxide (III) to form the new complex (IV). The hydride transfer reaction in the complex (IV) gives the ester (V); this is the "Tischtschenko Reaction". The transfer of alkoxide anion in the complex (IV) produces a metal alkoxide (VI) of higher order. The repetition of two consecutive steps, *viz.* the co-ordination of aldehyde and the transfer of alkoxide anion, results in the chain-propagation of polymerization; this continues until the hydride ion transfer intervenes in a higher "Meerwein Complex".

Thus, the co-ordination of acetaldehyde to aluminium is common to both alumina and aluminium alkoxide, but the stereoselectivities of these two catalysts differ from each other. Alumina gives an amorphous atactic

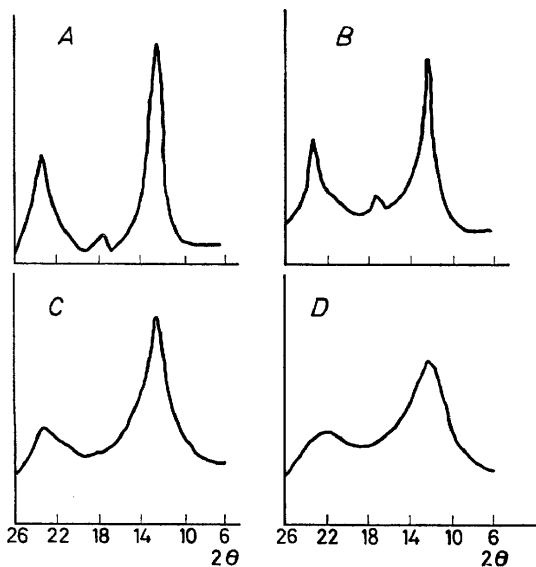


Scheme 1

polymer while alkoxide affords a crystalline isotactic polymer. One of the factors which controls the stereoregularity is steric hindrance in the surroundings of the co-ordination site. It is known that aluminium alkoxides form tetramers or hexamers by co-ordination between oxygen and aluminium<sup>32-34</sup>. The aggregation is represented in *Figure 1*. In these aggregates, the aluminium atoms of the outer alkoxides are 4-co-ordinated, and those of the inner alkoxides are 6-co-ordinated. Carbonyl groups will co-ordinate to aluminium atoms of the outer alkoxides. The alkoxy-groups of the latter will exert steric effects which lead to stereoregular co-ordination of the carbonyl compound. Asymmetric Meerwein-Ponndorf-Verley reduction<sup>35, 36</sup> may be taken to illustrate the stereo-selective co-ordination of carbonyl compounds to aluminium alkoxides. It may be assumed that the stereoregular polymerization of acetaldehyde by metal alkoxide catalysts is due to stereoregular co-ordination of the monomer.

The steric hindrance of the alumina surface is not large enough to cause stereoregular polymerization, although alumina is active and induces atactic polymerization.

We have studied the catalytic behaviour of a partially hydrolysed aluminium alkoxide in the polymerization of acetaldehyde<sup>5</sup>. The partially-hydrolysed alkoxide was prepared by treating the aluminium alkoxide with up to 1.5 moles of water. The alcohol produced was removed by distillation. The product may be of intermediate character between aluminium



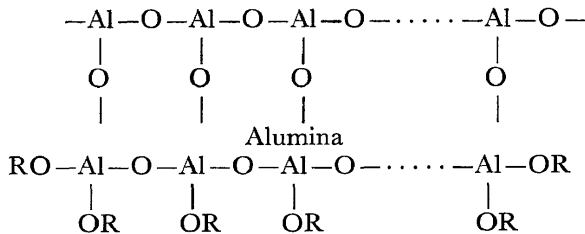
*Figure 2.* X-ray diffraction patterns of polyacetaldehydes of various crystallinities: *A*, insoluble fraction of blend in methanol-chloroform (600 : 30); *B*, insoluble fraction in methanol-chloroform (600 : 30); *C*, soluble fraction in methanol-chloroform (600 : 30); *D*, soluble fraction of blend in methanol-chloroform (600 : 30)

Table 5. Polymerization of acetaldehyde by partially-hydrolysed aluminium alkoxide: acetaldehyde, 0.25 moles; tri-isopropoxy aluminium, 0.005 moles; heptane, 30 ml for 40 h at  $-78^{\circ}$

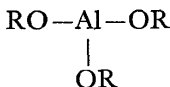
$H_2O/Al(OR)_3$ (molar ratio)	Total	Yield of polymer (%)		
		Methanol-soluble fraction	Chloroform-soluble fraction	Insoluble fraction
0	43	5	19	19
0.25	54	10	30	14
0.50	66	8	56	2
0.75	67	5	35	27
1.00	76	4	69*	3
1.25	12	2	2	8
1.50	8	1	3	4

\*  $[\eta] = 5.9$  in chloroform at  $25^{\circ}$ .

alkoxide and alumina. The following formulae will explain the relation, although it is oversimplified to some extent:



Partially-hydrolysed aluminium alkoxide



Aluminium alkoxide

The results of polymerization of acetaldehyde by a partially-hydrolysed aluminium alkoxide are shown in Table 5. The amounts of methanol-soluble and chloroform-soluble fractions, increased with the degree of hydrolysis of the catalyst. Soluble fractions produced by a partially-hydrolysed alkoxide had crystallinities intermediate between those of isotactic and atactic polymers as is shown in Figure 2. The possibility that these fractions are mechanical mixtures of atactic and isotactic polymers is ruled out by the infra-red spectra shown in Figure 3. Curves B and C represent the methanol-insoluble (chloroform-soluble) and the methanol-soluble fractions, respectively, of polyacetaldehyde produced by a partially-hydrolysed alkoxide catalyst. Curves A and D are the methanol-insoluble (chloroform-soluble) and the methanol-soluble fractions which were obtained by using the same fractionation procedure on an artificial mixture of crystalline and amorphous polymers. The crystalline polymer employed as the reference was prepared with a diethylzinc catalyst<sup>7, 8</sup>. The amorphous polymer was prepared with an alumina catalyst<sup>1</sup>. The separation



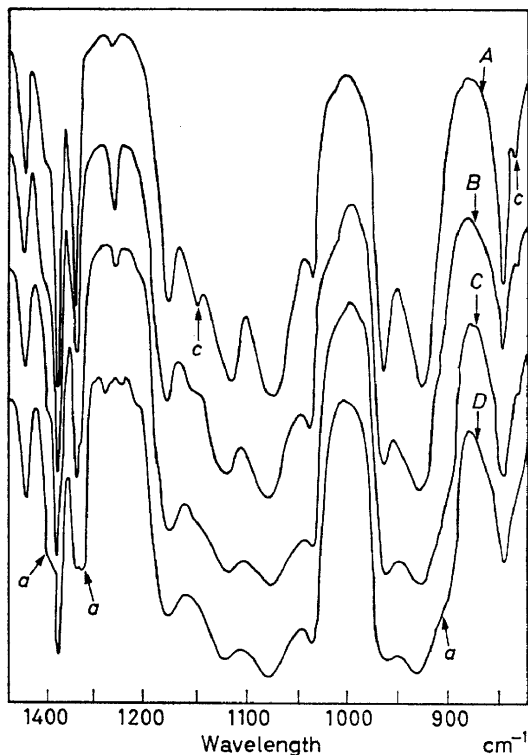


Figure 3. Infra-red spectra of polyacetaldehydes of various crystallinities; *A*, insoluble fraction of blend in methanol-chloroform (600 : 30); *B*, insoluble fraction in methanol-chloroform (600 : 30); *C*, soluble fraction in methanol-chloroform (600 : 30); *D*, soluble fraction of blend in methanol-chloroform (600 : 30); *a* = amorphous band (shoulder); *c* = crystalline band

of crystalline and amorphous polymers was considered to have been good. Therefore, the fact that curves *B* and *C* have bands characteristic of both crystalline (bands at  $1158\text{ cm}^{-1}$  and at  $835\text{ cm}^{-1}$ ) and amorphous (shoulder at  $1400\text{ cm}^{-1}$ , band at  $1339\text{ cm}^{-1}$  and shoulder at  $915\text{ cm}^{-1}$ ) polymers may be taken to indicate that these two fractions are stereo-block polymers consisting of crystalline (isotactic) and amorphous (atactic) blocks. Curve *B* is richer in isotactic block, and poorer in atactic block, than curve *C*.

During hydrolysis, alkoxy groups are replaced by oxide linkages, and, consequently, steric hindrance on the catalyst surface is reduced. This is reflected in the stereoregularity of the polymer produced.

Stereo-block polyacetaldehyde, consisting of isotactic and atactic blocks, has also been prepared by using a combination of two types of catalyst, *viz.* alumina and diethylzinc<sup>3</sup>. These are typical catalysts for atactic and isotactic polymers respectively. Alumina was treated with diethylzinc in *n*-hexane in an atmosphere of anhydrous nitrogen, and then the excess diethylzinc was removed by repeated washing with *n*-hexane. Polymerization of acetaldehyde by the modified alumina thus prepared gave a polymer which was soluble in chloroform but insoluble in methanol. Comparison

of the infra-red spectrum of this polymer with those of the fractions obtained by application of the same fractionation procedure to a polymer blend established that the polymer produced by the modified alumina catalyst had a stereo-block structure.

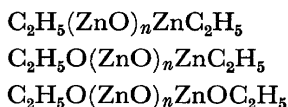
### POLYMERIZATION OF ALKYLENE OXIDES

Although organometallic compounds, such as diethylzinc and triethylaluminium, polymerize alkylene oxides, they are not very active and do not give high polymer<sup>12-15</sup>. We discovered that the catalytic activity of diethylzinc was much enhanced when a controlled amount of water was present as co-catalyst<sup>37, 38</sup>. The effect of water on the course of polymerization of propylene oxide by diethylzinc is illustrated in *Table 6*. The optimum

*Table 6.* Polymerization of propylene oxide by diethylzinc and water<sup>37</sup>; propylene oxide 3.5 ml; hexane 3.5 ml; diethylzinc 5 mole %, under nitrogen, at room temperature for 24 h

$\text{H}_2\text{O}/\text{Zn}(\text{C}_2\text{H}_5)_2$ (molar ratio)	Yield (%)	$[\eta]$ (100 ml/g)
0	0	—
0.25	Small	—
0.50	10.7	2.3
1.00	78.3	5.4
2.00	0	—
3.00	0	—

ration of water to diethylzinc is 1 : 1. When one mole of water was added to a hexane solution of diethylzinc, a yellow substance was obtained which was shown to be very active for the polymerization of propylene oxide. From the results of elementary analyses, and the determination of the volume of ethane gas evolved by acid decomposition, it was concluded that the yellow substance was a mixture of the following three species,



where  $n$  refers to a positive integer which is probably not very large<sup>38</sup>.

The catalytic system of diethylzinc and water was also found to be very active for the polymerization of ethylene oxide. We tried the polymerization of ethylene oxide under atmospheric pressure by using a simple apparatus depicted in *Figure 4*<sup>39</sup>. In the reactor, a controlled amount of water was added to a heptane solution of diethylzinc to prepare the active catalyst system. Gaseous ethylene oxide generated in the vaporizer was introduced into the reaction medium at a rate sufficient to keep the reaction medium saturated with the monomer. The excess monomer was allowed to pass through the water-cooled reflux condenser and was condensed in the trap which was placed in a solid carbon dioxide acetone bath. When an aliphatic hydrocarbon, *e.g.* heptane, was employed as the reaction medium, and the reaction temperature was below the melting point of poly(ethylene

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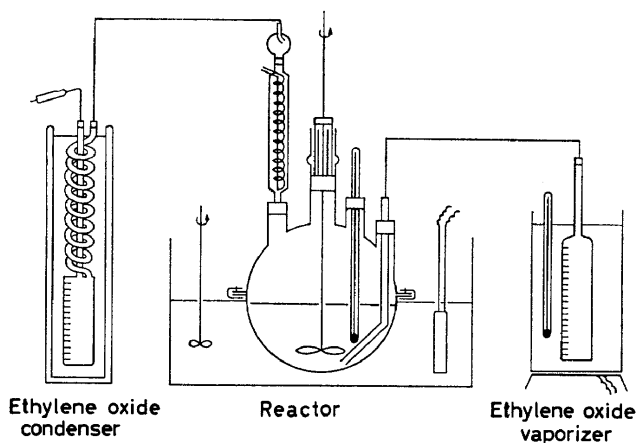


Figure 4. Apparatus for polymerization of ethylene oxide under atmospheric pressure

oxide) (about  $66^\circ$ ), polymer was formed continuously as small particles dispersed in the medium. The difference between the readings of the vaporizer and the condenser corresponded to the amount of monomer consumed by solution in the fresh solvent and by polymerization.

It was found that the activity of the catalyst was much affected by the reaction conditions. First, the presence of the monomer during the preparation of the catalytic system seems to be important for the production of a highly active catalyst. Good results were obtained when diethylzinc was reacted with water in the presence of monomer. Catalyst systems which were obtained by the reaction of diethylzinc and water in the absence of the monomer were much less active, and sometimes even inactive.

The second finding regarding the reaction conditions was the profound influence of ethers. Several ethers such as diethyl ether, di-isopropyl ether, dioxan, tetrahydrofuran, and trioxan increased the activity of the catalyst when they were added to the medium either before or after the preparation of the catalyst. The addition of an ether before the reaction of diethylzinc and water can sometimes render the presence of monomer unnecessary. The effects of ethers are exemplified in Table 7. Figure 5 indicates the

Table 7. Polymerization of ethylene oxide by diethylzinc and water, effect of ethers<sup>a</sup>: diethylzinc, 0.03 mole; water, 0.03 moles; heptane, 450 ml or 500 ml, at  $70^\circ$ , 3 h

Ether		Polymer produced (g)
Nature	Moles	
None	0	32.0
Dioxan	0.09	70.8
Dioxan	0.30	89.1
Trioxan <sup>a</sup>	0.09	79.5
Diethyl ether	0.30	137.5
Di-isopropyl ether	0.09	61.8
Di-isopropyl ether	0.30	125.9

<sup>a</sup> Reaction medium, 400 ml of heptane and 50 ml of benzene.

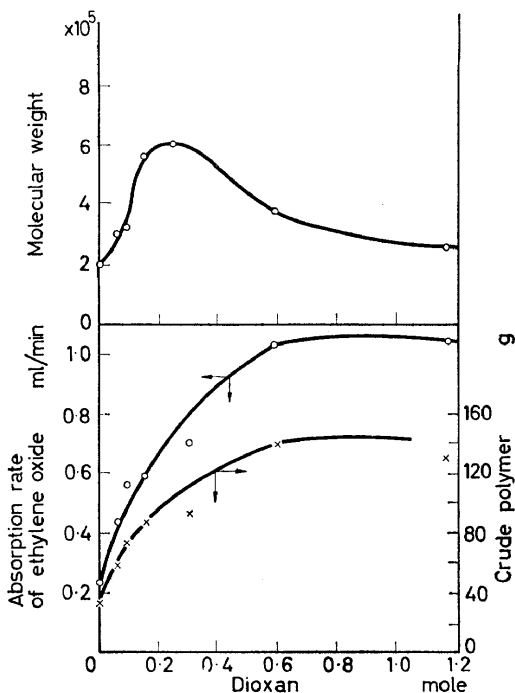


Figure 5. Polymerization of ethylene oxide by diethylzinc-water; effect of dioxan

effect of the amount of dioxan on the activity of the catalyst, and on the molecular weight of the polymer produced. The polymerization procedure was as follows. In the nitrogen-filled reaction vessel, 0.03 mole (3.1 ml) of diethylzinc was dissolved in 450 ml of dry, anhydrous heptane containing 50 ml (0.6 mole) of dioxan. To the solution 0.03 mole (0.54 ml) of water was added while gaseous monomer was introduced gradually. The temperature was then raised to 70° over a period of 40 minutes. At this temperature the gaseous monomer was added rapidly (1.3–1.4 ml of liquid monomer/minute the gaseous monomer was added rapidly (1.3–1.4 ml of liquid monomer/min), whereupon an immediate formation of polymer particles was observed. During 3 hours, 303 ml of liquid ethylene oxide was evaporated and 130 ml of the excess monomer was condensed. When the polymer suspension was exposed to air (to destroy the catalyst), filtered and dried, 140 g of snow-white polymer was obtained with a molecular weight of 370,000.

The over-all activation energy of this polymerization was calculated by using the relative rates at several reaction temperatures. In order to obtain the relative rate, the apparent rate was divided by the saturated concentration of the monomer in heptane at the corresponding temperature. The apparent rate was given both by the rate of consumption of the monomer, and by the actual weight of polymer produced. The values for the activation energy, 14.9 and 15.4 kcal/mole, respectively, agreed well with one another (Table 8).

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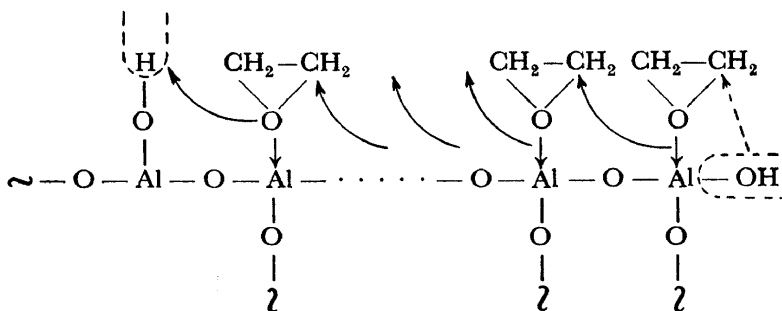
Table 8. Rate of polymerization of ethylene oxide by diethylzinc and water<sup>39</sup>

Temperature (°C)	Solubility (mole/l)	$-\frac{dM}{dt}$ <sup>a</sup> (ml/h)	$\frac{dP}{dt}$ <sup>b</sup> (g/h)
40	1.09	6.8	4.1
60	0.51	13.7	7.3
70	0.33	14.3	10.7
90	0.11	18.7	12.6
Activation energy (kcal/mole)		14.9	15.4

<sup>a</sup> Rate of monomer consumption.  
<sup>b</sup> Rate of polymer production.

As mentioned before, co-ordinate catalysts have a metal-oxygen linkage as a common feature, which may be regarded as the active constituent.  $\gamma$ -Alumina consists of aluminium-oxygen linkages, and in fact it was found to be active for the polymerization of ethylene oxide<sup>2</sup>. However, alumina alone does not give high molecular weight polymers.

We suggested<sup>4</sup> the following mechanism for the behaviour of an alumina catalyst. Hydroxyl groups on the alumina surface induce the anionic polymerization of neighbouring ethylene oxide monomer absorbed on the surface.



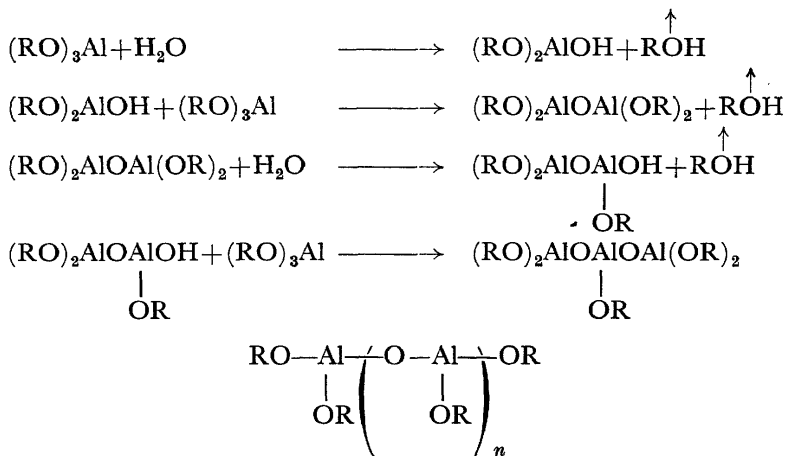
But a hydroxyl group can function also as an acid because of the amphoteric character of aluminium. Thus the propagating anionic chain is terminated by a proton which originates in one of the alumina hydroxyl groups. If alumina is treated with diethylzinc, some hydroxyl groups are converted into ethylzinc-oxy groups (IX) with the evolution of ethane gas.



An ethylzinc-oxy group cannot terminate the anion propagation, although it can still initiate the polymerization. This mechanism may explain the fact that extremely high molecular weight polymers of ethylene oxide are obtained by the binary mixture of alumina and diethylzinc<sup>4</sup>.

According to the above consideration, any other modified alumina which has alkoxy groups instead of hydroxyl groups should also afford high

molecular weight polymers of ethylene oxide. We have confirmed that partially hydrolysed aluminium isopropoxide, which should have such a structure, did, in fact, give high molecular weight poly(ethylene oxide)<sup>6</sup>. The formation of the catalyst may be represented in the following way:



A desired amount of water was added gradually to a stirred solution of aluminium isopropoxide in decahydronaphthalene, in a dry atmosphere. When the isopropyl alcohol produced had been distilled off from the mixture, partially hydrolysed aluminium isopropoxide was obtained as a fine suspension in decahydronaphthalene. The suspension was diluted with heptane, and gaseous ethylene oxide was then introduced under atmospheric pressure. Poly(ethylene oxide) of reasonably high molecular weight was produced in the form of fine particles dispersed in the medium. The activity of the catalyst depended upon the degree of hydrolysis, *i.e.*, the amount of water added. *Figure 6* shows the effect of the amount of

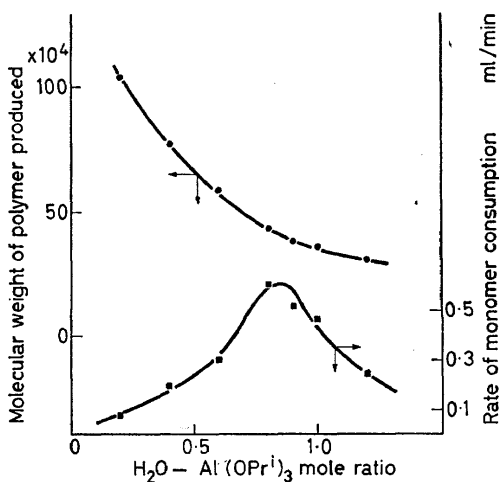
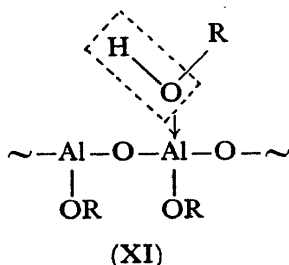
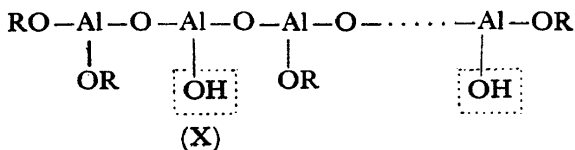


Figure 6. Polymerization of ethylene oxide by tri-isopropylaluminium; effect of water

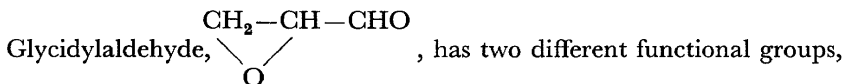
POLYMERIZATION OF ALDEHYDES, ALKYLENE OXIDES, DIKETENE

water on the course of the polymerization, the catalytic activity being expressed by the rate of ethylene oxide consumption. The decrease in molecular weight of the polymer with increase in the amount of water added may be ascribed either to the increasing proportion of hydroxyl groups (X) due to the incompleteness of the reaction of hydroxyl and alkoxide groups, or to the hydroxyl groups of isopropyl alcohol molecules (XI) adsorbed on alumina:

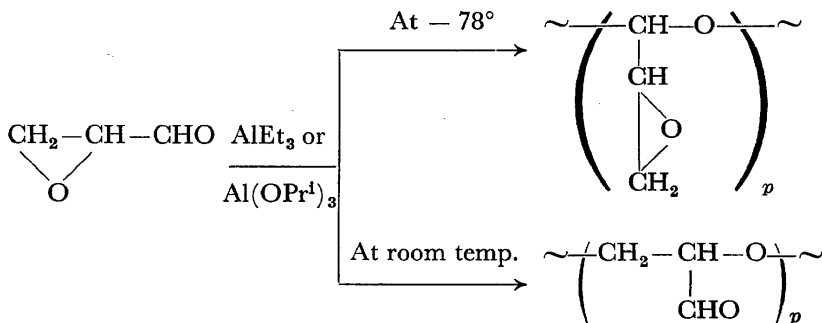


The activation energy was calculated by the method mentioned before; the value (15.7 kcal) was almost the same as that of the diethylzinc and water system.

POLYMERIZATION OF GLYCIDYLALDEHYDE



aldehyde and epoxide. Although both groups can be polymerized by metal alkyl or metal alkoxide, the polymerization temperature ranges differ. Polymerization of aldehydes is possible only below  $-40^\circ$ , while that of an epoxide ring can be accomplished efficiently at a higher temperature, preferably above  $0^\circ$ . By suitable selection of the temperature range, we obtained two types of polymers, polyaldehyde and poly(alkylene oxide)<sup>40</sup>:



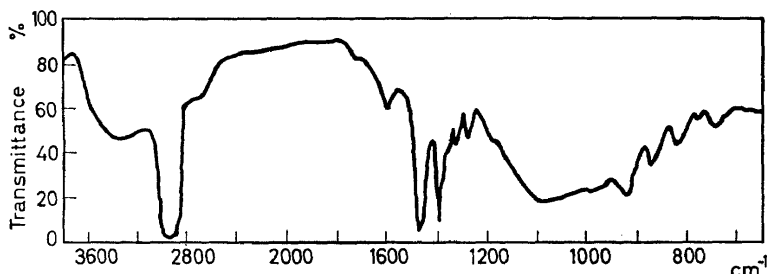
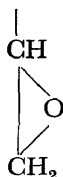


Figure 7. Infra-red spectrum of poly(glycidylaldehyde) (triethylaluminum catalyst, at  $-78^{\circ}$ )

Figure 7 shows the infra-red spectrum of polyglycidylaldehyde prepared by triethylaluminum catalyst at  $-78^{\circ}$ . No absorption band due to a carbonyl group can be observed. The polymer was insoluble in organic solvents. Functional group analysis showed that this polymer had 68 per cent of the epoxide unit,  $-\text{CH}-\text{O}-$ . Aluminium isopropoxide gave a similar result.



Polymerization at room temperature by an aluminium isopropoxide catalyst afforded a polymer which consisted of water-soluble and water-insoluble

Table 9. Functional group analysis of polyglycidylaldehyde obtained by tri-isopropoxyaluminium catalyst at room temperature<sup>40</sup>

	$-\text{CH}_2\text{CHO}-$   CHO (%)	$-\text{CH}_2\text{CH}-$   COOH (%)	Epoxide
Water-soluble fraction	20.1	18.3	0
Water-insoluble fraction	14.9	26.7	—

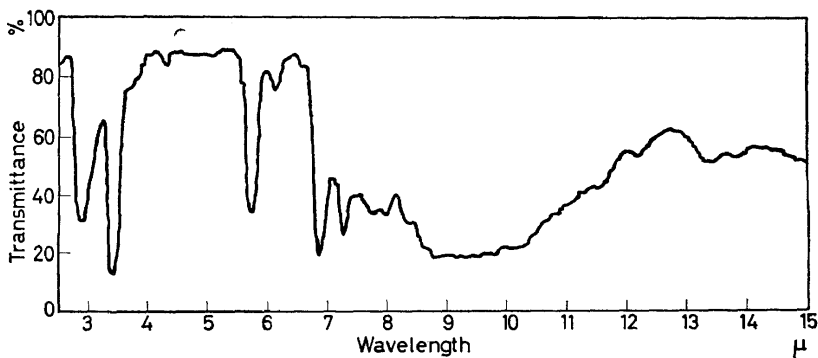


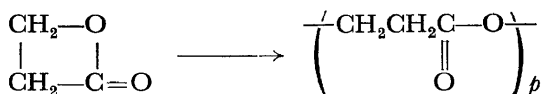
Figure 8. Infra-red spectrum of poly(glycidylaldehyde) (tri-isopropylaluminum catalyst, at room temperature)



fractions. The composition of these fractions is shown in *Table 9*. Both fractions were soluble in 50 per cent acetic acid. By the cryoscopic method the molecular weight of the water-soluble fraction was found to be 1,200. The infra-red spectrum of the water-insoluble fraction is given in *Figure 8* and indicates the presence of carbonyl (at 1740  $\text{cm}^{-1}$ ) and carboxylate (at 1640  $\text{cm}^{-1}$ ) groups.

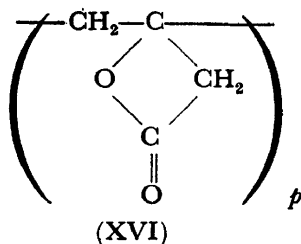
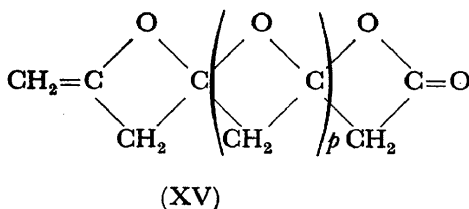
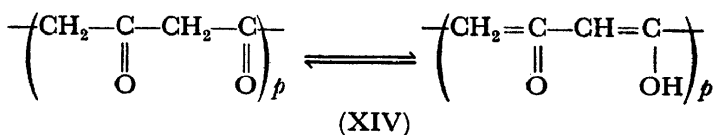
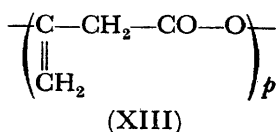
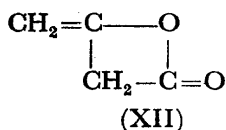
### RING OPENING POLYMERIZATIONS OF $\beta$ -PROPIOLACTONE AND DIKETENE

Poly- $\beta$ -propiolactone itself is not a new polymer, but a high molecular weight polymer has not yet been reported. We found<sup>14</sup> that a polymer of reasonably high molecular weight, having a reduced viscosity of 0.5, was produced in good yield when  $\beta$ -propiolactone was treated with aluminium isopropoxide in the temperature range  $-20$  to  $0^\circ$ .

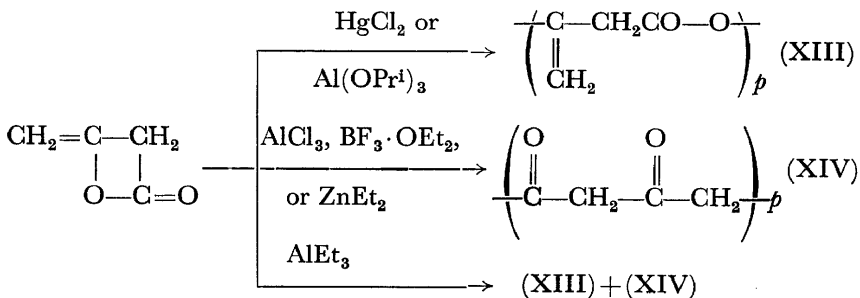


For the polymerization of  $\beta$ -propiolactone, an organometallic compound such as triethylaluminium was not active, but it became active when it was used in the presence of a controlled amount of air. It seems that the real active species is an aluminium alkoxide which is produced by the reaction of triethylaluminium with oxygen.

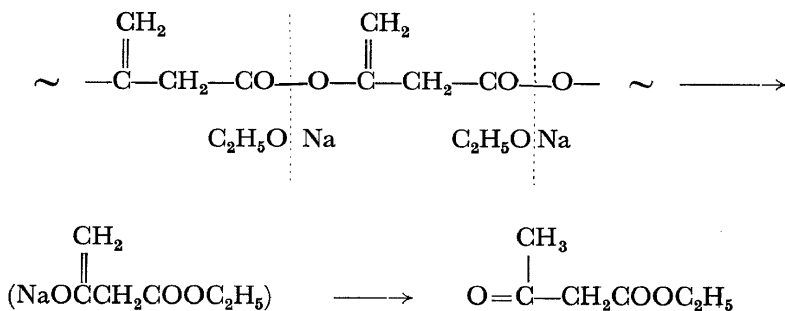
Diketene (XII) is a very interesting compound from the view-point of polymer chemistry. For the structure of the polymer, there are four possibilities, (XIII)—(XVI).



We studied the polymerization of diketene by using various types of catalysts<sup>41, 42</sup>. The results are summarized below:



The polymerizations were carried out at a temperature in the vicinity of 0°, both with and without solvent. The structure of the polymer produced was determined by its infra-red spectrum. The structure (XIII) was further confirmed by alkali-catalyzed alcoholysis which gave ethyl acetoacetate:



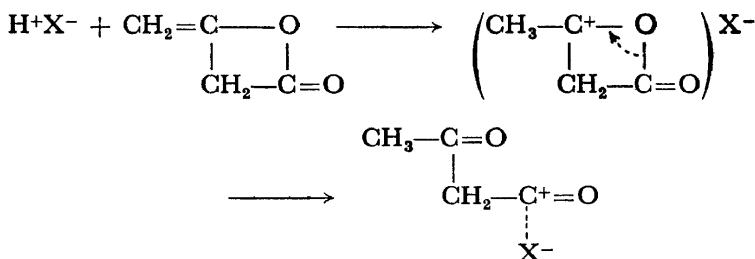
Polymers produced by mercuric chloride or by aluminium isopropoxide were of the polyester type and were not of high molecular weight; their reduced viscosities were between 0.1 and 0.2. The gross polymer obtained by triethylaluminium was shown to contain the polyester type of polymer (II) and the copolymer composed of both the structures (XIII) and (XIV). These two different polymers were separated by extraction with hot acetone. The polymer with the polyketone structure (XIV) was prepared with Lewis acid catalysts and with diethylzinc; it was soluble in dimethylformamide and *m*-cresol. The polymerization of diketene by a boron fluoride (etherate) catalyst has been reported by Oda *et al.*<sup>14</sup>. In our study, similar results were obtained with an aluminium chloride catalyst. The infra-red spectrum afforded evidence of keto-enol tautomerism in the polyketone (XIV).



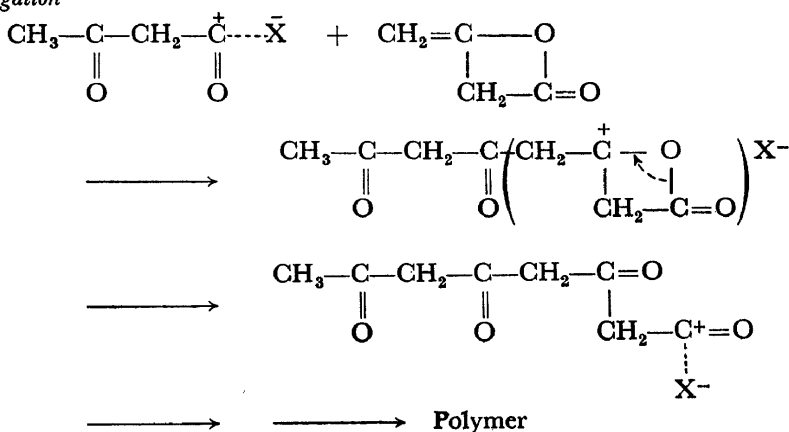
POLYMERIZATION OF ALDEHYDES, ALKYLENE OXIDES, DIKETENE

The polymerization of diketene in the presence of a Lewis acid catalyst may proceed by the following mechanism:

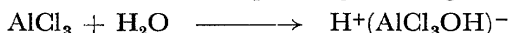
*Initiation*



*Propagation*



where X<sup>-</sup> indicates a counter-ion in the proton-generating reaction:



**Summary**

Alumina, alumina-alkylmetal, alkylmetal, alkylmetal-water, metal alkoxide, and metal alkoxide-water, induce the polymerization of acetaldehyde and of alkylene oxides. The active species of these catalysts appears to be a metal-oxygen linkage which induces "co-ordinate polymerization". According to the degree of steric hindrance of the surroundings of the co-ordination site, isotactic, stereo-block (isotactic and atactic blocks), and atactic polyacetaldehydes are prepared. The results of the polymerization of ethylene oxide by diethylzinc-water, and by aluminium isopropoxide-water, and of the stereo-block polymerization of acetaldehyde by aluminium isopropoxide-water system, are described. Glycidylaldehyde was polymerized by both triethylaluminium and aluminium isopropoxide. Polymerization at low temperature (-78°) gave a polyacetal, and that at room temperature gave a poly(alkylene oxide). Diketene was polymerized with various catalysts. Mercuric chloride and aluminium isopropoxide gave a polyester-type polymer, whilst aluminium chloride, boron fluoride (etherate), and diethylzinc afforded a polymer of the polyketone type. Triethylaluminium gave a polymer embodying both structures.

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