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CATALYTIC POLYMERISATION OF 1,2-EPOXIDES

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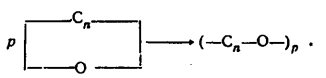
CONTENTS

1. Introduction 335
2. Structural features of monomers containing the epoxide group 335
3. Catalysts for the polymerisation of epoxides 336
4. Mechanism of polymerisation 338
5. Properties and structure of polymerised oxides 340

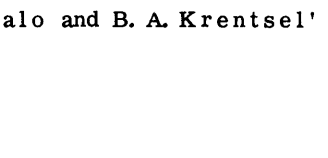
1. INTRODUCTION

Following the discovery that the simplest aldehyde would yield a stable polymer, polyformaldehyde, which possesses valuable complex technological properties, greater interest was shown in the various problems of polymerising aldehydes and ketones using the C = O bond and polymerising 1,2-epoxyalkanes by opening the three-membered heterocyclic ring[1-15]. Thanks to their valuable properties the polyethers so formed, which possess hetero-chains, have found application in many fields of present-day technology.

The polymerisation of oxygen-containing monomers to form polyethers can be represented in general as follows:



Various types of polymer are formed depending on the value of n: polyaldehydes (polyformaldehyde, polyacetaldehyde, etc.) when $n = 1$, polyoxyalkenes when $n = 2$,



, Penton, when $n = 3$, and polytetrahydrofuran when $n = 4$.

In this article we shall consider only one of the possible ways of obtaining polyethers — the catalytic polymerisation of 1,2-epoxyalkanes and their derivatives.

2. STRUCTURAL FEATURES OF MONOMERS CONTAINING THE EPOXIDE GROUP

Organic oxides can be considered to be internal ethers of 1,2-glycols, but they possess a higher reactivity than ordinary ethers, as noted by Würtz[1] and Brühl[2]. The explanation of the increased reactivity as due to the presence of strain in the three-membered ring, in accordance with Baeyer's theory[3], was widely accepted. Zimakov[4] made a detailed study of the structural features of epoxyethane in relation to its chemical and physical properties. Epoxyethane was found to be similar in its reactions to ethylene; this similarity must arise from the structures of the two molecules being analogous[5]. In 1947 there was some discussion in "Nature" on the structure of epoxyethane and cyclopropane[6], which led to Walsh's paper[7]. He concluded, from experimental results, that epoxyethane contains electron bonds which, in their lability, are more like the π bonds in alkenes than normal C–C and C–O bonds. It was shown by independent methods that in the epoxyethane and cyclopropane molecules the hybridisation of the valence electrons of the carbon atoms is not sp^3 as in alkanes, but sp^2 as in alkenes. At the present time it is widely acknowledged that the bonds in alkenes and 1,2-epoxides are of a related type[8]. The particular reactivity of 1,2-epoxides is attributed to a change in the valence state as a consequence of the considerable distortion of the

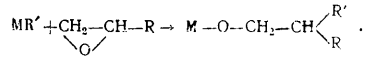
valence angles in the molecule. This results in the formation of easily polarisable bonds of a new type which are therefore very reactive. Different substituents in the three-membered ring either weaken or strengthen the polarisation and hence affect the reactivity of the oxide substantially. It follows, from the similarity between the structures of ethylene and epoxyethane, that, under certain conditions, epoxides can undergo polymerisation, like the alkenes, to form macromolecular compounds.

3. CATALYSTS FOR THE POLYMERISATION OF EPOXIDES

There has been considerable research on the polymerisation of 1,2-epoxides, and in particular of epoxyethane [9,10] and 1,2-epoxypropane [11-25].

The catalytic polymerisation of epoxyethane was first carried out by Staudinger and Schweitzer [5,6,26,27]. The catalysts used were alkali metals (Na, K), their hydroxides, and ammines. The catalytic action of a number of Lewis acids ($AlCl_3$, $FeBr_3$, $SnCl_4$), metal oxides (Al_2O_3, SiO_2), and organometallic catalysts was investigated [9,12,17,28-31]. The polyoxyalkenes so obtained are liquid or waxy with molecular weights of the order of several ten thousand. With alkaline-earth metal hydroxides, in particular $Be(OH)_2$ and $Mg(OH)_2$, as catalysts the molecular weight of the polymer was increased to a hundred thousand [31].

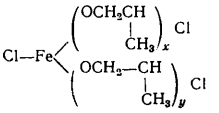
The active catalysts for the polymerisation of organic oxides are shown in Table 1. Catalysts I, II, and III are metal alkoxides with or without added metal halides [12,14,15,32,33]. Catalysts IV and V [13,34] are organometallic compounds which react with epoxides to form the corresponding metal alkoxide:



The activity of the catalyst in the polymerisation process is therefore determined to a considerable extent by the reactivity of the corresponding alkoxide.

The following structures are proposed for the active catalysts VI [16,35,36]: $RMO(MO)_pMR$, $ROM(OM)_pOMR$, $ROM(OM)_pOMOR$. Catalyst VII is not very active and gives low-molecular-weight polymers [17]. However, in the presence of organometallic cocatalysts (AlR_3, ZnR_2) it will produce high-molecular-weight polymers from epoxyethane and 1,2-epoxypropane [13]. Catalyst IX, the so-called "complex" catalyst of Pruitt and Baggett [18], is obtained from anhydrous ferric chloride or bromide and 1,2-epoxypropane. Price and coworkers [11], and later Colclough and Gee [12], observed that the polymerisation of 1,2-epoxypropane on anhydrous ferric chloride takes place in two stages. The first, which is fast, proceeds at room temperature but the polymerisation goes no further at this temperature. On raising the temperature to 80° (optimum), polymerisation occurs with 100% conversion of the monomer.

Colclough and Gee [12] examined the product from the first stage. They found that five moles of 1,2-epoxypropane are combined with each mole of anhydrous ferric chloride, and showed that the Cl^- content in the catalyst obtained slightly exceeds one equivalent on the basis of the original $FeCl_3$-1,2-epoxypropane complex. This indicated that only two chlorine atoms in the ferric chloride molecule are replaced by 1,2-epoxypropane. The structure proposed for the reaction product is



where $x + y = 5$.

It was shown in our paper [20] on the production and investigation of this catalytic system that the catalysts prepared according to Pruitt and Baggett [18] and Price [11] on the one hand, and according to Bořkovec and Jackson [19] on the other, have different elemental composition, infra-red spectra, and catalytic activity in the polymerisation of 1,2-epoxypropane and 3-chloro-1,2-epoxypropane. The difference in their composition is shown in Table 2.

TABLE 1. Catalysts for the polymerisation of organic oxides*.

No.	Name	Formula	References
I.	Metal alkoxides	Al $(OR)_3$; Zn $(OR)_2$; Fe $(OR)_3$	12, 14, 3, 2
II.	Alkoxide complexes	$MgAl(OR)_5$; $CaAl(OR)_5$	15
III.	Metal alkoxides + metal halides	Al $(OR)_3 + ZnCl_2 + FeCl_3$ Ti $(OR)_4 + ZnCl_2$	32, 33
IV.	Metal alkyls	AlR_3, ZnR_2, MgR_2	13, 34
V.	Metal alkyls + metal halides	$AlR_3 + FeCl_2$; $AlR_3 + NaF$	15, 34
VI.	Metal alkyls + water	AlR_3, MgR_2, $ZnR_2 + H_2O$	16, 35, 36
VII.	Alumina	Al_2O_3 (activated)	13, 17
VIII.	Aluminosilicate + metal alkyls	$Al_2O_3 : SiO_2$ (13 : 87 by weight) $+ZnR_2$, AlR_3	13
IX.	Pruitt-Baggett catalyst	$FeCl_3$-1,2-epoxypropane complex	11, 18, 19, 37
X.	Partly hydrolysed $FeCl_3$-1,2-epoxypropane	$FeCl_3$-1,2-epoxypropane + water	12, 38
XI.	Alkaline-earth metal carbonates	$SrCO_3$; $CaCO_3$; $BaCO_3$	23
XII.	Alkali metal hydroxides	KOH, NaOH (powdered)	11, 39
XIII.	Lewis acids	$FeCl_3$; $AlCl_3$; $SnCl_4$; BF_3	12, 40
XIV.	Boron trifluoride-ether complex	$BF_3 \cdot Et_2O$	41

* The catalysts listed are active in the polymerisation of various epoxides. The polymers obtained have different molecular weights and, therefore, different properties.

TABLE 2. Composition of $FeCl_3$-1,2-epoxypropane catalysts.

Catalyst		C, %	H, %	Cl, %	Fe, %
$FeCl_3$-1,2-epoxypropane	ether	41.31 41.35	7.35 7.40	18.90 18.88	11.95 11.36
$FeCl_3$-1,2-epoxypropane	CCl_4	30.45 30.25	5.58 5.44	21.26 21.28	16.22 16.12
$FeCl_3$ – ether		11.02 12.05	4.11 4.17	38.51 38.49	24.17 24.40

In our opinion this difference is explained by the occurrence of coordinate bonding of ether to anhydrous $FeCl_3$ or to the $FeCl_3$-1,2-epoxypropane catalyst when the catalyst is prepared in ether, an oxonium type compound being formed. This produces additional steric hindrance in polymerisation. To confirm this hypothesis, anhydrous ferric chloride was dissolved in dry ether under the conditions for synthesis of the "complex". After removing the ether and evacuating to a very low pressure, the residue had the composition indicated above (see Table 2).

1,2-Epoxypropane was polymerised on this catalyst to a degree of conversion not exceeding 40–50%, giving a low-molecular-weight polymer (intrinsic viscosity in benzene 0.08–0.1). We showed that four moles of 1,2-epoxypropane are combined with one mole of anhydrous ferric chloride and this is confirmed by results on the preparation and examination of the catalyst obtained[20]. This catalyst is of great interest because polymerisation of a number of epoxides (1,2-epoxypropane, epoxybutane, 3,4-epoxybut-1-ene, 3-chloro-1,2-epoxypropane) takes place on it stereospecifically, like the polymerisation of alk-1-enes on Ziegler–Natta catalysts[21,22]. The catalyst dissolves in the monomer and can be modified by various additives so that polyoxyalkenes with regular structure and different molecular weights are obtained[12].

Catalysts XI (see Table 1), the alkaline-earth metal carbonates, are extremely active in the polymerisation of epoxyethane[23]. Powdered alkali metal hydroxides are also active in polymerisation. Price and coworkers[11,24] showed that potassium hydroxide is an active catalyst for the polymerisation of 1,2-epoxypropane at room temperature.

TABLE 3. Polymerisation of epoxyethane on the catalysts Al_2O_3, SiO_2, and Al_2O_3–SiO_2, with metal alkyls (0.25 mole monomer, 5 g of first component, 0.0125 mole metal alkyl, room temperature, 20 h, nitrogen atmosphere).

Catalyst	Solvent	Percentage conversion	$[\eta]$
Al_2O_3[a]	benzene	56	1.0
$Al_2O_3 + B(n\text{-}C_4H_9)_3$	benzene	40	0.6
$Al_2O_3 + Zn(C_2H_5)_2$	benzene	87	4.1
$Al_2O_3 + Cd(C_2H_5)_2$	benzene	34	9.4
$Al_2O_3 + C_2H_5MgBr$	ether + benzene	29	3.4
$Al_2O_3 + C_4H_9Li$	benzene	2.7	3.5
SiO_2	hexane	0	—
$SiO_2 + Zn(C_2H_5)_2$	hexane	0	—
$Al_2O_3 : SiO_2$[b]	benzene	0	—
$Al_2O_3 + B(n\text{-}C_4H_9)_3$	benzene	13	
$Al_2O_3 + Zn(C_2H_5)_2$	benzene	26	2.9
$Al_2O_3 + Cd(C_2H_5)_2$	benzene	3	
$Al_2O_3 + C_2H_5MgBr$	ether + benzene	44	1.7
$Al_2O_3 + C_4H_9Li$	benzene	traces	—
Pure metal alkyls are inactive		0	—

[a] Industrial catalyst (8–14 mesh).
[b] Catalyst for cracking petroleum, $Al_2O_3 : SiO_2$ (13:87).

TABLE 4. Polymerisation of 1,2-epoxypropane on the catalysts Al_2O_3, SiO_2, and Al_2O_3–SiO_2, with metal alkyls (0.25 mole monomer, 5 g of first component, 0.0125 mole metal alkyl, room temperature, 65 h, nitrogen atmosphere).

Catalyst	Solvent	Percentage conversion	$[\eta]$
Al_2O_3[a]	hexane	24	0.6
$Al_2O_3 + B(n\text{-}C_4H_9)_3$	benzene	10	slightly viscous
$Al_2O_3 + Al(C_2H_5)_3$	hexane	21	1.3
$Al_2O_3 + Zn(C_2H_5)_2$	hexane	27	2.3
$Al_2O_3 + Cd(C_2H_5)_2$	benzene	38	4.2
$Al_2O_3 + C_2H_5MgBr$	ether + benzene	9	0.5
$Al_2O_3 + C_4H_9Li$	hexane + benzene	8	0.9
SiO_2	hexane	0	—
$SiO_2 + Al(C_2H_5)_3$	hexane	20	1.9
SiO_2 + remaining metal alkyls	benzene, hexane	0	—
$Al_2O_3 + SiO_2$[b]	hexane	3	liquid
$Al_2O_3 + B(n\text{-}C_4H_9)_3$	benzene	32	liquid
$Al_2O_3 + Al(C_2H_5)_3$	hexane	23	0.4
$Al_2O_3 + Zn(C_2H_5)_2$	hexane	60	3.1
$Al_2O_3 + Cd(C_2H_5)_2$	benzene	1	0.6
$Al_2O_3 + C_2H_5MgBr$	ether + benzene	20	viscous semi-solid
$Al_2O_3 + C_4H_9Li$	hexane + benzene	1	liquid
Pure metal alkyls, other than $Al(C_2H_5)_3$, are inactive			

[a] Industrial Al_2O_3 (8–14 mesh).
[b] Catalyst for cracking petroleum, $Al_2O_3 : SiO_2$ (13:87).

Furukawa and coworkers[13] propose a binary system consisting of industrial granulated aluminium oxide or a catalyst for petroleum cracking, $Al_2O_3 : SiO_2$ (13 : 87 by weight) and an organometallic compound.

The catalytic activity of a large number of metal alkyls has been examined, the polymerisation of epoxyethane and 1,2-epoxypropane being widely studied (Tables 3 and 4).

It is interesting, and it has been noted a number of times, that polymerisation of 1,2-epoxyalkanes on pure organometallic systems does not produce regular polymers of high molecular weight[16,35]. Water and alcohols play a definite part. The work of Furukawa *et al.*[35] illustrates this cocatalytic effect.

The optimum molar ratio of water to diethylzinc is 1 : 1. This catalyst gives a crystalline polymer of racemic 1,2-epoxypropane (15.9% crystalline). When water is added to diethylzinc in hexane, a semisolid precipitate is formed and the solution turns yellow. After the hexane and excess diethylzinc had been removed by evacuating, a yellow, viscous oil, named fraction A, which was extremely active in polymerisation, was obtained from the residue. Its composition is 15.4% C, 3.27% H, 14.2% O, 67.1% Zn, gramme-atomic ratios C : H : O : Zn = 4.0 : 10.1 : 2.8 : 3.2. The following reactions have been proposed:

$$C_2H_5ZnC_2H_5 + H_2O \rightarrow C_2H_5ZnOH + C_2H_6,$$
$$C_2H_5ZnOH + C_2H_5ZnC_2H_5 \rightarrow C_2H_5ZnOZnC_2H_5 + C_2H_6,$$
$$C_2H_5ZnOZnC_2H_5 + H_2O \rightarrow C_2H_5ZnOZnOH + C_2H_6,$$
$$C_2H_5ZnOZnOH + C_2H_5ZnC_2H_5 \rightarrow C_2H_5ZnOZnOZnC_2H_5 + C_2H_6, \text{ etc.}$$

TABLE 5. Conditions: 3.5 ml 1,2-epoxypropane, 3.5 ml hexane, 3 mole % diethylzinc, room temperature, 24 h, nitrogen atmosphere.

$H_2O/Zn(C_2H_5)_2$, mole/mole	Conversion, %	$[\eta]$
0	0	—
0.25	traces	—
0.50	10.7	2.3
1.00	78.3	5.4
2.00	0	—
3.00	0	—

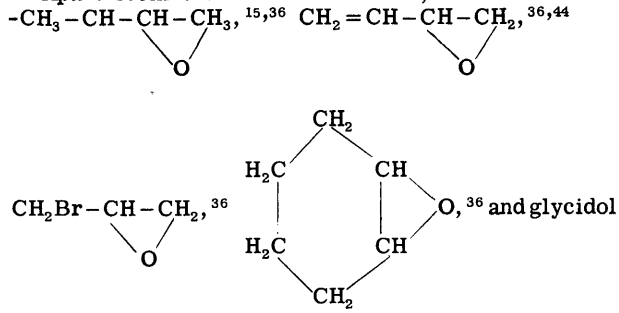
TABLE 6.

Monomer	Catalyst	Polymerisation conditions		Conversion, %	Yield of solid polymer, %	Physical properties		References
		T, °C	time			m.p., °C	$[\eta]$	
	Al_2O_3+Zn $(C_2H_5)_2$	room	20 h	87			4.1	42
	$FeCl_3$-1,2-epoxypropane	80	55 h	80	10	71—77		11
	Al $(CH_3)_3$ in n-hexane	(78) room	6 days	57.2	91.4	155		41
	$BF_3 \cdot Et_2O$	(—68) room	24 h	98	viscous liquid			41
	$BF_3 \cdot Et_2O$	room	72 h	51.3	does not melt even above 300°			41
	$FeCl_3$-1,2-epoxypropane	80	41 h	78.5	60.7	115		43
	KOH, NaOH	80				180—190		39
	$AlCl_3$	80	3 days	52	viscous liquid		0.018	12

We thus obtain a mixture of compounds of general formula $C_2H_5ZnO(ZnO)_pZnC_2H_5$, where $p = 0$ or any positive integer. These catalysts are insoluble in the reaction medium.

Okazaki[25] has examined the properties of a large group of inorganic oxides used in conjunction with diethylzinc. The binary catalysts were prepared by treating previously activated oxides with various amounts of diethylzinc. Bi_2O_3, MgO, CaO, BaO, Cr_2O_3, MoO_3, WO_3, TiO_2, SnO, MnO_2, V_2O_5, Sb_2O_3, ZnO, and also CaF_2 and NaF, were examined, the monomer being 1,2-epoxypropane. The yield of polymer and its intrinsic viscosity depended on the amount of diethylzinc added. The catalytic activity of the system is higher, the more ionic the binding in the metal oxide or fluoride.

Results on the synthesis of polyepoxy compounds using the catalytic systems described above are given in Table 6. Experiments have been selected which produce solid polymers of high molecular weight in good yield, or, if a solid polymer has not been obtained in a particular case, high-molecular-weight liquids.

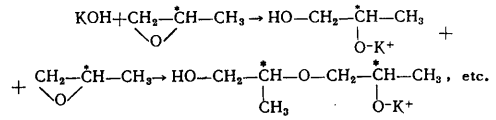
Apart from the monomers listed, *cis*- and *trans*-  ethers (methyl, ethyl, isopropyl, isobutyl, allyl) can undergo polymerisation. However, there are only isolated data, in patents[15,44] and letters to editors[36], on the polymerisation of these monomers.

4. MECHANISM OF POLYMERISATION

Mechanisms of the polymerisation of organic oxides are only hypothetical as there has been almost no specialised research on this point[45]. The polymerisation is said to be a chain process involving slow production of active centres and fast chain propagation with a comparatively small increase in molecular weight from the start of the reaction to the end[23].

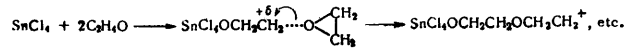
The polymerisation of epoxyethane on a $Be(OH)_2$ catalyst is different from this, the molecular weight of the polymer rising continuously during the process[30,31]. As the total amount of polymer formed grows, there is an almost parallel increase in molecular weight (Table 7).

There are various hypotheses as to the nature of the polymerisation. Price[11] showed that two polymers can be formed from 1,2-epoxypropane using a powdered potassium hydroxide catalyst — a crystalline polymer with m.p. 55.5° — 56.5° from the *l*-form of the monomer, and a liquid amorphous product of the same molecular weight (of the order of tens of thousands) from the racemic mixture. Retention of configuration of the asymmetric carbon atom is attributed to the ring's breaking at the primary carbon atom to give a secondary alkoxide of potassium:



A racemic mixture of polymer molecules is obtained from a racemic monomer. The polymerisation is anionic.

Worsfold and Eastham[40] proposed a cationic mechanism for the polymerisation of epoxyethane with Lewis acids as catalysts:



As noted above, polymerisation on anhydrous ferric chloride takes place in two stages. Gee[12] found, by studying the product from the first stage, that it proceeds by a cationic path:

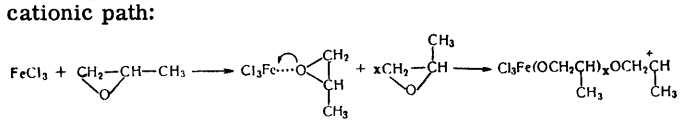
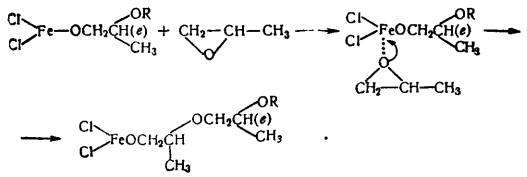


TABLE 7. Polymerisation of epoxyethane on $Be(OH)_2$ at 75°.

Polymerisation time, h	Polymer yield, %	η_{sp}/C	Mol. wt.
4	5.7	0.17	6200
9	50.3	0.48	28600
20	78	0.73	72500
29	90	0.85	115000

The second polymer chain grows at the iron atom similarly. The first stage is terminated by transfer of chloride ions with formation of a compound to which the structure $ClFe(OR)_2Cl_2$ is ascribed.

Further polymerisation occurs by a coordination mechanism. Price's scheme [11] for the complex formation and growth is given below for one OR group (it is similar for the second).



In this instance, besides the crystalline polyoxypropene, an amorphous material is always formed which has the same molecular weight regardless of whether it is obtained from the *l*- or *d*-monomer, or even from the racemic mixture. We may therefore suppose that a change in configuration of the asymmetric carbon atom is possible in the polymerisation process. Corey [45] agrees with the "coordination polymerisation" mechanism proposed by Price [11] but considers that polymerisation on ferric chloride takes place with retention of configuration because the polymer obtained from *l*-epoxypropane has the same specific rotation as that obtained using a potassium hydroxide catalyst. However, he does not take into consideration that, in the polymerisation of *l*-epoxypropane, an amorphous, optically inactive polymer is obtained as well as the crystalline, optically active one. He considers that, in the polymerisation of the *dl*-epoxide, the growing chain reacts selectively with that enantiomer which is involved in the catalyst formation stage, because such addition is the most favourable sterically. The polymeric racemate is shown to be a mixture of *l*- and *d*-macromolecules by the melting points of the crystalline fractions from *l*- and *dl*-monomers being the same and by the lack of optical activity in the crystalline polymer obtained from the racemate monomer.

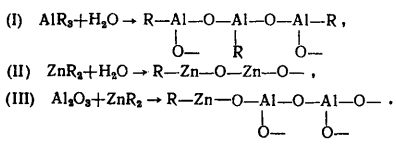
In Price's opinion the steric regularity is due to the heterogeneity of the catalytic system used. Formation of the coordination complex occurs as a result of chemisorption of the monomer on microcrystals of catalyst dispersed in the reaction medium [11]. However, this hypothesis of Price is open to argument because we have shown that the monomer–catalyst system ($FeCl_3$-1,2-epoxypropane + + 3-chloro-1,2-epoxypropane) is completely homogeneous [20]. The latter was confirmed by filtering a solution of the catalyst in the monomer through a bacteria filter with a pore size of 0.7–1 μ. The filtrate was just as active as the original solution.

In our view the cause of the steric regularity is the optically active nature of the monomers and the extremely complex structure of the catalysts, of the alkoxide type, which result in steric hindrance in the addition of a monomer molecule. The orientation of the monomer molecule takes place at the stage in which the coordination complex of the monomer and catalyst is formed. Coordination is achieved because there is a lone pair of electrons on the oxygen of the three-membered ring and an unfilled *d*-electron shell in the iron atom.

In the presence of water the third chlorine is removed from the $Cl-Fe(OR)_2$ catalyst on heating to the polymerisation temperature (80°).[12] It is still not known whether this hydrolysed catalyst is a compound of the type $OHFeOR_2$, $Fe(OR)_3$, or $(OR)_2Fe-O-Fe(OR)_2$. The action of water raises the yield of crystalline polymer and therefore such a catalyst must result in great steric hindrance to the addition of the monomer.

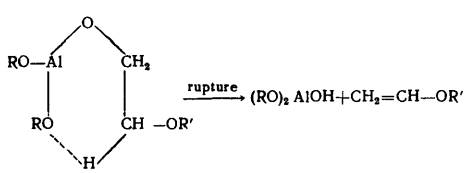
It has been noted that, in polymerisation of epoxy-compounds on organometallic and alkoxide systems, the cause of steric regularity is the heterogeneity of the system. Ebert and Price [46] report that catalytic solutions of triethylaluminium give a Tyndall cone and therefore contain colloidal particles, which are probably formed by reaction of the alkylaluminium with water or oxygen. The surface of these colloids creates a general steric hindrance and provides the necessary short-range order in the system being polymerised.

The structure of the alkylaluminium + water catalytic system is to some extent similar to the diethylzinc + water and Al_2O_3 + $ZnEt_2$ systems, suggested by Furukawa [35]:



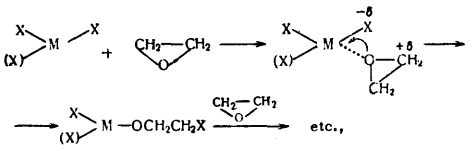
Although the surface of these structures provides activity, it also causes the chief steric hindrance which results in the monomer being absorbed regularly.

Proposals as to the mechanism of polymerisation on aluminium propoxide and isopropoxide in conjunction with anhydrous zinc chloride are not quite clear. In their earlier work, Price and coworkers [32] noticed that, in the polymerisation of 1,2-epoxypropane with aluminium isopropoxide, the reaction stopped after an initial period in which it proceeded rapidly. This "autoinhibition" was prevented by adding anhydrous zinc chloride. Starting from the "coordinate propagation" scheme, it was proposed that chain initiation and growth take place on the Al(iso-$-OC_3H_7)_3$. Rupture of the chain produces an unsaturated polymeric molecule and inactive $(OR)_2AlOH$:



The action of the zinc chloride is to change the inactive $Al(OR)_2OH$ into the active $Al(OR)_2Cl$.

In later work[10] it was found that the two catalysts (aluminium alkoxide and zinc chloride) react with the epoxyethane or epoxypropane independently of each other and a "coordinate propagation" scheme can be proposed for each:



where M = Zn or Al, and X = Cl or $OCH(CH_3)_2$.

As only a monomeric molecule is coordinated with the metal atom, the cationic character of the carbon atom bound to the oxygen is highly developed. The anionic character of the chlorine atom or isopropoxide group also increases, promoting migration of the monomer. Furthermore, zinc chloride by itself is a catalyst for polymerisation of epoxyethane and 1,2-epoxypropane.

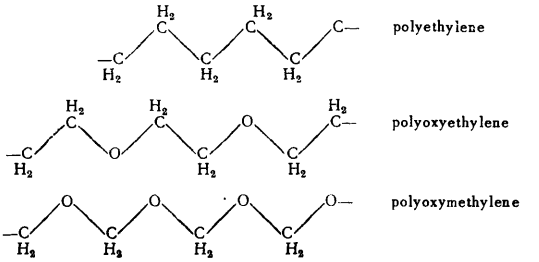
5. PROPERTIES AND STRUCTURE OF POLYMERISED OXIDES

The properties of known polyethers have been little studied. There are several references to melting points, intrinsic viscosities, solubilities, and, less often, X-ray diffraction patterns and infra-red spectra, but only a few to determinations of molecular weights by various methods[10,13,24,33]. Terminal hydroxyl groups have been determined by esterification with phthalic anhydride[10], and the possible unsaturation by bromination of the polymer dissolved in chloroform[10]. Polyoxypropylene prepared on powdered potassium hydroxide at room temperature contained both hydroxyl groups and double bonds[24]. The ratio of the hydroxyl number to the bromine number was 1 : 0.67.

There are contradictory data for the properties of the epoxyethane polymer obtained on the aluminium isopropoxide + zinc chloride system. Miller and Price[33] found one double bond per polymeric molecule, but Ebert and Price[10] did not detect any double bonds in polyoxyethylene prepared under similar conditions. Our determination of hydroxyl groups and the degree of unsaturation in polyoxychloropropylene prepared on Pruitt and Baggett's catalyst ($FeCl_3$--1,2-epoxypropane), using the methods described[10,47], did not give reproducible results. The reasons for this are unknown.

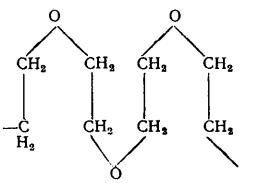
The molecular weights of liquid polymers were determined cryoscopically in benzene, by Rast's method in cyclopentadecanol (K_f = 21.3) or *p*-nitrotoluene (K_f = 7.8),[10] or by calculation from the intrinsic viscosity. For polyoxypropylene in benzene, $[\eta] = 1.4 \times 10^{-4} M^{0.8}$.[46] For polyoxyethylene in aqueous solution at 20°, the formula $\eta_{sp}/C = 9.8 \times 10^{-4} M^{0.59}$ was used[33].

No papers specially devoted to the structure of the main chain in polymerised oxides have been published. According to Staudinger[26], if crystalline polyoxyalkenes are assumed to have a chain structure similar to the paraffins and polyoxymethylene, these materials should have similar melting points and solubilities, polyoxyethylene occupying a position intermediate between polyethylene and polyoxymethylene.



However, the properties of polyoxyethylene do not agree with this hypothesis. Thus polyethylene with a degree of polymerisation equal to 90 has m.p. 110° and is soluble in chloroform with difficulty. The dimethyl ether of polyoxymethylene with $\bar{p}$ = 44 has m.p. 160° and is also soluble in $CHCl_3$ with difficulty. Polyoxyethylene with $\bar{p}$ = 30 has m.p. 40°–55° and dissolves easily in $CHCl_3$.

The viscosity of its solutions shows, moreover, that for the same degree of polymerisation the chain of polyoxyethylene is considerably shorter than expected (and in fact equal in length to the chain of polyoxymethylene). This, and also the extremely high solubility of polyoxyethylene in water, can be explained by a twisted or puckered form of chain[26].



In mono- and di-substituted polyoxyethylenes, all the forms of chain proposed for substituted polyalkenes (isotactic, syndiotactic, atactic) are probably obtained. The course of oxygen ring opening on polymerisation is determined by the nature of the substituents and the reaction conditions[48]. There is a greater probability of breaking the bond between the primary carbon atom and the oxygen than of the bond between the secondary carbon and the oxygen. This leads to retention of configuration in the polymer link after migration of the monomeric, optically active molecule. An isotactic polymer chain structure has been proposed for polyoxypropylene[47]. Its supermolecular structure is spherulitic[13].

The properties of the known polymerised epoxides show an extreme variety, and therefore some of these polymers have already found application in many branches of industry. Polyoxyethylene of various molecular weights is widely used in the pharmaceutical industry as a hydrophilic base, owing to its high solubility in water and its complete physiological inactivity[50,51]. It is also used as a plasticiser for polyurethane resins[41].

Solid polymers of 1,2-epoxides (of 1,2-epoxypropane, 3-chloro-1,2-epoxypropane, epoxybutane, etc.) can be used to produce castings, films, fibres, and in various compositions for coatings. They possess high strength, owing to their regular structure, good dielectric properties, and keep their elasticity even at temperatures as low as -70°.[23]

It is clear that the polymerisation of 1,2-epoxides and investigation of the structure and properties of the polymers obtained are of great theoretical and practical interest. The synthesis of sterically regular polyether compounds from optically active monomers and racemic mixtures forms part of the extremely interesting and complex problem of directed stereosynthesis.

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APPLICATION OF POLAROGRAPHY TO ORGANIC CHEMISTRY

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CONTENTS

I.	Introduction	341
II.	Investigation of structure and the effect of substituents on the reactivity of organic compounds	342
III.	Detection of hydrogen bonds and chelate rings	347
IV.	Study of tautomeric changes	348
V.	Study of the stereoisomerism of organic compounds	351
VI.	Study of the kinetics of chemical reactions	353
VII.	Study of molecular rearrangements and reactions	356
VIII.	Relation between polarographic data and those of other methods of investigation	357

I. INTRODUCTION

The present review is dedicated to the centenary of Butlerov's theory of the structure of organic compounds and to the fortieth anniversary of the invention by J. Heyrovský of the polarographic method of analysis, which is being successfully employed at the present time for the investigation of the structure, properties, and reactions of organic compounds.