Anionic Polymerization of Epichlorhydrin

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Introduction

Epichlorhydrin was polymerized by cationic catalysts such as boron trifluoride[1] leading to very low melting linear polymers. Amorphous polymers were also obtained with aluminum triethyl, zinc diethyl, or zinc chloride-aluminum isopropoxide catalysts,[2] which gave fast polymerization at room temperature. Recently, linear crystalline polyepichlorhydrin (m.p. 119°C.) was prepared using ferric chloride-propylene oxide complexes[2,3] or alkyls of zinc, magnesium, or aluminum with appropriate quantities of water as catalysts.[4]

Polyepichlorhydrin was used for the preparation of polymers in which the chlorine was replaced by tertiary amines such as pyridine.[1] Epichlorhydrin is used in the preparation of ion-exchange resins based on cellulose,[5] or polyamines;[6] with the latter it leads to crosslinking, and to alkylation of the amino groups.

In the anionic polymerization of epichlorhydrin there is the possibility of interaction of the basic catalyst with the chlorine atom. Therefore, the catalyst must be used in equivalent molar amounts for a high conversion, and the resultant polymers will have a low chlorine content. Under this condition, epichlorhydrin may behave as a trifunctional monomer causing crosslinking.

These crosslinked polymers can be converted to exchange resins by the reaction of various reagents with the free hydroxyl groups of the polymers or with their chlorine atoms. These reactions, if carried out to a high degree of substitution, may yield resins having a large equivalent capacity as compared with resins based on epichlorhydrin and cellulose,[5] etc., in being based solely on epichlorhydrin.

These considerations prompted the investigation of the polymerization of epichlorhydrin by basic catalysts.

Results

The following basic reagents were investigated as possible catalysts for the polymerization of epichlorhydrin both in bulk and in toluene solution, at room temperature and at 110–120°C: butyl lithium, sodamide, sodium methoxide, alkali metal carbonates, alkaline earth metal hydroxides (such as barium hydroxide octahydrate), and alkali metal hydroxides. Only potassium hydroxide at about 100°C. was found to be an active catalyst. Sodium hydroxide was a very weak catalyst and gave some polymer only when an equivalent amount of water was added to the catalyst suspension at 110–120°C. Lithium hydroxide gave no polymer, showing that the catalytic strength of the alkali metal hydroxides depends largely on the electropositivity of the attached metal.

In all cases the polymers obtained were crosslinked, as shown by their complete insolubility in a large number of solvents. They were stable at relatively high temperatures and decomposed above 300°C. Boiling with dilute acid caused no decomposition. In boiling dilute alkali they lost all their chlorine with ease. In fact the chlorine content of the polymers as determined by analyses was the same as that determined by hydrolysis with alkali. Infrared spectra of the polymers showed absorptions at 5.7–5.8 and at 6.05–6.2 μ, showing the presence of C=O and C=C bonds.

Large amounts of catalyst were needed for the polymerization, and even on using 150 mole-% of potassium hydroxide, the yield of the polymer was only about 50–55%. The polymers obtained had a low chlorine content varying from about 2 to 7%, depending on polymerization conditions, as compared with 38.5% for pure polyepichlorhydrin.

Carrying out the polymerization in bulk (Table I) at 115–120°C., using ground potassium hydroxide (75.6%), and varying the amount of catalyst, it was shown that under otherwise constant conditions the degree of conversion increased with increasing amount of catalyst. Thus the polymer yield was 8% on using 20 mole-% catalyst and 55% on using 150 mole-% catalyst. The catalyst, even at the lower molar ratios, was only partially consumed. In the various runs the

TABLE I
Effect of Catalyst Amount on the Polymerization of
Epichlorhydrin in Bulk[a]

Catalyst,[b] mole-%	Yield		Chlorine in polymer, %
	g.,	%	
20	0.4	(8)	3.4[c]
50	1.2	(25)	6.2
80	2.2	(47)	7.3
100	2.4	(51)	6.6[d]
120	2.6	(55)	6.25[e]

[a] The experiments were carried out using ground potassium hydroxide (75.6%) and 5 ml. of epichlorhydrin (0.064 mole): polymerization temperature, 115–120°C.; reaction time 30 min.

[b] The mole per cent is based on moles epichlorhydrin.

[c] Analysis: C, 51.3; H, 7.7.

[d] Analysis: C, 50.5; H, 7.4.

[e] Analysis: C, 50.6; H, 7.2. (The C content of the polymers is even higher than for polyglycidol (C, 48.7; H, 8) due to loss of chlorine by crosslinking or by epoxide formation.)

catalyst consumptions varied between 20 and 70%. This may be due to the heterogeneity of the polymerization medium and the insolubility of the catalyst and the precipitating polymer.

TABLE II
Effect of Catalyst Amount on the Polymerization of
Epichlorhydrin in Toluene

Catalyst, mole-%	Yield		Chlorine in polymer, %
	g.,	%	
	A[a]		
20	0.6	(13)	3
20	0.6	(13)	3.2
50	1.5	(32)	3.5
100	1.9	(40)	5.3
150	2.3	(50)	4.8
150	2.2	(47)	5
	B[b]		
20	0.6	(13)	2.6
100	2.4	(51)	4
150	2.6	(55)	4.3
	C[c]		
20	0.6	(13)	2.7
100	1.2	(25)	2
150	1.9	(40)	2

[a] The experiments were carried out using 86% potassium hydroxide pellets, these being added to a solution of 5 ml. of epichlorhydrin (0.064 mole) in 15 ml. of toluene; polymerization temperature, 115–120°C.; time, 30 min.

[b] Experimental conditions as in A except that ground potassium hydroxide was used.

[c] Experimental conditions as in A except that 75.6% potassium hydroxide pellets were used.

Carrying out the polymerization in toluene under otherwise constant conditions (Table IIC) showed that the yield was comparatively lower and the chlorine content of the polymers generally smaller.

Polymerization experiments (Table IIA, IIB) showed that the state of the catalyst (whether ground or in pellet form) affected the polymerization to a small extent. With ground catalyst a slightly better yield of polymer was obtained and the chlorine content was generally a little lower. The amount of water of hydration in the potassium hydroxide had a greater effect on the polymerization. This is seen from Table IIA and IIC, which shows the effects of 86 and 75.6% potassium hydroxide ($^1/_2$ mole and 1 mole of water of hydration, respectively). The yields of polymer and the chlorine content were both lowered with increase in the water content.

The effect on the polymerization of ethereal solvents (which are capable of complex formation with the catalyst or with the growing end of the polymers) was also studied (Table III). With dioxan (b.p. = 101°C.) the yield was lower than in toluene. With the polyether 1,2-bis-(2-methoxyethoxy)-ethane at 140°C. the results were similar

TABLE III
Effect of Catalyst Amount on the Polymerization of
Epichlorhydrin in Ethereal Solvents

Catalyst, mole-%	Yield		Chlorine in polymer, %
	g.,	%	
	A[a]		
20	0.2	(4)	4
100	0.9	(19)	3
150	1.8	(38)	3.5
	B[b]		
20	0.2	(4)	4.6
100	0.5	(11)	2.8
150	1	(21)	3.3
	C[c]		
20	0.5	(11)	2.9
80	1.7	(36)	—
100	1.9	(40)	2
150	2.2	(47)	4

[a] The experiments were carried out using 86% potassium hydroxide pellets and 5 ml. epichlorhydrin (0.064 mole) in 15 ml. of dioxan; polymerization temperature, 105–110°C.; reaction time, 1 hr.

[b] Experimental conditions as in A except that 75.6% potassium hydroxide pellets were used.

[c] Experimental conditions as in A except that 1,2-bis(2-methoxyethoxy)ethane was used; polymerization temperature, 140°C.; reaction time, 30 min.

to those obtained in toluene except that the chlorine content of the latter polymers was lower.

Using nitrobenzene as solvent, no polymerization occurred, probably due to interaction with the catalyst or with the growing chain end. Using concentrated aqueous potassium hydroxide solutions no polymerization occurred.
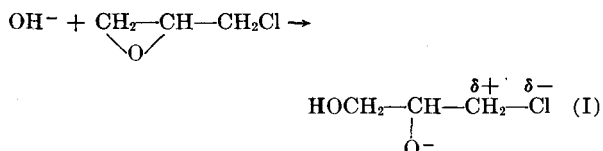
Discussion

The special features of the anionic polymerization of epichlorhydrin by potassium hydroxide are the formation of insoluble crosslinked polymers and the low chlorine content of these polymers.
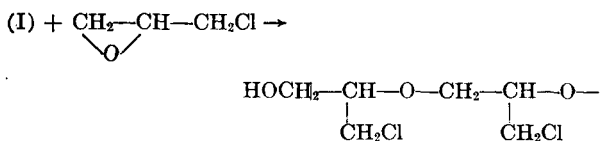
Initiation

. The initiation of the polymerization is by the hydroxyl anion, as is the case in the polymerization of propylene oxide by potassium hydroxide.[7] The anionic nature of the polymerization is also supported by the dependence of the catalyst strength on the electropositivity of the attached metal.

From what is generally known, reaction of the hydroxyl ion with epoxides leads to addition at the methylene group

$$OH^- + CH_2-CH-CH_2Cl \rightarrow$$
$$\underset{O}{\diagdown\diagup}$$

$$HOCH_2-CH-\overset{\delta+}{CH_2}-\overset{\delta-}{Cl} \quad (I)$$
$$\underset{O^-}{\vert}$$

This is the case, for example, in the preparation of epoxy resins by the reaction of phenoxide ions with epichlorhydrin.[8] On reaction with further monomer, (I) can lead to propagation of the polymerization:

$$(I) + CH_2-CH-CH_2Cl \rightarrow$$
$$\underset{O}{\diagdown\diagup}$$

$$HOCH_2-CH-O-CH_2-CH-O-$$
$$\underset{CH_2Cl}{\vert} \qquad \underset{CH_2Cl}{\vert}$$

An intramolecular attack of the negative alkoxide ion on the partially positive carbon attached to the chlorine atom, (the -I effect of the chlorine), can also occur, leading to the formation of glycidol as follows:

$$(I) \rightarrow HOCH_2-CH-CH_2 + Cl^-$$
$$\underset{O}{\diagdown\diagup}$$
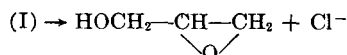
Glycidol is not obtained by direct substitution of the chlorine atom of epichlorhydrin by hydroxyl ions:

$$ClCH_2-CH-CH_2 + KOH \rightarrow KCl + HOCH_2-CH-CH_2$$
$$\underset{O}{\diagdown\diagup} \qquad\qquad\qquad \underset{O}{\diagdown\diagup}$$
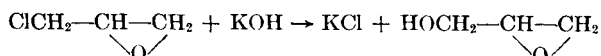
because the epoxide ring is much more reactive than the chlorine atom as is seen from its reaction with phenoxide ion in the preparation of epoxy resins[8] and from its reaction with amines whereby chlorohydroxy amines are formed.[9] Thus glycidol is likely to be formed only by the above reaction, that is, after initiation.
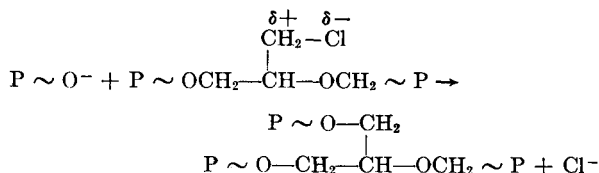
Since glycidol can be formed after initiation, we investigated its polymerization by potassium hydroxide. It was found that glycidol was very reactive and even at room temperature polymerized explosively to a water-soluble polymer. Epichlorhydrin, on the other hand, required heating to about 100°C. for polymerization. It is very improbable, because of this reactivity, that a significant part of the epichlorhydrin converts to glycidol and is then polymerized. The small amount of glycidol formed may either enter copolymerization or homopolymerize immediately, leading to a water-soluble polyglycidol.

Propagation

As stated above, there is the possibility that during the propagation of polymerization the growing anion either attacks further monomer to cause propagation or yields a terminal epoxide by intramolecular reaction. A chain having a terminal epoxide can continue propagation only if the epoxide ring is opened by hydroxide ion or by a propagating chain end. The latter will lead to the formation of crosslinked polymers as follows:

$$P \sim O^- + P \sim OCH_2-CH-CH_2 \rightarrow$$
$$\underset{O}{\diagdown\diagup}$$

$$P \sim OCH_2-CH-CH_2O \sim P$$
$$\underset{O^-}{\vert}$$
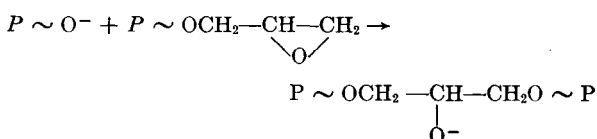
Crosslinked polymers can also be formed by the attack of a growing chain end of a polymer on the positive carbon attached to the chlorine atom:

$$\overset{\delta+}{CH_2}-\overset{\delta-}{Cl}$$
$$\vert$$
$$P \sim O^- + P \sim OCH_2-CH-OCH_2 \sim P \rightarrow$$

$$P \sim O-CH_2$$
$$\vert$$
$$P \sim O-CH_2-CH-OCH_2 \sim P + Cl^-$$

However, owing to the lower reactivity of the CH_2—Cl bond as compared with an epoxide, the formation of crosslinking by interaction with epoxide may be more dominant. On the other hand, the concentration of the chloromethyl group is large, and this may increase the crosslinking by the above reaction.

Crosslinking is also possible if an equilibrium between the free hydroxyl groups of the polymer and the potassium hydroxide exists forming a new alkoxide group which can initiate polymerization.

$$P \sim \underset{\underset{OH}{|}}{CH} \sim P + KOH \rightleftharpoons P \sim \underset{\underset{O^-K^+}{|}}{CH} \sim P + H_2O$$
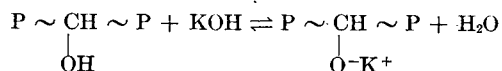
However this does not seem to take place to a significant extent, as glycidol polymerized by potassium hydroxide gives a linear polymer, although polyglycidol has a very high concentration of hydroxyl groups.

Effect of Water Content of Potassium Hydroxide on Polymerization

The water of hydration in the catalyst is tightly held and cannot be removed by azeotropic distillation with benzene. During polymerization when a large part of the potassium hydroxide catalyst has been consumed, this water of hydration is released. It is difficult to say whether the tightly held water of hydration in the catalyst is able to cause termination to a considerable extent, but in the course of polymerization the concentration of "free" water increases and this can lead to termination of anionic polymerization. As was found, concentrated solutions of potassium hydroxide in water caused no polymerization, and it may well be that the concentration of free water in the polymerization mixture reaches a limit where further polymerization is not possible. This may be one of the main reasons for the low degree of conversion—only about 50%. Side reactions such as hydrolysis of the monomer by the alkaline medium may also contribute to the lowering of the conversion.

Termination by water keeps the concentration of hydroxyl ions constant, while there is an increase in the hydroxyl content of the polymer. The presence of free water in relatively appreciable concentrations in the latter stages of polymerization will also lower the chlorine content of the polymers due to its polar nature and hydrolytic capabilities.

The presence of small amounts of water tends to assist polymerization, as is seen from the fact that water added to sodium hydroxide leads to some polymerization. The polar effect of the water and especially its hydration capability seem to help polymerization by increasing the ionization of the sodium hydroxide.
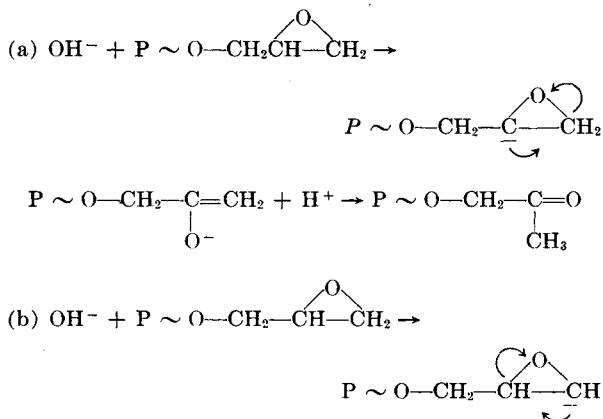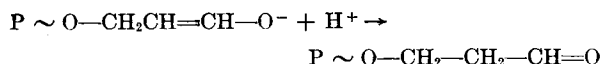
Surface Area of the Catalyst

The surface area of the catalyst has some effect on the course of the polymerization. A larger surface area leads to a somewhat greater conversion due to the larger contact area between the catalyst and the monomer. Because of the heterogeneity of the catalyst and the precipitating polymer the catalyst is not completely consumed.

Origin of the C=O and C=C Double Bonds in the Polymers

The formation of double bonds was also observed in the base-catalyzed polymerization of propylene oxide. St. Pierre and Price[7] suggested that these C=C double bonds are formed when a negative oxygen atom on a growing chain end abstracts a hydrogen of a methyl group six atoms away, followed by the elimination of the anion of 1,2-propanediol. Simons and Verbanc[10] proposed the formation of allyloxy groups as a result of the base abstracting a proton from the methyl group of propylene oxide and a subsequent base-catalyzed rearrangement to allyloxy radical. Gee[11] suggested a transfer reaction whereby a growing polymer chain abstracts a hydrogen atom from the middle carbon atom of propylene oxide giving a terminated polymer and isopropenyloxy anion which starts a new chain.

In the crosslinked polymers of epichlorhydrin, C=O and C=C double bonds were found to occur together. This may suggest the possibility that the formation of both is due to a single cause. It is known[12] that rearrangement reactions of epoxides occur under basic conditions whereby ketones or aldehydes are formed. In the polymerization of epichlorhydrin such a rearrangement may occur as a result of an attack of a hydroxyl ion on a terminal epoxide as follows:

(a) $OH^- + P \sim O-CH_2\overset{O}{\overset{/\backslash}{CH}}-CH_2 \rightarrow$

$$P \sim O-CH_2-\overset{O}{\overset{/\backslash}{C}}-CH_2$$

$$P \sim O-CH_2-\underset{\underset{O^-}{|}}{C}=CH_2 + H^+ \rightarrow P \sim O-CH_2-\underset{\underset{CH_3}{|}}{C}=O$$

(b) $OH^- + P \sim O-CH_2-\overset{O}{\overset{/\backslash}{CH}}-CH_2 \rightarrow$

$$P \sim O-CH_2-\overset{O}{\overset{/\backslash}{CH}}-CH$$

$$P \sim O-CH_2CH=CH-O^- + H^+ \rightarrow$$
$$P \sim O-CH_2-CH_2-CH=O$$

The base abstracts a hydrogen atom from the epoxide, either from the —CH— or the —CH₂— groups, although one of the positions may be favored. In both cases rearrangement can occur due to shifting of the electrons and an enolate ion formed. If propagation is continued by these ions then the polymers formed would have double bonds. On the other hand if no propagation occurs then the enolate ion can abstract a proton and convert to an aldehyde or a ketone. In confirmation of the above, it was found that the polymers obtained gave 2,4-dinitrophenyl hydrazones as is consistent with the presence of carbonyl groups of aldehydes or ketones. The polymers also gave a weak reaction with Fehling's reagent. However this test cannot be conclusive evidence for the presence of aldehyde groups since the double bonds found in the polymer may also reduce the reagent. Reaction with fuchsin reagent as a test for aldehydes was not conclusive.

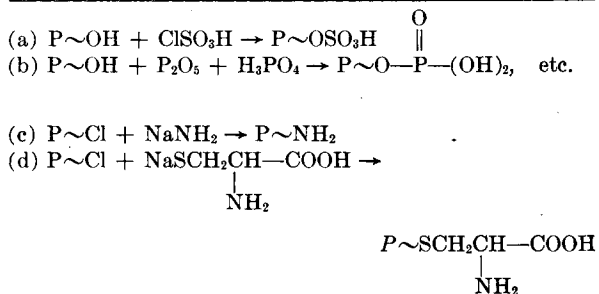### Preparation of Exchange Resins from Polyepichlorhydrin

Various preliminary experiments on the possibilities of converting the insoluble crosslinked polyepichlorhydrins to exchange resins were investigated. These experiments were carried out in two main directions, one utilizing the hydroxyl groups of the polymers and the other its reactive chlorine. In connection with the former method it was found that the residual chlorine in the polymer can be hydrolyzed quantitatively on boiling for about 1 hr. with dilute sodium hydroxide. The resulting polymers had about 19–20% hydroxyl groups as compared with 23% for polyglycidol. The lower hydroxyl content is likely due to the chlorine lost by crosslinking, which now cannot be replaced by hydroxyl.

We attempted the conversion of the polyhydroxy polymer to a sulfate ester having free sulfonic acid groups which can act as a cation exchange resin. On reaction of the polymer with chlorosulfonic acid in chloroform suspension [Table IV(a)], an acidic polymer was obtained. This polymer proved to be a reversible cation-exchange resin. Phosphorylation of the polyhydroxy polymer [Table IV-(b)] succeeded with polyphosphoric acid at 60–70°C. The polymer obtained was also a reversible cation-exchange resin.

The reactivity of the chlorine in polyepichlorhy-

drin was made use of for the introduction of amino groups in the polymer by reaction with sodamide in liquid ammonia [Table IV(c)]. The new polymer can act as an anion-exchange resin. Reaction of the chlorine with cysteine in liquid ammonia [Table IV(d)] incorporated this amino acid in the polymer. The new polymer gave positive reaction with ninhydrin, the blue coloration appearing in solution showing the presence of free amino and carboxyl groups. This insoluble crosslinked polymer can act both as a cation and an anion-exchange resin. Due to the proximity of the amino and carboxy groups it may act as a chelating agent for heavy metal ions. Furthermore, the sulfur atoms can be oxidized reversibly to sulfoxide or sulfone, so that it may act as an electron-exchange resin.

TABLE IV
Polymer Reaction

(a) $P \sim OH + ClSO_3H \rightarrow P \sim OSO_3H$

(b) $P \sim OH + P_2O_5 + H_3PO_4 \rightarrow P \sim O-\overset{O}{\overset{\|}{P}}-(OH)_2$, etc.

(c) $P \sim Cl + NaNH_2 \rightarrow P \sim NH_2$

(d) $P \sim Cl + NaSCH_2CH-COOH \rightarrow$
$\qquad\qquad\qquad\qquad |$
$\qquad\qquad\qquad\quad NH_2$

$P \sim SCH_2CH-COOH$
$\qquad\qquad |$
$\qquad\quad NH_2$

Experiments with various chlorinating agents can be carried out to replace the hydroxyl groups in the polyepichlorhydrin with chlorine to increase the chlorine content of the polymer, so that the above-mentioned reactions can be carried out to yield a high degree of substitution of various groups in the polyepichlorhydrin polymer.

Experimental

Purification of Reagents

Epichlorhydrin (BDH) was fractionally distilled under nitrogen, the fraction boiling at 112.5°C./690 mm. being used. Toluene and dioxan were refluxed over sodium wire and distilled under nitrogen. 1,2-Bis-(2-methoxyethoxy)-ethane (Eastman) was fractionally distilled in vacuo, the middle fraction boiling at 121°C./29 mm. being used. Potassium hydroxide (BDH Analar) was used and its concentration was checked by titration with standard acid. Nitrogen was purified from oxygen as described previously.[13]

Polymerization Procedure

The polymerizations were carried out in three-necked flasks, fitted with a high speed stirrer with a mercury seal, reflux condenser equipped with a calcium chloride tube, thermometer, and a gas adapter for introducing nitrogen. The catalyst, solvent, and monomer were added and the polymerization mixture was heated in an oil bath and kept at the required temperature. The polymer started to precipitate as brown particles. At the end of the polymerization, the contents were cooled and then added slowly with rapid stirring to excess of cold hydrochloric acid (1N) and left overnight. The now yellow polymer was filtered, washed with ethanol, water, and ethanol and then dried to constant weight.

The polymer is insoluble in the following solvents whether cold or hot: water, acetone, methanol, glycerine, dimethylformamide, and phenol. It darkens in concentrated sulfuric acid.

This polymerization procedure can be used also for polymerization on a large scale. In a typical experiment 100 ml. of epichlorhydrin (1.22 moles) in 400 ml. of toluene was added to 60 g. of potassium hydroxide pellets (86%) (72 mole-%). At about 100°C. an exothermic reaction set in which caused reflux of the toluene and continued for about 30 min. The polymerization mixture was heated for another 30 min. at 115–120°C. to complete the reaction. The polymer was added to excess dilute hydrochloric acid, filtered and washed as above. Yield: 40 g. polymer; chlorine content of polymer = 4.6%.

In all the tables, the yield was, for simplicity, calculated on the basis of polyglycidol (i.e., chlorine-free. polyepichlorhydrin) owing to the low chlorine content of the polymers.

Preparation of 2,4-Dinitrophenyl Hydrazone of Polymer

Polyepichlorhydrin was heated on a water bath for 20 min. with a solution of 2,4-dinitrophenyl hydrazine in ethanol acidified with a drop of hydrochloric acid. The polymer (colored orange-brown) was filtered and washed with ethanol. Purification was carried out by boiling the polymer several times with ethanol and with dioxan until no solute passed over. A typical 2,4-dinitrophenyl hydrazone had 2.5% nitrogen, which is approximately equivalent to one 2,4-dinitrophenyl hydrazone group for about every 25 units of epichlorhydrin. Infrared spectra of the polymer showed that the original

carbonyl absorption at 5.8 μ was still present but much weaker, and to the original double bond absorption at 6.15 μ, new absorptions for double bonds at 6.2 and 6.3 μ (C=N of the hydrazone and benzene) also appeared. The polymer had the absorptions of nitro groups at 6.6, 6.7, and 7.5 μ.

Reaction of Polymer with Fehling's Reagent

Polyepichlorhydrin was heated with Fehling's reagent for 20 min. in a water bath. It was filtered and washed with water until the filtrate was free of cupric ions, then with dilute ammonia solution and finally with water. It was heated with dilute nitric acid and filtered. The acid solution was made basic with ammonia and the blue color of the complex between cupric ions and ammonia appeared, showing that there was a positive reaction with the reagent and that some cuprous oxide was formed which precipitated with the polymer.

Determination of Chlorine and Hydroxyl Content of the Polymers

The chlorine content of the polymers was determined by refluxing about 0.1 g. of polymer in 10 ml. of sodium hydroxide (0.1N) for 1 hr. and back-titrating with hydrochloric acid (0.1N). The consumed sodium hydroxide gave the amount of chlorine in the polymer. These analyses were checked with microcombustion analyses for chlorine and found to be the same.

The hydroxyl content of the polymers was determined by acetylation with acetic anhydride-pyridine.[14]

Preparation of "Polyglycidol" from Polyepichlorhydrin

Polyepichlorhydrin containing 2–6% chlorine was heated in a water bath with excess dilute sodium hydroxide. The polymer was filtered and washed with water. It was completely free of chlorine. It swelled in diethylene glycol, pyridine, and dimethylformamide.

Sulfonation of Polyglycidol .

To a three-necked flask fitted with a mechanical stirrer, calcium chloride tube and a funnel fitted with a calcium chloride guard tube, 2 g. of dry polymer (having 20% hydroxyl) and 30 ml. of dry chloroform were added. The flask was cooled to 0°C. and a solution of 3.3 g. of chlorosulfonic acid (20% molar excess) in 20 ml. of chloroform was added drop-wise with rapid stirring over a 20-min.

period. The cooling bath was then removed, the mixture stirred for 2 hr. at room temperature and then poured slowly onto crushed ice. The polymer was filtered and washed with water until free of acid and dried. The capacity of the resin for exchanging cations as determined by elution with sodium chloride solution and titrating the resultant hydrochloric acid was 4 meq./g.

Phosphorylation of Polyglycidol

To a three-necked flask equipped with a mechanical stirrer and a calcium chloride tube, 2 g. of dry polymer (having 20% hydroxyl groups) and 20 ml. of polyphosphoric acid (80% phosphorous pentoxide) were added. The mixture was heated with stirring for 1 hr. at 60–70°C. and then was left overnight at room temperature. It was poured slowly into cold water, stirred for 15 min., filtered and washed with water until the washings were free from acid. The exchange capacity of the resin for cations was 3.1 meq./g.

Reaction of Cysteine with Polyepichlorhydrin

Cystine (0.75 g.) (excess) was dissolved in liquid ammonia (30 ml.) and reduced to cysteine by the addition of small pieces of sodium until a permanent blue solution of excess sodium was obtained. This excess sodium was destroyed by the addition of a small crystal of cysteine. Two grams of polyepichlorhydrin (having 5% chlorine) were added and the mixture stirred until all the ammonia was evaporated. The polymer was filtered, washed with acetic acid, water, dilute hydrochloric acid, and hot water until the filtrate gave negative reaction for free cysteine with nitroprusside. The polymer contained 0.5% nitrogen as compared with 1.75% if total replacement of the chlorine with cysteine had occurred. It was found to be a reversible chelating agent for ferric ions.

Reaction of Polyepichlorhydrin with Sodamide

Two grams of polymer (having 5% chlorine) were added to a solution of 50% molar excess of sodamide in 50 ml. of liquid ammonia. The reaction mixture was stirred for 2 hr. until all the ammonia evaporated. The polymer was filtered and washed with water, dilute hydrochloric acid, water, and dried. The nitrogen content of the polymer was 0.7% as compared with about 1.9% when complete replacement of the chlorine by amine occurs.

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Synopsis

The anionic polymerization of epichlorhydrin with potassium hydroxide was studied at 110–120°C. in bulk and in solution. Large molar equivalent ratios of catalyst were needed for polymerization and even when using 150 mole-% catalyst, the conversion was only about 50%. The polymers obtained were crosslinked and had a low chlorine content. Crosslinking may be due to attack of a propagating chain end on the partially positive carbon attached to the chlorine atom in a polymer, or on a terminal epoxide formed by an intramolecular elimination of chlorine. The water of hydration in the catalyst influenced the polymerization in that it was released on consumption of catalyst causing termination of the polymerization, relatively low conversion, and low chlorine content of the polymers. The polymers had infrared absorptions for both carbonyl and carbon double bonds and gave dinitrophenyl hydrazones that indicate the presence of aldehydes or ketones. Preliminary experiments showed that the crosslinked polyepichlorhydrins obtained can be converted to exchange resins by utilizing either the hydroxyl or the chlorine functions of the polymer. Thus sulfonation and phosphorylation of the polyhydroxy polymer obtained by alkaline hydrolysis of residual chlorine in the polyepichlorhydrin gave inorganic esters that had free acid groups and served as reversible cation-exchange resins. Amination of the polymers with sodamide gave an anion-exchange resin, while replacement of the chlorine with cysteine gave a resin that can be used as a chelating agent for heavy metals.

Résumé

On a étudié la polymérisation anionique en masse et en solution de l'épichlorhydrine avec de l'hydroxyde de potassium à 110–120°C. De grandes quantités molaires équivalentes de catalyseur sont nécessaires pour la polymérisation et, même lorsqu'on utilise 150 mole-% de cataly-

seur, la conversion est seulement de 50% environ. Les polymères obtenus sont pontés et ne contiennent qu'une faible quantité de chlore. Le pontage peut être dû à l'attaque d'une fin de chaîne en croissance sur le carbone partiellement positivé et attaché à l'atome de chlore dans le polymère, ou sur un époxyde terminal formé par réaction intramoléculaire avec élimination de chlore. L'eau d'hydratation du catalyseur influence la polymérisation en ce sens qu'elle est libérée lors de la consommation du catalyseur provoquant l'arrêt de la polymérisation, un taux de conversion relativement faible et une faible teneur en chlore des polymères. Les polymères présentent à l'infra-rouge les bandes d'absorption caractéristiques du groupe carboxyle et des doubles liaisons carbonées, et donnent des dinitrophényl-hydrazones, ce qui indique la présence d'aldéhydes ou de cétones. Des expériences préliminaires ont montré que les polyépichlorhydrines pontées obtenues pouvaient être transformées en résines échangeuses en utilisant soit la fonction hydroxyle soit la fonction chlorée du polymère. La sulfonation et la phosphorylation du polymère polyhydroxylé obtenu par hydrolyse alcaline du chlore résiduel dans la polyépichlorhydrique donnent donc des esters inorganiques possédant des fonctions acides libres et servant comme résines échangeuses de cations. L'amination des polymères avec l'amidure de sodium donne une résine pouvant être utilisée comme agent chélatant pour des métaux lourds.

Zusammenfassung

Die anionische Polymerisation von Epichlorhydrin mit Kaliumhydroxyd wurde bei 110–120° in Substanz und in Lösung untersucht. Grosse Molverhältnisse an Katalysator wurden für die Polymerisation bonötigt und sogar bei 150 Molprozent Katalysator betrug der Umsatz nur ungefähr 50%. Die erhaltenen Polymeren waren vernetzt und besassen einen geringen Chlorgehalt. Die Vernetzung kann auf einen Angriff des wachsenden Kettenendes auf das teilweise positive Kohlenstoffatom, an dem das Chloratom im Polymeren hängt, oder auf eine Epoxydgruppe zurückgeführt werden, die durch eine intramolekulare Chlorabspaltung gebildet wurde. Das Hydrationswasser des Katalysators beeinflusste die Polymerisation, da es bei Verbrauch des Katalysators in Freiheit gesetzt wurde und einen Abbruch der Polymerisation, relativ geringen Umsatz und einen geringen Chlorgehalt der Polymeren verursachte. Die Polymeren besassen im Infraroten Absorptionsbanden sowohl für Carbonyl- als auch für Kohlenstoffdoppelbindungen und lieferten Dinitrophenylhydrazone, was das Vorhandensein von Aldenhyden oder Ketonen aufzeigt. Verläufige Versuche zeigten, dass die erhaltenen vernetzten Polyepichlorhydrin mittels der Hydroxyl- oder Chlorgruppen des Polymeren zu Austauscherharzen umgesetzt werden können. So ergab Sulfonierung und Phosphorylierung des Polyhydroxypolymeren, das durch alkalische Hydrolyse des restlichen Chlors im Polyepichlorhydrin erhalten wurde, anorganische Ester, die freie Säuregruppen besassen und als reversible Kationenaustauscherharze dienten. Aminierung der Polymeren mit Natriumamid ergab ein Anionenaustauscherharz; ein Austausch des Chlors gegen Cystein ergab ein Harz, das als Chelierungsmittel für Schwermetalle verwendet werden kann.