Investigation of the elementary reactions in the synthesis of poly(hydroxethers) in dipolar, aprotic solvents

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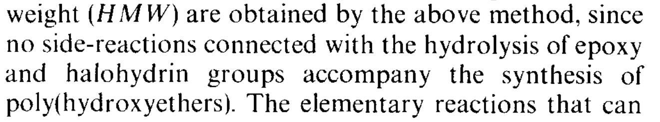
The effect of the hydroxyl groups of various phenols on the course of the reaction of their alkali metal salts with epichlorohydrin in dipolar, aprotic solvents has been studied. It was found that the presence of phenols in the system leads to the formation of a complex salt of the type $(ArO \ldots H \ldots OAr)^{-}Mt^{+}$, and to a considerable decrease in the reaction rate. The mechanism of the reaction of chlorohydrin ethers of phenols with alkali metal phenolates was also studied. The effect of various factors on the course of the reaction of glycidyl ethers with phenols was determined by kinetic measurements.

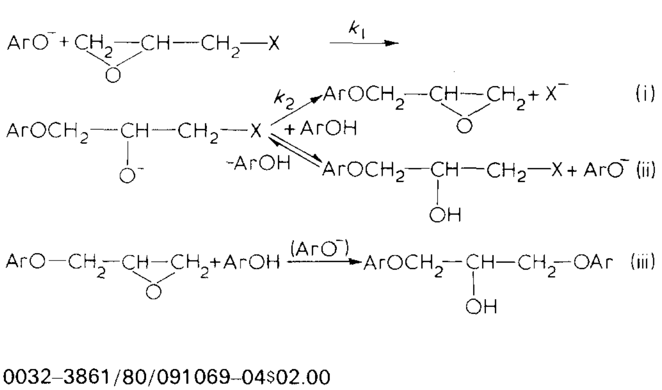
INTRODUCTION

A new method for the synthesis of poly(hydroxyethers), based on the reaction of monoalkali metal salts of diphenols with epihalohydrins at reactant mole ratio 1:1 (Equation 1), and carried out in a homogeneous system in an aprotic polar solvent, has been described previously[1].



Mt = Na, K; X = Cl, Br (1)

Thanks to the anhydrous reaction medium, poly(hydroxyethers) of a considerably high molecular weight (*HMW*) are obtained by the above method, since no side-reactions connected with the hydrolysis of epoxy and halohydrin groups accompany the synthesis of poly(hydroxyethers). The elementary reactions that can proceed in the course of synthesis of *HMW* poly(hydroxyethers) in a system containing monoalkali metal salts of diphenol and epihalohydrin in an anhydrous medium are presented by Reactions (i–iii).



The elementary reactions taking place during the synthesis of low molecular weight epoxy resins from alkali metals bisphenolates and epihalohydrins in dipolar aprotic solvents have been described and discussed by us elsewhere[2].

Since free phenol hydroxyl groups are present in an equimolar number with respect to the number of phenolate groups and epihalohydrin in systems in which *HMW* poly(hydroxyethers) are formed, it seemed worthwhile to study model reactions in systems containing simple monofunctional compounds.

The purpose of this work was to study the effect of the presence of hydroxyl groups of various phenols on the kinetics and mechanism of the reaction of their alkali metal salts with epichlorohydrin (Reaction i) in dipolar, aprotic solvents in an anhydrous medium. We also decided to study the mechanism of the reaction of phenyl chlorohydrin ethers with alkali metal phenolates (Reaction ii).

It also seemed worthwile to study the kinetics and mechanism of the reaction of phenyl glycidyl ethers with phenols in the presence of phenolates and alkali metal halides (Reaction iii) leading to the formation of oxy(2-hydroxytrimethylene)oxy groups, $[O-CH_2-CH(OH)-CH_2-O]$, which are characteristic of poly(hydroxyethers).

EXPERIMENTAL

Materials

Phenols and diphenols were prepared by conventional methods described in the literature and purified by distillation or recrystallization: 2,2-bis[4-(2,3-epoxypropoxy)phenyl]propane, bis[4-(2,3-epoxypropoxy)-phenyl]-2,2-dichloroethene were prepared according to the methods reported[3,4]. 2,3-Epoxypropoxyphenyl-

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Table 1 Dependence of rate constants of reactions of various sodium phenolates with epichlorohydrin carried out in different solvents on the presence of equimolar amounts of free phenols[a]

Sodium salt	Free phenol	Solvent	Reaction temperature (°C)	$10^2.k_2$ $dm^3\ mol^{-1}\ s^{-1}$
m-cresol	–	DMSO	70	3.1
"	*m*-cresol	"	70	0.53
"	phenol	"	70	0.47
"	*p*-nitrophenol	"	70	0.015
p-nitrophenol	–	"	110	0.32
"	*p*-nitrophenol	"	110	0.098
m-cresol	–	diglyme	70	0.20
"	*m*-cresol	"	70	0.17
"	–	sulpholane	70	0.61
"	*m*-cresol	"	70	0.35
"	–	isopropanol	70	0.55
"	*m*-cresol	"	70	0.45
bisphenol A	–	DMSO	70	3.2
"	bisphenol A	"	70	0.51[b]

[a] Exact details on the reaction conditions – s. Exp. part.
[b] At the beginning of the reaction

Table 2 Effect of *m*-cresol on the rate constant of the reaction of sodium *m*-cresolate with epichlorohydrin in DMSO at 70°C[a]

Mol ratio *m*-cresol/sodium *m*-cresolate	$10^2.k_2$ $dm^3\ mol^{-1}\ s^{-1}$
20	0.097
5	0.098
2	0.18
1	0.53
0.5	0.84[b]
0.1	2.1[b]
0	3.1

[a] Exact details on the reaction conditions – s. Exp. part.
[b] At the beginning of the reaction

(phenyl glycidyl ether) (Koch–Light Laboratory Ltd) was used after fractionation under reduced pressure. Solvents were purified by the usual procedures.

Analytical methods

Determination of the content of alkali metal phenolates has been described[2]. The content of epoxy groups in the samples of the reaction mixture was determined by titration with a solution of HCl in 1, 4-dioxane.

The content of *m*-cresol was determined by examining the absorption of its complex with 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (4-amino-antipyrine) in dimethylformamide using a SFR-1 spectrometer at a wave length of 580 nm[5].

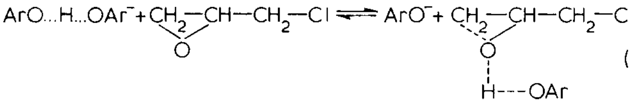
Kinetic measurements

The kinetic studies of the reaction of alkali metal phenolates and bisphenolates with epichlorohydrin in the presence of free phenols were carried out as in Reference 2, the only difference being the introduction an additional amount of free phenol or bisphenol to the reaction mixture.

Studies on the rate of conversion of epoxy groups in the reaction of glycidyl ethers with phenols and diphenols were carried out in a nitrogen atmosphere in an apparatus described in Reference 2. Firstly, the salt of the respective phenol was obtained and then, the free phenol and respective glycidyl ether were added. The concentration of phenols and glycidyl ethers in DMSO was 0.15 M dm^{-3}.

RESULTS AND DISCUSSION

The addition of an equimolar amount of free phenol to the reaction system sodium pheolate–epichlorhydrin in DMSO was found to cause a considerable decrease of the rate constant of Reaction (i) (*Table* 1). This effect is particularly clear for phenolates of a relatively high nucleophility, e.g. for *m*-cresolate and bisphenolate A. The introduction of a phenol characterized by strong acidic properties, e.g. *p*-nitrophenol, to the system studied causes a further decrease of the rate constant of Reaction (i). The changes in the rate of Reaction (i) are probably connected with the possibility of formation in the system containing a dipolar aprotic solvent of a complex salt of the type $(ArO \ldots H \ldots OAr)^-Na^+$. The presence of such complex salts in solutions containing phenols and their salts was proved by Bruss and Harlow[6]. At the same time, the oxygen atom in the oxirane ring of epichlorohydrin can be protonated by molecules of free phenol. Thus, an equilibrium is established in the system (Equation 2).



$$ArO \ldots H \ldots OAr^- + CH_2{-}CH{-}CH_2{-}Cl \rightleftharpoons ArO^- + CH_2{-}CH{-}CH_2{-}Cl \qquad (2)$$

Protonation of the oxirane ring should facilitate its opening and, hence, cause an increase in the rate of the reaction studied (i). On the other hand, the complex salt is characterized by a remarkably lower reactivity than the free phenolate anion or ion pair separated by solvent and, therefore, a decrease in the rate of the investigated reaction of alkali metal phenolate with epihalohydrin should be observed. Since a considerable decrease of the reaction rate is observed after the addition of free phenol, the latter effect dominates and the equilibrium (2) is shifted to the left (the complex salt is favoured).

When carrying out the reaction in solvents characterized by a lower ability to solvate cations than DMSO (sulpholane, diglyme), the presence of free phenol does not cause such a clear decrease in the rate of the reaction under discussion (*Table* 1). A similar phenomenon is observed for the reaction carried out in isopropanol as the reaction medium; the reaction rate constant changes only slightly after the addition of an equimolar amount of *m*-cresol to the system (*Table* 1). This results from the fact

Table 3 Effect of 2,6-disubstituted phenols on the rate constants of the reaction of their sodium salts with epichlorohydrin in DMSO[a]

Sodium salt	Free phenol	Reaction temp. (°C)	$10^2.k_2$ $dm^3\ mol^{-1}\ s^{-1}$
2,4,6-tribromo-phenol	–	110	0.53
"	2,4,6-tribromo-phenol	110	0.60
2,6-dimethyl phenol	–	70	1.7
"	2,6-dimethyl-phenol	70	1.3
2,6-di-t-butyl--p-cresol	–	70	0.055
"	2,6-di-t-butyl--p-cresol	70	0.056

[a] Exact details on the reaction conditions — s. Exp. part.

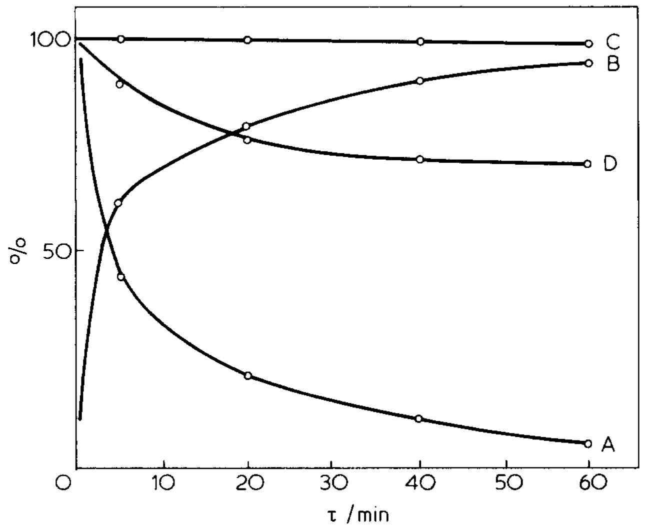


Figure 1 Conversion of cresolate (A) and epoxy (B) groups and *m*-cresol (C) in the reaction of phenyl chlorohydrin ether ($C_6H_5OCH_2CH(OH)CH_2Cl$) with sodium *m*-cresolate in DMSO (Reaction ii) at 30°C, and the conversion of *m*-cresol (D) in the reaction of epichlorohydrin with sodium *m*-cresolate (Reaction i) in DMSO at 30°C

that the solvation of the cresolate anion by isopropyl alcohol considerably hinders the formation of the complex salt.

In *Table* 2, the values of rate constants of the reaction of sodium *m*-cresolate with epichlorohydrin in DMSO at 70°C, carried out at different *m*-cresol/*m*-cresolate mol ratios, are present. It was observed that the reaction rate constant does not change for the *m*-cresol/*m*-cresolate mol ratio greater than 2. For small concentrations of *m*-cresol, the rate constant increases with time. This can be explained by the fact that *m*-cresol, besides complexing the cresolate anion, can also react with the simultaneously formed glycidyl ether of *m*-cresol (Equation 3). The secondary hydroxyl groups formed in this reaction complex the cresolate anion to a smaller degree.

The results of studies on the effect of the presence of *o*-disubstituted phenols by sterically large groups, CH_3, Br, $C(CH_3)_3$ on the rate of the reaction of their salts with epichlorohydrin in DMSO are presented in *Table* 3. It was found that the introduction of such phenols to the investigated system does not influence the reaction rate constant. The steric hindrances caused by the *ortho* substituents in these compounds are great enough to prevent the formation of a hydrogen bond between the phenol and its salt. Thus, these studies confirm the effect of complex salts on the rate of the described reaction.

The conversions of phenolate and epoxy groups and *m*-cresol during the model reaction of phenyl chlorohydrin ether with sodium *m*-cresolate (Reaction ii) are presented in *Figure* 1. As appears from curves 1 and 2, the overall concentration of epoxy and phenolate groups hardly changes during 60 min. Also the overall concentration of free *m*-cresol and sodium *m*-cresolate does not change. However, a complete conversion of phenolate groups (curve 1) is observed. This shows that the substitution of the chlorine atom by the cresolate anion does not take place, and only internal nucleophilic substitution with the

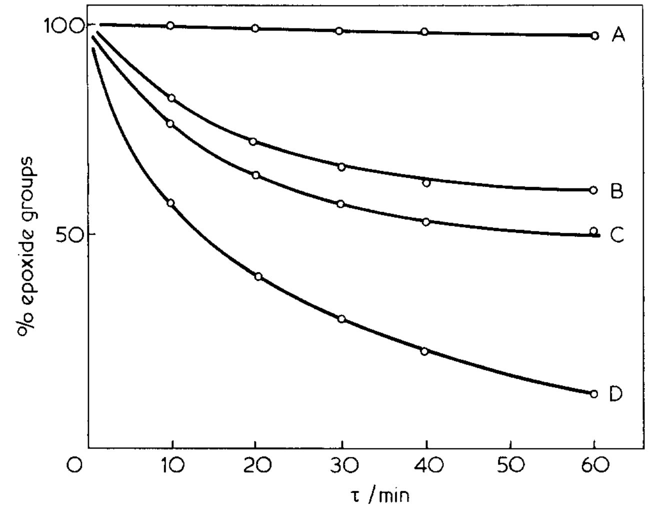


Figure 2 Effect of catalysts on the conversion of epoxy groups in phenyl glycidyl ether in the reaction with *m*-cresol in DMSO at 155°C. A, without catalyst; B, with 0.01 m NaCl; C, with 0.01 m KCl; D, in the presence of an equimolar amount of sodium *m*-cresolate (at 70°C)

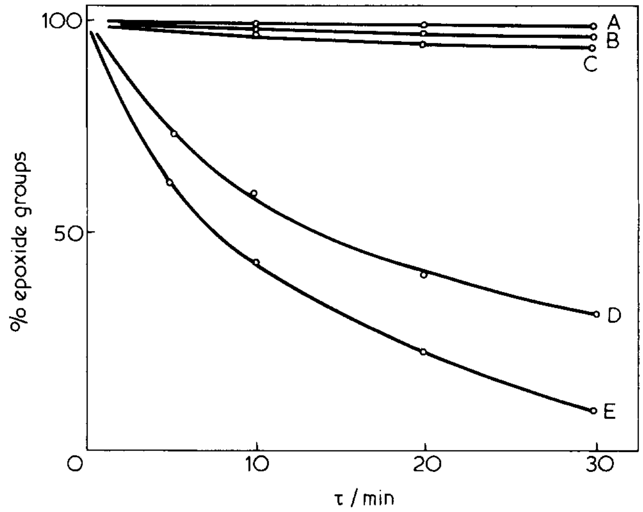


Figure 3 Effect of the structure of phenols on the rate of their reactions with phenyl glycidyl ether ($C_6H_5OCH_2–CH–CH_2$, epoxide O bridging CH and CH₂) in the presence of equimolar amounts of sodium salts of these phenols in DMSO (at 70°C). A, *p*-nitrophenol; B, 4,4′-sulphonyldiphenol, (bisphenol S); C, 4,4′-(2,2-dichlorovinylidenediphenol); D, *m*-cresol; E, 4,4′-isopropylidenediphenol, (bisphenol A)

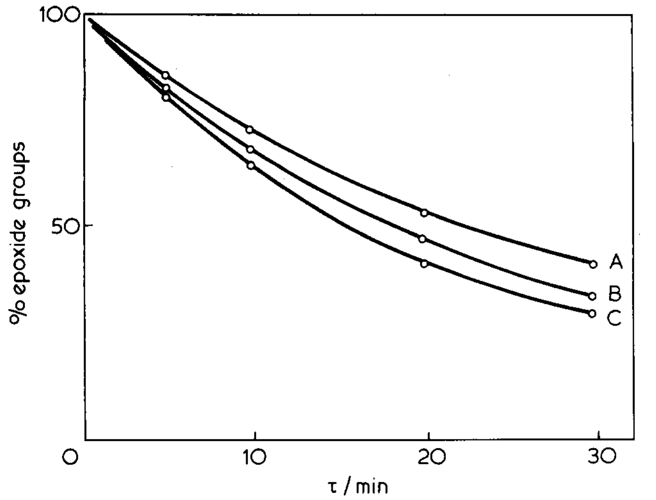


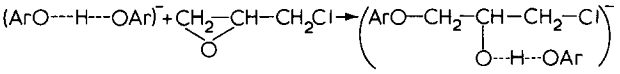
Figure 4 Effect of the structure of glycidyl ethers on the rate of their reactions with *m*-cresol in the presence of an equimolar amount of sodium *m*-cresolate in DMSO at 70°C. A, bis[4-(2,3-epoxypropoxy) phenyl]-2,2-dichloroethene; B, 2,3-epoxypropoxyphenyl, (phenyl glycidyl ether); C, 2,2-bis[4-(2,3-epoxypropoxy)phenyl] propane

formation of an oxirane ring occurs. Probably anchimeric acceleration plays an essential role here.

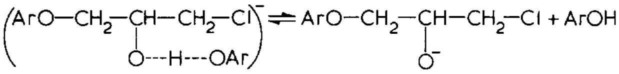
From the comparison of the rate of conversion of cresolate with simultaneous regeneration of the oxirane ring (in the reaction of chlorohydrin ether with soduim *m*-cresolate) [Equations (ii) and (i)] curves A, B in *Figure* 1) and the rate of the reaction of epichlorohydrin with sodium *m*-cresolate [Equation (2)] (curve D in *Figure* 1), it appears that the first step (k_1), i.e. the nucleophilic attack of the phenoxide anion at the α carbon atom in the oxirane ring, and not the repeated oxirane regeneration step (k_2), is the reaction rate determining step. The conversions of epoxy groups in the model reaction of phenyl glycidyl ether (PGE) with *m*-cresol in DMSO in the presence of different catalysts (Reaction iii) are given in *Figure* 2. The introduction of sodium *m*-cresolate to the system has the greatest effect on the kinetics of the reaction. Sodium *m*-cresolate is not used up in this reaction and acts as a catalyst. *Figures* 3 and 4 show the effect of the structure of phenols and glycidyl ethers on the rate of their reaction in DMSO. It was observed that, in the case of phenols characterized by a relatively high acidity, the conversion of epoxy groups of PGE does not exceed 5%, even after 1.5 h at 150°C. The character of phenyl groups in glycidyl ethers does not have an essential on the rate of the reaction studied (iii). The transfer of induction effects of $C=CCl_2$ and $C(CH_3)_2$ groups through the ether bond and aliphatic chain of the epichlorohydrin molecule is small here.

On the basis of these studies on the elementary reactions in model systems, the following mechanism of elementry reactions in the synthesis of poly(hydroxyethers) in anhydrous conditions can be proposed:

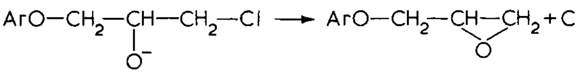
$$\mathrm{ArO^- + HOAr \rightleftharpoons (ArO{-}{-}{-}H{-}{-}{-}OAr)^-} \qquad (3)$$



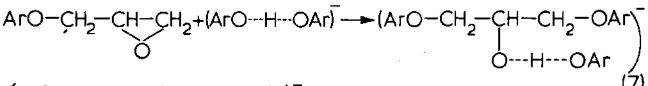
$$\mathrm{(ArO{-}{-}{-}H{-}{-}{-}OAr)^- + \underset{\diagdown\, O\, \diagup}{CH_2{-}CH}{-}CH_2Cl \rightarrow \left(ArO{-}CH_2{-}\underset{O{-}{-}H{-}{-}OAr}{\underset{|}{CH}}{-}CH_2{-}Cl\right)^-} \qquad (4)$$



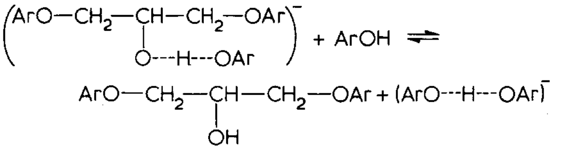
$$\mathrm{\left(ArO{-}CH_2{-}\underset{O{-}{-}{-}H{-}{-}{-}OAr}{\underset{|}{CH}}{-}CH_2{-}Cl\right)^- \rightleftharpoons ArO{-}CH_2{-}\underset{O^-}{\underset{|}{CH}}{-}CH_2{-}Cl + ArOH} \qquad (5)$$



$$\mathrm{ArO{-}CH_2{-}\underset{O^-}{\underset{|}{CH}}{-}CH_2{-}Cl \longrightarrow ArO{-}CH_2{-}\underset{\diagdown\, O\, \diagup}{CH{-}CH_2} + Cl^-} \qquad (6)$$



$$\mathrm{ArO{-}CH_2{-}\underset{\diagdown\, O\, \diagup}{CH{-}CH_2} + (ArO{-}{-}H{-}{-}OAr)^- \longrightarrow \left(ArO{-}CH_2{-}\underset{O{-}{-}{-}H{-}{-}{-}OAr}{\underset{|}{CH}}{-}CH_2{-}OAr\right)^-} \qquad (7)$$



$$\mathrm{\left(ArO{-}CH_2{-}\underset{O{-}{-}{-}H{-}{-}{-}OAr}{\underset{|}{CH}}{-}CH_2{-}OAr\right)^- + ArOH \rightleftharpoons ArO{-}CH_2{-}\underset{OH}{\underset{|}{CH}}{-}CH_2{-}OAr + (ArO{-}{-}H{-}{-}OAr)^-} \qquad (8)$$

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