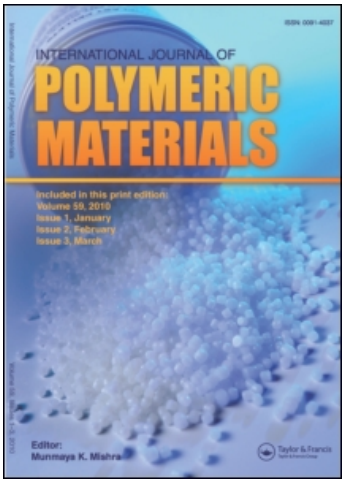

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Thioetherglycidyl resins: Synthesis, structure, and properties of glycidyl thioethers of aliphatic, aliphatic-aromatic, aromatic dithiols, and epichlorohydrin

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THIOETHERGLYCIDYL RESINS: SYNTHESIS, STRUCTURE, AND PROPERTIES OF GLYCIDYL THIOETHERS OF ALIPHATIC, ALIPHATIC-AROMATIC, AROMATIC DITHIOLS, AND EPICHLOROHYDRIN

Władysław Charmas
Department of Organic Chemistry and Technology,
Maria Curie-Skłodowska University, Lublin, Poland

The structure of thioetherglycidyl resins diglycidylthioethylformal [DGTEF]; (1-glycidylthiomethyl)naphthalene [1-GTMN]; 1,4-di(glycidylthiomethyl)-naphthalene [1,4-DGTMN]; 1,5-di(glycidylthiomethyl)-naphthalene [1,5-DGTMN]; mixture 1,4- and 1,5-[DGTMN]; bis-(4-glycidylthiomethyl-phenyl)ether [BGTMPE]; bis-(4-glycidylthiomethyl-phenyl) methane [BGTMPM]; [4, 5-di(glycidylthiomethyl)-o-xylene] [o-DGTMX]; [4, 6-di(glycidylthiomethyl)-m-xylene] [m-DGTMX]; [2, 6-di(glycidylthiomethyl)-p-xylene] [p-DGTMX]; glycidylthiophenyl [GTPh]; glycidylthio-p-tolyl [GTMPh]; glycidyl-p-chlorothiophenyl [GTClPh]; 1,4-di(glycidylthio)naphthalene [1, 5-DGTN]; 1,5-di(glycidylthio)naphthalene [1, 4-DGTN]; bis(4-glycidylthiophenyl)ether [BGTPhEe]; bis(4-glycidylthiophenyl)-methane [BGTPhE]; bis(4-glycidylthiophenyl) sulfide [BGTPhS] and bis(4-glycidylthiophenyl)sulfone [BGTPhSO$_2$] was determined from chemical investigations and elemental as well as IR and ^{1}H-NMR spectra analyses. Essential technological and processing properties such as viscosity, reactivity and thermal resistance were determined. The oxirane ring opening under the influence of temperature was examined based on model systems, mainly on glycidylthiophenol. The reaction products were separated and the structure of isolated compounds was determined by means of chromatographic and IR, ^{1}H-NMR and ^{13}C-NMR spectral methods.

Keywords: thioetherglycidyl resins, epoxy, synthesis

INTRODUCTION

Oxiranes are cyclic ethers of significant reactivity due to the presence of a three-member ring [1 – 2]. Ethylene oxide, which is the simplest epoxide compound, does not play a significant role in epoxide resin chemistry. However, epichlorohydrin, which is an essential raw material for synthesis of the most important types of epoxide resins, is of great significance.

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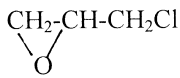
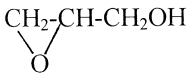
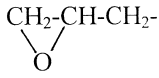
Glycidyl compounds whose name is derived from glycide its derivative, come from it.



Epichlorohydrin



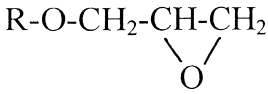
Glycidol

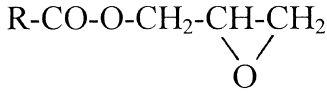


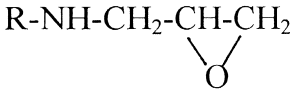
Glycidyl Groups

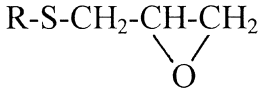
Individual chemical compounds or oligomer mixtures including at least two oxirane groups in the molecule are called epoxide resins.

Among epoxy resins, where an oxirane ring is a part of the glycidyl group, the following types of epoxides can be distinguished based on the nature of the atom to which this group is attached: glycidyl ethers, glycidyl esters, glycidyl amine derivatives, and glycidyl thioethers.









Recent numerous publications indicate that the research concerning epoxide resins include the cognitive aspects i.e., synthesis, kinetics of curing mechanism and application to increase the number of resin types as well as to modernize their production technology [2]. Great interest results from chemical technological and practical properties of the cured compositions. The high reactivity of the epoxide group creates a wide choice of curing agents and knowledge of curing mechanisms makes it possible to regulate the course of cross–linking process which affects significantly epoxide material properties.

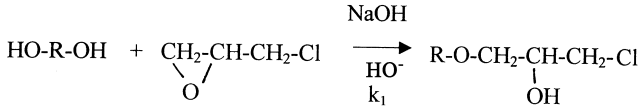
Despite a great number of epoxide resin preparation methods only a few, including the commercial ones, have been applied.

Of the direct methods of preparation there should be mentioned glycidylation with epichlorohydrin in an alkaline medium of the compounds including a mobile hydrogen atom as in phenols, alcohols, amines, acids, mercaptans etc., as well as oxidation of unsaturated compounds. Oxidation is usually carried out using organic peracids including peracetic acid. The

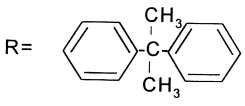
third method worth mentioning is polyaddition of proton-donor and epoxide compounds causing the molecule growth using up part of the epoxide groups.

The results of many researches [3–8] on kinetics and mechanism of the reaction of etherglycidyl resin formation, particularly derivatives of 2,2-bis(p-hydroxyphenyl)propane (Bisphenol A, Diane) and epichlorohydrin, indicate that the process is complicated and the following elementary reactions take part in it:

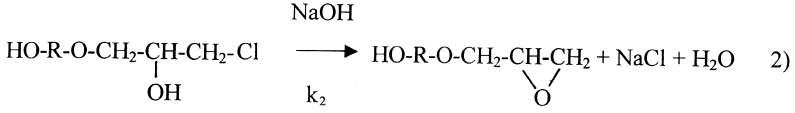
– **addition**



1)

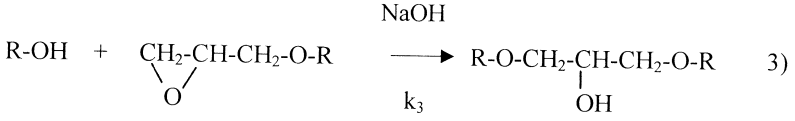


– **dehydrohalogenation**



2)

– **chain growth (oligomerization)**



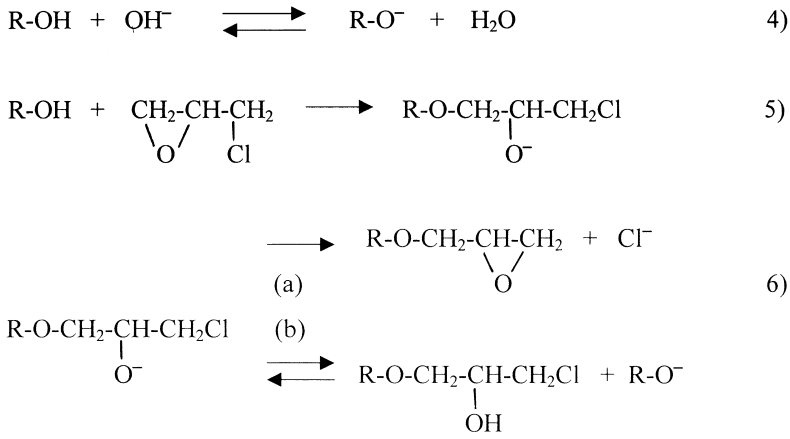
3)

The second diane group reacts in an analogous way and the reactivity of both groups is the same.

Main reactions are accompanied by the alkaline side process of epichlorohydrin hydrolysis. The addition reaction is always exothermic (74.4 kJ/mole). Dehydrohalogenation is a reversible reaction in which sodium hydroxide is used and the reaction heat is lower being 8.75 kJ/mole.

The addition and de hydrohalogenation stages of the resin synthesis are confirmed by kinetic, calorimetric and chromatographic studies. The ratio of the addition rate constant (k_1) and the dehydrohalogenation rate constant

(k_2) depends on the way of introducing NaOH into the reaction medium. The divergent data concerning the reaction rate constants published by various authors were explained by Rozentuler et al. [9–12] proposing an ionic mechanism of initiation and the following system of equilibrium reactions:



If the whole stoichiometric amount of NaOH is introduced at once in the beginning of the reaction, then almost a complete shift of reaction (4) towards the phenolate ion takes place. There is acceleration of the reaction (5) in which alcoholate ion is formed as well as of that (6a) when the reaction equilibrium (6b) is completely shifted left and glycidyl ethers are formed. In the model of etherglycidyl resins (1) and (2) process, the global reactions (1)+(2) proceeds very quickly, k_2 is larger by an order of magnitude than k_1 and the formed chlorohydrin groups react immediately giving epoxide groups.

Under the conditions of stepwise introduction of NaOH, only a part of diane phenol groups undergoes ionization. In the initial phase of the process, the reaction equilibrium (6b) is shifted right with predominance of chlorohydrin ethers. In the model of reactions (1) and (2) there occurs an inverse phenomenon i.e., a larger rate of addition reaction (1) (measured by the phenolate group conversion) than that of dehydrohalogenation.

However, the oligomerization process depends on the amount and way of introducing NaOH, particularly on the reaction medium pH. The phenomenon of chain growth was explained also on the basis of ion-equilibrium mechanism. With the increase of OH^- ions concentration, the reaction equilibrium (4) shifts right and the reaction (6b) left. The reaction (6a) is accelerated which leads to the increase of glycidyl ethers concentration

and thus to acceleration of oligomerization. It was also stated that with increased reaction temperature, the condensation process rate increases and an increase is observed of the ratio of dehydrohalogenation rate and addition which, in turn, further accelerates the oligomerization.

Synthesis of epoxide resins proceeds in a multi-phase system which makes this process even more complicated. In the simplest case this is a two-phase system: liquid-liquid, consisting of the organic and aqueous phases. Studies [11, 12] showed that the process of formation of diane chlorohydrin ethers (addition) takes place in both phases but the dehydrohalogenation reaction is localized in the organic phase. Protonic diluents, particularly isopropanol and isobutanol accelerate the addition and dehydrohalogenation reactions due to the increase of NaOH solubility in these solvents.

The high-molecular compounds including heteroatoms such as oxygen (whose representative are etherglycidyl resins) as well as nitrogen, boron, silica or sulfur are a common object of investigations. Aliphatic polysulfides i.e., polysulfide rubber, aromatic polyphenylsulfide (PPS, Ryron) and polyarylsulfone (Under Polysulfone, Astrel 360) are widely applied polymers.

However, there has been much smaller interest in thioeterglycidyl resins which are analogues of the well known and fully described etherglycidyl resins. Etherglycidyl compounds of aliphatic, aliphatic-aromatic and aromatic phenols and alcohols with epichlorohydrin have been already studied as far as synthesis, structure and physico-chemical properties are concerned. Also their cured compounds have found various applications owing to various curing agents of the amine and anhydride types. They are mainly used as cast, impregnated, glue, varnish or binding compositions, characterized by their application qualities.

There has been little interest in their sulfur analogues i.e., thioetherglycidyl compounds of aliphatic, aliphatic-aromatic and dimercaptans with epichlorohydrin. Only a few patents are found in the literature describing the possibility of their preparation without giving basic properties of the monomeric compounds and their cured compositions. The compounds of this group can be applied as the initial substances to obtain other sulfur–organic systems or as active diluents used as plasticizers of commercial epoxide resins. There is no complete information in the literature about the mechanism of curing reaction of this type of resins which affect the properties of the epoxide materials. Therefore studies of this group of compounds have both cognitive and application importance thus filling the gaps in the existing knowledge. The aims of the research are as follows:

– To carry out synthesis of new aliphatic, aliphatic-aromatic and aromatic thioetherglycidyl resins in the condensation reaction of bis(marcaptomethyl)- and bis(mercapto)-derivatives with epichlorohydrin.

- To work out, using a model system consisting of the isomeric mixtures of 1.4- and 1.5- di(mercaptomethyl)napthalenes and epichlorohydrin, such conditions of the condensation process which will enable the synthesis with good yield and good chemical properties i.e., epoxide number close to that calculated theoretically.
- Using glycidylthiophenol, to obtain the reaction products of the oxirane ring opening under the influence of temperature and their structure by means of chromatographic methods and IR spectra, ^{1}H-NMR and ^{13}C-NMR.

SYNTHESIS AND STRUCTURE OF THIOETHERGLYCIDYL COMPOUNDS

The scientific literature on thioetherglycidyl compounds i.e., the products of condensation of dithiols with epichlorohydrin is not aboundant and there are only patents. Two methods of resin preparation have been described.

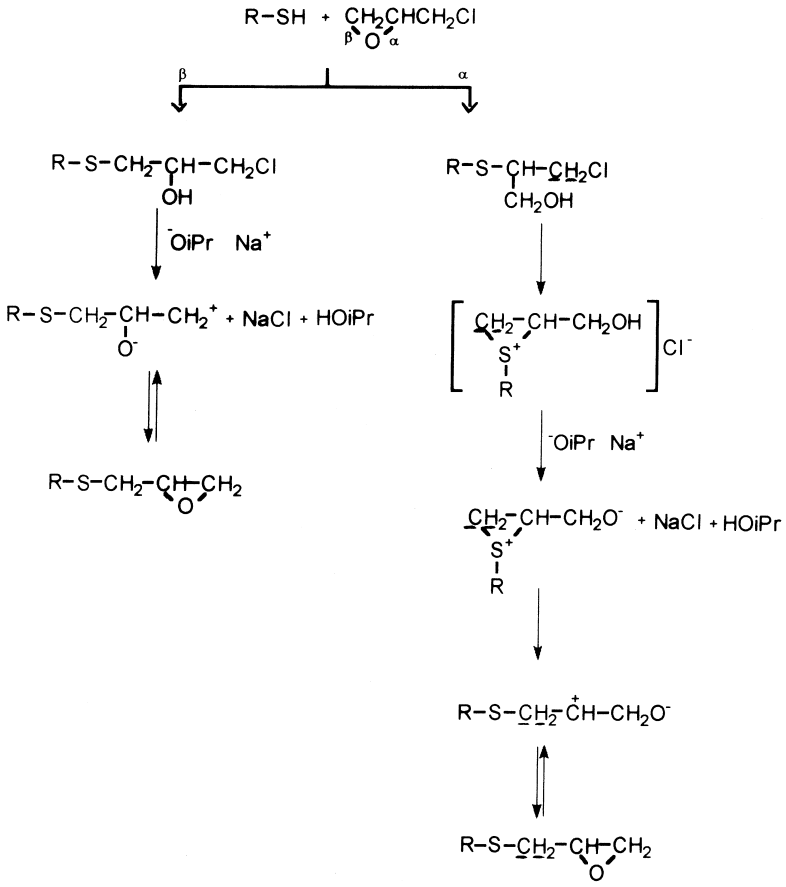
In the first method, as initial products there were used dithiols, derivatives of diphenyloxide, diphenylsulfide and diphenylmethane which were condensed with epichlorohydrin in the aqueous solution of alkaline hydroxide [37, 39]. The resins obtained by this method (based on oxide analogs) were sparsely soluble and had a much lower epoxide number compared with that theoretically calculated.

Using the other method, mercapto- or mercaptomethyl sodium salts, derivatives of benzene, isomeric xylenes, durene, methylbenzenes, biphenyl, tetraline or naphthalene, formed by the reaction of dithiols in toluene with the simultaneous azeotropic distillations of water [13 – 16], were subjected to the condensation reaction with epichlorohydrin. This method, though more arduous because of using mercaptides, gives more readily soluble products, but the epoxide group content did not exceed 80%.

It should be noted that the patent literature gives only the methods of thioetherglycidyl resins preparation determining the reaction yield, and only in few cases the quantity of epoxide number and chlorine content without detailed information about the synthesis and structure of resins as well as their physico-chemical properties and curing conditions. Our research team published several papers on thioetherglycidyl resins in 1980 – 1990 [17 – 24]. The resins presented in Scheme 1 were the subject of these studies.

Resin formation from dithiol and epichlorohydrin in the alkaline medium, similar to etherglycidyl resins, is a complex process involving some successive and parallel reactions.

The elementary reactions include addition, dehydrohalogenation and chain increase (oligomerization). At the same time the side reaction, mainly hydrolysis of epichlorohydrin into glycerol and hydrolysis of resin epoxide groups can take place.



SCHEME 1

The optimal conditions of synthesis were established from the isomeric reactions of 1.4- and 1.5- di(mercaptomethyl)naphtalenes with epichlorohydrin as the model system.

The following variable factors were considered:

- kind of organic phase
- molar ratios: epichlorohydrin/mercaptan
  alcohol/marcaptan
  alkaline hydroxide/mercaptan
- amount and kind of alkaline hydroxide for dehydrohalogenation
- concentration of alkaline hydroxide
- temperature of the process.

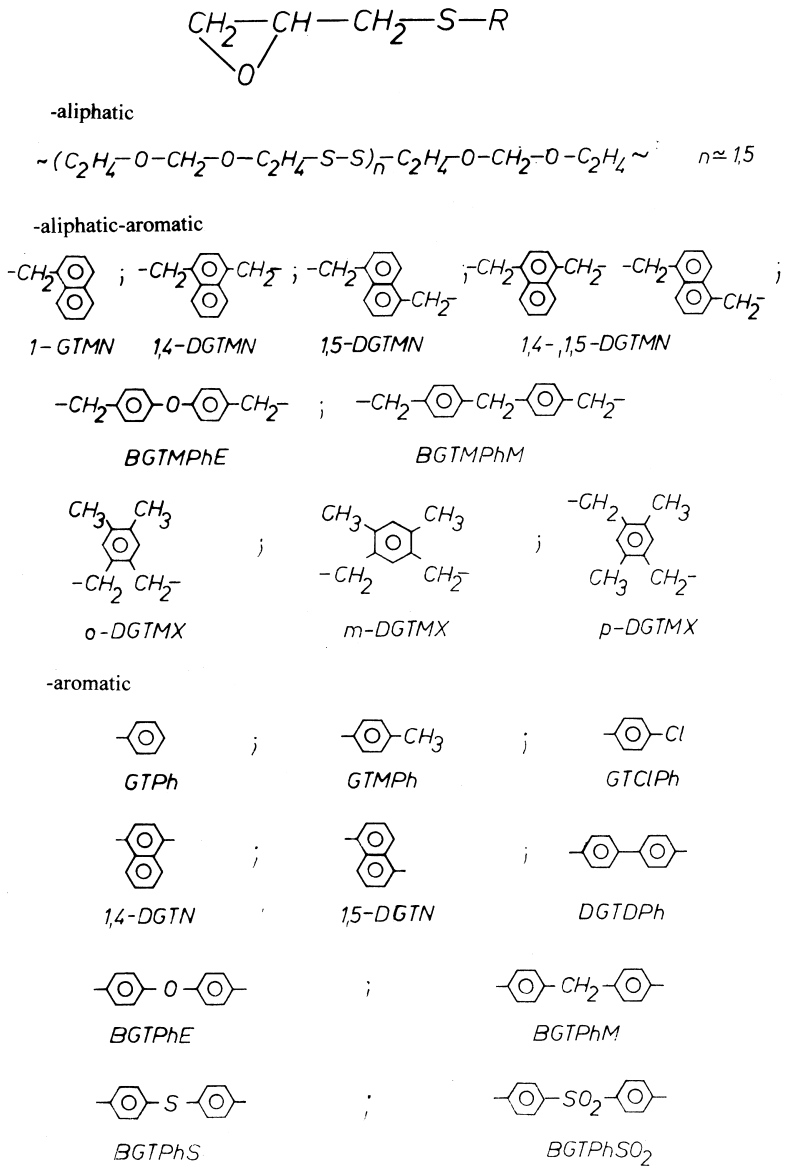


FIGURE 1 Aliphatic, aliphatic-aromatic and aromatic systems used for preparation of thioetherglycidyl resins.

The effect of the variable factors on resin formation was determined from the epoxide number contents, reaction yield and total chlorine contents. The studies showed that the method of heterophase, alkaline condensation of

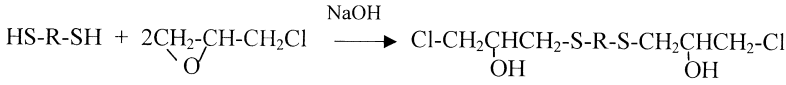
dimercapto compounds with epichlorohydrin in the aqueous -isopropanol medium by means of sodium hydroxide at the molar ratios:

mercaptan/epichlorohydrin	1:5
mercaptan/alcoho	1:1
mercaptan/alkaline hydroxide	1:3

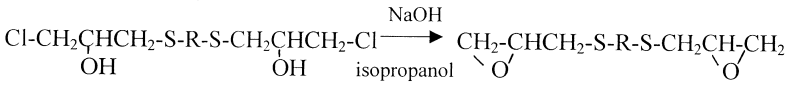
proved to be the most effective.

The time of dehydrohalogenation is 20 minutes, concentration of alkaline hydroxide is 20% w/w and the temperature of the process is 60°C.

addition:



dehydrohalogenation:



From the agreement between the obtained and calculated results of IR and ^{1}H-NMR spectra analysis it can be stated that the resins possess the structure of pure monomeric compounds whose viscosity values depending on temperature are presented in Figures 2 and 3.

The detailed data concerning structure, synthesis conditions and basic physico-chemical properties of newly obtained combinations are given in papers [17–24].

The results of the studies on synthesis of thioetherglycidyl resins indicate that when mercapto derivatives are used as substrates of greater acidity than that of phenols, low molecular weight resins are obtained under the conditions of much lower epichlorohydrin excess. It was observed that epichlorohydrin excess in the synthesis decreases the reaction mass viscosity and accelerates the process of resin isolation (it causes mainly a physical activity).

In the initial stage of reaction, relative share of dehydrohalogenation products and lengthening of the chain due to the stepwise mode of introducing alkaline hydroxide is insignificant. The addition reaction is predominant. As shown by Romanian researchers in 1935, the use of the thiophenol reaction with epichlorohydrin, produces a mixture of isomeric thiophenol chlorohydrins [25]. The first attempts to prepare thioetherglycidyl resins using the methods for etherglycidyl resins were not effective and multi- component products of low epoxide number were obtained.

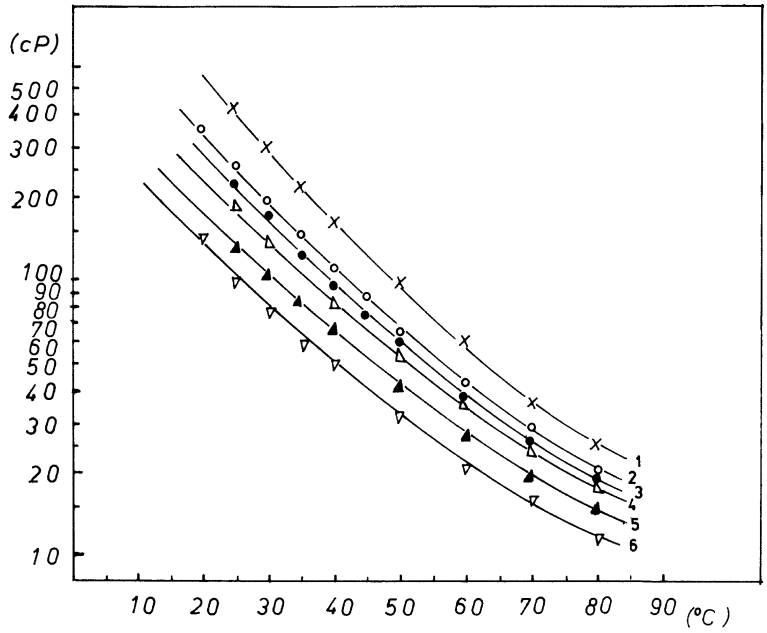


FIGURE 2 Dependence on temperature of viscosity of aliphatic-aromatic thioetherglycidyl resins: 1. DGTMPhS, 2. m-DGTMX, 3. o-DGTMX, 4. DGTMPhM, 5. DGTMPhE, 6. DGTEF.

The reaction mixture and alkaline hydroxide used in 50% excess affect the synthesis significantly. The positive effects of proton solvents, particularly of alcohols (in this case of isopropanol) can be explained by the increase of the medium polarity. In such a system there takes place a decrease of the distribution coefficient of alkaline hydroxide between the phases of the system, thus increasing the dechlorohydrogenation reaction rate with the decrease of epoxide groups hydrolysis rate.

From the literature on addition of thiophenol to epichlorohydrin, rates and effects of temperature, effects of addition reactions as well as influence of the reaction medium, it can be stated that the opening of the epichlorohydrin oxirane group in the β position in the first stage of synthesis leads to addition of mercaptan and then to epoxide compound as a result of intramolecular reaction S_N2 consisting in abstracting a proton from the hydroxide group by means of alkaline hydroxide.

However, in the case of opening in the α position, the β-halogen sulfide system is formed. From such systems, as a result of suitable reaction medium choice (isopropanol, alkaline hydroxide), and interaction of the neighboring group which is sulfur with a free pair of electrons a transitory ionic form is

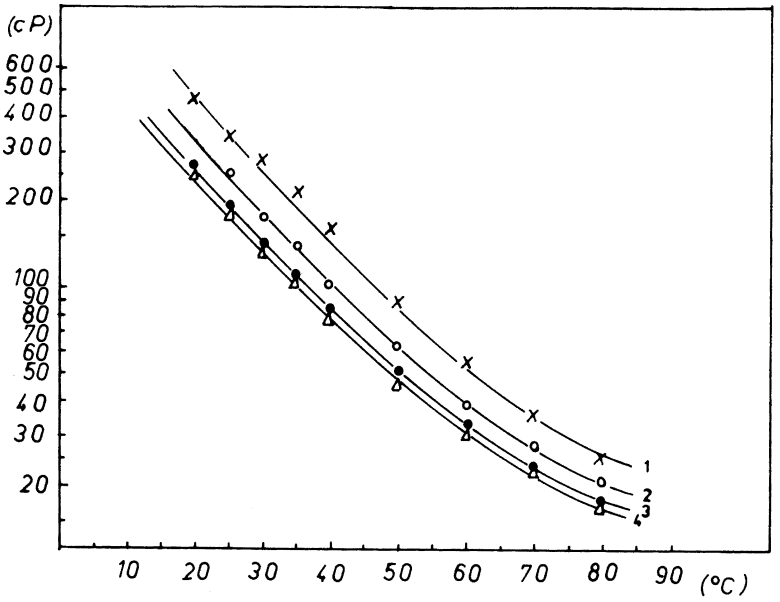


FIGURE 3 Dependence on temperature of viscosity of aliphatic thioetherglycidyl resins: 1. 1,4-DGTN, 2. DGTPhM, 3. DGTPhE, 4. DGTPhS.

created from the cyclic sulfone salt through intramolecular rearrangement and then oxirane ring is formed.

Formation of thioetherglycidyl resins can be presented as follows:

OPENING OF RESIN OXIRANE RING UNDER THE EFFECT OF TEMPERATURE

As follows from the literature, the stability of the oxirane ring in the glycidyl group depends on the neighboring atom or group of atoms bound to it. As shown by the studies etherglycidyl resins are relatively stable [26]. However, replacement of ether oxygen atom at the glycidyl group by the sulfone group (-SO_2-) makes the oxirane ring so active that its closure is impossible [27].

Thioether glycidyl resins prepared in our laboratory proved to be intermediate systems as far as oxirane ring reactivity is concerned. Already in the initial studies on synthesis of thioether glycidyl resins it was observed that under the influence of temperature the resin of this type becomes more viscous, undergoes mutual reactions (the epoxide number decreases) and forms a stable cured polymer insoluble in organic solvents typical of epoxide resins.

To explain this phenomenon there were undertaken some studies on the oxirane ring opening under the influence of temperature, using monosubstituted asymmetric oxiranes of the type of glycidyl thioethers-derivatives of thiophenol, p-methylthiophenol and p-chlorothiophenol:

1.2-epoxy-3-(phenylthio)-propane [GTPh]
1.2-epoxy-3-(p-tolilothio)-propane [GTMPh]
1.2-epoxy-3-(p-chlorophenylthio)-propane [GTClPh]

As the model system, GTPh- was accepted, a compound of low functionality including the oxirane group causing the reactions not to lead to the formation of multi- molecular compounds. They can be inspected by means of common kinetic measurements and chromatographic analysis.

Thermal stability of the resins was studied by an isothermal method, observing the typical epoxide group loss at 100, 110 and 120°C and obtaining typical kinetic dependence in the system: yield (epoxide group loss) – time [22].

It was found that the ring opening process satisfies the conditions of pseudostationary process (slow initiation and termination as well as the presence of rectilinear section on the kinetic curve).

Analysis of the experimental data shows that the second stage of reaction (rectilinear section) can be described using a first order dependence on monomer concentration. The values of rate constant of the reaction (k), oxirane ring opening, activation enthalpy (ΔH^*) and activation entropy (ΔS^*) were calculated.

Significantly, the negative value of activation enthalpy shows that the complex or the cyclic compounds, in which the decrease of translatory and rotational motions freedom is observed, is the intermediate stage. The value of activation enthalpy indicates a very small energetic barrier of oxirane ring opening.

The next stage consisted of the separation of reaction products by various fractionation methods and the determination of their structure using elementary analysis, IR spectra, ^{1}H-NMR and ^{13}C-NMR. Based on the chromatographic studies it was found that in the post- reaction mass there are seven groups of the reaction products, three of which occur in predominant amounts:

(I) fr. 3-(phenylthio)- 1.2-propanodiol (5%)
(II) fr. "*cis*" and "*trans*" mixture of 3-(phenylthio)allyl (34%) alcohols
(III) fr. 1.2-epoxy-3-(phenylthio)propane (3%)
(IV) fr. polymer products (30%)
(V) fr. 2.6-bis(phenylthiomethyl)-p-dioxane (19%)
(VI) fr. not isolated products- most probably geoisomer or conformer fr.
(VII) (5%)
(VIII) fr. 2.5 bis(phenylthiomethyl)-p-dioxane (5%)

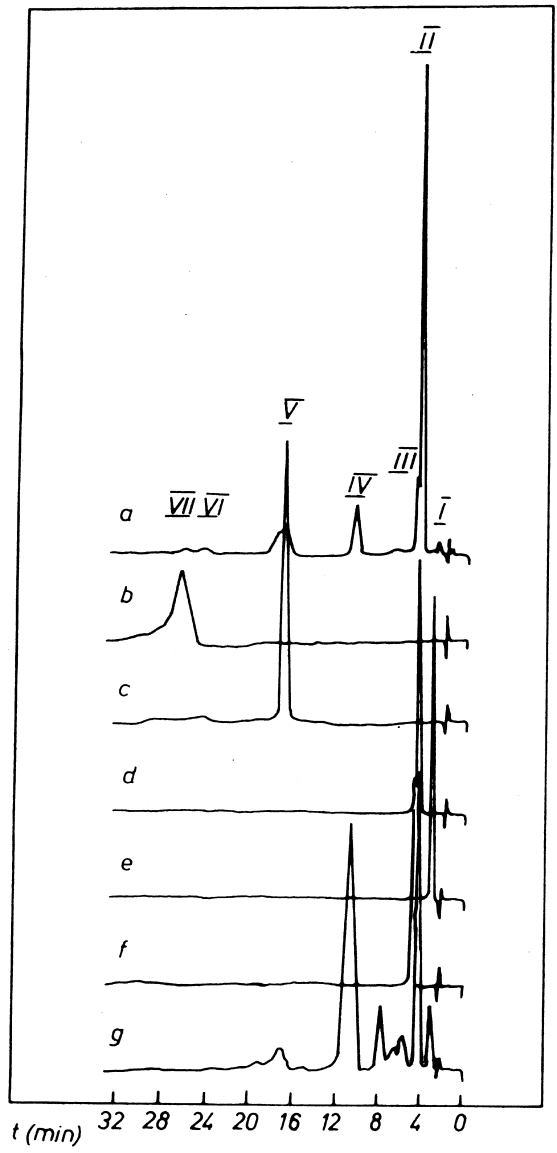


FIGURE 4 Chromatogram of the reaction mixture formed after heating GTPh at 120°C for 120h (a) after polymerization by BF_3 (g) and of separated reaction products (b-f).

Fractions II, V and VII proved to be interesting from the research point of view. A "*cis*" and "*trans*" mixture of unsaturated alcohols of 3-(phenylthio)-propane-2-en-1-ol constitutes fraction II.

As follows from the kinetic investigations, formation of unsaturated alcohols from thioether glycidyl resins under the influence of temperature can be presented as follows:

$$\text{GTMPh} > \text{GTPh} > \text{GTClPh}$$

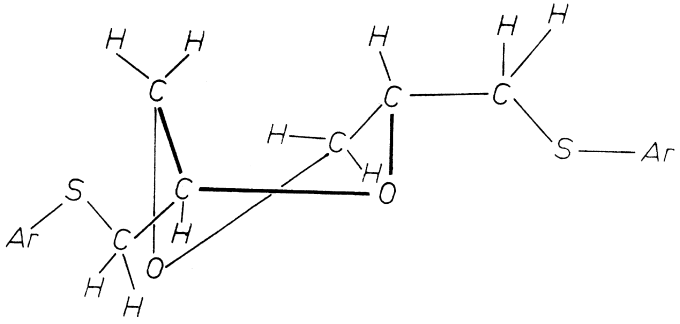


FIGURE 5

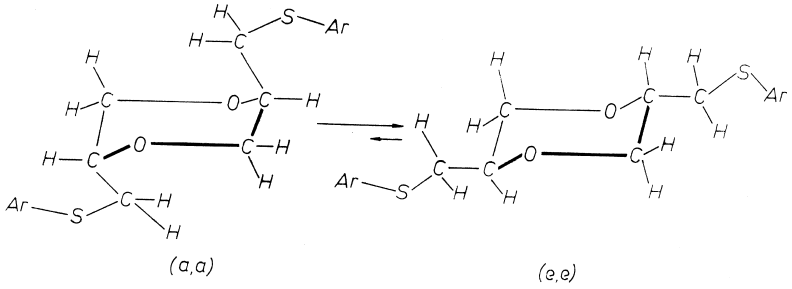
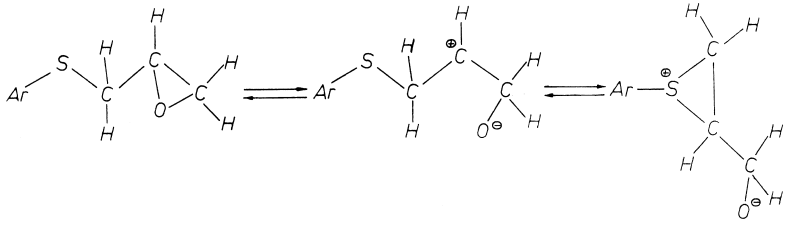
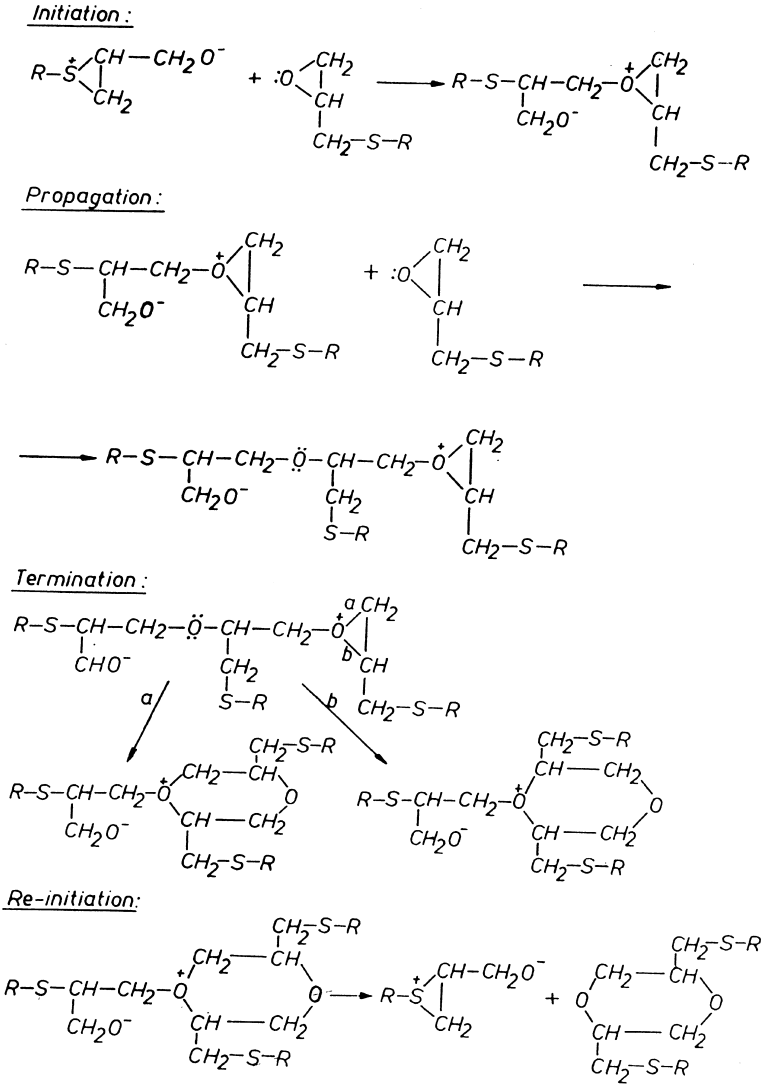


FIGURE 6



SCHEME 2



SCHEME 3

The crystalline compound of m.p. 108–109°C constitutes fraction V. The molecular mass determined by the cryoscope method in camphor equals to double the value of the initial monomer.

Analysis of the substance and IR as well as ^{1}H-NMR spectra identified fraction V as 2.6-bis(phenylthiomethyl)-p-dioxane.

Because of 2.6-substitution by large volume groups, the p-dioxane ring probably assumes the structure of a twisted conformer despite the fact that the chair conformation (e, e) in most cases is the lowest energy from of a six-member ring.

Molecular weight determined by the cryoscope method in camphor corresponds to double the value of the initial monomer. The spectral analysis IR and ^{1}H-NMR of large separability (300 MHz) confirms that fraction VII is a geometric "trans" isomer of 2.5-bis(phenylthiomethyl)-p-dioxane of the chair conformation (e, e).

It has been known that in the ether glycidyl systems of epoxy resins, particularly in asymmetric ones, mesomerism appears between the ring and ionic structures. Ionic structure in thioether glycidyl resins as sulfur analogs of ether glycidyl resins may form sulfonium systems which can provide suitable conditions, e.g., under the increased temperature.

The cyclic products (fractions V and VII) isolated from the reaction mixture suggest the mechanism of p-dioxane structure formation as follows:

On the basis of the experimental data it can be said that the direction of ring opening of the oxonium salt obtained in the process of propagation and termination does affect the p-dioxane structure.

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