

Thioetherglycidyl Resins. I. Products of Condensation of 1-Mercaptomethylnaphthalene and 1,4-, 1,5-Di-(Mercaptomethyl)naphthalene and Their Mixtures with Epichlorohydrin

WŁADYSŁAW CHARMAS and WAWRZYNIEC PODKOŚCIELNY,
Institute of Chemistry, Maria Curie-Skłodowska University, Lublin, Poland

Synopsis

New thioetherglycidyl resins produced by condensation of 1-mercaptomethylnaphthalene, 1,4-di(mercaptomethyl)naphthalene, 1,5-di(mercaptomethyl)naphthalene, and their mixture of 1,4- and 1,5-di(mercaptomethyl)naphthalene with epichlorohydrin were obtained. The condensation was carried out in two ways. In the first way, potassium salt of mercaptans and epichlorohydrin were used. In the second, epichlorohydrin was added to mercaptans and then the obtained chlorohydrin thioether was dehydrohalogenated by the alkaline hydroxide in water and *n*-butanol or isopropyl alcohol solution. The method of heterogeneous condensation of dithiol with epichlorohydrin in water and isopropyl alcohol solution proved to be the most effective. Yield, the epoxide content, and the total chlorine content for all resins were found. The structure of thioetherglycidyl resins with the highest epoxide content was determined by elementary analysis, and infrared (IR) and NMR spectra. Thermal stability of resins was studied during long controlled heating at unchanged temperature and short heating carrying the thermal gravimetric analysis (TGA) mainly in air. As follows from the studies, thioetherglycidyl resins can be cured both chemically and thermally.

INTRODUCTION

Among epoxy resins, where an oxirane ring is part of the glycidyl group, the following types of epoxides can be distinguished in relation to the nature of the atom to which this group is attached: glycidyl ethers, glycidyl esters, glycidyl amine derivatives, and glycidyl thioethers. Their synthesis, properties, and applications were studied thoroughly. However, literature concerning thioetherglycidyl resins, i.e., the products of condensation of dithiol with epichlorohydrin, is poor.

There are only few patents that can help to find methods of thioetherglycidyl resin production. In one, the dithiol derivatives of diphenyloxide, diphenylsulfide, and diphenylmethane were used as the initial products which were then condensed with epichlorohydrin in an aqueous solution of sodium hydroxide.^{1,2} The obtained resins were sparingly soluble and possessed lower epoxide content in comparison with the theoretical calculations.

Using another method, various sodium salts of the mercapto- or mercaptomethyl- of benzene, xylene, durene, methylbenzene, diphenyl, tetralin, and naphthalene derivatives obtained by the reaction of dithiol ether with sodium in the anhydrous ethanol,³ or sodium hydroxide in the toluene with simultaneous azeotropic distilling of water were condensed with epichlorohydrin. The second method though a little laborious, because of use of mercaptides, gives the resins

that are more readily soluble than those obtained by the first method, but their epoxy content is lower and does not exceed 80%. The patent literature gives only the methods for thioetherglycidyl resin production, the yield of reaction, and in some cases, the epoxy and chlorine content. It does not provide much information about their syntheses, structures, and physical and chemical properties.

For this reason it seemed useful to study the synthesis of thioetherglycidyl resins with di(mercaptomethyl)naphthalenes which were used effectively in polythioester synthesis earlier.^{5,6} Thioetherglycidyl resins were obtained by two methods: by reaction of 1-mercaptomethylnaphthalene, 1,4- and 1,5-di(mercaptomethyl)naphthalene with epichlorohydrin. In the first method epichlorohydrin and potassium mercaptide obtained by dissolving mercaptan in a methanol solution of potassium hydroxide were used as the initial products. In the second method, the heterogeneous alkaline condensation of epichlorohydrin with mercaptans in water and butanol or in water and isopropyl alcohol solution was used. The investigations also covered the determination of some properties of resins cured thermally or chemically with different curatives, thermal and mechanical properties of the cured compounds.

EXPERIMENTAL

Reagents

1-Mercaptomethylnaphthalene (1-MMN), which boils at 156–161°C at 12 Torr, 1,4-di(mercaptomethyl)naphthalene (1,4-DMMN), which melts at 86–87°C, 1,5-di(mercaptomethyl)naphthalene (1,5-DMMN), which melts at 153–154°C, and their mixture of 1,4-, and 1,5-di(mercaptomethyl)naphthalene (1,4- and 1,5-MDMMN), which melts at 80–120°C, were obtained from the corresponding chloromethylnaphthalene through the thiouronic salts.⁷ Epichlorohydrin (1-chloro-2,3-epoxypropane), boiling temperature 114–117°C, manufactured by Fluka AG, Buchs SG was used. We also used methylbicyclo(2,2,1)hept-5-ene-2,3-dicarboxylic anhydride-NMA (Allied Chemical Dye Corp.); hexahydrophthalic anhydride (HHPA) (Allied Chemical Dye Corp.); and triethylenetetraamine (TETA) (curative Z-1 produced by Chemical Plant Sarzyna).

Caution: The above mentioned mercaptans have a slightly unpleasant smell. In their preparation and handling some care must be taken to prevent dermatitis.

Measurement of Properties

Spectral Analysis

The infrared (IR) spectra were obtained with a Beckman 42-40 spectrophotometer. NMR spectra were carried out with a Tesla BS-487-C apparatus, frequency (MHz): 80, reference: TMS, solvent: CCl₄, temperature (°C): 25.

TABLE I
Synthesis in Water and *n*-Butanol Solution

Synthesis No.	1,4- and 1,5-MDMMN		Epichlorohydrin (g)	n -Butanol (g)	Initial temperature (°C)	Alkaline hydroxide		Yield (g)	Epoxy content	Chlorine (%)	\bar{M}_n^a
	(g)	(mole)				Kind	(ml)				
1	22	0.1	60	60	60	KOH	—	33	0.53	0.63	
2	22	0.1	60	60	60	KOH	67	31	0.53	0.84	
3	22	0.1	60	60	60	KOH	48	35	0.42	3.34	
4	22	0.1	60	60	60	NaOH	48	35	0.54	0.51	
5	22	0.1	23	45	60	NaOH	48	32	0.50	0.51	
6	22	0.1	23	45	25	NaOH	48	32	0.53	0.58	
7	22	0.1	60	45	60	NaOH	80	32	0.54	0.54	326
8	22	0.1	92	—	60	NaOH	48	36	0.18	9.63	328

^a Molecular weight was determined by cryoscopy in dioxane.

TABLE II
 Synthesis in Water and Isopropyl Alcohol Solution

Synthesis No.	Mercaptan		Epichlorohydrin (g)	Isopropyl alcohol (g)	Addition 15% NaOH		Yield (g)	Epoxy content	Chlorine (%)
	Kind	(g)			(mole)	(ml)			
9	1,4- and 1,5-MDMMN	33	139	90	1.5	5.5	50	0.56	0.35
10 ^a		33	46.2	90	1.5	5.5	51	0.56	0.36
11 ^a		33	46.2	60	1.0	5.5	50	0.57	0.32
12 ^a		33	46.2	60	1.0	5.5	50	0.57	0.35
13 ^a		33	46.2	60	1.0	5.5	50	0.55	0.40
14		33	139	—	—	8.5	56	0.17	10.33
15		33	139	90 ^b	1.0	8.5	49	0.55	0.38
16	1-MMN	34.8	139	90	1.5	5.5	49	0.43	0.28
17	1,4-DMMN	19.2	92	60	1.0	3.7	33	0.57	0.32
18	1,5-DMMN	19.2	92	60	1.0	3.7	26 ^c	0.59	0.12

^a 70 g of epichlorohydrin dropped additionally after dehydrohalogenation to break the solution.

^b Isopropyl alcohol dropped in after addition, i.e., before the second portion of NaOH.

^c Resin crystallizes from toluene solution after cooling to room temperature; melting point 111–112°C (ref. 4—oil).

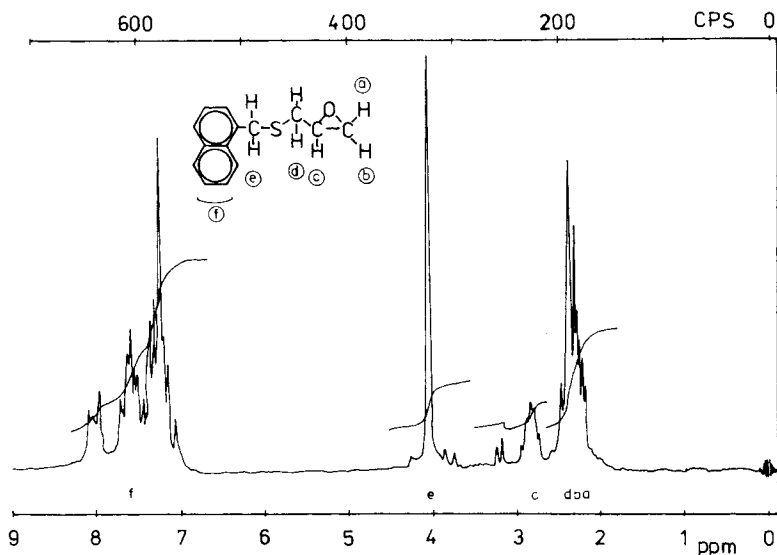


Fig. 1. NMR spectra of 1-GTMN resin. Assignments: $\delta_{(a,b,d)} = 2.00 \dots 2.50$, $\delta_{(c)} = 2.82$, $\delta_{(e)} = 4.08$, $\delta_{(f)} = 7.05 \dots 8.25$.

Thermogravimetric Analysis

Measurement of weight loss was conducted in a MOM derivatograph (Paulik, Paulik and Erdey, Budapest).

Epoxy Content

Epoxy content was expressed in epoxy gram-equivalent content in 100 g of resin and determined according to PN-69/C-8905 by HCl solution in dioxane. The calculated epoxy content is for glycidylthioethermethylnaphthalene 0.43 and di(glycidylthioethermethyl)naphthalene 0.60.

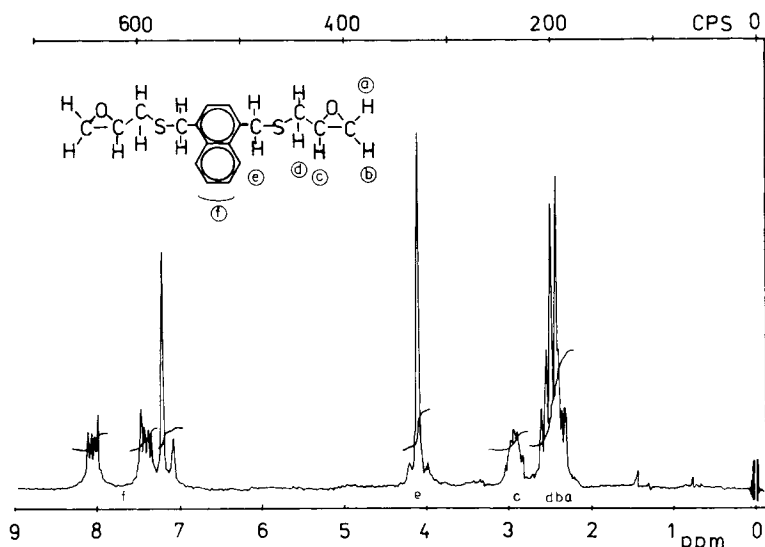


Fig. 2. NMR spectra of 1,4-DGTMN resin. Assignments: $\delta_{(a,b,d)} = 2.12 \dots 2.70$, $\delta_{(d)} = 2.93$, $\delta_{(e)} = 4.13$, $\delta_{(f)} = 7.10 \dots 8.25$.

Determination of Optimal Conditions of Resin Synthesis

In this article studies of resin syntheses, curing conditions, and properties of cured compounds were carried out on the most available di(mercaptomethyl)naphthalene, i.e., 1,4- and 1,5-DGTMN used as a model system. New thioetherglycidyl resins were obtained: 1-[(2,3-epoxypropyl)thiomethyl]naphthalene (1-glycidylthiomethyl-naphthalene—GTMN), 1,4-di[1-(2,3-epoxypropyl)thiomethyl]naphthalene [1,4-di(glycidylthiomethyl)naphthalene—1,4-DGTMN], 1,5-di[1-(2,3-epoxypropyl)thiomethyl]naphthalene [1,5-di(glycidylthiomethyl)naphthalene—1,5-DGTMN], and their mixture 1,4- and 1,5-di[1-(2,3-epoxypropyl)thiomethyl]naphthalene [1,4- and 1,5-di(glycidylthiomethyl)naphthalene—1,4- and 1,5-DGTMN].

Thioetherglycidal Resin Synthesis from Potassium Salts of Mercaptans and Epichlorohydrin

Into a four-necked flask of 500 cm³ volume, equipped with a reflux condenser, mechanical stirrer, thermometer, and dropper, 184 g (2.0 mole) of epichlorohydrin was poured. Then a solution of 44 g (0.2 mole) of 1,4- and 1,5-MDMMN, 28 g (0.5 mole) of solid KOH in 80 ml of methane was dropped within 1 hr at 30–40°C and stirred continuously. During the reaction KCl evolved. After the distillation of methanol, KCl was filtered. The excess of epichlorohydrin was distilled under the reduced pressure (12 Torr) and 76 g of yellow–orange resin of epoxy content 0.25 g and 12.5% of chlorine was obtained. Crude resin after dissolving in 300 ml of toluene was dehydrochlorinated at 50°C by means of 16 g (0.29 mole) of solid KOH, i.e., the amount calculated from the chlorine content. The mixture was washed with (3 × 30 ml) water. After the solvent had been distilled under the reduced pressure, 5.7 g of yellow–orange resin of 0.45 epoxy content and 1.87% of chlorine was obtained.

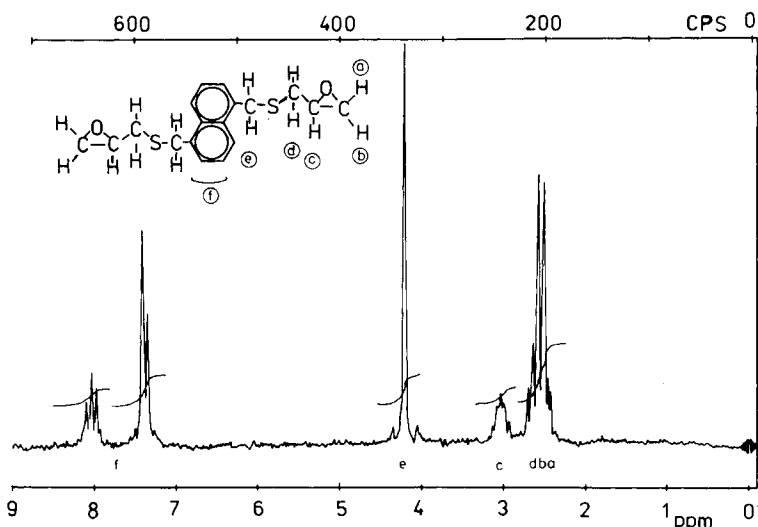


Fig. 3. NMR spectra of 1,5-DGTMN resin. Assignments: $\delta_{(a,b,d)} = 2.25 \dots 2.75$, $\delta_{(c)} = 3.03$, $\delta_{(e)} = 4.25$, $\delta_{(f)} = 7.15 \dots 8.24$.

TABLE III
 Results of Elementary Analysis

Thioetherglycidyl resins	Analysis					
	% C		% H		% S	
	Calc	Found	Calc	Found	Calc	Found
GTMN	73.0	73.04	6.13	6.46	13.92	13.64
1,4-DGTMN		64.98		5.95		18.98
1,5-DGTMN	65.02	65.00	6.06	6.04	19.19	19.62
1,4- and 1,5-MDGMN		65.23		6.11		19.53

Thioetherglycidyl Resin Synthesis by Heterogeneous Alkaline Condensation of Mercaptans with Epichlorohydrin

The influence of the following factors on yield of the reaction, epoxide, and chlorine content was studied: the mole ratios of epichlorohydrin: mercaptan, alcohol: mercaptan, and alkaline hydroxide: mercaptan, the amount of the addition catalyst, time of the addition and dehydrohalogenation, concentration of the alkaline hydroxide solution, temperature of the reaction, and kind of alcohol.

Synthesis in Water and Butanol Solution

Into a four-necked round-bottom flask of 500 cm³ volume, equipped with a mechanical stirrer, reflux condenser, thermometer, and dropper, 1,4- and 1,5-MDMMN, epichlorohydrin, *n*-butanol (number values are given in Table I) were poured. After heating in the water bath to a suitable temperature (values are

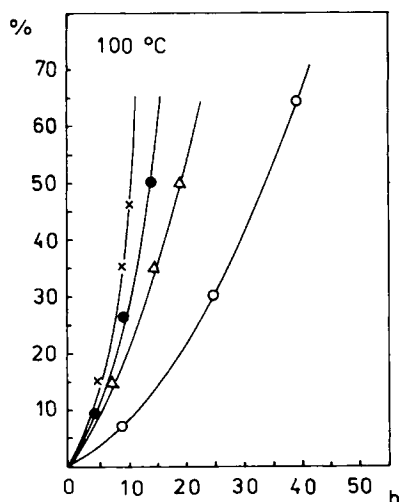


Fig. 4. Loss of epoxy groups in percent in relation to heating time at 100°C of the resins: (○) 1,4-GTMN; (Δ) 1,5-DGTMN; (●) 1,4- and 1,5-DGTMN; (X) 1,4-DGTMN.

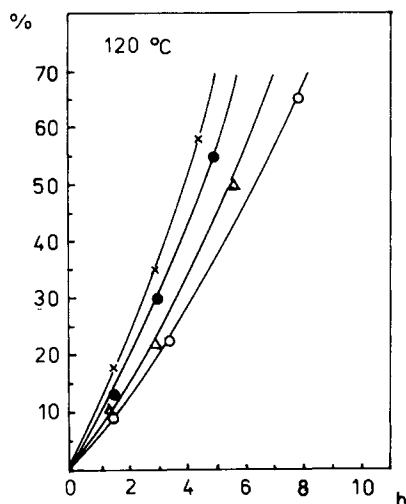


Fig. 5. Loss of resin epoxy groups in percent in relation to heating time at 120°C. The symbols are the same as in Fig. 4.

given in Table I), the aqueous solution of the alkaline hydroxide was dropped in during stirring for $\frac{1}{2}$ hr, then heated again and stirred for another $\frac{1}{2}$ hr. The aqueous layer was separated at 60°C, then from the organic layer *n*-butanol and excess of epichlorohydrin were distilled under the reduced pressure (12 Torr). The resins were dissolved in 70 ml of toluene, washed with water (3×20 ml), and the solvent was distilled again under the reduced pressure.

TABLE IV
Thermal Resistance of the Resins and Compositions

Resin	Kind	Epoxy content	Thermal analysis				
			T_1^a	T_2^b	T_3^c	U^d	T_4^e
1-GTMN	Uncured	0.43	—	175–310	235	1.5	315
	Thermal curing	0.25	—	175–270	220	1.5	310
	Thermal curing	0.00	—	—	220	0.0	310
1,4-DGTMN	Uncured	0.57	—	160–275	230	2.0	290
1,5-DGTMN	Uncured	0.59	118	160–290	265	2.0	320
	Uncured ^f	0.59	118	170–280	280	3.5	310
	Thermal curing	0.27	—	180–250	220	0.0	320
1,4- and 1,5-DGTMN	TETA	—	—	—	240	2.0	330
	HHPA	—	—	—	290	2.0	335
	NMA	—	—	—	250	2.0	340

^a T_1 : (°C) melting temperature from the curve DTA.

^b T_2 : (°C) homopolymerization temperature from the curve DTA.

^c T_3 : (°C) initial mass loss temperature from the curve TG.

^d U : (%) mass loss in the temperature T_3 from the curve TG.

^e T_4 : (°C) temperature of intensive mass loss from the curve DTG.

^f DGA was carried out under nitrogen.

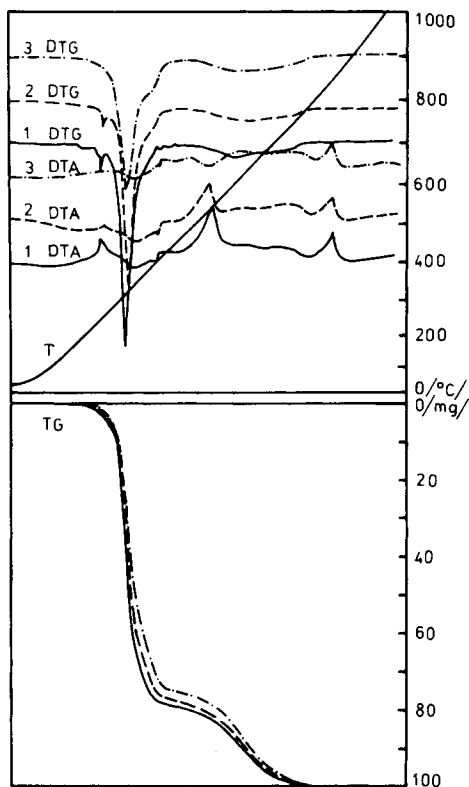


Fig. 6. TGA and DTA of uncured and thermally cured resin 1-GTMN of epoxy contents 0.40 (—), 0.25 (---), and 0.00 (-·-·-). Heating time in air, 100 min; heating rate, 10°C/min; amount of resins, 100 mg; measurements relate to Al_2O_3 .

TABLE V
Composition and Cure Conditions for the Epoxy Resin^a

Resin	Composition No.		
	I	II	III
1,4- and 1,5-DGTMN (g)	100	100	100
TETA (g)	13	—	—
HHPA (g)	—	70	—
NMA (g)	—	—	80

^a Cure schedules: (I) 48 hr at room temperature, 24 hr at 60°C; (II) 24 hr at 80°C, 24 hr at 110°C, 24 hr at 130°C, and 5 hr at 150°C; (III) 24 hr at 80°C, 24 hr at 120°C, 24 hr at 150°C, and 2 hr at 170°C.

Synthesis in Water and Isopropyl Alcohol Solution

The resin synthesis was carried out in the apparatus as in the preceding section. To obtain the chlorohydrin thioesters, the mixture of mercaptans, epichlorohydrin, isopropyl alcohol (amounts are given in Table II) was heated in the water bath to the required temperature, the first portion of 15% solution of NaOH which is the addition catalyst was dropped in very carefully for 10 min. Then another portion of the NaOH solution was added for 5 min and stirred for another 10 min. The organic layer was separated, and the alcohol and the excess of

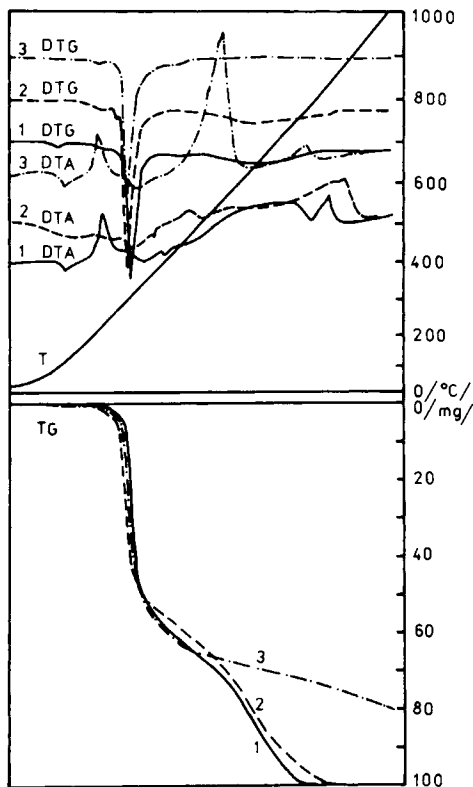


Fig. 7. TGA and DTA of the uncured and thermally cured resin 1,5-DGTMN of epoxy contents 0.59 (—), 0.59 under nitrogen (- · - · -), and 0.27 (- - -). Heating time in air, 100 min; heating rate, 10°C/min; amount of resins, 100 mg; measurements relate to Al_2O_3 .

TABLE VI
Gelation Time of Composition in Minutes in Relation to Temperature

Composition No.	Gelation Time (min)				
	25 (°C)	40 (°C)	50 (°C)	60 (°C)	80 (°C)
I	360	110	12	—	—
II	—	—	—	195	35
III	—	—	—	720	270

epichlorohydrin were distilled under the reduced pressure. In every synthesis the resin yield, its epoxy, and chlorine contents were determined. Values are presented in Tables I and II.

IR and NMR spectra were made for GTMN, 1,4-DGTMN, and 1,5-DGTMN. IR spectra of the resins showed strong absorption at 945–920 and 840–835 cm^{-1} , which are characteristic of the epoxy valency band; at 720–700 and 635–630 cm^{-1} , which are characteristic of —C—S— stretching; and at 1420 cm^{-1} , which is characteristic of —CH₂—S— groups.

NMR spectra of the resins (Figs. 1–3) consist of four separate groups of signals for GTMN: six for 1,4-DGTMN and five for 1,5-DGTMN. The ratio of their

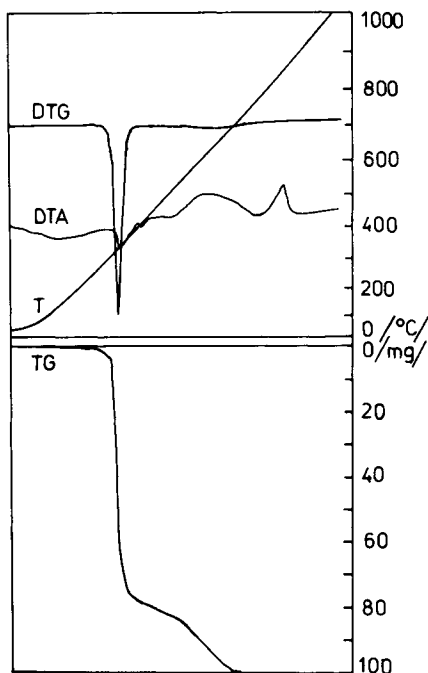


Fig. 8. TGA and DTA of the cured composition 1,4- and 1,5-DGTMN with HHPA. Heating time in air, 100 min; heating rate, 10°C/min; amount of resins, 100 mg; measurements relate to Al_2O_3 .

intensity in the direction of the increasing field according to the drop of the integral curve is 7:2:1:4, 2:2:2:4:2:8, and 2:4:4:2:8, which equals 14 protons in monothioetherglycidyl and 20 protons in dithioetherglycidyl. The value of chemical shifts is given under the figures presenting spectra.

Studies on the Structure of Thioetherglycidyl Resins

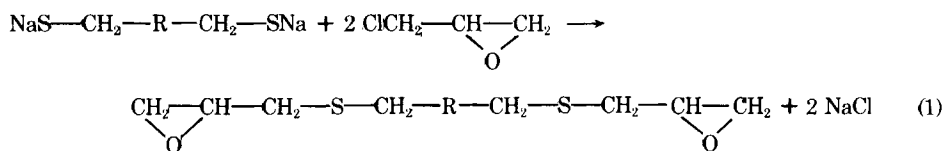
It follows from the experiments that resins obtained from mercaptide derivatives of naphthalene and epichlorohydrin have much lower contents of epoxy groups. The synthesis carried out by heterogeneous alkaline condensation of mercaptans with epichlorohydrin in *n*-butanol, or better in isopropenyl alcohol, gives the resins of epoxy group content close to the theoretically calculated value

TABLE VII
Flammability, Thermal, and Mechanical Properties of the Cured Compositions

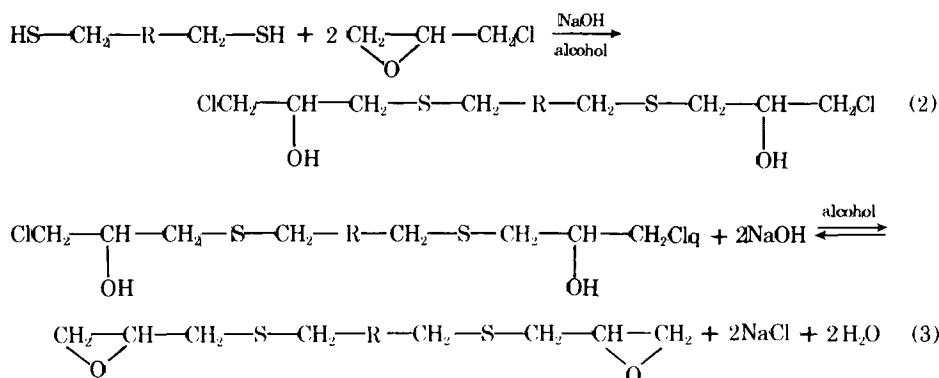
Test	Composition No.		
	I	II	III
Limiting oxygen index (%)	22.1	20.7	21.6
Martens softening point (°C)	70	92	116
Vicat softening point (°C)	80	102	133
Bending strength (kg/cm ²)	1105	726	743
Compressive strength (kg/cm ²)	1520	1630	1785
Tensile strength (kg/cm ²)	587	445	457
Brinnell hardness (kg/mm ²)	17.3	16.1	14.6
Impact strength (kg/cm ²)	11.6	6.1	8.3

with a minimal chlorine content which is within the measurement error limit. Using this method independent of the molar ratio of mercaptans and epichlorohydrin, low-molecular-weight epoxides in which one molecule of epichlorohydrin falls to a mercaptan group are always obtained. We have not observed high-molecular-weight compounds as in the resin synthesis from bisphenol-A. Such results may be due to the greater acidity of thiol groups in comparison with hydroxyl groups of phenols.

The reaction of mercaptans and epichlorohydrin in the presence of the alkaline hydroxide and alcohol as solvents can be taken two ways. In the first way the alkaline mercaptide may be formed before condensation with epichlorohydrin formation taking place:



In the second case a two-stage reaction takes place, i.e., the addition of thiol groups to oxirane groups first while chlorohydrin thioethers are formed, and then dehydrohalogenation with formation of oxirane groups:



where R denotes naphthalene. This is the two-stage reaction, because while dropping the alkaline hydroxide into the mixture of mercaptan, epichlorohydrin, and alcohol, the addition [eq. (2)] mainly takes place in the first stage which is recognized by strong thermal effects. In this case the alkaline hydroxide is not bound stoichiometrically but acts as a catalyst. Further addition of alkaline hydroxide gives very weak exothermic effects which indicate the dehydrohalogenation process [eq. (3)].

The good effects of alcohol, in particular of isopropenyl, on addition and mainly on dehydrohalogenation (synthesis No. 15, Table II), as in epoxy resins of bisphenol-A,⁸⁻¹⁰ is a result of the increased polarity of the reaction medium and the decreased coefficient of NaOH distribution between the phases of the system that causes increase of addition and dehydrochlorination rate and decrease of epoxy group hydrolysis rate.

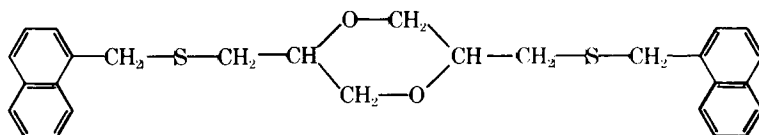
On the basis of good agreement of the found and calculated analytical data (Table III), the observed thermal effects of the reaction, IR and NMR spectra, the resin structure of the type of a pure monomeric compound is assumed.

Resin Curing

One of the most important characteristics of thioetherglycidyl resins observed is the easy metamorphosis caused by controlled heating. Like polyphenylene sulfide,¹¹⁻¹³ resins become more and more viscous while heating in air, reacting with one another to yield a solid cured polymer insoluble in common organic solvents. This indicates crosslinking formation between polymer chains.

To explain the changes caused by thermal curing of thioetherglycidyl resins, some studies were carried out on a monomeric thioetherglycidyl resin 1-GTMN. A relation between epoxy content and molecular weight of the thermally cured thioetherglycidyl resin has been observed. The molecular weight (\bar{M}_n) determined from cryometry in dioxane of the uncured resin 1-GTMN at the epoxy content 0.63 is 230; after heating at 100°C at an epoxy content of 0.25, it is 295; and at the complete loss of the epoxy number it reaches 450. Hence, molecular weight of the cured resin does not exceed a double quantity of monomer molecular weight.

One may suppose that linear lengthening does not occur during process but a *p*-dioxane structure of the type has been formed:

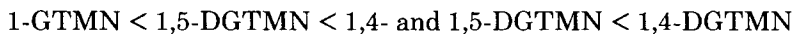


Such a *p*-dioxane structure resulting from epoxy-epoxy reactions for etherglycidyl resins has been used to interpret the β -transition mechanism studying dynamic mechanical properties of resins from bisphenol-A.¹⁴

Thermal Stability

Thermal stability of new resins was determined during controlled heating at different temperatures, from the epoxy group loss (Figs. 4 and 5), and derivatographic analysis (TGA) carried mainly in air for uncured resins and those cured in a thermal or chemical way. Figures 6-8 present some results of the derivatographic analysis. Thermal resistance of other resins and their compounds is similar to that shown in Table IV.

From the curves presented in Figures 4 and 5 it can be seen that temperature affects rate of thioetherglycidyl resin thermal curing. Resin reactivity according to the increasing rate of curing is the following:



Melting temperature, homopolymerization temperature, initial decomposition temperature, mass loss in percentage, and temperature of intensive decomposition have been determined from the curves of thermal derivatographic analysis (DTG) (Figs. 6-8).

From differential thermal analysis (DTA) of uncured resins, exothermic reaction is detected in the range 160-310°C and appears to be independent of oxidation. That proves to be a homopolymerization reaction of epoxy groups. A fairly sharp onset of weight loss is noted around 220-290°C. Using a mechanical or chemical method, the upper limits of stability of both uncured and

cured resins appear to be governed by the stability of the thioether linkage. Decomposition of polymers gives hydrogen sulfide, which identifies the thioether linkage as the weakest in the chain. The highest stability is reached by the resin 1,5-DGTMN and the lowest by 1,4-DGTMN.

Chemical Curing of Resins

Chemical curing of thioetherglycidyl resins was carried out in hot setting using acid anhydride and in cold setting using aliphatic amine. Chemical structure of the compound determined from stoichiometric calculations (0.85 mole of anhydride per epoxide equivalent) and curing conditions are given in Table V. Time of resin compound gelation in relation to the temperature has been determined (Table VI). To examine the application of cured resins, some cast profiles have been prepared. After mixing the components at the increased temperature, the fluid compound was vented, poured into a metal mold covered with an antiadhesive coating of silicone resin varnish, and cured. Cast profiles obtained according to Polish standards were studied to determine their flammable, thermal mechanical, and mechanical properties. From the results of these investigations (see Table VII), it can be seen that thioetherglycidyl resin derivatives of naphthalene can be cured by means of common curatives used for epoxy resins.

On the basis of the determined gelation time we can say that epoxy compounds cured in cold-setting TETA reveal good technological and processing properties at about 25°C, but those cured with anhydride are good at about 60°C. The compound cured by NMA is characterized by longer gelation time and the highest temperature of thermal deformation. The mechanical properties of the examined compounds are similar to those of the cured resins from bisphenol-A. The technological, processing, and mechanical properties of thioetherglycidyl resins are dependent on a curative. This fact should be taken into account in cast resin, laminated plastics, glue, and varnish coat production.

References

1. W. Werner and W. Hechtenberg, Ger. Pat. No. 1006618 (1957).
2. B. J. Bremmer, U.S. Patent No. 3328353 (1967).
3. H. Pietsch and R. Köhler, Ger. Pat. No. 1027403 (1958).
4. L. Orthner, K. Horst, and R. Bollinger, Ger. Pat. No. 971835 (1959).
5. W. Podkościelny and Wł. Charmas, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 2429 (1979).
6. W. Podkościelny and Wł. Charmas, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 3811 (1979).
7. W. Podkościelny and Wł. Charmas, in preparation.
8. J. Wiesner, *Chem. Prum.*, **20**(55), 270 (1970).
9. J. Stevens, *J. Am. Chem. Soc.*, **70**, 2449 (1948).
10. S. M. Rozentuler, A. G. Pozamantir, and A. F. Nikolajew, *Zh. Prikl. Khim.*, **47**, 187 (1974).
11. A. D. Macallum, *J. Org. Chem.*, **13**, 154 (1948).
12. J. T. Edmouds and H. W. Hill, U.S. Pat. No. 3354129 (1967).
13. H. W. Hill and J. T. Edmouds, *Adv. Chem. Ser.*, **129**, 80 (1973).
14. E. Cuddihy and J. Moacanin, *Adv. Chem. Ser.*, **92**, 96 (1970).

Received April 15, 1980

Accepted April 30, 1980