

Thioether Glycidyl Resins. V. Products of Condensation of 1,4-, 1,5-Di(mercapto)naphthalene and 4,4'-Di(mercapto)diphenyl with Epichlorohydrin

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Synopsis

Thioether glycidyl resins produced by condensation of isomeric 1,4-, 1,5-di(mercapto)naphthalenes and of 4,4'-di(mercapto)diphenyl with epichlorohydrin were obtained by heterophase alkaline condensation in water and isopropyl alcohol solution by sodium hydroxide solution. Their structure was determined by elemental analysis and IR and NMR spectra. The physical and chemical properties were determined. Some properties of the resins were determined during thermal and chemical curing with the curatives typical for epoxy resins. The cured compounds were characterized from derivatographic, thermomechanical, and mechanical studies.

INTRODUCTION

There has been observed great interest in polymers of increased thermal resistance in each type of plastics. It also refers to thioether glycidyl resins obtained so far which reveal too little thermal resistance but possess some advantageous properties. As shown in the previous articles,¹⁻⁴ some improvement in thermal resistance of epoxy compositions can be achieved using special curatives. The synthesis of new thioether glycidyl resins including condensed aromatic rings seems to be more effective.

For this reason it seemed useful to study the synthesis of resins including thioether sulfur directly connected with the phenol conjugated ring system in a naphthalene or diphenyl molecule.

The model studies of thioether glycidyl resin structure showed that heterophase, alkaline condensation of thiols with epichlorohydrin in water and isopropyl alcohol solution using sodium hydroxide was the most effective.¹⁻³

This article gives the results of the studies on synthesis, structure, and physical and chemical properties of thioether glycidyl resins derivatives of 1,4-di(mercapto)naphthalene, 1,5-di(mercapto)naphthalene and 4,4'-di(mercapto)diphenyl with epichlorohydrin.

The investigations also covered the determination of some properties of resins cured thermally, or chemically with curatives typical for epoxy resins, and the thermal and mechanical properties of the cured compounds.

I would like to explain that thioether glycidyl resin of 4,4'-di(mercapto)diphenyl has already been obtained by condensation with epichlorohydrin in anhydrous ethanol using metallic sodium.⁵

EXPERIMENTAL

Reagents

Di(mercapto)compounds were obtained from the corresponding disulfonyl chlorides through the reduction by stannous chloride in acetic acid solution saturated with the gaseous hydrogen chloride.

Disulfonyl chlorides were prepared directly through chlorosulfonation of hydrogen chlorides or indirectly through disulfonyl acids.

1,4-Di(mercapto)naphthalene (1,4-DMN), mp 70–71°C (lit.^{6,7} 71–71.5°C) was obtained from chloride of 1,4-naphthalenedisulfonyl acid. Disulfonyl chloride was obtained by the Janczewski method⁸ of diazotization of naphthionic acid through acidic sodium salt of naphthalene-1-sulfonic-4-sulfonyl acid and sodium salt of 1,4-naphthalenedisulfonyl acid which was treated with phosphorus pentachloride.

1,5-Di(mercapto)naphthalene (1,5-DMN) at mp 119–121°C (lit.^{7,9} 119–121°C) was obtained from 1,5-naphthalenedisulfonyl acid chloride. Disulfonyl chloride was obtained using the Marotta method¹⁰ of naphthalene chlorosulfonation by chlorosulfonyl acid.

4,4'-Di(mercapto)diphenyl (4,4'-DMDP) at mp 175–178°C (lit.⁹ 179–180°C) was obtained from 4,4'-diphenyldisulfonyl acid dichloride. Disulfonyl chloride was obtained using Dutta method¹¹ of diphenyl sulfonation by the concentrated sulfuric acid through the potassium salt of 4,4'-diphenyldisulfonyl acid which was treated with phosphorus pentachloride.

Naphthalene mercapto compounds were crystallized from the mixture of 10 parts of glacial acetic acid and one part of the concentrated hydrochloric acid (1 g of 1,4-DMN from 12 cm³ of solvent and 1 g of 1,5-DMN from 14 cm³ of solvent).

Epichlorohydrin (1-chloro-2,3-epoxypropane) boiling at 114–117°C, manufactured by Fluka AG, Buchs SG, methylbicyclo(2,2,1)-hept-5-ene-dicarboxylic anhydride—NMA (Allied Chemical Dye Corp.), anhydride HY-905 (Ciba-Geigy), and triethylenetetraamine (TETA), curative Z-1 produced by Chemical Plant Sarzyna were used.

Caution: The above-mentioned mercaptans have a slightly unpleasant smell. In their preparation and handling some care must be taken to prevent dermatitis. This does not refer to the newly obtained resins.

Measurement of Properties

Spectral Analysis. The infrared (IR) spectra were obtained with a Beckman 42-40 spectrophotometer. ¹H-NMR spectra were carried out with a Tesla BS-487-C apparatus, frequency 80 MHz, reference, TMS; solvent, CCl₄ and CCl₃; temperature, 25°C.

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

Mechanical Analysis. The analysis was conducted in a resistance machine 1231-U-10 produced in the Soviet Union.

Epoxy Content. Epoxy content was expressed in epoxy gram-equivalent content in 100 g (val/100 g) of resin and determined according to the Polish Norm PN-69/C-8905 by HCl solution in dioxane.

Resin Synthesis

Based on the results of model compound investigations there were obtained the following resins: 1,4-di[(2,3-epoxypropyl)thio]naphthalene [1,4-di(glycidylthio)naphthalene (1,4-DGTN)], 1,5-di[(2,3-epoxypropyl)thio]naphthalene [1,5-di(glycidylthio)naphthalene (1,5-DGTN)], and 4,4'-di[(2,3-epoxypropyl)thio]diphenyl [4,4'-di(glycidylthio)diphenyl (4,4'-DGTDP)].

The detailed studies of their structure, physicochemical properties, and curing conditions were presented. In a further stage thioether glycidyl resins with curatives were prepared. The cured resins were described from derivatographic, thermomechanical, and mechanical analyses.

1,4- or 1,5-[Di-(2,3-epoxypropyl)thio]naphthalene Resin Synthesis. Into a four-necked flask of 500 mL volume, equipped with a mechanical stirrer, reflux condenser, thermometer, and dropper, 19.2 g (0.1 mol) of 1,4-DMN or 1,5-DMN, 92.5 g (1.0 mol) of epichlorohydrin, and 60 g (1.0 mol) of isopropanol were placed. The mixture was heated in the water bath to 60°C. The first portion 5 mL of 15% solution of sodium hydroxide as an addition catalyst was dropped in very carefully. After 10 min the second portion 65 mL of 15% solution of sodium hydroxide was added for 5 min and stirred for another 10 min.

The organic layer was separated in a distributor; the solvent and excess of epichlorohydrin were distilled under reduced pressure (12 Torr). The remains of epichlorohydrin were distilled azeotropically under reduced pressure adding 2×10 mL of toluene into resin and filtered.

Twenty-nine grams of 1,4-DGTN resin, light brown color, of the epoxide content 0.62 val/100 g (the theoretical epoxide content 0.65 val/100 g) and viscosity 310 cP at 25°C or 28 g of 1,5-DGTN resin, light brown color of the epoxide content 0.62 val/100 g solidifying at room temperature was obtained.

4,4'-[Di-(2,3-epoxypropyl)thio]diphenyl Resin Synthesis. Into a four-necked flask of 1 L volume, equipped with a mechanical stirrer, reflux condenser, thermometer, and dropper, 66 g (0.3 mol) of 4,4'-di(mercapto)diphenyl and 370 g (4.0 mol) of epichlorohydrin were placed and heated in the water bath to 60°C. Then 25 mL of 15% solution of sodium hydroxide as an addition catalyst was dropped in at such a rate that the mixture temperature would not exceed 80°C. After 15 min 100 mL of isopropanol and the second portion 240 mL of 15% solution of sodium hydroxide were added and stirred for another 20 min.

TABLE I
Results of Elemental Analysis

Thioether glycidyl resins	Analysis					
	% C		% H		% S	
	Calcd	Found	Calcd	Found	Calcd	Found
1,4-DGTN		62.77		5.57		21.23
	63.12		5.30		21.06	
1,5-DGTN		63.39		5.06		21.15
4,4'-DGTDP	65.42	64.98	5.40	5.30	19.37	19.21

The organic layer was separated in a distributor and filtered through a crimped filter; 500 mL of methanol was added to the filtrate. The separated sediment of diglycidyl compound was filtered, washed with methanol, and dried in air; 47 g of crude product at mp 117–122°C was obtained. After crystallization from carbon tetrachloride (1 g of substance in 10 mL of solvent) 40 g of crystalline compound of mp 121–123°C (lit.⁵ 116–117°C) of the epoxide content 0.58 val/100 g was obtained.

The resin dissolves well in toluene, epichlorohydrin, and dioxane, moderately in carbon tetrachloride, and poorly in methanol and ethanol.

RESULTS AND DISCUSSION

Studies of Thioether Glycidyl Resin Structure

The chemical structure of the resins: 1,4-DGTN of the epoxide content 0.62 val/100 g (the theoretical epoxide content 0.65 val) 100 g and viscosity 350 cP at 25°C, 1,5-DGTN of the epoxide content 0.62 val/100 g and mp 62°C (from derivatograph) and 4,4'-DGTDP or the epoxide content 0.58 val/100 g (the theoretical epoxide content 0.60 val/100 g) and mp 121–123°C was determined from the analytical and spectral data. Elemental analysis (Table I) for C, H, and S showed the agreement with theoretical values.

IR spectra of the resin showed strong adsorption at 1265–1245, 954–920, and 850–840 cm^{-1} , which are characteristic of the epoxy valency band, and at 1100–1080 cm^{-1} , which are characteristic of Ar—S— stretching, and at 1420–1400 cm^{-1} and 1240–1220 cm^{-1} , which is characteristic of —S—CH₂— groups.

¹H-NMR spectroscopic studies of the resins (Figs. 1–3) show two basic group signals. The first group δ 7.03–8.55 for 1,4-DGTN, δ 7.05–8.65 for 1,5-DGTN, and 7.55 ppm for 4,4'-DGTDP comes from the aromatic rings. The second group δ 2.28–3.25 for 1,4-DGTN, δ 2.28–3.30 for 1,5-DGTN and δ

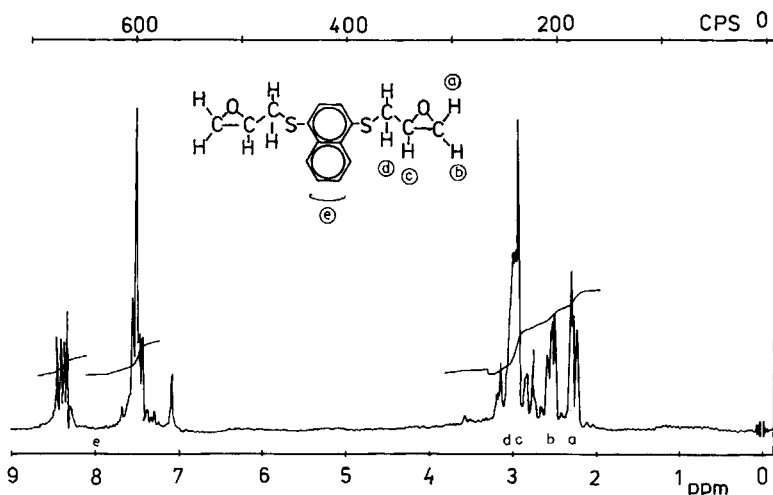


Fig. 1. NMR spectra of 1,4-DGTN resin. Assignments: $\delta_a = 2.28$, $\delta_b = 2.55$, $\delta_{c,d} = 2.68$ – 3.25 , and $\delta_e = 7.03$ – 8.55 ppm (solvent CCl_4).

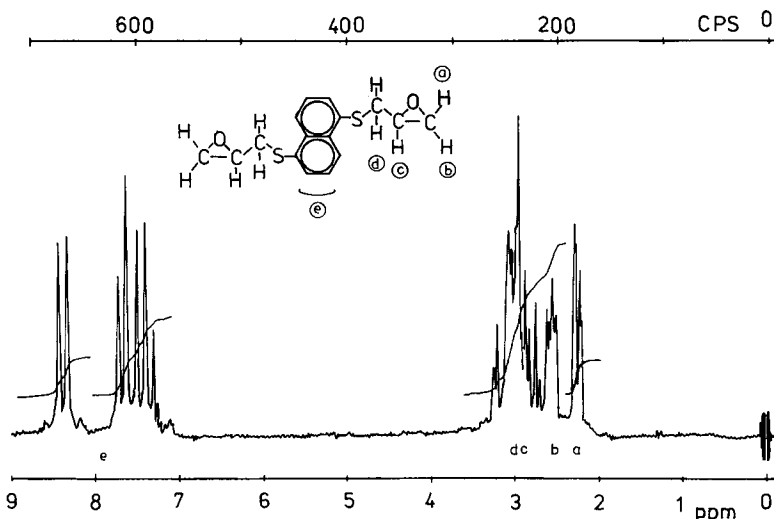


Fig. 2. NMR spectra of 1,5-DGTN resin. Assignments: $\delta_a = 2.28$, $\delta_b = 2.58$, $\delta_{c,d} = 2.73$ – 3.30 , and $\delta_e = 7.05$ – 8.65 ppm (solvent CCl_4).

2.50 to 3.40 ppm for 4,4'-DGTDP comes from glycidyl group. Intensity ratios for each band calculated from the integration curve are in agreement with the number of magnetically nonequivalent protons in a resin molecule and are 2:4:6:2:2 for 1,4-DGTN and 1,5-DGTN, which equals 16 protons, and 8:6:2:2 for 4,4'-DGTDP, which equals 18 protons. The values of proton chemical shifts are given under the figures presenting spectra. Good agreement of elemental analyses and IR and NMR spectra assumes pure monomeric structure of resins.

Thermal Stability

Thermal stability of new resins was studied by isothermal and dynamic methods. Isothermic studies were carried out controlling epoxy group loss during heating at 100°C , 110°C , and 120°C for 1,4-DGTN and 1,5-DGTN resins and at 130°C , 150°C , and 170°C for 4,4'-DGTDP.

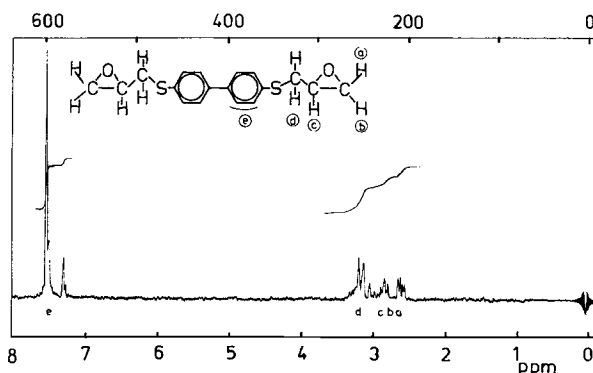


Fig. 3. NMR spectra of 4,4'-DGTDP resin. Assignments: $\delta_a = 2.60$, $\delta_b = 2.80$, $\delta_{c,d} = 3.00$ – 3.50 , and $\delta_e = 7.50$ ppm (solvent CDCl_3).

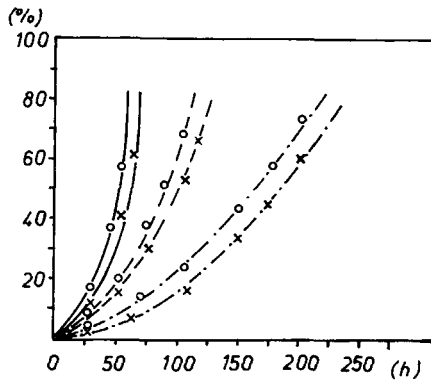


Fig. 4. Loss (%) of epoxy groups of 1,4-DGTN (X) and 1,5-DGTN (O) resins in relation to heating time (h) at 100°C (---), 110°C (—), and 120°C (—).

From the curves presented in Figures 4 and 5 it can be seen that reactivity of both resins is similar and considerably higher than that of 4,4'-DGTDTP. Temperature affects rate of resin thermal curing.

Some results of studies of uncured and thermally or chemically cured resins using the dynamic method (temperature increase of 10°/min in air) are presented in Figures 6-8. As follows from the values given in Table II, thermal resistance of composition is similar.

Melting point, homopolymerization temperature, maximum homopolymerization temperature, initial decomposition temperature, mass loss in percentage, and the temperature at which the highest rate of resin decomposition takes place have been determined from the curves of thermal derivatographic analysis (TGA). From differential thermal analysis (DTA) of uncured resins exothermic reaction is detected in the range 200-360°C and indicates a polymerization reaction of epoxy groups. A fairly sharp onset of weight loss is noted at 250-310°C. The upper limits of stability of both uncured and thermally or chemically cured resins appear to be governed mainly by the stability of thioether linkage and additionally by initial monomer molecule architecture. Monomers of symmetric structure increase temperature, but those of disturbed symmetry cause its decrease. 4,4'-

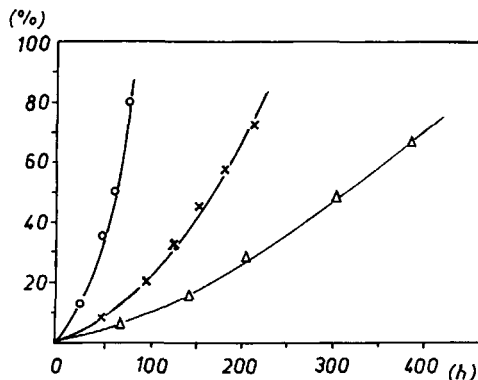


Fig. 5. Loss (%) of epoxy groups of 4,4'-DGTDTP resin in relation to heating time (h) at 130°C (Δ), 150°C (X), and 170°C (O).

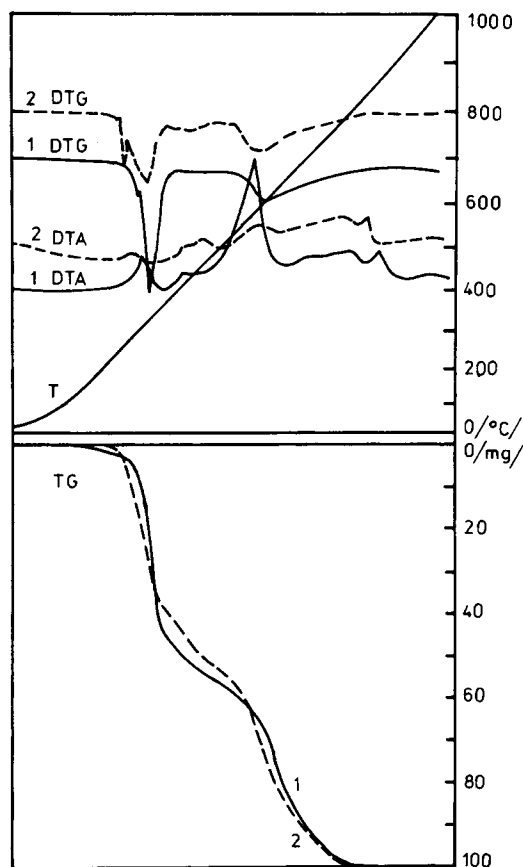


Fig. 6. TGA and DTA of uncured and thermally cured resin 1,4-DGTN of epoxy contents 0.62 (—) and 0.20 (---). Heating time in air, 100 min; heating rate, 10°C/min; amount of resins, 100 mg; measurements related to Al_2O_3 .

DGTDP resin is characterized by the highest thermal stability, but 1,4-DGTN resin possesses the lowest thermal stability.

Chemical Curing of Resins

Chemical curing of thioether glycidyl resins was carried out in one case (1,4-DGTN) using aliphatic amine but in others using acid anhydride. Chemical structure of the compound was determined from stoichiometric calculations. Numerical values and curing conditions are given in Table III.

To examine the application of cured resins, the time of gelation with curatives in relation to the temperature has been determined (Table IV), and some compositions have been prepared whose curing conditions are given in Table III. Cast profiles obtained according to Polish standards were studied to determine their thermal mechanical properties, which are presented in Table V.

From the results of these investigations, it can be seen that 1,4-DGTN, 1,5-DGTN, and 4,4'-DGTDP resins can be cured by means of common curatives used for ether glycidyl resins. On the basis of the determined gelation

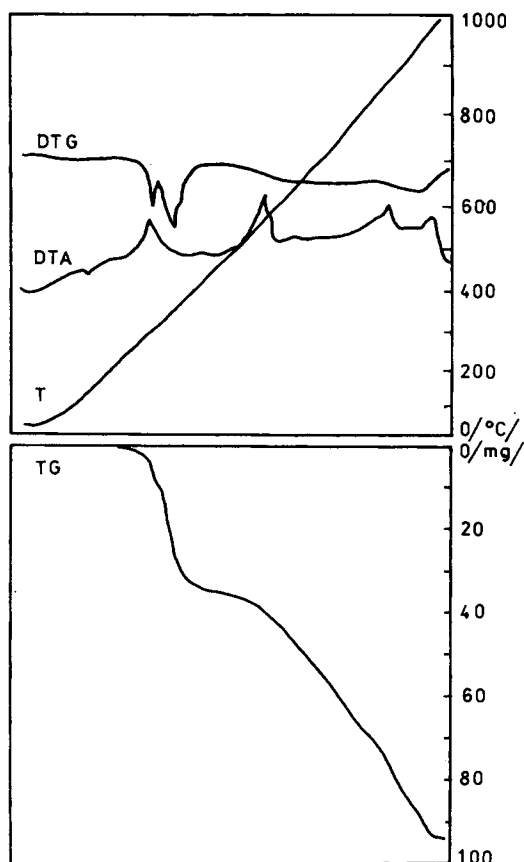


Fig. 7. TGA and DTA of uncured resin 4,4'-DGTDN of epoxy content 0.58. Heating time in air, 100 min; heating rate, 10°C/min; amount of resin, 100 mg; measurements related to O_2 .

TABLE V
Thermal and Mechanical Properties of Cured Composition

TEST	1,4-DGTN			1,5-DGTN		4,4'-DGTDP	
	TETA	HY-905	NMA	HY-905	NMA	HY-905	NMA
Vicat thermal resistance after Martens (°C)	84	73	132	79	139	92	98
Softening temp after Vicat (°C)	126	87	183	90	210	104	129
Bending strength (MPa)	12.4	54.9	64.4	85.0	61.5	80.8	65.3
Compressive strength (MPa)	118.7	106.9	175.5	157.9	104.1	132.0	148.6
Tensile strength (MPa)	8.9	17.5	29.6	24.3	21.8	36.2	10.2
Brinnell Hardness (MPa)	17.7	15.0	16.8	15.2	21.3	16.2	13.0
Charpy impact (kJ/m ²)	16.6	6.7	12.5	13.5	3.8	10.2	4.4

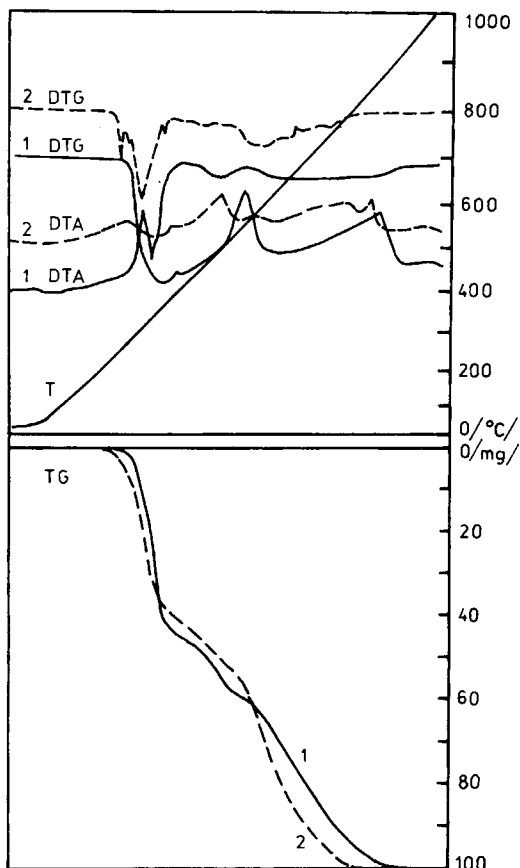


Fig. 8. TGA and DTA of uncured and thermally cured resin 1,5-DGTN of epoxy contents 0.62 (—) and 0.23 (---). Heating time in air, 100 min; heating rate, 10°C/min; amount of resins, 100 g; measurements related to Al_2O_3 .

time we can say that the compounds reveal good technological processing properties at 25–30°C, 90–100°C, and 110–120°C for 1,4-DGTN-TETA, 1,4- and 1,5-DGTN-HY-905, and 4,4'-DGTDP-HY-905, respectively. The compounds cured by NMA are characterized by longer gelation time.

For the studied compositions thermal stability is of the same order as in the case of uncured resins. Using NMA anhydride causes increase of thermomechanical resistance according to Martens and Vicat and greater bending and impact strength but decrease of elasticity. It is due to endomethyl bridges which make any changes of cyclohexane ring shape of the cured composition lattice structure impossible.

Summing up, it can be said from the studies of the three thioether glycidyl resins derivatives of aromatic hydrocarbon dimercaptans possessing condensed phenyl rings that thermal stability is affected not only by bond energy but also by monomer molecule symmetry and accumulation of a greater number of aromatic and cycloaliphatic rings.

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