

Synthesis, Structure, and Properties of the Addition Products Bis[*p*-(2,3-epoxypropyl)thiophenyl]methane with Methacrylic Acid

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ABSTRACT: The synthesis of bis(thiophenol-F) glycidyl methacrylate (BIS-GMTF) by the addition reaction between epoxide resin and methacrylic acid is described. The reaction was carried out without a solvent (in the alloy) and with the solvent (xylene). The reaction kinetics between the epoxide and carboxyl group during the BIS-GMTF reaction was observed by chemical analytical methods and infrared radiation (IR). The esterification is a second-order reaction at temperatures $>45^{\circ}\text{C}$ in the alloy and 70°C in the solvent. The spectroscopic characteristics of unsaturated BIS-GMTF resin were determined from IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectra. Epoxymethacrylate was subjected to photocuring, with the addition of IRGACURE 651, with a high-pressure mercury lamp in an oxygen-free atmosphere. The cured foil was subjected to thermal, thermomechanical, and mechanical investigations. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1806–1813, 2002

Keywords: epoxymethacrylate; bis(thiophenol-F)glycidyl methacrylate resin; structure; kinetic parameter; curing

INTRODUCTION

Resins and epoxide oligomers based on 2,2'-di(4-hydroxyphenyl)propane (Diane) have been commonly applied in the industry.^{1,2} Oligomers from other dihydroxyl phenols are also of great interest because of their specific properties. Such oligomers include epoxide derivatives of 4,4'-dihydroxy-diphenylsulphone, 4,4'-dihydroxydiphenyl oxide, and 4,4'-dihydroxydiphenyl methane.³

Epoxide resins of the aforementioned bisphenols require various modifications in practical applications. These modifications are mainly reduction of viscosity, improvement of filler wettability, reactivity regulation, improvement of fluidity, reduction of polymerization contraction, as well as

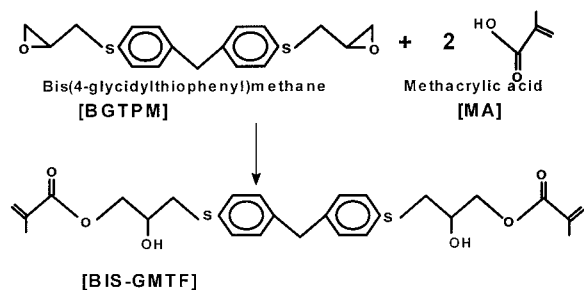
improvement of physical and mechanical properties of the cured resins.

Esterification with (meth)acrylic acids is one of modified types of epoxide resins from bisphenols. As a result of the epoxide groups reaction with carboxyl groups, epoxide resins transform into corresponding esters or diesters.^{4–6} The obtained products are liquids of great viscosity or solids that are easily dissolved in styrene and monomeric acrylates. However, their solutions, cross-linked in a classical way by means of a radical mechanism or various kinds of radiation, are used as binding material for plastics strengthened with glass fiber as well as microlithography, dentistry, opto-electric and printing industry, and protective layers.^{7–11}

Complex work on application of aliphatic, aliphatic–aromatic, and aromatic dimercaptans for the synthesis of monomers and polymers including sulfur have been carried out in our laboratory

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Scheme 1 Addition reaction of epoxide groups of bis[*p*-(2,3-epoxypropyl)thiophenyl]methane resin with the carboxyl group of methacrylic acid to form a new unsaturated vinyl bis[4-(2-hydroxy-3-methacryloyloxypropoxy)thiophenyl]methane or [bisthiophenol F-glycidyl methacrylate-(BIS-GMTF) resin].

for many years. Sulfide groups improve significantly the product properties after curing. From a practical point of view, they increase thermooxidation resistance, decrease water absorbing capacity, and increase the refractive index because of the significant polarizability of the sulfur atom.

Some new thioetherglycidyl resins were obtained from the reaction of glycerol epichlorohydrin with thiophenols.^{12–14} Further research has been carried out in which epoxide resins are chemically modified to improve their properties and increase their application.

The aim of this article is to describe the preparation of a new unsaturated vinyl bis[4-(2-hydroxy-3-methacryloyloxypropoxy)thiophenyl]methane resin [i.e., bis(thiophenol-F) glycidyl methacrylate (BIS-GMTF)] by the addition reaction

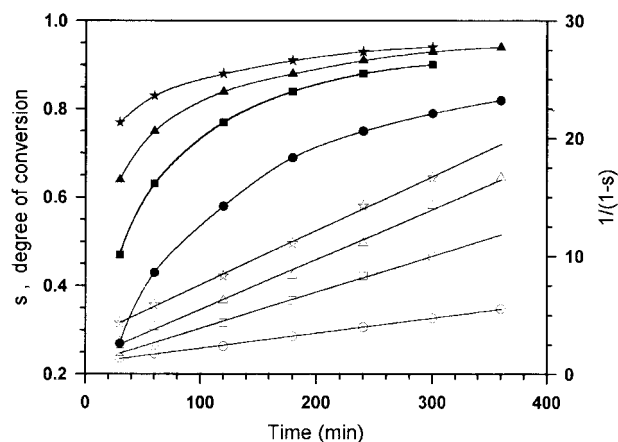


Figure 1 Reaction between the epoxy resin BGTPM and methacrylic acid (MA) without a solvent. Temperature key: (○, ●) 45°C; (□, ■) 55°C; (△, ▲) 65°C; (☆, ★) 75°C.

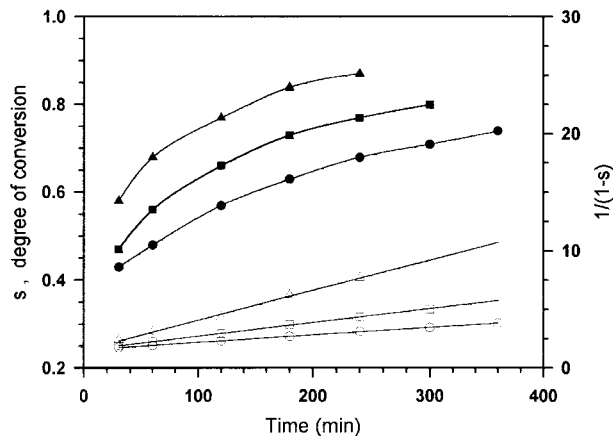


Figure 2 Reaction between the epoxy resin BGTPM and MA, with xylene at 0.86 M. Temperature key: (○, ●) 70°C; (□, ■) 80°C; (△, ▲) 90°C.

of epoxide groups of bis[*p*-(2,3-epoxypropyl)thiophenyl]methane resin with the carboxyl group of methacrylic acid (MA). In addition, the structure and basic properties of this product were determined and are presented.

A simplified reaction scheme is shown in Scheme 1. As a result of the reaction shown, thioetherglycidyl resin transforms into diester, which can polymerize because of the double bonds passing into the cross-linking state.

EXPERIMENTAL

Materials

Bis(4-glycidylthiophenyl)methane (BGTPM)¹³ was used for the synthesis determined in this work

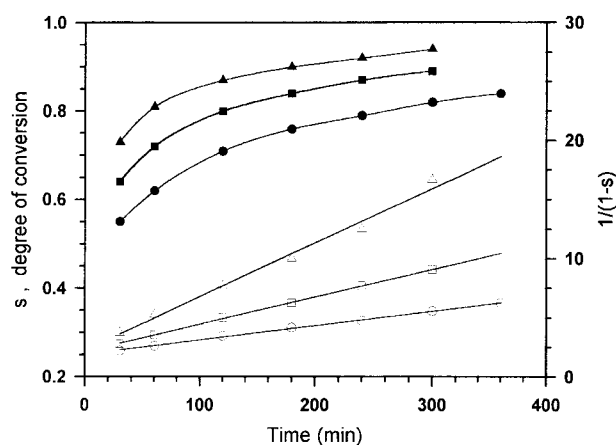


Figure 3 Reaction between the epoxy resin BGTPM and MA, with xylene at 1.29 M. Temperature key: (○, ●) 70°C; (□, ■) 80°C; (△, ▲) 90°C.

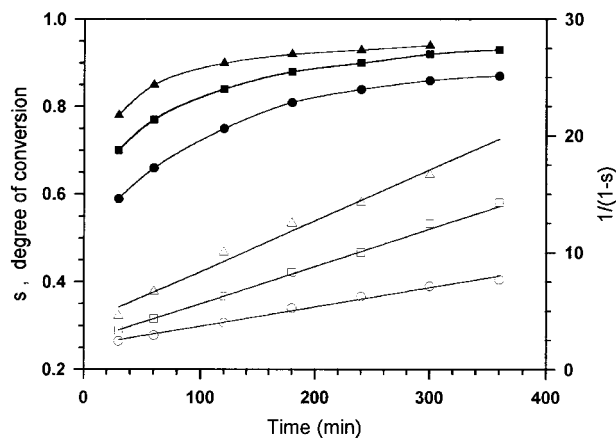


Figure 4 Reaction between the epoxy resin BGTPM and MA, with xylene at 1.72 M. Temperature key: (○, ●) 70°C; (□, ■) 80°C; (△, ▲) 90°C.

following analysis of its structure by infrared (IR) spectroscopy and examination of its epoxide groups. The following agents were also used: methacrylic acid (MA; Fluka Chemie, Buchs, Switzerland; purum; monomer, >98% [GC]), initiator IRGACURE 651 (2,2-dimethoxy-2-phenylacetophenone; Aldrich Chemie, Steinheim, Germany; purum; >99%), and xylene.

Methods

Synthesis of BIS-GMTF Resin

The reaction between BGTPM and MA was carried out in a nitrogen atmosphere without a solvent (in the alloy; Figure 1) at 45, 55, 65, and 75°C with or without the addition of catalyst (TEBA).

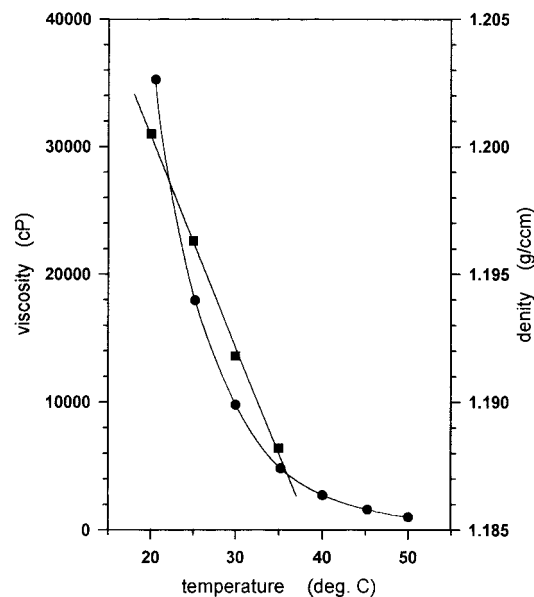
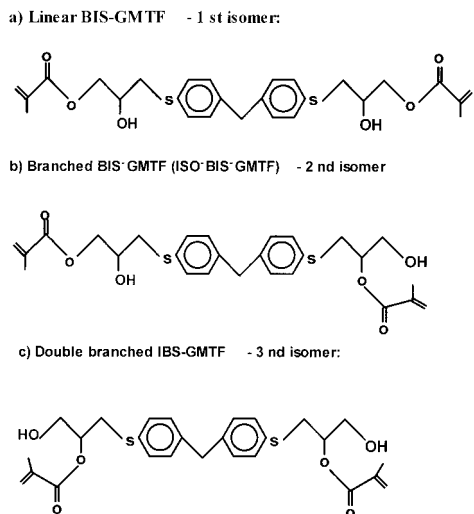


Figure 5 Viscosity (●) and density (■) of the BIS-GMTF resin depending on temperature.

The reaction was also carried out with the solvent (xylene; Figures 2–4) at reaction mixture concentrations of 0.86, 1.29, and 1.72 at 70, 80, and 90°C without a catalyst using a polymerization inhibitor (hydroquinone 0.1% by weight). The syntheses were carried out until the reaction yield was >0.8. The esterification reaction progress was monitored by the disappearance of adsorption band in the IR spectrum at 920 cm^{-1} , which is characteristic of the epoxide groups, and by determination of the MA concentration in the reaction mixture by chemical analysis (acid number). The reaction

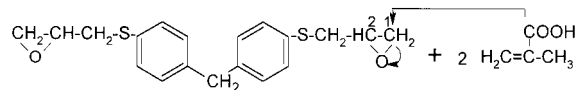
Table I Reaction Parameters of Addition of BGTPM and MA

Temperature K (°C)	Concentration BGTPM [mol]	$K \times 10^{-3}$ [$\text{mol}^{-1} \text{min}^{-1}$]	$E_a \times 10^3$ [J/mol]	ΔG^\ddagger [kJ/mol]	ΔH^\ddagger [kJ/mol]	ΔS^\ddagger [kJ/mol deg]
343.15 (70)	0.86	8.05	71.84	100.84	68.99	-92.82
353.15 (80)	0.86	15.37	71.84	102.00	68.90	-93.73
363.15 (90)	0.86	24.55	71.84	102.78	68.82	-93.52
343.15 (70)	1.29	18.06	67.05	98.97	64.20	-101.33
353.15 (80)	1.29	32.31	67.05	100.09	64.11	-101.88
363.15 (90)	1.29	54.07	67.05	101.03	64.03	-101.89
343.15 (70)	1.72	20.69	53.88	98.12	51.03	-137.27
353.15 (80)	1.72	40.50	53.88	99.17	50.94	-136.57
363.15 (90)	1.72	57.07	53.88	100.89	50.86	-137.77
328.15 (55)	in alloy	14.83	21.30	92.13	18.58	-224.15
338.15 (65)	in alloy	19.06	21.30	94.32	18.49	-224.23
348.15 (75)	in alloy	23.21	21.30	96.62	18.41	-224.65



Scheme 2 Three isomers of BIS-GMTF.

product was purified by treatment with an acid or base and stabilized by the addition of 50 ppm inhibitor (hydroquinone). Then, 34.45 g (0.1 mol) BGTPM resin and 0.034 g (0.1% by weight) hy-



Formation of the bis-GMTF

Scheme 3 Formation of BIS-GMTF.

droquinone were put into a round-bottomed four-necked, 250-mL glass flask equipped with a mechanical stirrer, reflux condenser, thermometer, and a pipe to introduce nitrogen.

When the required reaction temperature (45, 55, 65, or 75°C) was reached, 17.22 g (0.2 mol) of MA was introduced. However, when the solvent (xylene) was used, the reaction was carried out at the three concentrations [0.86 M (0.44 g with 1 mL of solvents), 1.29 M (0.66 g with 1 mL of solvents), or 1.72 M (0.86 g with 1 mL of solvents)] and at three temperatures (70, 80, and 90°C). A mass sample of ~0.5 g was taken from the reaction mixture at predetermined time intervals, and the acid number was determined.

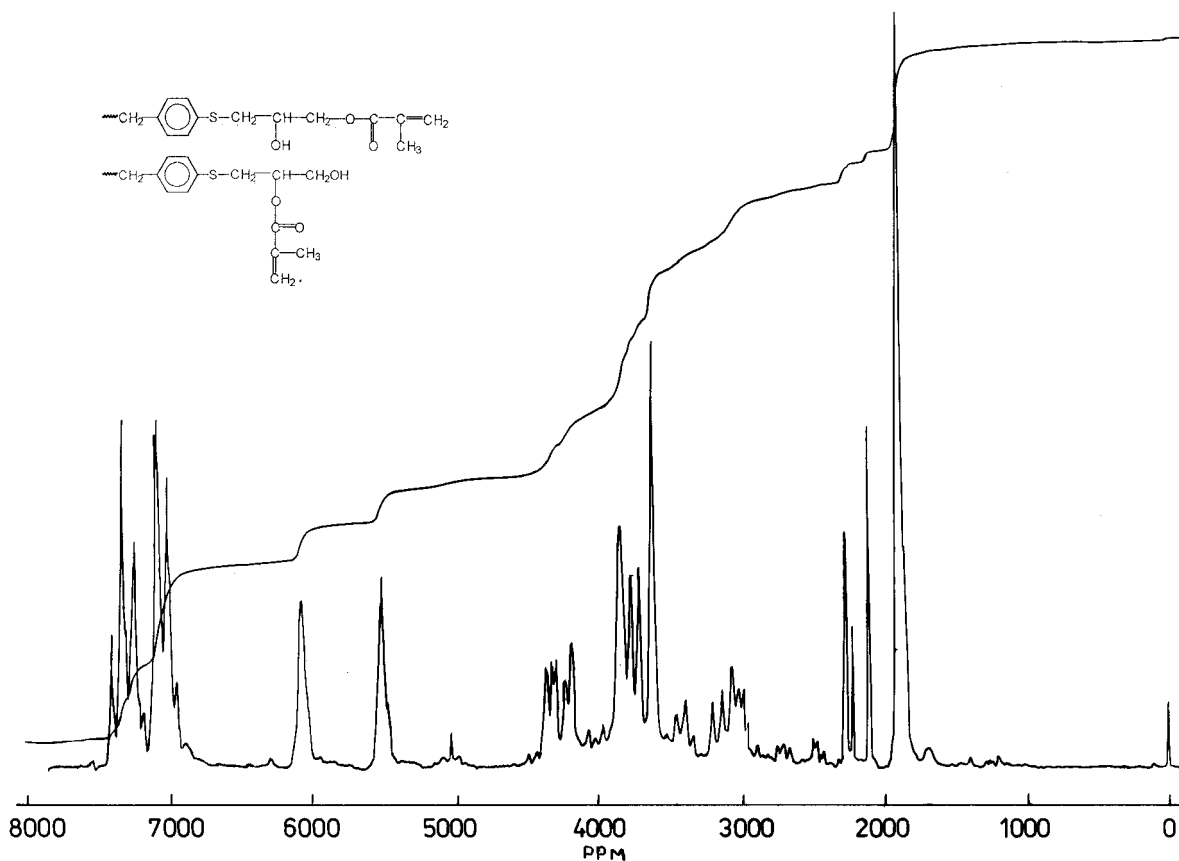
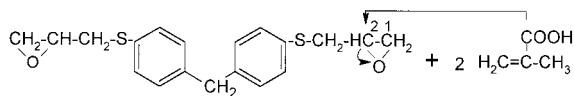


Figure 6 $^1\text{H-NMR}$ spectrum of the GMTF.



Formation of the iso-bis-GMTF

Scheme 4 Formation of iso-BIS-GMTF.

RESULTS AND DISCUSSION

Kinetic Studies

The reactions between etherglycidyl resins and (met)acrylic acids in the alloy and solvents have been the object of many investigations.¹⁵⁻¹⁷ The reaction mechanism between the epoxide and carboxyl group is complicated and has not been fully explained yet. In this article, the subject of the investigation is the reaction between BGTPM and MA. The reaction was carried out without the solvent in the presence of quaternary ammonium salt (TEBA) and without the catalyst as well as in the solvent (xylene).

The preliminary studies showed that the catalyst does not affect the addition reaction rate and further investigations were carried out without it. The reaction order, reaction rate constants, activation energy (E_a) and activation enthalpy (ΔH) were determined by the graphical method.¹⁸ A

drop in MA concentration (transformation degree) corresponds to a second-order rate. The activation parameters (ΔG), (ΔH), and (ΔS) were calculated as follows:

$$\Delta G^\ddagger = RT(23.764 - \ln k/T) \quad (1)$$

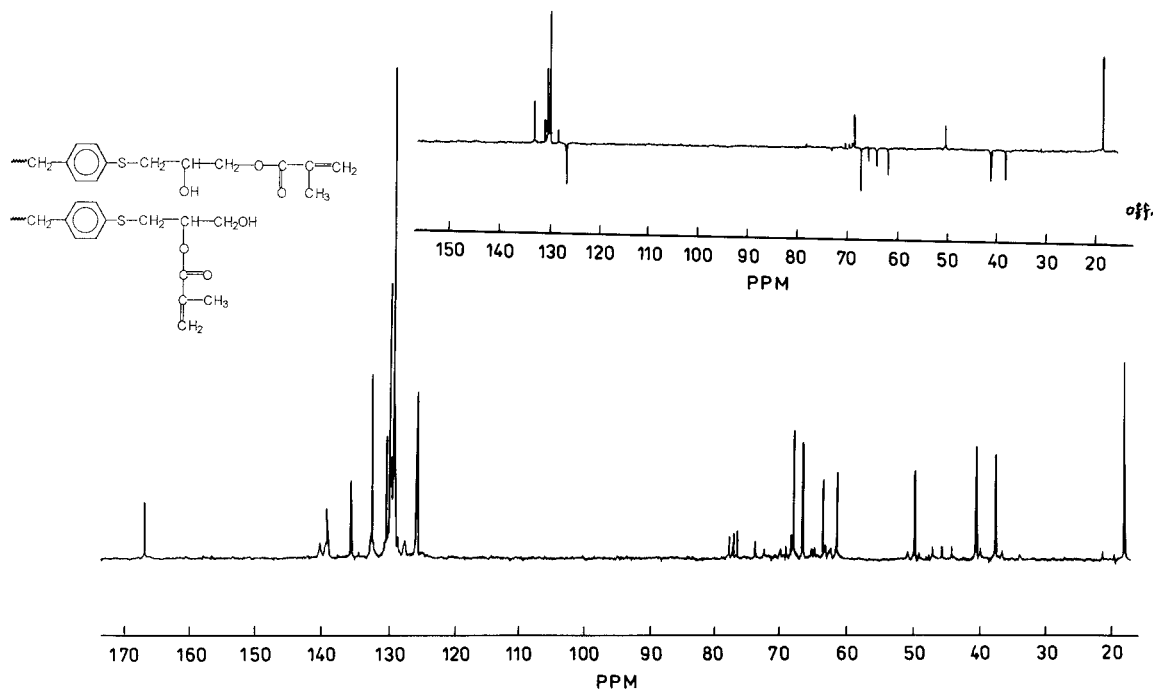
$$\Delta H^\ddagger = E_a - RT \quad (2)$$

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger - \Delta G^\ddagger}{T} \quad (3)$$

The numerical values are presented in Table I.

Characteristics of the BIS-GMTF Resin

The color of the obtained BIS-GMTF resin, depending on the synthesis conditions and process temperature, ranges from bright yellow to bright brown. The synthesized samples were analyzed by such techniques like elementary analysis, and IR, proton nuclear magnetic resonance ($^1\text{H-NMR}$), and carbon-13 NMR ($^{13}\text{C-NMR}$) spectroscopy. Solubility viscosity (at 25°C, 18 000 cP, and density of 1.197 g/cm³), refractive index ($n = 1.5675$), and thermal resistance were determined derivatographically. The character of BIS-GMTF solubility was tested in different polar

**Figure 7** $^{13}\text{C-NMR}$ spectrum of the GMTF.

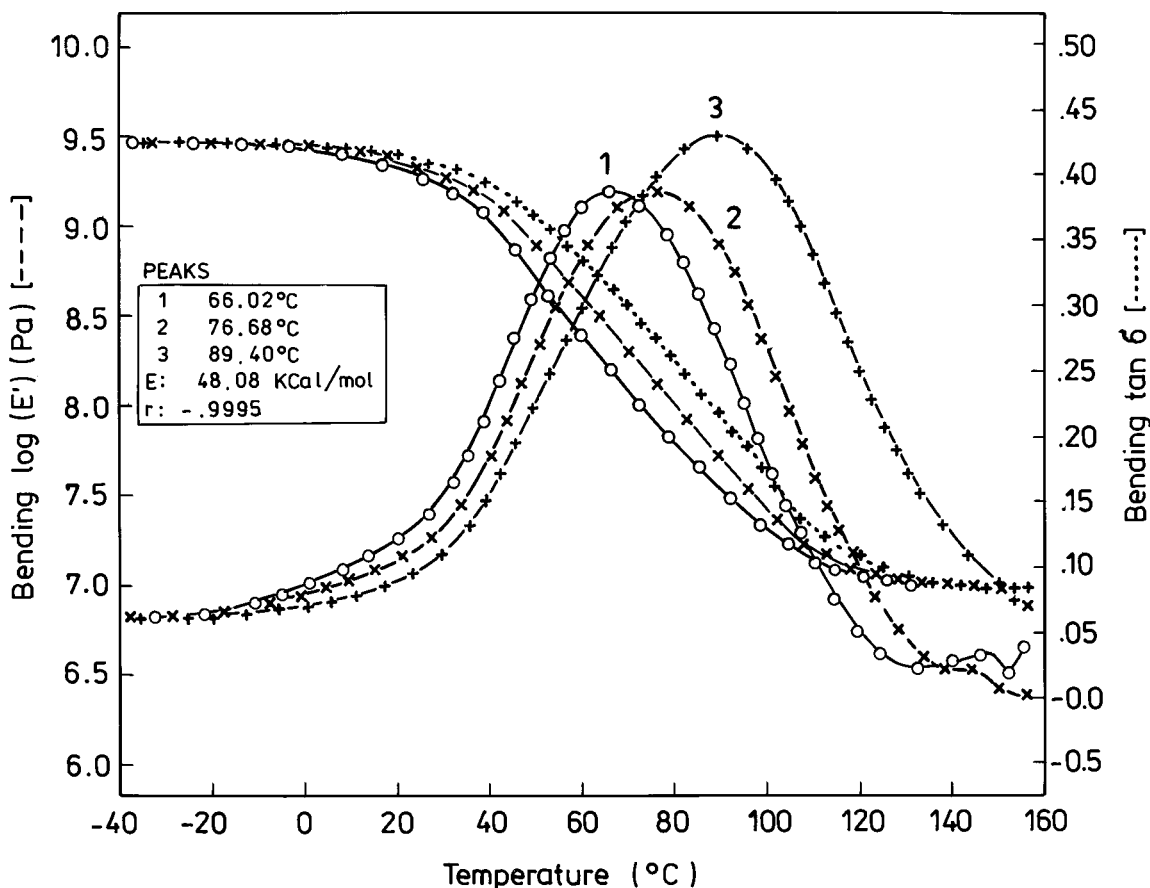


Figure 8 Changes of dynamic module and attenuation of the cured resin GMTF depending on temperature.

and nonpolar solvents; it is soluble in CHCl_2 , CH_2Cl_2 , dimethylformamide (DMF), dimethyl sulfoxide (DMSO), benzene, toluene, xylene, and CCl_4 , but does not dissolve in water. The dependence of viscosity and density on temperature is presented in Figure 5.

The IR spectrum of BIS-GMTF resin confirms formation of the product of thioetherglycidyl resin esterification with MA. The peak of the final epoxide group adsorption disappears at $920\text{--}925\text{ cm}^{-1}$. Other characteristic absorption peaks occur at 939 cm^{-1} (C--CH_2 , bending), 1639 cm^{-1} (C--CH_2 , stretching), 1665 cm^{-1} (carboxyl group), and 3400 cm^{-1} (hydroxyl group).

The product of diglycidyl ether bisphenol-A and MA synthesis is a mixture of isomers of similar chemical structure, as shown by $^1\text{H-NMR}$ spectra. These isomers are called bisphenol-A glycidyl methacrylate and iso-bisphenol-A glycidyl methacrylate (BIS-GMA and ISO-BIS-GMA, respectively).¹⁹⁻²²

Analysis of the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of BIS-GMTF resin prepared indicates a mixture of isomers. It is obvious that these two isomers differ in the mutual position of OH-groups in relation to the methacrylic unit. As each of two epoxide groups of BGTPM can react with MA independently, the reaction product may be a mixture of the three isomers shown in Scheme 2.

In the $^1\text{H-NMR}$ spectrum (Figure 6) of GMTF resin, characteristic peaks of the isomer BIS-GMTF are evident, and peaks of another structure of the monomer, of similar chemical structure, which was identified as the isomer ISO-BIS-GMTF. The characteristic peaks for these components are 1.96 ppm (CH_3 methacrylate), 2.82 ppm (OH), 2.50–4.00 ppm ($\text{S-CH}_2\text{-CH(OH)-CH}_2\text{-O}$), 3.90 ppm ($\text{Ar-CH}_2\text{-Ar}$), 5.10–6.18 ppm ($\text{CH}_2\text{=}$ methacrylate), 7.08–7.35 ppm (*p*-substituted aromatic ring), 4.4 ppm ($\text{-C-CH}_2\text{-OH}$). As indicated by the integration data, ~10–20% of the total final groups present in the isomeric form

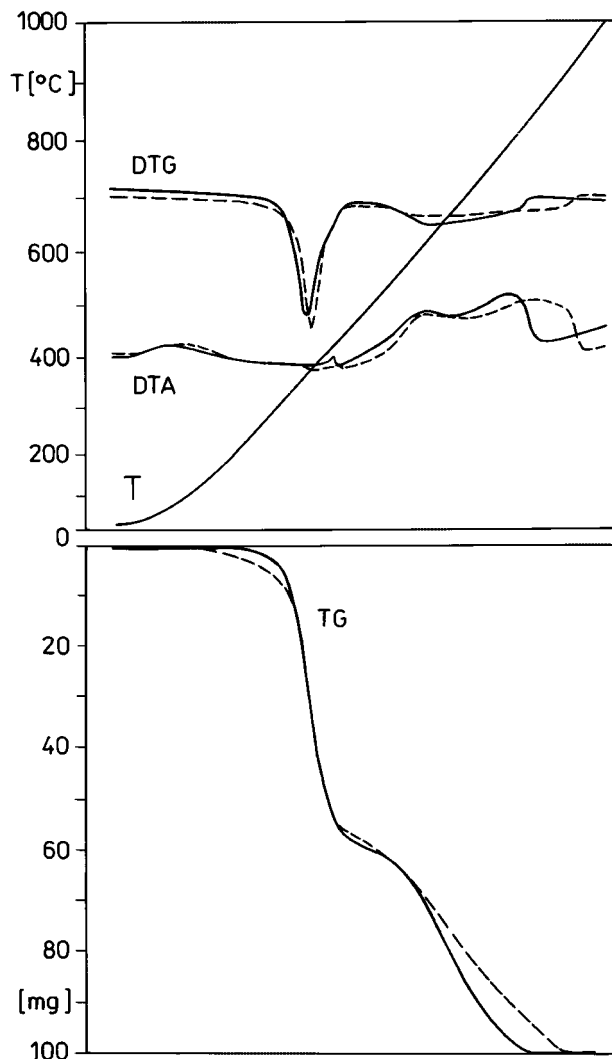


Figure 9 TGA and DTA of the uncured (solid line) and the cured (dashed line) BIS-GMTF resin (heating time in air, 100 min; heating rate, 10°C/min; amount of resins, 100 mg; measurements related to Al_2O_3).

comes from the branched BIS-GATM. The mutual relation of two isomers present in the synthesis product depends on such factors as reagents concentration, process temperature, reaction time, or synthesis method. Generally, it is connected with the reaction of epoxide group ring opening. During the attack on carbon C_1 , ring opening follows the direction shown in Scheme 3. Some of the MA reacts with carbon C_2 , and ring opening follows another direction. The latter reaction, in which ISO-BIS-GMTF is formed, is shown in Scheme 4. Both epoxide groups of the molecule react independently and it is quite probable that a large part of ISO-BIS-GMTF has a mixed structure as suggested.

Analysis of the ^{13}C -NMR spectrum (Figure 7) confirms that the BIS-GMTF resin is the mixture of BIS-GMTF and ISO-BIS-GMTF isomers. The signals in the range $\delta = 37\text{--}68$ ppm come from the open ring of the glycidyl unit; the signals in the range $\delta = 139\text{--}129$ ppm come from the aromatic carbon rings; and the signals at $\delta = 17.9$, $\delta = 125\text{--}132$ ppm, and $\delta = 187$ ppm are from the molecule fragment connected with the acid unit. Four main lines in the spectrum (i.e., 49.8, 61.2, 66.5, and 67.8 ppm) confirm that the ISO-BIS and BIS-GMTF structures are found in the resin.

It is surprising that the signal from the carbon of methine unit has such a significant chemical shift. Off-resonance of the new resin and the literature data of other systems including sulfur in the main chain indicate that these signals of the ^{13}C -NMR spectrum correspond to the methine unit. One signal in the ^{13}C -NMR spectrum of the BIS-GMTF resin (i.e., 63.4 ppm) is not connected with the resin structure. This signal is probably from impurities of the reaction mixture with "cis", "trans"-3-(*p*-phenylthio)propane-2-en-1-ol formed during the synthesis. The heated thioetherglycidyl resin transforms partially into unsaturated alcohol of the type confirmed in our paper.¹⁴

Curing of the BIS-GMTF Resin

The deaerated unsaturated BIS-GMTF resin with the addition of the photoinitiator in the amount of 2% by weight was put into a mould made of two glass plates (10 × 15 cm; thickness, 0.3 cm) covered with adhesive lubricant and separated by a 1-mm thick piece. The mould with the resin was placed in the exposure chamber and subjected to two-sided ultraviolet (UV) radiation using two high-pressure mercury lamps, with a total power of 500 W, at a distance of 20 cm for 5 min. The foil prepared in this way was cut into 120 × 10-mm strips, which were used for the studies of strength on the tensile testing machine, thermal resistance on the UTS-50, and thermal-mechanical resistance (PL-DMTA).

The studies included elasticity, strength, relative elongation, hardness and thermal resistance, vitrification temperature (T_g), changes of dynamic, and suppression modules. Dynamic-mechanical studies of the cured BIS-GMTF resin were carried out with the PL-DMTA apparatus (Figure 8). Changes of the dynamic and suppression modules were determined in the temperature range $-40\text{--}+180^\circ\text{C}$ at the frequencies 0.10, 1.00, and 10.00 Hz during the transformation (α) defin-

Table II Properties of BIS-GMTF

BIS-GMTF Resin	Thermal Properties				Mechanical Properties			
	T_1^a	U^b	T_2^c	T_3^d	Hardness (Brinell) [MPa]	Tensile Strength [MPa]	Elongation at Break [%]	Young's Modulus [MPa]
Uncured	280	4.0	380	420	—	—	—	—
UV-cured	290	2.5	380	420	157.4	28.54	1.7	1794.0

^a T_1 (°C), temperature of initial mass loss from the DTG and TG curves.

^b U (%), mass loss at the temperature T_1 from the TG curve.

^c T_2 (°C), temperature of intensive mass loss from the DTG curve.

^d T_3 (°C), temperature of 50% mass loss from the TG curve.

ing the T_g . A rapid drop of the elasticity module value is observed near the T_g of the cured resin changing from the elastic state into the highly flexible state.

Dynamic studies of decomposition of the uncured or UV-cured BIS-GMTF resin were carried out with the derivatograph MOM (Paulik, Paulik and Erdey, Budapest, Hungary; temperature increase 10 °C/min in air; Figure 9). The decomposition temperature is in the range 240–260 °C regardless of whether it is estimated from the mass loss curve (T_g) or the differential thermal analysis curve (DTA) showing a rapid mass loss. Therefore, the decomposition may begin from the structural elements of the molecule chain (i.e., from the thioether sulfur from weakest link in the chain structure). The cured BMS-GMTF resin was subjected to mechanical investigations according to the Polish Standard PN-81/C-89034 using a UTS-50 apparatus. The obtained numerical values are presented in Table II.

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