

Thioether glycidyl resins II.  
Synthesis, structure and properties of the addition  
products bis[p-(2,3-epoxypropyl)thiophenyl]methane  
with acrylic acid

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The synthesis of bithiophenol-F glycidyl acrylate (BIS-GATF) was described in the addition reaction between epoxide resin and acrylic acid. The reaction was carried out without a solvent (in the alloy) and in the solvent (xylene). The reaction kinetics between the epoxide and carboxyl groups during the BIS-GATF reaction was observed using chemical analytical methods and in the infrared radiation (IR). It was found that the esterification reaction is of II order at a the temperatures over 45°C in the alloy and 70°C in the solvent. The spectroscopic characteristics of unsaturated resin BIS-GATF was determined from IR spectra, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. Epoxyacrylate 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, thermo-mechanical, and mechanical investigations.

Keywords: epoxyakrylate; bis(thiophenol-F)glycidyl acrylate resin; structure; kinetic parameters; curing

## 1. INTRODUCTION

Diesters obtained from the addition of (meth)acrylic acids to the epoxide diene resin are well described in literature. They can be cured by radical polymerization of unsaturated bonds occurring in them. Good physical and

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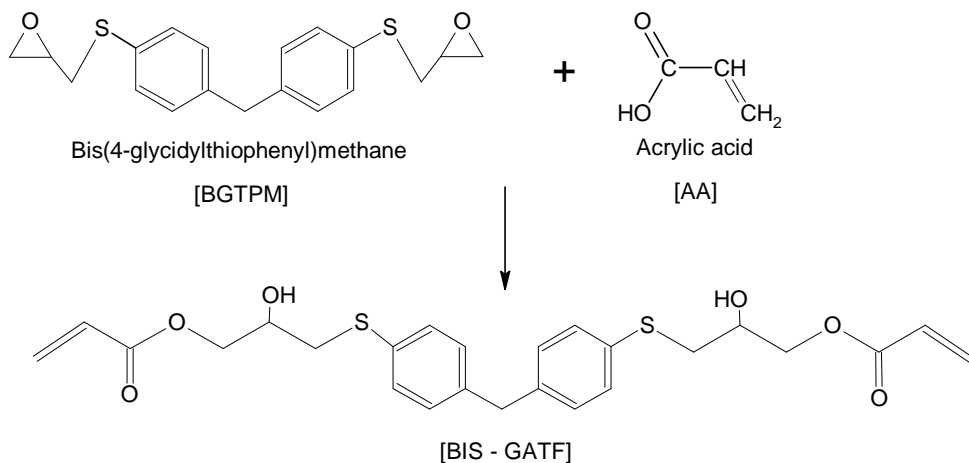
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mechanical properties as well as great curing rate promote numerous practical application of the products of this type.

Literature on synthesis, properties and application of this type diesters of various bisphenols as well as sulfur analogue with methacrylic acid was presented in the previous publication [1].

The aim of this paper is to prepare new unsaturated vinyl bis[4-(2-hydroxy-3-acryloyloxypropoxy)thiophenyl]methane or bis(thiophenol-F) glycidyl acrylate resin (BIS-GATF) the by addition reaction of epoxide groups of bis[p-(2,3-epoxypropyl)thiophenyl]methane resin with carboxyl group of acrylic acid (AA), to determine its structure and basic properties.

A simplified reaction scheme is shown in Scheme 1.



Scheme 1. Addition reaction of epoxide groups of bis[p-(2,3-epoxypropyl) thiophenyl] methane resin with the carboxyl group of acrylic acid to form a new on saturated vinyl bis[4-(2-hydroxy-3-acryloyloxypropoxy) thiophenyl]methane or [bisthiophenol F-glycidyl acrylate-(BIS-GATF) resin]

As a results of the reaction shown, thioetherglycidyl resin transforms into diester, which can polymerize because of the double bonds passing into the cross-linking state.

## 2. EXPERIMENTAL

**Materials.** Bis(4-glycidylthiophenyl)methane (BGTPM) [2] was applied after the analysis of its structure by means of the IR spectra and examination of the epoxide groups content according to the synthesis worked out by us.

Acrylic acid ([AA], Fluka Chemie, Buchs, Switzerland; purum; monomer, >98%, {GC}).

Initiator IRGACURE 651 (2,2-dimethoxy-2-phenylacetophenone, Aldrich Chemie, D-7924 Steinheim, Germany, purity; >99%).

Xylene (Mixture of isomers), POCh, Gliwice, Poland, pure.

**Methods.** *Synthesis of BIS-GATF resin.* The reaction between BGTPM and acrylic acid (AA) was carried out in the nitrogen atmosphere without a solvent (in the alloy) (Fig.1) at 45, 55, 65 and 75°C with or without the addition of a catalyst (TEBACI). The reaction was also carried out with the solvent (xylene) (Figs.2-4) with the reaction mixture concentrations: 0.86, 1.29 and 1.72 M at 70, 80 and 90°C without a catalyst using a polymerization inhibitor (hydroquinone 0.1% by weight). The syntheses were carried out till the reaction yield was over 0.8. The esterification reaction progress was observed from the disappearance of adsorption band in the IR spectrum at  $920\text{ cm}^{-1}$  characteristic of determination of the epoxide groups and from determination of the acrylic acid concentration in the reaction mixture by means of the chemical analysis (acid number). The reaction product was purified by treatment with an acid or base and stabilized with the addition of 50 ppm inhibitor (hydroquinone).

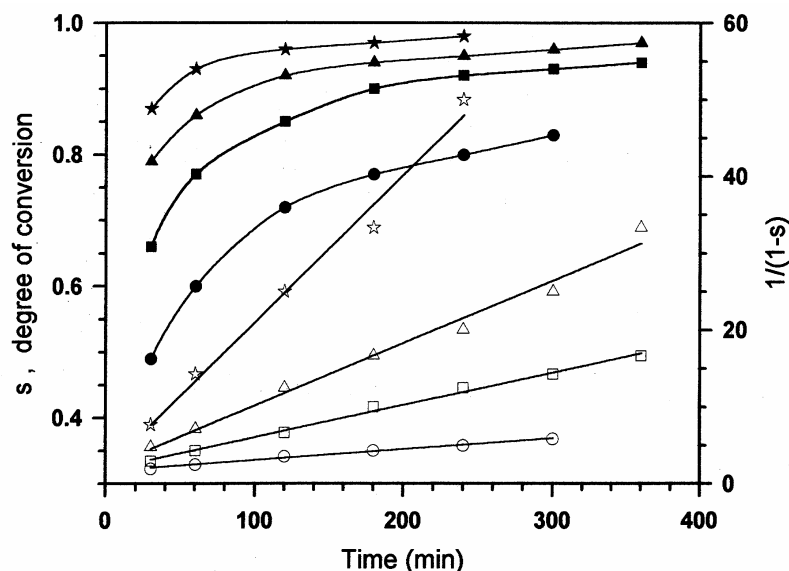


Fig. 1. Reaction between the epoxy resin BGTPM and acrylic acid (AA) without a solvent. Temperature key: (●, ○) 45°C; (■, □) 55°C; (▲, △) 65°C; (★, ☆) 75°C

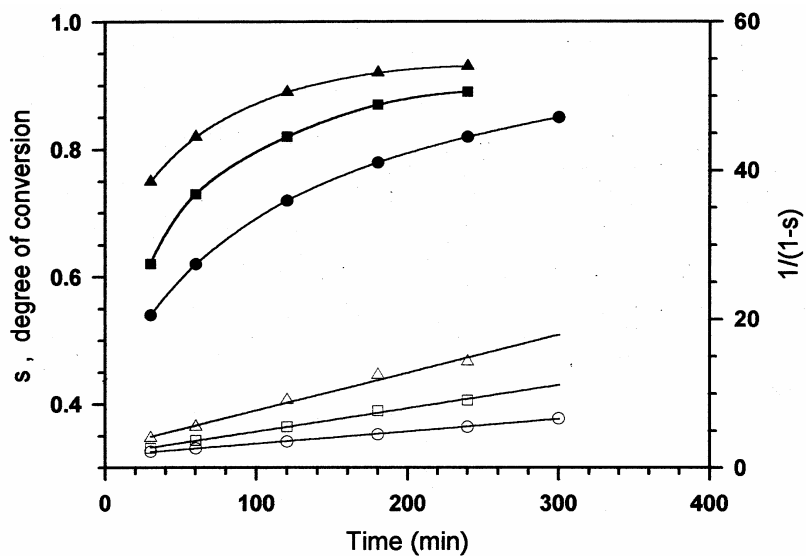


Fig. 2. Reaction between the epoxy resin BGTPM and AA with xylene at 0.86 M. Temperature key: (•, ◯) 70°C; (■, □) 80°C; (▲, △) 90°C

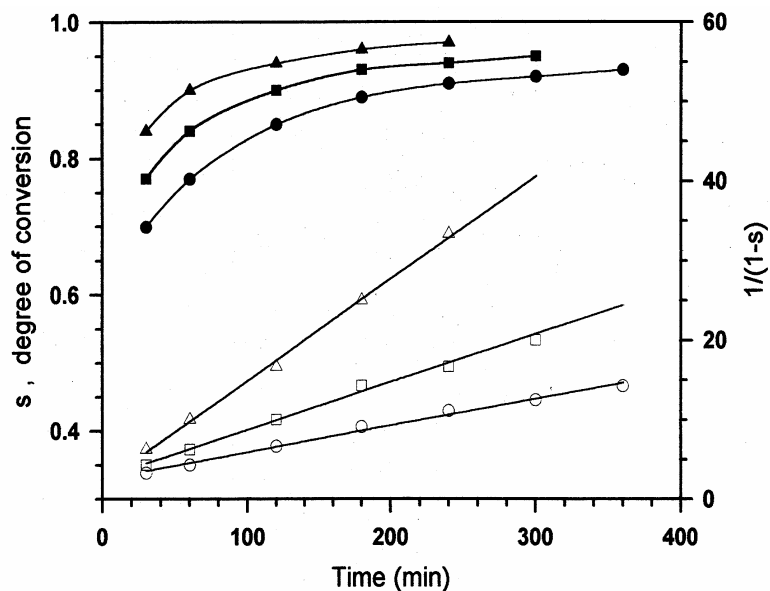


Fig. 3. Reaction between the epoxy resin BGTPM and AA with xylene at 1.29 M. Temperature key: (•, ◯) 70°C; (■, □) 80°C; (▲, △) 90°C

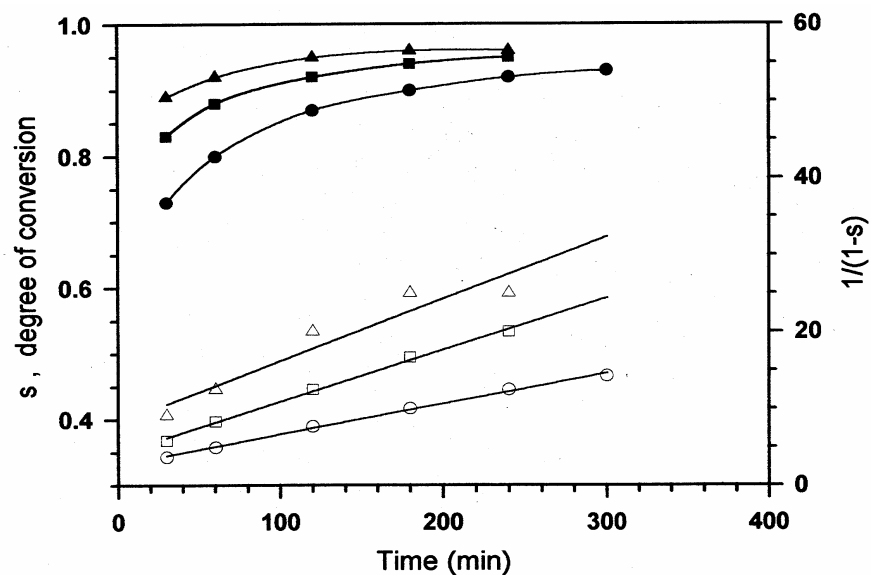


Fig. 4. Reaction between the epoxy resin BGTPM and AA with xylene at 1.72 M. Temperature key: (•,◦) 70°C; (◼,◻) 80°C; (▲,△) 90°C

34.45 g (0.1 mole) BGTPM resin and 0.034 g (0.1% by weight) hydroquinone were put into a round-bottom four necked glass flask of a volume 250 mL 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, 14.4 g (0.2 mole) acrylic acid (AA) was introduced. However, when the solvent (xylene) was used, the reaction was carried out at three concentrations: 0.86 mole (0.44 g of resin with 1 mL of solvent), 1.29 mole (0.66 g of resin with 1 mL of solvent), or 1.72 mole (0.86 g of resin with 1 mL of solvent) at three temperatures (70, 80 and 90°C). The mass sample about 0.5 g was taken from the reaction mixture at predetermined time intervals and the acid number was determined.

### 3. RESULTS AND DISCUSSION

**Kinetic studies.** The reactions between etherglycidyl resins and (meth)acrylic acids in the alloy and solvents have been the object of many investigations [3-5]. The reaction mechanism between the epoxide and carboxyl groups is complicated and has not been fully explained yet.

In this article, the subject of the investigation is the reaction between thioether glycidyl resin (BGTPM) and acrylic acid. The reaction was carried

out without the solvent in the presence of quaternary ammonium salt (TEBACl) 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 ( $\Delta H^\ddagger$ ) were determined by the graphical method [6]. A drop of acrylic acid concentration (transformation degree) corresponds to a second-order rate.

The activation parameters ( $\Delta G^\ddagger$ ), ( $\Delta H^\ddagger$ ) and ( $\Delta S^\ddagger$ ) were calculated from the dependence:

$$\Delta G^\ddagger = RT(23,764 - \ln k/T)$$

$$\Delta H^\ddagger = E_a - RT$$

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger - \Delta G^\ddagger}{T}$$

The numerical values are presented in Table 1.

Tab. 1 Reaction Parameters of Addition of BGTPM and AA

Temperature [K]	Concentration BGTPM [mol]	$K \times 10^{-3}$ [mol <sup>1</sup> min <sup>-1</sup> ]	$E_a$ [kJ/mol]	$\Delta G^\ddagger$ [kJ/mol]	$\Delta H^\ddagger$ [kJ/mol]	$\Delta S^\ddagger$ [kJ/mol deg]
343.15	0.86	8.05	57.47	98.21	54.62	-127.03
353.15	0.86	15.37	57.47	99.26	54.53	-126.66
363.15	0.86	24.55	57.47	100.74	54.45	-127.49
343.15	1.29	18.07	56.26	95.90	53.41	-123.82
353.15	1.29	32.31	56.26	97.07	53.33	-123.86
363.15	1.29	54.07	56.26	98.35	53.24	-124.22
343.15	1.72	20.69	53.68	95.52	49.83	-133.15
353.15	1.72	40.50	53.68	96.41	49.74	-132.15
363.15	1.72	57.07	53.68	98.19	49.66	-133.64
328.15	in alloy	22.31	69.23	91.02	66.51	-74.69
338.15	in alloy	40.43	69.23	92.22	66.42	-76.29
348.15	in alloy	100.67	69.23	92.37	66.34	-74.77

**Characteristics of the BIS-GATF resin.** The colour of the obtained BIS-GATF resin depending on the synthesis conditions and process temperature, ranges from bright yellow to bright brown. The synthesized samples were analyzed using such techniques as: elementary analysis, IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. Solubility, viscosity (at 25°C, 17905 cP), density (1.177 g/cm<sup>3</sup>),

refractive index ( $n=1.5755$ ) and thermal resistance were determined derivatographically. The character of BIS-GATF solubility was tested in different polar and nonpolar solvents. It was stated that it is well soluble in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , DMF, DMSO, benzene, toluene and xylene but does not dissolve in water. Viscosity and density depending on the temperature are presented in Figure 5.

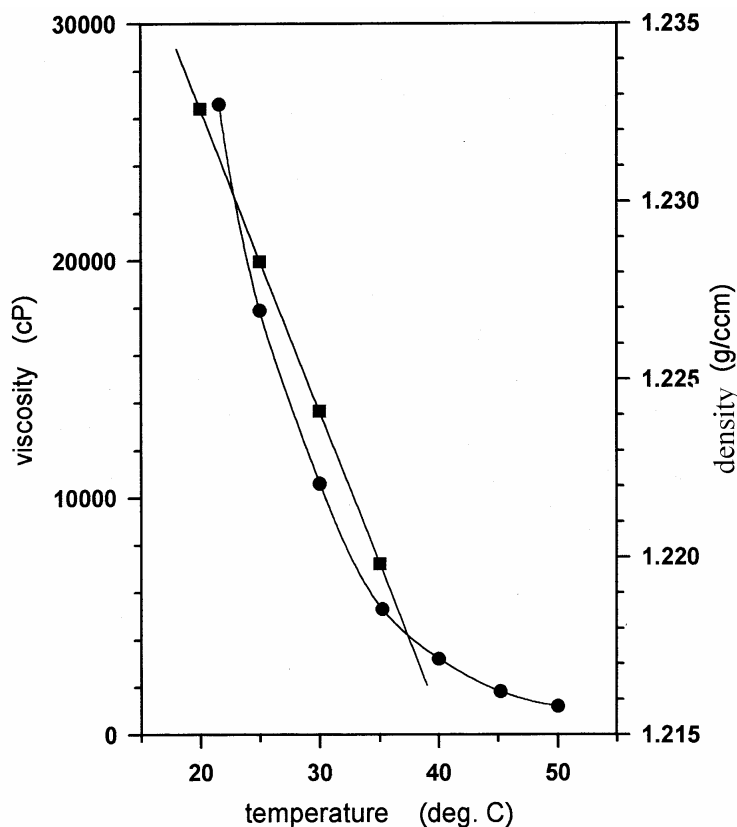


Fig. 5. Viscosity (●) and density (■) of the BIS-GATF resin depending on temperature

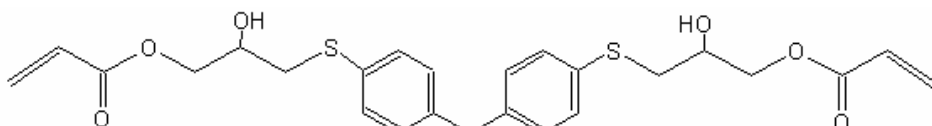
The infrared (IR) spectrum of BIS-GATF resin confirms formation of the product of thioetherglycidyl resin esterification with acrylic acid. The peak of the final epoxide group absorption disappears at  $920\text{-}925\text{ cm}^{-1}$ . Other characteristic absorption peaks occur at  $939\text{ cm}^{-1}$  ( $\text{C}=\text{CH}_2$ , bending),  $1639\text{ cm}^{-1}$  ( $\text{C}=\text{CH}_2$ , stretching),  $1722\text{ cm}^{-1}$  (carbonyl group) and  $3444\text{ cm}^{-1}$  (hydroxyl group).

The product of diglycidyl ether bisphenol-A and methacrylic acid synthesis is a mixture of isomers of similar chemical structure as shown by means of

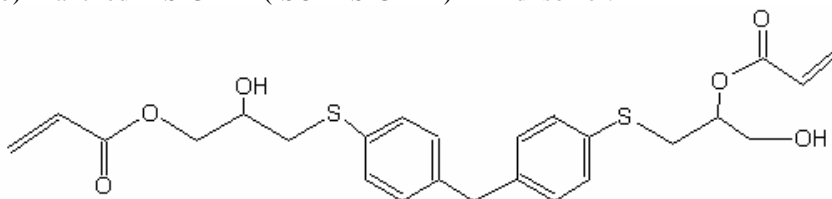
$^1\text{H-NMR}$  spectra. These isomers are called bisphenol-A glycidyl methacrylate and iso-bisphenol-A glycidyl methacrylate (BIS-GMA and ISO-BIS-GMA) [7-10].

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

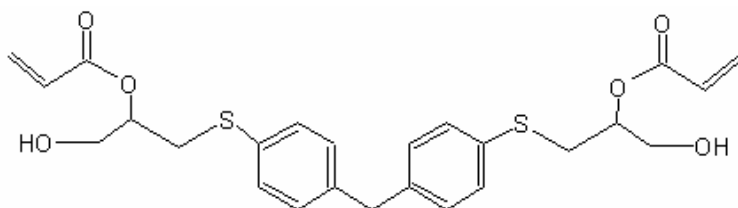
a) Linear BIS-GATF – 1-st isomer:



b) Branched BIS-GATF (ISO-BIS-GATF) – 2-nd isomer:



c) Double branched BIS-GATF – 3-rd isomer:



Scheme 2. Three isomers of BIS-GATF

In the  $^1\text{H-NMR}$  spectrum (Fig. 6.) of GATF resin there occur characteristic peaks of the isomer BIS-GATF and also another structure of the monomer of similar chemical structure which was identified as the isomer ISO-BIS-GATF. The characteristic peaks for these components are: 2.55-2.8 ppm (OH) in linear BIS-GATF and 4.8–5.2 ppm (OH) in branched BIS-GATF, 2.9–3.25 ppm ( $\text{S-CH}_2\text{-CH(OH)-O}$ ), 3.1–3.9 ppm ( $\text{Ar-CH}_2\text{-Ar}$ ), 5.6-6.6 ppm ( $\text{CH}_2=\text{acrylate}$ ), 6.0–6.2 ppm ( $\text{CH}_2=\text{CH}$ ), 6.9–7.4 ppm (p-substituted ring).



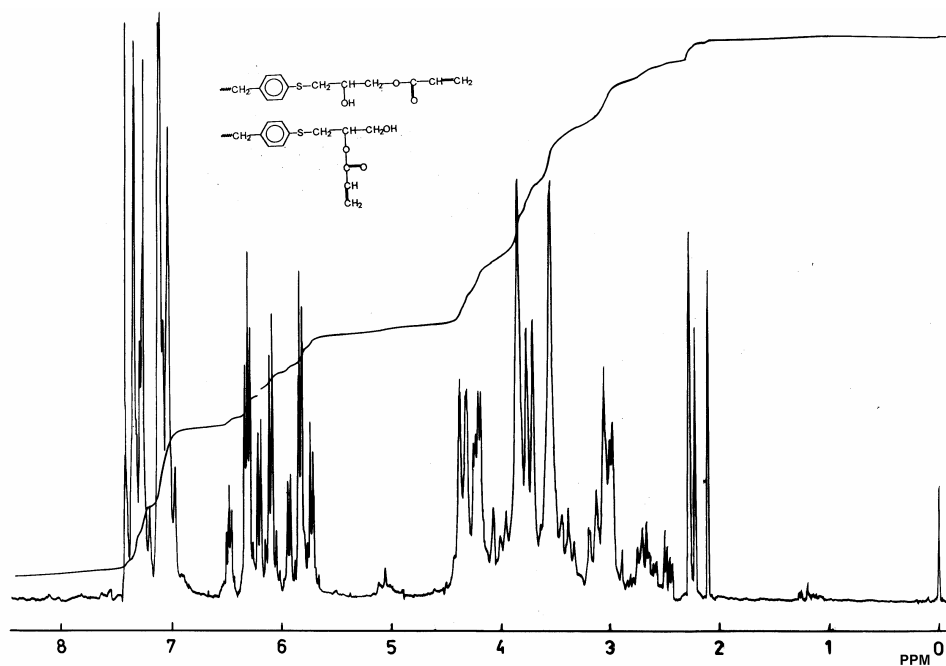


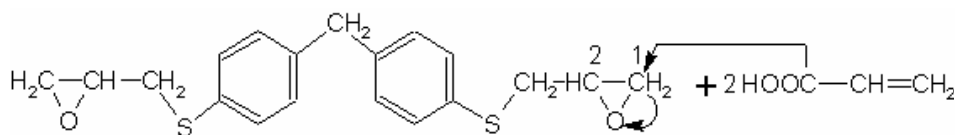
Fig. 6. <sup>1</sup>H-NMR spectrum of the GATF

Occurrence of the isomer ISO-BIS-GATF in the postreaction mixture is evidenced by the multiplet observed in the spectrum at 4.95–5.15 ppm coming from tertiary methine proton (-CH(OH)) and the signal at 4.15–4.50 ppm corresponding to methylene protons coming from the group (C-CH<sub>2</sub>-OH).

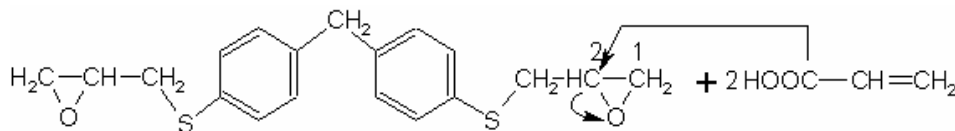
As follows from the integration data, about 10–20% of the total final groups present in the isomeric form comes from the branched BIS-GATF. The mutual relation of two isomers present in the synthesis product depends on such factors as reagents concentration, process temperature, reaction time or synthesis method. Generally, it is connected with the reaction of epoxide group ring opening. During the attack on carbon C<sub>1</sub>, ring opening follows the direction shown in Scheme 3.

Some of the acrylic acid reacts with carbon C<sub>2</sub>; and ring opening follows another direction. The latter reaction, in which ISO-BIS-GATF is formed, is shown in Scheme 4.

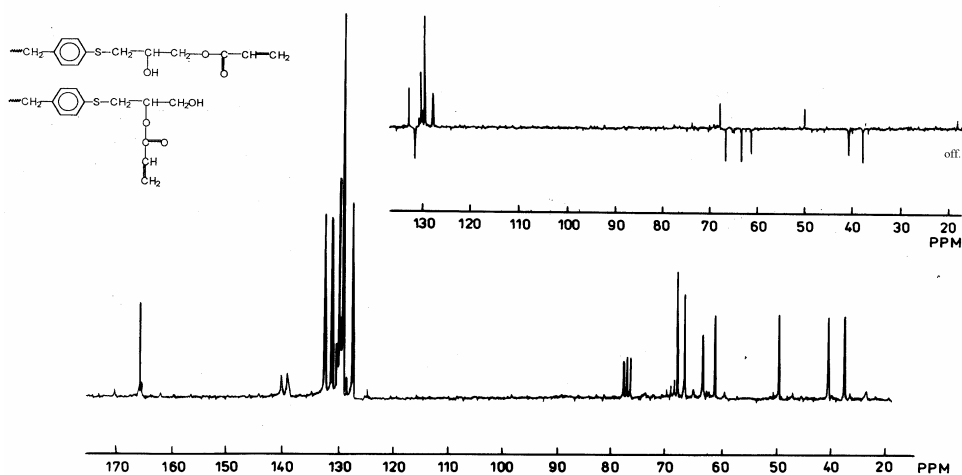
Both epoxide groups of the molecule react independently and it is quite probable that a large part of ISO-BIS-GATF has a mixed structure as suggested.



Scheme 3. Formation of BIS-GATF



Scheme 4. Formation of ISO-BIS-GATF

Fig. 7.  $^{13}\text{C}$ -NMR spectrum of the GATF

The analysis of  $^{13}\text{C}$ -NMR spectrum (Fig. 7) confirms that the BIS-GATF resin is the mixture of BIS-GATF and ISO-BIS-GATF isomers. The signals in the range  $\delta=37$  to  $\delta=68$  ppm come from the open ring of the glycidyl unit, the signals in the range  $\delta=129$  to  $\delta=134$  ppm come from the aromatic carbon rings and the signals  $\delta=128$ ,  $\delta=131$ ,  $\delta=166$  ppm from the molecule fragment connected with the acid unit. Four main lines in the spectrum (i.e. 49, 61.3, 69.9 and 67.3 ppm) confirm that the ISO-BIS-GATF 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  $^{13}\text{C}$ -NMR spectrum correspond to the methine unit.

**Curing of the BIS-GATF resin.** The deaerated unsaturated BIS-GATF resin with the addition of the photoinitiator in the amount of 2% weight was put into a mould made of two glass plates, (size 10 x 15 cm and 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 the two-sided UV radiation using two high pressure mercury lamps, with a total power of 500 W, at a distance of 20 cm for 5 minutes. The foil prepared in this way was cut into 120 x 10 mm strips, which were used for the studies of strength on the tensile testing machine, thermal resistance (derivatograph UPS-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.

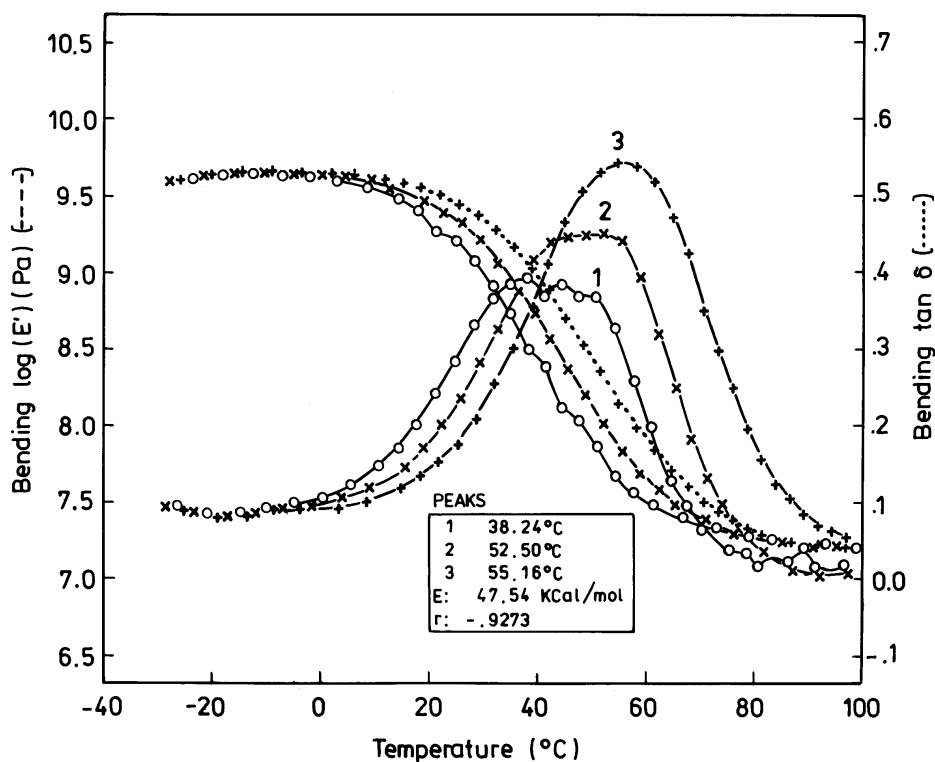


Fig. 8. Changes of dynamic module and attenuation of the cured resin GATF depending on temperature. 1 - 0.10Hz; 2 - 1.00Hz; 3 - 10.00Hz

Dynamic-mechanical studies of the cured BIS-GATF resin were carried out using the PL-DMTA apparatus (Fig. 8). Changes of the dynamic and suppression modules were determined in the temperature range  $-40^{\circ}\text{C}$  to  $180^{\circ}\text{C}$  at the frequencies 0.10, 1.00 and 10.00 Hz during the transformation ( $\alpha$ ) defining the vitrification temperature ( $T_g$ ). A rapid drop of the elasticity module value is observed near the vitrification temperature ( $T_g$ ) of the cured resin changing from the elastic state into the highly flexible state.

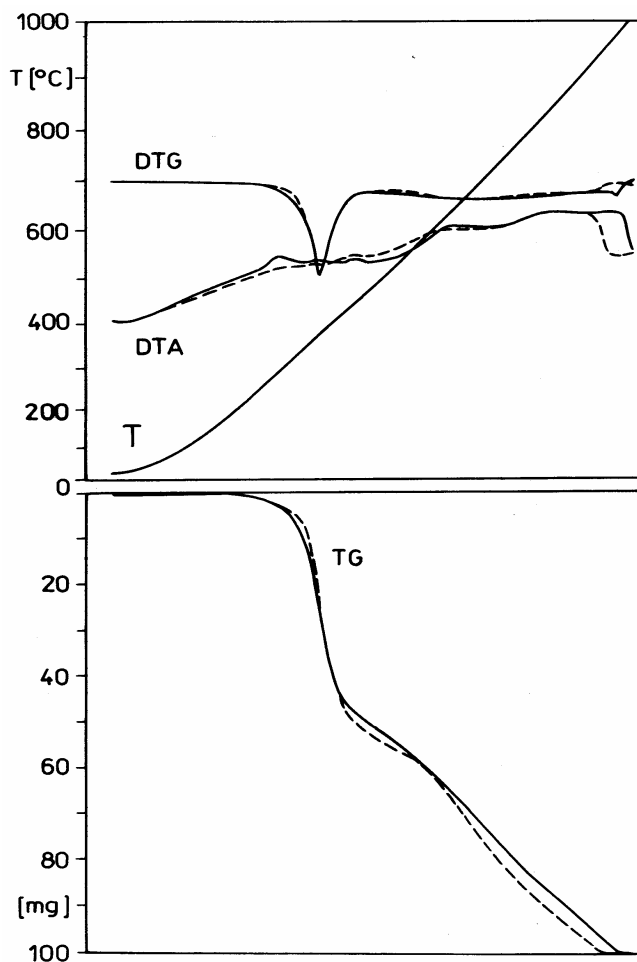


Fig. 9. TGA and DTA of the uncured (solid line) and the cured (dashed line) BIS-GATF resin (heating time in air, 100 min; heating rate  $10^{\circ}\text{C}/\text{min}$ ; amount of resins, 100 mg; measurements related to  $\text{Al}_2\text{O}_3$ )

Dynamic studies of decomposition of the uncured or UV cured BIS-GATF resin were carried out using the derivatograph MOM (Paulik, Paulik, and Erdey, Budapest, Hungary); temperature increase 10°C/min in air; (Fig.9). The decomposition temperature is in the range 230-250°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 thioether sulfur from the weakest link in the chain structure).

The cured BIS- GATF resin was subjected to the mechanical investigations according to the Polish Standard PN-81/C-89034 using the UTS-50 apparatus. The obtained numerical values are presented in Table 2.

Tab. 2 Properties of BIS-GATF

BIS-GATF 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	2.5	370	470	-	-	-	-
UV-cured	290	2.0	370	440	91.6	11.07	6.55	273.8

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

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

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

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

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## CURRICULUM VITAE



**Władysław Charmas** was born on 4 September 1937 in Majdan Surhowski, Krasnystaw District. After finishing the secondary school he studied chemistry at the Mathematics-Physics-Chemistry Faculty graduating in 1963. In the same year he was employed as the assistant in the Department of Organic Chemistry. He obtained the Doctor title in 1970. His doctoral thesis was supervised by Prof. Marian Janczewski. After presenting the habilitation thesis at the Faculty of Chemistry, University in Poznań he obtained the Dr hab. title in 1991. In 2001 he was nominated for the post of associate professor of University. Since 2002 he has been the head of Chemistry and Organic

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Research areas: synthesis and studies of chiral compounds, polymers with sulfur in the main chain; polymers, chiral packing for HPLC; polymers with "reactive" groups based on methacrylate monomers.

The results of his research are published in 88 papers and communiqués as well as 26 patents.