

# Linear Polythioesters. XII. Products of Polycondensation Some Isomeric Di(mercaptomethyl)trimethylbenzenes with Isophthaloyl and Terephthaloyl Chlorides

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## Synopsis

New polythioesters by interfacial polycondensation of 4,6-di(mercaptomethyl)-1,2,3-trimethylbenzene, 3,5-di(mercaptomethyl)-1,2,4-trimethylbenzene, and 2,4-di(mercaptomethyl)-1,3,5-trimethylbenzene with isophthaloyl and terephthaloyl chlorides were obtained. Polycondensation was carried out under the same conditions as established earlier as optimum for synthesis of polythioesters from 2,5-di(mercaptomethyl)-1,4-dimethylbenzene and isophthaloyl chloride. The conditions of polycondensation were as follows: the organic phase benzene/hexane, ratio of aqueous to organic phase 1:1, presence of 100% excess of NaOH as hydrogen chloride acceptor, temperature of reaction 15°C, little excess of acid dichloride with addition time of 8 min, catalyst benzyltriethylammonium chloride. Yield, reduced viscosity and molecular weight for reaction products have been found. The structure of all polythioesters was determined from elemental analysis, infrared (IR) spectra and x-ray analysis. Thermal properties were defined from the curves of thermogravimetric analysis. Some mechanical and electrical properties of the polythioesters obtained from di(mercaptomethyl)-trimethylbenzenes and isophthaloyl chloride were determined.

## INTRODUCTION

In the last several years systematic studies of the synthesis, structure, and properties of polythioesters prepared from various dimercapto compounds and acid dichlorides were undertaken.

Studies connected with the optimization synthesis and properties of polythioesters three di(mercaptomethyl) derivatives of isomeric xylenes with isophthaloyl and terephthaloyl chlorides were discussed in our article.<sup>1</sup> The synthesis of polythioesters from 4,5-di(mercaptomethyl)-1,2-dimethylbenzene, 4,6-di(mercaptomethyl)-1,3-dimethylbenzene, and 2,5-di(mercaptomethyl)-1,4-dimethylbenzene and isophthaloyl as well as terephthaloyl chlorides were carried out by means of low temperature, and high temperature in solution and by interfacial polycondensation. We stated that the best value of reduced viscosity and the highest yield were obtained using interfacial polycondensation. Moreover, we found that many factors greatly influence the properties of polythioesters. Among these are: kind of organic phase, contribution of catalyst, concentration of acceptor of hydrogen chloride, time and temperature of the reaction.

The purpose of this article was to describe new polythioesters obtained from di(mercaptomethyl) derivatives of isomeric trimethylbenzenes and iso-

phthaloyl as well as terephthaloyl chlorides. Di(mercaptomethyl) trimethylbenzenes are formed from suitable di(chloromethyl)compounds by thiouronic salts.<sup>2-4</sup>

In suitable conditions chloromethylation reaction of isomeric trimethylbenzenes obtains the following products with the greatest yield: 4,6-di(chloromethyl)-1,2,3-trimethylbenzene, from hemimellitene,<sup>5</sup> 3,5-di(chloromethyl)-1,2,4-trimethylbenzene from pseudocumene,<sup>6</sup> and 2,4-di(chloromethyl)-1,3,5-trimethylbenzene from mezytylene.<sup>7</sup> The above mentioned di(chloromethyl) compounds were used for synthesis of corresponding di(mercaptomethyl)-trimethylbenzenes.

Preparation of polythioesters from 4,6-di(mercaptomethyl)-1,2,3-trimethylbenzene [4,6-DMM-1,2,3-TMB], 3,5-di(mercaptomethyl)-1,2,4-trimethylbenzene [3,5-DMM-1,2,4-TMB], or 2,4-di(mercaptomethyl)-1,3,5-trimethylbenzene [2,4-DMM-1,3,5-TMB] and isophthaloyl as well as terephthaloyl chlorides were carried out under the same optimum conditions, established earlier for the interfacial polycondensation 2,5-di(mercaptomethyl)-1,4-dimethylbenzene with isophthaloyl chloride.<sup>1</sup> Structure of polythioesters was determined from infrared, x-ray, and elementary analysis.

Chemical and thermal resistance, mechanical and electrical properties were determined. The molecular weight of polythioesters were determined by gel chromatography only for polymers soluble in tetrachloroethane.

## EXPERIMENTAL

### Reagents

4,6-di(mercaptomethyl)-1,2,3-trimethylbenzene [4,6-DMM-1,2,3-TMB], mp 60°C (after crystallization from methanol), 3,5-di(mercaptomethyl)-1,2,4-trimethylbenzene [3,5-DMM-1,2,4-TMB], bp 158°C/1.5 mmHg and 2,4-di(mercaptomethyl)-1,3,5-trimethylbenzene [2,4-DMM-1,3,5-TMB], mp 68°C (after crystallization from ethanol) were obtained from the suitable di(chloromethyl)compounds through the thiouronic salts.<sup>2-4</sup> Isophthaloyl chloride, mp 44°C, and terephthaloyl chloride, mp 83°C were obtained by the reaction of phosphorus pentachloride with isophthalic or terephthalic acids. Elemental analyses (C,H,S,Cl) were completed for all the above monomers.

### THE SYNTHESIS OF POLYTHIOESTERS

In a three-necked, round-bottomed flask of 500 cm<sup>3</sup>, equipped with a mechanical stirrer (2000 rpm), thermometer, and dropper, 2.12 g (0.01 mol) of dithiol, 50 cm<sup>3</sup> benzene and sodium hydroxide solution (1.6 g NaOH in 100 cm<sup>3</sup> of water) were placed. Then 0.063 g of catalyst benzyltriethylammonium chloride was mixed in. After thorough mixing the solution of 2.233 g (0.011 mol) isophthaloyl or terephthaloyl chloride in 50 cm<sup>3</sup> hexane was added for a period of 8 min at 15°C under vigorous stirring. After the addition of the acid chloride was completed the stirring was continued for 30 min and the mixture was then acidified with hydrochloric acid (Congo red). The isolated product of polycondensation was filtered and boiled in 100 cm<sup>3</sup> water for 10 min. After cooling and filtration, the polythioester was washed with hot water (2 × 100 cm<sup>3</sup>) and acetone (30 cm<sup>3</sup>) and dried under reduced pressure (15 mmHg) at 60°C to a constant weight.

## MEASUREMENT OF PROPERTIES

**Melting Point.** Melting point determinations were made on a Boetius apparatus.

**Viscosity.** The reduced viscosity (dL/g) of a 1% solution of polythioesters in tetrachloroethane was measured in a Ubbelohde viscometer at 25°C.

**Thermogravimetric Analysis.** Measurement of weight loss was taken in a MOM derivatograph (Paulik, Paulik and Erdey, Budapest) at a heating rate of 10°C/min in air.

**X-ray Analysis.** X-ray photographs were obtained by the Debye-Scherer's powder method with a camera 64 mm in diameter and an x-ray tube Cu without filters. Exposure time was 8 h, tube voltage was 32 kV, and anodic intensity was 12 mA. The apparatus was a URS-60 type.

**Molecular Weight.** The average molecular weights ( $M_w$ ) of polythioesters were calculated on the basis of gel permeation chromatographic data.<sup>8,9</sup> The chromatographic measurements were carried out applying Varian Aerograph liquid chromatograph type 4100 with RI detector and orlite pump AF 10-4. As mobile phase tetrachloroethane was used. The investigated polythioesters as filtrated solution (0.5–1.0 g of polymer in 100 cm<sup>3</sup> of tetrachloroethane) has been injected on the column system consisted of two chromatographic columns. The columns (300 mm long × 7.8 mm i.d.) were filled with Lichrospher Si-100 and Si-500 (Merck, Darmstadt, FRG). The measurements were carried out at 18°C.

**Glass Transition Temperature.** Measurement of glassy temperature was taken in a DSC-IB Perkin-Elmer differential microcalorimeter, at a heating rate of 32°C/min, nitrogen flow rate of 30 cm<sup>3</sup>/min, sensibility of apparatus 4 mcal/sec, weight of sample 16 mg.

**Infrared Analysis.** Infrared (IR) spectra were obtained with UNICAM SP-200 spectrophotometer.

**Solubility.** In a flask of 200 cm<sup>3</sup> volume, attempts were made to dissolve 1 g of polythioesters in several different solvents at room temperature.

## RESULTS AND DISCUSSION

New polythioesters from 4,6-di(mercaptomethyl)-1,2,3-trimethylbenzene [4,6-DMM-1,2,3-TMB], 3,5-di(mercaptomethyl)-1,2,4-trimethylbenzene [3,5-DMM-1,2,4-TMB], and 2,4-di(mercaptomethyl)-1,3,5-trimethylbenzene [2,4-DMM-1,3,5-TMB] and isophthaloyl as well as terephthaloyl chlorides were carried out by means of interfacial polycondensation under the optimal conditions used for the polycondensation of 2,5-di(mercaptomethyl)-1,4-

TABLE I  
Properties of Polythioesters from Dithiols and Acid Dichlorides

Polythioester		$\eta$ red (dL/g)	Yield (%)	Glassy temperature (°C)	Softening range (°C)	Molecular weight ( $M_w \times 10^3$ )
Dithiol	Acid chloride					
4,6-DMM-1,2,3-TMB		—	86.1	150.0	195–235	—
3,5-DMM-1,2,4-TMB	isophthaloyl	0.52	85.9	124.5	180–205	58
2,4-DMM-1,3,5-TMB		0.54	88.6	125.5	195–225	—
4,6-DMM-1,2,3-TMB		—	91.5	99.5	240–260	—
3,5-DMM-1,2,4-TMB	terephthaloyl	0.48	84.8	94.0	200–215	57
2,4-DMM-1,3,5-TMB		0.79	84.3	94.5	220–240	68

TABLE II  
 Results of Elementary Analysis of Polythioesters

Polythioester		% C		% H		% S	
Dithiol	Acid chloride	Calcd	Found	Calcd	Found	Calcd	Found
4,6-DMM-1,2,3-TMB	isophthaloyl		66.70		5.20		18.46
3,5-DMM-1,2,4-TMB		66.63	66.48	5.30	5.21	18.72	18.55
2,4-DMM-1,3,5-TMB		66.50	66.50		5.23		18.60
4,6-DMM-1,2,3-TMB	terephthaloyl		66.52		5.23		18.52
3,5-DMM-1,2,4-TMB		66.63	66.50	5.30	5.30	18.72	18.50
2,4-DMM-1,3,5-TMB			66.45		5.20		18.58

dimethylbenzene and isophthaloyl chloride.<sup>1</sup> Table I shows values of reduced viscosity, yields, glassy temperature, softening point, and molecular weight. The molecular weight and reduced viscosity were determined only for polythioesters soluble in tetrachloroethane.

### STRUCTURE OF POLYTHIOESTERS

The structure of all polythioesters was determined by elementary analysis, infrared spectra, and x-ray analysis. The results of elementary analysis are given in Table II.

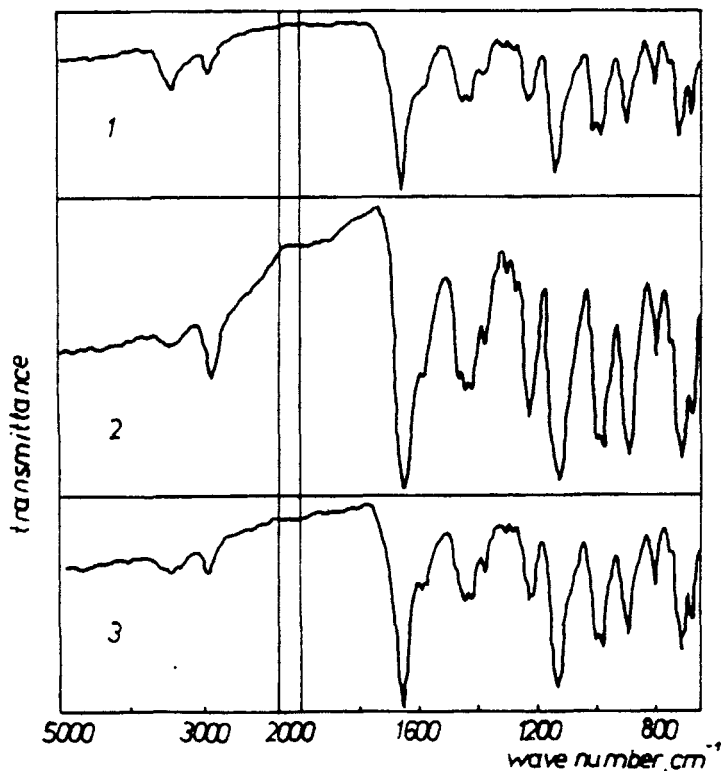


Fig. 1. Infrared spectra of polythioester derivatives of isophthaloyl chloride and isomeric di(mercaptomethyl)trimethylbenzenes: 4,6-DMM-1,2,3-TMB (1), 3,5-DMM-1,2,4-TMB (2), and 2,4-DMM-1,3,5-TMB (3).

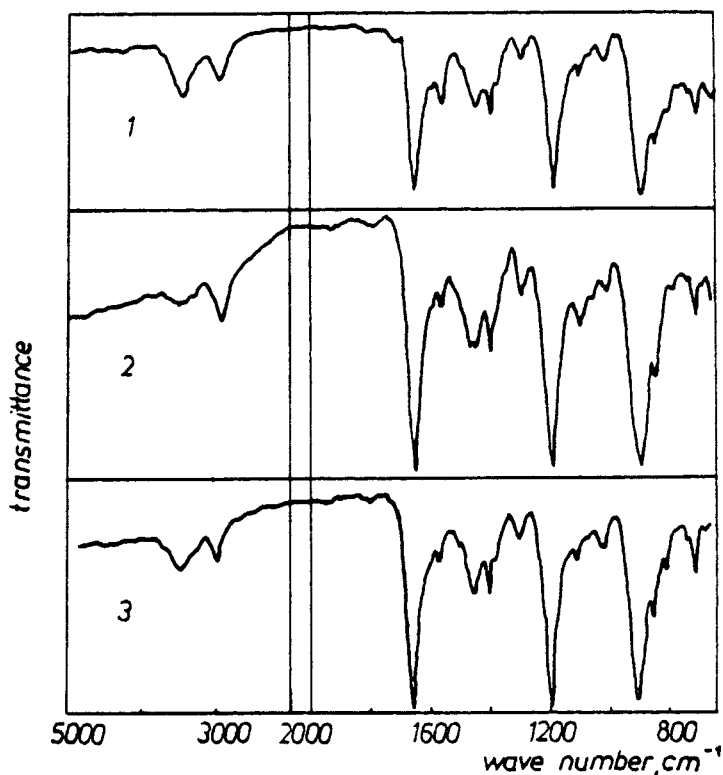
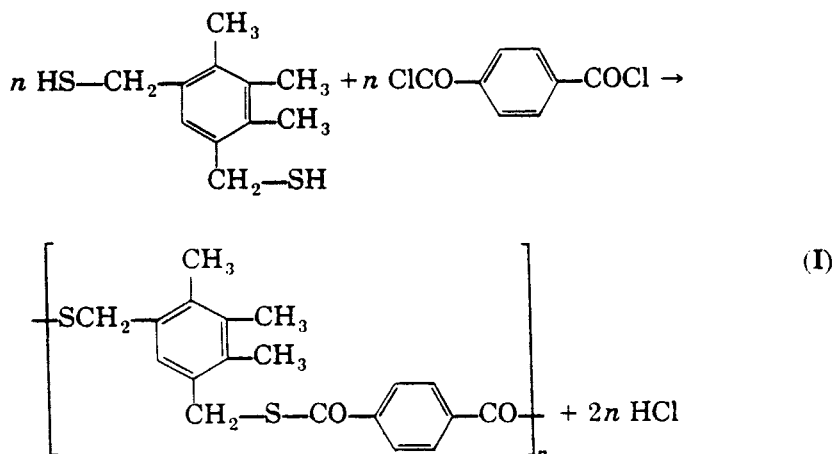


Fig. 2. Infrared spectra of polythioester derivatives of terephthaloyl chloride and isomeric di(mercaptomethyl)trimethylbenzenes: 4,6-DMM-1,2,3-TMB (1), 3,5-DMM-1,2,4-TMB (2), and 2,4-DMM-1,3,5-TMB (3).

IR spectra of polythioesters showed strong absorption at  $1660\text{--}1680\text{ cm}^{-1}$  which is characteristic of carbonyl valency bond; at  $1420\text{--}1445\text{ cm}^{-1}$  characteristic of the  $-\text{CH}_2\text{-S-}$  group; bands at  $900\text{--}1000\text{ cm}^{-1}$  are attributed to the  $-\text{COS}$  stretch vibration.



On the basis of good agreement of the calculated and found analytical data (Table II) and IR spectra (Figs. 1 and 2), the reaction scheme (I) for

4,6-di(mercaptomethyl)-1,2,3-trimethylbenzene and terephthaloyl chloride as an example was assumed:

### X-RAY ANALYSIS

Polythioesters obtained from isomeric di(mercaptomethyl)-trimethylbenzenes and isophthaloyl as well as terephthaloyl chlorides were examined by

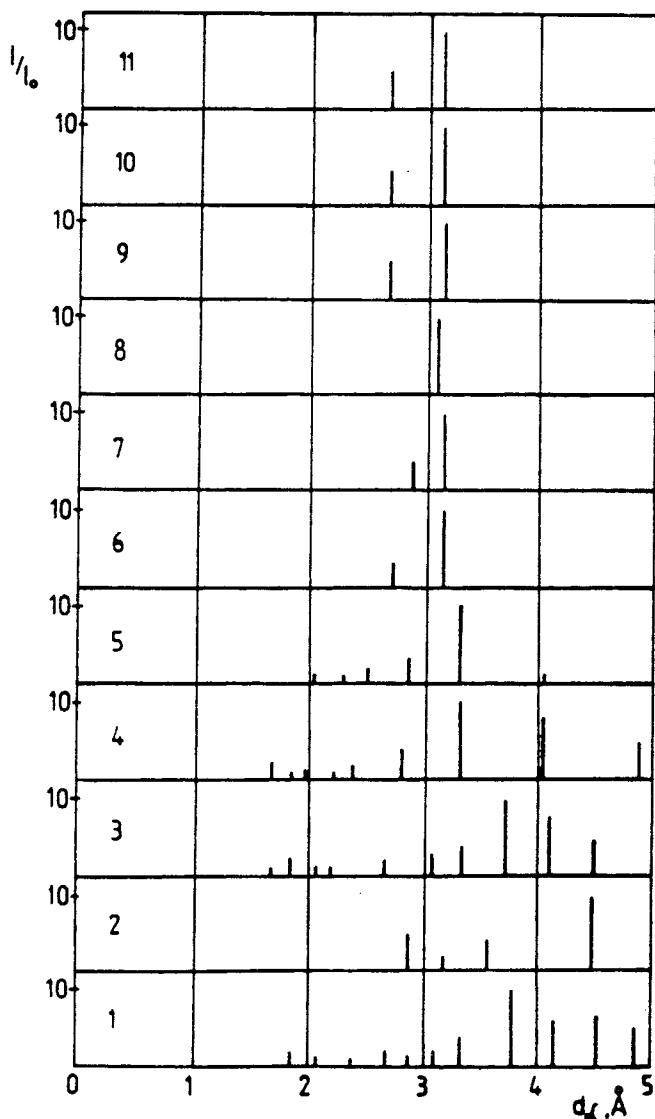


Fig. 3. X-ray diffraction patterns of 4,6-DMM-1,2,3-TMB (1), 3,5-DMM-1,2,4-TMB (2), 2,4-DMM-1,3,5-TMB (3), isophthaloyl chloride (4), terephthaloyl chloride (5), polythioester from 4,6-DMM-1,2,3-TMB and isophthaloyl chloride (6), polythioester from 4,6-DMM-1,2,3-TMB and terephthaloyl chloride (7), polythioester from 3,5-DMM-1,2,4-TMB and isophthaloyl chloride (8), polythioester from 3,5-DMM-1,2,4-TMB and terephthaloyl chloride (9), polythioester from 2,4-DMM-1,3,5-TMB and isophthaloyl chloride (10), polythioester from 2,4-DMM-1,3,5-TMB and terephthaloyl chloride (11).

TABLE III  
 Thermal Properties of Polythioesters

Polythioester		Thermal analysis <sup>a</sup>				Mass loss, %				
Dithiol	Acid chloride	$T_1$ (°C)	$K_1$ (%)	$T_2$ (°C)	$K_2$ (%)	300	400	500	600	700
4,6-DMM-1,2,3-TMB		310	0.5	360	20	—	35	44	62	77
3,5-DMM-1,2,4-TMB	isophthaloyl	320	1.5	365	22	1	42	52	70	84
2,4-DMM-1,3,5-TMB		325	3	365	25	3	41	52	71	86
4,6-DMM-1,2,3-TMB		300	1.5	365	20	1	34	44	64	80
3,5-DMM-1,2,4-TMB	terephthaloyl	300	1	365	22	1	40	51	73	88
2,4-DMM-1,3,5-TMB		320	1	360	20	1	40	51	75	92

<sup>a</sup> $T_1$  = temperature of initial exothermic effect from the curve DTA;  $K_1$  = mass loss in the temperature  $T_1$ ;  $T_2$  = temperature of initial intensive decomposition from the curve DTA;  $K_2$  = mass loss in temperature  $T_2$ .

means of x-ray diffraction analysis. In Figure 3 presents the diffraction diagrams showing the interplanar spacings  $d_n$  and relative intensity  $I/I_0$  of reflections for polythioesters and as well as for monomers. The diffraction patterns of all monomers show many x-ray diffraction lines, which indicates the high crystalline degree of these compounds. X-ray diffraction patterns

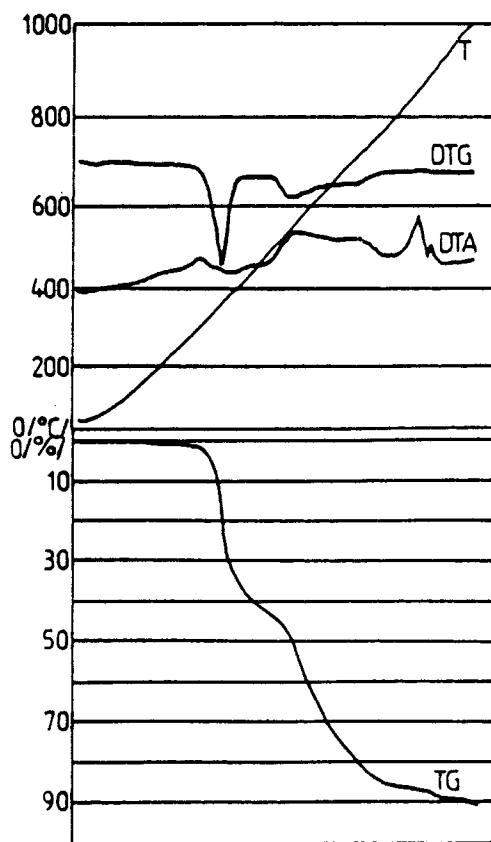


Fig. 4. TGA and DTA of polycondensation product of 4,6-DMM-1,2,3-TMB with terephthaloyl chloride; heating time in air 250 min, heating rate 4°C/min, amount of polythioester 100 mg, measurement relative to  $Al_2O_3$ .

TABLE IV  
Temperature of Pressing and Mechanical Properties of Polythioesters from Isomeric  
Di/mercaptomethyl/trimethylbenzenes and Isophthaloyl Chloride

Test	Dithiol		
	4,6-DMM-1,2,3-TMB	3,5-DMM-1,2,4-TMB	2,4-DMM-1,3,5-TMB
Temperature of pressing, °C	200	205	220
Vicat softening point, °C	152	146.5	167
Tensile strength, kG/cm <sup>2</sup>	159.02	26.04	104.43
Impact strength, kG/cm <sup>2</sup>	2.27	1.43	1.67
Bending strength, kG/cm <sup>2</sup>	407.93	97.64	230.22
Brinnell hardness, kG/cm <sup>2</sup>	12.90	—	7.13
Modulus of elasticity, kG/cm <sup>2</sup>	2721.01	—	2485.94

also show many diffraction lines, but they are other values of  $d_{\alpha}$ . The presence of these lines indicate the high crystalline degree of polymers.

### THERMAL PROPERTIES

The polythioesters obtained were examined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The temperature of initial decomposition, its mass loss in percent, and the temperature of the fastest decomposition process, mass loss percentage at 300–700°C were defined from the curves. The numerical data are presented in Table III. The results of examination are shown only for polythioester from 4,6-di(mercaptomethyl)-1,2,3-trimethylbenzene and terephthaloyl chloride as an example (Fig. 4).

### MECHANICAL AND ELECTRICAL PROPERTIES

Some mechanical and electrical properties of the polythioesters obtained from 4,6-DMM-1,2,3-TMB, 3,5-DMM-1,2,4-TMB, and 2,4-DMM-1,3,5-TMB and isophthaloyl chloride have been studied after pressing first, at room temperature under a pressure of 600 kg/cm<sup>2</sup> and then at increased temperature at a pressure of 150 kg/cm<sup>2</sup> in the upper range of the softening

TABLE V  
Some Electrical Properties of Polythioesters from Isomeric  
Di/mercaptomethyl/trimethylbenzenes and Isophthaloyl Chloride

Test	Dithiol		
	4,6-DMM-1,2,3-TMB	3,5-DMM-1,2,4-TMB	2,4-DMM-1,3,5-TMB
Dielectric constant ( $\epsilon$ )			
at frequency (kHz) – 0.05	4.00	2.40	4.19
1	3.95	2.42	4.17
10	3.89	2.43	4.15
100	3.83	2.42	4.14
Dielectrical loss factors ( $tg\theta \times 10^{-4}$ )			
at frequency (kHz) – 0.05	55	37	61
1	66	40	30
10	106	41	36
100	320	42	65



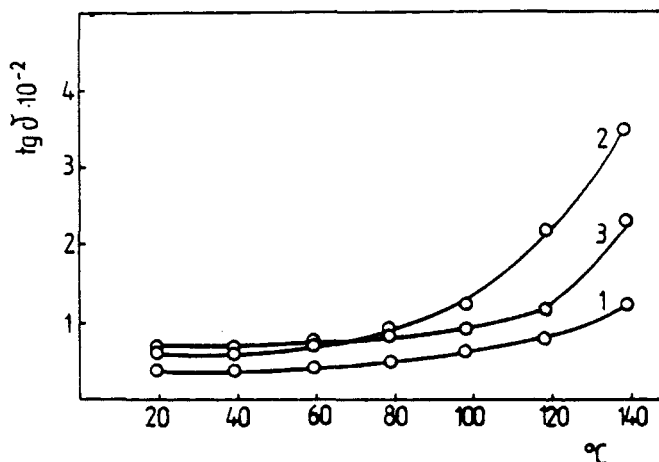


Fig. 5. The dependence of dielectric loss factor ( $tg\theta$ ) on temperature at frequency 0.05 kHz of polythioesters derivatives of isophthaloyl chloride and isomeric di(mercaptomethyl)trimethylbenzenes: 4,6-DMM-1,2,3-TMB (1), 3,5-DMM-1,2,4-TMB (2), and 2,4-DMM-1,3,5-TMB (3).

temperature of every polymer. Samples for electrical tests were additionally metallized by silver in vacuum. Pressing temperature and numerical data are given in Table IV. Electric properties of polythioesters were characterized by dielectric constant ( $\epsilon$ ), dielectric loss factor ( $tg\theta$ ), and volume resistivity ( $\rho$ ) as a function of temperature. Samples were examined at a frequency of 0.05 kHz at 20, 40, 60, 80, 100, 120 and 140°C. Values of  $\epsilon$  and  $tg\theta$  at 20°C and at frequencies of 0.05, 1, 10, and 100 kHz were obtained. Results are given in Table V and in Figures 5-7.

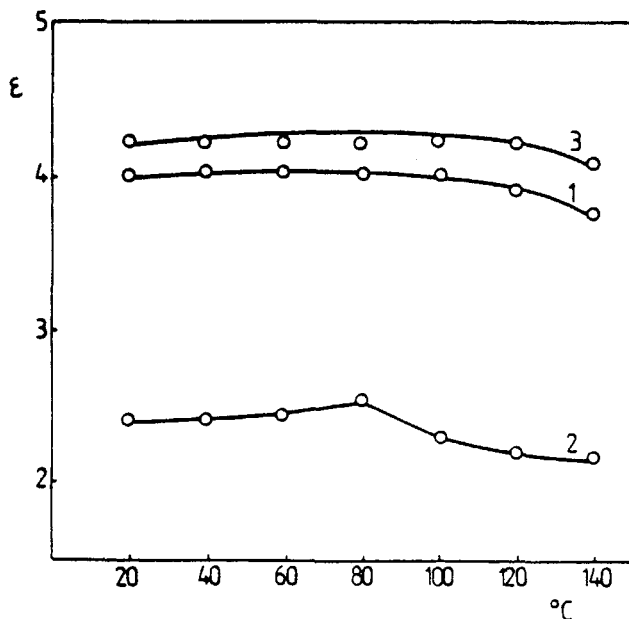


Fig. 6. The dependence of dielectric constant ( $\epsilon$ ) on temperature at frequency 0.05 kHz of polythioesters derivatives of isophthaloyl chloride and isomeric di(mercaptomethyl)trimethylbenzenes: 4,6-DMM-1,2,3-TMB (1), 3,5-DMM-1,2,4-TMB (2), and 2,4-DMM-1,3,5-TMB (3).

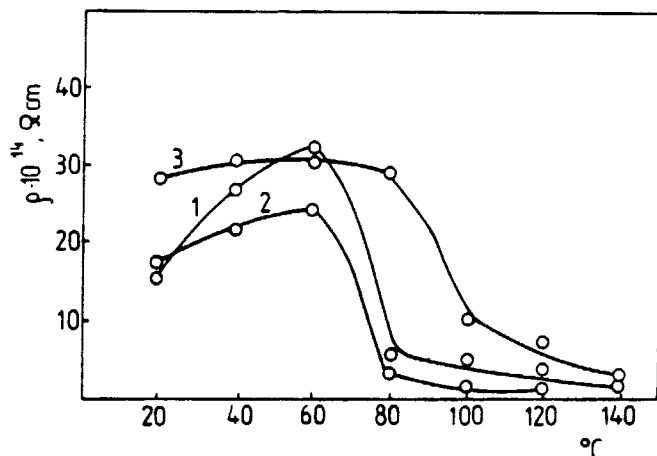


Fig. 7. The dependence of volume resistivity ( $\rho$ ) on temperature at frequency 0.05 kHz of polythioesters derivatives of isophthaloyl chloride and isomeric di(mercaptomethyl)trimethylbenzenes: 4,6-DMM-1,2,3-TMB (1), 3,5-DMM-1,2,4-TMB (2), and 2,4-DMM-1,3,5-TMB.

### SOLUBILITY

The polythioesters were treated with some organic solvents: acetone, benzene, chloroform, methylene chloride, dimethylformamide, nitrobenzene, tetrachloroethane and a mixture of phenol and tetrachloroethane (1 : 1), 10% and concentrated hydrochloric, sulfuric and nitric acids, 10 and 50% sodium hydroxide. They show good resistance to organic solvents, mineral acids and sodium hydroxide. Some of them are soluble in tetrachloroethane and in mixture of phenol/tetrachloroethane (1 : 1), but all react with concentrated nitric and sulfuric acids.

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Received July 1, 1986

Accepted September 5, 1986