

# Linear Polythioesters. X. Products of Interfacial Polycondensation of Bis(4-Mercaptophenyl)ether with Isomeric Phthaloyl Chlorides

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## Synopsis

New polythioesters were obtained by interfacial polycondensation of bis(4-mercaptophenyl)ether with phthaloyl, isophthaloyl, and terephthaloyl chlorides. To determine the optimal conditions for interfacial polycondensation, the influence of the following factors on yield and value of reduced viscosity were studied: organic phase, 100% excess of sodium hydroxide, contribution of benzyltriethylammonium chloride as a catalyst, and the temperature of the reaction. A thorough examination of the process was carried out only for polycondensation of dithiol with phthaloyl chloride. Yield of all reaction products as well as reduced viscosity of only polythioesters from dithiol and phthaloyl chloride were found because these were the ones which were soluble in tetrachloroethane. The structure of all polythioesters was determined by elemental analysis and infrared spectra. Initial decomposition and initial intensive decomposition temperature were defined by the curves of thermogravimetric analysis. Some mechanical and electrical properties of polythioesters were determined.

## INTRODUCTION

For several years studies have been carried out on the synthesis, structure, and properties of polythioesters obtained in our laboratory by means of polycondensation of aliphatic-aromatic dithiols with aliphatic and aromatic acid chlorides.<sup>1-3</sup>

In one of the previous articles<sup>4</sup> we presented the results of our investigations concerning the determination of optimal conditions in synthesis of polythioesters by interfacial polycondensation of bis(4-mercaptophenyl) ether with aliphatic acid dichlorides. We found that many factors greatly influence the properties of polythioesters. Among those there are: kind of organic phase, contribution of catalyst, concentration of acceptor of hydrogen chloride, and temperature of the reaction.

To obtain more information about properties of polythioesters which depend on conditions of their synthesis and kind of reagents used, it seemed to be interesting to use isomeric phthaloyl chlorides for their synthesis from bis(4-mercaptophenyl)ether.

## EXPERIMENTAL

### Reagents

Bis(4-mercaptophenyl)ether, mp 98–100°C (after crystalization from hexane), was obtained from 4,4'-diphenyletherdisulphonyl chloride by reduction according to Marvel and Caesar.<sup>5</sup>

Terephthaloyl chloride, mp 83°C, and isophthaloyl chloride, mp 44°C (after crystallization from hexane), were obtained by the reaction of phosphorus pentachloride with terephthalic or isophthalic acids. Phthaloyl chloride, bp 131–133°C (9–10 mm Hg) was obtained through the reaction of phthalic anhydride with phosphorus pentachloride.<sup>6</sup>

### Synthesis of Polythioesters

The synthesis of all polythioesters were carried out in the way described below.

In a three-necked round-bottomed flask of 500 cm<sup>3</sup> volume, equipped with a mechanical stirrer, thermometer, and dropper, 2.34 g (0.01 mol) of dithiol, 50 mL of benzene–hexane (1:1), and a suitable quantity of sodium hydroxide, that is, a stoichiometric quantity 0.8g (0.02 mol) or a 100% excess (0.04 mol) and 0.01 g of the emulsifier (Mersolan) and catalyst dissolved in 100 mL of water were added.

The solution was stirred vigorously and 2.23 g (0.011 mol) of acid chloride in 50 mL of benzene–hexane 1:1 was being added for 10 min.

After the addition of acid chloride was completed, stirring was continued for 30 min. The mixture was then acidified with hydrochloric acid (Kongo red), and the separated product of polycondensation was filtered or isolated by decantation and boiled in water (100 mL) for 15 min. The polythioester was washed with hot water, acetone, or methanol and dried under reduced pressure (15 mm Hg) at 60°C to a constant weight.

### Measurement of Properties

#### Melting Point

Melting point determinations were carried out on a Bötius apparatus.

#### Viscosity

Reduced viscosity [ $\eta_{\text{red}}$  (dl/g)] of tetrachloroethane of 1% polythioester solution was measured in a Ubbelohde viscometer at 25°C.

#### Thermogravimetric Analysis

Measurement of weight loss was conducted in a MOM derivatograph (Paulik, Paulik and Erdey, Budapest) at a heating rate of 4°C/min in air.

#### Infrared Analysis

Infrared (IR) spectra were obtained with a Unicam SP-200 spectrophotometer.

#### X-Ray Investigations

X-Ray photographs were obtained by the Debye–Scherrer powder method with a Camera 64 mm in diameter and an X-ray tube Cu without filters. Exposure time was 2 h, tube voltage was 32 kW, and anodic intensity was 15 mA. The apparatus was a URS-60 type.

### Optimal Conditions in Interfacial Polycondensation

To determine the optimal conditions of interfacial polycondensation, polythioesters from bis(4-mercaptophenyl)ether, and isomeric phthaloyl dichlorides, phthaloyl chloride was chosen as a model system. The choice was determined by the fact that its polythioesters are easily dissolved in tetrachloroethane, which permits the measurement of the reduced viscosity value.

To establish optimal conditions, yield of the process and reduced viscosity were taken into consideration. The influence of the following parameters on interfacial polycondensation was studied: kind of organic phase, concentration of sodium hydroxide (stoichiometric quantity and 100% excess), contribution of benzyltriethylammonium chloride as a catalyst, as well as temperature of the reaction.

Having determined the initial reaction conditions, that is, the aqueous to organic phase ratio 1:1, molar ratio of the reagents dithiol/acid dichloride 1:1.1, reaction temperature 25°C, and the rate of chloride addition 10 min, the influence of the kind of organic solvent on yield and reduced viscosity was examined. The applied solvents and physicochemical values obtained are listed in Table I. From the data presented it follows that the solvent considerably influence the yield and reduced viscosity of the polycondensation polymers. The best yield and the highest value of reduced viscosity were obtained with benzene-hexane (1:1) as organic phase.

The contribution of catalyst (5% weight in relation to dithiol) to interfacial polycondensation was studied with stoichiometrically necessary quantity of sodium hydroxide and with its 100% excess.

As follows from Table II, the use of catalyst increase the value of reduced viscosity and yield of polythioesters obtained both with and without 100% excess of sodium hydroxide.

From the data presented in Table II it is evident that some lowering of temperature of the reaction to 15°C doesn't exert a great effect on the process of polycondensation. Yield and value of reduced viscosity both increase to a small extent.

## RESULTS AND DISCUSSION

To establish the optimal conditions of interfacial polycondensation, we had to select phthaloyl chloride because its polythioesters were easily dis-

TABLE I  
The Organic Phase Effect on the Yield and Reduced Viscosity of Polythioester from Bis(4-Mercaptophenyl)ether and Phthaloyl Chloride<sup>a</sup>

Organic phase	Yield (%)	$\eta_{red}$ (dL/g)	Softening range (°C)
Chloroform	30	0.19	186-189
Benzene	64	0.38	187-220
Benzene/hexane /1:1/	67	0.49	196-230
Tetrachloromethane	50	0.47	187-220

<sup>a</sup> Conditions of the reaction: ratio of aqueous to organic phase 1:1; reagent ratio 1:1.1; rate of chloride addition 10 min; temperature of the reaction 25°C.

TABLE II  
Influence of Catalyst, 100% Excess of NaOH and Temperature on the Reduced Viscosity and Yield of Polythioesters from Bis(4-Mercaptophenyl)ether and Phthaloyl Chloride<sup>a</sup>

Catalyst	100% excess of NaOH	Temperature (°C)		Yield (%)	$\eta_{red}$ (dL/g)	Softening range (°C)
		25	15			
		+		67	0.49	196-230
+		+		75	0.60	220-241
+			+	77	0.82	228-248
+	+	+		79	1.34	230-250
+	+		+	81	1.39	239-252

<sup>a</sup> Conditions of the reaction: ratio of aqueous to organic phase 1:1; reagent ratio 1:1.1; rate of chloride addition 10 min.

solved whereas polythioesters from isophthaloyl and terephthaloyl chloride were only partly soluble in organic solvents.

The best results for polythioesters from phthaloyl chloride were obtained by using benzene-hexane (1:1) as an organic phase, 100% excess of hydrogen chloride acceptor, benzyltriethylammonium chloride as a catalyst (5% weight in relation to amount of dithiol), and the reaction temperature at about 15°C. Investigating the influence of these parameters on interfacial polycondensation, we assumed that the excess of acid chloride was 10% and the ratio of its addition about 10 min.

Polythioester synthesis from dithiol and the remaining two chlorides, isophthaloyl and terephthaloyl, was carried out according to the conditions for phthaloyl chloride defined experimentally.

However, because there were some difficulties in polythioester synthesis and isolation of the product of the reaction, 0.01 g Mersolan was used as an emulsifier in relation to 0.01 mol of dithiol.

Polythioesters obtained from dithiol and phthaloyl chloride were yellowish glass masses easily soluble in chlorinated aliphatic and aromatic hydrocarbons. Compared to these, however, polythioesters from dithiol and isophthaloyl and terephthaloyl chlorides were yellowish solids hardly soluble in organic solvents and in the mixture of phenol/tetrachloroethane, independently of whether stoichiometric quantity of sodium hydroxide or its 100% excess were used.

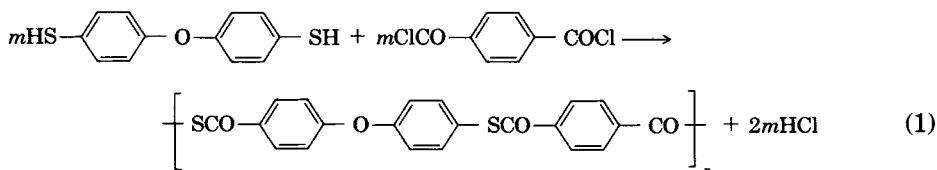
These polythioesters reveal chemical resistance to diluted acids and alkali.

TABLE III  
Results of Elementary Analysis of Polythioesters

Acid chlorides	% C		% H		% S	
	Calcd	Found	Calcd	Found	Calcd	Found
Phthaloyl		65.61		3.02		17.89
Isophthaloyl	65.91	64.90	3.32	2.89	17.56	17.60
Terephthaloyl		64.61		3.18		16.57

Infrared (IR) spectra for polythioesters from dithiol and isomeric phthaloyl chlorides showed strong adsorption at  $1670\text{--}1690\text{ cm}^{-1}$ , which is characteristic for a carbonyl valency band, at  $1230\text{--}1240\text{ cm}^{-1}$  which is characteristic for an ether band and at  $910\text{--}990\text{ cm}^{-1}$  attributed to the  $\text{—COS—}$  stretch.

On the basis of good agreement among calculated and found analytical data (Table III) and IR spectra, the following reaction scheme for dithiol and terephthaloyl chloride was assumed:



### X-Ray Investigations

On the basis of powder diffraction patterns the interplanar distances  $d\alpha$  and the relative intensities ( $I/I_0$ ) have been obtained. Numerical data presented in Figure 1 indicate some degree of order in the structure of solid state of the polythioesters that are under investigation. It may be supposed that polythioester from isophthaloyl chloride reveals a better ordered structure.

### Thermal Properties

Polythioesters were also examined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The results of the examination of these polythioesters are shown in Figure 2.

It can be seen from thermal curves that decomposition of these polymers begins at  $240\text{--}350^\circ\text{C}$  and is fastest at  $320\text{--}400^\circ\text{C}$ .

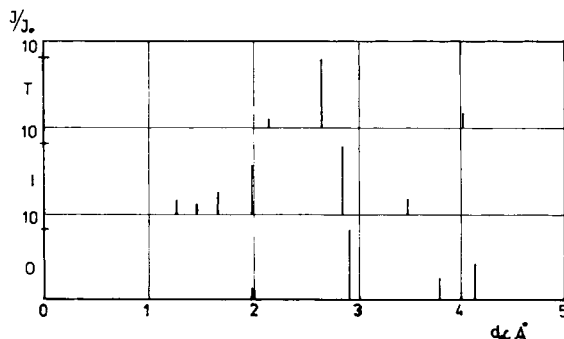


Fig. 1. X-Ray diffraction patterns of polythioester from dithiol and phthaloyl chloride (O); polythioester from dithiol and isophthaloyl chloride (I); polythioester from dithiol and terephthaloyl chloride (T).

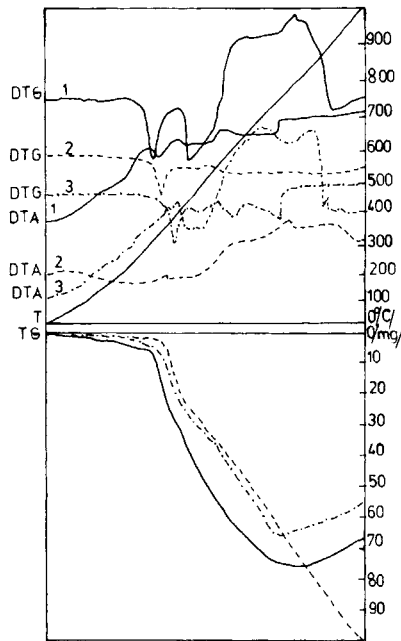


Fig. 2. TGA and DTA of polycondensation product of bis(4-mercaptophenyl)ether with phthaloyl chloride (—), isophthaloyl chloride (---), and terephthaloyl chloride (-·-). Heating time in air, 250 min; heating rate, 4°C/min; amount of polythioester 100 mg; measured relative to  $\text{Al}_2\text{O}_3$ .

### Mechanical and Electrical Properties

To examine mechanical and electrical properties, the polythioesters were pressed in a steel mold under pressure of 200 kg/cm<sup>2</sup>. Numerical data given in Table IV show that polythioesters from dithiol and isophthaloyl and terephthaloyl chlorides possess interesting mechanical properties. Because of this, they may find practical application, especially as modifiers of commercial polyesters.

TABLE IV  
Temperature of Pressing and Mechanical Properties of Polythioesters

Test	Chloride		
	Phthaloyl	Isophthaloyl	Terephthaloyl
Temperature of pressing (°C)	135	230	160
Vicat softening point (°C)	114	136	118
Rupture strength (kg/cm <sup>2</sup> )	—	353	155
Impact strength (kg/cm <sup>2</sup> )	—	355	172
Bending strength (kg/mm <sup>2</sup> )	—	4.4	0.68
Brinell hardness (kg/cm <sup>2</sup> )	21.0	20.3	20.3
Dielectrical constant	3.0	2.3	3.7
Tan $\delta$ at 170 kHz, 21°C	0.0101	0.0400	0.0207

### CONCLUSIONS

New polythioesters from bis(4-mercaptophenyl)ether and isomeric phthaloyl chlorides were obtained with great yield and considerably high thermal and chemical resistance only in the case of polythioesters from chlorides: isophthaloyl and terephthaloyl.

In contrast to these, polythioesters from phthaloyl chloride were obtained with both smaller yield and lower thermal and chemical resistance.

It was found that the use of 100% excess of sodium hydroxide exerts a beneficial influence both on yield and value of reduced viscosity which was, however, determined only for polythioesters from phthaloyl chloride.

The use of catalyst favourably influences the reaction of polycondensation.

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