

Linear Polythioesters. XI.* Products of Polycondensation of Some Isomeric Di(mercaptomethyl)Dimethylbenzenes with Isophthaloyl and Terephthaloyl Chlorides

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Synopsis

New polythioesters have been obtained by polycondensation of 4,5-di(mercaptomethyl)-1,2-dimethylbenzene, 4,6-di(mercaptomethyl)-1,3-dimethylbenzene, and 2,5-di(mercaptomethyl)-1,4-dimethylbenzene with isophthaloyl and terephthaloyl chlorides. To define the optimal conditions of polycondensation, polythioester from 2,5-di(mercaptomethyl)-1,4-dimethylbenzene and isophthaloyl chloride was chosen as a model system. The optimization of the polycondensation conditions was carried out by low-temperature and high-temperature solution polycondensation as well as by interfacial polycondensation. To determine the optimal conditions for polycondensation the following parameters have been studied. The kind of organic solvent, concentration of reagents, temperature and time of reaction, and, in the case of interfacial polycondensation additional, the ratio of aqueous to organic phase, kind and concentration of hydrochloride acceptor, kind and concentration of catalyst and concentration of emulsifier (Mersolan) were taken into consideration. The synthesis of all described polythioesters obtained by polycondensation di(mercaptomethyl)-dimethylbenzenes with isophthaloyl and terephthaloyl chlorides was carried out under the same optimal conditions, established for the reaction 2,5-di(mercaptomethyl)-1,4-dimethylbenzene with isophthaloyl chloride. The structure of polythioesters was determined from infrared, X-ray, and elementary analysis. Some physicochemical, thermal, mechanical, and electrical properties as well as molecular weight of polythioesters have been determined.

INTRODUCTION

In earlier articles¹⁻⁴ systematic studies on the optimization of the synthesis, structure, and properties of new polythioesters, mainly formed by interfacial polycondensation of aromatic and aliphatic-aromatic dithiols with aromatic or aliphatic acid dichlorides, were described. Until now di(mercaptomethyl) derivatives of benzophenone, naphthalene, tetramethylbenzene, and diphenylether were used. The purpose of this study was to obtain new polythioesters from easily accessible di(mercaptomethyl) derivatives of isomeric xylenes.

Di(mercaptomethyl)xylenes are formed from suitable di(chloromethyl) compounds by thiouronic salts.⁵ It was experimentally stated that in suitable conditions chloromethylation reaction of isomeric xylenes leads to obtaining the following products with the greatest yield^{5,6}: 4,5-

* For Part X of this series, see *J. Appl. Polym. Sci.*, Vol. 30, 1579 (1985).

di(chloromethyl)-1,2-dimethylbenzene, from *o*-xylene, 4,6-di(chloromethyl)-1,3-dimethylbenzene from *m*-xylene, and 2,5-di(chloromethyl)-1,4-dimethylbenzene from *p*-xylene. These above-mentioned di(chloromethyl)xylenes were used to the synthesis responsible di(mercaptomethyl)xylenes. Preparation of polythioesters from 4,5-di(mercaptomethyl)-1,2-dimethylbenzene (4,5-DMM-1,2-DMB), 4,6-di(mercaptomethyl)-1,3-dimethylbenzene (4,6-DMM-1,3-DMB), and 2,5-di(mercaptomethyl)-1,4-dimethylbenzene (2,5-DMM-1,4-DMB) and isophthaloyl as well as terephthaloyl chlorides was carried out by means of low- and high-solution polycondensation and by interfacial polycondensation.

To determine the optimal conditions required in the all kinds of processes of polycondensation, the influence of some factors on yield and reduced viscosity was considered. The reaction of polycondensation of 2,5-di(mercaptomethyl)-1,4-dimethylbenzene (2,5-DMM-1,4-DMB) with isophthaloyl chloride was chosen as a model system and thoroughly studied. It was stated that the best results were obtained by using interfacial polycondensation.

The structure of all polythioesters obtained under model conditions was determined by elemental analysis, infrared (IR) spectra, and X-ray. Chemical and thermal resistance and mechanical and electrical properties were determined. The molecular weights of polythioesters obtained by interfacial polycondensation were determined by gelchromatography only for polymers soluble in tetrachloroethane.

EXPERIMENTAL

Reagents

4,5-Di(mercaptomethyl)-1,2-dimethylbenzene (4,5-DMM-1,2-DMB), mp 68–69°C (after crystallization from ethanol),⁷ 4,6-di(mercaptomethyl)-1,3-dimethylbenzene (4,6-DMM-1,3-DMB), mp 48–49°C (after crystallization from isopropanol),⁸ and 2,5-di(mercaptomethyl)-1,4-dimethylbenzene (2,5-DMM-1,4-DMB), mp 75–77°C (after crystallization from ethanol)⁹ were obtained from the suitable di(chloromethyl) compounds thorough the thio-uronic salts.⁵ Isophthaloyl chloride, mp 44°C, and terephthaloyl chloride, mp 83°C (after crystallization from hexane), were obtained by the reaction of phosphorous pentachloride with isophthalic or terephthalic acid.

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-Scherrer'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 weight (\bar{M}_w) of polythioesters were calculated on the basis of gel permeation chromatographic data.^{10,11} The chromatographic measurements were carried out applying Varian Aerograph liquid chromatograph Type 4100 with RI detector and orlite pompe AF 10-4. As a mobile phase tetrachloroethane was used. The investigated polythioester as filtrated solution (0.5–1.0 g of polymer in 100 cm³ 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, West Germany). The measurements were carried out at 18°C.

Glassy Temperature

Measurement of glassy temperature was taken in a DSC-IB Perkin-Elmer Differential Microcalorimeter, at a heating rate of 32°C/min, a nitrogen flow rate of 30 cm³/min, sensibility of apparatus 4 mcal/s, and the weight of the sample 16 mg.

Chemical Resistance

In a flask of 200 cm³ volume, 1 g of polythioester tried to dissolve in a 50 cm³ of different several solvents at room temperature.

Infrared Analysis

Infrared (IR) spectra were obtained with a UNICAM SP-200 Spectrophotometer.

The Synthesis of Polythioesters

The synthesis of polythioesters from isomeric di(mercaptomethyl)xylenes and isophthaloyl or terephthaloyl chlorides were carried out by low-temperature solution polycondensation, high-temperature solution polycondensation, and interfacial polycondensation. For every polycondensation method as a model system for determining the optimal conditions, 2,5-di(mercaptomethyl)-1,4-dimethylbenzene and isophthaloyl chloride were chosen. In the choice of optimal conditions, a yield of the process and value of the reduced viscosity were considered.

Determination of Optimal Conditions in Low-Temperature Solution Polycondensation

The following factors, which influenced the process, were studied: the kind of organic solvent, concentration of monomers, time, and the temperature of the reaction. The initial reaction conditions were: organic solvent benzene, concentration of monomers 0.1M, temperature of the reaction 10°C, and time of the reaction 1 h. The applied solvents and physicochemical values obtained are listed in Table I. From the data presented it follows that the solvent influences the reduced viscosity and the yield imperceptibly. The best yield, highest value of reduced viscosity, and highest of softening range of polythioesters were obtained with chlorobenzene.

In the optimalization process only this solvent was used. In further investigations the influence of concentration of reagents, temperature of reaction and time of reaction on yield and value of reduced viscosity were studied.

As Figures 1–3 show, polythioesters of the highest yield and reduced viscosity were received with concentration of reagents 0.1M, temperature of reaction 20°C, and time of reaction 1 h. Polythioester synthesis from 2,5-DMM-1,4-DMB and isophthaloyl chloride according to the best experimentally defined conditions was carried out as follows:

In a three-necked round-bottomed flask of 250 cm³ volume, equipped with a mechanical stirrer (1600 rpm), dropper, thermometer, and reflux condenser, 1.98 g (0.01 mol) 2,5-DMM-1,4-DMB in 50 cm³ chlorobenzene and 2.02 g (0.02 mol) of triethylamine were added. To this solution 2.03 g (0.01 mol) of isophthaloyl chloride in 50 cm³ chlorobenzene was slowly added with stirring at 10°C. Stirring was continued at 20°C for 1 h, and then 100 cm³ of acetone was added. The isolated product was filtered, washed with hot water and acetone, and dried under reduced pressure (11 mm Hg) at 60°C. Yield of polythioester 92%, η_{red} 0.27 (dL/g), and softening range 195–230°C.

Determination of Optimal Conditions of High-Temperature Solution Polycondensation

To determine the optimal conditions for solution polycondensation of 2,5-DMM-1,4-DMB with isophthaloyl chloride, the influence of the kind of organic solvent and the temperature reaction on yield and value of reduced

TABLE I
Effect of Solvent on Properties of Polythioester from 2,5-DMM-1,4-DMB and Isophthaloyl Chloride^a

Solvent	η_{red} (dL/g)	Yield (%)	Softening range (°C)
Benzene	0.20	84	182–212
Chlorobenzene	0.27	92	195–230
Dioxane	0.24	79	172–231
Dichloromethane	0.25	81	180–235

^a Conditions of the reaction: concentration of reagents 0.1M; temperature 10°C; time of the reaction 1 h.

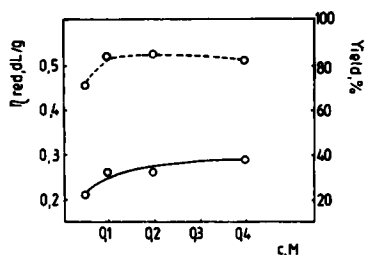


Fig. 1. The influence of concentration on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and isophthaloyl chloride. Conditions of the reaction: chlorobenzene, reaction temperature 10°C, reaction time 1 h.

viscosity were studied. The initial reaction conditions were organic solvent xylene, concentration of monomers 0.5M, reaction temperature 140°C, reaction time 5 h, and nitrogen atmosphere. Table II shows values of reduced viscosity, yields, and softening point ranges of obtained polythioesters in xylene, *o*-dichlorobenzene, and α -chloronaphthalene. The highest values of reduced viscosity and the best yields of polythioesters were obtained with chlorohydrocarbons. In the further optimization process *o*-dichlorobenzene was chosen as a organic solvent. The effect of temperature on yield and value of reduced viscosity is shown in Table III. The best results of the polycondensation were achieved at applied highest temperature near boiling point of *o*-dichlorobenzene. It was Experimentally affirmed that the best advantageous results of polycondensation were obtained in the way described below.

In a four-necked round-bottomed flask of 250 cm³ volume, equipped with a mechanical stirrer (1600 rpm), thermometer, reflux condenser, and tube to introduce of nitrogen 3.98 g (0.02 mol) of 2,5-DMM-1,4-DMB, 4.06 g (0.02 mol) of isophthaloyl chloride were placed and 40 cm³ of *o*-dichlorobenzene was added. The mixture was stirred vigorously and heated at 175°C for 5 h. Then it was cooled to room temperature. Precipitated polythioester was separated by filtration, boiled for 15 min in water (100 cm³), filtered again, washed with acetone, and dried under reduced pressure (15 mm Hg) at 60°C to constant weight. Yield 86%, η_{red} = 0.36 dL/g, and softening range 200–240°C.

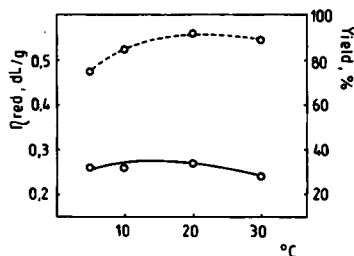


Fig. 2. The influence of reaction temperature on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and isophthaloyl chloride. Conditions of the reaction: chlorobenzene, concentration of reagents 0.1M, reaction time 1 h.

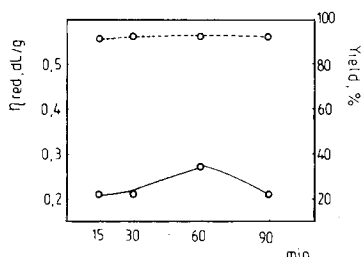


Fig. 3. The influence of reaction time on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and isophthaloyl chloride. Conditions of the reaction: chlorobenzene, concentration of reagents 0.1M, reaction temperature 20°C.

Determination of Optimal Conditions in Interfacial Polycondensation

In determining the optimal conditions of interfacial polycondensation of 2,5-DMM-1,4-DMB with isophthaloyl chloride, the yield of the process and reduced viscosity were taken into consideration. The influence of the following factors was studied: the kind of organic phase, the quantitative ratio of aqueous to organic phase, the kind and concentration of hydrogen chloride acceptor, the concentration and molar ratio of monomers, the temperature of reaction, and the kind and the contribution of catalysts.

The initial reaction conditions were: organic solvent benzene, hydrogen chloride acceptor 0.2M NaOH, concentration of dithiol 0.1M, concentration of acid dichloride 0.11M, rate of acid dichloride addition 5 min, and temperature of the reaction 15°C. The applied organic phase and some physicochemical values obtained are listed in Table IV. From the data presented it follows that the solvent influences the yield and reduced viscosity of the polycondensation polymers considerably. The best yield and the highest value of reduced viscosity were obtained with a benzene/hexane mixture in a volume ratio 1:1.

In the further optimization process only this mixture was used as an organic phase. The influence of the kind of hydrogen chloride acceptor, that is, NaOH, KOH, and Na₂CO₃, is shown in Table V. From the data presented it follows that the most useful hydrochloride acceptor is sodium hydroxide. The amount of sodium hydroxide exerts considerable influence on the results of polycondensation.

As Figure 4 shows, the use of excess sodium hydroxide in relation to the amount stoichiometrically necessary (0.2M) causes an increase in the value

TABLE II
Effect of Solvent on Properties of Polythioester from 2,5-DMM-1,4-DMB and Isophthaloyl Chloride*

Solvent	η_{red} (dL/g)	Yield (%)	Softening range (°C)
Xylene	0.09	45	167–226
<i>o</i> -Dichlorobenzene	0.26	76	194–236
α -Chloronaphthalene	0.21	73	185–243

* Conditions of the reaction: concentration of reagents 0.5M; reaction time 5 h; reaction temperature 140°C; nitrogen atmosphere.

TABLE III
Effect of Reaction Temperature on Properties of Polythioester from 2,5-DMM-1,4-DMB and Isophthaloyl Chloride

Reaction temp (°C)	η_{red} (dL/g)	Yield (%)	Softening range (°C)
140	0.26	76	194–237
160	0.29	81	198–235
175	0.36	86	200–240

* Conditions of the reaction: *o*-dichlorobenzene, concentration of reagents 0.5*M*; reaction time 5 h; nitrogen atmosphere.

of reduced viscosity and a gradual decreases in yield. In further studies of optimization of the process, 100% excess of hydrogen chloride acceptor was used, which caused a good yield and simultaneously a good value of reduced viscosity. The influence of the kind and concentration of catalyst on the value of reduced viscosity by using benzyltriethylammonium chloride, benzyltriphenylphosphonium chloride, and methyltriphenylarsonium iodide in the range 0.5–5% by weight in relation to the amount of dithiol was studied.

Figure 5 shows that the highest value of reduced viscosity was obtained with contribution 3% benzyltriethylammonium chloride. The effect of monomer concentration on reduced viscosity and yield of polythioester in the range 0.01–0.3*M* at a constant volume of water and organic phases was determined.

Figure 6 shows that the highest value of reduced viscosity and the best yield were obtained with a 0.1*M* solution of monomers. The effect of the ratio of the aqueous to the organic phase on the value of reduced viscosity and the yield of the polythioester was studied with different quantities of water at the constant volume of organic phase. The ratio of aqueous to organic phase was 0:1–0.1:1, which corresponded to the concentration of dithiol in the aqueous-basic phase in the range of 0.1–1.0 mol/L.

TABLE IV
Organic Phase Effect on the Yield and Reduced Viscosity of Polythioester from 2,5-DMM-1,4-DMB and Isophthaloyl Chloride*

Organic phase	η_{red} (dL/g)	Yield (%)	Softening range (°C)
Benzene	0.28	71	166–192
Chlorobenzene	0.23	82	176–203
Hexane	0.28	78	153–180
Dichloromethane	0.14	61	158–188
Chlorophorm	0.14	65	164–186
Tetrachloromethane	0.56	76	170–208
Dichloroethane	0.62	68	160–210
Benzene–hexane (1:1)	0.64	84	176–218

* Conditions of the reaction: phase ratio 1:1; hydrogen chloride acceptor 0.2*M* NaOH; concentration of dithiol 0.1*M*; concentration of acid chloride 0.11*M*; rate of acid chloride addition 5 min; temperature 15°C.

TABLE V
Influence of the Kind of Hydrogen Chloride Acceptor on Properties of Polythioester from 2,5-DMM-1,4-DMB and Isophthaloyl Chloride*

Hydrogen chloride acceptor	η_{red} (dL/g)	Yield (%)	Softening range (°C)
NaOH	0.64	84	176–218
KOH	0.44	71	176–210
Na ₂ CO ₃	0.32	64	168–186

* Conditions of the reaction: organic phase, benzene/hexane (1:1); phase ratio 1:1; concentration of hydrogen chloride acceptor, stoichiometric; concentration of dithiol 0.1M; concentration of acid chloride 0.11M; rate of chloride addition 5 min; temperature 15°C.

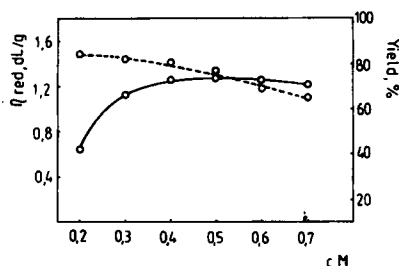


Fig. 4. The influence of concentration of hydrogen chloride acceptor (NaOH) on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and isophthaloyl chloride. Conditions of the reaction: organic phase benzene/hexane (1:1); concentration of dithiol 0.1M; concentration of acid chloride 0.11M; rate of chloride addition 5 min; temperature 15°C.

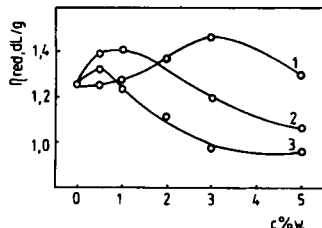


Fig. 5. The influence of kind and contribution of catalyst on reduced viscosity of polythioester from 2,5-DMM-1,4-DMB with isophthaloyl chloride: (1) benzyltriethylammonium chloride (TEBA); (2) benzyltriphenylphosphonium chloride; (3) methyltriphenylarsonium iodide. Conditions of the reaction: organic phase, benzene/hexane (1:1); phase ratio 1:1; concentration of dithiol 0.1M; concentration of acid chloride 0.11M; concentration of hydrogen chloride acceptor 0.4M NaOH; rate of acid chloride addition 5 min; temperature 15°C.

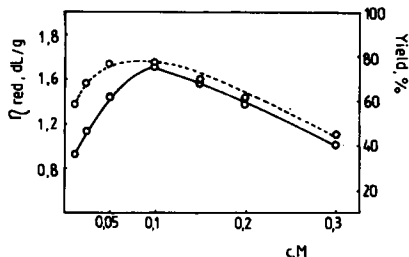


Fig. 6. The influence of concentration of monomers on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and isophthaloyl chloride. Conditions of the reaction: organic phase, benzene/hexane (1:1); phase ratio 1:1; 100% excess of NaOH; catalyst 3% TEBA (3% weight in relation to dithiol); rate of acid chloride addition 5 min; temperature 15°C.

Figure 7 shows that the best results were achieved with a 0.2M solution of dithiol (phase ratio 1:1). The emulsifier (Mersolan) effect was studied in a range of 0–1% weight in relation to aqueous phase.

The curve in Figure 8 shows the negative contribution of the emulsifier on reduced viscosity and insignificant its effect on yield.

Figure 9 shows the effect of the ratio of acid chloride addition on the value of reduced viscosity and the yield of polythioester. It can be seen that the optimal time of acid chloride addition is 7–10 min. The effect of temperature on the value of reduced viscosity and yield was studied in the range 6–55°C.

As Figure 10 shows the best results were obtained at 15°C. On the basic above experiments it can be stated, that the best results of polycondensation process were achieved if the synthesis of polythioester were carried out in the way described below. In a three-necked, round-bottomed flask of 500 cm³, equipped with a mechanical stirrer (2000 rpm), thermometer, and dropper, 1.98 g (0.01 mol) 2,5-DMM-1,4-DMB, 50 cm³ benzene and a sodium hydroxide solution (1.6 g NaOH in 100 cm³ water) were placed. After thorough mixing, 2.233 g (0.011 mol) of an isophthaloyl chloride solution in 50 cm³ hexane was added over a period 8.5 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 cm³ water for 10 min. After cooling and filtration the polythioester was washed with hot water (2 × 100 cm³) and acetone (30 cm³) and dried under reduced pressure (15 mm Hg) at 60°C to a constant weight.

Comparison of Methods of Polythioester Synthesis

In the Table VI are presented some physicochemical properties of polythioesters showing the greatest value of reduced viscosity, obtained by low-temperature and high-temperature solution polycondensation as well as interfacial polycondensation. Comparison of these three methods shows that suitably chosen conditions of interfacial polycondensation make polythioesters with the best properties. Polythioester syntheses from 4,5-DMM-1,2-DMB, 4,6-DMM-1,3-DMB, and 2,5-DMM-1,4-DMB and with isophthaloyl or terephthaloyl chloride were carried out according to these

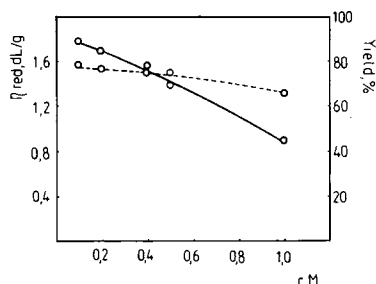


Fig. 7. The influence of concentration on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and isophthaloyl chloride. Conditions of the ratio; organic phase, benzene/hexane (1:1); 100% excess of NaOH; concentration of acid chloride 0.11M; catalyst, TEBA (3% weight in relation to dithiol); rate of chloride addition 5 min; temperature 15°C.

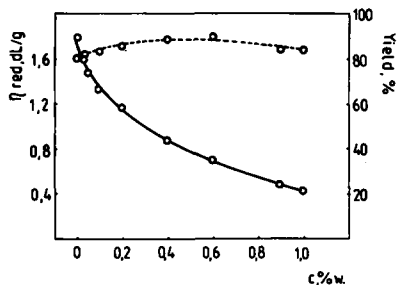


Fig. 8. The influence of concentration of emulsifier (Mersolan) on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and isophthaloyl chloride. Conditions of the reaction: organic phase, benzene/hexane (1:1); 100% excess of NaOH; concentration of dithiol 0.1M; concentration of acid chloride 0.11M; catalyst, TEBA (3% weight in relation to dithiol); rate of chloride addition 5 min; temperature 15°C.

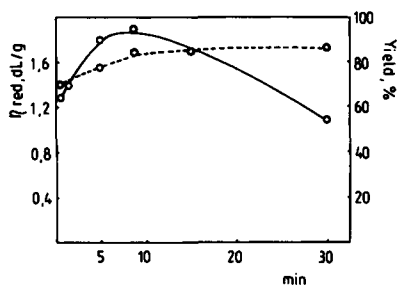


Fig. 9. The influence of rate of acid chloride addition on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and isophthaloyl chloride. Conditions of the reaction: organic phase, benzene/hexane (1:1); 100% excess of NaOH; concentration of dithiol 0.1M; concentration of acid chloride 0.11M; catalyst, TEBA (3% weight in relation to dithiol); temperature 15°C.

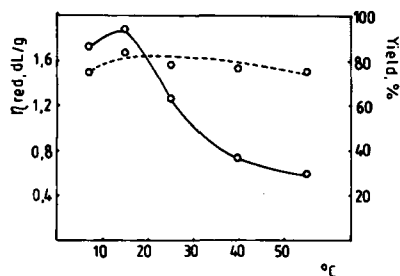


Fig. 10. The influence of the reaction temperature on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and isophthaloyl chloride. Conditions of the reaction: organic phase, benzene/hexane (1:1); 100% excess of NaOH; concentration of dithiol 0.1M; concentration of acid chloride 0.11M; catalyst, TEBA (3% weight in relation to dithiol); rate of acid chloride 5 min.

TABLE VI

Effect of Polycondensation Method on Properties of Polythioester from 2,5-DMM-1,4-DMB and Isophthaloyl Chloride Obtained in Optimal Conditions for Each Method

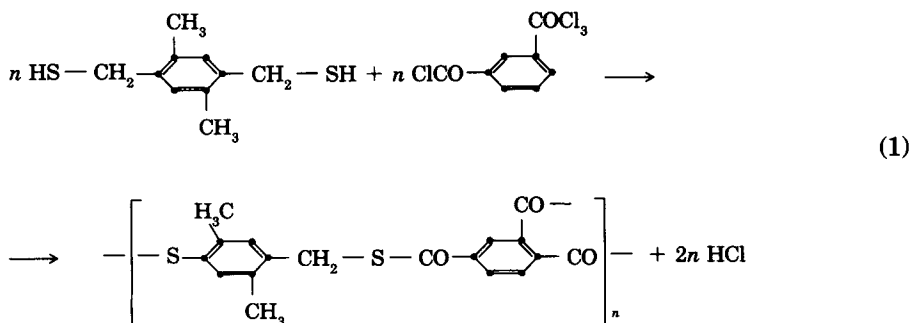
Method of polycondensation	Yield (%)	η_{red} (dL/g)	Softening range (°C)
Interfacial	84	1.89	200–230
Low-temperature	92	0.27	195–230
High-temperature	86	0.36	200–240

conditions defined experimentally for 2,5-DMM-1,4-DMB and isophthaloyl chloride. Table VII shows values of reduced viscosity, yields, and softening point ranges of all obtained polythioesters.

Structure of Polythioesters

The structure of all polythioesters obtained by interfacial polycondensation under the model conditions was determined by elemental analysis, infrared spectra, and X-ray analysis. The results of elementary analysis are given in Table VIII.

IR spectra of polythioesters showed strong absorptions at 1650–1680 cm^{-1} which is characteristic of carbonyl valency bond; at 1420–1450 cm^{-1} characteristic of the $-\text{CH}_2-\text{S}-$ group, bands at 900–950 are attributed to the $-\text{CO}-\text{S}-$ stretch vibration. On the basis of good agreement of the calculated and found analytical data (Table VIII) and IR spectra (Fig. 11) the following reaction scheme (1) for 2,5-DMM-1,4-DMB and isophthaloyl chloride as an example was assumed:



Molecular Weight

Molecular weight of polythioesters (\bar{M}_w) obtained by interfacial polycondensation isomeric di(mercaptomethyl)dimethylbenzenes with isophthaloyl and terephthaloyl chlorides are presented in Table VII. Molecular weight was measured only for these polythioesters which were soluble in tetrachloroethane. A gel permeation chromatography system was calibrated in the range 2.1×10^3 – 3.1×10^6 by means of polystyrene standards (PS) from Water Associates (U. S.). Eleven PS standards of a known average molecular weight characterized by ultranarrow distribution of molecular weight were applied.

In order to calculate the molecular weights of polythioesters, the universal calibration curve was used. According to Benoit,¹² the elution volume of macromolecule depends on the hydrodynamic volume of macromolecule

$$\lg[\eta]M = f(V_e)$$

where $[\eta]$ = intrinsic viscosity and V_e = elution volume.

TABLE VII
Properties of Polythioesters Obtained in Optimal Conditions by Interfacial Polycondensation

Polythioester		η_{red} (dL/g)	Yield (%)	Glassy temperature (°C)	Softening range (°C)	Molecular weight ($\bar{M}_n \times 10^3$)
Dithiol	Acid chloride					
4,5-DMM-1,2-DMB	Isophthaloyl	1.76	83	116.5	185-215	241
4,6-DMM-1,3-DMB		1.22	77	103	155-200	147
2,5-DMM-1,4-DMB		1.89	84	127	200-230	350
4,5-DMM-1,2-DMB	Terephthaloyl	0.84	79	104.5	164-195	103
4,6-DMM-1,3-DMB		—	81	97.5	200-230	—
2,5-DMM-1,4-DMB		—	87	97	245-265	—

TABLE VIII
Results of Elemental Analysis of Polythioesters

Polythioester		% C		% H		% S	
Dithiol	Acid chloride	Calcd	Found	Calcd	Found	Calcd	Found
4,5-DMM-1,2-DMB	Isophthaloyl		65.63		4.75		19.29
4,6-DMM-1,3-DMB		65.70		4.91	4.85	19.52	19.30
2,5-DMM-1,4-DMB		65.69			4.81		19.36
4,5-DMM-1,2-DMB	Terephthaloyl		65.70		4.80		19.18
4,6-DMM-1,3-DMB		65.73		4.91	4.78	19.52	19.21
2,5-DMM-1,4-DMB		65.70			4.75		19.25

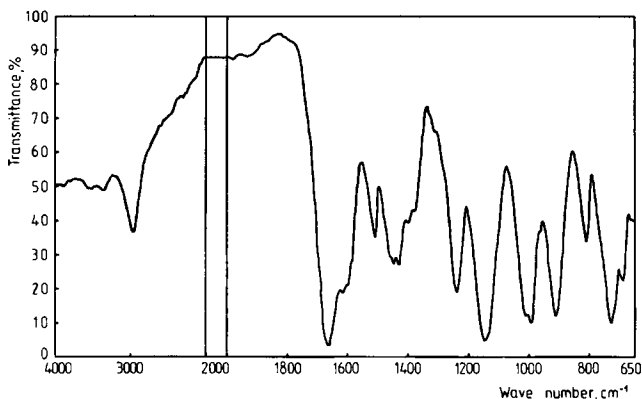


Fig. 11. Infrared spectra of polythioester from 2,5-DMM-1,4-DMB and isophthaloyl chloride.

According to a previous paper,^{12,13} the hydrodynamic volume of macromolecules is a decisive parameter of elution behavior of polymers in GPC column at a given solvent and is proportional to $[\eta]M$.

The $[\eta]$ values were calculated by extrapolation of η_s/c specific $c = f(c)$ functions. The measurements of (η) were carried out for polythioester solution of 0.2, 0.4, 0.6, 0.8, and 1 g/dL in tetrachloroethane.

X-Ray Analysis

Polythioesters obtained by interfacial polycondensation of isomeric di(mercaptatomethyl)dimethylbenzenes with isophthaloyl and terephthaloyl chlorides were examined by means of X-ray diffraction analysis. In Figure 12 are presented the diffraction diagrams showing the interplanar spacings d_n and relative intensity I/I_0 of reflections for polythioesters 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 show also many diffraction lines but they are other values of d . The presence of these lines indicate the high crystalline degree of polymers.

Thermal Properties

The polythioesters obtained were examined by differential 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 percent for polythioesters at 300, 400, 500, and 600°C are listed in Table IX. The results of the examination are shown only for polythioester from 2,5-DMM-1,4-DMB and isophthaloyl chloride as an example (Fig. 13).

Mechanical and Electrical Properties

Some mechanical and electrical properties of the polythioesters obtained from 4,5-DMM-1,2-DMB, 4,6-DMM-1,3-DMB, and 2,5-DMM-1,4-DMB with

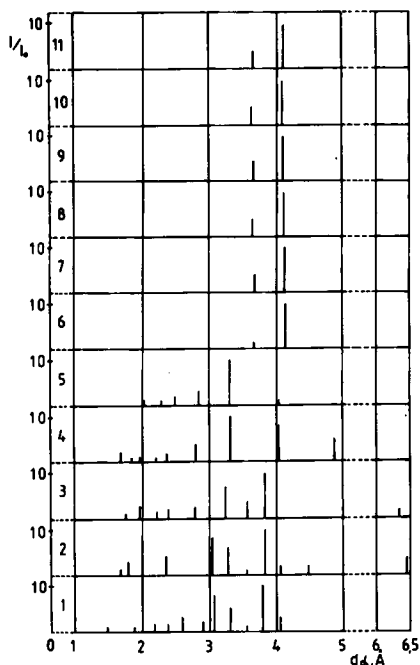


Fig. 12. X-Ray diffraction patterns of: (1) 4,5-DMM-1,2-DMB; (2) 4,6-DMM-1,3-DMB; (3) 2,5-DMM-1,4-DMB; (4) isophthaloyl chloride; (5) terephthaloyl chloride; (6) polythioester from 4,5-DMM-1,2-DMB and isophthaloyl chloride; (7) polythioester from 4,5-DMM-1,2-DMB and terephthaloyl chloride; (8) polythioester from 4,6-DMM-1,3-DMB and isophthaloyl chloride; (9) polythioester from 4,6-DMM-1,3-DMB and terephthaloyl chloride; (10) polythioester from 2,5-DMM-1,4-DMB and isophthaloyl chloride; (11) polythioester from 2,5-DMM-1,4-DMB and terephthaloyl chloride.

isophthaloyl chloride have been studied after pressing at first at room temperature under a pressure of 600 kg/cm^2 and then at increased temperature at a pressure of 150 kg/cm^2 in the upper range of the softening temperature of every polymer. Samples for electrical tests were additionally metalized by silver in vacuum. Pressing temperature and numerical data are given in Table X. Electric properties of polythioesters were characterized by dielectric constant ϵ , dielectric loss factor ($\tan \delta$), and volume resistivity ρ 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 ϵ and $\tan \delta$ at 20°C and at frequency of 0.05, 1, 10, and 100 kHz were obtained. The temperature range was limited by thermal properties of polythioesters. Results are given in Table XI and in Figures 14–16.

The dependences of $\tan \delta$ on temperature show some differences for various polythioesters which is determined by their chemical structure. Figure 14 shows that polythioesters lose their electrical properties above 100°C, which is connected with their glassy temperature. Values of dielectric constant and dielectric loss factor in function of frequency in temperature 20°C show small changes in these conditions (Table XI). Figure 16 shows the dependence of volume resistivity (ρ) in function of temperature at frequency of 50 Hz.

TABLE IX
Thermal Properties of Polythioesters

Polythioester	Thermal analysis ^a				Mass loss (%)			
	T_1 (°C)	K_1 (%)	T_2 (°C)	K_2 (%)	300	400	500	600
Dithiol								
Acid chloride								
Isophthaloyl								
4,5-DMM-1,2-DMB	300	1.5	335	14	2	33	44	64
4,6-DMM-1,3-DMB	290	3	320	11	3.5	30	42	68
2,5-DMM-1,4-DMB	300	1	325	9	1.3	27.5	40	67
Terephthaloyl								
4,5-DMM-1,2-DMB	300	2	345	25		32	43.5	61
4,6-DMM-1,3-DMB	285	1.5	320	8	3	28	40	59
2,5-DMM-1,4-DMB	290	1.5	325	9	2	25	37.5	56

^a 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 .

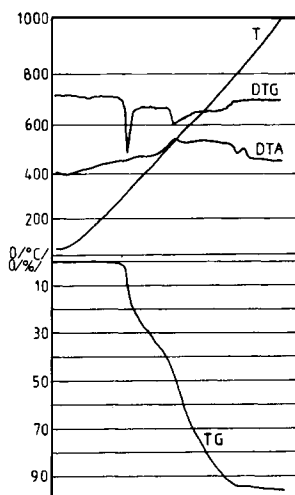


Fig. 13. TGA and DTA of polycondensation product of 2,5-DMM-1,4-DMB with isophthaloyl chloride. Heating time in air 250 min; heating rate 4°C/min; amount of polythioester 100 mg; measured relative to Al_2O_3 .

Chemical Resistance

The obtained polythioesters show good resistance to acetone, benzene, dioxane, dimethylsulfoxide, 10% and concentrated hydrochloric acid, 10 and 50% sodium hydroxide, and 10% sulfuric and nitric acids. Some of them are soluble in tetrachloroethane and in mixture of phenol/tetrachloroethane (1:1), but all react with concentrated nitric and sulfuric acids.

CONCLUSION

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 solution polycondensation, and by interfacial polycondensation. It was stated that the best results, i.e., the best value of reduced viscosity and the highest yield were obtained using interfacial polycondensation. About 100% excess of acceptor hydrogen chloride (NaOH) exerts considerable influence on the results of polycondensation.

Polythioesters with the best properties were obtained when the ratio of the aqueous to organic phase was 1:1, when a phase transfer catalyst was used, when the time required in the reaction mixture was 7–10 min, and when the process of polycondensation was carried out at 15°C.

Emulsifier decreases the value of reduced viscosity, exerting insignificant effect on the yield. Considering their good thermal and mechanical properties as well as good chemical resistance the polythioesters obtained can be widely applied, particularly as modifiers of commercial polyesters.

TABLE X
 Temperature of Pressing and Mechanical Properties of Polythioesters from Isomeric D(mercaptomethyl) Dimethylbenzene and Isophthaloyl Chloride

Test	Dithiol		
	4,5-DMM-1,2-DMB	4,6-DMM-1,3-DMB	2,5-DMM-1,4-DMB
Temperature of pressing (°C)	190	180	190
Vicat softening point (°C)	123	137	128.5
Tensile strength (kg/cm ²)	49.27	314.02	310.97
Impact strength (kg/cm ²)	1.97	4.40	4.16
Bending strength (kg/cm ²)	298.02	623.25	516.28
Brinnell hardness (kg/mm ²)	8.16	7.69	10.00
Modulus of elasticity (kg/cm ²)	1078.16	2594.07	2510.78

TABLE XI
Some Electrical Properties of Polythioesters from Isomeric Di(mercaptomethyl) Dimethylbenzene and Isophthaloyl Chloride

Test	Dithiol		
	4,5-DMM-1,2-DMB	4,6-DMM-1,3-DMB	2,5-DMM-1,4-DMB
Dielectrical constant at frequency (kHz)			
0.05	3.71	4.10	4.16
1	3.81	4.01	4.11
10	3.75	3.95	4.05
100	3.70	3.89	3.99
Dielectrical loss factor at frequency (kHz)			
0.05	55	89	134
1	46	76	97
10	71	100	100
100	97	148	127

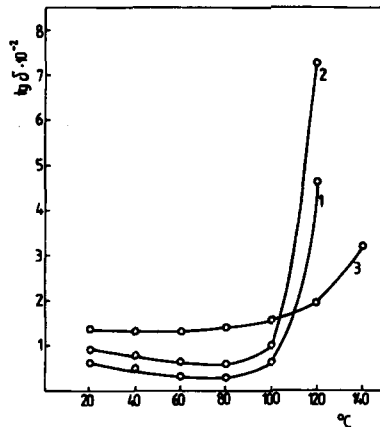


Fig. 14. The dependence of dielectric loss factor ($\tau\delta$) on temperature at frequency 0.05 kHz of polythioesters from: (1) 4,5-DMM-1,2-DMB and isophthaloyl chloride; (2) 4,6-DMM-1,3-DMB and isophthaloyl chloride; (3) 2,5-DMM-1,4-DMB and isophthaloyl chloride.

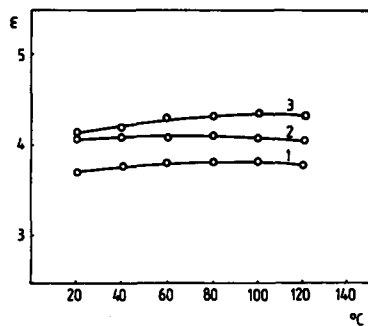


Fig. 15. The dependence of dielectric constant on temperature at frequency 0.05 kHz of polythioesters from: (1) 4,5-DMM-1,2-DMB and isophthaloyl chloride; (2) 4,6-DMM-1,3-DMB and isophthaloyl chloride; (3) 2,5-DMM-1,4-DMB and isophthaloyl chloride.

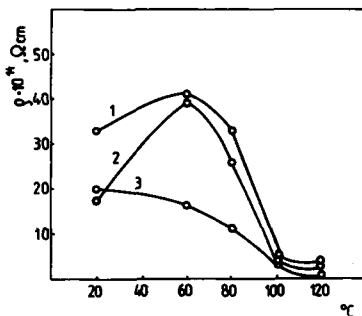


Fig. 16. The dependence of volume resistivity (ρ) on temperature at frequency 0.05 kHz of polythioesters from: (1) 4,5-DMM-1,2-DMB and isophthaloyl chloride; (2) 4,6-DMM-1,3-DMB and isophthaloyl chloride; (3) 2,5-DMM-1,4-DMB and isophthaloyl chloride.

References

1. W. Podkościelny and A. Kultys, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 655 (1976); **22**, 2265 (1984).
2. W. Podkościelny, and W. Charmas, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 2429 (1979); **17**, 3811 (1979).
3. W. Podkościelny and W. Kowalewska, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1025 (1984); **22**, 1579 (1984).
4. W. Podkościelny and D. Wdowicka, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 2961 (1983).
5. C. D. Shacklett and H. A. Smith, *J. Am. Chem. Soc.*, **73**, 766 (1951).
6. W. D. Szein, G. S. Mironow, and M. I. Farbierow, *Zh. Prikl. Khim.*, **40**, 2006 (1967).
7. J. Shahak and E. Bergman, *J. Chem. Soc., C. Org.*, **11**, 1005 (1966).
8. U. S. Pat. 3,208,969 (1965); *Chem. Abstr.*, **63**, 18377a (1965).
9. Ch. Nakashima and R. Oda, *Nippon Kagaku Zasshi*, **86**, 645 (1965); *Chem. Abstr.*, **65**, 633 g (1965).
10. A. L. Dawidowicz, A. Waksmundzki and S. Sokołowski, *Wiadomości Chem.*, **31**, 553 (1977).
11. A. L. Dawidowicz and S. Sokołowski, *J. Chromatogr.* **125**, 428 (1976).
12. H. Benoit, Z. Grubisic, P. Rempp, D. Decker and J. Zilliox, *J. Chem Phys.*, **63**, 1507 (1966).
13. Z. Grubisic, P. Rempp and H. Benoit, *J. Polym. Sci. Part B*, **5**, 753 (1967).

Received November 20, 1985

Accepted January 12, 1986