

Linear Polythioesters. XIII.* Products of Polycondensation of Isomeric Di(mercaptomethyl)-Dimethylbenzenes with Adipoyl and Sebacoyl Chlorides

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Synopsis

The synthesis of a new aliphatic-aromatic polythioesters 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 adipoyl and sebacoyl chloride is described. To define the optimal condition of the process, the polythioester from 2,5-di(mercaptomethyl)-1,4-dimethylbenzene and sebacoyl chloride was chosen as a model system and obtained by interfacial polycondensation as well as by low- and high-temperature solution polycondensation. To determine the optimal conditions for polycondensation the following parameters have been studied: kind of organic solvent, concentration of reagents, temperature and time of reaction and, in the case of interfacial polycondensation additional, ratio of aqueous to organic phase, kind and concentration of hydrochloride acceptor, and kind and concentration of catalyst were taken into consideration. The quality of the obtained polycondensates was estimated on the basis of values of the reduced viscosity and yield. The structure of the aliphatic-aromatic polythioesters was determined from elementary analysis, infrared spectra, and X-ray analysis. Some thermal, mechanical, electrical, and chemical properties as well as molecular weights of obtained polycondensates have been determined.

INTRODUCTION

Within the systematic studies on the synthesis, structure, and properties of polythioesters prepared from various dimercapto compounds and acid dichlorides, during the last years our interest was concentrated on the synthesis of polythioesters from methyl derivatives of benzene, i.e. toluene, xylenes, tri- and tetramethylbenzenes.

In earlier articles^{1,2} studies on the synthesis and properties of polythioesters formed from 1,4-di(mercaptomethyl)-2,3,5,6-tetramethylbenzene and aromatic or aliphatic acid dichlorides as well as formed from di(mercaptomethyl)-isomeric xylenes and di(mercaptomethyl)-trimethylbenzenes and isomeric phthaloyl chlorides were described.

The purpose of this study was to obtain new 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 from adipoyl and sebacoyl acid dichlorides.

*For Part XII of this series, see Ref. 2.

Process of polycondensation dimercaptomethyl compounds with acid dichlorides was carried out by means of low- and high-temperature 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-DMM-1,4-DMB with sebacyl chloride was chosen as a model system and thoroughly studied. It was stated that the best results were obtained by using interfacial polycondensation.

EXPERIMENTAL

Reagents

4,5-Di(mercaptomethyl)-1,2-dimethylbenzene (4,5-DMM-1,2-DMB), mp 68–69°C (after crystallization from ethanol)³; 4,6-di(mercaptomethyl)-1,3-dimethylbenzene (4,6-DMM-1,3-DMB), mp 48–49°C (after crystallization from isopropanol)⁴ and 2,5-di(mercaptomethyl)-1,4-dimethylbenzene (2,5-DMM-1,4-DMB), mp 75–77°C (after crystallization from ethanol)⁵ were obtained from the suitable di(chloromethyl)-compounds⁶ through the thio-uronic salts. Adipoyl chloride with bp 125–128°C/18 mmHg and sebacyl chloride with bp 166–168°C/11 mmHg were obtained by chlorination of the suitable acids with thionyl chloride.

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 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 (\bar{M}_w) of polythioesters were calculated on the base of gel permeation chromatographic data.^{7,8} The chromatographic measurements were carried out applying Varian Aerograph liquid chromato-

graph Type 4100 with RI detector and orlite pumps 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, FRG). The measurements were carried out at 18°C.

Glassy Temperature

Measurement of glassy temperature was taken in a DSC-1B Perkin-Elmer differential microcalorimeter, at a heating rate of 32°C/min, nitrogen flow rate of 30 cm³/min, sensibility of apparatus 4 mcal/s, weight of sample 16 mg.

Chemical Resistance

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

Infrared Analysis

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

The Synthesis of Polythioesters

Polythioesters derivatives of 4,5-di(mercaptomethyl)-1,2-dimethylbenzene, 4,6-di(mercaptomethyl)-1,3-dimethylbenzene, 2,5-di(mercaptomethyl)-1,4-dimethylbenzene and adipoyl or sebacoyl chlorides can be obtained by low- and high-temperature solution polycondensation. For every polycondensation method as a model system for determining the optimal conditions 2,5-di(mercaptomethyl)-1,4-dimethylbenzene and sebacoyl chloride were chosen. In the choice of optimal conditions, 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, time of the reaction 1 h. The applied solvents and physiochemical values obtained are listed in Table I. As it follows from data in Table I the best yield and highest value of reduced viscosity were obtained with chlorobenzene. In further optimization processes only this solvent was used.

The influence of concentration of monomers, reaction temperature and reaction time on reduced viscosity, and yield of polythioester from 2,5-DMM-1,4-DMB and sebacoyl chloride is presented in Figures 1–3. Polythioesters of the highest yield and reduced viscosity were received with

TABLE I
Effect of Solvent on Properties of Polythioester from 2,5-Di(mercaptomethyl)-
1,4-Dimethylbenzene and Sebacoyl Chloride^a

Solvent	η_{red} (dL/g)	Yield (%)	Softening (range (°C))
Benzene	0.29	75	107-122
Chlorobenzene	0.46	80	104-120
Dioxane	0.24	73	110-120
Dichloromethane	0.28	74	100-128

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

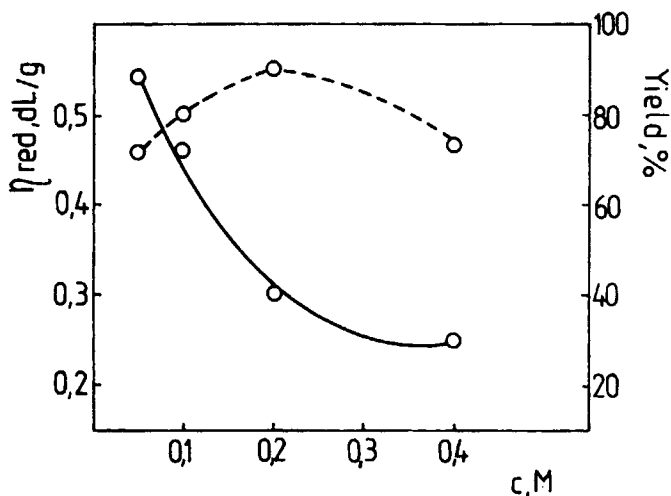


Fig. 1. The influence of concentration of reagents on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and sebacoyl chloride. Conditions of the reaction: chlorobenzene; catalyst triethylamine; reaction temperature 10°C; reaction time 1 h.

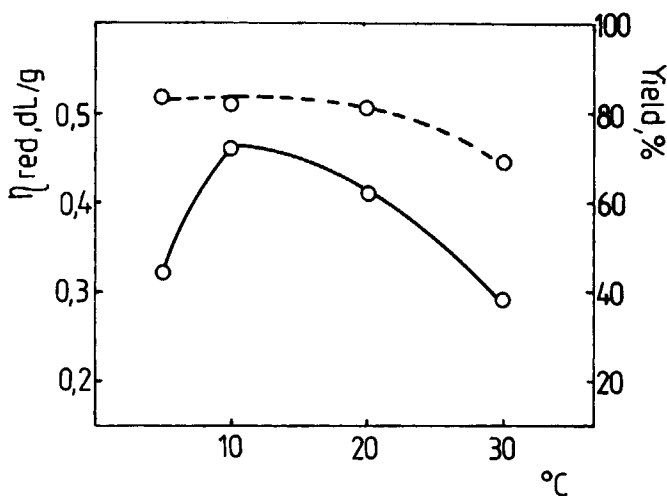


Fig. 2. The influence of reaction temperature on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and sebacoyl chloride. Conditions of the reaction: chlorobenzene; concentration of reagents 0.1M; concentration of catalyst triethylamine 0.2M; reaction time 1 h.

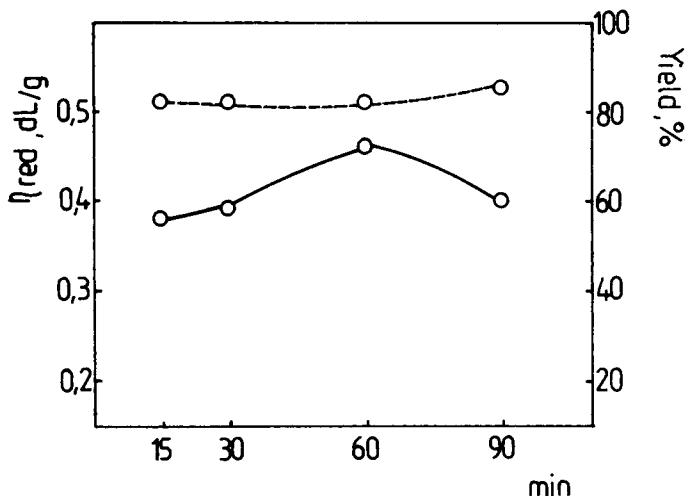


Fig. 3. The influence of reaction time on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and sebacyl chloride. Conditions of the reaction: chlorobenzene; concentration of reagents 0.1M; concentration of catalyst triethylamine 0.2M; reaction temperature 10°C.

concentration of monomers 0.1M, temperature of reaction 10°C, and time of reaction 1 h.

Polythioester synthesis from 2,5-DMM-1,4-DMB and sebacyl chloride according to the best experimentally defined condition 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 catalyst triethylamine were added. To this solution 2.39 g (0.01 mol) sebacyl chloride in 50 mL chlorobenzene was slowly added with stirring at 10°C. Stirring was continued at this temperature for 1 h; then 100 ml acetone was added. The isolated product was filtered, washed with hot water and acetone and dried under reduced pressure (15 mm Hg) at 60°C. The yield of polythioester was 82%, η_{red} 0.46 dL/g, and softening range 100–130°C.

Determination of Optimal Conditions of High-Temperature Solution Polycondensation

To determine the optimal conditions for high-temperature solution polycondensation of 2,5-DMM-1,4-DMB with sebacyl chloride, the influence of the kind of organic solvent and reaction temperature on value of reduced viscosity and yield was studied. The initial reaction conditions were: organic solvent xylene; concentration of monomers 0.5M; reaction temperature 140°C; reaction time 5 h; nitrogen atmosphere.

In the Table II are presented properties of obtained polythioesters in xylene, *o*-dichlorobenzene, and α -chloronaphthalene. Polythioesters with the highest values of reduced viscosity and the best yields were obtained in chlorohydrocarbons. The further optimization processes were carried out only in *o*-dichlorobenzene as an organic solvent.

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

Solvent	η_{red} (dL/g)	Yield (%)	Softening range (°C)
Xylene	0.18	68	80-127
<i>o</i> -Dichlorobenzene	0.62	90	83-136
α -Chloronaphthalene	0.58	93	91-145

^a 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 Sebacoyl Chloride^a

Reaction temperature	η_{red} (dL/g)	Yield (%)	Softening range (°C)	Form of compound
140	0.62	90	83-136	White powder
160	0.55	92	94-142	Beige powder
175	0.50	92	102-156	Beige powder

^a Conditions of the reaction: *o*-dichlorobenzene; concentration of monomers 0.5M; reaction time 5 h; nitrogen atmosphere.

It is worth mentioning that extension of time of the reaction from 5 to 7 h did not influence imperceptibly on the yield, value of reduced viscosity, and softening range of polymer.

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 temperature 140°C. Experimentally affirmed, the best advantageous results of polycondensation were obtained in the way described below.

In a 250-cm³, round-bottomed, four-necked flask fitted with a mechanical stirrer, thermometer, reflux condenser, and a tube to introduce of nitrogen 3.98 g (0.02 mol) of 2,5-DMM-1,4-DMB, 4.78 g (0.02 mol) of sebacoyl chloride were placed and 40 mL *o*-dichlorobenzene was added. The mixture was stirred rigorously and heated at 140°C for 5 h. Then it was cooled to room temperature. Isolated polythioester was filtered, boiled for 15 min in water (100 mL), filtered again, washed with acetone, and dried under reduced pressure (15 mm Hg) at 60°C. The yield of polythioester was 90%, η_{red} 0.62 dL/g, and softening range 83-136°C.

Determination of Optimal Conditions of Interfacial Polycondensation

To determine the optimal conditions for the interfacial polycondensation of 2,5-DMM-1,4-DMB with sebacoyl chloride, the influence of the following factors on properties of polythioesters was studied: kind of organic solvent, aqueous and organic phase ratio, kind and concentration of hydrogen chloride acceptor, concentration of monomers, reaction temperature, kind and contri-

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

Organic phase	η_{red} (dL/g)	Yield (%)	Softening range (°C)
Benzene	0.19	69	107-119
Chlorobenzene	0.16	71	72-105
Hexane	0.25	63	96-123
Tetrachloromethane	0.01	69	88-115
Dichloromethane	0.11	65	93-106
Chlorophorm	0.10	53	82-115
Dichloroethane	0.20	60	112-123
Benzene-hexane (1 : 1)	0.29	75	90-120

^a Conditions of the reaction: phase ratio 1 : 1; hydrogen chloride acceptor 0.2M NaOH; concentration of dithiol 0.1M; concentration of acid chloride 0.11M; rate of acid chloride addition 10 min; reaction temperature 25°C.

bution of catalyst. Yield, reduced viscosity, and softening range were determined for the obtained polythioesters. 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 10 min, and temperature of the reaction 25°C.

The effect of applied organic phase on properties of obtained polythioesters is listed in Table IV. From these data it follows that 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 processes only this mixture was used as an organic phase.

The influence of kind of hydrogen chloride acceptor on properties of polythioesters is shown in Table V. From presented data it follows that sodium hydroxide is a more useful hydrochloride acceptor than potassium hydroxide.

In the next experiment an effect of excess of sodium hydroxide on the results of polycondensation was studied. As shown in Figure 4, an increase in the amount of hydroxide influences the value of reduced viscosity very much and does not cause a decrease in the yield of polymer. When a 100% excess of NaOH is used, reduced viscosity increases about four times. In the further optimization processes an excess of NaOH like this was used.

TABLE V
Influence of Kind of Hydrogen Chloride Acceptor on Properties of Polythioester
from 2,5-DMM-1,4-DMB and Sebacyl Chloride^a

Hydrogen chloride acceptor	η_{red} (dL/g)	Yield (%)	Softening range (°C)
NaOH	0.29	75	90-120
KOH	0.21	43	83-115

^a Conditions of the reaction: organic phase benzene/hexane (1 : 1); phase ratio 1 : 1; concentration of hydrogen chloride acceptor 0.2M; concentration of dithiol 0.1M; concentration of acid chloride 0.11M; rate of acid chloride addition 10 min; reaction temperature 25°C.

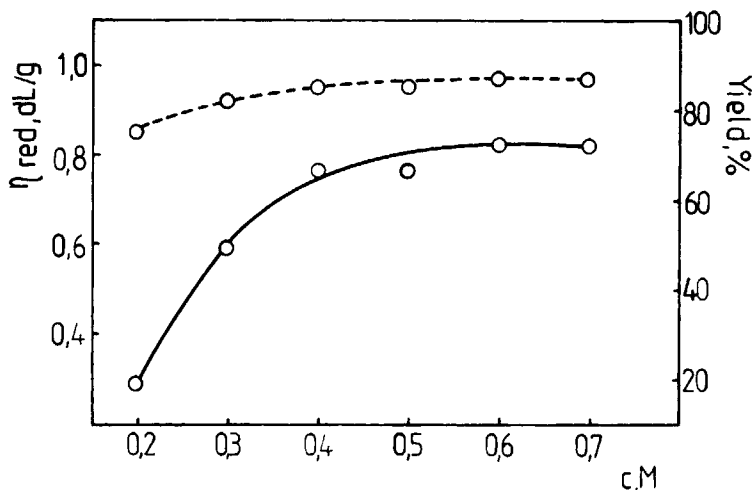


Fig. 4. The influence of concentration of optimal hydrogen chloride acceptor (NaOH) on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and sebacoyl chloride. Conditions of the reaction: organic phase benzene/hexane (1:1); phase ratio 1:1; concentration of dithiol 0.1M; concentration of acid chloride 0.11M rate of acid chloride addition 10 min; temperature 25°C.

The influence of kind and concentration of catalyst on value of reduced viscosity by using benzyltriethylammonium chloride (TEBA), benzyltriphenylphosphonium chloride, and methyltriphenylarsonium iodide in the range 0.5–5% by weight in relation to the amount of dithiol was studied. From Figure 5 it follows that, in the presence of catalysts, obtained polymers had

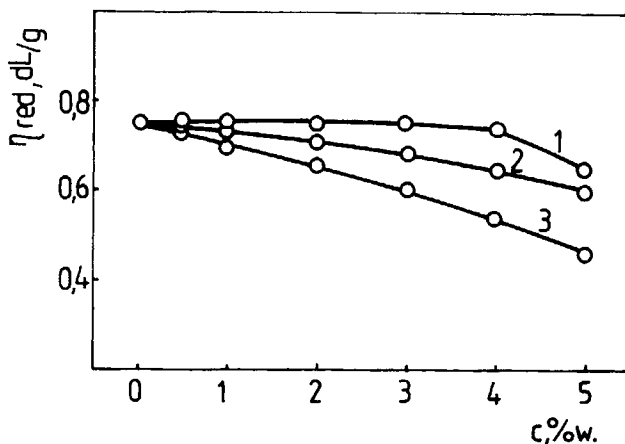


Fig. 5. The influence of kind and contribution of catalyst on reduced viscosity of polythioester from 2,5-DMM-1,4-DMB and sebacoyl chloride: (1) benzyltriethylammonium chloride; (2) benzyltriphenylphosphonium chloride; (3) methyltriphenylarsonium iodide. Conditions of the reaction: organic phase benzene/hexane (1:1); phase ratio 1:1; concentration of dithiol 0.1M; concentration of acid chloride 0.11M; concentration of acid chloride acceptor (NaOH) 0.4M (100% excess); rate of acid chloride addition 10 min; temperature 25°C.

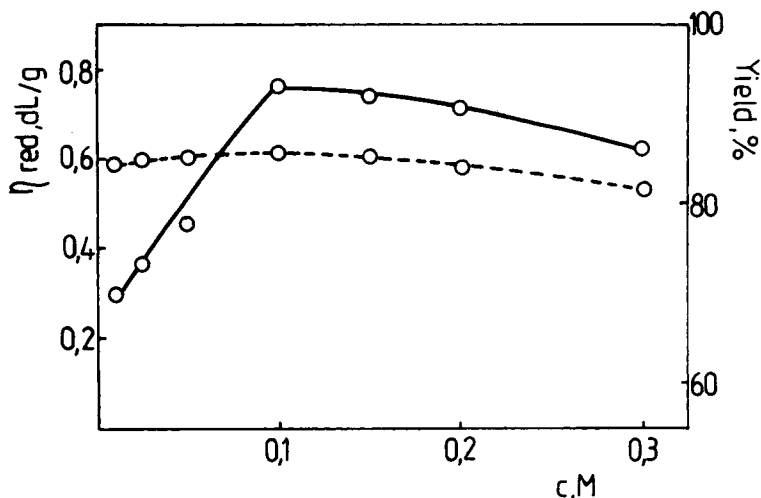


Fig. 6. The influence of concentration of monomers on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and sebacyl chloride. Conditions of the reaction: organic phase benzene/hexane (1:1); phase ratio 1:1; 100% excess of NaOH; rate of acid chloride addition 10 min; temperature 25°C.

the lower value of reduced viscosity. The further experiments were carried out without catalyst.

The effect of concentration of monomers on the reduced viscosity and yield of polythioester was studied in the range of 0.01–0.3M. A constant volume of water and organic phase was used, and the amount of dithiol and acid chloride

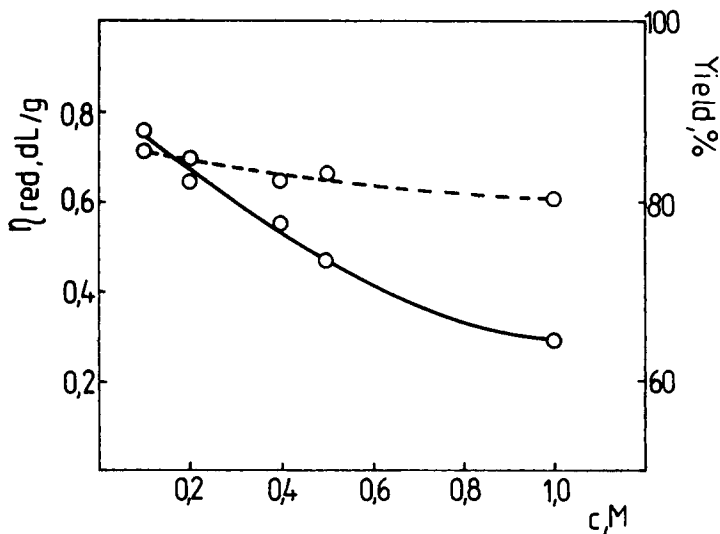


Fig. 7. The influence of concentration of dithiol on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and sebacyl chloride. Conditions of the reaction: organic phase benzene/hexane (1:1); 100% excess of NaOH, concentration of acid chloride 0.11M; rate of acid chloride addition 10 min; temperature 25°C.

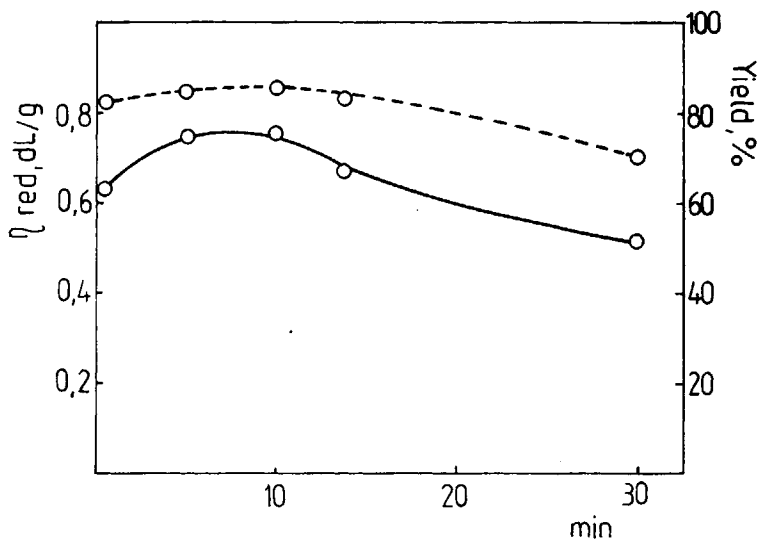


Fig. 8. The influence of rate of acid chloride addition on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and sebacyl chloride. Conditions of the reaction: organic phase benzene/hexane (1:1), 100% excess of NaOH, concentration of dithiol 0.1M, concentration of acid chloride 0.11M; temperature 25°C.

was changed. From obtained results (Fig. 6) it follows that the best properties of polythioesters were obtained in 0.1M solution of monomers.

The effect of ratio of water to organic phase on the value of reduced viscosity and yield of polythioester was investigated at various amounts of water and constant volume of organic phase. The ratio of water to organic phase was formed from 1:1 to 0.1:1 and corresponded to a concentration of dithiol in water/basic phase in the range of 0.1–1.0M. From Figure 7 it follows that the highest value of reduced viscosity was obtained using 0.1M dithiol (phase ratio of 1:1).

The effect of the rate of acid chloride addition on reduced viscosity is shown in Figure 8. It can be seen that the optimal time of acid chloride addition is 5–10 min.

The synthesis of polythioesters was carried out in the range of temperature of 6–55°C. As follows from Figure 9, the best results were obtained in temperature 15–25°C.

On the basis of the above experiments it was stated that the best results of polycondensation process were achieved when synthesis of polythioester was carried out in the way described below.

In a three-necked, round-bottomed flask of 250 cm³ volume, equipped with a mechanical stirrer (2000 rpm), thermometer and dropper, 1.98 g (0.01 mol) 2,5-DMM-1,4-DMB, 50 mL benzene, and sodium hydroxide solution (1.6 g NaOH in 100 ml water) were placed. After thorough mixing, the solution of 2.629 g (0.011 mol) sebacyl chloride in 50 mL hexane was added for a period 5 min and stirred in temperature of 15°C. After addition of acid chloride, stirring was continued for 0.5 h in this temperature, and then the mixture was acidified with hydrochloric acid (Congo Red). The isolated product of polycondensation was filtered and boiled in 100 mL water for 15 min. After

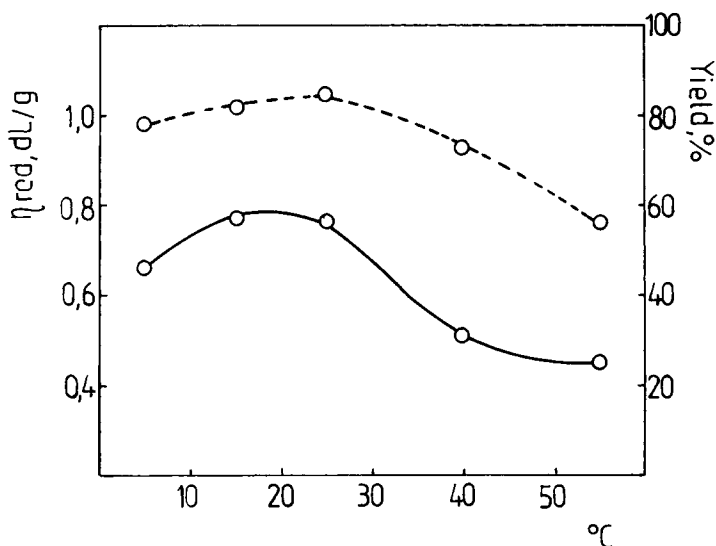


Fig. 9. The influence of reaction temperature on reduced viscosity (—) and yield (---) of polythioester from 2,5-DMM-1,4-DMB and sebacyl chloride. Conditions of the reaction: organic phase benzene/hexane (1 : 1); 100% excess of NaOH; concentration of dithiol 0.1M; concentration of acid chloride 0.11M; rate of acid chloride addition 5 min.

cooling the polythioester was washed with acetone and dried under reduced pressure (15 mm Hg) at 60°C. The yield of polymer was 85%, η_{red} 0.76, and softening range 125–133°C.

Comparison of Methods of Polythioester Synthesis

In Table VI are presented some physiochemical properties of polythioesters from 2,5-DMM-1,4-DMB and sebacyl chloride, having the greatest value of reduced viscosity and yield, obtained by interfacial polycondensation as well as by low- and high-temperature solution polycondensation.

Keeping the experimentally stated optimal conditions of interfacial polycondensation of 2,5-DMM-1,4-DMB with sebacyl chloride, the synthesis of polythioesters from 4,5-DMM-1,2-DMB, 4,6-DMM-1,3-DMB, and 2,5-DMM-1,4-DMB with adipoyl and sebacyl chlorides was carried out. The properties of obtained polythioesters are presented in Table VII.

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

Method of polycondensation	η_{red} (dL/g)	Yield (%)	Softening range (°C)
Interfacial	0.76	85	125–133
Low temperature	0.46	82	100–130
High temperature	0.62	90	83–136

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 ($\bar{M}_w \times 10^3$)
Dithiol	Acid chloride					
4,5-DMM-1,2-DMB	Adipoyl	0.17	71	117	137-165	10.5
4,6-DMM-1,3-DMB	Adipoyl	0.37	70	111.5	142-154	45
2,5-DMM-1,4-DMB	Adipoyl	0.36	78	111	147-166	47
4,5-DMM-1,2-DMB	Sebacoyl	0.21	78	104	110-124	26
4,6-DMM-1,3-DMB	Sebacoyl	0.37	77	98	120-130	49
2,5-DMM-1,4-DMB	Sebacoyl	0.76	85	112	125-133	100

RESULTS AND DISCUSSION

Structure of Polythioesters

Chemical structure of polythioesters derivatives of isomeric di(mercaptomethyl)dimethylbenzenes with adipoyl and sebacoyl chlorides was determined by elementary analysis, infrared spectra, and X-ray analysis. The results of elementary analysis are given in Table VIII. Infrared spectra of aromatic-aliphatic polythioesters, presented on Figure 10 only for polythioester from 4,5-DMM-1,2-DMB and adipoyl chloride as an example, showed

TABLE VIII
Results of Elementary Analysis of Polythioesters

Polythioester		% C		% H		% S	
Dithiol	Acid chloride	Calcd	Found	Calcd	Found	Calcd	Found
4,5-DMM-1,2-DMB	Adipoyl		62.14		6.50		20.62
4,6-DMM-1,3-DMB	Adipoyl	62.30	62.15	6.54	6.40	20.79	20.55
2,5-DMM-1,4-DMB	Adipoyl		62.20		6.30		20.65
4,5-DMM-1,2-DMB	Sebacoyl		65.60		7.60		17.48
4,6-DMM-1,3-DMB	Sebacoyl	65.89	65.71	7.74	7.55	17.59	17.40
2,5-DMM-1,4-DMB	Sebacoyl		65.78		7.48		17.35

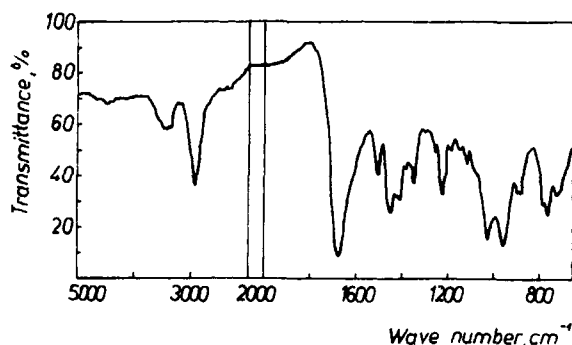
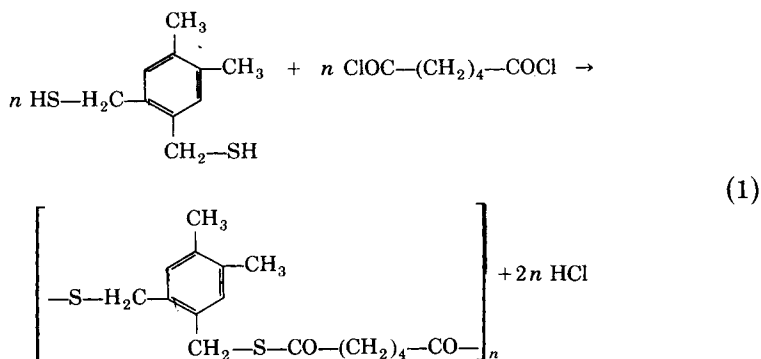


Fig. 10. Infrared spectrum of polythioester from 4,5-DMM-1,2-DMB and adipoyl chloride.

strong absorptions at 1660–1700 cm^{-1} which is characteristic of carbonyl valency band; at 900–1000 cm^{-1} characteristic of COS group and at 1400–1460 cm^{-1} characteristic of the $\text{CH}_2\text{—S}$ group.

On the basis of good agreement of the calculated and found analytical data and infrared spectra, the reaction scheme (1) for 4,5-DMM–1,2-DMB and adipoyl chloride as an example was assumed:



X-Ray Analysis

Obtained polythioesters and initial isomeric dithiols were examined by X-ray analysis. Diffraction diagrams show the interplanar spacings d_α and relative intensity I/I_0 of the reflections. Numerical data are presented in Figure 11. Comparison of reflections of polythioesters with these for suitable dithiols permits us to state that reflections existing on the röntgenograms of polythioesters do not origin from substrates.

Polythioesters from 4,5-DMM–1,2-DMB and adipoyl as well as sebacoyl chlorides are amorphous, whereas polythioesters derivatives of 2,5-DMM–1,4-DMB have the high crystalline degree.

Thermal Properties

All polythioesters 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 of 2,5-DMM–1,4-DMB and sebacoyl chloride (Fig. 12).

Mechanical and Electrical Properties

Some mechanical and electrical properties was determined only for the most interesting polythioesters: mechanical properties for polythioesters derivatives of 2,5-DMM–1,4-DMB and adipoyl as well as sebacoyl chloride and electrical properties for polythioester of 2,5-DMM–1,4-DMB and sebacoyl chloride. Polymers have been studied after pressing at first at the room temperature

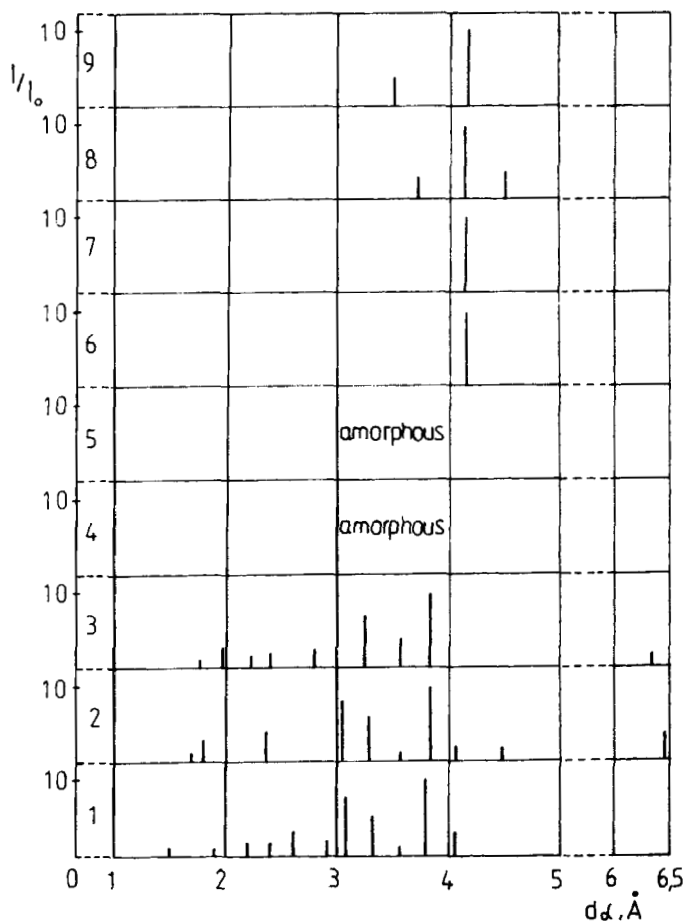


Fig. 11. X-ray diffraction patterns of: (1) 4,5-DMM-1,2-DMB; (2) 4,6-DMM-1,3-DMB; (3) 2,5-DMM-1,4-DMB; (4) polythioester of 4,5-DMM-1,2-DMB and adipoyl chloride; (5) polythioester of 4,5-DMM-1,2-DMB and sebacyl chloride; (6) polythioester of 4,6-DMM-1,3-DMB and adipoyl chloride; (7) polythioester of 4,6-DMM-1,3-DMB and sebacyl chloride; (8) polythioester of 2,5-DMM-1,4-DMB and adipoyl chloride; (9) polythioester of 2,5-DMM-1,4-DMB and sebacyl chloride.

TABLE IX
Thermal Properties of Polythioesters

Polythioester		Thermal analysis ^a				Mass loss (%)				
						%C				
Dithiol	Acid chloride	T_1 (°C)	K_1 (%)	T_2 (°C)	K_2 (%)	300	350	400	500	600
4,5-DMM-1,2-DMB	Adipoyl	280	1	350	43	4	43	66	70	79
4,6-DMM-1,3-DMB	Adipoyl	290	0.5	340	28	2	35	51	56	69
2,5-DMM-1,4-DMB	Adipoyl	280	0.5	350	35	1.5	40	63	69	83
4,5-DMM-1,2-DMB	Sebacyl	280	0.5	360	32	1.5	25	52	66	76
4,6-DMM-1,3-DMB	Sebacyl	300	1	360	22	1	17	44	58	67
2,5-DMM-1,4-DMB	Sebacyl	300	1.5	380	39	1.5	16	55	70	80

^a T_1 = temperature of initial exothermic effect from the curve DTA (°C). K_1 = mass loss in the temperature T_1 (%). T_2 = temperature of initial intensive decomposition from the curve DTA (°C). K_2 = mass loss in the temperature T_2 (%).

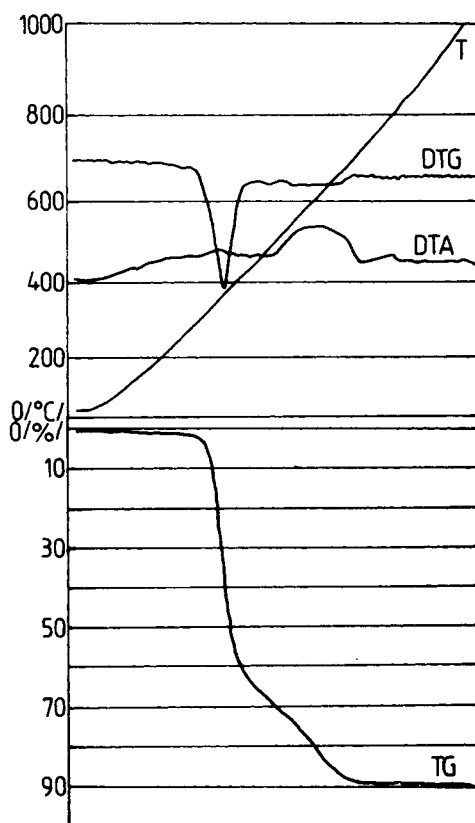


Fig. 12. TGA and DTA of polycondensation product of 2,5-DMM-1,4-DMB with sebacyl chloride. Heating time in air 250 min, heating rate 4°C/min, amount of polythioester 100 mg, measured relative to Al_2O_3 .

under a pressure of 600 kg/cm² and then at increased temperature at a pressure of 150 kg/cm² 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.

TABLE X
Temperature of Pressing and Mechanical Properties of Polythioesters
from 2,5-DMM-1,4-DMB with Adipoyl and Sebacyl Chlorides

Test	Acid chloride	
	Adipoyl	Sebacyl
Temperature of pressing (°C)	150	125
Vicat softening point (°C)	112	114
Tensile strength (kg/cm ²)	53.97	93.26
Impact strength (kg/cm ²)	0.87	2.32
Bending strength (kg/cm ²)	—	216.96
Brinell hardness (kg/mm ²)	5.39	7.69
Modulus of elasticity (kg/cm ²)	1250.00	1694.57

TABLE XI
Some Electrical Properties of Polythioester from 2,5-DMM-1,4-DMB
and Sebacyl Chloride in Temperature of 20°C

Frequency (kHz)	Dielectric constant ϵ	Dielectric loss factor $\tan \delta \times 10^{-4}$
0.05	5.59	108
1	3.46	111
10	3.40	157
100	3.40	395

Electric properties of polythioester from 2,5-DMM-1,4-DMB and sebacyl chloride were characterized by dielectric constant (ϵ), dielectric loss factor ($\tan \delta$), and volume resistivity (ρ) in the function of temperature. The examinations were made at frequency of 0.05 kHz at 20, 40, 60, 80, 100, and 120°C. Furthermore, the values of ϵ and $\tan \delta$ at 20°C and at frequency of 0.05, 1, 10, and 100 kHz were obtained. Results are given in Table XI and in Figure 13.

From Table XI it follows that the values of ϵ and $\tan \delta$ of polythioester from 2,5-DMM-1,4-DMB and sebacyl chloride show small changes in range of frequency of 0.05–100 kHz.

The temperature characteristics of the changes of $\tan \delta$, ϵ , and ρ at frequency of 0.05 kHz are presented in Figure 13. The point of inflexion of the curve $\tan \delta = f(t)$, stating the loss of electric properties of polythioester is found at a temperature of 80°C. The changes of dielectric constant of polythioester with the increasing temperature in the range of 20–120°C at a

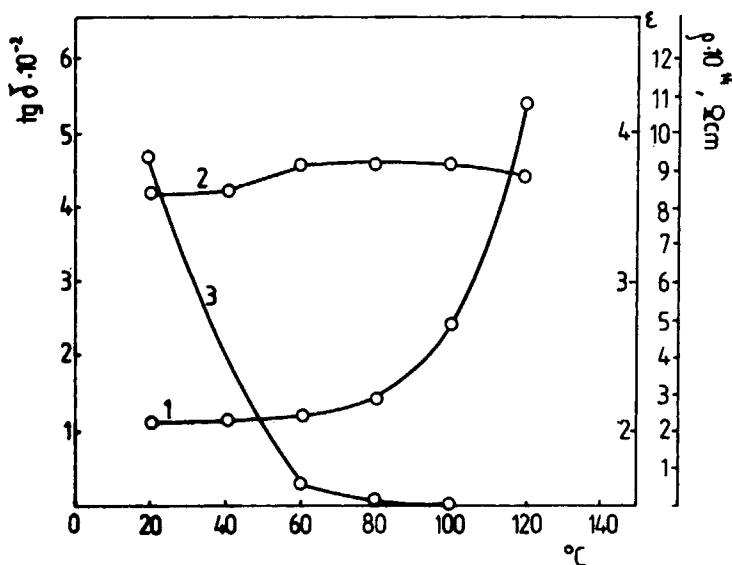


Fig. 13. The changes of electric properties of polythioester from 2,5-DMM-1,4-DMB and sebacyl chloride dependence on temperature at frequency 0.05 kHz: (1) dielectric loss factor $\tan \delta$; (2) dielectric constant ϵ ; (3) volume resistivity ρ .

frequency of 0.05 kHz are usually small and the values of ϵ testify to the polar character of the compound studied.

Chemical Resistance

The polythioesters were treated with some organic solvents, i.e., acetone, benzene, chlorophorm, methylene chloride, dioxane, dimethylphormamide, DMSO, nitrobenzene, tetrachloroethane, a mixture of phenol and tetrachloroethane (1 : 3), and 10% and concentrated mineral acids as well as 10 and 50% sodium hydroxide. The studied compounds are dissolving partially in chlorophorm, completely in tetrachloroethane and in mixture of phenol : tetrachloroethane (1 : 3). They are resistant against diluted alkali and mineral acids but decompose against concentrated H_2SO_4 and HNO_3 .

CONCLUSION

Polycondensation of isomeric di(mercaptomethyl)-dimethylbenzenes with aliphatic acid dichlorides was carried out by low- and high-temperature solution methods and an interfacial one. Interfacial polycondensation proved to be the most useful because of the short time it demands, good yield, and the high value of reduced viscosity.

In the preparation of polythioesters by interfacial polycondensation the best results were obtained for polymers of 2,5-di(mercaptomethyl)-1,4-dimethylbenzene.

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