Linear Polythioesters. XXII. Products of Interfacial Polycondensation of Bis(4-mercaptomethylphenyl)Sulfide with Some Aliphatic and Isomeric Phthaloyl Dichlorides

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SYNOPSIS

New polythioesters were obtained by interfacial polycondensation of bis(4-mercaptomethylphenyl)sulfide with some aliphatic and isomeric phthaloyl dichlorides. To determine optimal conditions for polycondensation, the polythioester from bis(4-mercaptomethylphenyl)sulfide and sebacoyl dichloride was chosen as a model system. The influence of some factors on the reduced viscosity and the yield were studied. Polythioesters from aliphatic and isomeric phthaloyl dichlorides were prepared under the same optimal conditions as those established for the reaction of the dithiol with sebacoyl dichloride. The structure of all polythioesters was determined by elementary, infrared spectra, and X-ray analysis. Initial decomposition temperature and maximum rate of decomposition temperature were defined from the curves of thermogravimetric analysis. Some physicochemical, mechanical, and electrical properties have been determined. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polythioesters that contain in their structure the characteristic group –SCO– are the sulfur analogues of polyesters. One of the best methods of obtaining both polyesters and polythioesters is the reaction of acid dichlorides with aromatic compounds endining with dihydroxyl or dithiol groups. As it is known, polythioesters are generally obtained by three methods: in bulk with evolution of HCl, in solution using alcali as a hydrochloride acceptor, and by interfacial polycondensation. As the last method turned out to be the most effective in the synthesis of polyesters and polythioesters, it seemed interesting for us to devote more attention to this method. Because of the simple equipment required, the process rate, and the possibilities of obtaining high molecular mass, the process of obtaining polymers by interfacial polycondensation has been studied in detail and widely applied.

Numerous publications, monographs, and encyclopedia entries by Morgan and Korshak[1-3] give evidence to the effect that the process depends on many factors that influence molecular mass and yield. They are high purity of semiproducts, adequate mixing, swelling or solubility of polymers, the kind and purity of solvent, organic/aquaous ratio, concentration of reagents, excess of alkali as a hydrochloric acceptor, as well as the presence of catalyst for some systems.

As follows from the current research, the solvent greatly influences molecular weight and yield of polycondensation process. Predominantly, it turns out, the solvent should dissolve acid chloride, next, it should influence reagents diffusion rate, and cause swelling or polymer precipitation. It has not been yet determined whether solvent should dissolve or only swell the polymer being obtained. Wittbacker[4] maintains that it is enough for solvent to only swell the polymer and achieve high molecular weight, while Eareckson[5] states it should dissolve it. On the other hand, according to Korshak and co-workers it is difficult to foresee which of the solvents used will produce the best result for the reagent applied. The

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process conducted with chlorine solvents rather than with the use of hydrocarbones in some cases gives better results[6] but worse in some other.[7]

It is known that the mixing of the reactive mixture results in higher surface tension and helps to achieve a quicker reaction time than without mixing. The example of bisphenol A with isophthalic chloride in interfacial polycondensation shows that mixing rate results in higher molecular mass and yield.[8,9]

Also, the influence of concentration and the ratio of substrates has been widely studied to show that the best results are achieved with the use of $0.1 M$ concentration of reagents at their ratio of $1 : 1$.[3,5,10-12] Further, literature on the subject shows that of the studied hydrochloride acceptors, e.g., KOH, NaOH, Na_2CO_3, the best result are obtained with the use of NaOH. It serves a double function, first as a component necessary to produce reactive phenolane sodium, next as an acceptor of hydrochloride.

Korshak and co-workers show that in some cases high molecular mass polyeters are obtained using excess of NaOH above the amount necessary to change diphenol into suitable phenolane. The amount of alkali higher than the optimal excess reduces both the value of reduced viscosity and yield; this is due to the higher rate of acid chloride groups hydrolysis.[13] In some interfacial polycondensation process polymers with highest molecular mass are obtained using small excess of acid chloride, this is the result of hydrolysis reaction of the used dichloride. On the contrary, increased excess of dichloride above stochiometrically necessary results in lower molecular mass.[14]

Another important parameter is the time needed for the addition of acid chloride to influence the value of reduced viscosity and polyester yield. It has been established that a very short time (1–10 min) is beneficial for a reaction to be fast. Longer acid chloride addition time is detrimental for the increase of polymer chain.[15-17]

The advantage of interfacial polycondensation is the low temperature of the reaction, usually in the 20–30°C range. In some cases, however, the lowering of temperature to even −20°C gives a considerable increase of molecular mass and yield; that is probably the result of slower acid dichlorides hydrolysis. The increase in temperature above 30°C increases hydrolysis reaction that leads to the break in the chain and hence lower yield.[9,18,19] In various cases interfacial polycondensation in the presence of catalyst produces polymers with high molecular mass.

Most frequently the catalysts quaternary ammonium, phosphonium, arsonium, and sulfonium compounds were used as phase-transfer agents especially in estrification. Addition of phase-transfer agents increases the rate of polymer formation and results in higher molecular weight and yield.[20]

Our research so far allows us to state that the parameters mentioned above in an important manner influence the properties of polythioesters obtained by interfacial polycondensation of dithiol derivatives of different aromatic compounds with some aliphatic and isomeric phthaloyl chlorides.[21-24] We may also assume that the conditions of optimization of the process should be defined experimentally, however, they are contained within the well-accepted rules of interfacial polycondensation.

Making attempts at synthesis of polythioesters by means of melt, high- and low-temperature solution polycondensation, as well as interfacial polycondensation it was stated that the best properties of polythioesters were achieved in properly chosen conditions for interfacial polycondensation.[25] Similar results have been obtained from analysis presented in the earlier papers and patents.[26-30] Among the known methods, the melt polycondensation is the least useful in preparation of polymers because its products are of small molecular weight and also unpleasant smell.[31]

Systematic investigations have been undertaken in our laboratory for the last 15 years and have given more information not only on the choice of the method of synthesis of polythioesters but also in the study of their structure, physicochemical, thermal, mechanical, and electric properties.

Recently for synthesis of polythioesters from aliphatic and isomeric phthaloyl chlorides bis(4-mercaptophenyl)sulfide[32] and sulphone[33] have been used. Carrying out the optimization process in which value-reduced viscosity and yield were taken into consideration, we found that the some factors greatly influence the quality and quantity of polycondensation product. To obtain more information about synthesis and properties of polythioesters in this study we present the results of our investigations concerning utilization of bis(4-mercaptomethylphenyl)sulfide for synthesis of polythioesters.

EXPERIMENTAL

Reagents

Bis(4-mercaptomethylphenyl)sulfide, m.p. 93–94°C (after crystallization from cyclohexane), was

obtained from bis(4-chloromethylphenyl)sulfide through the thiouronic salt.[34] Starting bis(4-chloromethylphenyl)sulfide, m.p. 97–98°C (after crystallization from hexane) was obtained by chloromethylation diphenyl sulfide with formaldehyde and concentrated hydrochloric acid in acetic and sulfuric acids medium in the presence of NaCl, according to the Massarani and Mauri prescription.[35] Glutaroyl chloride (b.p. 107–108°C/16 mmHg), adipoyl (b.p. 128–130°C/18 mmHg), pimeloyl (b.p. 137°C/15 mmHg), suberoyl (b.p. 143–147°C/12 mmHg), azelainoyl (b.p. 166°C/18 mmHg), and sebacoyl (b.p. 166–168°C/11 mmHg) were obtained by chlorination of the suitable acids with thionyl chloride.

Terephthaloyl chloride (m.p. 83°C) and isophthaloyl chloride (m.p. 44°C) (after crystallization from hexane) were obtained by the reactions of phosphorous pentachloride with suitable acids. Phthaloyl chloride (b.p. 131–133°C/9–10 mmHg), was obtained through the reaction of phthalic anhydride with phosphorous pentachloride.

Synthesis of Polythioesters

The synthesis of polythioesters by interfacial polycondensation of bis(4-mercaptomethyl)sulfide with aliphatic and isomeric phthaloyl dichlorides was achieved as follows: In the three-necked, round-bottomed flask of 500 cm^3 volume, equipped with a mechanical stirrer (2000 rpm), thermometer and dropper, 0.01 mol dithiol, 50 cm^3 benzene and sodium hydroxide (0.04 mol) dissolved in 100 cm^3 of water and 5% by weight of benzyltriphenylphosphonium chloride were added. After thorough mixing 0.011 mol of acid chloride solution in 50 cm^3 hexane was added over a period 5 min at 10°C under vigorous stirring. After the addition of the acid chloride was completed, the stirring was continued for 15 min, and the mixture was then acidified with hydrochloric acid (Congo red). The isolated product of polycondensation was filtered and boiled in water (50 cm^3) for 10 min. After cooling and filtration the polythioester was washed with hot water (2 × 50 cm^3) and acetone (50 cm^3) 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 Böetius apparatus at a heating rate of 6°C/min.

Viscosity

The reduced viscosity (dL/g) of a 1% solution of polythioesters in a phenol–tetrachloroethane mixture with a weight ratio of 1 : 3 was measured with a Ubbelohde viscometer at 25°C.

Infrared Analysis

Infrared (IR) spectra were accorded in KBr discs with a Carl-Zeiss UR-20 spectrophotometer.

X-ray Analysis

X-ray photographs were obtained by the Debye–Scherer powder method with a camera 64 mm in diameter and an X-ray Cu tube 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.

Glass Transition Temperature

Measurement of glass temperature was taken in a DSC-12 Perkin-Elmer differential microcalorimeter, at a heating rate of 32°C/min, nitrogen flow rate of 30 cm^3/min, sensibility of apparatus 4 mcal/s, weight of sample 16 mg.

Thermogravimetric Analysis

Measurement of weight loss was taken in a MOM derivatograph (Paulik, Paulik and Erdey, Budapest). Heating time in air, 100 min; measurements relative to Al$_2$O$_3$; heating rate, 10°C/min; amount of polythioester, 100 mg.

Chemical Resistance

In a flask of 200 cm^3 volume, we tried to dissolve 1 g of polythioester in 50 cm^3 of different solvents at room temperature during 48 h.

Mechanical Tests

Vicat Softening Point

Measurement was taken in a Vicat apparatus FWV type (Germany) with 5-kg weight and heating rate 50°C/h.

Tensile Strength

Measurement was taken in a strength machine 1231-U 10 type (S.U.) in the range of weight 0–200 kg.

Impact Strength

Measurement was taken in a Dynstat apparatus (Germany) in the range of measurement 0–10 kG/cm.

Bending Strength

Measurement was taken in a As-102 apparatus (Hungary) with 0–50 kg weight at a gap of supports 60 mm and deformation rate 4 mm/min.

Brinnell Hardness

Measurement was taken in a As-111 apparatus (Hungary) with 31.25 kg/mm^2 weight ball ϕ 5 mm.

Electrical Tests

Measurements were taken at 200-V alternating current in Schering's system Tetex firm and at higher frequencies by using a low-voltage Rhode-Schwarz bridge.

RESULTS AND DISCUSSION

To determine the optimal conditions in interfacial polycondensation of bis(4-mercaptomethylphenyl)sulfide with aliphatic and isomeric phthaloyl acid dichlorides, sebacoyl chloride was chosen as a model system. In the choice of optimal conditions of polycondensation, the highest value of reduced viscosity and the best yield of the process were taken into consideration.

The influence of the following factors on the results of interfacial polycondensation was studied: the kind of organic phase, the concentration and molar ratio of monomers, the quantite ratio of

Table I   Organic Phase Influence on the Reduced Viscosity and Yield of Polythioester from Bis(4-mercaptomethylphenyl)Sulfide with Sebacoyl Chloride[a]

| | Polythioester | |
Organic Phase	η_{red} (dL/g)	Yield (%)
Benzene	0.17	27.0
Benzene–hexane	0.42	85.6
Tetrachloromethane	0.31	45.0
Chlorobenzene	0.32	32.5

[a] Conditions for the reaction: phase ratio 1 : 1; reagents ratio 1 : 1, period for chloride addition 5 min; temperature 20°C.

Table II   Influence of Concentration of Monomers on Reduced Viscosity and Yield of Polythioester from Bis(4-mercaptomethylphenyl)Sulfide and Sebacoyl Chloride[a]

| | Polythioester | |
Molar Concentration of Monomers	η_{red} (dL/g)	Yield (%)
0.20	0.25	75.6
0.15	0.31	76.6
0.10	0.42	85.6
0.05	0.38	73.1

[a] Conditions for reaction are the same as in Table I by using a mixture of benzene–hexane (1 : 1) as an organic phase.

aqueous to organic phase, concentration of hydrogen chloride acceptor, acid chloride excess, rate of addition of acid chloride, the temperature of reaction, and the kind and contribution of catalyst.

The initial reaction conditions were: organic solvent benzene, hydrogen chloride acceptor 0.2M NaOH, concentration of monomers 0.1M, rate of acid dichloride addition 5 min, and temperature of the reaction 20°C.

From the data presented in Table I it follows that the solvent has considerable influence over the reduced viscosity and yield of the polycondensation products. The highest value of reduced viscosity and the best yield was obtained with a benzene–hexane solution in a volume ratio 1 : 1. The higher yield

Table III   Influence of Concentration of Dithiol in the Aqueous Basic Phase on the Reduced Viscosity and Yield of Polythioester from Bis(4-mercaptomethylphenyl)Sulfide with Sebacoyl Chloride[a]

| Concentration of Dithiol (M) | Ratio Organic to Aqueous Phase | Polythioester | |
		η_{red} (dL/g)	Yield (%)
0.1	1 : 1	0.42	85.6
0.2	1 : 0.5	0.38	81.1
0.4	1 : 0.25	0.33	81.0
0.8	1 : 0.125	0.29	76.6
1.0	1 : 0.1	0.26	76.1

[a] Conditions for the reaction: reagents ratio 1 : 1; period for chloride addition 5 min; temperature 20°C; organic phase benzene–hexane.

Table IV   Influence of the Excess of Hydrogen Chloride Acceptor (NaOH) on the Reduced Viscosity and Yield of Polythioester from Bis(4-mercaptomethylphenyl)Sulfide with Sebacoyl Chloride[a]

Excess of NaOH (%)	Polythioester	
	η_{red} (dL/g)	Yield (%)
0	0.42	85.6
50	0.64	86.6
100	0.67	87.2
200	0.50	86.1

[a] Conditions for the reaction: reagents ratio 1 : 1; phase ratio 1 : 1; organic phase benzene–hexane; period for chloride addition 5 min; temperature 20°C.

and the higher value of reduced viscosity of product while using this mixture in comparison with benzene alone are probables caused by increased solubility of the organic phase in water in the presence of hexane. Additionally, it was found that the obtained product is easier to reparate by filtration than while using other solvents. Furthermore, in the optioptimization process only a benzene–hexane mixture was used for polycondensation as an organic phase. The effect of monomers concentration on reduced viscosity and yield polythioester in the range 0.05–0.2M was determined. A constant volume of water and organic phase was used and the amount of dithiol and acid chloride was changed.

Table V   Influence of the Excess of Acid Chloride on the Reduced Viscosity and Yield of Polythioester from Bis(4-mercaptomethylphenyl)Sulfide with Sebacoyl Chloride[a]

Excess of Acid Chloride (% M)	Polythioester	
	η_{red} (dL/g)	Yield (%)
0	0.67	87.2
10	0.61	82.1
20	0.46	81.8
30	0.42	80.2
40	0.39	82.0
50	0.40	83.0

[a] Conditions for the reaction are the same as in Table IV except using 100% excess of NaOH.

Table VI   Influence of Time of Acid Chloride Addition on the Reduced Viscosity and Yield of Polythioester from Bis(4-mercaptomethylphenyl)Sulfide with Sebacoyl Chloride[a]

Time (s)	Polythioester	
	η_{red} (dL/g)	Yield (%)
10	0.46	78.8
60	0.52	81.2
120	0.62	84.8
300	0.67	87.2
600	0.53	82.1
1200	0.48	83.2

[a] Conditions for the reaction: reagents ratio 1 : 1; phase ratio 1 : 1; organic phase benzene–hexane; temperature 20°C; 100% excess of NaOH.

From Table II it follows that the highest value of reduced viscosity and the best yield was 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 1 : 1–0.1 : 1, which corresponded to the concentration of dithiol in the aqueous–basic phase 0.1 : 1.0 mol/L.

The results presented in Table III show that the highest value of reduced viscosity and the best yield of the polythioester was obtained with a 0.1 M solution of dithiol (phase ratio 1 : 1) in aqueous water

Table VII   Influence of Temperature on the Reduced Viscosity and Yield of Polythioester from Bis(4-mercaptomethylphenyl)Sulfide with Sebacoyl Chloride[a]

Temperature (°C)	Polythioester	
	η_{red} (dL/g)	Yield (%)
10	0.60	78.8
15	0.58	83.3
20	0.67	87.2
25	0.55	85.1
35	0.44	82.2
50	0.32	81.0

[a] Conditions for the reaction are the same as in Table VI by using period for chloride addition, 5 min.

Table VIII   Influence of Kind and Concentration of Catalyst on the Reduced Viscosity and Yield of Polythioester from Bis(4-mercaptomethylphenyl)Sulfide and Sebacoyl Chloride[a]

| Catalyst (% wt) | Polythioester | |
	η_{red} (dL/g)	Yield (%)
—	0.67	87.2
BTEA (5)	0.53	86.0
BTPP (5)	0.93	92.3
MTPA (5)	—	—
BTPP (1)	0.68	86.1
BTPP (3)	0.70	90.2
BTPP (4)	0.82	92.7
BTPP (5)	0.93	92.3
BTPP (6)	0.85	91.7

[a] Conditions for the reaction are the same as in Table VII.

phase. It is in agreement with experimental data obtained by many autors who have produced different polycondensates including also polythioesters.

In the further optimization process, influence of excess sodium hydroxide as a hydrogen chloride acceptor on the results of polycondensation was studied. As shown in Table IV, use of excess sodium hydroxide in relation to the amount stoichiometrically necessary at first causes increases and then decreases in the value of reduced viscosity. The highest value of reduced viscosity and yield are achieved by using 50–100% excess of sodium hydroxide. The advantageous influence of some excess of NaOH may be explained by increased activity of tiolane with simultaneous increase in their solubil-

ity. Excess of NaOH over 100% results in accelerated acid dichloride hydrolysis of COCl and groups of polymer chain as well as removing unreacted monomers. Probably reaction rate of tiolane with acid chloride is higher than hydrolysis rate of COCl groups.

In the further investigations, 100% molar excess of sodium hydroxide was used. The molar excess effect of acid chloride on the value of reduced viscosity and yield of polythioester is shown in Table V. The negative contribution of the excess of acid chloride is observed. The effect of the rate of addition of acid chloride on the value of reduced viscosity and yield is shown in Table VI. It can be seen that the optimal time of acid chloride addition is 2–5 min; either shorter or longer time decreases the value of reduced viscosity and yield.

The effect of temperature on the value of reduced viscosity and yield was studied in the 10–50°C range. As Table VII shows, the best results of polycondensation are achieved in the 15–25°C range. The influence of the kind and concentration of catalyst on the value of reduced viscosity by using benzyltriethylammonium chloride (BTEA) and benzyltriphenylphosphonium chloride (BTPP) was studied.

At first, by using the above-mentioned 5% weight in relation to the volume of dithiol, the best result of polycondensation with BTPP was obtained. In the further investigations influence of concentration of BTPP in the range 1–6% by weight on the value of reduced viscosity and yield was defined. As shown in Table VIII, the best results for obtaining the polythioesters were achieved with contribution of BTPP in the range of 4–6% by weight in relation to the amount of dithiol.

Polythioesters from glutaroyl, adipoyl, pimeloyl, suberoyl, azelainoyl, phthaloyl, isophthaloyl, and

Table IX   Some Physiocochemical Properties of Polythioester Derivatives Bis(4-mercaptomethylphenyl)Sulfide and Acid Dichlorides[a]

Acid Dichlorides	η_{red} (dL/g)	Yield (%)	Softening Range (°C)	Glass Temperature (°C)
Glutaroyl	0.74	73.4	162–179	114
Adipoyl	0.96	88.8	180–199	108; 124
Pimeloyl	0.65	80.1	115–124	—
Suberoyl	0.80	96.0	192–208	84
Azelanoyl	0.83	95.2	148–167	84.5; 113.5
Sebacoyl	0.93	92.3	138–156	77
Phthaloyl	0.23	78.3	164–181	84.5; 109
Isophthaloyl	0.66	88.1	205–226	90
Terephthaloyl	—	95.5	194–225	140

Table X   Results of Elementary Analysis of Polythioesters Derivatives Bis(4-mercaptomethylphenyl)Sulfide and Acid Dichlorides

Acid Dichlorides	Analysis					
	C (%)		H (%)		S (%)	
	Calcd	Found	Calcd	Found	Calcd	Found
Glutaroyl	60.93	60.18	4.84	4.44	25.68	25.36
Adipoyl	61.82	61.28	5.19	5.23	24.76	24.08
Pimeloyl	62.65	62.21	5.52	4.93	23.90	23.41
Suberoyl	63.42	62.99	5.81	5.13	23.09	22.78
Azelanoyl	64.14	64.33	6.09	5.74	22.33	22.19
Sebacoyl	64.82	64.40	6.35	5.91	21.63	21.07
Phthaloyl	64.67	64.37	3.95	3.56	23.55	24.05
Isophthaloyl	64.67	63.88	3.95	3.23	23.55	23.92
Terephthaloyl	64.67	64.12	3.95	3.56	23.55	23.11

terephthaloyl chlorides were prepared under the same optimal conditions as for sebacoyl chloride.

Table IX lists the values of reduced viscosity, yield, softening range, and glass temperature of all polythioesters obtained from bis(4-mercaptomethylphenyl)sulfide and some aliphatic and isomeric phthaloyl dichlorides.

Structure of Polythioesters

The structure of all polythioesters obtained under the model conditions was determined by elemental

analysis, infrared spectra, and X-ray analysis. The results of elementary analysis are given in Table X.

X-ray Analysis

It follows from the X-ray analysis data that all polythioesters indicate various degrees of crystallinity. Numerical data were estimated according to the accepted scale[32]: high, low, and insignificant degree of crystallinity. Thus, polythioesters obtained from bis(4-mercaptomethylphenyl)sulfide and glutaroyl, adipoyl, pimeloyl, sebacoyl, and phthaloyl chlorides belong to group with high degree of crystallinity.

Table XI   Thermal Properties of Polythioesters from Bis(4-mercaptomethylphenyl)Sulfide and Acid Dichlorides
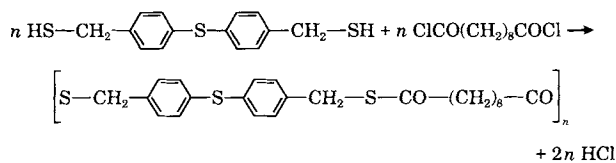
Acid Dichlorides	Thermal Analysis[a]			Mass Loss, (%)				
	T_1 (°C)	U (%)	T_2 (°C)	Temperature (°C)				
				300	350	400	450	500
Glutaroyl	290	0.5	330	1.0	33.5	39.0	41.0	43.0
Adipoyl	295	1.0	345	2.5	40.0	54.5	57.0	59.5
Pimeloyl	290	1.0	370	1.0	14.0	52.0	57.0	60.0
Suberoyl	295	1.5	370	1.5	12.0	43.0	49.5	53.0
Azelanoyl	295	0.5	380	0.5	11.0	49.0	60.5	67.0
Sebacoyl	295	2.0	370	2.5	14.0	45.0	52.5	57.0
Phthaloyl	270	3.5	310	16.0	39.0	41.5	42.0	44.0
Izophthaloyl	28.0	1.0	350	1.5	12.5	19.0	23.0	26.0
Terephthaloyl	290	0.5	330	1.0	12.5	18.5	21.5	27.0

[a] T_1 = temperature of initial exothermic effect from the curve DTA; U = mass loss in temperature T_1; T_2 = temperature for maximum velocity of decomposition from the curve DTA.

Polythioesters obtained from dithiol and azelainoyl and isophthaloyl chlorides have low crystallinity. Polythioesters from dithiol and suberoyl and terephthaloyl chlorides show insignificant crystallinity.

IR spectra of polythioesters showed strong absorptions at 1660–1680 cm^{-1} and are characteristic for carbonyl valency band; those at 937–975 are attributed to the $-S-CO-$ stretch vibration; those at 645–680 cm^{-1} are characteristic for sulfide band. The absorption bands in the regions 820–840 cm^{-1} show disubstitution of benzene rings in para position.

On the basis of good agreement between the calculated and the obtained analytical data and IR spectra, reaction scheme for bis(4-mercaptomethylphenyl)sulfide and sebacoyl chloride as an example was taken as:

$$n\ HS-CH_2-\bigcirc-S-\bigcirc-CH_2-SH + n\ ClCO(CH_2)_8COCl \rightarrow$$

$$\left[S-CH_2-\bigcirc-S-\bigcirc-CH_2-S-CO-(CH_2)_8-CO \right]_n$$

$$+ 2n\ HCl$$

Thermal Properties

The thermal resistance of the polythioesters were examined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The temperature of initial decomposition of its mass loss in percent, the temperature of the fastest decomposition process, and percentage mass loss at 300–500°C were deduced from the curves. Numerical data are presented in Table XI.

Mechanical and Electrical Properties

Some mechanical and electrical properties were determined only for polythioesters from sebacoyl and

Table XII   Mechanical Properties of Polythioesters from Bis(4-mercaptomethylphenyl)Sulfide and Acid Dichlorides

Test	Sebacoyl	Isophthaloyl
Temperature of pressing (°C)	150	220
Vicat softening point (°C)	107	205
Tensile strength (kg/cm²)	102.2	124.7
Impact strength (kg/cm²)	5.8	1.3
Bending strength (kg/cm²)	108.1	171.5
Brinnell hardness (kg/mm²)	320.0	650.0
Modulus of elasticity (kg/cm²)	743.2	2361.6

Table XIII   Some Electric Properties of Polythioesters from Bis(4-mercaptomethyl phenyl)Sulfide and Acid Dichlorides at 20°C

Test	Acid Dichloride	
	Sebacoyl	Isophthaloyl
Dielectrical constant ε at frequency (kHz)		
0.05	5.91	4.06
1	5.36	4.08
10	4.89	3.97
100	4.50	3.85
Dielectrical loss factor tan $\delta \times 10^{-4}$ at frequency (kHz)		
0.05	600	106
1	585	101
10	535	123
100	380	180
Volume resistivity $\Omega \times$ cm at frequency		
0.05	1.3×10^{14}	1.6×10^{14}

isophthaloyl chlorides. For mechanical properties moldings (90 × 10 × 4 mm) and for electrical properties discs (ϕ 35 × 0.5 mm) were used. Above moldings and discs were obtained by pressing, at first at room temperature under a pressure 500 kg/cm² and then at 150°C for sebacoyl and 220°C for isophthaloyl dichloride at a pressure 160 kg/cm². Numerical data are given in Table XII.

Disc electrical tests were metallized by silver in vacuum. Electrical properties were characterized by dielectric constant (ε), dielectric loss factor (tan δ), and volume resistivity (ρ). The examinations were made at a frequency 0.05 kHz, at 20, 40, 60, and 80°C for sebacoyl and additionally at 100 and 120°C for isophthaloyl chloride. The values of ε, tan δ, and ρ at a frequency 0.05, 1, 10, and 100 kHz at 20°C were determined. Results are given in Tables XIII and XIV.

From Tables XIII and XIV it follows that ε values of polythioesters show small changes in the frequency range of 0.05–100 kHz. Dielectric loss factor decreases with increase of frequency for sebacoyl chloride and increase with increase of frequency for isophthaloyl chloride. The changes of dielectric constant of polythioester from sebacoyl chloride with temperature in the range of 20–40 are small, but its value at 80°C is seven times higher than at 20°C. In the case of isophthaloyl chloride, the

Table XIV   Changes of Electric Properties of Polythioesters from Bis(4-mercaptomethylphenyl)Sulfide and Acid Dichlorides[a]

Test	Acid Dichloride	Temperature (°C)				
		40	60	80	100	120
ε	Sebacoyl	7.80	15.66	42.1	—	—
$\tan \delta \times 10^{-4}$		826	1231	63600	—	—
$\Omega \times cm$		1.8×10^9	7.2×10^9	2.5×10^9		
ε	Isophthaloyl	3.97	3.94	3.96	4.85	5.76
$\tan \delta \times 10^{-4}$		70	40	23	839	913
$\Omega \times cm$		7.6×10^{14}	1.1×10^{15}	1.4×10^{12}		7.2×10^{10}

changes of dielectric constant are very small with increase temperature. The values of $\tan \delta$ and ρ undergo clear changes with increase of temperature.

Chemical Resistance

The polythioesters show good resistance to acetone, benzene, dioxane, dimethylsulphoxide, dimethylformamide, and methylene chloride. Derivatives of pimeloyl, suberoyl, azelainoyl, and sebacoyl dichlorides dissolve partially in chloroform and tetrachloroethane. All polythioesters dissolve completely in a mixture of phenol–tetrachloroethane (1 : 3 weight) except the polythioesters from terephthaloyl dichlorides. All are resistant to dilute alkali and mineral acids but decompose in conc. H_2SO_4 and HNO_3.

CONCLUSION

Polythioesters derivatives of bis(4-mercaptomethylpfenyl)sulfide and some aliphatic as well as isomeric phthaloyl dichlorides were obtained by interfacial polycondensation with good yield and reduced viscosity.

The best properties of these polymers were obtained when the molar concentration of monomers was $0.1 M$, ratio of the aqueous to organic phase (mixture benzene–hexane 1 : 1) was 1 : 1, temperature 20°C, and period for acid chloride addition was 5 min. Clear improvement of results of polycondensation were achieved when 50–100% molar excess of NaOH and catalyst; BTPP about 5% by weight was used.

All polythioesters obtained by interfacial polycondensation in the optimal conditions have good thermal and chemical resistance. Polythioester from bis(4-mercaptomethylphenyl)sulfide and isophthaloyl chloride shows much better dielectric properties than polythioester obtained with dithiol and sebacoyl chloride.

REFERENCES

1. P. W. Morgan, *Condensation Polymers by Interfacial and Solution Methods*, Wiley-Interscience, New York, 1965.
2. V. V. Korshak and S. V. Vinogradova, *Nieravnoviesnaja Polycondensacja*, Izdatielstwo Nauka, 1972.
3. P. W. Morgan, Interfacial Polymerization, *Encyclopedia of Polymer Science and Technology*, Vol. 8, p. 221 (1987).
4. E. L. Wittbacker and P. W. Morgan, *J. Polym. Sci.*, **40**, 289 (1959).
5. W. E. Earecson, *J. Polym. Sci.*, **40**, 399 (1959).
6. V. V. Korshak, S. V. Vinogradova, and A. S. Lebedeva, *Vysokomol. Soedin.*, **2**, 1162 (1960).
7. V. V. Korshak and S. V. Vinogradova, *Russ. Chem. Rev.* (English Transl.), **30**, 171 (1961).
8. V. V. Korshak, S. V. Vinogradova, and A. S. Lebedeva, *Vysokomol. Soedin.*, **2**, 61 (1960).
9. E. E. Magaz, U.S. Pat. 2,831,834 (1958).
10. S. A. Sundet, W. A. Harpkey, and S. B. Speck, *J. Polym. Sci.*, **40**, 389 (1959).
11. S. B. Speck, U.S. Pat. 2,808,394 (1957).
12. E. L. Wittbacker, U.S. Pat. 2,816,879 (1957).
13. V. V. Korshak and S. V. Vinogradova, *Vysokomol. Soedin.*, **4**, 982 (1962).
14. V. V. Korshak, T. M. Frunze, S. V. Vinogradova, V. V. Kurashev, and A. S. Lebedeva, *Vysokomol. Soedin.*, **3**, 371 (1961); *Polym. Sci.* (S.U.) (English Transl.), **3**, 109 (1962).
15. M. S. Akutin and L. A. Rodilova, *Plast. Massy*, **19**, 14 (1960).
16. T. M. Frunze, V. V. Korshak, V. V. Kurashev, and P. A. Alievski, *Vysokomol. Soedin.*, **1**, 1795 (1959).

17. V. V. Korshak, S. V. Vinogradova, P. M. Valeckij, and Ju. Mirnow, *Vysokomol. Soedin.*, **3**, 66 (1961).
18. A. I. Conix, *Ind. Eng. Chem.*, **51**, 147 (1959).
19. V. V. Korshak, S. V. Vinogradova, T. M. Frunze, A. S. Lebedeva, and V. V. Kurashev, *Vysokomol. Soedin.*, **3**, 984 (1961).
20. A. I. Conix, Fr. Pat. 1,284,226 (1962); RFN Pat. 1,162,079 (1964).
21. W. Podkościelny and A. Kultys, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 655 (1976); **22**, 2265 (1984).
22. W. Podkościelny and W. Kowalewska, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 1025 (1984); **22**, 1579 (1984).
23. W. Podkościelny and W. Kowalewska, *J. Appl. Polym. Sci.*, **39**, 1649 (1990).
24. W. Podkościelny and D. Wdowicka, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 2961 (1983).
25. W. Podkościelny and S. Szubińska, *J. Appl. Polym. Sci.*, **32**, 3277 (1986); **34**, 143 (1987); **35**, 85, 1853 (1988).
26. C. S. Marvel and A. J. Kotek, *J. Am. Chem. Soc.*, 1100 (1951).
27. Brit. Pat. 783,546; 786,178 (1957).
28. U.S. Pat. 2,870,126 (1959).
29. U.S.S.R. Pat. 203,902 (1967).
30. Ger. Pat. 2,016,031 (1971).
31. U.S. Pat. 2,510,567 (1950).
32. W. Podkościelny and W. Rudż, *J. Appl. Polym. Sci.*, **47**, 1523 (1993).
33. W. Podkościelny and W. Rudż, *Eur. Polym. Sci.*, **29**, 69 (1993).
34. W. Rudż, Doctoral Dissertation, Maria Curie-Skłodowska University, Lublin, Poland, 1981.
35. E. Massarani and L. Mauri, *Farmaco (Pavia), Ed. Prac.*, **19**, 958 (1964).