

Linear Polythioesters. XVIII. Products of Interfacial Polycondensation of Bis(4-Mercaptophenyl)Sulfide with Aliphatic and Aromatic Acid Dichlorides

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SYNOPSIS

New polythioesters were synthesized by interfacial polycondensation of bis(4-mercaptophenyl)sulfide with aliphatic and isomeric phthaloyl chlorides. To determine the optimal conditions for polycondensation, we studied the influence of the following factors on the yield and reduced viscosity: type of organic solvent, concentration and molar ratio of monomers, ratio of aqueous to organic phase, concentration of hydrogen chloride acceptor (NaOH), acid chloride excess, rate of addition of acid chloride, the temperature of reaction, and the kind and the contribution of catalyst. A thorough examination was carried out for the polycondensation of dithiol, with sebacoyl and isophthaloyl chlorides chosen as a model systems. Polythioesters from aliphatic dichlorides were prepared under the optimal conditions used for sebacoyl chloride. For polythioesters from phthaloyl and terephthaloyl chlorides, the conditions were those used for isophthaloyl chloride. The structure of polythioesters was determined from infrared, X-ray, and elementary analysis. Some physico-chemical, thermal, mechanical, and electrical properties are reported. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Bis(4-mercaptophenyl)sulfide is used with success for the synthesis of many kinds of polymers.

Preparation of polythioethersulfones, derivatives of the above compound, was described in 1970 in a German patent.¹ The reaction was carried out by means of high-temperature solution polycondensation with the use of dimethylformamide and sodium hydroxide at a temperature of 130–140°C. Polythioethersulfones, with great thermal and chemical resistance, obtained in such a way were subsequently oxidized to suitable polyarylsulfones.

In 1968, a British patent² reported the synthesis of polymers that showed high thermal resistance by polycondensation of bis(4-mercaptophenyl)sulfide with 4,4'-dibromobenzophenone, as well as with 2,5-dibromo-1,4-dinitrobenzene, under similar conditions, that is, using dimethylformamide KOH at 130–140°C.

In 1957,³ attempts at preparation of thioetherglycidyl resins were undertaken by means of polycondensation of bis(4-mercaptophenyl)sulfide with epichlorohydrin in the aqueous solution of sodium hydroxide, which were then cured chemically using acid anhydrides. Resins obtained by this method were brittle solids with very low reduced epoxide content in comparison with the theoretical calculations.

However, the thioetherglycidyl resins from bis(4-mercaptophenyl)sulfide and epichlorohydrin have since been prepared with high epoxide content by heterophase alkaline condensation using NaOH in water or isopropanol.⁴ It is worth noting that these resins have good thermal and mechanical properties. Our current efforts concentrate on how to utilize bis(4-mercaptophenyl)sulfide for synthesis of polythioesters. It should be noted that work on the preparation, structure, and properties of these polymers has been conducted systematically in our laboratory for more than 15 years. Investigations previous to this study have been concerned with synthesis of polythioesters by polycondensation of

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dithiol derivatives of benzophenone,⁵ diphenylether,⁶ and naphthalene,⁷ with some aliphatic and isomeric phthaloyl dichlorides. Synthesis, structure, and properties of polythioesters, derivatives of di(mercaptomethyl)-xylenes, -trimethylbenzene,⁸ and -tetramethylbenzene,⁹ were also studied in great detail. In the applied dithiols, SH groups were attached directly to a benzene ring or thorough the $-\text{CH}_2$ group. All syntheses of polythioesters were carried out by means of interfacial, low-temperature, and high-temperature solution polycondensation, but interfacial polycondensation proved to be the most useful.

We found that the following factors greatly influence this process: catalyst, excess of hydrochloride acceptor, temperature, and rate of addition of acid dichloride. To obtain more information on the general properties of polythioesters, polymers from bis(4-mercaptophenyl)sulfide and aliphatic dichlorides and isomeric phthaloyl chlorides were synthesized.

EXPERIMENTAL

Reagents

Bis(4-mercaptophenyl)sulfide, with a melting point (m.p.) of 116–118°C (after crystallization from cyclohexane) was obtained from bis(4-chlorosulfonylphenyl)sulfide by reduction with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in acetic acid saturated with dry hydrogen chloride by the Marvel and Caesar method used to prepare bis(mercaptophenyl)oxide.¹⁰

The synthesis of dithiol is described in our earlier publications.^{4,11}

Malonyl [boiling point (b.p.) 53–54°C/19 mm Hg], glutaroyl (b.p. 107–108°C/16 mm Hg), adipoyl (b.p. 128–130°C/18 mm Hg), pimeloyl (b.p. 137°C/15 mm Hg), suberoyl (b.p. 143–147°C/12 mm Hg), azelainoyl (b.p. 166°C/18 mm Hg), and sebacoyl (b.p. 166–168°C/11 mm Hg) chlorides were obtained by chlorination of the suitable acids with thionyl chloride. Succinyl chloride (b.p. 103–104°C/25 mm Hg), was obtained from the reaction of succinic acid and phosphorous pentachloride. Commercial oxaloyl chloride (b.p. 63°C), was purified by distillation. Terephthaloyl chloride (m.p. 83°C), isophthaloyl chloride (m.p. 44°C, after crystallization from hexane), and phthaloyl chloride (b.p. 131–133°C/9–10 mm Hg) were obtained by the reactions of phosphorous pentachloride with suitable acids.

The Synthesis of Polythioesters

The synthesis of polythioesters for the polycondensation of bis(4-mercaptophenyl)sulfide with sebacoyl and isophthaloyl was achieved as follows:

Polythioester from Sebacoyl Chloride

In a three necked, round-bottomed flask of 500 cm³ volume, equipped with a mechanical stirrer (2000 rpm), thermometer, and dropper, 2.5 g (0.01 mol) of bis(4-mercaptophenyl)sulfide, 50 cm³ of benzene and sodium hydroxide solution (0.08 g NaOH in 50 cm³ of water), and 5% by weight of benzyltriphenylphosphonium chloride were added. After thorough mixing, 2.3 g (0.011 mol) of sebacoyl chloride solution in 50 cm³ hexane was added over a period 3 min at 20°C under vigorous stirring.

After the addition of the acid chloride was complete, stirring was continued for 15 min and the mixture was then acidified with hydrochloric acid (Kongo Red). The isolated product of polycondensation was filtered and boiled in water (50 cm³) for 10 min. After cooling and filtration, the polythioester was washed with hot water ($2 \times 100 \text{ cm}^3$) and acetone (50 cm³) and was dried under pressure (15 mm Hg) at 60°C to a constant weight.

Polythioester from Isophthaloyl Chloride

As in the first method, 2.5 g (0.01 mol) of bis(4-mercaptophenyl)sulfide, 50 cm³ benzene, and a sodium hydroxide solution (1.2 g in 100 cm³ of water) and 5% by weight of benzyltriphenylphosphonium chloride were added. After thorough mixing, 2.23 g (0.011 mol) of an isophthaloyl chloride solution in 50 cm³ hexane was added over a period of 5 min at 20°C under vigorous stirring. After the complete addition of the acid chloride, the procedure was as described previously.

MEASUREMENT OF PROPERTIES

Melting Point

Melting point determinations were made on a Boettius apparatus.

Viscosity

The reduced viscosity (dL/g) of a 1% solution of polythioesters in a phenol/tetrachloroethane mix-

ture, with a weight ratio of 1 : 3, was measured with a Ubbelohde viscometer at 25°C.

Infrared Analysis

Infrared (IR) spectra were obtained with a Carl Zeiss UR-20 spectrophotometer.

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.

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, with a nitrogen flow rate of 30 cm³/min. The apparatus sensitivity was 4 mcal/sec and the weight of sample was 16 mg.

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.

Table I Organic Phase Effect on the Reduced Viscosity and Yield Polythioesters from Bis(4-Mercaptophenyl)Sulfide with Sebacyl (Polythioester 1) and Isophthaloyl (Polythioester 2) Chlorides

Organic Phase	Polythioester 1		Polythioester 2	
	η Red (dL/g)	Yield (%)	η Red (dL/g)	Yield (%)
Benzene	1.20	93.7	2.02	94.7
Benzene/Hexane	1.22	96.1	1.26	81.6
Tetrachloromethane	1.20	91.3	0.82	63.2
Chlorobenzene	1.04	81.7	1.78	86.8
Methylene chloride	0.17	57.3	—	—
Chloroform	0.08	79.3	1.21	68.4
Tetrachloroethane	0.16	52.9	—	—

Table II The Influence of Concentration of Monomers on Reduced Viscosity and Yield of Polythioester from Bis(4-Mercaptophenyl)Sulfide with Sebacyl (Polythioester 1) and Isophthaloyl (Polythioester 2) Chlorides

Molar Concentration of Monomers	Polythioester 1		Polythioester 2	
	η Red (dL/g)	Yield (%)	η Red (dL/g)	Yield (%)
0.20	0.79	93.7	1.40	89.5
0.15	1.12	96.1	—	—
0.10	1.22	96.1	2.02	94.7
0.05	1.20	91.3	1.86	97.4

Chemical Resistance

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

RESULTS AND DISCUSSION

To determine the optimal conditions of interfacial polycondensation, bis (4-mercaptophenyl) sulfide with sebacyl and isophthaloyl chlorides were chosen as model systems. In the choice of optimal conditions, 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 quantitative ratio of 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 0.2 M NaOH, concentration of dithiol 0.1 M, concentration of acid dichloride 0.1 M, rate of acid dichloride addition 5 min, and temperature of the reaction 20°C.

The applied organic phase, and some physico-chemical values obtained, are listed in Table I. From the data presented, it follows that the solvent considerably influences the yield and reduced viscosity of the polycondensation products. The best yield and the highest value of reduced viscosity were obtained with a benzene/hexane mixture in a volume ratio 1 : 1 for polythioesters from sebacyl chloride and with benzene for polythioester from isophthaloyl chloride.

Table III The Influence of Concentration of Dithiol in the Aqueous-Basic Phase on the Reduced Viscosity and Yield of Polythioester from Bis(4-Mercaptophenyl)Sulfide with Sebacyl (Polythioester 1) and Isophthaloyl (Polythioester 2) Chlorides

Concentration of Dithiol	Ratio Organic to Aqueous Phase	Polythioester 1		Polythioester 2	
		η Red (dL/g)	Yield (%)	η Red (dL/g)	Yield (%)
0.1	1 : 1	1.26	96.1	2.02	94.7
0.2	1 : 0.5	1.32	96.1	1.32	89.5
0.4	1 : 0.25	1.26	91.3	—	—
0.8	1 : 0.125	1.17	81.7	—	—
1.0	1 : 0.1	1.04	72.1	1.22	52.6

In the further optimized process, only the benzene/hexane mixture was used for polycondensation with sebacyl chloride and benzene with isophthaloyl chloride. The effect of the monomer concentration in the range 0.05–0.2 M on reduced viscosity and yield of polythioesters was determined.

A constant volume of water and organic phase was used and the amount of dithiol and acid chloride was changed. From the data presented in Table II, it follows that the highest reduced viscosity and the best yield were obtained with 0.1 M solutions.

The influence 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 con-

Table IV The Influence of the Excess of Hydrogen Chloride Acceptor (NaOH) on the Reduced Viscosity and Yield of Polythioester from Bis(4-Mercaptophenyl)Sulfide with Sebacyl (Polythioester 1) and Isophthaloyl (Polythioester 2) Chlorides

Excess of NaOH (%)	Polythioester 1		Polythioester 2	
	η Red (dL/g)	Yield (%)	η Red (dL/g)	Yield (%)
0	1.32	96.1	2.02	94.7
50	1.18	96.0	2.15	94.7
100	1.08	95.8	2.11	89.5
200	0.92	93.7	1.80	89.4

Table V The Influence of the Excess of Acid Chloride on the Reduced Viscosity and Yield of Polythioester from Bis(4-Mercaptophenyl)Sulfide with Sebacyl (Polythioester 1) and Isophthaloyl (Polythioester 2) Chlorides

Excess of Acid Chloride (% M)	Polythioester 1		Polythioester 2	
	η Red (dL/g)	Yield (%)	η Red (dL/g)	Yield (%)
0	1.32	96.1	2.15	94.7
10	1.38	91.3	2.13	94.7
20	1.30	93.7	2.05	94.6
30	1.28	91.3	1.96	89.5
40	1.10	93.7	1.74	89.5
50	1.01	96.1	1.59	89.5

centration 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 polythioesters were obtained with a 0.2 M solution of dithiol (phase ratio 1 : 2) in aqueous water phase with sebacyl chloride and with 0.1 M (phase ratio 1 : 1) solution of dithiol for isophthaloyl chloride. Probably these results are connected with the different reactivity of the dichlorides used.

In the process of further optimization, influence of excess sodium hydroxide as a hydrogen chloride acceptor on the results of polycondensation were studied.

As shown in Table IV, the use of excess sodium hydroxide, in relation to the amount stoichiometrically necessary, causes decreases in the value of

Table VI The Influence of Time of Acid Chloride Addition on the Reduced Viscosity and Yield of Polythioester from Bis(4-Mercaptophenyl)Sulfide with Sebacyl (Polythioester 1) and Isophthaloyl (Polythioester 2) Chlorides

Time (sec)	Polythioester 1		Polythioester 2	
	η Red (dL/g)	Yield (%)	η Red (dL/g)	Yield (%)
10	1.29	93.7	1.75	89.5
60	1.32	96.1	—	—
120	1.37	96.1	1.93	84.2
300	1.34	96.2	2.16	94.7
600	1.26	93.1	2.01	94.7
1200	0.73	86.5	1.86	94.7

reduced viscosity and in the yield of polythioesters from sebacoyl chloride. The highest value of reduced viscosity, and the good yield of polythioesters from isophthaloyl chloride, are achieved by using a 50% excess of sodium hydroxide. A further increase in acceptor excess decisively decreases the reduced viscosity and yields of the process, probably because of an increase in the adjacent hydrolysis process.

In further investigations, 50% molar excess of sodium hydroxide was used for polycondensations with isophthaloyl chloride. The molar excess effect of acid chloride on the value of reduced viscosity and yield of polythioesters is shown in Table V. A slight beneficial influence of a 10% excess of acid chloride on reduced viscosity and yield was observed. The effect of the rate of addition of acid chloride on the value of reduced viscosity and yield is shown in Table VI.

The optimal time for the addition of acid chloride was 2–5 min; either shorter or longer time decreased 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 highest value of reduced viscosity and the best yield were achieved in the 10–25°C range. The influence of the kind and concentration of catalyst on the value of reduced viscosity, by using benzyltriethylammonium chloride (BTEA), benzyltriphenylphosphonium chloride (BTPP), and methyltriphenylarsonium iodide (MTPA), 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 investigations that followed, the influence of the concentration of BTPP in the range 1–5% by

Table VII The Influence of Temperature on the Reduced Viscosity and Yield of Polythioester from Bis(4-Mercaptophenyl)Sulfide with Sebacoyl (Polythioester 1) and Isophthaloyl (Polythioester 2) Chlorides

Temperature (°C)	Polythioester 1		Polythioester 2	
	η Red (dL/g)	Yield (%)	η Red (dL/g)	Yield (%)
10	1.32	91.3	2.07	97.4
15	1.35	96.1	2.10	97.4
20	1.38	96.1	2.15	94.7
25	1.30	91.0	2.10	94.7
35	1.10	81.7	2.08	94.7
50	0.69	52.9	1.93	94.7

Table VIII The Influence of Kind and Concentration of Catalyst on the Reduced Viscosity and Yield of Polythioester from Bis(4-Mercaptophenyl)Sulfide with Sebacoyl (Polythioester 1) and Isophthaloyl (Polythioester 2) Chlorides

Catalyst	(% wt)	Polythioester 1		Polythioester 2	
		η Red (dL/g)	Yield (%)	η Red (dL/g)	Yield (%)
—	—	1.38	96.1	2.02	94.7
BTEA	(5)	1.02	97.5	1.58	76.3
BTPP	(5)	2.32	96.4	2.38	94.8
MTPA	(5)	1.60	90.8	—	—
BTPP	(1)	1.44	93.7	2.08	94.6
BTPP	(2)	1.57	94.0	2.15	94.6
BTPP	(3)	1.89	94.3	2.25	94.8
BTPP	(4)	2.05	95.1	2.22	94.7
BTPP	(5)	2.32	96.4	2.38	94.8

weight on the value of reduced viscosity and yield was defined.

Table VIII shows that the best results for obtaining the polythioesters were achieved with the contribution of PTPP in the range 5–6% by weight in relation to the amount of dithiol. Polythioesters from oxalyl, malonyl, succinyl, glutaroyl, adipoyl, pimenoyl, suberoyl, and azelanoyl dichlorides were prepared under the same optimal conditions as for sebacoyl chloride, and from phthaloyl and terephthaloyl chlorides as those used for isophthaloyl chloride.

Table IX lists the values of reduced viscosity, yield, softening range, and glass transition temperature of all polythioesters obtained from bis(4-mercaptophenyl)sulfide and acid dichlorides.

STRUCTURE OF POLYTHIOESTERS

The structure of all polythioesters obtained under the model conditions was determined by elemental analysis, infrared spectroscopy, 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 a small or high degree of crystallinity. X-ray analysis was carried out with the

Table IX Some Physicochemical Properties of Polythioesters Derivatives Bis(4-Mercaptophenyl)Sulfide and Acid Dichlorides

Acid Dichlorides	η Red (dL/g)	Yield (%)	Softening Range (°C)	Glassy Temperature (°C)
Oxalyl	—	55.9	185–203	—
Malonyl	—	12.6	—	—
Succinyl	—	84.2	188–201	105.5
Glutaroyl	1.02	89.5	146–164	130.5
Adipoyl	0.71	65.3	182–205	—
Pimenoil	0.72	82.8	128–149	—
Suberoyl	1.00	79.8	138–154	—
Azelanoyl	1.58	94.4	151–169	91.5
Sebacoyl	2.18	96.1	135–150	—
Phthaloyl	0.40	71.0	223–239	135 (164)
Isophthaloyl	2.54	97.4	227–248	113.5
Terephthaloyl	—	98.7	238–265	199.0

use of the Debye–Scherrer powder method. The Results of the analysis were that numerical data were estimated according to the accepted scale: high, low, and insignificant degrees of crystallinity. Thus, polythioesters obtained from bis(4-mercaptophenyl)sulfide and adipoyl, seberoyl, sebacoyl, oxalyl, glikoroyl, simeroyl, and phthaloyl chlorides show high degrees of crystallinity. However, polythioesters obtained from dithiol and succinyl, azelanoyl, and therephthaloyl chlorides have low degrees of crystallinity. Finally, polythioester derivatives of

dithiol and isophthaloyl chloride show insignificant degrees of crystallinity.

IR spectra of polythioesters showed strong absorptions at 1660–1690 cm^{-1} (characteristic of carbonyl bond), 920–980 cm^{-1} (attributed to the —COS stretch vibration), and 640–680 cm^{-1} (characteristic of sulfides). The absorption bands in the regions 810–850 cm^{-1} show disubstitution of benzene rings in para position. On the basis of good agreement of the calculated and the obtained analytical data (Table X) and IR spectra, the following

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

Acid Dichlorides	Analysis					
	C (%)		H (%)		S (%)	
	Calcd	Found	Calcd	Found	Calcd	Found
Oxalyl	55.23	55.01	2.65	2.43	31.60	30.68
Succinyl	57.80	56.28	3.64	3.04	28.94	28.15
Glutaroyl	58.93	57.87	4.07	3.91	27.91	26.90
Adipoyl	59.96	59.08	4.47	4.10	26.68	25.93
Pimenoil	60.93	60.02	4.84	4.71	25.68	25.14
Suberoyl	61.82	60.99	5.19	4.82	24.76	23.97
Azelanoyl	62.65	62.29	5.51	5.03	23.89	23.09
Sebacoyl	63.42	63.10	5.81	5.10	23.09	22.87
Phthaloyl	63.13	62.71	3.18	2.80	25.28	24.83
Isophthaloyl	63.13	62.46	3.18	2.96	25.28	25.00
Terephthaloyl	63.13	62.37	3.18	2.95	25.28	24.49

Table XI Thermal Properties of Polythioesters from Bis(4-Mercaptophenyl)Sulfide and Acid Dichlorides

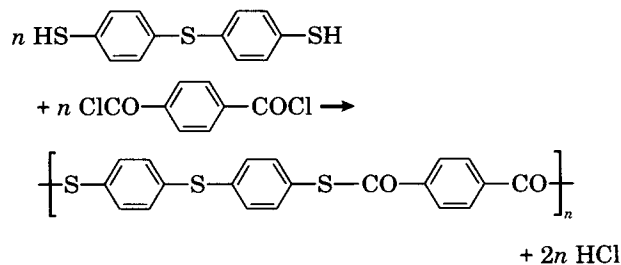
Acid Dichlorides	Thermal Analysis ^a			Mass Loss (%)				
	T_1 (°C)	U (%)	T_2 (°C)	300°C	350°C	400°C	450°C	500°C
Oxalyl	190	1.0	315	11.5	18.5	20.5	22.5	27.0
Succinyl	255	3.0	315	8.0	25.0	27.0	28.5	31.5
Glutaroyl	300	1.0	360	1.0	13.0	36.0	36.5	40.5
Adipoyl	280	1.0	315	3.0	25.0	33.0	34.0	37.0
Pimenoyl	270	1.0	360	2.5	20.5	41.0	42.0	45.0
Suberoyl	300	1.0	360	1.0	5.5	38.0	44.0	47.0
Azelanoyl	310	0.0	370	0.0	5.0	38.0	44.0	47.0
Sebacoyl	330	1.0	380	0.0	5.0	34.0	48.5	52.0
Phthaloyl	280	2.0	340	3.0	19.0	27.0	32.0	90.0
Isophthaloyl	380	2.5	415	1.0	1.5	4.5	19.5	23.5
Terephthaloyl	350	3.0	430	1.5	3.0	6.0	19.5	24.0

^a T_1 = Temperature of initial exothermic effect from the curve DTA.

U = Mass loss in temperature T_1 .

T_2 = Temperature maximum velocity of decomposition from the curve DTA.

reaction scheme (1) for bis(4-mercaptophenyl)sulfide and terephthaloyl chloride, as an example, was assumed:



THERMAL PROPERTIES

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

The greatest thermal resistance is revealed by the polythioethers from glutaroyl, suberoyl, azelanoyl, sebacoyl, isophthaloyl, and terephthaloyl chlorides.

MECHANICAL AND ELECTRICAL PROPERTIES

Some mechanical and electrical properties were determined for polythioesters from sebacoyl and isophthaloyl chlorides. Polymers have been studied after pressing at first at room temperature under a

Table XII Temperature of Pressing and Mechanical Properties of Polythioesters from Bis(4-Mercaptophenyl)Sulfide and Acid Dichloride

Test	Sebacoyl	Terephthaloyl
Temperature of pressing (°C)	140.00	240.00
Vicat softening point (°C)	131.00	270.00
Tensile strength (kg/cm ²)	64.41	29.80
Impact strength (kg/cm ²)	2.50	1.30
Bending strength (kg/cm ²)	174.60	70.70
Brinnell hardness (kg/mm ²)	750.00	530.00
Modulus of elasticity (kg/cm ²)	2577.10	458.40

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

Test	Acid Dichloride	
	Sebacoyl	Terephthaloyl
Dielectrical constant (ϵ) at frequency (kHz)		
0.05	3.89	4.96
1	3.99	4.68
10	3.93	4.59
100	3.87	4.51
Dielectrical loss factor $\tan \delta \times 10^{-4}$ at frequency (kHz)		
0.05	126.0	156
1	60.0	110
10	66.0	200
100	81.0	570
Volume resistivity $\rho \Omega \times \text{cm}$ at frequency 0.05	1×10^{15}	2.1×10^{15}

pressure of 650 Kg/cm², and then at increased temperature at a pressure of 150 Kg/cm² in the upper range of the softening temperature of each polythioester. Moldings for electrical tests were additionally metallized by silver in vacuum. Pressing temperature and numerical data are given in Table XII.

Electric properties were characterized by dielectric constant (ϵ), dielectric loss factor ($\tan \delta$), and volume resistivity (ρ). The examinations were made at a frequency of 0.05 kHz at 20, 40, 60, 80, 100, 120, and 140°C. Furthermore, the values of (ϵ), $\tan \delta$ and (ρ) at frequency 0.05, 1, 10, and 100 kHz were

obtained. Results are given in Tables XIII and XIV. From Table XIII it follows that values of polythioesters show small changes in the frequency range of 0.05–100 kHz. The changes of dielectric constant of polythioesters with the increasing temperature in the range 20–140°C at a frequency of 0.05 kHz are small for terephthaloyl chloride. In the case of sebacoyl chloride, the values of significance increased over 100°C (Table XIV).

CHEMICAL RESISTANCE

The polythioesters show good resistance to acetone, benzene, dioxane, dimethylsulfoxide, dimethylphormamide, and methylene chloride. The polymers from phthaloyl, pimenoyl, suberoyl, azelanoyl, and sebacoyl dichlorides dissolve partially in chloroform, tetrachloroethane, and chlorobenzene. All polythioesters dissolve completely in the mixture of phenol: tetrachloroethane (1 : 3), except the polythioesters from oxalyl, succinyl, and terephthaloyl chlorides. These are resistant to diluted alkali and mineral acids, but decompose in concentrated H₂SO₄ and HNO₃.

CONCLUSION

Most of polythioesters by interfacial polycondensation from bis(4-mercaptophenyl)sulfide and some aliphatic and isomeric phthaloyl dichloride were obtained in high yield with good reduced viscosities. The best results of polycondensation were obtained with 0.2 M solution of dithiol with sebacoyl chloride and with 0.1 M solution of dithiol with isophthaloyl chloride.

Table XIV The Changes of Electric Properties of Polythioesters from Bis(4-Mercaptophenyl)Sulfide and Acid Dichlorides

Test	Acid Dichlorides	Temperature (°C)					
		40	60	80	100	120	140
ϵ		4.22	4.72	5.46	11.90	42.5	54.0
$\tan \delta \times 10^{-4}$	Sebacoyl	32	1086	2080	618	1160	3000
$\rho \Omega \times \text{cm}$		7.4×10^{13}	5.1×10^{12}	1.5×10^{12}	4.4×10^{10}	3.3×10^9	6.4×10^8
ϵ		4.62	4.51	4.61	4.64	4.75	4.87
$\tan \delta \times 10^{-4}$	Terephthaloyl	83	74	53	67	150	308
$\rho \Omega \times \text{cm}$		6.2×10^{14}	3.4×10^{14}	3.1×10^{14}	5.4×10^{13}	3.6×10^{13}	1.5×10^{13}

Dependence on temperature at frequency 0.05 KHZ: dielectrical constant; dielectrical loss factor: volume resistivity.

Excess NaOH (as the hydrogen chloride acceptor) is detrimental for the process with sebacoyl chloride, but produces good results with isophthaloyl chloride. Polythioesters with the highest value of reduced viscosity and good yield were obtained when the time required in the reaction mixture was 2–5 min, and when the polymerization was carried out at 10–25°C. A dependence of the results of polycondensation on the kind and concentration of catalyst is observed. It was found that the use of phase transfer catalyst–BTTP, 5% by weight in relation to the amount of dithiol, increases the value of reduced viscosity twice for polythioester from sebacoyl chloride, but in the case of polythioester synthesis from isophthaloyl chloride it is less effective. Because of their good thermal and chemical resistance, the polythioesters obtained may find use as modifiers of commercial polyesters.

REFERENCES

1. J. Studinka and R. Gabler, German Pat. No. 1938806 (1970).
2. British Pat. No. 1 124 200 (1968), *Chem. Abstr.*, **69**, 97357 g (1969).
3. W. Zerweck and W. Hechtenberg, German Pat. No. 100618 (1957).
4. W. Charmas, W. Podkościelny, and W. Rudź, *J. Appl. Polym. Sci.*, **39**, 1623 (1990).
5. W. Podkościelny and A. Kultys, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 655 (1976); **19**, 2167 (1981); **22**, 2265 (1984).
6. W. Podkościelny and D. Wdowicka, *J. Polym. Sci.*, **30**, 1579 (1985).
7. W. Podkościelny and W. Charmas, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 2429, 3811 (1979).
8. W. Podkościelny and S. Szubińska, *J. Appl. Polym. Sci.*, **32**, 3277 (1986); **34**, 143 (1987); **35**, 85 (1988).
9. W. Podkościelny and W. Kowalewska, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 1025, 1579 (1984); *J. Appl. Polym. Sci.*, **39**, 1649 (1990).
10. C. S. Marvel and P. D. Caesar, *J. Am. Chem. Soc.*, **73**, 1097 (1951).
11. W. Rudź, Doctoral Dissertation, Maria Curie–Skłodowska University, Lublin, Poland, 1981.

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