Modification of Polythioesters from Bis(4-mercaptophenyl)ether with Adipoyl, Sebacoyl, and Isophthaloyl Chlorides with the Use of 2,2-Bis(4-hydroxyphenyl)propane

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SYNOPSIS

Modification of polythioesters obtained by interfacial polycondensation bis(4-mercaptophenyl)ether and adipoyl, sebacoyl, or isophthaloyl chlorides with the use of 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) has been described. Polycondensates with 10, 50, or 90% molar of bisphenol A in relation to dithiol were obtained under the same conditions as those established earlier as optimal for synthesis of polythioesters from dithiol and adipoyl, sebacoyl, or isophthaloyl chlorides. The structure of all the polycocondensates was determined by infrared spectra and X-ray analysis. Thermal and some mechanical and electrical properties for polycocondensates containing 50% molar bisphenol A in relation to dithiol were defined. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyesters—derivatives of bisphenol A with aliphatic and aromatic acid dichlorides—have been described,[1-6] in particular, with regard to methods of synthesis, structure, and properties. They were obtained mainly in melt, in solvent, or by interfacial polycondensation. As follows from the literature review,[7,8] polyesters having very interesting properties are formed by interfacial polycondensation. Thus, for instance, applying the above method, linear thermoplastic polyarylate from bisphenol A and adipoyl chloride (η = 0.62, mp 82°C, tensile strength 410 kG/cm^2, elongation 3%) was obtained by using methylene chloride as the organic phase, in the presence of benzyltriethylammonium chloride (TEBA) at temperature 20°C. But *o*-phthaloyl polyester obtained under the same conditions has the following values: η = 0.76, mp 214°C, tensile strength 700 kg/cm^2, and elongation 1%. Polyarylate derivatives of 2,2-(4-hydroxyphenyl)propane (diane) and isophthalic or terephthalic acid produced on industrial scale possess the value of tensile strength and elongation equal 850 kG/cm^2 and 35%, and 750 kG/cm^2 and 60%, accordingly.[9]

It is difficult to compare our results with the properties of polyesters from bisphenol A and acid dichlorides described in the literature because the conditions of their preparation differ from ours. Isophthaloyl polyester (η = 1.5–1.7 dL/g, mp 280°C, 80% yield) was obtained by interfacial polycondensation with the use *p*-xylene as the organic phase, TEBA, and the emulsifier Mersolan.[7]

Until now, there has been no mention in the literature about the preparation of polymer sulfur derivative of dithiol analogous of diane. For this reason, it is difficult to compare their properties with analogous polyesters. But in our laboratory, for several years, systematic investigations concerning the preparation of polythioesters from dithiols and acid dichlorides by interfacial polycondensation have been conducted. This led to the conclusion that the method we use is the best available.[10]

Studying the process of this kind of polycondensation, we found that the following factors mainly influence the values of reduced viscosity and yield

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reaction: kind of organic phase, molar ratio of reagents, catalyst TEBA, and concentration of the NaOH-acceptor of hydrochloride.

The best results for polythioesters derivatives bis(4-mercaptophenyl)ether and adipoyl chloride are achieved under optimal conditions, using benzene as the solvent, a 0.1 molar solution of dithiol, ratio of aqueous to organic phase equal to 1 : 1, 5% excess of acid chloride, time of addition of acid chloride about 5 min, temperature of reaction of 15°C, and 100% excess of NaOH.

Polythioesters from dithiol and sebacoyl chloride were obtained using a mixture of solvents benzene–hexane (1 : 1), a 0.2 molar solution of dithiol, ratio of aqueous to organic phase of 1 : 2, 5% concentration of TEBA, equimolar ratios of reagents, time of addition of acid chloride about 12 min, temperature of reaction about 15°C, and 100% excess of sodium hydroxide.

Interfacial polycondensation of dithiol with isophthaloyl chloride has been carried out under the following conditions: a mixture of benzene–hexane as the organic phase, ratio of aqueous to organic phase of 1 : 1, ratio of reagents dithiol / acid chloride of 1 : 1.1, molar ratio of dithiol to sodium hydroxide equal to 1 : 2, without contribution of catalyst, time of addition of acid chloride about 10 min, and temperature of reaction about 25°C.

The results of the investigations undertaken by us were presented in our previous papers.[11,12] It appears that polythioesters obtained from aliphatic dichlorides under optimal conditions are highly fusible powders that are hard to dissolve in common organic solvents. They are only soluble in a mixture of phenol–tetrachloroethane at room temperature. They are also partly dissolved in diluted and concentrated alkali. Polythioester derivatives of dithiol and isophthalic acid are also highly fusible powders. They reveal good resistance to common organic solvents. They are not soluble even in mixtures of phenol–tetrachloroethane solvents. It seemed interesting for us to try and improve some properties of polythioesters derivatives of dithiol and chlorides: adipoyl, sebacoyl, and isophthaloyl, by using the mixture of this compound and commercial bisphenol A instead of dithiol.

The influence of the added diol has been studied taking the same concentration of acid chloride equal to 0.1 molar under the established optimal conditions for polythioesters synthesis from adipoyl, sebacoyl, and isophthaloyl chlorides, but changing the concentration of the two remaining components: dithiol and bisphenol A. The latter was used in the amount of 10, 50, or 90% molar in relation to dithiol.

Some thermal, mechanical, and electrical properties of chosen polycondensates obtained from bis(4-mercaptophenyl)ether, bisphenol A with molar ratio (50 : 50), and dichlorides: adipoyl, sebacoyl, or isophthaloyl, have been studied.

EXPERIMENTAL

Reagents

Bis(4-mercaptophenyl)ether, which melts at 98–100°C (after crystallization from hexane) was obtained from 4,4′-diphenyletherdisulfonyl chloride by reduction with $SnCl_2 x 2H_2O$ in acetic acid saturated with dry HCl.[13] Adipoyl chloride (bp 128–130°C [18 Torr]) and suberoyl chloride (bp 143–147°C [12 Torr]) were obtained by the reaction of thionyl chloride with the corresponding acids. Isophthaloyl chloride, mp 44°C (after crystallization from hexane), was obtained by isophthaloyl acid reaction with phosphorous pentachloride. 2,2-Bis(4-hydroxyphenyl)propane, mp 157–158°C, was a commercial product of the "Sarzyna" firm, purified by crystallization from chlorobenzene.

Measurement of Properties

Melting Point

The melting point was determined by using a Böetius apparatus.

Viscosity

Reduced viscosity (η red dL/g) of phenol/tetrachloroethane at a ratio 3 : 2 by weight of 1% polymers solution was measured in a Ubbelohde viscometer at 25°C.

Thermogravimetric Analysis

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

Infrared Analysis

IR spectra were obtained with UNICAM SP-200 spectrophotometer.

X-ray Analysis

X-ray photographs were obtained by the Debye–Scherrer powder method from 64 mm-diameter cammera using X-ray tube Cu without filters; exposure time was 2 h; tube volgate, 32 kW; and anodic

intensity, 15 mA. The apparatus was of the URS-60 type.

RESULTS AND DISCUSSION

Polythioesters obtained under optimal conditions using interfacial polycondensation from 4,4'-dimercaptodiphenylether and aliphatic acids turned out to be powders hardly soluble in common organic solvents. They are completely soluble only in the mixture of phenol–tetrachloroethane at room temperature and partly in diluted and concentrated solutions of alkali. Aliphatic polythioesters reveal thermal resistance and have some good mechanical properties. With regard to electric properties, i.e., the values of the dielectric constant $\mathcal{E}$ and dielectric loss factor tan δ, the properties of sebacic polythioester are equal to the properties of the polyester obtained from bisphenol A and isophthaloyl chloride.

To determine the usefulness of chosen polythioesters, some thermal mechanical and electrical properties have been studied. They have both good thermal and electrical properties. Polythioester derivatives of dithiol and isomeric phthaloyl chlorides are powders with high melting points, nonsoluble in common organic solvents. They also reveal thermal resistance and are not soluble even in the mixture of solvents such as phenol–tetrachloroethane. It should be added that sulfuric acid and nitric acid do not dissolve them.

The subject of this paper was the modification of some properties of polythioesters obtained from dithiol and adipoyl, sebacoyl, or isophthaloyl chlorides using bisphenol A. These polycocondensates were obtained under optimal conditions for polythioesters as described below.

In a three-necked round-bottomed, 500 cm^3 flask with a mechanical stirrer (2000 rpm), thermometer, and dropper, 1.17 g (0.005 mol) bis(4-mercaptophenyl)ether, 1.14 g (0.005 mol) 2,2-bis(4-hydroxyphenyl)propane, 50 mL benzene, and 1.6 g sodium hydroxide solution in 100 cm^3 water were placed.

While the solution was vigorously stirred, and the temperature was reduced to 15°C, the solution of 2.01 g (0.011 mol) adipoyl chloride in 50 cm^3 benzene was added over 5 min and stirring was continued for 0.5 h at this temperature. Subsequently, the mixture was acidified with hydrochloric acid (Kongo Red). The isolated product of polycondensation was filtered and boiled in 100 mL water for 15 min. After cooling, the polycondensate was washed with acetone and dried under reduced pressure (15 mmHg) at 60°C. The influence of the amount of bisphenol A on the yield value of reduced viscosity has been studied using 10, 50, or 90% molar of this compound in relation to the amount of dithiol. Values of some physicochemical properties have been listed in Table I.

On the basis of the experimental data, we found out that better values of yield and reduced viscosity were obtained in the case of adipoyl chloride with the use of 50% molar of bisphenol A in relation to dithiol. These polymers are better soluble in common organic solvents in contrast to polythioesters obtained from these acid dichlorides. However, polycocondensates obtained from dithiol, bisphenol A, and isophthaloyl chloride reveal similar properties as those of polythioesters from this chloride. They are only partly soluble in common organic solvents and completely soluble in the mixture of solvents phenol–tetreachloroethane. Resistance of the studied polymers to mineral acids and alkali-aggressive factors is the same as that of polythioesters.

The structure of obtained polymers was determined from infrared and X-ray analyses. Infrared spectra (IR) for polycocondensates from 4,4'-bis(4-mercaptophenyl)ether, bisphenol A (50 : 50), and

Table I Properties of Polycocondensates Obtained from Bis(4-mercaptophenyl)ether, Bisphenol A, and Acid Chlorides

	Acid Chloride					
	Adipoyl		Sebacoyl		Isophthaloyl	
Bisphenol A (% molar)	Yield (%)	η_{red} (dL/g)	Yield (%)	η_{red} (dL/g)	Yield (%)	η_{red} (dL/g)
10	69.30	3.55	78.75	5.43	38.00	0.48
50	70.10	3.64	79.25	5.55	50.00	0.70
90	51.10	0.23	65.00	0.56	70.00	0.60

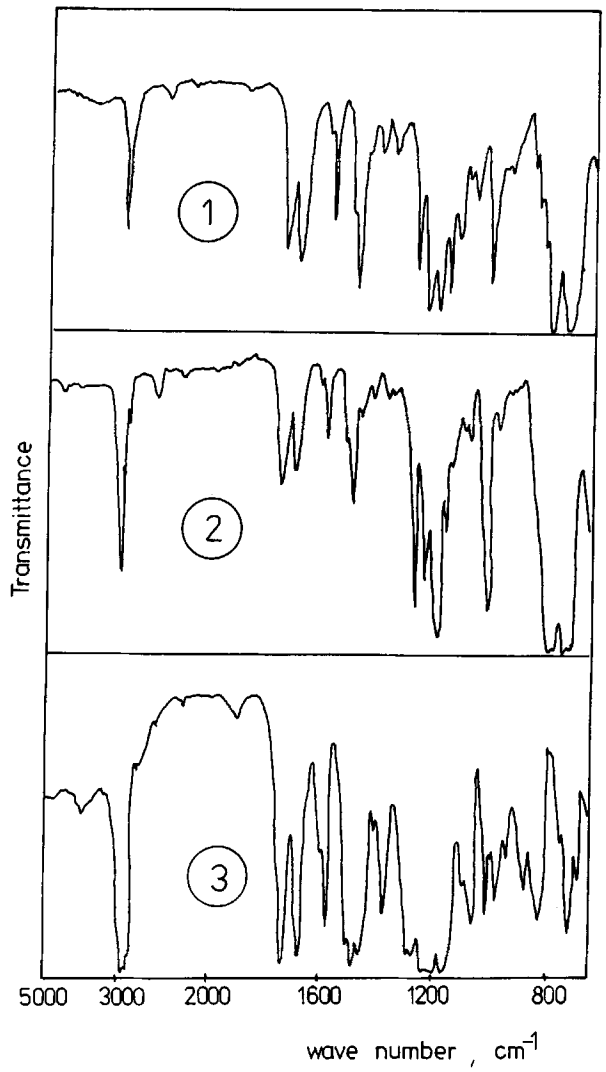

Figure 1 Infrared spectrum of polycocondensates from dithiol, bisphenol A, and acid chlorides: (1) adipoyl; (2) sebacoyl; (3) isophthaloyl.

adipoyl chloride showed strong absorption at 1680 cm^{-1}, which is characteristic for polythioester with S—CO— stretching, at 1160–1220 cm^{-1}, characteristic for the ether band; at 1580 cm^{-1}, for the benzene ring; and at 1720 cm^{-1}, for polyester —COO— stretching. The results are presented for three spectra in Figure 1.

The polycondensates derivatives of dithiol, bisphenol A (50 : 50), and adipoyl, sebacoyl, or isophthaloyl chlorides were also examined by means of X-ray analysis. They all show an insignificant degree of crystallinity. It also seemed interesting to study some thermal mechanical and electrical properties of polycocondensates obtained from 4,4′-dimercaptodiphenylether, bisphenol A (50 : 50), and adipoyl, sebacoyl, and isophthaloyl chlorides.

Thermal Properties

These polymers were examined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The temperature of initial decomposition, its mass loss in percent, and the temperature of the fastest decomposition process as well as mass loss percent at 200, 300, 400, and 500°C are listed in Table II, and the results of examination are shown in Figure 2. It can be seen from the obtained data that decomposition of these polymers begins at 260–360°C and is fastest at 320–480°C.

Mechanical and Electrical Properties

The examined polymers were pressed in a steel mold at a pressure of 200 kG/cm^2 and the obtained moldings were examined. Numerical data are given in Table III.

We could not carry out measurements of some mechanical properties of polycocondensates derived from sebacoyl chloride because of their brittleness, similar to the case of polythioesters obtained from this chloride. On the other hand, polycocondensates obtained from adipoyl and sebacoyl chlorides show generally lower values of mechanical properties than do polythioesters from these chlorides.

However, they exceed considerably the latter with regard to values of relative lengthening at rupture.

Table II Thermal Properties of Polycocondensates

Acid Chloride	Thermal Analysis[a] T_1 (°C)	U (%)	T_2 (°C)	Mass Loss (%) 200°C	300°C	400°C	500°C
Adipoyl	270	2.0	320	1.0	51.0	51.0	60.0
Sebacoyl	320	1.5	430	—	0.5	22.5	80.0
Isophthaloyl	380	4.0	470	1.0	2.0	7.0	42.0

[a] T_1 = temperature of initial decomposition from curve DTA (°C); U = mass loss in temperature T_1 (%); T_2 = temperature maximum velocity of decomposition from curve DTA (°C).

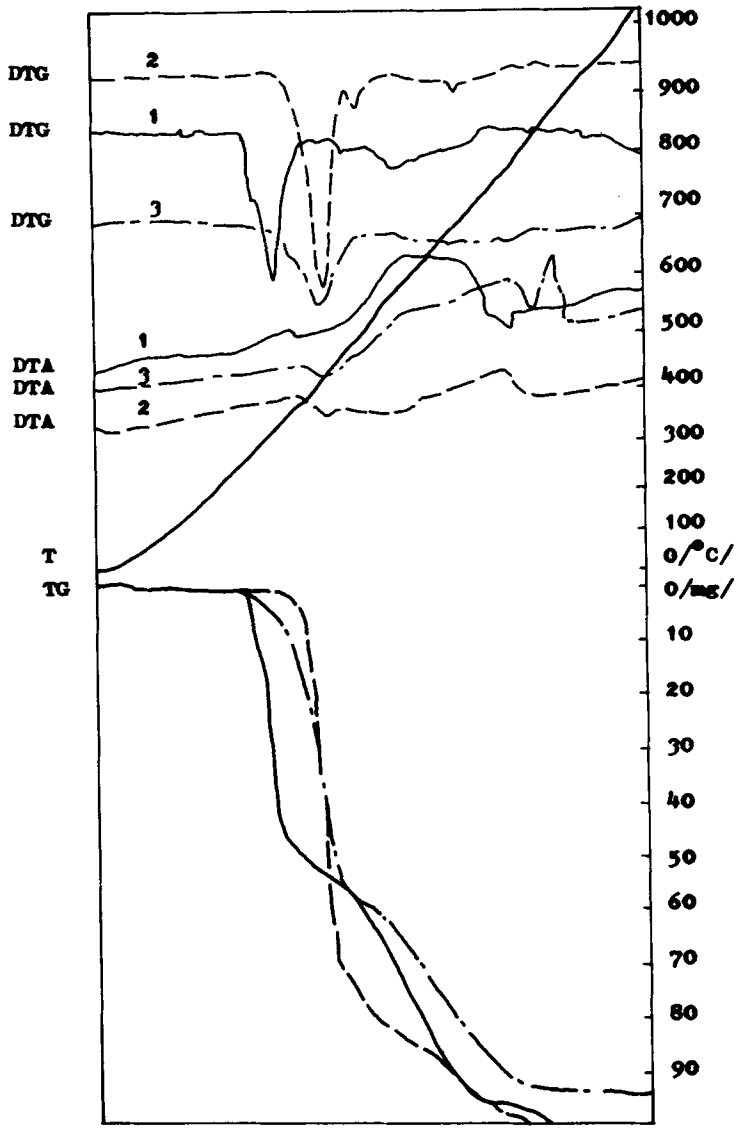

Figure 2 TGA and DTA of polycocondensates from dithiol, bisphenol A (50 : 50), and acid chlorides: (—) adipoyl; (- - - -) sebacoyl; (- · - · -) isophthaloyl.

Obtained values are 110 and 120%, respectively, for polycocondensates from adipoyl and sebacoyl chloride. In this respect, they are much better than is commercial polycarbonate Bistan AW (84.5%) or even hard polyvinyl chloride (2–4%).[14] The test specimens 4 mm thick were employed.

Polycocondensate from sebacoyl chloride reveals a much larger value in respect to resistance at rupture or bending than that of polythioester from this chloride. Polycocondensates obtained from sebacoyl and isophthaloyl chlorides are distinguished by better thermal resistance than that of the pure polythioesters. Their mass loss at temperature 400°C is equal 22.5 and 7% in comparison with polythioesters, whose values are 44 and 10%, respectively. Polycocondensates from isophthaloyl chloride are characterized by a nearly twice higher value of impact strength according to the method of Dynstat and by higher values of dielectrical constant $\mathcal{E}$ and tan δ than those of polythioesters from this chloride.[10,11]

Chemical Resistance

Polycocondensates were treated with some organic solvents, i.e., acetone, benzene, chloroform, methylene chloride, dioxane, dimethylformamide (DMF), nitrobenzene, tetrachloroethane (TCE), dimethyl sulfoxide (DMSO), a mixture of phenol and tetrachloroethane (3 : 2), 10% and concentrated mineral acids, and 10% and 50% sodium hydroxide.

Polycocondensates from adipoyl of sebacoyl

Table III Temperature of Pressing: Mechanical and Electrical Properties of Polycocondensates

Test	Bis(4-mercaptophenyl)ether–Bisphenol A (50 : 50)		
	Adipoly Chloride	Sebacoyl Chloride	Isophthaloyl Chloride
Temperature of pressing (°C)	65	90	190
Vicat softening (°C)	47	—	164
Rupture strength (MPa)	13.34	8.14	7.26
Relative lengthening at rupture (%)	110	122	5
Bending strength (MPa)	41.5	27.96	22.66
Impact strength (kJ/m^2)	2.65	—	7.85
Brinell hardness (MPa)	1.01	—	1.87
Relative dielectrical constant	3.5	1.9	2.5
Tan δ at 170 kHz (20°C)	0.00109	0.0521	0.0177

chlorides are soluble in methylene chloride, DMF, TCE, and DMSO as well as in the mixture of phenol and TCE (3 : 2). Polymers from isophthaloyl chloride are only soluble in a mixture of phenol and TCE (3 : 2). All polycocondensates are resistant to diluted mineral acids and alkali, but they react with concentrated nitric and sulfuric acids.

CONCLUSIONS

Polycocondensates by interfacial polycondensation of 4,4′-bis(4-mercaptophenyl)ether, bisphenol A, and adipoyl, sebacoyl, or isophthaloyl chlorides were obtained under optimal conditions established for pure polythioesters. The best results of yield, reduced viscosity, thermal resistance, and some good mechanical and electrical properties were obtained using 50% molar of bisphenol A in relation to dithiol. The examined polycocondensates are more soluble in organic solvents than are pure polythioesters obtained from these chlorides.

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