Linear Polythioesters. XV. Products of Interfacial Polycondensation of 1,4-Dimercapto-Tetramethylbenzene with Some Aliphatic and Aromatic Acid Dichlorides

WAWRZYNIEC PODKOŚCIELNY and WANDA KOWALEWSKA,
Institute of Chemistry, Maria Curie-Skłodowska University, Lublin, Poland

Synopsis

New polythioesters by interfacial polycondensation of 1,4-dimercaptomethyl–tetramethylbenzene with oxalyl, succinyl, adipoyl, suberoyl, sebacoyl, and isomeric phthaloyl dichlorides were obtained. To define the optimal conditions for interfacial polycondensation, the influence of the following factors on yield and value of reduced viscosity were studied: type of organic phase, concentration of hydrogen chloride acceptor, the quantitative ratio of aqueous to organic phase, molar ratio of reagents rate of acid chloride addition, contribution of benzyltriethylammonium chloride as a catalyst, and the temperature of the reaction. Thorough studies were carried out only for polycondensation of the dithiol with adipoyl, sebacoyl, and isophthaloyl chlorides. The structure of polythioesters obtained under the model conditions was determined by elementary analysis and infrared spectra. Initial decomposition temperature, mass loss in percentage at the same temperature, maximum rate of decomposition, and mass loss percentage at 100–400°C were defined from the curves of thermogravimetric analysis. Chemical resistance of the polythioesters was determined by treatment with some organic solvents, mineral acids (concentrated and 10%) and sodium hydroxide (10% and 50%). The molecular weight was not measured because of the low solubility of the polythioesters.

INTRODUCTION

During the last year our interest was concentrated on the synthesis, structure, and properties of polythioesters from mercaptomethyl derivatives xylenes, tri- and tetramethylbenzenes.[1,2] Studies on optimization of synthesis process polythioesters obtained by high- and low-temperature solution polycondensation as well as by interfacial polycondensation from dimercaptomethyl compounds and aliphatic acid dichlorides or izormeric phthaloyl chlorides were described. It was stated that the best results were obtained using interfacial polycondensation. Results of the investigations concerning the synthesis of polythioesters derivatives of 1,4-dimercaptomethyl–tetramethylbenzene with aliphatic and aromatic acid dichlorides were discussed in earlier articles.[2]

It has been found that many factors influence properties of polythioesters significantly. Among them are: kind of organic phase, contribution of catalyst,

Journal of Applied Polymer Science, Vol. 39, 1649–1656 (1990)
 CCC 0021-8995/90/081649-08$04.00

concentration of hydrogen chloride acceptor, and temperature of the reaction. It seems appropriate to use for synthesis of polythioesters dithiols derivatives of tetramethylbenzene in which SH groups are directly attached to the aromatic ring. As in the previous articles, influence of some parameters on yield and reduced viscosity is studied. The reactions of polycondensation of 1,4-dimercapto-tetramethylbenzene with adipoyl, sebacoyl, and isophthaloyl chlorides were chosen as a model system and thoroughly studied.

The structure of all polythioesters obtained under model conditions was determined by elemental analysis and infrared (IR) spectra. Chemical and thermal resistance and mechanical and electrical properties were determined. Molecular weight was not determined because of the low solubility of the polythioesters.

EXPERIMENTAL

Reagents

1,4-Dimercapto-tetramethylbenzene, mp 201°C (after crystallization from cyclohexane) was obtained from 1,4-disulfonyl chloride-tetramethylbenzene by reduction with $SnCl_2.2H_2O$ in acetic acid saturated with dry hydrogen chloride.[3] Adipoyl chloride, bp 128–130°C/18 torr, suberoyl chloride, bp 143–147°C/12 torr, and sebacoyl chloride, bp 166–169°C/11 torr were obtained by the reaction of thionyl chloride with respective acids. Succinyl chloride, bp 103–104°C/25 torr was obtained from succinic acid and phosphorous pentachloride. Commercial oxalyl chloride bp 63°C was purified by distillation. Terephthaloyl chloride mp 83°C and isophthaloyl chloride mp 44°C (after crystallization from hexane) were obtained by the reaction of phosphorous pentachloride with suitable acids. Phthaloyl chloride bp 131–133°C/9–10 torr was obtained through the reaction of phthalic anhydride with phosphorous pentachloride.

Synthesis of Polythioesters

The synthesis of all polythioesters, whose yield and some physicochemical properties are listed in Table III, were carried out as follows: in a three-necked, round-bottomed flask of 500 cm^3 volume, equipped with a mechanical stirrer (2000 rpm/min), thermometer, and dropper, 0.01 mol of dithiol, 50 cm^3 of benzene–hexane (1 : 1) mixture, and a suitable quantity of sodium hydroxide, that is, a stoichiometric quantity (0.02 mol) or a 100% excess (0.04 mol) dissolved in 100 cm^3 of water. After thorough mixing 0.011 mol of acid chloride dissolved in 50 cm^3 of a benzene–hexane (1 : 1) mixture was added over a period of 2, 3, or 5 min at 25°C and vigorously stirred. After the complete addition of acid chloride the stirring was continued for 15 min. The mixture was then acidified with hydrochloric acid (Congo Red). The precipitated product of polycondensation was filtered and boiled in water (100 cm^3) for 15 min. After filtration the polythioesters were washed with water and acetone and dried under reduced pressure (15 mm Hg) at 60°C to a constant weight.

Measurement of Properties

Melting Point

Melting point determinations were carried out with a Boetius apparatus.

Viscosity

Reduced viscosity (dL/g) on 0.7% solution of polythioesters in a phenol/tetrachloroethane mixture in the weight ratio 1 : 3 was measured with 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

The IR spectra were obtained with a UNICAM SP-200 spectrophotometer.

RESULTS AND DISCUSSION

Determination of Optimal Conditions in Interfacial Polycondensation

To determine optimal conditions of interfacial polycondensation, 1,4-dimercapto-tetramethylbenzene with adipoyl and sebacoyl chlorides, as well as isophthaloyl chloride were chosen as a model system. In the choice of optimal conditions the best yield of the process and the highest value of reduced viscosity were taken into consideration. The influence of the following factors on interfacial polycondensation was studied: the kind organic phase, concentration of hydrogen chloride acceptor, the quantitative ratio of aqueous and organic phases, molar ratio of reagents, rate of acid chloride addition, contribution of benzyltriethylammonium chloride as a catalyst, and the temperature of the reaction. After determining preliminary reaction conditions, that is, the aqueous to organic phase ratio 1 : 1, molar ratio of the reagents : dithiol/acid chloride 1 : 1, reaction temperature 25°C, and the rate of acid chloride addition 2 min, the influence of the kind of organic solvent on yield and reduced viscosity was examined.

As the organic phase chloroform, benzene, as well as a mixture of benzene/hexane in a volume ratio 1 : 1, were used. From the data presented in Table I it follows that the solvent influences the yield and reduced viscosity of the polycondensation polymers significantly. The best yield and the highest value of reduced viscosity were obtained with the benzene/hexane mixture.

In the further optimalization process only this mixture was used as an organic phase. The effect of an excess of sodium hydroxide as a hydrogen acceptor on the results of polycondensation is illustrated in Table II.

Using excess of sodium hydroxide in relation to the amount stoichiometrically necessary causes a decrease in the value of reduced viscosity and the

TABLE I
Effect of Solvent on Properties of Polythioesters from 1,4-Dimercaptotetramethylbenzene Adipoyl, Sebacoyl and Isophthaloyl Chlorides[a]

Organic phase	Acid chlorides	Yield (%)	η_{red} (dL/g)	Softening range (°C)
Chloroform	Adipoyl	52	0.09	200–218
	Sebacoyl	76	0.05	138–151
	Isophthaloyl	91	0.09	310–325
Benzene	Adipoyl	81	0.21	212–227
	Sebacoyl	84	0.06	150–165
	Isophthaloyl	77	0.41	325–347
Benzene/hexane	Adipoyl	85	0.36	220–236
	Sebacoyl	87	0.23	175–188
	Isophthaloyl	97	1.39	330–350

[a]Conditions of the reaction: phase ratio, 1 : 1, reagents ratio, 1 : 1 rate of chloride addition, 2 min, temperature 25°C.

yield of polythioesters from adipoyl and sebacoyl chloride. In the case of polythioesters from isophthaloyl chloride, using excess of sodium hydroxide causes an increase in reduced viscosity, and a slight decrease in yield. In further investigations a stoichiometrically necessary amount of a hydrogen chloride acceptor for adipoyl and sebacoyl chloride was used. Instead of synthesis polythioester with isophthaloyl chloride 100% molar excess of sodium

TABLE II
Influence of Excess of Hydrogen Chloride Acceptor (NaOH) and Catalyst Benzyltriethylammonium Chloride on Yield and Reduced Viscosity of Polythioesters from 1,4-Dimercaptotetramethylbenzene, Adipoyl, Sebacoyl, and Isophthaloyl Chlorides

Acid chlorides	NaOH[a] (excess %)	η_{Red} (dL/g)	Yield (%)
Adipoyl	0	0.36	85
	50	0.32	82
	100	0.29	81
	150	0.25	78
	200	0.21	70
	0[b]	0.44	92
Sebacoyl	0	0.23	87
	50	0.22	85
	100	0.20	83
	150	0.18	80
	200	0.15	78
	0[b]	0.32	94
Isophthaloyl	0	1.39	97
	50	1.70	92
	100	2.00	90
	150	1.61	80
	200	1.50	78
	100[b]	3.19	99

[a]Hydrogen chloride acceptor.
[b]Contribution of catalyst.

hydroxide was used. The effect of a catalyst for example of benzyltriethylammonium chloride (5% weight in relation to dithiol) was determined. As Table II shows, when the catalyst is used the value of reduced viscosity and yield increase for the polythioester from adipoyl, sebacoyl, and isophthaloyl chlorides.

In further investigations the influence of the ratio of the aqueous to organic phase on the value of reduced viscosity and yield of polythioesters was examined by using different quantities of water at the constant volume of organic phase. The ratio of aqueous to organic phase was from 1 : 1 to 0.1 : 1, which corresponded to the concentration of dithiol in the aqueous-basic phase in the range of 0.1–1.0 mol/L. It was found that the highest value of reduced viscosity and the best yield of polythioesters from adipoyl, sebacoyl, and isophthaloyl chlorides were obtained with 0.4*M* solution of dithiol (phase ratio 1 : 4).

The molar ratio excess of acid chloride, the effect of the rate of acid chloride addition, and the effect of temperature on the value of reduced viscosity and yield of polythioesters were also studied. It was stated that the best results are achieved, with 10% molar excess of acid chloride at the optimal time of acid chloride addition 2 min for sebacoyl chloride, 3 min for isophthaloyl chloride, and 5 min for adipoyl chloride. The greatest value of reduced

TABLE III
Some Physicochemical Properties of Polythioesters

Acid chlorides	Yield (%)	η_{red}	Softening range (°C)
Oxalyl	85	—	307–312
Succinyl	97	—	280–290
Adipoyl	98	0.62	220–235
Suberoyl	95	0.70	160–166
Sebacoyl	98	0.78	145–154
Phthaloyl	85	0.69	310–322
Isophthaloyl	96	3.51	340–357
Terephthaloyl	98	—	< 360

TABLE IV
Results of Elementary Analysis of Polythioesters Derivatives 1,4-Dimercaptotetramethylbenzene and Acid Chlorines

	Analysis					
	C %		H %		S %	
Acid chloride	Calcd	Found	Calcd	Found	Calcd	Found
Oxalyl	57.11	57.41	4.79	4.34	25.41	25.59
Succinyl	59.96	59.21	5.75	5.21	22.87	22.93
Adipoyl	62.30	62.49	6.53	6.47	20.79	20.16
Suberoyl	64.24	63.87	7.18	7.52	19.05	18.65
Sebacoyl	65.89	65.03	7.74	7.94	17.59	17.61
Phthaloyl	65.82	65.60	4.91	4.51	19.32	19.60
Isophthaloyl	65.82	65.21	4.91	4.27	19.32	19.66
Terephthaloyl	65.82	65.32	4.91	4.44	19.32	19.80

viscosity and very good yield were achieved at polycondensation of dithiol with using acid chlorides at temperature in the range 6–25°C.

Polythioesters from oxalyl and succinyl chlorides were prepared under in the same optimal conditions as for adipoyl chloride and from phthaloyl and terephthaloyl chlorides as those used for isophthaloyl chloride. Table III lists the values of reduced viscosity, yields and softening range of all polythioesters.

Infrared spectra of polythioesters show strong absorptions at 1665–1675 cm^{-1}, which is characteristic of carbonyl valency band C=O, at 650–680 cm^{-1} for the valency band —C—S, and at 1450–1470 cm^{-1} for the benzene ring. On the basis of good agreement of the calculated and found analytical data (Table IV) and infrared spectra, linear structure of polythioester was affirmed.

Thermal Properties

The polythioesters were examined by means of differential analysis (DTA) and thermogravimetric analysis (TGA). The temperature of initial decomposition, the percentage of its mass loss, the temperature of the fastes decomposition process, and the percentage mass loss at 100–400°C were defined from the curves. The numerical data are presented in Table V. The greatest thermal resistance is revealed by the polythioesters from adipoyl, suberoyl, and sebacoyl chlorides. The results of the examination are given as an example of polythioester from suberoyl chloride (Fig. 1).

Chemical Resistance

The polythioesters were treated with some organic solvents, i.e., acetone, benzene, chloroform, methylene chloride, dioxane, dimethylformamide, nitrobenzene, tetrachloroethane, and a mixture of phenol and tetrachloroethane

TABLE V
Thermal Properties of Polythioesters from 1,4-Dimercaptotetramethylbenzene and Acid Dichlorides

	Thermal analysis[a]			Mass loss (%) (°C)						
Acid chloride	T_1 (°C)	U (%)	T_2 (°C)	100	150	200	250	300	350	400
Oxalyl	240	3	320	0.1	1.0	1.5	3.0	16.0	48.0	54.0
Succinyl	260	5	350	0	0.5	3.0	5.0	10.0	48.0	59.0
Adipoyl	290	2	380	0	0	0.5	0.8	2.0	32.0	63.0
Suberoyl	320	2	390	0	0	0.4	0.6	1.0	11.0	55.0
Sebacoyl	340	3	400	0	0	1.0	1.5	2.0	10.0	63.0
Phthaloyl	280	4	320	0	1.0	2.0	3.0	4.0	40.0	52.0
Isophthaloyl	320	2	365	0	1.0	1.5	2.0	5.0	10.0	21.0
Terephthaloyl	340	3	385	0.5	1.5	2.5	4.5	7.0	10.0	53.0

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

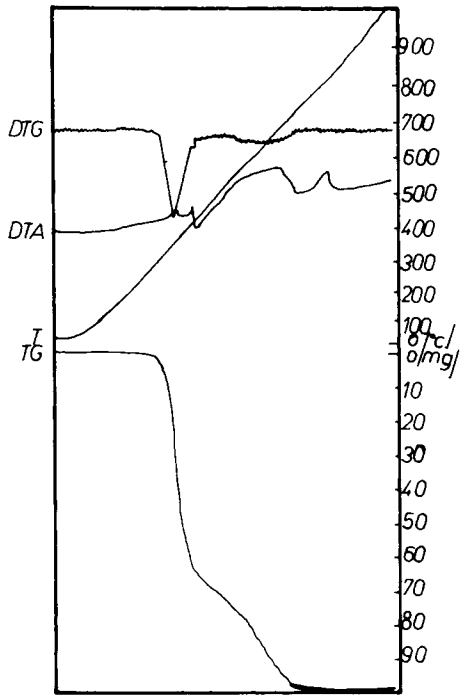

Fig. 1. TGA and DTA polythioesters from 1,4-dimercaptotetramethylbenzene and suberoyl chloride. Heating time in air, 100 min; measurements relative to Al_2O_3; heating rate, 10°C/min; amount of polythioester, 100 mg.

(1 : 3), 10% and concentrated mineral acids as well as 10 and 50% sodium hydroxide.

All polythioesters dissolve partially in benzene, and completely indissoluble in acetone, dioxane, and dimethylformamide. Then are good dissolve in chlorohydrocarbons except the polythioesters from oxalyl, succinyl, and terephthaloylchlorides. The polythioesters show good resistance to 10 and 50% sodium hydroxide and mineral acids, except nitric acid in which almost completely dissolubility is observed.

TABLE VI
Temperature of Presing and Mechanical and Electrical Properties of Polythioesters

Test	1,4-Dimercaptotetramethylbenzene		
	Succinyl	Isophthaloyl	Terephthaloyl
Temperature of pressing (°C)	140	280	270
Vicat softening point (°C)	129	240	240
Rupture strength (kg/cm^2)	—	37	48
Impact strength (kg/cm^2)	—	2.2	2.5
Bending hardness (kg/cm^2)	—	39.3	86.6
Brinnel hardness (kg/cm^2)	—	Brittle	Brittle
Dielectrical constant	4.8	2.4	1.7
tan δ at 170 kHz, 20°C	0.030	0.064	0.0138

Mechanical and Electrical Properties

Polythioesters are light yellow or colorless solids. To examine their mechanical and electrical properties polythioesters obtained from dithiol and succinyl, isophthaloyl and terephthaloyl chlorides were pressed in a steel mold at a pressure of 200 kg/cm^2. The cream-colored moldings obtained were the subject of examination. Pressing temperatures and numerical data are given in Table VI.

CONCLUSION

The polythioesters from 1,4-dimercapto–tetramethylbenzene and some alphatic and isomeric phthaloyl dichlorides were obtained in high yield and high values of reduced viscosity only for polythioesters from adipoyl, suberoyl, sebacoyl, and isophthaloyl chlorides using interfacial polycondensation.

Good results were obtained without excess of hydrochloric acid acceptor (for aliphatic acid dichlorides, and with 100% excess for phthaloyl dichlorides) and at using benzyltriethylammonium chloride as a catalyst.

It was shown that polythioester with the highest reduced viscosity and yield were obtained when the ratio of the aqueous to organic phase was 1 : 4. Because of their good thermal and chemical resistance, the polythioesters may find various application especially as modifiers of commercial polyesters.

References

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Received April 26, 1989
Accepted May 1, 1989