

Linear Polythioesters. IV.* The Effect of Hydrogen Chloride Acceptor on Interfacial Polycondensation of 4,4'-Di(mercaptomethyl)benzophenone with Isomeric Phthaloyl Chlorides

WAWRZYNIEC PODKOSCIELNY and ANNA KULTYS, *Institute of Chemistry, Maria Curie-Skłodowska University, Lublin, Poland*

Synopsis

New polythioesters of better physicochemical and mechanical properties have been obtained by interfacial polycondensation of 4,4'-di(mercaptomethyl)benzophenone with terephthaloyl, isophthaloyl, and phthaloyl chlorides with the use of sodium hydroxide excess as a hydrogen chloride acceptor. According to preliminary experiments, the best yield and the highest reduced viscosity are reached when the polycondensation at a 1:1 ratio of the aqueous to the organic phase is carried out at a temperature of 5–7°C with a little excess of acid chloride with addition time of 0.5–2 min in the presence of 100% excess of NaOH as hydrogen chloride acceptor. The structure of the polythioesters was determined from elemental analysis and infrared spectra. Thermal properties of all polythioesters were determined. Mechanical and electrical properties of only the most interesting polythioesters obtained from isophthaloyl chloride were determined.

INTRODUCTION

In a previous report¹ on polythioester synthesis we attempted to establish the optimal conditions of interfacial polycondensation of 4,4'-di(mercaptomethyl)benzophenone with terephthaloyl, isophthaloyl, and phthaloyl acid chlorides studying various factors influencing yield and reduced viscosity. Using the stoichiometric quantity of dithiol and sodium hydroxide as a hydrogen chloride acceptor, the most advantageous conditions for interfacial polycondensation were defined: organic phase 1:1, some molar excess of acid chloride, reaction temperature in the range of 5–7°C, and addition of emulsifier.

Further studies on polythioester synthesis by the interfacial polycondensation of di(mercaptomethyl)naphthalene with acid chlorides^{2,3} proved that excess of sodium hydroxide used as a hydrogen chloride acceptor in the polycondensation effects the yield, reduced viscosity, and properties of polythioesters. It seemed to be interesting to investigate the effect of sodium hydroxide excess on the polythioester synthesis from 4,4'-di(mercaptomethyl)benzophenone and isomeric phthaloyl chlorides.

* For Parts I–III of this series, see references 1–3.

EXPERIMENTAL

Reagents

4,4'-Di(mercaptomethyl)benzophenone (mp 113–114°C), isophthaloyl chloride (mp 44°C), terephthaloyl chloride (mp 83°C), and phthaloyl chloride (bp 131–133°C/9–10 torr) were obtained as previously.

Measurement of Properties

Melting Point. Melting point determinations were carried out by using a Bötius apparatus.

Viscosity. Reduced viscosity of phenol–tetrachloroethane at a ratio of 1:3 by weight of 0.7% polythioester 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 2.5°C/min in air.

Infrared Analysis. The infrared spectra were obtained with a Unicam SP-200 spectrophotometer.

RESULTS

Determination of Optimal Conditions in Interfacial Polycondensation using Sodium Hydroxide as Hydrogen Chloride Acceptor

To determine the optimal conditions in interfacial polycondensation using sodium hydroxide as a hydrogen chloride acceptor, 4,4'-di(mercaptomethyl)-benzophenone and isophthaloyl acid chloride were chosen as model system. Based on previous results, benzene has been introduced as organic solvent and the ratio of aqueous to organic phase is 1:1. The influence of the following conditions on yield and reduced viscosity of polythioesters was studied: rate of acid chloride addition (Fig. 1), sodium hydroxide excess as hydrogen chloride acceptor (Fig. 2), isophthaloyl chloride excess (Fig. 3), contribution of catalyst (Table I), and reaction temperature (Fig. 4).

The rate of acid chloride addition influences the reduced viscosity and yield of polythioesters to a great extent. As shown in Figure 1, the short time of 0.5–2 min of addition is the most advantageous.

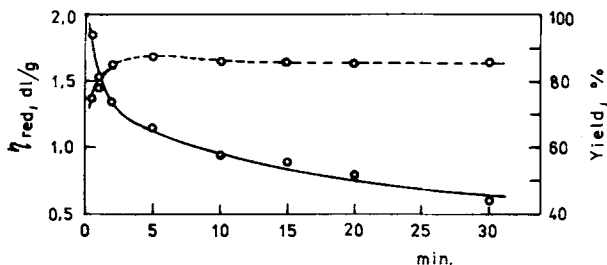


Fig. 1. Influence of time of isophthaloyl chloride addition on reduced viscosity (—) and yield (---) of the polythioester: stoichiometric quantity of NaOH; temperature 25°C; 10% excess isophthaloyl chloride; emulsifier (Mersolan) 1% by weight in relation to reagents.

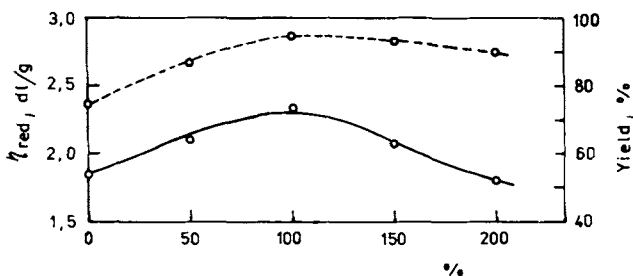


Fig. 2. Influence of sodium hydroxide excess on reduced viscosity (—) and yield (---) of the polythioester from dithiol and isophthaloyl chloride: temperature 25°C; time of chloride addition $\frac{1}{2}$ min; 10% excess isophthaloyl chloride; emulsifier (Mersolan) 1% by weight in relation to reagents.

Using sodium hydroxide excess in relation to the amount stoichiometrically necessary in mercaptide production is very important in polycondensation. The highest value of reduced viscosity and the best yield are achieved with a 100% molar excess of sodium hydroxide (Fig. 2). Excess of acid chloride affects the value of reduced viscosity slightly because of the high rate of reaction. The yield of the reaction decreases slightly with over 10% excess of acid chloride (Fig. 3).

The influence of a catalyst on interfacial polycondensation was examined with benzyltriethylammonium chloride (TEBA) added in the amount of 5% by weight in relation to dithiol into the reaction medium before the process has begun. It can be seen in Table I that the presence of a catalyst decreases the value of reduced viscosity and increases the yield of the polythioester.

The influence of temperature on interfacial polycondensation in the presence of a 100% molar excess of hydroxide was studied at 6–70°C. Figure 4 shows that the polythioester of the greatest reduced viscosity and good yield was obtained at 6°C. It follows from the experiments that the best method of obtaining polythioesters is the polyreaction of 4,4'-di(mercaptomethyl)benzophenone with isophthaloyl chloride.

In a round-bottomed, 500-cm³ flask equipped with a mechanical stirrer (2000 rpm), thermometer, and dropper, 2.74 g (0.01 mole) 4,4'-di(mercaptomethyl)-benzophenone, 50 ml benzene, sodium hydroxide solution (1.6 g NaOH in 100 cm³ water), and 0.05 g emulsifier (Mersolan) were poured. After thorough mixing, the solution of 2.03 g (0.01 mole) of isophthaloyl chloride in 50 ml benzene was added and stirred for a period of 0.5 min at about 6°C. After addition of the acid chloride was completed, stirring was continued for 15 min.

The isolated product of polycondensation was filtrated and washed with ac-

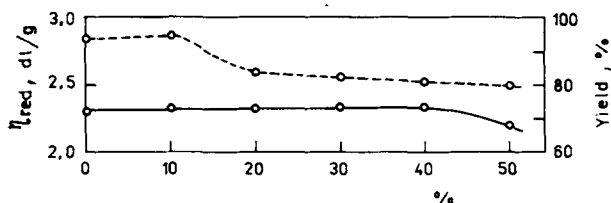


Fig. 3. Influence of isophthaloyl chloride excess on reduced viscosity (—) and yield (---) of the polythioester: temperature 25°C; 100% excess NaOH; time of chloride addition $\frac{1}{2}$ min; emulsifier (Mersolan) 1% by weight in relation to reagents.

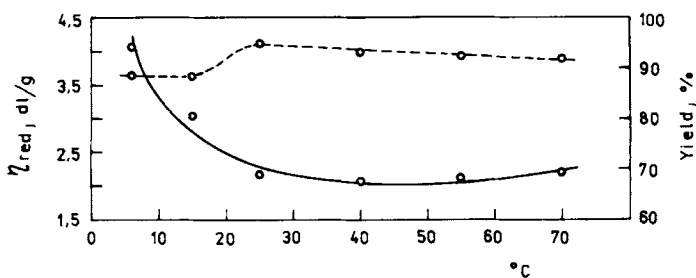


Fig. 4. Influence of temperature on reduced viscosity (—) and yield (---) of the polythioester from dithiol and isophthaloyl chloride: 100% excess NaOH; 10% excess isophthaloyl chloride; time of chloride addition $\frac{1}{2}$ min; emulsifier (Mersolan) 1% by weight in relation to reagents.

etone (100 ml), hot water (2×100 ml), and again acetone (55 ml). This purified polythioester was dried in a vacuum dryer at 60°C to constant weight. Then its yield and reduced viscosity were determined. A similar procedure was used to prepare polythioesters from dithiol and terephthaloyl chlorides. Table II presents yield and values of reduced viscosity of the prepared polythioesters.

The polycondensation products of 4,4'-di(mercaptomethyl)benzophenone with isophthaloyl and terephthaloyl chlorides are hardly soluble in common organic solvents. The polythioester from phthaloyl chloride reveals the greatest solubility.

IR spectra of the polythioesters show strong absorptions at $1675\text{--}1660\text{ cm}^{-1}$ (which are characteristic of the carbonyl valency band), at $1440\text{--}1420\text{ cm}^{-1}$ (which are characteristic of the $\text{—CH}_2\text{—S—}$ group), at $685\text{--}660\text{ cm}^{-1}$ (which are characteristic of —C—S— stretching), and at 1615 cm^{-1} (which are characteristic of benzene ring vibrations). Infrared spectra and good agreement between calculated and found analytic data (Table III) prove the linear structure of polythioesters.

TABLE I
Influence of Catalyst (Benzyltriethylammonium Chloride) on Yield and Reduced Viscosity of Polycondensation of 4,4'-Di(mercaptomethyl)benzophenone with Isophthaloyl Chloride

100% excess of NaOH	Catalyst	Yield, %	η_{red} , dl/g	Melting range, $^\circ\text{C}$
—	—	75.3	1.85	205–250
—	+	82.7	1.01	170–230
+	+	92.1	1.89	165–220
+	—	95.0	2.34	200–260

TABLE II
Yield and Reduced Viscosity of Polythioesters from 4,4'-Di(mercaptomethyl)benzophenone and Acid Chlorides

Acid dichloride	Yield, %	η_{red} , dl/g
Phthaloyl	80.0	0.63
Isophthaloyl	88.8	4.15
Terephthaloyl	88.8	5.14

TABLE III
Results of Elementary Analysis of Polythioesters from 4,4'-Di(mercaptomethyl)benzophenone and Acid Dichlorides

Acid chloride	Percent C		Percent H		Percent S	
	Calcd	Found	Calcd	Found	Calcd	Found
Phthaloyl		68.17		4.54		15.36
Isophthaloyl	68.29	68.24	3.98	4.03	15.85	15.42
Terephthaloyl		68.69		4.11		15.97

Thermal Properties

The polythioesters of highest reduced viscosity were examined by differential analysis (DTA) and TGA. The numerical data of the examination are presented in Table IV. It can be seen from the DTG curves that the temperature of initial decomposition is in the range of 275–295°C, the temperature of initial intensive decomposition is in the range of 300–330°C, and the temperature of intensive decomposition is in the range of 570–590°C. The TG curve also shows a percentage mass loss at 100, 150, 200, 250, 300, and 350°C. The greatest thermal resistance is revealed by the polythioester from terephthaloyl chloride, while the weakest is revealed by that from phthaloyl chloride.

Mechanical and Electrical Properties

The polythioesters obtained are colorless solids. To examine their mechanical and electrical properties, they were pressed in a steel mold at a pressure of 200 kg/cm². The obtained yellow bright moldings were the subject of examination;

TABLE IV
Thermal Properties of Polythioesters^a

Chloride	Melting range, °C	Thermal analysis			% Mass loss at					
		T ₁ , °C	T ₂ , °C	T ₃ , °C	100°C	150°C	200°C	250°C	300°C	350°C
Phthaloyl	125–160	275	300	570	1.0	1.3	1.5	1.9	30.0	48.0
Isophthaloyl	220–260	290	320	585	0.0	0.5	0.7	0.8	5.0	18.8
Terephthaloyl	265–280	295	330	590	0.5	0.7	0.8	0.9	1.5	16.8

^a T₁, is the temperature of initial decomposition from the DTG curve; T₂, temperature of initial intensive decomposition from the DTG curve; T₃, temperature of intensive decomposition from the DTG curve.

TABLE V
Mechanical and Electrical Properties of Polythioester from 4,4'-Di(mercaptomethyl)-benzophenone and Isophthaloyl Chloride

Test	Reduced viscosity, dl/g	
	1.1	4.15
Temperature of pressing, °C	83	140
Vicat softening point, °C	112	127
Rupture strength, kg/cm ²	106	265
Impact strength, kg/cm ²	1.56	3.2
Bending strength, kg/cm ²	172	331
Brinell hardness, kg/cm ²	23.9	19.3
Dielectrical constant	2.34	2.70
tan δ at 170 kHz, 20°C	0.0149	0.0660

results were given for the polythioester prepared from isophthaloyl chloride chosen as an example. The properties of the polythioester of reduced viscosity 1.1 obtained as described before and of reduced viscosity 4.15 prepared using sodium hydroxide as a hydrogen chloride acceptor are presented in Table V. From Table V it follows that the use of 100% excess alkali results in production of higher reduced viscosity and thereby of high molecular weight polythioesters. These have better properties, especially mechanical properties.

CONCLUSIONS

A 100% excess of sodium hydroxide as hydrogen chloride acceptor has a beneficial effect on the interfacial polycondensation of 4,4'-di(mercaptomethyl)-benzophenone with phthaloyl chlorides. Polythioesters obtained in high yield possess high reduced viscosity, good thermal properties, very good chemical resistance, and interesting mechanical properties. Because of these, they may find practical application, especially as modifiers of commercial polythioesters.

References

1. W. Podkościelny and A. Kultys, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 655 (1976).
2. W. Podkościelny and W. Charmas, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2429 (1979).

Received May 27, 1980

Accepted August 11, 1980