Linear Polyesters. Products of Interfacial Polycondensation of Bis(4-hydroxyphenyl)ether with Isomeric Phthaloyl Chlorides

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SYNOPSIS

New polyesters were obtained by interfacial polycondensation of bis(4-hydroxyphenyl)ether with phthaloyl, isophthaloyl, and terephthaloyl chlorides. The initial reaction conditions were as follows: the aqueous to organic phase ratio 1 : 1, reaction temperature 25°C, the rate of chloride addition about 10 min, and molar ratio of the reagents diol/acid dichloride 1 : 1.1, benzene–hexane as an organic phase. To determine the optimal conditions for interfacial polycondensation, the influence of the following factors on yield and value of reduced viscosity were studied: organic phase, excess of sodium hydroxide as an acceptor of HCl, contribution of benzyltriethylammonium chloride as a catalyst, and contribution of an emulsifier, Mersolan. The structure of all polyesters was determined by elemental analysis and infrared spectra. Initial decomposition and initial intensive decomposition temperature were defined by the curves of thermogravimetric analysis. Some mechanical and electrical properties of isophthaloyl polyester, only partly soluble in organic solvents, were determined.

INTRODUCTION

In the previous paper[1] we presented the results of our investigations concerning the determination of optimal conditions in synthesis of polyesters by interfacial polycondensation of bis(4-hydroxyphenyl)ether with aliphatic acid dichlorides. We found that a number of factors greatly influences the properties of polyesters. Among those there are: the kind of organic phase, contribution of catalyst, temperature of reaction, concentration of acceptor of hydrogen chloride, concentration and molar ratio of reagents, and rate of addition of acid chloride.

As concerns polyesters obtained from bis(4-hydroxyphenyl)ether with isomeric phthaloyl chlorides, the only mention about isophthaloyl polyester is to be found in publication by Eklers which was published only in 1969.[2]

We found it interesting, in the light of the abovementioned paper, to determine the optimal conditions for interfacial polycondensation for polyesters from bis(4-hydroxyphenyl)ether and isomeric phthaloyl dichlorides as well as to define some physicochemical, mechanical, electrical, and thermal properties of these polymers.

EXPERIMENTAL

Reagents

Bis(4-hydroxyphenyl)ether, m.p. 160–161°C (after crystallization from benzene), was obtained by condensation of the hydroquinone in an inert solvent at 180–195°C in the presence of acid-activated montmorillonite as catalyst.[3] Therephthaloyl chloride, m.p. 83°C, and isophthaloyl chloride, m.p. 44°C (after crystallization from hexane), were obtained by the reaction of phosphorous pentachloride, with terephthalic or isophthalic acids. Phthaloyl chloride, b.p. 131–133°C (9–10 mm Hg), was obtained

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through the reaction of phthalic anhydride with phosphorous pentachloride.[4]

Measurement of Properties

Melting Point. Melting point determinations were carried out on a Böetius apparatus.

Viscosity. Reduced viscosity (η_{red} dL/g) of phenol–tetrachloroethane at a ratio of 3 : 2 by weight of 0.5% polyester solution was measured in a Ubbelohde viscometer at 25°C.

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

Infrared Analysis. Infrared (IR) spectra were obtained with a UNICAM SP-200 spectrophotometer.

X-Ray Investigations. X-ray photographs were obtained by the Debye–Scherrer powder method with a camera 64 mm in diameter and an X-ray tube Cu without filters. Exposure time was 2 h, tube voltage was 32 kW, and anodic intensity was 15 mA. The apparatus was a URS-60 type.

RESULTS AND DISCUSSION

In the previous article we found that the reaction of interfacial polycondensation of bis(4-hydroxyphenyl)ether with aliphatic acid dichlorides was greatly influenced by such parameters as the kind of organic phase, contribution of benzyltriethylammonium chloride catalyst, concentration of sodium hydroxide, and temperature of reaction, as well as the rate of acid chloride addition.

Table I The Influence of Organic Phase on Physicochemical Properties of Polyesters from Diol and Isophthaloyl Chloride

Phase	Yield (%)	Melting Point (°C)	η_{red}[b]
Chloroform	90.36	240–247	—
Ethylene chloride	88.85	236–244	—
Tetrachloroethane	74.40	255–262	0.40
Chlorobenzne	90.36	248–260	2.1
Benzene	92.77	250–276	1.78
Benzene–hexane	94.88	266–292	0.64
p-Ksylene	90.36	249–260	0.52

[a] Conditions of the reaction: molar ratio of aqueous to organic phase 1 : 2; molar ratio of the reagents diol/acid chloride 1 : 1.1; temperature of the reaction 25°C; rate of addition of acid chloride, 5 min.

[b] 0.5% solution of phenol/tetrachloroethane 3 : 2 by weight, temperature 25°C.

Table II The Influence of the Catalyst (TEBA) on the Properties of Polyesters from Diol and Isophthaloyl Chloride[a]

Catalyst	Yield (%)	Melting Point (°C)	η_{red}[b]
+	94.87	274–280	1.8
−	90.36	248–260	2.1

[a] Conditions of the reaction: organic phase–chlorobenzene; molar ratio of the reagents diol/acid chloride 1 : 1.1; ratio of aqueous to organic phase 1 : 2; concentration of catalyst, 5% in relation to diol; temperature of the reaction, 25°C; rate of addition of acid dichloride, 5 min.

[b] 0.5% solution of phenol/tetrachloroethane 3 : 2 by weight, temperature 25°C.

The reaction of polycondensation of diol with isomeric phthaloyl acid dichlorides was carried out at first having determined the initial reaction conditions: the aqueous to organic phase ratio 1 : 2, molar ratio of the reagents diol/dichloride 1 : 1.1, and temperature of reaction 25°C, without a catalyst with stoichiometric quantity of sodium hydroxide and at the rate of chloride addition about 15 min. To establish optimal conditions, yield of the process and reduced viscosity were taken into consideration.

Polyester from diol and isophthaloyl chloride was chosen as a model system. The influence of the following parameters on interfacial polycondensation was studied: kind of organic phase, contribution of catalyst (benzyltriethylammonium chloride), concentration of sodium hydroxide (stoichiometric quantity) and 50% excess, and influence of emulsifier, Mersolan, as well as the temperature.

The applied solvent and physicochemical values of obtained polyesters are listed in Table I. From the data presented it follows that the solvent considerably influenced the yield and reduced viscosity of the polycondensation polymers. The best yield and highest value of reduced viscosity were obtained with chlorobenzene as organic phase.

The contribution of catalyst (5% weight in relation to diol) to interfacial polycondensation was studied with stoichiometrically necessary quantity of sodium hydroxide with its 50% excess.

As follows from Table II, a small quantity of catalyst decreased the value of reduced viscosity and increase only in a small degree yield of the obtained polyesters. The contribution of other parameters such as molar excess of sodium hydroxide, the rate addition of acid dichloride, temperature of reaction,

Table III Influence of Catalyst, 50% Excess of NaOH, Marsolan and Temperature on the Reduced Viscosity and Yield of Polyesters from Bis(4-hydroxyphenyl)ether and Isophthaloyl Chloride[a]

Catalyst	50% Excess of NaOH	Mersolan	Temperature 25°C	Temperature 15°C	Yield (%)	η_{red} (dL/g)	Soft Range (°C)
+			+		90.36	2.1	248–260
			+		94.87	1.8	274–280
				+	100.00	2.2	249–265
		+		+	89.85	0.93	240–256
	+			+	81.91	0.68	244–260

[a] Conditions of the reaction: rate of aqueous to organic phase 1 : 1, reagents ratio 1 : 1.1, rate of chloride addition 10 min.
[b] 0.5% solution of phenol/tetrachloroethane 3 : 2 by weight, temperature 25°C.

and contribution of emulsifier, Mersolan, was studied. From the data presented in Table III it is evident that molar excess of sodium hydroxide decreases both yield and value of reduced viscosity. The best yield and highest value of reduced viscosity were obtained lowering temperature of the reaction to 15°C at the rate of addition of acid chloride about 10 min, without using Mersolan.

On the basis of experimental data, the best results for polyesters from isophthaloyl chloride were obtained by using chlorobenzene as an organic phase, ratio aqueous to organic phase 1 : 1, molar ratio of the reagents diol/acid chloride 1 : 1.1, rate of chloride addition about 10 min, and temperature of the reaction 15°C.

Polyesters synthesis from diol and the remaining two chlorides, phthaloyl and terephthaloyl, was carried out according to the conditions for isophthaloyl chloride defined experimentally.

The synthesis of all polyesters were carried out in the way described below.

In a three-necked, round-bottomed flask of 500 cm^3 volume, equipped with a mechanical stirrer, thermometer, and dropper, 2.02 g (0.01 mol) of diol,

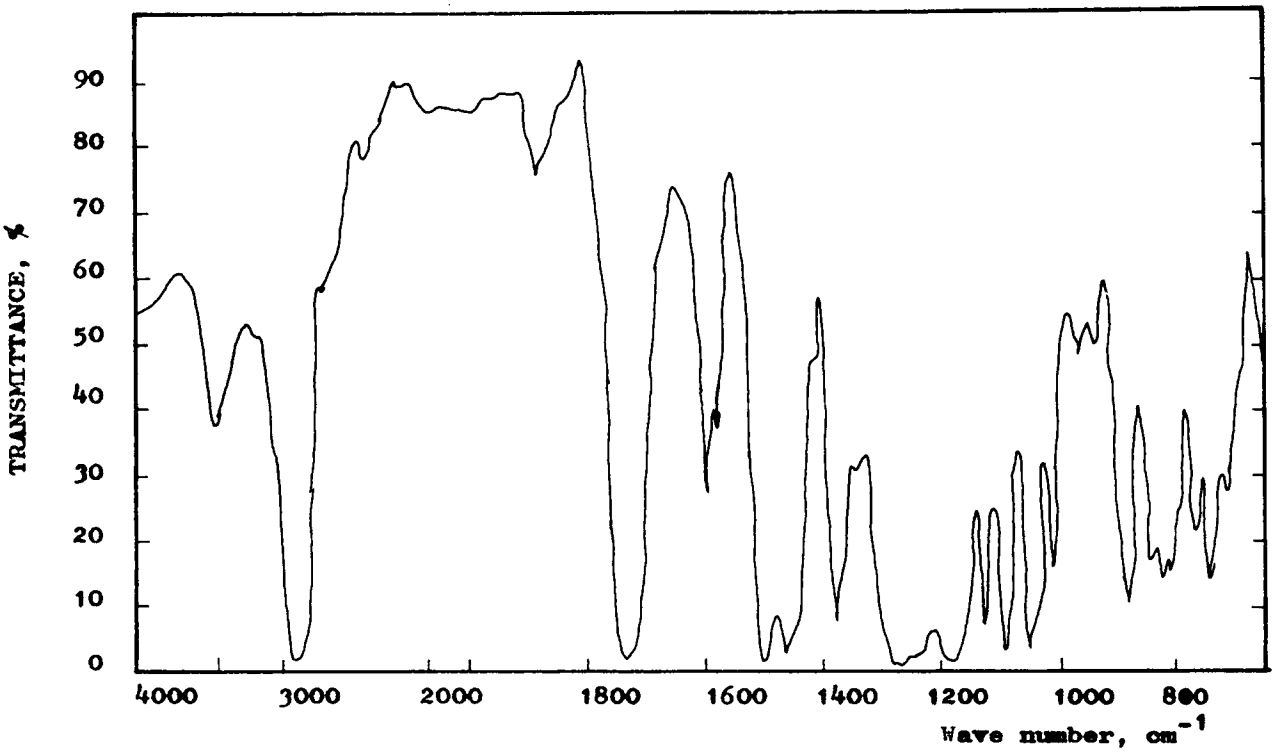


Figure 1 Infrared spectrum of polyester from diol and isophthaloyl chloride.

Table IV Results of Elementary Analysis of Polyesters

	% C		% H	
Acid Chlorides	Calcd	Found	Calcd	Found
Phthaloyl		71.92		4.07
Isophthaloyl	72.28	71.45	3.64	3.55
Terephthaloyl		70.38		3.28

50 mL of chlorobenzene, and what is a suitable quantity of sodium hydroxide stoichiometric quantity, 0.8 g (0.02 mol) of sodium hydroxide dissolved in 100 mL of water, was added. The solution was stirred vigorously and 2.23 g (0.011 mol) of acid chloride in 50 mL of chlorobenzene was added for 10 min. After the addition of acid chloride was completed, stirring was continued for 30 min. The mixture was then acidified with hydrochloric acid (Kongo red) and the separated product of polycondensation was filtered and washed with acetone or methanol (100 mL) and hot water (3 × 100 mL) and then with methanol. Polyester was dried under reduced pressure (15 mm Hg) at 60°C to a constant weight.

Polyesters obtained from diol and isophthaloyl chloride were colorless powders soluble only in mixture of phenol and tetrachloroethane.

Polyesters from terephthaloyl chloride were colorless powders practically insoluble in common solvents and in the mixture of phenol and tetrachloroethane. Polyesters from phthaloyl chloride were obtained as thick oils freezing into glassy mass. They are easily soluble in chlorinated aliphatic and aromatic hydrocarbons.

Infrared (IR) spectra for polyesters from diol and aromatic dichlorides (Fig. 1) showed strong absorption characteristic for ether bond aromatic ring and absorption at 1720 cm^{-1}, which is characteristic for —O—CO— stretching.

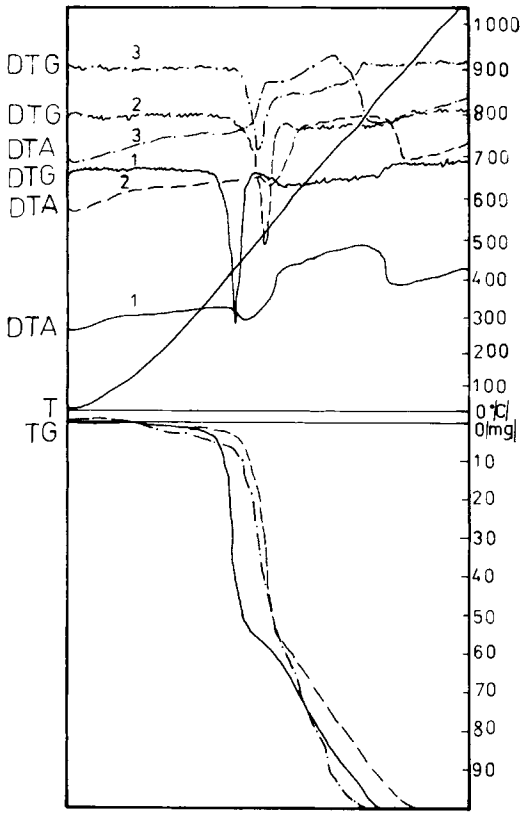


Figure 2 TGA and DTA of polycondensation product of bis(4-hydroxyphenzyl)ether with phthaloyl (——), isophthaloyl (— —) and terephthaloyl (- · -) chlorides. Heating rate, 4°C/min; amount of polyester 100 mg, measured to Al_2O_3.

Polyesters showing the highest value of reduced viscosity were examined by X-ray analysis. It was found that they are either of low crystallinity or amorphous white powders, revealing chemical resistance to diluted acids and alkali.

On the basis of good agreement between calculated and found analytical data (Table IV) and IR spectra, the following reaction scheme for diol and terephthaloyl chloride was assumed:

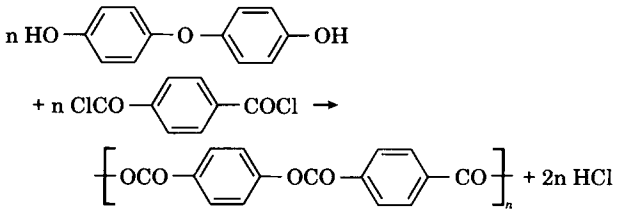
Table V Thermal Properties of Polyesters

Acid Chlorides	Thermal Analysis[a]				Mass Loss (%)			
	T_1	K_1	T_2	K_2	300	400	500	600
Phthaloyl	380	2.0	430	23.0	2.0	13.0	56.0	68.0
Isophthaloyl	400	3.0	500	20.0	2.0	4.0	40.0	65.0
Terephthaloyl	420	8.04	480	34.0	5.0	9.0	42.0	70.0

[a] T_1 = temperature of initial exothermic effect from the curve DTA (°C); K_1 = mass loss in the temperature T_1 (%); T_2 = temperature of initial intensive decomposition from the curve DTA (°C); K_2 = mass loss in the temperature T_2 (%).

Table VI Temperature of Pressing: Mechanical and Electrical Properties of Polyester from Diol and Isophthaloyl Chloride

Test	
Temperature of pressing (°C)	230
Vicat softening point (°C)	200
Rupture strength (kg/cm^2)	78
Impact strength (kg/cm^2)	271
Bending strength (kg/mm^2)	3.1
Brinnel hardness (kg/cm^2)	28.5
Dielectrical constant	2.64
Tan δ at 170 kHz (20°C)	0.0108



Thermal Properties

Aromatic polyesters obtained from bis(4-hydroxyphenyl)ether and isomeric phthaloyl chlorides were examined by differential thermal analysis (DTA).

The temperature of initial decomposition, its mass loss in percent and the temperature of the fastest decomposition process, its mass loss percent, for polyesters in the 200–800°C range are listed in Table V. It can be seen from data in Figure 2 that the decomposition begins at about 300°C and is fastest at 600°C.

Mechanical and Electrical Properties

To examine mechanical and electrical properties, the polyesters obtained from diol and isophthaloyl chloride were presented in a steel mold at a pressure of 200 kg/cm^2. Numerical data are given in Table VI.

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