Linear Polyesters Products of Interfacial Polycondensation of *Bis*(4-Hydroxyphenyl)Ether with Some Aliphatic Acid Dichlorides

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Synopsis

New polyesters were obtained by interfacial polycondensation of *bis*(4-hydroxyphenyl)ether with succinyl, adipoyl, suberoyl, or sebacoyl chlorides. To define the optimal conditions of the process, the polyesters of diol and adipoyl or sebacoyl chlorides were chosen as a model system. Yield for all reaction products and reduced viscosity were found. The following factors were studied: organic phase, contribution of catalyst, concentration and molar ratio of reagents, rate of addition of acid chloride, temperature of reaction and concentration of hydrochloride acceptor. The structure of all polyesters was determined by means of elementary analysis, infrared spectra, and X-ray. Initial decomposition and initial intensive decomposition temperatures were defined by the curves of thermogravimetric analysis. Thermal and electrical properties of polyesters from diol and adipoyl or sebacoyl chlorides were studied. The molecular weights for these polymers were also determined by gel chromatography.

INTRODUCTION

It is known from chemical literature, that *bis*(4-hydroxyphenyl)ether is used for the synthesis of different kinds of polyesters, (e.g., polysulfonates, polycarbonates and polyarylates). It has been found that polysulfonates[1] obtained by interfacial polycondensation from *bis*(4-hydroxyphenyl)ether and disulfoxides are resistant to hydrolysis and aminolysis and at the same time, reveal desirable chemical resistance to alkali, acids, and oils.

Aromatic polycarbonate resins[2,3] apart from good physical, chemical, and electrical properties also have excellent resistance to light and ionizing radiation. The polyesters mentioned above were prepared from diol and phosgene by means of solvent polycondensation at 20–30°C or from diaryl carbonate, especially Ph_2CO_3, at 150–300°C *in vacuo*.

Polyarylates[4-6] from *bis*(4-hydroxyphenyl)ether and aromatic acid dichlorides obtained by melt, solvent, and interfacial polycondensation reveal good mechanical properties. What is more, diol—the object of our research—is utilized to obtain various copolymers[7] of good adhesive properties for different surfaces. In the search for new polyesters it is interesting to study the synthesis of polymer from *bis*(4-hydroxyphenyl)ether and aliphatic acid dichlorides.

The purpose of this study is to determine the optimal conditions for interfacial polycondensation and to define some physicochemical, electrical, and thermal properties of polyesters.

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EXPERIMENTAL

Reagents

Bis(4-hydroxyphenyl)ether, m.p. 160–1°C was prepared by diazotization of *bis*(4-aminophenyl)ether in aq. H_2SO_4 and HCl, followed by decomposition of the salt with refluxing 50% H_2SO_4.[8] Adipoyl chloride with bp 128–130°C (18 torr), suberoyl chloride with bp 143–147°C (12 torr), and sebacoyl chloride with bp 166–168°C (11 torr) were obtained by the reaction of thionyl chloride with corresponding acids. Succinyl chloride with bp 103–104°C (25 torr) was obtained from succinic acid and phosphorous pentachloride.

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

Molecular Weight. Molecular weight was determined by gel chromatography on a Varian Aerograph MOD–4100 apparatus, detector 4V, 2540 A, dosage WATERS 46 K, liquid pump ORLIT.

RESULTS AND DISCUSSION

Optimal Conditions in Interfacial Polycondensation

To determine the optimal conditions of interfacial polycondensation, polyesters from *bis*(4-hydroxyphenyl)ether as well as adipoyl and sebacoyl chlorides, were chosen as a model system. Melting point, yield, and reduced viscosity were determined for the polyesters obtained. The following factors, which influenced the process, were studied: kind of organic phase, contribution of catalyst (benzyltriethylammonium chloride), concentration and molar ratio of reagents, rate of acid chloride addition, temperature of reaction, contribution of emulsifier, and hydrogen chloride acceptor concentration.

After determining the initial reaction conditions, that is, the aqueous to organic phase ratio 1:2, molar ratio of the reagents diol/acid dichloride 1:1.1, reaction temperature 25°C, and the rate of chloride addition 5 min, the influence of the kind of organic solvent on yield and reduced viscosity was examined. The applied solvents and physicochemical values obtained are listed in Table I. From the data presented it follows that the solvent greatly

TABLE I
The Organic Phase Effect on the Yield and Reduced Viscosity of Polyesters from *Bis*(4-hydroxyphenyl)Ether and Adipoyl or Sebacoyl Chloride[a]

Organic phase	Acid chlorides	Yield (%)	η red. (dL/g)	Melting range (°C)
Chloroform	Adipoyl	35.9	0.19	178–186
	Sebacoyl	—	—	oil
Tetrachloromethane	Adipoyl	57.21	0.37	172–178
	Sebacoyl	33.60	0.16	116–119
Benzene	Adipoyl	54.84	0.20	152–158
	Sebacoyl	24.24	0.20	116–122
Benzene/hexane (1 : 1)	Adipoyl	55.12	0.26	181–185
	Sebacoyl	46.36	0.30	139–150
Chlorobenzene	Adipoyl	50.38	0.28	103–108
	Sebacoyl	43.59	0.14	152–158
p-Xylene	Adipoyl	45.51	0.35	176–186
	Sebacoyl	20.66	0.17	120–126

[a] Conditions of the reaction: rate of aqueous-organic phase 1 : 2; reagent ratio 1 : 1, 1, rate of chloride addition 5 min; temperature of the reaction 25°C.

influences the yield and reduced viscosity of the polycondensation polymers. The best yield and the highest value of reduced viscosity were obtained with carbon tetrachloride as organic phase for adipoyl chloride. The highest value of reduced viscosity for sebacoyl chloride was obtained with benzene-hexane (1 : 1) as solvent.

The contribution of catalyst concentration to interfacial polycondensation in the range of 0–10% by weight in relation to the amount of diol was studied. The results presented in Figure 1 show, that catalyst in the case of polyesters derived from adipoyl chloride maintains the value of reduced viscosity on the same level, and slightly increases the yield.

By using a catalyst in the preparation of polyesters from sebacoyl chloride, a considerable increase in reduced viscosity and slight changes in yield take place. Taking these results into consideration, further diol polycondensation from adipoyl chloride was carried out without a catalyst, but in polyester preparation from sebacoyl chloride, an excess of 5% by weight was used.

Polyester from *bis*(4-hydroxyphenyl)ether and adipoyl or sebacoyl chlorides were obtained using 0.1 *M*/L concentration of acid chloride in organic phase.

The influence of the ratio of the aqueous to organic phase on the value of reduced viscosity and yield of polyesters was examined using different quantities of water on the same quantity of organic phase. The ratio of the aqueous to organic phase was 2 : 1–1 : 12, which corresponds to diol concentration in the water-base phase in the range of 0.1–1.2 *M*/L.

From the curves in Figure 2, it follows that the best results in both chlorides are achieved by using 0.2 *M* diol solution (phase ratio 1 : 1). The effect of an excess of acid chloride in range of 0–25% mol on the value of reduced viscosity and yield of polyester from adipoyl and sebacoyl chlorides is also illustrated in Figure 3. In polyester preparation from both chlorides the best results are achieved with a 5% molar excess of acid chloride. Effect of temperature on polyester properties was examined at 0–50°C. The curves in Figure 4 show

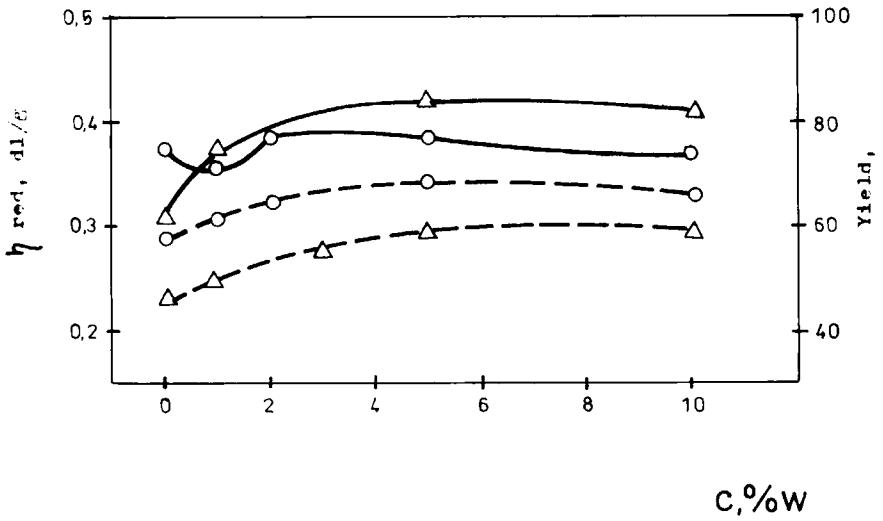

Fig. 1. The influence of the concentration of catalyst on reduced viscosity (—) and yield (- - -) of polyesters from *bis*(4-hydroxyphenyl)ether and adipoyl (○), and sebacoyl (△) chlorides: organic phase CCl_4 for (○) and benzene-hexane for (△) phase ratio 1 : 2 time of chloride addition, 5 min, 10% excess acid chloride, temperature 25°C.

that with increased temperature the values of reduced viscosity and yield increase and then decrease. The best results were achieved in the polycondensation of diol with both acid chlorides in the range of 15–25°C. The effect of acid chloride addition time on the value of yield and reduced viscosity was also studied. As shown in Figure 5, the optimal time of acid chloride addition is 5–10 min for adipoyl chloride and about 8–12 min for sebacoyl chloride.

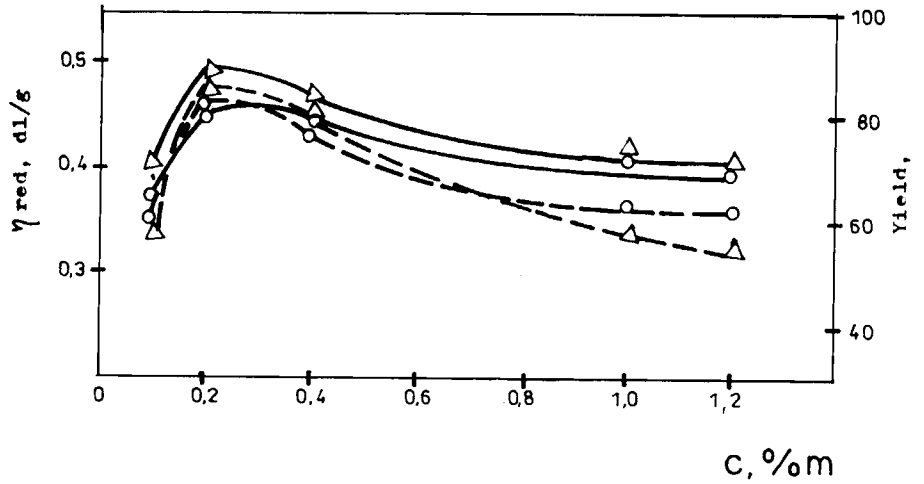

Fig. 2. The influence of the concentration of diol on reduced viscosity (—) and yield (- - -) of polyesters from *bis*(4-hydroxyphenyl)ether and adipoyl (○) and sebacoyl (△) chlorides: organic phase CCl_4 for (○), and benzene-hexane for (△), phase ratio 1 : 2, time of chloride addition 5 min, 10% excess acid chloride, temperature 25°C.

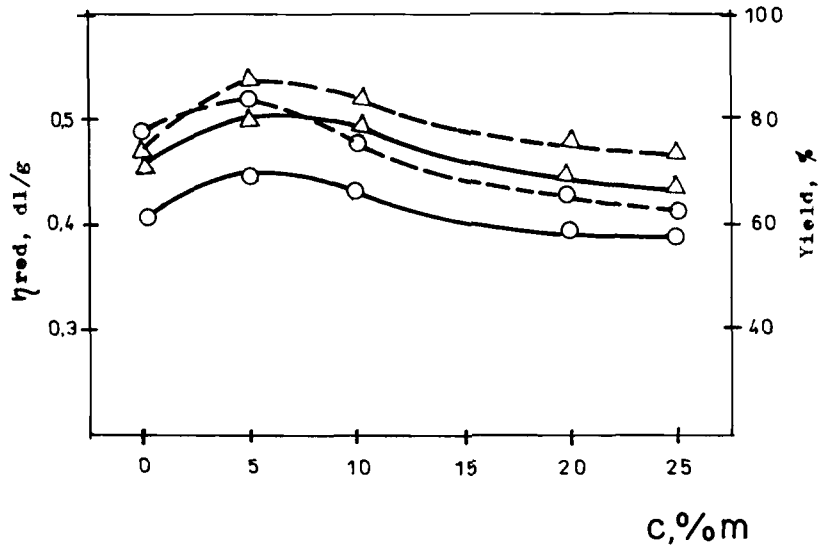

Fig. 3. The influence of acid chloride excess on reduced viscosity (—) and yield (- - -) of polyesters from *bis*(4-hydroxyphenyl)ether and adipoyl (○), and sebacoyl (△) chlorides: organic phase CCl_4 for (○), and benzene-hexane for (△), phase ratio 1 : 1, catalyst 10%, time of chloride addition 5 min, temperature 25°C.

The emulsifier (Mersolan) effect was studied in the range of 0–0.2% wt in relation to aqueous phase. The curves in Figure 6 show negative contribution of the emulsifier on yield and reduced viscosity for the two dichlorides applied. Both these values decreased considerably. The influence of the amount of sodium hydroxide as a hydrogen chloride acceptor was studied in

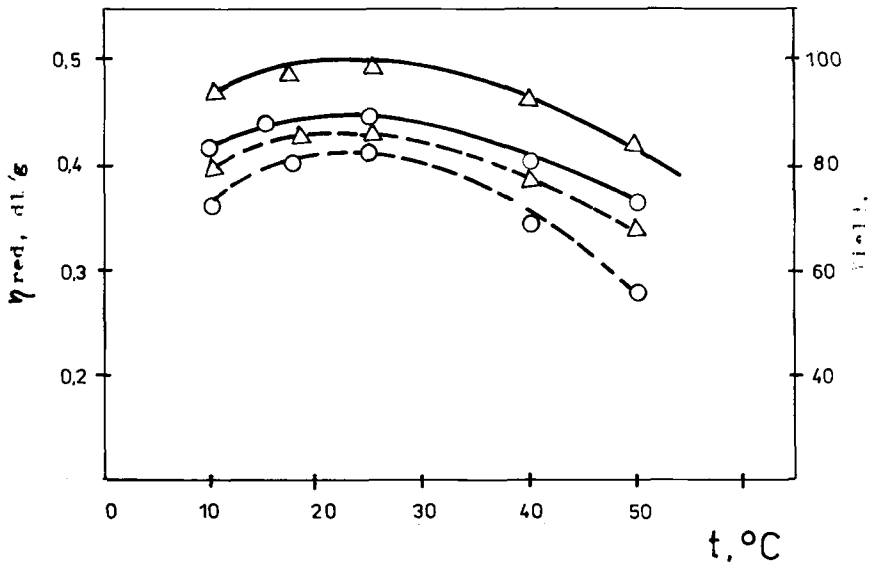

Fig. 4. The influence of temperature on reduced viscosity (—) and yield (- - -) of polyesters from *bis*(4-hydroxyphenyl)ether and adipoyl (○), and sebacoyl (△) chlorides: organic phase CCl_4 for (○), and benzene-hexane for (△), phase ratio 1 : 1, catalyst 10%, time of chloride addition 5 min.

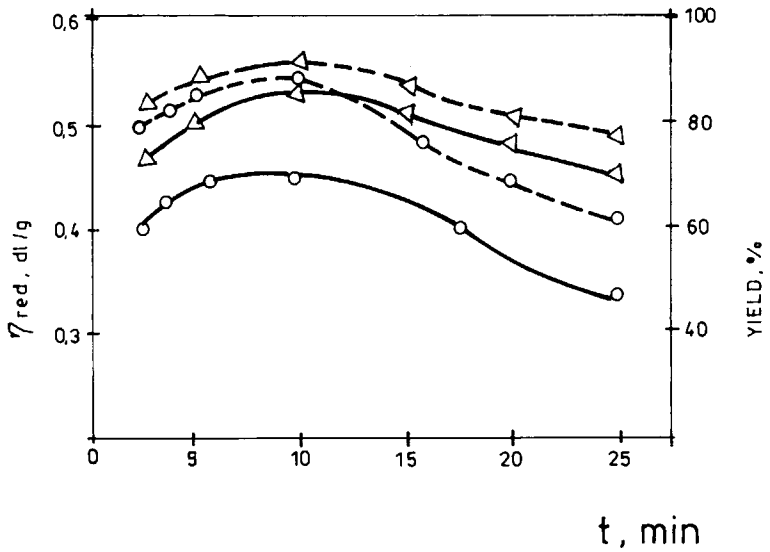

Fig. 5. The influence of time of chloride acid addition on reduced viscosity (—), and yield (- - -) of polyesters from diol and adipoyl (○) and sebacoyl (△) chlorides: phase CCl_4 for (○) and benzene-hexane for (△), phase ratio 1 : 1, catalyst 10%, excess of chloride 10%, temperature 25°C.

the range of 0–150% wt and results are presented in Figure 7. The addition of 30% excess of NaOH is useful, because the increased value of reduced viscosity and yield of polycondensation reaction for the two dichlorides applied. Adding more than 30% excess to the reaction is unfavorable, because yield and reduced viscosity of polyesters decreased. Considering the experimental results, the interfacial polycondensation conditions for polyester preparation

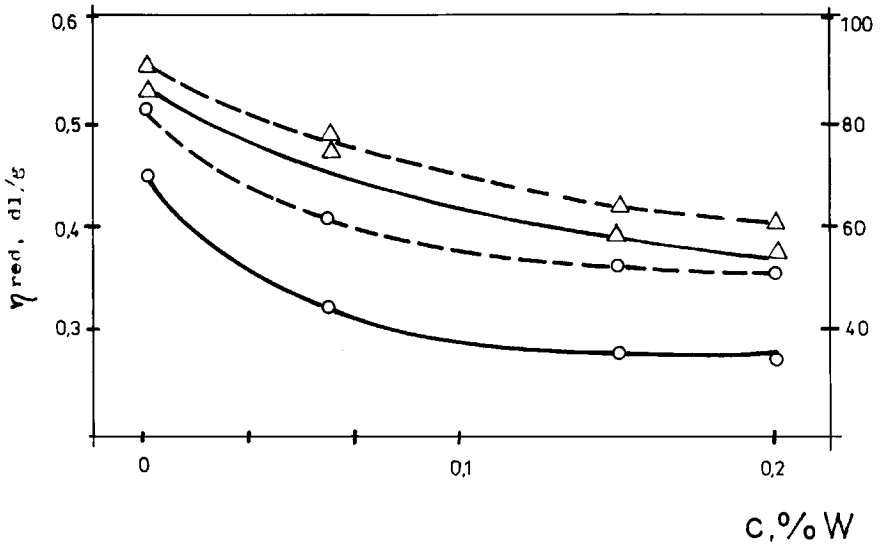

Fig. 6. The influence of concentration of emulsifier on reduced viscosity (—) and yield (- - -) of polyesters from diol and adipoyl (○), and sebacoyl (△) chlorides: organic phase CCl_4 for (○), and benzene-hexane for (△), phase ratio 1 : 1, catalyst 10%, excess of chloride 10%, temperature 25°C.

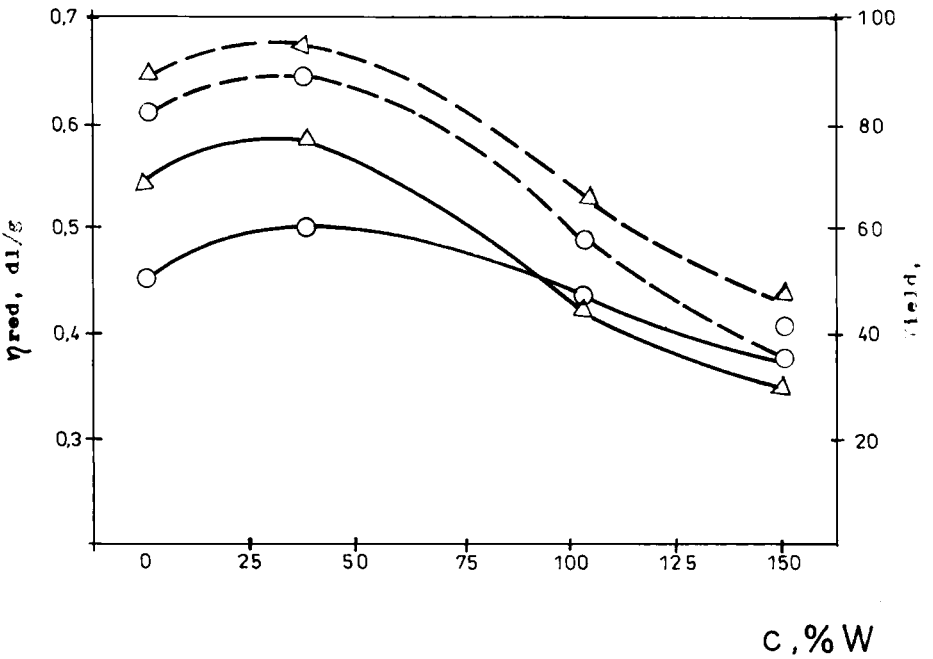

Fig. 7. The influence of sodium hydroxide excess on reduced viscosity (—) and yield (- - -) of polyesters from diol and adipoyl (○) and sebacoyl (△) chlorides: organic phase CCl_4 for (○) and benzene-hexane for (△), phase ratio 1 : 1, catalyst 10%, excess of chloride 10%, temperature 25°C.

from *bis*(4-hydroxyphenyl)ether and adipoyl and sebacoyl chlorides were defined.

The best results for polyesters from adipoyl chloride were obtained using tetrachloromethane as an organic solvent, 0.1 *M* diol solution, aqueous to organic phase ratio 1 : 1, molar ratio of the reagents diol-acid dichloride 1 : 1.1, rate of chloride addition 5–10 min, reaction temperature of 15–25°C, and 30% excess of hydrogen chloride acceptor. Best results for polyesters from sebacoyl chloride were obtained using organic phase benzene/hexane (1 : 1), concentration of catalyst 5% wt, aqueous to organic phase ratio 1 : 1, molar ratio of the reagents diol-acid dichloride 1 : 1.1, rate of chloride addition 8–12 min, reaction temperature of 15–25°C, and 30% excess of hydrogen chloride acceptor.

The definition of optimal polycondensations in the preparation of polyesters from adipoyl and sebacoyl chlorides results from the different reactivities of the chlorides. In diol polycondensation with less reactive sebacoyl chloride better results are obtained with a catalyst and a longer time of chloride addition. Polyesters from succinyl chloride were prepared under optimal conditions used for adipoyl chloride, and, in the case of suberoyl chloride, the conditions were those used for sebacoyl chloride.

The synthesis of polyesters from diol and adipoyl chloride was carried out as follows: 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, 50 mL of tetrachloromethane, and a suitable quantity of sodium hydroxide, that is, a stoichiometric quantity (0.02 mol) or 30% excess (0.026 mol) dissolved in 100 mL of water was added. A 5% excess (0.0105 mol) of

adipoyl chloride in 50 mL of tetrachloromethane was added for 5–10 min at 15–25°C and stirred vigorously. After the addition of acid chloride was completed stirring was continued for 30 min. The mixture was then acidified with hydrochloric acid (Congo red) and the isolated 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 pressured (15 mm Hg) at 60°C to a constant weight.

Synthesis from *bis*(4-hydroxyphenyl)ether and sebacoyl chloride were carried out as follows. 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, 50 mL of benzene-hexane volume ratio (1 : 1), and a suitable quantity of sodium hydroxide, that is, a stoichiometric quantity (0.02 mol) or 30% excess (0.026 mol) in 100 mL water and 0.1 g of catalyst (benzyltriethylammonium chloride) was added. Then a solution of 2.26 g (0.15 mol) acid chloride in 50 mL of a benzene-hexane (1 : 1) was added during 8–12 min at 15–25°C at vigorous stirring. After the addition of acid chloride was completed, stirring was continued for 30 min. The mixture was then acidified with hydrochloric acid (Congo red) and the isolated product of polycondensation was filtered and washed with acetone (100 mL) and hot water (3 × 100 mL) and then with methanol. The polymer was dried under reduced pressure (15 mm Hg) at 60°C to a constant weight.

Polyesters obtained without an excess of hydrogen chloride acceptor are highly soluble in chlorinated aliphatic hydrocarbons while those obtained with 30% excess of sodium hydroxide are hardly soluble. They dissolve only in the solvent mixture of phenol-tetrachloroethane. The reduced viscosity was determined for 0.5% solutions in the mixture of phenol-tetrachloroethane used in the weight ratio 3 : 2 at 25°C.

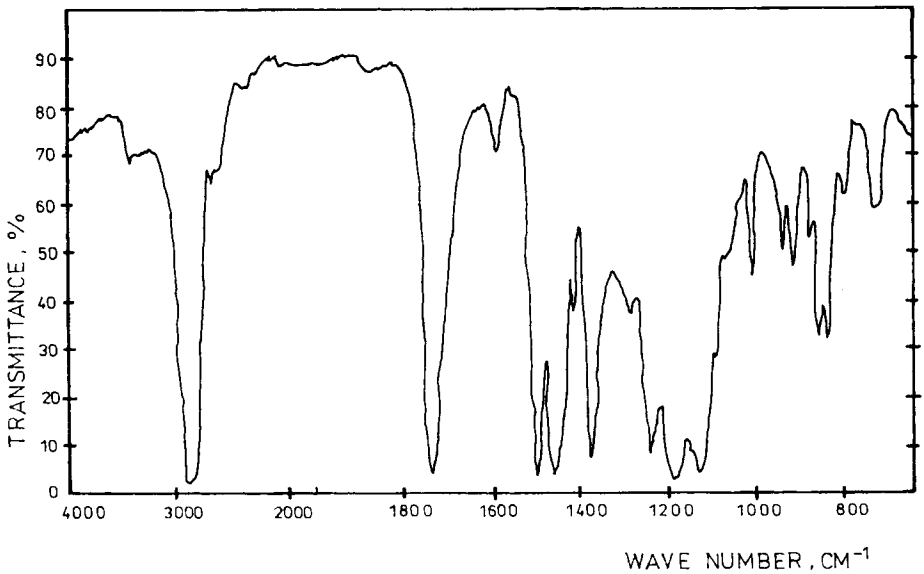

Fig. 8. Infrared spectrum of polyester from diol and adipoyl chloride.

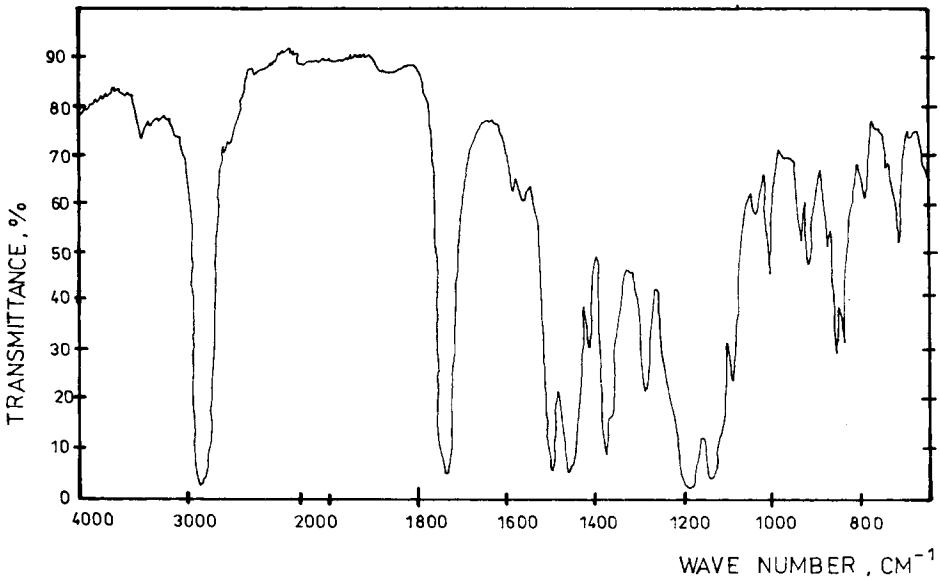

Fig. 9. Infrared spectrum of polyester from diol and sebacoyl chloride.

Infrared (IR) spectra for polyesters from adipoyl and sebacoyl chlorides (Figs. 8 and 9 showed strong adsorption characteristics for ether band, aromatic ring, and strong adsorption at 1720 cm^{-1}, which is characteristic for —O—CO— stretching.

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 (except for polyester from diol and succinyl chloride, which is cream colored) insoluble in common organic solvents. They dissolve only in the solvent mixture of phenol/tetrachloroethane. These polyesters reveal chemical resistance to diluted acids and alkali.

Thermal Properties

Aliphatic-aromatic polyesters obtained from *bis*(4-hydroxyphenyl)ether and adipoyl or sebacoyl chlorides under optimal conditions 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 of mass loss-percent for polyesters in the 300–700°C range are listed in

TABLE II
Results of Elementary Analysis of Polyesters

Acid chlorides	% C		% H	
	Calcd.	Found.	Calcd.	Found.
Succinyl	67.60	67.24	4.25	5.00
Adipoyl	69.22	68.10	5.16	4.82
Suberoyl	70.57	69.48	5.92	5.80
Sebacoyl	71.72	70.68	6.57	6.72

TABLE III
Thermal Properties of Polyesters

Acid chlorides	Thermal analysis[a]				Mass loss, %			
	T_1	K_1	T_2	K_2	400°C	500°C	600°C	700°C
Succinyl	320	2.0	420	28	21.0	52.5	68.0	80.0
Adipoyl	260	1.5	340	16	55.0	59.0	70.0	77.0
Suberoyl	340	3.0	450	32.5	10.0	67.0	80.0	97.0
Sebacoyl	315	0.5	480	52	9.0	75.0	88.0	100.0

[a] T_1 = temperature of initial exotermic 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; %

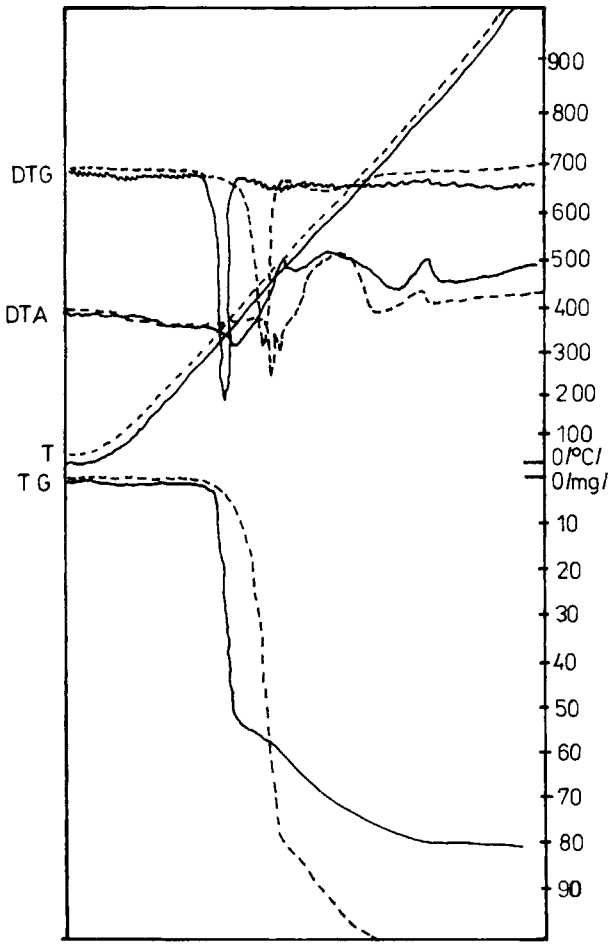

Fig. 10. TGA and DTA of polycondensation product of *bis*(4-hydroxyphenyl)ether with adipoyl (—) and sebacoyl (- - -) chlorides. Heating time in air, 250 min; heating rate, 4°C/min; amount of polyester 100 mg; measured relative to Al_2O_3.

Table III. The results of the examination are shown only for diol and adipoyl and sebacoyl chlorides. It can be seen from the data (Fig. 10) that the decomposition begins at about 300°C and is fastest at 500–700°C.

Electrical Properties

To examine electrical properties the polyesters obtained from diol and adipoyl or sebacoyl chlorides were pressed in a steel mold at 200 kG/cm^2 pressure. The value of dielectrical constant for polyester from diol and adipoyl chloride equals 2.0 and 1.5 for sebacoyl chloride, and the tan δ values at 170 kHz, 20°C equal 0.0037 and 0.0161, respectively.

Molecular Weight Determination

The molecular weights of polyesters obtained by interfacial polycondensation from *bis*(4-hydroxyphenyl)ether and adipoyl or sebacoyl chlorides without an excess of sodium hydroxide and thereby soluble in tetrachloroethane were determined by gel chromatography. The value for the former was 37,400–37,800 and for the latter, 40,600–43,000.

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