Synthesis of Rigid Polyurethane Foams from Oligoester Alcohols Based on the Residues from the Distillation of Crude Dimethyl Terephthalate and Recrystallization of the Dimethyl Terephthalate/Dimethyl Isophthalate Fraction

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Synopsis

Oligoester alcohols are synthesized from the residues from the distillation of crude dimethyl terephthalate and recrystallization of the fraction dimethyl terephthalate/dimethyl isophthalate, diols, triols, tetrols, and tall oil. The polyol component containing various oligoester alcohols is suitable for preparing rigid polyurethane foams with good thermal stability and improved resistance to combustion.

INTRODUCTION

The industrial production of dimethyl terephthalate via oxidation of *p*-xylene with air followed by esterification with methanol also affords waste products consisting mainly of methyl esters of aromatic carboxylic acids.

The waste products[1] can be used in transesterification with the hydroxyl group containing compounds as a raw material for synthesizing oligoester alcohols, with the view to using them in the preparation of rigid polyurethanes. They possess good physical and mechanical characteristics and have considerably improved resistance to combustion compared to rigid polyurethanes prepared from aliphatic acids, diols, and triols. Industrial production of oligoester alcohols can be carried out by using waste products from the production of dimethyl terephthalate.

The aim of this work is the synthesis of oligoester alcohols by simultaneously using the residues from the distillation of crude dimethyl terephthalate (residue 1) and from the recrystallization of the dimethyl terephthalate/dimethyl isophthalate fraction (isophthalic fraction). The synthesis is based on the waste mixture with a constant methoxycarbonyl group (32.98%), thus paving the way for the industrial production of the oligoester alcohols.

EXPERIMENTAL

Starting compounds. The residue from the distillation of crude dimethyl terephthalate (residue 1); the residue from the recrystallization of the fraction dimethyl terephthalate/dimethyl isophthalate (isophthalic fraction); diethylene glycol; trimethylolpropane; pentaerythritol; triethanol amine; tall oil.

Synthesis of Oligoester Alcohols

Synthesis of Oligoester Alcohol from Residue 1, the Isophthalic Fraction, Diethylene Glycol, and Trimethylolpropane in Ratio of OH:(COOH + COOCH$_3$) = 4.25:1 (Oligoester Alcohol A)

Diethyleneglycol (371 g, 3.5 mol) and tetrabutyl titanate (0.4 g) are placed in a four-necked flask provided with a stirrer, thermometer, Vigreux column, and a condensor. The temperature is brought to 130°C and trimethylol propane (67 g, 0.5 mol) added. Residue 1 (methoxycarbonyl group content 5.3%) (194 g) is added to the reaction mixture after the dissolution of trimethylol propane followed by isophthalic fraction (methoxycarbonyl group content 11.90%) (191 g), bringing in this manner the total methoxycarbonyl group content to 32.98%. The temperature is brought to 180°C and evolution of methanol begins. The temperature is increased at the rate of 10°C/h to 220°C. The reaction is continued until an acid value of 1–2 mg KOH/g is reached. The temperature is brought down to 120°C after the end of the reaction, and the mixture is subjected to reduced pressure.

The product obtained is a dark-brown viscous liquid which was characterized by the hydroxyl value, acid value, methoxycarbonyl content, moisture content, density, and viscosity (see Table III).

Synthesis of Oligoester Alcohol from Residue 1, the Isophthalic Fraction, Diethylene Glycol, and Trimethylolpropane in Ratio of OH:(COOH + COOCH$_3$) = 2.87:1 (Oligoester Alcohol B)

Diethyleneglycol (84.8 g, 0.8 mol) and tetrabutyl titanate (0.4 g) are placed in a four-necked flask provided with a thermometer, a Vigreux column, and a condensor. The temperature is brought to 120°C and trimethylolpropane (201 g, 1.5 mol) introduced. Residue 1 (194 g, methoxycarbonyl content 5.3%) and isophthalic fraction (methoxycarbonyl content 11.90%) are added after trimethylolpropane has dissolved; the total methoxycarbonyl content is 32.98%. The temperature is increased to 180°C, and the evolution of methanol begins. The temperature rate of increasing is 10°C/h till 220°C. Tall oil (34.8 g, 0.12 mol) is added after the evolution of methanol ceases. The reaction is continued until an acid value of 1–2 mg KOH/g is reached, and then cooled to 130°C and subjected to reduced pressure.

The product obtained is a dark-brown strongly viscous liquid, characterized as the oligoester alcohol B (see Table III).

Synthesis of Oligosester Alcohol from Residue 1, Isophthalic Fraction, Diethyleneglycol, Trimethylolpropane, and Pentaerythritol in Ratio of OH: (COOH + COOCH$_3$) = 3.3:1 (Oligoester Alcohol C)

The synthesis is conducted, as with the oligoester alcohol A, at the following reactant ratios: diethyleneglycol (68.9 g, 0.65 mol), tetrabutyl titanate (0.4 g), trimethylolpropane (83.0 g, 0.62 mol), pentaerythritol (174 g, 1.28 mol), residue 1 (194 g), and isophthalic fraction (191 g). After the reaction has ended, 20% polyethyleneglycol (129.5 g) with molecular mass 200 is added to the synthesized oligoester alcohol.

TABLE I
Composition of Rigid Polyurethane Foams

No.	Starting compounds	Weight fractions	
		PP-1	PP-2
1	Oligoester alcohol A	16	16
2	Oligoester alcohol B	14	14
3	Oligoester alcohol C	9	9
4	Oligoester alcohol D	15	15
5	Polyethyleneglycol	11.2	11.2
6	Glycerol	3.9	3.9
7	Tris(β-chloroethyl) phosphate	—	7.2
8	Surfactant	1.3	1.3
9	Water	0.34	0.34
10	Stannous octanoate	0.09	0.09
11	Freon-11	20.80	20.80
12	Amine catalyst	1.20	1.20
13	Diisocyanate polymer	112.0	112.0

The characteristics of the prepared oligoester alcohol are listed in Table III.

Synthesis of Oligoester Alcohol from Residue 1, Isophthalic Fraction, Diethyleneglycol, and Triethanol amine in Ratio of $OH:(COOH + COOCH_3)$ = 5.35:1 (Oligoester Alcohol D)

Diethyleneglycol (265 g, 2.5 mol) and triethanol amine (283.1 g, 1.9 mol) are placed in a four-necked flask provided with a stirrer, thermometer, Vigreux column, and condensor. The temperature is increased to 120°C and residue 1 (194 g, methoxycarbonyl group content 5.3%) and isophthalic fraction (191 g, methoxycarbonyl group content 11.90%) are added, bringing the total methoxycarbonyl content to 32.98%. The reaction begins at 135°C. The temperature is brought to 165°C, and the process carried out at this temperature. The reaction mixture is cooled to 120°C after the evolution of methanol ceases and is subjected to reduced pressure.

The characteristics of the synthesized oligoester alcohol are given in Table III.

Synthesis of Rigid Polyurethane Foams

Starting compounds. Oligoester alcohol A, oligoester alcohol B, oligoester alcohol C, oligoester alcohol D, polyethyleneglycol with molecular mass 200, glycerol, tris(β-chloroethyl) phosphate, surfactant, stanous octanoate, freon-11, an amine catalyst, polymeric diphenyl methanediisocyanate.

The polyol component consisting of compounds 1–10 (Table I) exhibits the following characteristics: hydroxyl value mg KOH/g = 310.84, acid value, mg KOH/g = 8.1, moisture content (%) = 1.88, density at 20°C (g/cm³) = 1.0962, and viscosity at 20°C (cps) = 1887.

The component A consisting of the polyol component, freon-11, and the amine catalyst has a density of 1.2201 (at 20°C, g/cm³) and a viscosity of 880 (at 20°C, cps).

The polyurethane foams are synthesized at an isocyanate index of 112.

The rigid polyurethane foams were prepared in a 250-mL beaker by mixing the ingredients with a mechanical stirrer for 10 s (1350 rev/min). The reaction mixture is then poured onto a polyethylene foil. During the synthesis the starting time, crosslinking duration, and end of the crosslinking process (Table IV) were followed.

Characterization of the Oligoester Alcohols and the Polyurethanes

The hydroxyl value was determined according to the acetylation method; the acid value—by titrating a sample with KOH against phenolphthalein; methoxycarbonyl groups—by gas chromatography; moisture content—by Karl Fischer's procedure; viscosity—using a rotation viscosimeter (Brookfield, Model LVT).

The characteristics of the polyurethanes were determined using standard procedures. The oxygen index was obtained with samples of dimensions 100/10/10 mm on an FTA instrument. The thermal studies were conducted on a MOM derivatograph at a heating rate of 10°C/min in an air atmosphere.

RESULTS AND DISCUSSION

Studies on the composition of waste products from the production of dimethyl terephthalate, i.e., residue 1, residue 2, and the isophthalic fraction, indicated that the methoxycarbonyl group content in the residues 1 and 2 varies considerably. This observation necessitated a constant change in the ratios of the starting compounds used for the synthesis of the oligoester alcohols.[1] In order to avoid this disadvantage experiments were conducted with residue 1 and the isophthalic fraction premixed to give a methoxycarbonyl group content of 32.98%. The high methoxycarbonyl group content of this fraction and the constant composition of the isophthalic fraction resulted in minimal variations in the composition of the waste products used in the synthesis.

The polyester alcohols employed in the preparation of the rigid polyurethane foams have to satisfy certain conditions regarding the hydroxyl value, branching, reactivity, and compatibility with freon and viscosity.

In connection with these requirements for the synthesis of oligoester alcohols from residue 1 and the isophthalic fraction various ratios between OH and (COOH + $COOCH_3$) groups, various diols, and triols were used.

The experiments conducted using residue 1 and the isophthalic fraction (see Table II) indicate that the increase of the ratio of OH/(COOH + $COOCH_3$) leads to better completion of the transesterification and esterification processes, as

TABLE II
Characteristics of Residue 1 and the Isophthalic Fraction

Characteristics	Residue 1	Isophthalic fraction
Acid value (mg KOH/g)	15	5.4
Methoxycarbonyl content (%)	5.3	11.9
Moisture (%)	0.01	0.01

judged from the methoxycarbonyl content of the oligoester-alcohols and the acid values (the data from the synthesis of the oligoester alcohols A, B, and C will be discussed).
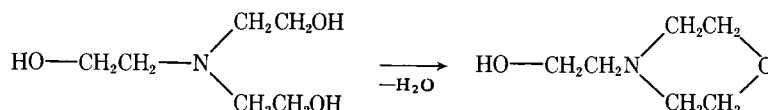
The highest degree of transesterification reaction was observed for the oligoester alcohol A at the highest ratio of OH/(COOH + COOCH$_3$) (Table III). Decreasing this ratio adversely affects the completion of the reaction. The esterification process is to a lesser extent dependent on this ratio.

The high OH vs. carboxylic and methoxycarbonyl groups ratio determines the hydroxyl group value and the low viscosity.

It is known[2] that the introduction of tall oil into the polyester alcohol fraction considerably improves its compatibility with freon 11 and reduces its viscosity. The experiments carried out corroborate these conclusions. Synthesizing oligoester alcohol from waste mixture, diethylene glycol, and trimethylolpropane in ratio of OH:(COOH + COOCH$_3$) = 3.05:1[3] yields a product with a viscosity of 71,200 cps. The latter goes down to 48,939 cps on introducing 0.12 mol tall oil (oligoester alcohol B) at a ratio of functional groups 2.87:1.

A synthesis using pentaerythritol (oligoester alcohol C) at a ratio of 3.3:1 was conducted with the view to improving the branching of the chain of the oligoester alcohol. The product obtained is considerably branched in comparison with the other oligoester alcohols.

In order to improve the reactivity of the oligoester alcohols a synthesis using triethanol amine (oligoester alcohol D) was carried out. The transesterification proceeds at considerably lower temperatures (135°C) than with other diols and triols even in the absence of a catalyst. This result is due to the higher basicity of triethanol amine. Conducting the synthesis under the conditions of preparing the oligoester alcohols A, B, and C indicated that the esterification and transesterification processes are accompanied by dehydration of the triethanol amine. Triethanol amine undergoes dehydration above

$$\text{HO---CH}_2\text{CH}_2\text{---N}\begin{array}{c}\diagup\text{CH}_2\text{CH}_2\text{OH}\\ \diagdown\text{CH}_2\text{CH}_2\text{OH}\end{array} \xrightarrow[-\text{H}_2\text{O}]{} \text{HO---CH}_2\text{CH}_2\text{N}\begin{array}{c}\diagup\text{CH}_2\text{CH}_2\diagdown\\ \diagdown\text{CH}_2\text{CH}_2\diagup\end{array}\text{O}$$

This reaction is reflected in a marked decrease in the hydroxyl value and an increase in the acid value. In spite of having carried out the process at 165°C, the oligoester alcohol possessed a strongly decreased hydroxyl value and a strongly increased acid one.

TABLE III
Characteristics of the Oligoester Alcohols

Indexes	Oligoester alcohols			
	A	B	C	D
OH/(COOH + COOCH$_3$)	4.25:1	2.87:1	3.3:1	5.35:1
Hydroxyl value (mg KOH/g)	403.4	354.0	310.8	171.65
Acid value (mg KOH/g)	1.37	1.85	1.97	28.05
Methoxycarbonyl content (%)	0.88	4.21	2.08	7.15
Moisture (%)	0.21	0.20	0.29	1.40
Density, at 20°C (g/cm^3)	1.2133	1.1972	1.1248	1.2203
Viscosity, at 20°C (cps)	2038	48,939	1939	18,951

TABLE IV
Characteristics of the Rigid Polyurethane

Characteristics	PU-1	PU-2
Density (kg/cm^3)	38	35
Resistance at 10% deformation (kg/cm^2)	1.05	1.8
Open	—	—
pores (%)		
Closed	98	95
Coefficient of thermal conductivity		
(kcal/m·h), 0°C	0.023	0.023
Oxygen index (%) O$_2$	20.2	22.0
Reaction times:		
Starting times (s)	21	18
Crosslinking time (s)	42	37
Time required for ending the rise (s)	61	44

From the oligoester alcohols a polyol component was prepared in this manner synthesized (Table I) which was further used in the preparation of rigid polyurethane foams.

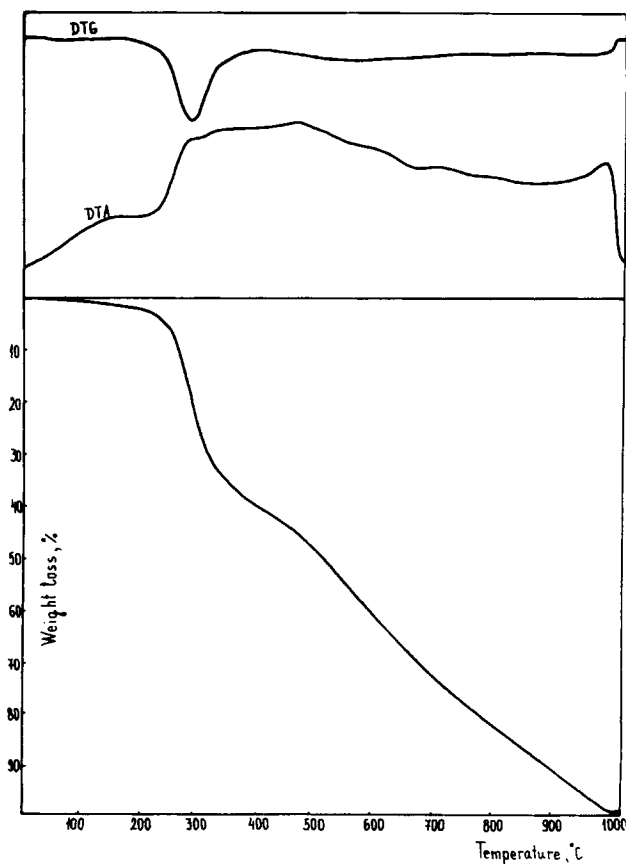Values shown in Table IV indicate that the used polyol component consisting

Fig. 1. DTG, DTA, and TG curves for PU-1.

of the four oligoester alcohols is suitable for the synthesis of rigid polyurethane foams.

A comparison between PU-2 [contains tris(β-chloroethyl)phosphate] and the rigid polyurethane foams on the basis of the oligoester alcohols from residue 1 and residue 2[1] shows that the latter have higher oxygen index values, i.e., 24.3 and 24.8, respectively. This difference can arise solely as a result of the two times lower content of condensed aromatic compounds in PU-2 since 50% of the waste mass consists of the isophthalic fraction. This assumption is also supported by the improvement in resistance to combustion of polymers containing condensed aromatic compounds.[5]

From the differential-thermal analysis curves (Fig. 1) for PU − 1 the apparent decomposition takes place at 200°C, while the maximal degradation rate is at 300°C coinciding with a well-marked exothermal effect associated with oxidative processes.

The comparison of the TG curves for PU-1 and polyurethane foam obtained on the basis of polyester alcohol prepared from laevoglucosane, adipic acid, and diethylene glycol (PU-3)[6] shows that the polyurethane foams begin to degrade at the same temperatures. A significant difference between the TG curves is observed above 300°C—PU-1 loses 50% of its mass at 540°C while PU-3[6] loses
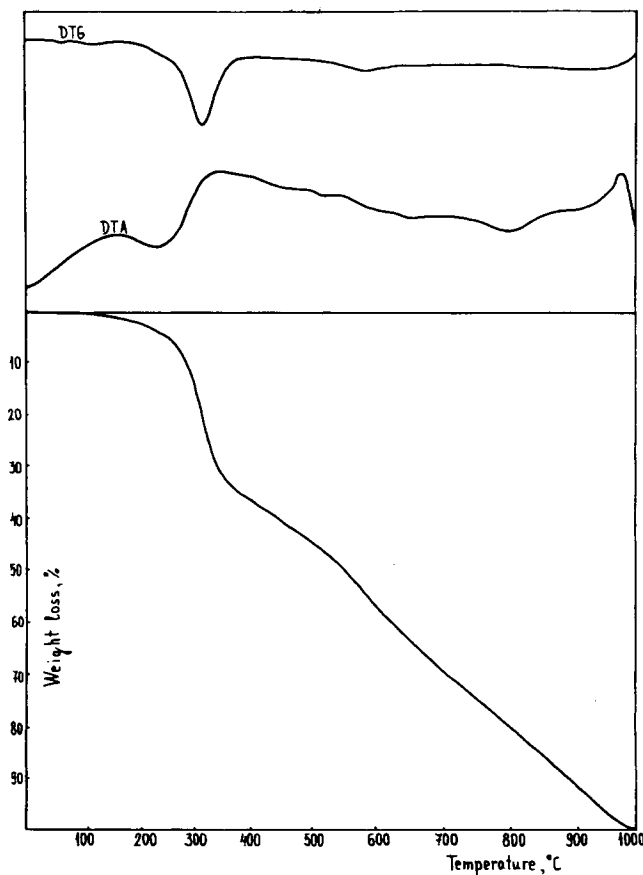

Fig. 2. DTG, DTA, and TG curves for PU-2.

50% of its mass at 370°C; at 600°C, PU-3 loses 85%, while PU-1 loses 56%. These results show that PU-1 is relatively thermostable.

A certain amount of tris(β-chloroethyl) phosphate[7] was introduced into the rigid polyurethane foams with the view to improving the compatibility of the polyol component with freon-11. Thermal analysis of PU-2 containing tris(β-chloroethyl phosphate) (Fig. 2) shows that its introduction does not significantly affect the TG curve. Destruction begins at 160°C (1.74%); however, the further course of the curve is the same as for PU-1. A difference is observed above 500°C—the losses for PU-2 are about 1.5–2% lower in comparison with PU-1. This is probably due to the presence of tris(β-chloroethyl phosphate) which as flame retardant increases the coke residue.[8]

It can be seen, from the course of the TG curves for PU-1 and PU-2, that destruction proceeds in two stages—the first from 200°C to 400°C and the second from 400°C to 900°C. In the first stage the destruction of the aliphatic part of the polyurethane foams takes place; while in the second stage the aromatic compounds are destroyed.

The following conclusion can be drawn: The oligoester alcohols based on residue 1 and the isophthalic fraction are suitable for synthesizing rigid polyurethane foams with good physical and mechanical properties and considerably improved thermal stability and flame resistance.

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