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Oligoesters on the Basis of Hydroxyethylated Derivatives of 4,4'-(Propan-2,2-diyl)diphenol

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Abstract—Equilibrium melt polycondensation was used to synthesize a series of oligoethers containing end hydroxy groups, starting with hydroxyethylated derivatives of 4,4'-(propan-2,2-diyl)diphenol and saturated aliphatic dicarboxylic acids. The structure of the oligoethers was assigned, and their physicochemical characteristics and thermal stability were determined.

Keywords: 4,4'-(propan-2,2-diyl)diphenol derivatives, aromatic oligoesters, physicochemical properties, thermal stability

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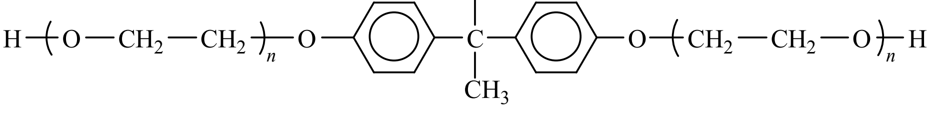
Synthesis of polyfunctional reactive oligomers is an important task of modern macromolecular chemistry. One of the lines of activities in this field relates to the synthesis of oligoesters which can be further used as starting materials for heat- and fire-resistant polyurethane materials. Phosphorus- and halogen-containing oligoesters for production of fire-resistant polyurethanes have been described in [1, 2]. However, such polymers have a fairly low thermal stability. One of the synthetic approaches to materials combining fire resistance and a high thermal stability consists in the introduction into the polymer chain of benzene rings, using aromatic oligoesters as the starting materials. Oligoesters on the basis of phthalic anhydride and diethylene glycol have been prepared [3]. Probably, the thermal stability of oligoesters can be further enhanced using monomers with coupled aromatic moieties as the component, containing hydroxyl groups.

In the present work we used hydroxy-ethylated 4,4'-(propan-2,2-diyl)diphenol derivatives **I** and **II** to synthesize oligoesters (Scheme 1).

The choice of compounds **I** and **II** is motivated by the fact that they contain two hydroxy groups capable of reacting with carboxylic acids to form ester bonds. The presence of benzene rings in monomers **I** and **II** makes it possible to include fragments containing two aromatic rings into the oligoester to be synthesized. The introduction of such fragments into the oligoester chain gives us grounds to expect that the polyurethane on its basis will feature enhanced thermal stability. Moreover, by varying the degree of hydroxyethylation of diphenol one will be able to vary the flexibility of oligoester units, which, in its turn, will open access to polymers with varied degree of flexibility.

Aromatic oligoesters were synthesized by polycondensation of aliphatic dicarboxylic acids with excess of compounds **I** and **II**. As the dicarboxylic acids we took adipic and sebacic acids, which have different numbers of methylene units between the carboxy groups. The temperature and time regimes of the synthesis and the characteristics of aromatic oligoesters are presented in the table.

Scheme 1.



I, II

$n = 1$ (**I**), 3 (**II**).

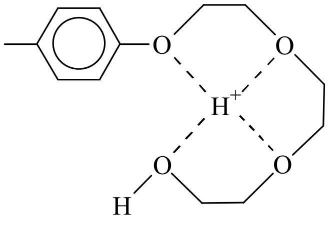
Conditions of synthesis and properties of aromatic esters synthesized by polycondensation of adipic (AA) and sebacic (SA) acids and diols **I** and **II**

Comp. no.	Monomer molar ratio	Stage 1		Stage 2		Yield, %	Acid number, mg KOH/g	Hydroxyl number, mg KOH/g	*M*		*n*
		time, h	*T*, °C	time, h	*T*, °C				found	calculated	
III	**I**–AA, 2 : 1	5	150	5	180	99	0.4	151.4	739	742	1
IV	**II**–AA, 2 : 1	5	150	28	180	95	2.6	101.8	1054	1094	1
V	**I**–AA, 1.5 : 1	2	160	19	180	98	1.4	95.5	1158	1168	2
VI	**II**–AA, 1.5 : 1	6	180	24	200	93	5.6	60.4	1700	1696	2
VII	**I**–SA, 1.5 : 1	2	160	18	180	98	1.2	88.3	1254	1280	2
VIII	**II**–SA, 1.5 : 1	6	180	24	200	93	7.9	54.9	1787	1808	2
IX	**I**–AA, 1.3 : 1	6	160	22	200	97	1.6	70.4	1560	1594	3
X	**I**–SA, 1.3 : 1	2	150	22	200	99	1.0	63.7	1733	1762	3

As seen from the table, the propose procedure allow synthesis of weakly acidic oligoesters on the basis of 2,2'-[propan-2,2-diylbis(*p*-phenyleneoxy)]diethanol (**I**). The reaction with 2,2'-[propan-2,2-diylbis(*p*-phenyleneoxydiethoxy)]diethanol (**II**) occurs much slower, as evidenced by the kinetic curves of polycondensation in Fig. 1. Analysis of the time dependences of the conversion of carboxy groups at the first stage of polycondensation shows that adipic acid faster reacts with monomer **I** than with monomer **II**: The half-conversion times are 3 h and 4 h, respectively.

The difference in the activities of diols **I** and **II** becomes even more appreciable at the second stage of polycondensation. As seen from the table, the polycondensation of adipic acid with diol **I** is complete in 5 h (the acid number decreases to 0.4 mg KOH/g, which implies a 99.8% conversion), whereas in the system adipic acid–diol **II** the acid number could only be decreased to 2.6 mg KOH/g after 28 h (conversion 97.5%).

The lower reactivity of diol **II** is probably explained by the fact that its polyoxyethylene fragments form multicenter complexes due to hydrogen bonding with the carboxyl proton of adipic acid.



Oligoesters **III–X** (see table) are colored resins soluble in ketones (acetone, cyclohexanone, methyl ethyl ketone), chloroform, ethyl acetate, and butyl acetate and insoluble in alcohols and carbon tetrachloride.

The structure of the synthesized aromatic oligoesters was assessed based on their IR spectra, ν, cm^{-1}: 3500–3200 (OH), 3030 (=C–H), 1608, 1507 (C=C), 2871 (CH_2 and CH_3), 1250, 1195 [$C(CH_3)_2$, shoulder], 1732 (C=O), 1250, 1190 (C–O). Thus, oligoesters **III–X** contain ester and hydroxy groups, and a little of carboxy groups. These results provide evidence for the suitability of the chosen synthetic strategy (Scheme 2).

The TG curves of the oligoesters (Fig. 2) reflect the process of their thermal decomposition. The weight loss onset temperature regularly increases with increasing molecular weight of the oilgoester. Oligoster **VI** proved to be the most stable: it started to decompose at 280–300°C. Thermal decomposition of oligoesters **V** and **VII** started at 250–270°C. As follows from the half weight loss temperatures, oligoester **VII** decomposes slower than oligoesters **VI** and **V**, which is explained by the fact that it was synthesized from sebacic acid and, therefore, contains more methylene groups which are thermally more stable than oxyethyl groups. The structure of the oligoester block was found to affect the thermal stability of the polyurethane coatings synthesized from oligoesters **V–VII** [4].

Thus, we have synthesized a series of bifunctional oligoesters containing both aromatic and aliphatic

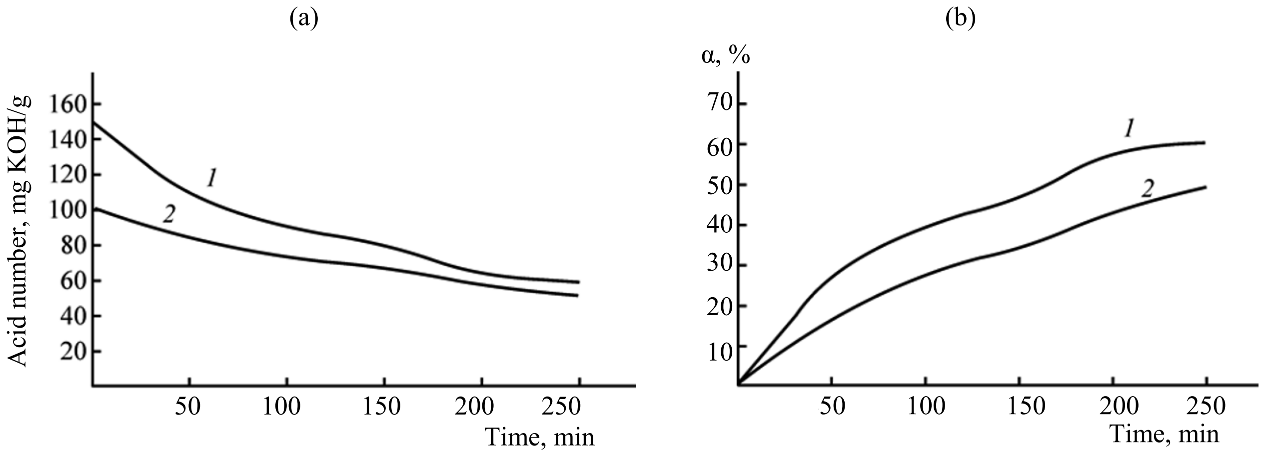
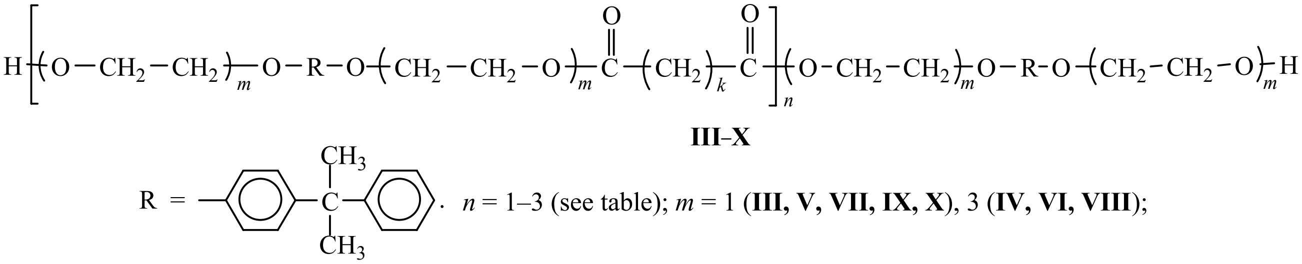


Fig. 1. Dependences of the (a) acid number and (b) conversion α on the time of reaction of adipic acid with diols (*1*) **I** and (*2*) **II** at the acid : diol molar ratio 2, 150°C.

Scheme 2.



$$\mathrm{H}\left[\left(\mathrm{O{-}CH_2{-}CH_2}\right)_m\mathrm{O{-}R{-}O}\left(\mathrm{CH_2{-}CH_2{-}O}\right)_m\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\left(\mathrm{CH_2}\right)_k\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\right]_n\left(\mathrm{O{-}CH_2{-}CH_2}\right)_m\mathrm{O{-}R{-}O}\left(\mathrm{CH_2{-}CH_2{-}O}\right)_m\mathrm{H}$$

III–**X**

R = , n = 1–3 (see table); m = 1 (**III, V, VII, IX, X**), 3 (**IV, VI, VIII**);

k = 4 (**III–VI, IX**), 8 (**VI**–**X**).

moieties, which allows these compounds to be used in the synthesis of thermally stable polymers with a desired combination of hardness and elasticity.

EXPERIMENTAL

The following chemical reagents and materials were used in the work: 4,4'-(propan-2,2-diyl)diphenol, *M* 228.3, bp 220°C, mp 156.7°C (Kazanorgsintez, Technical Specifications 2423-172-00203335-2007); ethylene carbonate, *M* 88.06, bp 248°C, mp 39°C (Sigma–Aldrich, USA); monomer **II**, hydroxyl number 220–235 mg KOH/g (Sigma–Aldrich, USA); adipic acid, *M* 146.14, bp 265°C, mp 153°C, State Standard 10558–80 (Sigma–Aldrich, USA); sebacic acid, *M* 202.25, bp 352°C, mp 134.5°C, State Standard 115582–70 (Vekton); argon, State Standard 10157–79.

2,2'-[Propan-2,2-diylbis(*p*-phenyleneoxy)]diethanol (I) [5]. 4,4'-(Propan-2,2-diyl)diphenol, ethylene carbonate, and catalyst were loaded into a four-necked flask equipped with a stirrer and reflux condenser. The process was performed at 150°C under argon for 8 h. The reaction product was washed out with water. Yield 99%, mp 110°C, hydroxyl number 10.7%.

Oligoesters were prepared by melt polycondensation. Monomer **I** or **II** and dicarboxylic acid were loaded into a four-necked flask equipped a thermometer, stirrer, Vigreux column, and Liebig condenser.

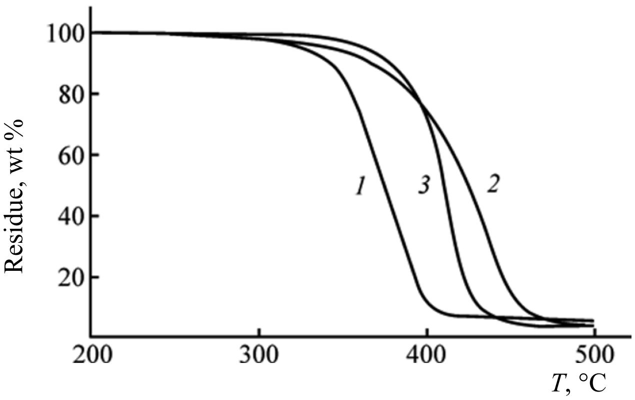


Fig. 2. Thermal gravimetry curves for oligoesters (*1*) **V**, (*2*) **VII**, and (*3*) **VI** (heating rate 2 deg/min, argon).

The first stage was performed under a stream of argon, and at the second stage volatile products were distilled off at 10 mmHg.

The IR spectra were measured on an InfraLYuM FT-08 FTIR spectrometer (LUMEX, Russia).

The acid numbers were determined by titration of oligoester dissolved in acetone with KOH (according to State Standard 25210–82). The hydroxyl numbers were determined by titration of oligoester dissolved in an acetylating mixture with KOH (according to State Standard 25261–82).

Thetmogravimetric analysis was performed by differential scanning calorimetry on a STA 6000 calorimeter (Perkin–Elmer, USA).

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