

FORMATION OF LINEAR OLIGOMERS IN THE INITIAL PHASE OF POLYESTERIFICATION OF TEREPHTHALIC ACID*

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Formation of linear poly(ethylene terephthalate) oligomers during the initial phase of polyesterification of terephthalic acid by ethylene glycol was studied under atmospheric pressure in a homogeneous system, corresponding at 196°C to the initial molar ratio of both components 1 : 73, in the presence or absence of zinc oxide as a catalyst. The main oligomers formed in the course of the catalysed reaction were the linear dimer-diol, 1,2-bis[*p*-(2-hydroxyethoxycarbonyl)benzoyloxy]ethane, and the monocarboxylic dimer, 1-(*p*-carboxybenzoyloxy)-2-[*p*-(2-hydroxyethoxycarbonyl)benzoyloxy]ethane. The uncatalysed reaction was less selective and besides the above dimer-diol and monocarboxylic-dimer it yielded also appreciable amounts of trimer- and tetramer-diols which were accompanied by small amounts of higher oligomer-diols (presumably pentamer and hexamer). Terephthalic acid is converted by two competitive reactions, which both are first-order in the acid, to 2-hydroxyethyl hydrogen terephthalate and to the monocarboxylic dimer. This dimer is esterified during the reaction to the dimer-diol. Oligomer-diols reach their concentration maximum at the same time at which all the 2-hydroxyethyl hydrogen terephthalate has reacted and then they undergo glycolysis in an excess of ethylene glycol. The product of the reaction is an equilibrium mixture of bis(2-hydroxyethyl)terephthalate and the dimer-diol.

The variety of intermediate products of the esterification of dicarboxylic acids by diols is well-known from the pioneering work of Carothers on polyesterification reactions¹⁻³. The difficult analysis and identification of mixtures of intermediate products, which in different phases of polyesterification are of different composition, is apparently the reason, why the mechanism of these reactions is not yet well elucidated. This has led to the suggestion of too simplified and idealised reaction models. In this respect the esterification reactions of benzenedicarboxylic acids with diols are not an exception, inclusive the reaction of terephthalic acid with ethylene glycol. The kinetics of this reaction was studied in the absence of catalysts, the assumption being made that single reactions in this system are only the esterification of terephthalic acid to give 2-hydroxyethyl hydrogen terephthalate and the consecutive esterification of this intermediate product to monomeric bis(2-hydroxyethyl)terephthalate^{4,5}. In the last two papers of this Series we discussed the kinetics of the esterification of 2-hydroxyethyl hydrogen terephthalate by ethylene glycol homogeneously catalysed by metal ions⁶ and the kinetics of the initial phase of polyesterification of terephthalic acid by ethylene glycol⁷, both reactions being studied under normal pressure

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and with the initial molar ratios of ethylene glycol to the monoester and to the acid equal or greater than 10. We have proved that, contrary to the current views, the transformations of the two above-mentioned compounds are in the phases preceding the equilibrium between bis(2-hydroxyethyl)terephthalate and its dimer, 1,2-bis[*p*-(2-hydroxyethoxycarbonyl)benzoyloxy]ethane (dimer *I*), represented by a system of six, eventually eight, irreversible or equilibrium, consecutive and competitive reactions. Along with the above formation of 2-hydroxyethyl hydrogen terephthalate and bis(2-hydroxyethyl)terephthalate, there occur also condensation reactions of bis(2-hydroxyethyl)terephthalate and of 2-hydroxyethyl hydrogen terephthalate with bis(2-hydroxyethyl)terephthalate to give dimer *I*, and the condensation of two molecules of 2-hydroxyethyl hydrogen terephthalate to give 1-(*p*-carboxybenzoyloxy)-2-[*p*-(2-hydroxyethoxycarbonyl)benzoyloxy]ethane (dimer *II*), which is also produced by the condensation reaction of terephthalic acid with bis-(2-hydroxyethyl)terephthalate. The last three reactions, similarly as the consecutive esterification of dimer *II* by ethylene glycol to dimer *I* in homogeneous phase of the reaction, are characterised by the highest reaction constants of the esterification, and that both in the case of the conversion of the starting 2-hydroxyethyl hydrogen terephthalate and in the case of the conversion of terephthalic acid. In view of these new facts relating to the course of the metal-ion homogeneously catalysed esterification of terephthalic acid with ethylene glycol, it was of interest to ascertain whether a similar reaction scheme holds also for the uncatalysed esterification reaction.

The present work is concerned with the formation of the monomeric and oligomeric intermediates and products of the initial phase of the polyesterifications of 2-hydroxyethyl hydrogen terephthalate and terephthalic acid by ethylene glycol, and with the determination of their time-concentration changes. The reactions were studied in homogeneous phase both in the presence and in the absence of a catalyst, under atmospheric pressure, using the initial molar ratios of ethylene glycol to the monoester and to the acid equal 24 and 73, respectively, within the temperature range of 190 to 196°C, and under the conditions which ensured immediate removal of the reaction water from the reaction system.

EXPERIMENTAL

Compounds used. Terephthalic acid, "fiber grade" (Mobil Oil Co., U.S.A.), free of isophthalic acid, contained 0.07% of phthalic acid, less than 0.005% of benzoic acid and was used without further purification. Ethylene glycol, commercial sample (Slovnaft, Bratislava), was distilled through a 30 TP column. The fraction boiling at 96°C/12 Torr was collected, which contained 0.07% of water and 0.02% of diethylene glycol (by g.l.c.). 2-Hydroxyethyl hydrogen terephthalate [acid number 264 (calc. 266.9), saponification number 529 (calc. 533.9), m.p. 183–184°C; ref.⁴ m.p. 180–181°C], bis(2-hydroxyethyl)terephthalate [saponification number 438 (calc. 441.4), m.p. 110.0–110.5°C; ref.⁴ m.p. 109–110°C], dimer *I* [saponification number 499 (calc. 502.8), m.p. 172–173°C; ref.⁸ m.p. 168–170°C], and dimer *II* [acid number 145 (calc. 139.4), m.p. 215–216°C; ref.⁸ m.p. 220°C] were prepared by the procedures described in a previous work⁶. *N,N*-Dimethylformamide (chemical purity grade) was used in a polarographic analysis without further purification. Gelatine for the same purpose was employed as an 1% aqueous solution. The preparation of Michaelis veronal buffer for polarography was described in the previous work⁷. Zinc oxide, analytical purity grade, which was used for comparative catalytic esterifica-

tion of terephthalic acid was not further purified. Melting points of the esters and dimers were determined with a Kofler hot stage microscope and are uncorrected.

Polarographic analysis of reaction mixtures. Individual reaction components from the esterification of 2-hydroxyethyl hydrogen terephthalate and from the polyesterification of terephthalic acid, *i.e.* besides the two compounds mentioned above also bis(2-hydroxyethyl)terephthalate, dimer *I*, and dimer *II*, were isolated from the samples of reaction mixtures (0.5–1 g) by procedures described in previous works^{6,7} and their concentrations were determined by polarographic method^{6,7,9,10}. The measurements were carried out in a temperature-controlled cell ($25.0 \pm 0.1^\circ\text{C}$) with mercury bed and a dropping mercury electrode; air oxygen was removed by a stream of nitrogen. Polarographic curves were recorded with a LP-50 polarograph which was connected to an EZ-2 recorder; the concentrations of the individual components were determined from the heights of polarographic curves by the method of calibration curves.

Analysis of reaction mixture by thin-layer chromatography. Samples of the reaction mixtures were introduced on a chromatographic plate (150 × 75 mm) covered by Silufol UV₂₅₄ (Kavalier), developed by a chloroform–ethanol mixture^{11,12} (9 : 1), and the spots were detected by their exposure to UV-light. Single spots were identified and the R_F values for terephthalic acid, 2-hydroxyethyl hydrogen terephthalate, bis(2-hydroxyethyl)terephthalate, dimer *I*, and dimer *II* were determined by co-chromatography with authentic samples of these compounds (see above).

Determination of diethylene glycol in the reaction mixture. Samples of the reaction mixture (1.5–2.0 g) taken at the end of each esterification experiment were subjected to hydrazinolysis, and the concentrations of the free and the ester diethylene glycol were determined by g.l.c. analysis¹³. The amount of diethylene glycol varied around 1.0 wt.% (with respect to bis (2-hydroxyethyl)terephthalate and the dimer *I* present in the resulting reaction mixture).

General esterification procedure. Experimental arrangement of esterification experiments was the same as in previous kinetic studies^{6,7}. The esterifications were carried out in an open reaction system at a temperature ranging from 190 to 196°C. To a stirred 300 ml-tubular glass reactor was weighed 2-hydroxyethyl hydrogen terephthalate (10 g, 0.58 mol/kg) or terephthalic acid (3.5 g, 0.21 mol/kg), along with ethylene glycol (70–100 g, 14–16 mol/kg) and, eventually, zinc oxide (8 mg, 0.001 mol/kg); the reactor was placed in a temperature-controlled silicone oil bath and the reaction mixture was warmed in a stream of nitrogen to the desired reaction temperature (8–10 min), while stirring. The temperature of the reaction mixture was kept within $\pm 0.1^\circ\text{C}$. The reaction water was removed from the reactor by a stream of nitrogen which was introduced above the level of the reaction mixture and then passed through a condenser heated at 105°C; this arrangement prevented the undesired loss of ethylene glycol from the reaction system. At a 40 ml per min nitrogen flow rate and the intensity of stirring 200 rev. per min, the esterification reactions took place in the kinetic region. Throughout this work the concentrations of reaction components are given in mol/kg.

RESULTS AND DISCUSSION

Terephthalic acid reacts with ethylene glycol in the presence of zinc catalyst from the beginning of the reaction in homogeneous phase, *i.e.* at initial molar ratio of both reactants equal 1 : 73 and under the conditions of the immediate removal of the reaction water from the reaction medium in a similar manner (Fig. 1) as in the more concentrated heterogeneous systems⁷. The only difference is the higher rate of over-all

conversion of the acid in homogeneous phase and the lower concentration of linear dimer *I* in its final equilibrium mixture with bis(2-hydroxyethyl)terephthalate. The latter fact may be accounted for by markedly higher initial concentration of ethylene glycol and then also by more extensive reverse glycolytic cleavage of dimer *I* to the bis-ester. In both cases the major intermediate product of the reaction is 2-hydroxyethyl hydrogen terephthalate. As proved by thin-layer chromatography, the main oligomers of poly(ethylene terephthalate), which are formed in the course of the reaction in kinetically significant concentration, are linear dimer *I* and monocarboxylic linear dimer *II*. Similarly to the heterogeneous esterification of terephthalic acid, dimer *II* is again gradually and completely converted to dimer *I*. With respect to the formation of oligomers, the metal-ion catalysed esterification of terephthalic acid by ethylene glycol in homogeneous phase does not differ even from the esterification of 2-hydroxyethyl hydrogen terephthalate⁶. Both oligomers, dimer *I* and dimer *II*, are accompanied only by trace amounts of linear trimer *IV* and, presumably, the dicarboxylic dimer, 1,2-bis(*p*-carboxybenzoyloxy)ethane (*III*). An analogous course of the reactions of terephthalic acid and of both intermediate products, 2-hydroxyethyl hydrogen terephthalate and dimer *II*, enables us to describe the over-all, metal-ion catalysed conversion of terephthalic acid in homogeneous phase up to the stage of the formation of a bis(2-hydroxyethyl)terephthalate-dimer *I* equilibrium mixture

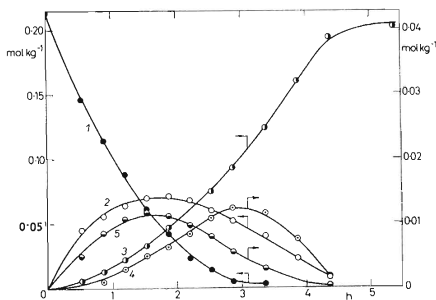
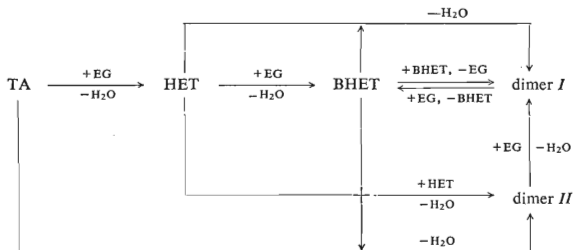


FIG. 1

Time-Concentration Changes of Reaction Components in the Initial Stage of the Polyesterification of Terephthalic Acid by Ethylene Glycol Catalysed by ZnO in Homogeneous System from the Beginning of the Reaction

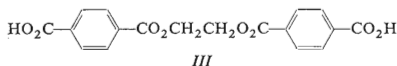
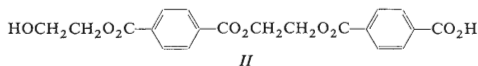
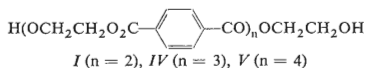
1 Terephthalic acid, 2 2-hydroxyethyl hydrogen terephthalate, 3 bis(2-hydroxyethyl)terephthalate, 4 dimer *I*, 5 dimer *II*; $[p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2]_0 = 0.213 \text{ mol/kg}$; $[\text{C}_2\text{H}_4(\text{OH})_2]_0 = 15.5 \text{ mol/kg}$; $[\text{ZnO}] = 0.001 \text{ mol/kg}$ ($8 \cdot 10^{-4} \text{ mol Zn/mol } p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$); temp. $196.0 \pm 0.1^\circ\text{C}$.

by Scheme 1, in which TA is terephthalic acid, HET is 2-hydroxyethyl hydrogen terephthalate, BHET is bis(2-hydroxyethyl)terephthalate, and EG is ethylene glycol.



SCHEME 1

The validity of Scheme 1 for the metal-ion catalysed esterification in a heterogeneous system consisting of terephthalic acid and ethylene glycol was established by us in a previous work⁷. A somewhat different situation arises in the case of uncatalysed reactions of 2-hydroxyethyl hydrogen terephthalate (Fig. 2) and of terephthalic acid (Fig. 3) with ethylene glycol in homogeneous phase. In both cases, and with high concentration of ethylene glycol, *i.e.* under the conditions clearly unfavourable for the condensation reactions of the monomer to occur, the concentration of dimer II and oligomer-diols are at maximum approximately doubled, compared to the reactions catalysed by metal ions^{6,7}. Maximum concentrations of the oligomer-diols and dimer II in the esterification of terephthalic acid amounted to 13 and 9% of the initial acid concentration, respectively. The only acidic oligomer identified during the reaction of 2-hydroxyethyl hydrogen terephthalate and of terephthalic acid was again dimer II; however, at maximum concentration of oligomer-diols, along with



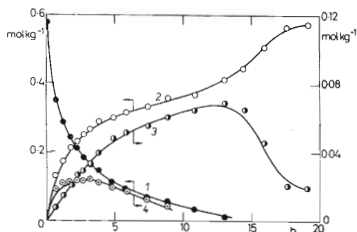


FIG. 2

Time-Concentration Changes of Reaction Components in Uncatalysed Esterification of 2-Hydroxyethyl Hydrogen Terephthalate by Ethylene Glycol

1 2-Hydroxyethyl hydrogen terephthalate, 2 bis(2-hydroxyethyl)terephthalate, 3 dimer I, 4 dimer II; $[p\text{-C}_6\text{H}_4(\text{CO}_2\text{CH}_2\text{CH}_2\text{OH})(\text{CO}_2\text{H})]_0 = 0.581 \text{ mol/kg}$; $[\text{C}_2\text{H}_4(\text{OH})_2]_0 = 14.1 \text{ mol/kg}$; temp. $190 \pm 0.1^\circ\text{C}$.

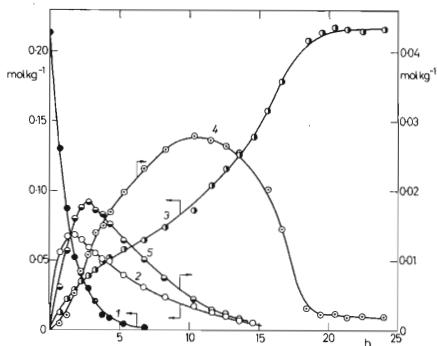


FIG. 3

Time-Concentration Changes of Reaction Components in the Initial Stage of Uncatalysed Polyesterification of Terephthalic Acid by Ethylene Glycol in Homogeneous System

1 Terephthalic acid, 2 2-hydroxyethyl hydrogen terephthalate, 3 bis(2-hydroxyethyl)terephthalate, 4 dimer I, 5 dimer II. $[p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2]_0 = 0.213 \text{ mol/kg}$; $[\text{C}_2\text{H}_4(\text{OH})_2]_0 = 15.5 \text{ mol/kg}$; temp. $196 \pm 0.1^\circ\text{C}$.

dimer *I*, which prevails, also higher oligomers were found by t.l.c. to be present in significant concentrations. Their relative R_F values (Table I) agree well with the R_F values determined by Gueris and Meybeck for the linear trimer *IV* and tetramer *V* isolated from the product of reesterification of dimethyl terephthalate by ethylene glycol¹⁴. Additional two, less intense spots detected on the chromatogram could by their sequence and in harmony with the results of thin layer chromatographic analysis of a mixture of the monomer and linear oligomers (dimer to nonamer), isolated by Peebles and coworkers¹¹ from poly(ethylene terephthalate), correspond to a linear pentamer and hexamer. As corresponding R_F values for these oligomers are not available, they could not be convincingly identified. As we found, quantitative differentiation of higher oligomer-diols from dimer *I* cannot be achieved by using either separation method or polarographic analysis, *i.e.* the methods employed with success in a kinetic investigation of the esterification of 2-hydroxyethyl hydrogen terephthalate and of terephthalic acid catalysed by metal ions^{6,7}. For that reason the time-concentration curves 3 in Fig. 2 and 4 in Fig. 3, with concentration maxima at 0.068 mol/kg and 12.25 h, and at 0.028 mol/kg at 10.5 h, respectively, correspond rather to an approximate sum of concentrations of the individual, above-mentioned oligomer-diols, determined as dimer *I*.

If the formation of already 5% of dimer *I* (calculated with respect to the initial

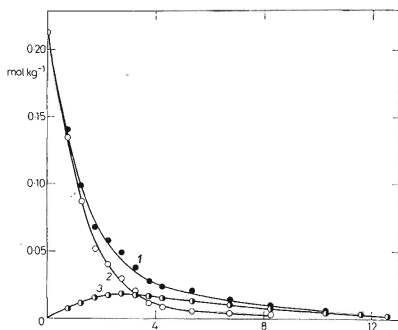


FIG. 4

Dependence of Concentration of a Terephthalic Acid-Dimer *II* Mixture (1), Terephthalic Acid (2), and Dimer *II* (3) on Time in the Initial Stage of Uncatalysed Homogeneous Polyesterification of Terephthalic Acid by Ethylene Glycol at $196 \pm 0.1^\circ\text{C}$

$[p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2]_0 = 0.213 \text{ mol/kg}$; $[\text{C}_2\text{H}_4(\text{OH})_2]_0 = 15.5 \text{ mol/kg}$.

concentrations of 2-hydroxyethyl hydrogen terephthalate and terephthalic acid) significantly affects the kinetics of catalysed esterification reactions^{6,7}, the formation of even higher concentrations of oligomer-diols during the uncatalysed reaction should in no case be neglected. Scheme 1 then does not give a true picture of the over-all course of the uncatalysed esterification of terephthalic acid, even though the

TABLE I

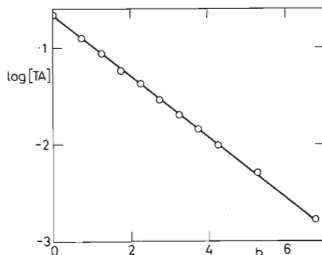
R_F Values of the Monomer and Linear Oligomer-Diols Identified by Thin-Layer Chromatography in the Reaction Mixture from Uncatalysed Esterification of 2-Hydroxyethyl Hydrogen Terephthalate and of Terephthalic Acid by Ethylene Glycol

For reaction conditions see Fig. 3. The samples were taken from the reaction mixture at the maximum concentration of oligomer-diols.

Compound	R_F^a	Relative values of R_F BHET ^b = 1.00	
		this work	ref. ^{14,c}
BHET	0.26	1.00	1.00
Dimer <i>I</i>	0.32	1.23	1.25
Trimer <i>IV</i>	0.37	1.42	1.38
Tetramer <i>V</i>	0.42	1.61	1.57

^a The spots were developed by 10% ethanol in chloroform; ^b BHET = bis(2-hydroxyethyl)-terephthalate; ^c the spots were developed by 5% methanol in chloroform; the relative values of R_F recorded for dimer *I*, the trimer, and the tetramer were calculated from the experimental values of R_F 0.59, 0.65, and 0.74, respectively, the experimental value of R_F for BHET, 0.47, being taken as 1.00.

FIG. 5
Dependence of the Logarithm of Terephthalic Acid Concentration (mol/kg) on Time (h) for Uncatalysed Esterification of the Acid by Ethylene Glycol at $196 \pm 0.1^\circ\text{C}$
 $[p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2]_0 = 0.213 \text{ mol/kg}$;
 $[\text{C}_2\text{H}_4(\text{OH})_2]_0 = 15.5 \text{ mol/kg}$.



resulting equilibrium mixture contains, similarly as in the case of the catalysed esterification, only bis(2-hydroxyethyl)terephthalate and dimer *I*.

Starting from the facts that the only acidic oligomer identified during the uncatalysed esterification of terephthalic acid was dimer *II*, and that the highest oligomer-diol present in significant amount was linear tetramer and considering the established irreversibility of the reactions connected with the formation of water which is immediately removed from the reaction mixture^{6,7}, then the over-all conversion of terephthalic acid to the bis-ester and to dimer *I* should be described by 19 single reactions. A successful analytical and kinetic solution of such a system seems to be extremely difficult.

Time-concentration dependences found for individual reaction components in the esterification of 2-hydroxyethyl hydrogen terephthalate and of terephthalic acid allow, nevertheless, to draw at least qualitative conclusions about single steps of the uncatalysed reaction. It can be expected that under the given experimental-conditions, similarly to the catalysed reaction, also here, besides esterification reactions, also those condensation reactions will be preferred which would be connected with the release of water and would lead to the formation of both the mono- and bis-esters, and the dimers *I* and *II* (Scheme 1). When compared to the catalytic reaction (Fig. 1), a relatively faster decrease in the concentrations of 2-hydroxyethyl hydrogen terephthalate and dimer *II* in the region of concentration maximum of oligomer-diols (Fig. 2 and 3) speaks, however, for the greater participation of the two compounds in condensation reactions. By analogy with the catalytic reaction, 2-hydroxyethyl hydrogen terephthalate can react with dimer *I* to give trimer *IV* and with the trimer to form tetramer *V*. With the condensation reactions of dimer *II* with bis(2-hydroxyethyl)terephthalate to give trimer, and of dimer *II* with dimer *I* to form the tetramer, which both also proceed under the formation of water, will obviously compete the esterification of dimer *II* by ethylene glycol, which is relatively fast^{6,7} also in the catalytic reaction. The inflex on the concentration curve of bis(2-hydroxyethyl)terephthalate in the region of the concentration maximum of oligomer-diols indicates that also the bis-ester significantly participates in polycondensation reactions. However, both the equilibrium condensation of bis(2-hydroxyethyl)terephthalate to dimer *I*, and the condensation of the bis-ester with dimer *I* giving trimer *IV*, and with the trimer to give tetramer *V*, proceed, similarly as an eventual condensation of dimer *I* to tetramer *V*, with the release of ethylene glycol. Hence, the equilibrium of these reaction, due to a considerable excess of the diol, will be shifted predominantly to the left-hand side. It can be then assumed that under the given conditions the main reaction by which bis(2-hydroxyethyl)terephthalate contributes to the formation of oligomer-diols would be rather its condensation with 2-hydroxyethyl hydrogen terephthalate to dimer *I* under the formation of water (Scheme 1). This assumption is supported by the time coincidence of the inflex on the concentration curve of the bis-ester with the decrease of the concentration of the mono-ester, both occurring

in the region of the concentration maxima of oligomer-diols. By this, it can also be explained why the excess of ethylene glycol causes the glycolytic cleavage of oligomer-diols only after the disappearance of 2-hydroxyethyl hydrogen terephthalate from the reaction mixture. This glycolytic cleavage leads to an equilibrium mixture of bis-(2-hydroxyethyl)terephthalate and dimer *I*, which contains, however, only c. 1 wt.% of the latter compound (based on the initial concentration of terephthalic acid).

The identification of monocarboxylic dimer *II* as an intermediate product of the esterification as well as the participation of 2-hydroxyethyl hydrogen terephthalate both in the consecutive formation of bis(2-hydroxyethyl)terephthalate, and in competitive condensation reactions, made it possible to explain some inconsistencies which appeared in the first part of this Series⁴ devoted to the kinetics of uncatalysed esterification of terephthalic acid by ethylene glycol. In the cited work the uncatalysed reaction was found to be second-order in terephthalic acid. Non-first order behaviour of the reaction with respect to 2-hydroxyethyl hydrogen terephthalate was explained either by the hydrogen-bond association of two molecules of 2-hydroxyethyl ester, or by the formation of some, not clearly defined inactive product of the association of the 2-hydroxyethyl ester with the bis-ester. The concentration of terephthalic acid during the esterification reaction was in that case determined by subtracting the amount of 2-hydroxyethyl hydrogen terephthalate, determined by polarographic method, from the total acidity of the reaction mixture, which was determined titrimetrically. This determination did not allow for the presence of monocarboxylic dimer *II*, which was simultaneously formed, as proved in our previous works^{6,7}.

The form of the curve 1 in Fig. 4, which is the sum of the concentrations of terephthalic acid and dimer *II*, does correspond to apparent second order in terephthalic acid. By subtracting the concentrations of dimer *II* (curve 3), which was determined by separation and polarographic method⁷, from the sum of the concentrations of terephthalic acid and dimer *II* (curve 1), one obtains the time-dependence of the actual concentration of terephthalic acid (curve 2). However, contrary to a previous work⁴, the so obtained dependence indicates first-order behaviour with respect to terephthalic acid (Fig. 5) through nearly the whole range of its conversions by the two competitive reactions, leading both to 2-hydroxyethyl hydrogen terephthalate and to dimer *II* (Scheme 1). The participation of 2-hydroxyethyl hydrogen terephthalate in several condensation reactions depicted in Scheme 1 and in the reactions leading to higher oligomer-diols explains also why the over-all conversion of 2-hydroxyethyl hydrogen terephthalate does not agree with the first-order kinetics, as considered earlier⁴.

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