

# Mechanism of the Reaction Involving the Formation of Dioxane Byproduct During the Production of Poly(ethylene Terephthalate)

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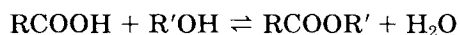
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## SYNOPSIS

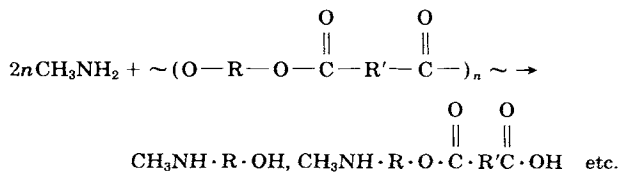
The formation of certain low molecular weight by-products during the esterification reaction between ethylene glycol and dimethyl terephthalate was investigated. The result obtained showed that the presence of incorporated diethylene glycol within the polymer led to the formation of low molecular weight side products. An alcoholysis reaction involving the ethylene glycol and the ester was found to show a mechanism that is analogous to that of an ester interchange resulting in the production of the acid and the diethylene glycol precursor of the dioxane by-product.

## INTRODUCTION

Generally, esters are prepared by acid-catalyzed reaction of alcohols and acids or acid derivatives such as acid chlorides and anhydrides. In the presence of the reaction mixtures, the polyesterification process is followed by a similar acid-catalyzed reversible hydrolytic degradation of the ester:



In an earlier study carried out on acid-catalyzed degradation of poly(ethylene terephthalate) (PET) using primary amines, formation of several low molecular weight side products in addition to the main amide that was formed on complete degradation in accordance to the following scheme was proposed<sup>1</sup>:



Similar low molecular weight side products are formed during direct esterification of terephthalic acid with ethylene glycol or during the ester interchange of dimethyl terephthalate with the glycol and to a smaller extent during the polycondensation of the low molecular weight ester that followed. The polymer itself (PET) contains a limited amount of incorporated diethylene glycol, the amount of which influences the properties of the polyester.<sup>2,3</sup> Diethylene glycol and dioxane were among the compounds formed in the side reaction during the esterification process and the subsequent polycondensation step that follows. From the experimental observation made in this work and the discussion on the data obtained, the mechanism that is consistent with the formation of these products is discussed.

## EXPERIMENTAL

Several low molecular weight polyesters differing in their degrees of polymerization were prepared by direct esterification of terephthalic acid with ethylene glycol. This was followed by a polycondensation step and removal of glycol by distillation. The esters were analyzed for free glycol by reacting the glycol with

periodate and subsequent iodometric titration of iodate plus excess periodate.

The number of alcoholic end groups was determined by nuclear magnetic resonance (NMR) analysis of solutions in hot nitrobenzene at 150°C. Five of the esters prepared were heated at 270°C in sealed capsule for varying times of 1, 2, 3, 4, 5, 6, and 7 h. The amounts of diethylene glycol in the heated samples were determined by refluxing for 15 min with hydrazine followed by gas chromatographic analysis at 215°C using wet N<sub>2</sub> as carrier gas and Porapak Q column material in a stainless steel column.

Similarly, the dioxane formed during the heating was determined by chromatographic technique using Carbowax-KOH on Chromosorb-W in a column at 100°C. Since the diethylene glycol is the precursor of dioxane, the amount of dioxane has to be added to that of diethylene glycol formed in calculating the total amount of diethylene glycol formed.

Carboxyl end groups were determined by photometric titration of solutions of PET in 25 mL *o*-cresol containing 10 mL chloroform with 0.03M alcoholic KOH using Bromophenol blue as indicator.

## RESULTS AND DISCUSSION

During the heating, it was found that the increase in carboxyl end groups exceeded that of diethylene glycol formed by a factor of 2, indicating that the amount of diethylene glycol formed is about half that of the acid main product. The sample details of the starting materials and the rate of formation of diethylene glycol are contained in Table I.

Some control experiments were performed with

**Table I Sample Details of the Starting Materials and Rate of Formation of Diethylene Glycol and Dioxane**

Sample	Glycol (mol/kg)	Alcoholic End Group (mol/kg)	Formation of DiethylGly + Dioxane (mol/kg h)
1	0.31	2.76	0.037
2	0.05	1.62	0.020
3	0.02	1.24	0.013
4	—	0.75	0.008
5	—	0.48	0.006
Glycol	16.1	—	0.010

pure glycol and with glycol to which small quantities of low molecular weight ester (1–10%) had been added. They showed that diethylene glycol formation in pure glycol is almost negligible but that the addition of small quantities of ester caused a marked increase in diethylene glycol formation, the increase being proportional to the amount of ester added.

From the control experiments with almost pure glycol, it was concluded that ester linkages are indispensable to formation of diethylene glycol. This conclusion cannot be drawn from the experiments with low molecular weight polymer as the concentration of ester linkages is almost independent of the degree of polymerization, as shown in Table II.

Since the sum of the concentration of the alcoholic groups seems to be another important parameter to the formation of the diethylene glycol, a simple kinetic equation describing the rate of formation of diethylene glycol is

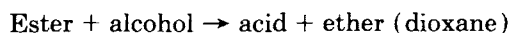
$$d[\text{DiethylGly} \cdot + \text{dioxane}]/dt = k[\text{OH}][\text{ester} \cdot]$$

Using this equation and Table II, consistent values are obtained for *k*. The formation of the dioxane is not catalyzed by the presence of carboxyl end groups. In all experiments a marked increase in carboxyl end groups occurred with heating time. The diethylene glycol formation, however, proceeded at a constant rate, indicating that it was independent of the carboxyl group content.

From the results obtained, diethylene glycol was not formed by a dehydration reaction between two alcoholic groups, as this will be expected to be proportional to the square of the alcoholic group concentration, i.e.,

$$d[\text{DiethylGly} \cdot + \text{dioxane}]/dt = k[\text{OH}]^2$$

The most feasible mechanism of the formation therefore involved the alcoholysis reaction of the ester:



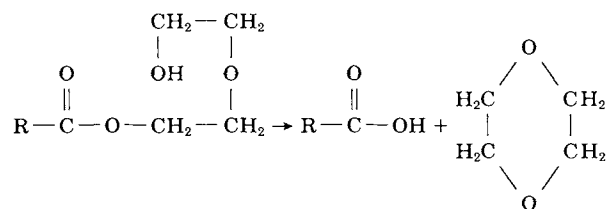
A similar reaction involving the heating of alcohols with concentrated sulfuric acid, leading to the formation of the ether, can be described by the same reaction path. When dimethyl terephthalate is heated with glycol and diethylene glycol, formation of the ether methyl cellosolve and carbitol, respectively, further gives credence to this reaction between ester and alcohol. The formation of dioxane

**Table II Calculation of Rate Constant for the Formation of Dioxane**

Sample	Alcohol Groups (mol/kg)	Ester Groups (mol/kg)	<i>k</i> (kg/mol h)
1	3.38	9	0.0012
2	1.72	10	0.0012
3	1.29	10	0.0011
4	0.75	10	0.0012
5	0.48	10	0.0014
			0.0012 <sup>a</sup>

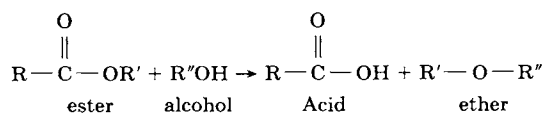
<sup>a</sup> Average value of *k*.

reported in this work can be explained by an intramolecular elimination reaction of half-esterified diethylene glycol followed by cyclization and proton transfer from the diethylene glycol to the acetate anion of the ester residue:

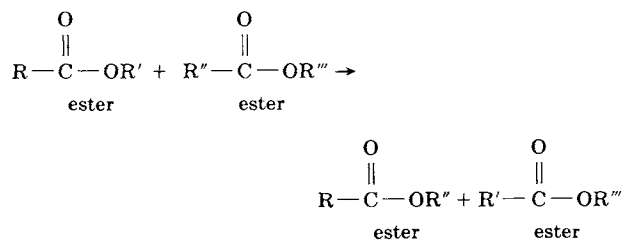


The reaction mechanism is analogous to the ester interchange reaction shown in the following reaction schemes:

#### Alcoholysis



#### Ester interchange



From the observed rapid increase of COOH groups during heating, it may be concluded that at least one other important side reaction occurs. A possible explanation is that glycolic end groups are degraded rapidly during heating.

#### REFERENCES

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