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### Influence of Metal Catalysts on the Formation of Ether Links in Polyethylene Terephthalate

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## **Influence of Metal Catalysts on the Formation of Ether Links in Polyethylene Terephthalate**

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### **ABSTRACT**

The formation of ether linkages in polyethylene terephthalate was investigated using three different metal acetates as catalysts. The zinc salt was found to produce more ether bonds than either lead(II) or manganese(II) acetate. The amount of diethylene glycol detected in the fibers increased with rising catalyst concentration as well as with increasing polycondensation time. Negligible at the reesterification temperature of 195°C, ether formation became more important during the preheating period during which the polycondensation temperature was achieved (280°C). Most of the ether linkages were formed during the first 30 min of polycondensation and only a slow increase was observed thereafter. Model experiments conducted by heating pure ethylene glycol with the catalysts were in agreement with the polycondensation results.

### **INTRODUCTION**

Metal catalysts employed to accelerate the polyesterification reaction leading to the formation of polyethylene terephthalate (PET) have also been found to promote certain undesirable side reactions. Such reactions include, in particular, the formation of ether links and the thermal degradation of the polyester formed. While the

latter reaction has been studied in detail by Zimmermann [1, 2], data concerning the etherification reaction are scarcer. Yoda [3] has carried out the polycondensation of bis( $\beta$ -hydroxyethyl) terephthalate in the presence of various metal catalysts. The melting point and the diethylene glycol (DEG) content were found to depend on the types of catalysts employed, and possible mechanisms of ether formation were discussed.

Recently Tomita and Ida [4] investigated the activity of various metal acetates in the transesterification of dimethyl terephthalate (DMT) with ethylene glycol (EG). Their study has shown that the most active catalysts are the acetates of zinc, lead, and manganese. The same three catalysts were selected in the present work. An analytical method described in a previous paper [5] was used to determine the amount of DEG formed. The formation of DEG was investigated both on model systems consisting solely of EG and the catalyst and on systems involving DMT and EG in various stages of reesterification and polycondensation.

## EXPERIMENTAL

### Reagents

DMT was a commercial product (Hercules). It was crystallized from ethanol and then vacuum-distilled before use.

EG (technical grade) was first dried 48 h over anhydrous  $\text{Na}_2\text{SO}_4$ . The product was then warmed up to  $100^\circ\text{C}$  and sodium metal was added (1 g Na/100 g EG). The mixture was maintained at  $100^\circ\text{C}$  for several hours followed by distillation on a vacuum column at 15-20 mmHg. The middle fraction was collected and stored in brown-glass storage bottles.

Sodium salt of dimethyl(5-sulfo)isophthalate (NaDMSIP) (Chemische Werke Witten) was used as such without purification.

All other chemicals employed in this work were of reagent purity and were used without additional purification.

### Reactor

The polyesters were prepared in a stainless steel tubular batch reactor. The reactor was equipped with a vacuum-tight hollow stirrer which also served for the introduction of nitrogen through holes in the impeller. A side arm connected to a condenser and a calibrated receiver permitted us to monitor the amount of methanol and EG distilled off. The bottom of the reactor was provided with a spinneret, which was capped during the reaction. At the desired time the spinneret was opened and the filament formed was then spun onto a rotating drum. The speed of the drum determined the thickness of the

fiber drawn. The temperature of the reactor was controlled by means of a thermostated aluminum block enclosing the reactor.

### Reesterification and Polycondensation

The reactor was charged with 0.2 mol of DMT and 0.5 mol of EG. The system was purged with nitrogen and the temperature was raised to  $195 \pm 1^\circ\text{C}$ . From the onset of reesterification (the moment methanol first appeared), the mixture was maintained at  $195^\circ\text{C}$  for 1 h. The amount of methanol freed by the reaction was measured in a calibrated receiver.

During the next 30 min the mixture was heated up to  $280^\circ$ . This was accompanied by the removal of most of the excess EG. Then the pressure was gradually brought down to 0.5-1 mmHg during 15 min and the flow of nitrogen was stopped. The reaction mixture was subsequently maintained at  $280^\circ$  for the required time. After the reaction was completed, the reactor was filled with nitrogen, the spinneret opened, and the polymer discharged.

The temperature-time regime of the reaction was carefully observed in order to obtain a good reproducibility of the experiments. In the preparation of polyesters modified with NaDMSIP, a proportionate molar amount of DMT was replaced with NaDMSIP.

### Etherification of EG

The etherification experiments were carried out in Pyrex glass ampules. The ampule was charged with the required amounts of EG and catalyst and subsequently flushed with dry nitrogen. The top of the ampule was then sealed off and the ampule was placed in a thermostated aluminum block maintained at the required temperature. After the desired reaction time, the ampule was quickly cooled down and opened. The contents were then analyzed for DEG content.

## RESULTS AND DISCUSSION

### Effect of Catalysts on Polycondensation

The effect of the three metal acetate catalysts on the formation of ether bonds and on the melting points of the resulting polyesters is shown in Tables 1, 2, and 3. The catalyst concentration range studied was from  $5-100 \times 10^{-4}$  mol/mol of DMT charged in the reactor and the time of polycondensation was 4 h. The data have shown an important difference between the zinc acetate catalyst and the other two catalysts in that the DEG levels found with the former were much higher. Even at the lowest concentration ( $5 \times 10^{-4}$  mol/mol DMT),

TABLE 1. Polycondensation Catalyzed by  $\text{Zn}(\text{OCOCH}_3)_2$ 

Sample	Catalyst concentration (mol/mol DMT) $\times 10^4$	% DEG <sup>a</sup>	Melting point ( $^\circ\text{C}$ )
Z1	5	2.94	262
Z2	8	2.84	263
Z3	12	3.05	261
Z4	20	3.17	263
Z5	27	3.17	264
Z6	32	3.28	263
Z7	37	3.30	259
Z8	43	3.46	259
Z9	50	3.53	260

<sup>a</sup>Average of three analyses.

TABLE 2. Polycondensation Catalyzed by  $\text{Pb}(\text{OCOCH}_3)_2$ 

Sample	Catalyst concentration (mol/mol DMT) $\times 10^4$	% DEG <sup>a</sup>	Melting point ( $^\circ\text{C}$ )
P1	1	1.25	264
P2	5	1.33	260
P3	10	1.44	261
P4	20	1.49	259
P5	30	1.66	259
P6	40	1.97	261
P7	50	2.51	260
P8	100	3.11	262

<sup>a</sup>Average of three analyses.

TABLE 3. Polycondensation Catalyzed by  $\text{Mn}(\text{OCOCH}_3)_2$ 

Sample	Catalyst concentration (mol/mol DMT) $\times 10^4$	% DEG <sup>a</sup>	Melting point ( $^{\circ}\text{C}$ )
M1	1	1.25	262
M2	5	1.39	264
M3	10	1.53	263
M4	20	1.71	261
M5	30	1.93	262
M6	40	2.16	263
M7	50	2.65	260
M8	100	2.71	260

<sup>a</sup> Average of three analyses.

zinc acetate already gave close to 3% DEG. The acetates of lead and manganese, on the contrary, produced only slightly over 1% DEG at the same concentration. However, they gave a steeper increase in DEG content with rising catalyst concentration.

The effect of polycondensation time, as well as the effect of the reesterification and heating stage on the formation of DEG, was also investigated. The results are summarized in Tables 4, 5, and 6 for zinc, lead, and manganese acetates, respectively. The catalyst concentration in all these experiments was held at  $2 \times 10^{-3}$  mol/mol DMT. The first two experiments listed in each table correspond to the samples withdrawn after the reesterification and after the preheating period, respectively. Each entry in the tables is the result of a separate polycondensation experiment.

The data indicate that no increase in DEG content is brought about by the reesterification reaction at  $195^{\circ}\text{C}$ . The DEG contents found after the reesterification for all three catalysts are within the error limit of the 0.25% DEG content determined for unreacted EG in the presence of DMT [5]. A steep rise in DEG content is then observed during the 15-min preheating period and during the first hour of polycondensation. Once again, zinc acetate is the strongest promoter of the etherification reaction. This is in agreement with the findings of Yoda [3], although the absolute values of DEG content observed in the present work were lower  $\sim 3.3\%$  as compared to 7.5% in Yoda's work).

The melting points shown in Tables 1, 2, and 3 display little variation. While Janssen et al. [6] observed a decrease in polyester melting point from 270 to  $250^{\circ}\text{C}$  coinciding with an increase in DEG content from 0.60 to 3.64%, the melting points found in this work are

TABLE 4. Effect of Reaction Time on DEG Content with  $\text{Zn}(\text{OCOCH}_3)_2$  as Catalyst (catalyst =  $2 \times 10^{-3}$  mol/mol DMT)

Sample	Time (h)	% DEG <sup>a</sup>
DZ1	Reesterification	0.25
DZ2	Preheat	1.07
DZ3	0.5	2.38
DZ4	1.0	2.55
DZ5	2.0	2.78
DZ6 <sup>b</sup>	4.0	3.17
DZ7	6.0	3.23
DZ8	8.0	3.42
DZ9	10.0	3.50

<sup>a</sup>Average of two analyses.

<sup>b</sup>Identical with Z4 (Table 1).

TABLE 5. Effect of Reaction Time on DEG Content with  $\text{Pb}(\text{OCOCH}_3)_2$  as Catalyst (catalyst =  $2 \times 10^{-3}$  mol/mol DMT)

Sample	Time (h)	% DEG <sup>a</sup>
DP1	Reesterification	0.26
DP2	Preheat	0.84
DP3	0.5	1.26
DP4	1.0	1.27
DP5	2.0	1.42
DP6 <sup>b</sup>	4.0	1.49
DP7	6.0	1.86
DP8	8.0	2.03
DP9	10.0	2.15

<sup>a</sup>Average of two analyses.

<sup>b</sup>Identical with P4 (Table 2).

TABLE 6. Effect of Reaction Time on DEG Content with  $\text{Mn}(\text{OCOCH}_3)_2$  as Catalyst (catalyst =  $2 \times 10^{-3}$  mol/mol DMT)

Sample	Time (h)	% DEG <sup>a</sup>
DM1	Reesterification	0.21
DM2	Preheat	0.79
DM3	0.5	1.39
DM4	1.0	1.41
DM5	2.0	1.56
DM6 <sup>b</sup>	4.0	1.71
DM7	6.0	2.02
DM8	8.0	2.18
DM9	10.0	2.18

<sup>a</sup>Average of two analyses.

<sup>b</sup>Identical with M4 (Table 3).

almost constant. They are very close to the values reported by Yoda [3] for comparable polyesters.

An addition of zinc acetate to a polycondensation already under way with another catalyst was found to substantially raise the DEG content of the fibers. In one experiment, polycondensation was carried out with  $2 \times 10^{-3}$  mol/mol DMT of  $\text{Mn}(\text{CH}_3\text{COO})_2$  during 4 h, whereupon  $2 \times 10^{-3}$  mol/mol DMT of  $\text{Zn}(\text{CH}_3\text{COO})_2$  was added. This resulted in an increase of DEG content from 1.78 to 3.26%.

### Polyesters Modified with NaDMSIP

NaDMSIP is a modifier which imparts flexibility to the rigid polyethylene terephthalate chain. The addition of the modifier, which is subsequently built into the chain, is expected to lower the melting point of the fiber. It is interesting to know whether NaDMSIP contributes to the formation of DEG units in the polyester.

Table 7 lists the results of polycondensation experiments in which a part of DMT was replaced with an equimolar amount of NaDMSIP. The reactions were catalyzed with zinc acetate in a concentration of  $2 \times 10^{-3}$  mol/mol (DMT + NaDMSIP). The results show that the DEG content found was almost independent of the NaDMSIP concentration. Consequently, it can be concluded that the rather large melting point drop occurring at NaDMSIF concentrations above 6% is brought about



TABLE 7. Polyesters Modified with NaDMSIP

Sample	NaDMSIP (% by mol)	% DEG <sup>a</sup>	Melting point (°C)
Z4	0.0	3.17	263
S1	0.2	3.94	257
S2	0.5	4.16	262
S3	1.0	3.93	257
S4	2.0	3.92	256
S5	3.0	3.86	257
S6	4.0	3.94	256
S7	5.0	4.02	257
S8	6.0	4.04	-
S9	7.0	4.30	253
S10	8.0	4.20	241
S11	10.0	4.29	244

<sup>a</sup> Average of three analyses.

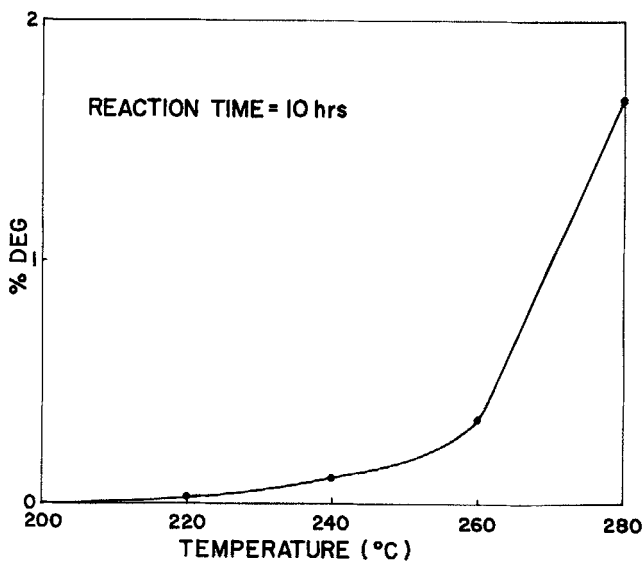


FIG. 1. Etherification of EG in the absence of catalyst.

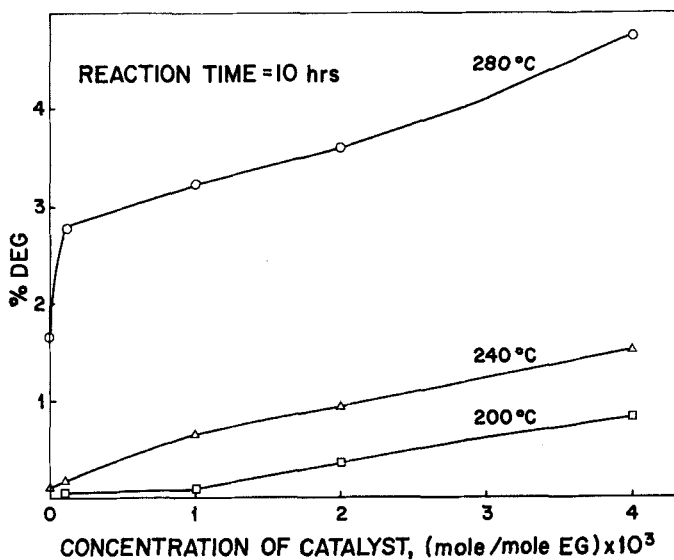


FIG. 2. Etherification of EG in the presence of zinc acetate.

solely by the loss of polymer regularity due to the addition of the modifier, and not through an increased formation of ether bonds.

### Etherification of EG

The formation of ether bonds in ethylene glycol containing systems was further investigated. A model system was used consisting of freshly distilled EG either alone or in the presence of one of the three catalysts studied. The formation of DEG in the absence of catalyst is shown in Fig. 1 for the temperature range 200–280°C. It is evident that noncatalyzed etherification becomes important only when the temperature exceeds approximately 250°C.

The addition of a metal acetate catalyst results in significantly higher levels of DEG being found, and this is already at 200°C. In comparison to the results of the polycondensation experiments, zinc acetate is the most active catalyst for etherification. The levels of DEG observed with the two other catalysts are significantly lower.

Yoda [3] proposed three reactions which could be responsible for the formation of DEG:

1. The self-dehydrating condensation of alcohol terminal groups by the catalysts

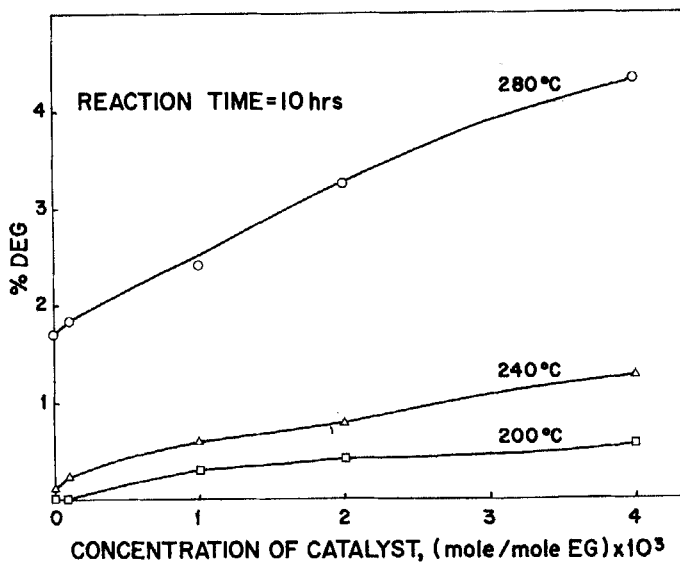
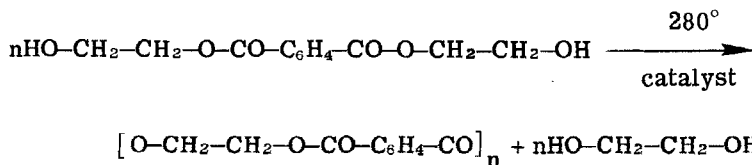


FIG. 3. Etherification of EG in the presence of lead acetate.

2. The thermal decomposition of the hydroxyethyl ester end group
3. The thermal decomposition of the main chain

Based on the results of model experiments (EG + catalyst) which produced little or no DEG, he concluded that Reaction (1) was of little significance except for one particular catalyst ( $\text{Sb}_2\text{O}_3$ ). Yoda's model experiments, however, were carried out at  $197^\circ\text{C}$ . The data obtained in this work have shown that only a small amount of DEG is formed at temperatures below  $250^\circ$ , even in the presence of a catalyst. On the contrary, the polycondensation is carried out at temperatures ranging from  $265$  to  $280^\circ$ . Although there is no free EG present when using bis( $\beta$ -hydroxyethyl) terephthalate as the monomer, the polyesterification reaction results in the formation of EG as a by-product:



The free EG then may undergo etherification into DEG. Because of its rather high boiling point ( $245^\circ$ ), DEG is not likely to be immediately removed from the reaction mixture by distillation with the

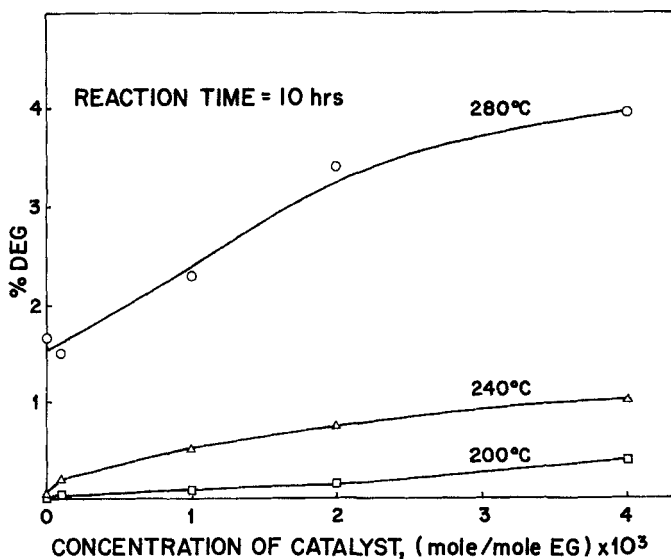


FIG. 4. Etherification of EG in the presence of manganese acetate.

EG, and will enter the polyester chain through a sequence of reesterification and polycondensation reactions.

The results reported in this work demonstrate that, at the polycondensation temperature (280°C), the percentual amount of DEG formed is very similar in the model system to the polycondensation system. This would indicate that the contribution of Reaction (1) is the most important. It is apparent from Tables 4-6 that the formation of DEG is the most rapid during the first 2 h of the reaction when the concentration of free EG is the highest. The observation that increasing the reaction time failed to produce any spectacular rise in DEG content of the fibers would indicate that the contribution of degradation reactions to the formation of ether links is less important.

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