

A Novel Catalyst for the Glycolysis of Poly(ethylene terephthalate)

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ABSTRACT: Poly(ethylene terephthalate) waste materials were depolymerized by ethylene glycol (EG), diethylene glycol (DEG), and propylene glycol (PG) in the presence of a novel catalytic system: titanium (IV)-phosphate. The new catalyst was synthesized through a reaction of TiCl_4 with triethyl phosphate ($\text{C}_2\text{H}_5\text{O}$)₃P(O). It was found that the depolymerization of poly(ethylene terephthalate) fiber proceeds faster in the presence of titanium (IV)-phosphate com-

pared with compounds traditionally used in this process like $\text{Zn}(\text{OOCCH}_3)_2$. The oligomer distribution in the glycolysis products was studied by size-exclusion chromatography. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1148–1152, 2003

Key words: catalysis; glycolysis; organometallic catalysts; poly(ethylene terephthalate); recycling; thermoplastics

INTRODUCTION

Increased environmental awareness, legislative measures, and public demand for environmental sustainability are leading to an increased interest in plastics recycling.¹ Poly(ethylene terephthalate) (PET), a high volume thermoplastic polyester² that is extensively used in diverse applications—textiles, high strength fibers, photographic films, soft-drink bottles (annually 1.5 million ton of PET are used in the production of bottles and jars alone),³ and others—is also one of the largest components of the postconsumer plastics waste in landfills⁴ (1,700,000 tons in the U.S. alone¹). Therefore, the chemical PET decomposition and conversion into reusable chemical products of added value is one of the important recycling strategies for this material.^{5,6} Glycolysis with ethylene glycol (EG)⁷ propylene glycol, and their derivatives is one of the most widely studied processes for PET degradation.⁸ The reaction is a very sluggish one when performed without a catalyst. It was found that the activation energy for the uncatalyzed glycolysis was 32 kcal/mol whereas the catalyzed process requires only 19 kcal/mol.⁹ Therefore various metal-containing catalysts, such as zinc acetate,^{8,10–12} lead-, cobalt-, or manganese acetate,^{10–12} and titanium alkoxides^{14–16} were used to facilitate the process. The reaction proceeds faster with

titanium alkoxides compared with the degradation catalyzed by metal acetates. Regrettably, the former compounds also catalyze side reactions that yield products with an undesirable yellowish color.¹⁴ On the other side, it was found that during the PET synthesis similar reactions could be avoided in the presence of thermal stabilizers like trialkyl- or aryl phosphates affording PET with good whiteness and transparency.^{17–20}

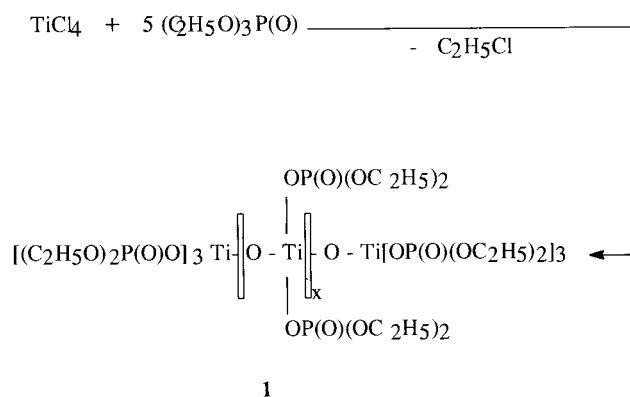
The primary goals of this study are the design, synthesis, and evaluation of a new catalyst for PET glycolysis that will combine the advantages of the previously applied compounds while avoiding their shortcomings. The leading idea is to incorporate titanium and alkyl phosphate moieties in a single molecule that could act simultaneously as a catalyst and as a thermal stabilizer during the process. Here we report the results from the synthesis of titanium (IV)-phosphate compound and its application in the glycolysis of PET wastes.

EXPERIMENTAL

Materials

PET pellets used for fiber production ($M_w = 30,000$) were supplied by Yambolen Ltd., Bulgaria. PET pellets for bottle manufacturing ($M_w = 51,000$) were supplied by Bulgarian private company. Ethylene glycol (EG), diethylene glycol (DEG), and 1,2-propylene glycol (PrG), TiCl_4 , triethyl phosphate, and $\text{Zn}(\text{OOCCH}_3)_2$ were purchased from Aldrich (Milwaukee, WI) and used without further purification.

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Scheme 1

Synthesis of titanium(IV)-phosphate catalyst, **1**

Triethyl phosphate 18.2 g (0.1 mol) and TiCl_4 3.78 g (0.02 mol) were placed into a three-necked flask, charged with 30 mL of high boiling gasoline, and equipped with a capillary for argon purging, thermometer, and reflux condenser. The reaction was performed at 120°C for 6 h. The contents in the flask were allowed to cool down to room temperature after the completion of the reaction (controlled by the amount of $\text{C}_2\text{H}_5\text{Cl}$ evolved). The precipitate formed was separated by filtration, washed several times with dry ethanol in order to separate the unreacted triethyl phosphate, and then dried at 50°C. Yield 7.9 g (60%).

General procedure of PET glycolysis

A typical experiment is performed as described: 25 g (0.13 mol/repeating unit) of PET pellets (fiber grade or bottle grade) were added to 0.36 mol of glycols (EG, DEG, or PrG). The molar ratio of PET repeating unit to glycol was 1:2.77. The mixtures, together with different amounts of titanium (IV)-phosphate catalyst **1**, (in wt% based on the weight of PET), were charged into a three-necked flask, equipped with a stirrer, thermometer, and reflux condenser. Comparative experiments in the presence of $\text{Zn}(\text{OOCCH}_3)_2$ (0.3 wt%) and with-

out a catalyst were also performed. The reaction was monitored by size-exclusion chromatography.

Measurements

The molecular weight characteristics and the oligomer distribution of the glycolysis products were determined by size-exclusion chromatography (SEC). The analyses were performed at 40°C on a Waters 244 instrument, equipped with differential refractive index detector R410, 450 UV-Vis detector (both from Waters), and 5 mm American Polymer Standards columns (Linear, 10^4 Å, and 500 Å) in tetrahydrofuran (THF) eluting at 1 mL/min. The molecular weights were calculated by a conventional calibration with polystyrene standards.

^{31}P NMR spectra were recorded on a Bruker 500 MHz spectrometer in solid state. Thermal studies were performed on a Perkin Elmer DSC-7 differential scanning calorimeter in nitrogen atmosphere and heating rate of 5°C/min. The instrument was calibrated by indium and lead standards. FTIR spectra were recorded on a Bruker Vector 22 instrument in KBr.

RESULTS AND DISCUSSION

Synthesis of titanium (IV)-phosphate catalyst

Titanium (IV)-phosphate ester is chosen as the catalyst in the PET glycolysis because of the known efficiency of phosphate compounds as thermal stabilizers.¹¹ The heterochain catalyst **1**, containing Ti-O-P sequences, is synthesized by reacting TiCl_4 with triethyl phosphate (Scheme 1).

Suggestions that polymeric compounds like **1** might be formed during this reaction were briefly mentioned in some early studies²¹⁻²⁴ without any experimental description and analytical evidence. The structure of the individual building block in **1** is confirmed by ^{31}P NMR and IR spectroscopy. The $^{31}\text{P}\{\text{H}\}$ NMR spectrum shows only one quintet signal at with $d = -0.24$ ppm

TABLE I
Reaction Conditions and Main Products During PET (Fiber Grade) Glycolysis with EG

| PET (mol/ repeating unit) | EG (mol) | Cat. (wt %) | Temperature (°C) | Reaction time (min) | SEC analysis of glycolyzed products | | | |
|---------------------------------|-------------|------------------|---------------------|---------------------------|-------------------------------------|-----------|------------|--------------|
| | | | | | BHET (%) | Dimer (%) | Trimer (%) | Tetramer (%) |
| 0.13 | 0.36 | — | 190–200 | 300 | 96.4 | 2.4 | 0.9 | 0.3 |
| 0.13 | 0.36 | 0.05 | 190–200 | 195 | 95.3 | 3.5 | 1.0 | 0.2 |
| 0.13 | 0.36 | 0.1 | 190–200 | 180 | 96.5 | 2.4 | 0.8 | 0.2 |
| 0.13 | 0.36 | 0.2 | 190–200 | 160 | 95.5 | 3.2 | 1.0 | 0.3 |
| 0.13 | 0.36 | 0.3 | 190–200 | 150 | 97.5 | 1.6 | 0.7 | 0.2 |
| 0.13 | 0.36 | 0.5 | 190–200 | 155 | 95.3 | 3.5 | 1.0 | 0.3 |
| 0.13 | 0.36 | 0.3 ^a | 190–200 | 150 | 62.8 | 26.8 | 8.6 | 1.8 |

^a Catalyst = $\text{Zn}(\text{OOCCH}_3)_2$.

TABLE II
Characterization Data for PET (Fiber Grade) Glycolysis with DEG

| PET (mol/ repeating unit) | DEG (mol) | Cat. (wt %) | Temperature (°C) | Reaction time (min) | SEC analysis of glycolyzed products | | | |
|---------------------------------|--------------|----------------|---------------------|---------------------------|-------------------------------------|-----------|------------|--------------|
| | | | | | BHEET (%) | Dimer (%) | Trimer (%) | Tetramer (%) |
| 0.13 | 0.36 | — | 220 | 50 | 12.8 | 2.8 | 81.8 | 2.0 |
| 0.13 | 0.36 | 0.3 | 220 | 12 | 91.2 | 4.5 | 2.8 | 1.5 |
| 0.13 | 0.36 | 0.5 | 220 | 13 | 90.4 | 4.6 | 3.1 | 1.9 |

and $^3\text{J}(\text{P,H}) = 7.7$ Hz. The phosphorus chemical shift is shifted upfield by 0.50 ppm with respect to triethyl phosphate ($d = 0.26$ ppm) due to the presence of an ionic bond in this structure.²⁵ In the IR spectrum of **1** the P = O stretching frequency is lowered by approximately 235 cm^{-1} when compared with the analogous band in triethyl phosphate. These data confirm that the phosphorus atom is surrounded by two ethoxy groups.

Glycolysis of fiber grade PET

The glycolysis is carried out with EG, DEG, or PrG with the molar ratio PET to glycol kept constant at 1:2.77.

During the glycolysis with EG the temperature of the oil bath is kept at 200°C, close to the boiling temperature of the glycol. It is also observed that the temperature of the system increases from 190 to 200°C during the depolymerization process. Different concentrations of the catalyst **1** were investigated (Table I, runs 2–5). It is found that the reaction proceeds faster in the presence of the titanium (IV)-phosphate ester, (Table I). At 0.3 wt % of **1**, the optimal concentration of the catalyst, the reaction time is reduced from 300 min (noncatalyzed glycolysis, Table I, run 1) to 150 min. SEC analysis shows (Table I) that the decomposition mixtures consist mainly of bis(2-hydroxyethyl) terephthalate (BHET). DSC thermograms of the products contain two endothermic peaks. The first peak at 107.8°C, can be attributed to the melting transition of BHET. The second peak at 124.8°C is small and well below the reported melting temperature of the BHET dimer (162°C).¹³ The glycolysis mixture produced in the presence of 0.3 wt % of $\text{Zn}(\text{OOCCH}_3)_2$ and 150 min

reaction time is more complex (Table I, run 7). It contains 62.8% BHET, 26.8% dimer, 8.6% trimer, and 1.8% tetramer. It is obvious that the full decomposition of PET is significantly facilitated in the presence of **1** compared with process catalyzed by $\text{Zn}(\text{OOCCH}_3)_2$ under identical reaction conditions.

In the case of DEG the depolymerization is performed at 220°C. The experimental results show that 0.3 wt % of **1** is again the optimal catalyst concentration because the decomposition is complete within 20 min, compared to the same process run for 65 min without a catalyst (Table II). Bis[2(2-hydroxyethoxy)ethyl] terephthalate (BHEET) is the main product of the glycolysis.

The depolymerization with PrG is carried out at the boiling temperature of the glycol (180°C). Similar to the EG case, the reaction temperature increases during the decomposition process. The optimal concentration of the catalyst **1** is also 0.3 wt %. The depolymerization proceeds at this concentration for 480 min, whereas depolymerization without catalyst runs for 885 min. SEC analysis shows that the main product is bis(2-hydroxypropyl) terephthalate (BHPT) (Table III).

Glycolysis of bottle grade PET

From the experimental data presented in Table IV it is clear that the reaction time with EG is reduced from 480 min for the noncatalyzed depolymerization (run 1) to 105 min for catalyzed process (0.3 wt % of **1**, run 2). It should be mentioned that the content of BHET at the catalyzed depolymerization (66.7%) is notably higher compared with the noncatalyzed process (37.4%). Surprisingly, the results obtained show that in this case of the glycolysis there is no substantial difference in the

TABLE III
Reaction Conditions and Main Products During PET (Fiber Grade) Glycolysis with PrG

| PET (mol/ repeating unit) | PEG (mol) | Cat. (wt %) | Temperature (°C) | Reaction time (min) | SEC analysis of glycolyzed products | | | |
|---------------------------------|--------------|----------------|---------------------|---------------------------|-------------------------------------|-----------|------------|--------------|
| | | | | | BHPT (%) | Dimer (%) | Trimer (%) | Tetramer (%) |
| 0.13 | 0.36 | — | 180–194 | 885 | 94.1 | 3.3 | 1.7 | 0.9 |
| 0.13 | 0.36 | 0.3 | 180–188 | 480 | 93.6 | 3.6 | 1.8 | 1.0 |
| 0.13 | 0.36 | 0.5 | 180–188 | 530 | 93.3 | 3.7 | 1.9 | 1.1 |

TABLE IV
Characterization Data for PET (Bottle Grade) Glycolysis with EG

| PET (mol/ repeating unit) | EG (mol) | Cat. (wt %) | Temperature (°C) | Reaction time (min) | SEC analysis of glycolyzed products | | | |
|---------------------------------|-------------|------------------|---------------------|---------------------------|-------------------------------------|-----------|------------|--------------|
| | | | | | BHET (%) | Dimer (%) | Trimer (%) | Tetramer (%) |
| 0.13 | 0.36 | — | 190–200 | 480 | 37.4 | 23.7 | 24.4 | 13.9 |
| 0.13 | 0.36 | 0.3 | 190–200 | 105 | 66.7 | 28.9 | 4.4 | — |
| 0.13 | 0.36 | 0.5 | 190–200 | 110 | 62.9 | 29.1 | 7.9 | — |
| 0.13 | 0.36 | 0.3 ^a | 190–200 | 105 | 61.1 | 28.5 | 8.7 | 1.7 |

^a Catalyst = Zn(OOCCH₃)₂.

TABLE V
Characterization Data for PET (Bottle Grade) Glycolysis with DEG

| PET (mol/ repeating unit) | DEG (mol) | Cat. (wt %) | Temperature (°C) | Reaction time (min) | SEC analysis of glycolyzed products | | | |
|---------------------------------|--------------|----------------|---------------------|---------------------------|-------------------------------------|-----------|------------|--------------|
| | | | | | BHEET (%) | Dimer (%) | Trimer (%) | Tetramer (%) |
| 0.13 | 0.36 | — | 220 | 16 | 9.7 | 21.0 | 32.0 | 37.3 |
| 0.13 | 0.36 | 0.3 | 220 | 8 | 64.2 | 3.3 | 2.1 | 30.4 |
| 0.13 | 0.36 | 0.5 | 220 | 8 | 58.0 | 8.6 | 6.5 | 26.9 |

TABLE VI
Reaction Conditions and Main Products During PET (Fiber Grade) Glycolysis with PrG

| PET (mol/ repeating unit) | PEG (mol) | Cat. (wt %) | Temperature (°C) | Reaction time (min) | SEC analysis of glycolyzed products | | | |
|---------------------------------|--------------|----------------|---------------------|---------------------------|-------------------------------------|-----------|------------|--------------|
| | | | | | BHPT (%) | Dimer (%) | Trimer (%) | Tetramer (%) |
| 0.13 | 0.36 | — | 180–194 | 1210 | 38.8 | 29.8 | 19.6 | 11.8 |
| 0.13 | 0.36 | 0.3 | 180–190 | 285 | 52.8 | 27.8 | 11.6 | 5.0 |
| 0.13 | 0.36 | 0.5 | 180–190 | 400 | 47.7 | 27.9 | 13.2 | 11.2 |

activity of catalyst **1** and Zn(OOCCH₃)₂. The glycolysis of bottle grade PET in the presence of 0.3 wt % of Zn(OOCCH₃)₂ (Table IV, run 4) generates the following decomposition products: BHET 61.1%, dimer 28.5%, trimer 8.7%, and tetramer 1.6%.

The depolymerization with DEG was carried out at 220°C. The glycolysis is faster in the presence of **1** (Table V, runs 2 and 3). The SEC analysis shows that the content of the monomer, dimer, trimer, and tetramer for the noncatalyzed depolymerization process is several times lower, compared with the process where the glycolysis is carried out in the presence of a catalyst **1** (Table 5).

The same trend is observed for the PET glycolysis by PrG. At the optimal concentration of **1** (0.3 wt %) the glycolysis proceeds for 285 min. In the absence of a catalyst the reaction time is significantly longer, at 1210 min. The content of BHPT is 52.8% for catalyzed depolymerization of PET whereas for the noncatalyzed process it is 38.8% as revealed by SEC analysis (Table VI).

CONCLUSIONS

The results obtained show that the titanium (IV)-phosphate (**1**) synthesized by reaction of titanium tetra-

chloride and triethyl phosphate can be used as a catalyst for PET glycolysis with EG, DEG, and PrG. It is found that the optimal concentration of **1** is 0.3 wt %. The depolymerization rate of fiber grade PET substantially increases in the presence of this catalyst. At comparable reaction times (195 min, Table I; 480 min, Table III) the depolymerization achieved by the uncatalyzed process is less than 60%. At these times the reaction produces mostly oligomers. The mechanism of the catalyzed reaction most probably involves complexes of the polymer, catalyst and the corresponding glycol through hydrogen bond formation.^{26,27} It should be mentioned that **1** shows markedly higher catalytic activity in this system compared with Zn(OOCCH₃)₂. In the case of the depolymerization of bottle grade PET no substantial difference in the activity of **1** and Zn(OOCCH₃)₂ is observed. However, the color of the degradation products is notably better. The good product whiteness observed in all depolymerizations studied is an additional advantage of the new catalyst system.

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