

Degradation of Poly(ethylene terephthalate) Waste with Dimethyl Tin Distanoxane as a Catalyst

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ABSTRACT: In this article, we report the degradation of poly(ethylene terephthalate) (PET), which occurs through glycolysis in the presence of dimethyl tin distanoxane $[(\text{CH}_3)_2\text{Sn}(\text{OCOCH}_3)_2]$ as a catalyst, triethylene glycol (TEG) as a nucleophilic agent, and decaline like a solvent. A number of experiments were executed, which were derived from a factorial experimental design, in which the reaction time was between 40 and 60 min, the amount of TEG was between 3.4 and 5.6 g, and the amount of catalyst was between 0.04 and 0.06% in ratio to PET. The reaction temperature was constant at 175°C in all of the experiments. Once the glycolytic depolymerization occurred, oligomers with a molecular weight around 6000 g/mol were obtained. These oligomers were analyzed through gel permeation chromatography, differential scanning calorimetry, Fourier transform infrared spectroscopy, and ¹H-NMR. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3482–3488, 2013

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INTRODUCTION

Poly(ethylene terephthalate) (PET) is a thermoplastic polymer used widely in the manufacturing of different products, for example, photographic films, audio and video tapes, automotive parts, toys, and especially in carbonated drink containers.¹ PET by itself is not harmful to the environment because it is non-toxic; however it is considered a harmful material because of its resistance to environmental biodegradation. The disposal of PET is critical because of the volume it occupies; it has reached a high degree of pollution.

The reuse of this material, its transformation by chemical degradation into a compound of lower molecular weight, is important so it can be used in the manufacturing of composite materials.² PET is synthesized by a polycondensation reaction between terephthalic acid and diethylene glycol; because this is a reversible process, PET degradation by glycolysis is possible under certain reaction conditions. The main mechanism that occurs is called transesterification, which is a reaction achieved in the presence of a catalyst.³ In our research group, we studied the degradation of PET with different types of catalysts; this consequently resulted in the study of other reaction parameters, such as glycol concentration, temperature, and glycolysis time.⁴

In previous research, the degradation of PET has reportedly used different metal acetates as catalysts, propylene glycol, and an excess of ethylene glycol (EG) as a nucleophilic agent at 190–200°C for 8 h. The products obtained were oligomers with molecular weights between 276 and 480 g/mol. Zinc acetate was the best in terms of the extent of depolymerization.^{5,6} Chen and coworkers^{5–7} reported the glycolysis of PET at 190°C with an excess of EG and zinc acetate as the catalyst; it was found that the higher catalyst concentration (0.5% with respect to PET) was, the higher the glycolysis rate was. After 2 h of reaction, an equilibrium state between the monomer and dimer was reached, whereas a reduced amount of EG in the initial feed resulted in a decrease in the glycolysis rate.^{7,8}

The ratio of EG to PET used was 2:1, the temperatures were 130 and 190°C, the times were 0.5 and 2.0 h, and the amounts of catalyst used were 0 and 0.004 mol.

Reports have confirmed the influence of the glycolysis conditions on the conversion of PET in studies with factorial experimental design that involved glycolysis conditions with cobalt acetate as a catalyst, and the formation of Bis (2-hydroxyethyl terephthalate) (BHET) as the main product of the degradation was found.^{9,10} In these reports, the sequence of the main effects on the glycolysis conversion in ascending order was

Table I. Factorial Experiment Design (2^3)

Experiment number	Time (min)	TEG (g)	Catalyst (g)
1	60	3.4	0.04
2	60	3.4	0.06
3	60	5.6	0.04
4	60	5.6	0.06
5	40	3.4	0.04
6	40	3.4	0.06
7	40	5.6	0.04
8	40	5.6	0.06

Time < Temperature < Amount of catalyst. Glycolysis was studied in the presence of different catalysts, including zinc chloride, lithium chloride, didymium chloride, magnesium chloride, and ferric chloride at concentrations between 0.1 and 0.3% w/w.¹¹ In that study, the authors reported the metal salts were ionized to form a complex with the carbonyl group of ester in PET; this complex facilitated the attack of glycol on PET, which in turn led to the formation of BHET.

The organocatalytic depolymerization of PET with a commercially available guanidine catalyst was executed with 1.0 mol of 1,5,7-triazabicyclo-[4,4,0]-dec-5-ene (the catalyst) at 190°C for 3.5 h under atmospheric pressure to obtain BHET at a 78% isolated yield.¹²

Research so far has reported glycolysis conditions of 2 h of reaction time and a temperature of 190°C. The main product of degradation under these conditions is BHET. The types of products that could be obtained by the reaction of glycolysis with triethylene glycol (TEG) as a nucleophilic agent and decalin as a reaction medium were investigated in this study; in addition, the reaction conditions were lower (in terms of time and temperature) than those previously reported.

According to literature reports and the experience of our research group, the type of catalyst plays an important role. We verified that a reaction with organometallic compounds completely degraded the PET under the same conditions as with another kind of catalyst.

Organotin compounds derived from organic ligands have potential applications as luminescent probes,¹³ in nonlinear optical applications,¹⁴ and as catalysts.¹⁵ Moreover, depolymerization reactions of PET with tin(II) octoate¹⁶ and tin(II) acetate have been reported.¹⁷ However, both tin derivatives must be handled under an inert atmosphere, and this is a disadvantage for potential industrial applications. On the other hand, $\text{Me}_2\text{Sn}(\text{OAc})_2$ has been reported as a catalyst in the acetylation of amines with ethyl acetate.¹⁸ It is stable at room temperature, has a high melting point, is soluble in most organic solvents, and gives good yields in the acetylation reaction.

EXPERIMENTAL

Materials

Chemicals, including TEG, decaline, and Me_2SnCl_2 , were obtained from Sigma Aldrich and were used as received without any previous purification. The benzene was dried with

Na/benzophenone. PET bottle waste (molecular weight = 28,000 g/mol) was obtained from M&G Polymers USA. The tin catalyst was synthesized as described in the literature.^{19,20}

Methodology

Catalyst Synthesis. A solution of dimethyl tin distanoxane (5 g, 0.03 mol) and acetic acid (1.82 g, 0.03 mol) in benzene (20 mL) was heated to boiling temperature for 6 h in a reaction system provided with a Dean–Stark trap used for the azeotropic removal of water and allowed to cool to room temperature. Afterward, the solvent was removed under reduced pressure to obtain a white crystalline powder (yield = 95%). The product was washed with distilled water until the washings were neutral. Recrystallization from benzene/methanol (10:50 mL) in a -10°C freezer for 6 days afforded a purity suitable for catalytic study.

PET Degradation. PET flakes (4.0 g), TEG (3.4 and 5.6 g), decaline (10 mL), and the catalyst (0.04 and 0.06) were added to a flask in specific quantities according to the experiment derived from the experimental design. The mixture was heated to 175°C for 1 h with constant agitation. Once the reaction was done, decaline was decanted. The residue was washed three times with toluene to eliminate any decaline residue and to extract the oligomers formed in the degradation of PET, and then, three extractions with 15 mL of distilled water were performed on it to eliminate any residual TEG. After the extractions, the product was dried in an oven set to 110°C for 24 h and then weighed; this fraction corresponded to the nondegraded PET [B in eq. (1)]. The fraction extracted with toluene was separated by evaporation, the residue obtained was dried in an oven set to 110°C for 24 h and weighed, and this fraction corresponded to the oligomers produced during the degradation of PET.

The conversion (percentage of PET degraded) for the glycolysis of the recycled PET flakes was determined with eq. (1):

$$\text{Degraded PET (\%)} = \frac{A-B}{A} \times 100 \quad (1)$$

where A is the initial amount of PET flakes (g) and B is the amount of undegraded PET flakes (g).

To determine the influence of the reaction time, the catalyst quantity, and the amount of TEG on the degradation of PET, eight experiments were designed (Table I).

Characterization. The glycolyzed PET was characterized with a Thermo Scientific IR200 attenuated total reflectance (SeZn crystal) Fourier transform infrared (FTIR) spectrometer with 32 scans per analysis from 650 to 4000 cm^{-1} and by gel permeation chromatography in an HP instrument (model 1100) under the following conditions: 10 μL was injected from a 6 mg/mL glycolyzed PET solution into a PL gels columns: 10^6 Å, 10 μm (400,000–40,000,000); 10^5 Å, 5 μm (400,000–40,000,000); 10^3 Å, 5 μm (1000–40,000); this was done at 40°C with THF as the mobile phase at a flow rate of 1.0 mL/min. The melting characteristics were determined by differential scanning calorimetry (DSC; PerkinElmer) at a heating rate of 20°C/min from 10 to 350°C under a nitrogen atmosphere, and the structure of the resulting oligomer in experiment 3 was determined with a $^1\text{H-NMR}$ JEOL Eclipse 300-MHz spectrometer (CDCl_3 , tetra methyl silane (TMS)).

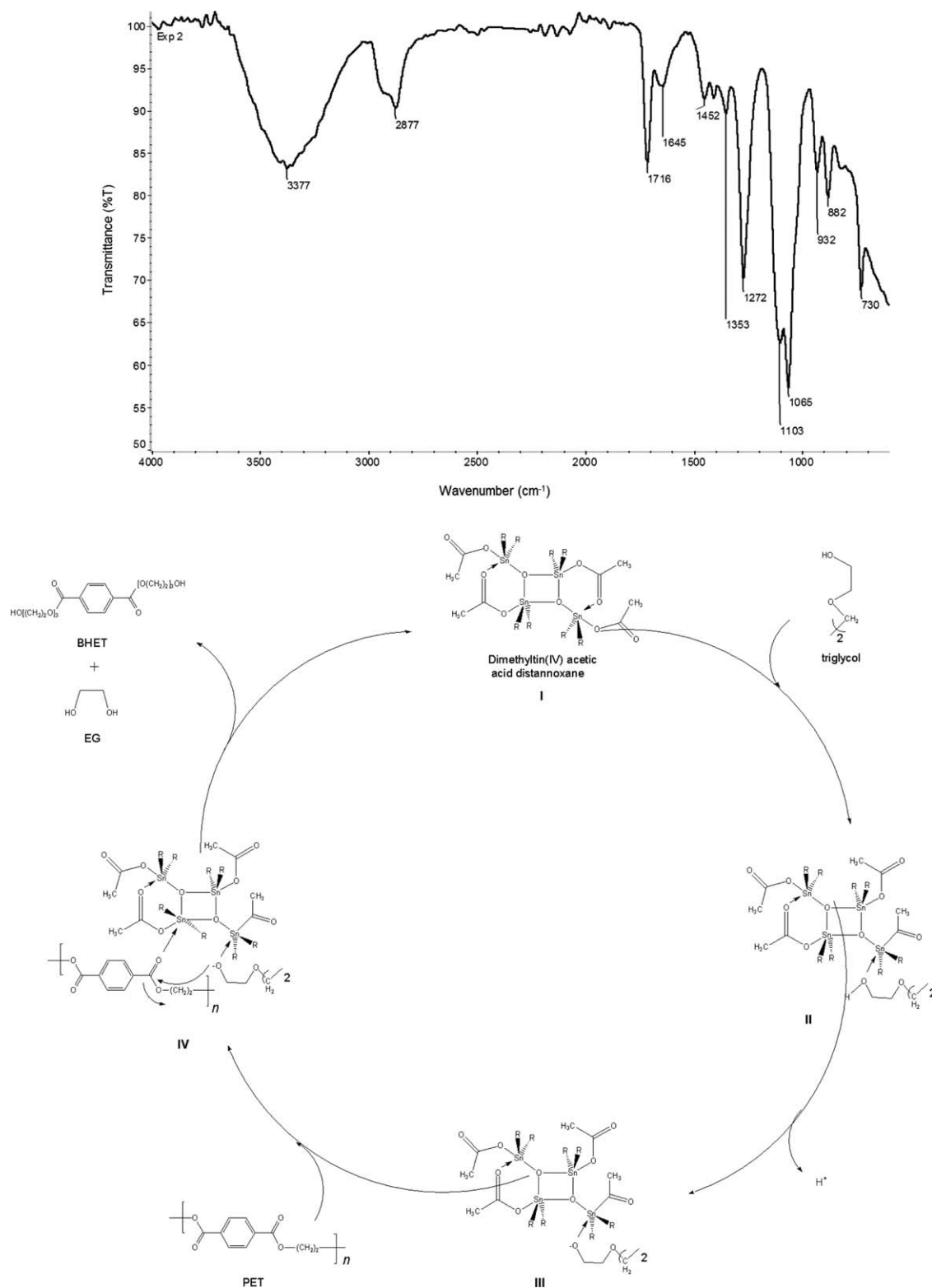


Figure 1. FTIR spectra of the oligomers obtained from PET glycolysis.

Kinetic Behavior. With the goal of determining the amount of degraded PET with the reaction time, we performed experiment 3 by taking a sample every 10 min. Chloroform was added to

each sample, and the solution was mixed, filtered, and dried in an oven at 80°C. The conversion was determined according to eq. (1).

Table II. Degraded PET from Experiments 1–8

Experiment number	Time (min)	TEG (g)	Catalyst (g)	PET degraded (%)
1	60	3.4	0.04	100
2	60	3.4	0.06	100
3	60	5.6	0.04	100
4	60	5.6	0.06	100
5	40	3.4	0.04	83
6	40	3.4	0.06	84
7	40	5.6	0.04	89
8	40	5.6	0.06	91

RESULTS AND DISCUSSION

The FTIR spectrum of the degraded PET is shown in Figure 1; the absorption bands were typical of a polyester resin: C–H at 2877 cm^{-1} , C=O at 1726 cm^{-1} , C–O at $1272\text{--}1065\text{ cm}^{-1}$, and aromatics at 882 cm^{-1} . The 3400-cm^{-1} absorption band belonged to the hydroxyl group that was absent in PET, and the increase of these groups was indicative of the fact that PET was glycolyzed by TEG in the presence of dimethyl tin distanoxane as the catalyst. This increase was highly significant because the residual TEG and water were removed completely after the end of the glycolysis reaction.

The relationships among the degraded PET and reaction time, catalyst quantity, and TEG amount are shown in Table II. The results show that the reaction time was a more influential parameter than the TEG and catalyst amounts. All of the experiments with the reaction time of 60 min accomplished 100% degradation, regardless of the amount of TEG.

The molecular weight distribution of the degraded PET from experiments 1–4 (Table III) with a yield of 100% were calculated. The concentration of TEG used in glycolysis led to the formation of short PET chains (oligomers) with a molecular weight between 6000 and 8000 g/mol. Because the repeating unit of PET had a molecular weight of 196, the molecular weight of the obtained oligomers (6000–8000 g/mol) suggested that they were formed with an average of 30–40 repeating units. The oligomers obtained with the reaction conditions used in this study suggested that they could be used in formulations

Table III. Molecular Weight Distribution of the Oligomers Obtained from Degraded PET

Experiment number	M_p	M_n	M_w	D
1	5553	3357	7404	2.206
2	6281	3551	8270	2.328
3	5076	3220	6549	2.034
4	5334	3379	7326	2.168

Molecular weight in number (M_n), Molecular weight in weight (M_w), Molecular weight on the top of the curve (M_p), Molecular weight in viscosity (M_v), Polidispersity (D).

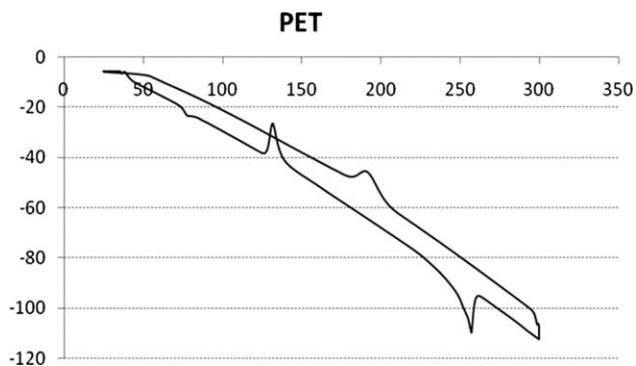


Figure 2. Thermal analysis of the undegraded PET.

that require polyester resins with medium molecular weights, such as unsaturated polyester resins.²¹

DSC thermograms of PET without degradation were registered from 10 to 350°C at a heating rate of $20^\circ\text{C}/\text{min}$ (Figure 2). The thermogram showed a glass-transition peak (T_g) at 84°C ; this was followed by two peaks at 264°C due to melting and 200°C , which indicated the degree of crystallinity. Figure 3 shows the thermogram of the oligomer from experiment 1. The thermogram indicated a T_g of 39°C and a melting at 136°C . This decay in T_g and melting temperature (T_m) demonstrated that the PET was degraded by the presence of tin catalyst to form chains with TEG groups in its structure. Figure 4 shows the $^1\text{H-NMR}$ spectrum of the oligomer resulting in the degradation of PET (experiment 3). The signals of TEG protons were visible to fields slightly higher than the protons of EG eliminated from the polymer during degradation; this indicated that the chains of the resulting oligomers were formed by the TEG groups included in its structure.

Table IV shows the results of T_g and T_m from experiments 1–4. The experiments with the highest amount of TEG (5.6 g) presented lower T_m 's; this was in accordance with the theory that with a higher glycol quantity, there is a higher possibility of a chain breaking and, thus, smaller chains will be produced than in the experiments with 3.4 g of TEG. The products obtained when with less TEG, because of its fewer points of rupture,

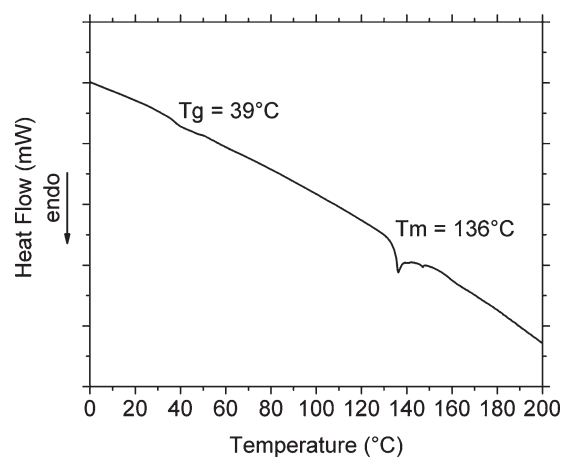


Figure 3. DSC of the PET glycolysis of Experiment 1.

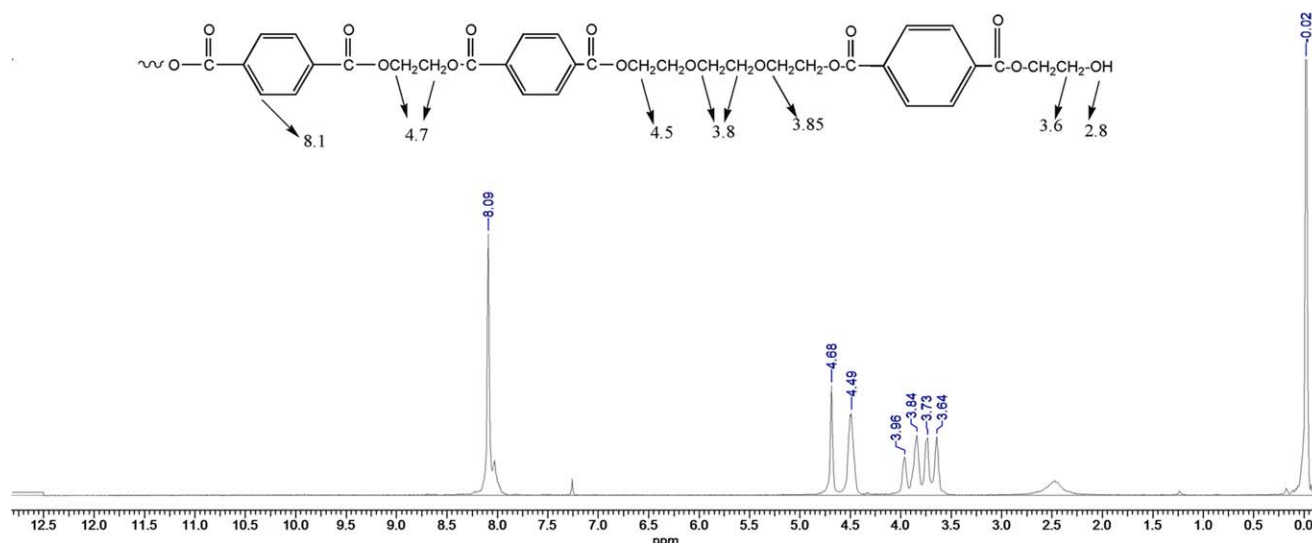


Figure 4. (a) Proposed repeating unit of the oligomer and (b) $^1\text{H-NMR}$ spectrum of the oligomer of experiment 3.

were longer chains with a greater probability of forming crystalline zones. Therefore, T_m was slightly higher.

The relationship between the degraded PET and the glycolysis time is represented in Figure 5; this experiment was realized only in the reactions with 1 h of glycolysis (experiments 1–4). The amount of degraded PET increased with the glycolysis time and approached a steady state after 40 min; during this time, the rate of degradation decreased, and almost 100% of the PET was degraded. Table V shows the distribution of the molecular weight of the experiment 3 values; the molecular weight within 30 min was very similar to that obtained after 1 h of reaction (see Table III). This agreed with the decay in the degradation rate of PET after 40 min, as pointed out in Figure 5.

The proposed mechanism for the degradation of PET with dimethyl tin distanoxane as a catalyst is shown in Scheme 1. The catalytic activity of dimeric $\text{Me}_2\text{Sn}(\text{OAc})_2$ was due to its behavior as a Lewis acid, which allowed coordination bonding with Lewis bases.¹⁷

The most likely mechanism of PET degradation started with the coordination of the hydroxyl groups of glycol with the tin atoms (step I). This kind of hypercoordination for diorganotin acetates has been reported.¹⁸ This coordination facilitated the loss of hydrogen (step II) and increased the reactivity of oxygen and the nucleophilic attack of oxygen to the carbonyl group of

PET (step III). Finally, the breaking of the Sn-O bond provided the products and recycled the catalyst (step IV).

CONCLUSIONS

The compound $(\text{CH}_3)_2\text{Sn}(\text{OCOCH}_3)_2$ accelerated the degradation of PET in the presence of TEG as a nucleophilic agent with decaline as a solvent with a reaction time of 1 h and a temperature of 175°C. These were mild conditions. Unlike the results reported so far, DSC analysis confirmed the T_m (136°C) and T_g (39°C) of the oligomers; this will be potentially useful for applications at room temperature. The molecular weight distribution obtained for the oligomers indicated that short-chain polyesters were obtained with a molecular weight of about 8000 g/mol, in which the catalyst was part of the degradation mechanism. According to the degradation rate, at 60 min, 100% of the PET was degraded. However, after 40 min of the glycolysis reaction,

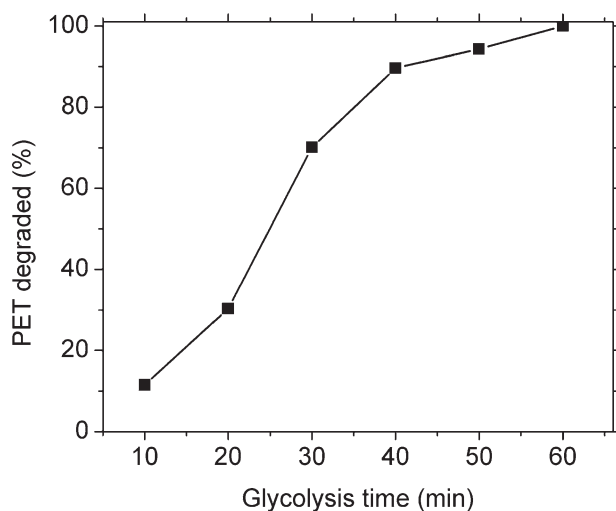
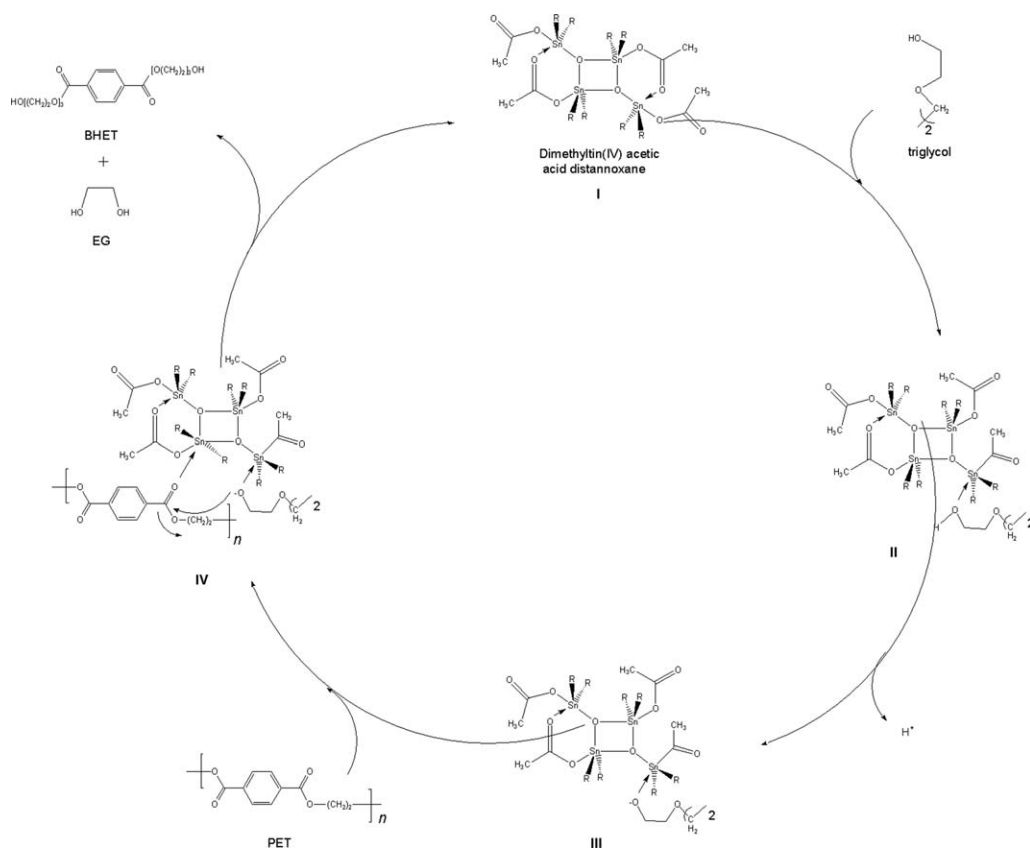


Figure 5. Relationship between the glycolysis time and amount of PET degraded in experiment 3.

Table IV. T_m and T_g Values and Amount of Glycol in the Glycolysis of PET

Experiment number	TEG (g)	Catalyst (g)	T_g (°C)	T_m (°C)
1	3.4	0.04	39	136
2	3.4	0.06	40	143
3	5.6	0.04	—	122
4	5.6	0.06	—	128



Scheme 1. Proposed mechanism for the degradation of PET with dimethyl tin distannoxane as the catalyst.

Table V. Molecular Weight Distribution with Glycolysis Time from Experiment 3

Time (min)	M_p	M_n	M_w	D
10	692	950	1067	1.123
20	4784	3087	6562	2.126
30	4505	2706	5785	2.137

Molecular weight in number (M_n), Molecular weight in weight (M_w), Molecular weight on the top of the curve (M_p), Molecular weight in viscosity (M_v), Polydispersity (D).

90% of the PET was degraded; this could be convenient because it saved energy in the process.

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