# Organocatalytic Depolymerization of Poly(ethylene terephthalate)

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ABSTRACT: We describe the organocatalytic depolymerization of poly(ethylene terephthalate) (PET), using a commercially available guanidine catalyst, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). Postconsumer PET beverage bottles were used and processed with 1.0 mol % (0.7 wt %) of TBD and excess amount of ethylene glycol (EG) at 190 °C for 3.5 hours under atmospheric pressure to give bis(2-hydroxyethyl) terephthalate (BHET) in 78% isolated yield. The catalyst efficiency was comparable to other metal acetate/alkoxide catalysts that are commonly used for depolymerization of PET. The BHET content in the glycolysis product was subject to the reagent loading. This

**INTRODUCTION** Advances in technology continue to present many environmental issues making waste management a significant challenge. Landfill space is at a premium, even if the total amount of municipal solid waste (MSW) going to landfills in US has dropped since 1990. The plastic refuse generated in US constitutes 12% of the MSW in 2008; while relatively modest as a percentage, plastic waste is the 4th major component of the MSW after paper, food, and yard trimmings.<sup>1</sup> Poly(ethylene terephthalate) (PET), a widely used commodity-grade thermoplastic contributes several billion pounds of waste to landfills every year, and the amount of PET needed is unlikely to diminish any time soon.<sup>2</sup> Recycling of petroleum-based plastics has recently attracted enormous attention to promote effective use of limited fossil resources to mitigate impacts on solid waste. According to the American Plastics Council, now only 27% of the PET bottles and jars are recycled and the PET market for packaging continues to grow due to the popularity of PET-packaged products, such as bottled water.<sup>3</sup>

The challenge for PET recycling is to achieve a closed-loop, bottle-to-bottle process, similar to the aluminum cans (48%

catalyst influenced the rate of the depolymerization as well as the effective process temperature. We also demonstrated the recycling of the catalyst and the excess EG for more than 5 cycles. Computational and experimental studies showed that both TBD and EG activate PET through hydrogen bond formation/activation to facilitate this reaction. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 1273– 1281, 2011

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recycled).<sup>1</sup> Two major conventional methods of recycling postconsumer PET exist: mechanical recycling and chemical recycling.4-7 The former is most commonly practiced and involves sorting, washing and drying postconsumer PET before melt-processing to produce a new material. The organometallic catalysts used to synthesize PET such as antimony, titanium or germanium<sup>8</sup> remain permanently in the fabricated item, leading to significant property deterioration during the secondary melt fabrication process.<sup>9</sup> As a consequence, mechanically-recycled PET generally ends up in secondary products such as fiber for clothing or carpeting, and engineering resins for reinforced automobile components.<sup>2,10</sup> Ultimately these all find their way to the landfill. The problem was, however, solved by solid state polymerization technique where the catalysts in the waste PET are applied to increase/maintain the molecular weight high enough for the fabrication.<sup>11</sup> Mechanical methods for bottle-to-bottle recycling are being established, but there still are some practical concerns especially when colored bottles are used as raw materials;<sup>12</sup> variation in the amounts and types of residual catalysts in the waste PETs create additional challenges.

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SCHEME 1 Glycolysis of poly(ethylene terephthalate) catalyzed by TBD.

Chemical recycling entails degradation of the polymer to its starting monomer, purification, and then subsequent repolymerization to yield high quality plastic.<sup>7</sup> Depolymerization processes for chemical recycling mainly include hydrolysis, methanolysis, and glycolysis<sup>13-15</sup> which are generally conducted at high temperature in the presence of catalysts such as metal (zinc, lead, cobalt, manganese) acetate, zeolite, titanium(IV) *n*-butoxide, and sodium/potassium sulfate, and under the pressure in some cases.<sup>15-20</sup> Hydrolysis and methanolysis are more common because the high crystalline monomers terephthalic acid (TA) and dimethylterephthalate (DMT) are easier to isolate than the glycolysis product bis(2hydroxyethyl) terephthalate (BHET). In addition, PET is generally prepared by a two step process: the condensation of TA or DMT with excess ethylene glycol (EG) to generate BHET followed by the self-condensation of BHET at high temperatures (270-290 °C) using mixed organometallic catalysts optimized for their reactivity and selectivity for each step of the process.<sup>5,21</sup> Current processes for the chemical recycling of PET are energy intensive, and consequently suffer from unfavorable economics relative to mechanical recycling, and are therefore not widely practiced.<sup>6,7</sup> Low monomer costs also contribute to the economic challenges for alternative technologies utilizing postconsumer PET as a monomer feedstock.<sup>22,23</sup> Moreover, the chemical approach to recycling of PET-based copolyesters<sup>24,25</sup> has advantages in terms of mechanical properties associated with the final product. It also can be readily extended to other polyesters.<sup>26,27</sup> Initiatives in the chemical recycling of PET are thus ideally focused on developing an environmentally safe, economically feasible, and industrially applicable process for wide-scale application. Chemical recycling methodologies that are energy efficient and do not involve heavy metals are highly desirable even though the catalysts are usually not contained in the purified monomers.

Organic catalysts are attractive alternatives to traditional organometallic reaction promoters. Organic phase transfer catalysts based on quaternary ammonium salts have been used for hydrolysis of PET where sodium hydroxide was used as a cocatalyst.<sup>14,28</sup> Organocatalysis has been shown to be a powerful strategy for polymer synthesis. As these catalysts typically operate by different mechanisms than metal alkoxides, they offer a diversity of mechanistic pathways that can provide new opportunities for selective polymerization and depolymerization processes.<sup>29</sup> We have developed several organic catalyst platforms for polymerization and transesterification reactions.<sup>30</sup> 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), a potent neutral base (pKa = 26 in acetoni-

trile)<sup>31</sup> well-known as a catalyst for a variety of reactions<sup>32</sup> is among the most active ring-opening polymerization (ROP) catalysts known. The ROP of lactide with 0.1% TBD in THF exhibits a turnover frequency of 80 s<sup>-1</sup> at room temperature, a rate comparable to that of the most active metal catalysts reported for ROP of lactide.<sup>33</sup> Computational studies suggest that TBD is such an effective catalyst because it activates both alcohol and monomer through hydrogen-bonds.<sup>34,35</sup> The high activity of TBD for transesterification reactions stimulated us to extend our investigation to depolymerization, rather than polymerization. Herein, we show that the guanidine TBD is an efficient catalyst for the glycolysis of PET to its monomer bis(2-hydroxyethyl)terephthalate (BHET)<sup>36,37</sup> and also demonstrate its recyclability (Scheme 1).

# **EXPERIMENTAL**

# Materials

PET beverage bottles were washed with water, dried, and shredded to around 3 mm squares prior to use. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), ethylene glycol (EG; anhydrous, 99.8%), and solvents were used as received (Sigma-Aldrich).

# Instruments

<sup>1</sup>H NMR spectra were obtained on a Bruker Avance 400 Instrument at 400 MHz. Size exclusion chromatography (SEC) was performed in THF at 30 °C using a Waters chromatograph equipped with four 5  $\mu$ m Waters columns (300 mm × 7.7 mm) connected in series with increasing pore size (10, 100, 1000, 105, 106 Å), a Waters 410 differential refractometer for refractive index (RI) detection, and calibrated with polystyrene standards (750 – (2 × 106) g/mol).

# **Typical Procedure of Glycolysis**

To a 25 mL Schlenk tube containing colorless PET flakes (0.96 g, 5.0 mmol),<sup>38</sup> previously dried at 80 °C for 1 h, was charged a mixture of EG (5.00 g, 80.6 mmol) and TBD (70 mg, 0.50 mmol) in a glove box. The tube was immersed in an oil bath heating at 190 °C to conduct the reaction with stirring. After 8 minutes the slurry turned into a clear and homogeneous liquid. The crude solid was purified by either of the following two methods.

A. Extraction: The reaction mixture was cooled to room temperature and dissolved in methylene chloride (100 mL) with slight heating to dissolve the solid. The solution was washed with 0.5 N HCl aqueous solution (100 mL) and extracted with methylene chloride (50 mL). The organic fractions were combined, stirred over MgSO<sub>4</sub>, evaporated, and dried in

vacuum to give the product bis(2-hydroxyethyl) terephthalate (BHET) as white powder (0.79 g, 62%).

B. Recrystallization: The crude solid was dissolved in DI water (200 mL) and a small amount of insoluble material was filtered (denoted as the water insoluble fraction below). The filtrate was then left in a refrigerator for 24 hours. Needle-like crystals formed were then filtered and dried in vacuum to yield BHET as white solid (1.00 g, 78%).

# **Glycolysis Using Recycled Reagent and Catalyst**

The first batch was conducted in the half scale of the procedure described earlier using PET (0.48 g, 2.5 mmol), EG (2.5 g, 40 mmol), and TBD (35 mg, 0.25 mmol). The crude product was purified by recrystallization and the filtrate was dried until most of water was evaporated, which was checked by NMR. The residue including EG and a small amount of TBD and BHET was used in the next batches where additional 0.48 g of PET flakes and supplemental fresh EG were added. No additional catalyst was charged. After the completion of the reaction, the crude product was purified and the excess EG and TBD were recovered in the same way and the reaction was repeated 9 times.

### Computation

To gain an understanding of the elementary processes during the polymer breakdown in the presence of TBD, we performed B3LYP/aug-cc-pVTZ//B3LYP/6-31+G\* density functional calculations<sup>39</sup> with a continuum dielectric using IEF-cPCM<sup>40</sup> as implemented in GAMESS-US.<sup>41</sup>

All calculations were run on IBM pSeries (pwr 4,5,6) workstation clusters. PCM parameters (solvent radius and dielectric) for the solvent in question under the experimental conditions (EG at 185 °C) do not exist. For the solvent radius we followed a recommendation by one of the authors of PCM, Bennedetta Mennucci, who suggested using the radius of a similarly sized known solvent. In doing so we discovered a correlation between the "size" of common solvent molecules and their PCM solvent radii (as implemented in GAMESS/US). Using said correlation, we estimated a PCM solvent radius for EG of 2.35Å. For the dielectric  $\varepsilon$  we used an equation of state and extrapolated  $\varepsilon(1/T)$  to T = 185 °C, giving a dielectric of 19.1.<sup>42</sup>

# **RESULTS AND DISCUSSION**

#### Glycolysis of PET Catalyzed by TBD

Glycolysis of the waste PET was carried out in a glass flask containing PET, TBD and EG at 190 °C under nitrogen atmosphere until the PET flakes disappeared. The disappearance time of PET flakes was used as a visual indicator for the end of the reaction. No change in product composition was observed when the reaction was allowed to run for longer time. The crude product was then purified by either extraction or recrystallization in water and the purified products were characterized by GPC, NMR, DSC, and GC (see Supporting Information Figs. S1 and S2 for DSC and GC charts). In addition, the water insoluble fraction obtained in the recrystallization process was also characterized by GPC and NMR.



**FIGURE 1** GPC (THF) chromatograms of (a) the crude glycolysis product, (b) the extraction product, (c) the crystallization product, and (d) the water insoluble fraction.

Following glycolysis, the crude product [Fig. 1(a)] showed two major peaks in the gel-permeation chromatogram (GPC) corresponding to the monomer BHET (42 min) and EG (46 min) as well as a small peak with a retention time of approximately 40 min. The latter peak was also observed in the extraction product [Fig. 1(b)] and corresponds to that fraction which is insoluble in water [Fig. 1(d)]. The major component of this water insoluble fraction was identified as the linear dimer of BHET [Fig. 2(b)] (rather than cyclic oligomers often generated by melt-processing of PET<sup>25,26</sup>), but this fraction likely also contains a mixture with other terephthalic esters, as PET bottles typically contain a small amount of isophthalic acid, diethylene glycol, and cyclohexane dimethanol for the improved moldability.<sup>5,21</sup> As found in the GPC chromatograms, the BHET dimer is difficult to remove by the extraction due to its limited solubility in water. In contrast, recrystallization affords pure BHET monomer that includes no impurities (the dimers, catalysts, additives, and other components (See Supporting Information Figs. S1 and S2 for comparison with a commercial sample of BHET).

# Influence of Reagent Loading on Dimer Content and Reaction Time

The ratio of ethylene glycol to PET influences both the product composition and the degradation time. The content of BHET dimer in the extraction product decreases with increasing EG loading in the reaction [Fig. 3(a)]. This is consistent with the previous reports showing the equilibrium between BHET and the dimer during glycolysis where excess EG is required for reducing the dimer formation.<sup>37,43,44</sup> However, with increasing EG loading, the degradation time





FIGURE 3 (a) BHET dimer content in the extraction product and (b) the degradation time of the glycolysis of PET as a function of the EG loading relative to PET. The reaction was conducted using 0.96 g of PET, 70 mg of TBD, and the varied amount of EG at 190 °C. The dimer content was calculated from the peak ratio of the GPC chart.



**FIGURE 4** Degradation time of glycolysis of PET as a function of the reaction temperature. The reaction was conducted using 0.96 g of PET, 70 mg of TBD, and 5.0 g of EG at the varied temperature.

increases [Fig. 3(b)] as a consequence of lower TBD concentration as the volume of the reaction media increases.

# **Catalytic Efficiency of TBD in Glycolysis**

We studied the catalytic efficiency of TBD in the glycolysis of PET as a function of the reaction time at the varied process temperature and catalyst loading. These studies were conducted using the same types of bottles; the TBD was stored in a nitrogen-filled glove box, an anhydrous grade of EG was used, because the bottle thickness, additives, and the purity of EG and TBD also influenced the reaction rate. These results are shown in Figures 4 and 5. The process temperature exponentially affected the reaction time when varied at the fixed condition using 0.1 equiv. of TBD and 16 equiv. of EG (relative to monomer unit, Fig. 4). Under these conditions at 190  $^\circ$ C, depolymerization was complete within 10 minutes, highlighting the efficiency of the TBD catalyst. At 140°C, depolymerization required 16 hours, implicating that glycolysis of PET with TBD could be carried out at these reduced process temperatures.

The catalyst loading also significantly influenced the rate of the glycolysis when the process temperature and the EG loading were fixed at 190 °C and 16 equiv, respectively (Fig. 5). At TBD loading of 0.1 equiv. (10 mol % relative to PET), glycolysis was complete within 8 minutes; with as little as 0.005 equiv. of TBD (0.5 mol %), glycolysis was complete within 325 minutes. These results demonstrate that TBD is as efficient as the other metal catalysts used for glycolysis of PET, where catalyst loadings of less than 1 mol % are typical.<sup>16–18,44,45</sup> As postconsumer PET typically contains catalyst residues from its synthesis, we carried out the degradation of PET in the absence of TBD as a control. In the absence of TBD, the PET flakes disappeared after 40 hours at 190 °C.

# **Recycle of the Reagent and Catalyst**

To assess the feasibility of catalyst recycling, we investigated the recovery and reuse of the TBD catalyst following recrystallization of BHET from water. A sample of PET flake (0.48 g) was treated with 2.5 g of EG (40 mmol) and 35 mg of TBD (0.25 mmol) and heated to 190 °C. Under these conditions, glycolysis of PET was complete within 10 minutes (Supporting Information Table S1). After isolation of the recrystallized BHET the aqueous filtrate was evaporated under vacuum to afford an oily residue that contained EG, TBD, and BHET (Supporting Information Fig. S3); no other products could be identified by <sup>1</sup>H NMR. To this residue, fresh EG and PET flake were added (to maintain a 16:1 ratio of EG:terephthalate) and the mixture was heated again to 190 °C. For this run, glycolysis required 80 min; the depolymerization time for subsequent runs (10 total) gradually increased, likely as a consequence of decreasing catalyst concentrations upon multiple recycling steps (Supporting Information Table S1). It is likely that some of the TBD was deactivated during purification and recovery steps (possibly formed the adduct with carbon dioxide upon exposure to air). This may explain significant increase of the degradation time at the second run. Nevertheless, the reaction was still completed in 150 min even after 9 catalyst recycling cycles. In addition, pure BHET was produced with high yields (>65%) at every batch. This result demonstrates that the reagent and catalyst are repeatedly recyclable. For these experiments, a relatively large amount of EG (16 equiv., 500 wt % relative to PET) was necessary to reduce the dimer content in the product below 10%.37 The use of the 16 equiv. of EG facilitates the dissolution of BHET in water at room temperature and contributes to easy purification. Although less than 6 equiv. of EG is typically used for the glycolysis of PET, the procedure requires elevated



FIGURE 5 Degradation time of glycolysis of PET as a function of catalyst loading relative to PET. The reaction was conducted using 0.96 g of PET and 5.0 g of EG at 190  $^{\circ}$ C.



SCHEME 2 Two possible pathways of TBD-catalyzed transesterification: (a) acyl transfer pathway and (b) hydrogen bonding pathway.

temperatures to dissolve PET and the products obtained under these conditions contain the dimer and oligomers of BHET.<sup>23,45</sup> There are a few techniques to polymerize the mixture of BHET oligomers obtained by glycolysis.<sup>46</sup> Therefore, breaking down PET into the monomer unit may not be required for some chemical recycling processes.

# **Color Bottle Recycling**

Postconsumer PET is often colored. For the chemical recycling of colored bottles, activated carbon can be used to remove residual pigments and dyes.<sup>47</sup> We demonstrated the depolymerization of green, blue, and white PET using the typical conditions (Supporting Information Table S2). The depolymerization was slower with the colored bottles. As many pigments contain somewhat acidic components,<sup>47</sup> these components may have inhibited the TBD catalyst. The crude products were purified by recrystallization that gave as white BHET crystals, comparable to those obtained from the clear bottles (Supporting Information Fig. S4). In our procedure, most of pigments were removed at the filtration step with the water insoluble fraction.

#### Investigation of the Mechanism of the Reaction

To gain an understanding of the elementary processes during the polymer breakdown in the presence of TBD, we conducted computational investigations of possible reaction pathways. This study was guided by prior experience with TBD as a catalyst in the ROP of L-lactide<sup>34,35</sup> where TBD interacts with both an alcohol initiator and the lactide monomer through hydrogen bonding. Recently Becker et al., reported that amino-oxazolines and amino-thiazoles are also effective in the ROP of lactide and have dual H-bonding interactions with the initiator and monomer as well as TBD.<sup>48</sup> Our primary interest was to determine whether the reaction would follow a purely hydrogen-bonding pathway where TBD acts as a bifunctional catalyst activating both the oxygen of the carbonyl group of the ester and as well as the hydrogen of the alcohol through hydrogen bonding interactions [Scheme 2(b)], or proceeds via a nucleophilic "acyl transfer" pathway in which, at one stage of the reaction, the TBD catalyst is covalently bound to the ester [Scheme 2(a)].

To make this computational study more tractable, we investigated the methanolysis of dimethylterephthalate (DMT) using TBD as a catalyst [Fig. 6(a)] modeled in the presence of an implicit solvent representing the experimental conditions (EG at 185 °C). The calculated energy profiles [Fig. 6(b,c)] suggest that the H-bonding pathway has a lower barrier than the nucleophilic acyl transfer pathway. The highest energy barrier in the reaction profile of the acyl transfer pathway was 24.8 kcal/mol [Fig. 6(b)] while the corresponding barrier for the competing H-bonding pathway was 15.9 kcal/mol, approximately 9 kcal/mol lower than the acyltransfer pathway [Fig. 6(c)]. A detailed analysis of the structures of the intermediates and transition states revealed that C-C-C-O dihedral angles of the structures identified along the H-bonding pathway trajectory [IRC, TS, INT, Fig. 6(c)] remained close to zero. As DMT is an aromatic ester, it would be expected to have a preference to retain the planar conformation of the ester group with respect to the aromatic ring. This is consistent with calculations that predict a cistrans isomerization barrier of 4.5 kcal/mol for DMT (Supporting Information Fig. S5). For the acyl transfer pathway [Fig. 6(b)], every species along the reaction profile has an approximately tetrahedral ester carbon, which contributes to the higher barrier for this pathway.

NMR experiments were carried out in an effort to provide support for calculated intermediates. The NMR studies provided supporting evidence for the formation of H-bond



FIGURE 6 TBD-catalyzed methanolysis of dimethylterephthalate (DMT) as a model reaction for PET breakdown. (a) Reaction scheme, (b) reaction profile of the acyl transfer pathway, and (c) reaction profile of the hydrogen bonding pathway. Note that due to the nature of the model reaction (methanolysis of DMT) the pathways are symmetric and products (not shown) are equivalent to reactants.

adducts of TBD with methanol (Supporting Information Fig. S9) whereas the interaction of TBD with DMT (Supporting Information Fig. S10) was not as strong as that with methanol. However, the interaction between TBD and DMT was larger than that expected from the fact that TBD can be regarded as a weak H-bond donor and just strong enough to see a weakly bound complex with DMT in the calculations

(2.22 Å H-bond length and -0.6 kcal/mol binding affinity without entropic considerations). Actually, the importance of TBD as an H-bond donor does not lie in its ability to activate reactants other than nucleophiles but rather in its ability to stabilize the reactive species along the pathway (TS and INT). These results provide strong support for an H-bonding mechanism for transesterification of aromatic esters.

**TABLE 1** Lowdin Charges and ESP Charges at the Oxygen of the Ester C=O Group of DMT for Various Reactive Species Along the Acyl and H-Bonding Pathways [Labeling of Species According to Figs. 6(b,c)]

Acyl pathway	q(O): INT1:-0.64 <sup>a</sup> ,-0.78 <sup>b</sup> ; INT2:-0.60 <sup>a</sup> ,-0.78 <sup>b</sup> TS2:-0.46 <sup>a</sup> ,-0.63 <sup>b</sup> ; INT3:-0.42 <sup>a</sup> ,-0.63 <sup>b</sup>
H-bonding pathway	q(O): TS:-0.53 <sup>a</sup> ,-0.69 <sup>b</sup> ; INT:-0.66 <sup>a</sup> ,-0.76 <sup>b</sup>
DMT	q(O): -0.40 <sup>a</sup> ,-0.61 <sup>b</sup>

<sup>a</sup> Lowdin charges.

<sup>b</sup> ESP charges fit to reproduce the total molecular charge and dipole.

Furthermore, calculations by ourselves and Simon and Goodman<sup>35</sup> on the corresponding reaction for a nonaromatic ester, methylacetate, illustrated that the difference in barrier heights between the two mechanisms: H-bonding and acylation, was not as large as for the aromatic ester (because of the absence of any stabilizing conjugation for the aliphatic ester), but nevertheless the calculations still substantially favored the H-bonding pathway [see Fig. 6(b,c) and Supporting Information Fig. S7(a,b)].

The calculations reveal that there is significant accumulation of negative charge at the oxygen of the ester carbonyl group of DMT at various stages along both pathways (Table 1). Stabilization of this charge results from the H-bond donating ability of TBD and supports the importance of TBD as a bifunctional catalyst. However, any species in the reaction vessel that is an H-bond donor could, in principle, also be beneficial. One obvious choice would be to consider excess alcohol, which is certainly present under the experimental conditions for the breakdown of PET (occurring at 185 °C with EG as solvent and reactant). We found that excess alcohol can actively stabilize all reactive species along the two reaction pathways especially the transition states (Supporting Information Fig. S8). The excess of EG lowers the reaction barrier of the acyl transfer pathway by 3.4 kcal/mol (to 21.4 kcal/mol) and that of the H-bonding pathway by 4.4 kcal/mol (to 11.5 kcal/mol). These calculations suggest that EG is ideally suited as a reaction medium as it can function both as a reagent and a catalyst, as implicated earlier in kinetic studies.<sup>43</sup> This interaction of the ester carbonyl group with the hydroxyl group of alcohols was supported by additional NMR experiments (Supporting Information Fig. S11).

# CONCLUSIONS

In summary, the depolymerization of PET by the organic guanidine catalyst, TBD, can be applied in the ethylene glycol to regenerate the monomer BHET in good yield. This catalysis occurs in a few hours with as a little loading as other conventional catalysts. The reagent loaded in excess and the catalyst can be recycled for the other batches repeatedly. This organocatalytic procedure, based on effective hydrogen bonding, is efficient with regards to energy consumption, atom economy, and accessibility and provides an attractive option for chemical recycling comparable to metal-based approaches.

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