Unexpected Efficiency of Cyclic Amidine Catalysts in Depolymerizing Poly(ethylene terephthalate)

Kazuki Fukushima,^{1,2} Daniel J. Coady,¹ Gavin O. Jones,¹ Hamid A. Almegren,³ Abdullah M. Alabdulrahman,³ Fares D. Alsewailem,³ Hans W. Horn,¹ Julia E. Rice,¹ James L. Hedrick¹

¹IBM Almaden Research Center, San Jose, California 95120

²Department of Polymer Science and Engineering, Yamagata University, Yonezawa, Yamagata 992-8510, Japan ³Petrochemicals Research Institute, King Abdul Aziz City for Science and Technology, Riyadh 11442, Saudi Arabia Correspondence to: J. L. Hedrick (E-mail: hedrick@almaden.ibm.com)

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ABSTRACT: This article describes studies on the catalytic activity of several nitrogen-based organic catalysts for the depolymerization of poly(ethylene terephthalate) (PET), in which a few cyclic amidines work more effectively than a potent, bifunctional guanidine-based catalyst 1,5,7-triazabicyclo-[4,4,0]dec-5-ene (TBD) in the presence of short chain diols that play a role in activation of carbonyl groups through hydrogen bonding. Further studies prove that the catalytic efficiency at the above specific conditions depends only on the extent of activa-

INTRODUCTION Recycling of plastic materials has an important role in the 21st Century in reducing environmental pollution and saving petroleum resources. Poly(ethylene terephthalate) (PET) is a commodity thermoplastic widely used in clothing fibers, fabrics, packaging films, food containers, and beverage bottles. The rate of collection of PET bottles in the United States was 27% as of 2008.¹ Several practical issues need to be solved before the collection rate can be improved, such as development of the nationwide infrastructure for bottle collection and establishment of facilities capable of accepting and reprocessing the recycled PET. There are two conventional methods of processing postconsumer PET (particularly bottle-grade PET): mechanical recycling and chemical recycling.

Bottle-to-bottle recycling of PET is currently the most commonly practiced mechanical recycling process. Bottle-to-bottle recycling entails sorting, washing, melt-processing, and remolding the postconsumer PET. This process benefits from several innovations such as solid-state polymerization,² the inclusion of additives such as chain extenders,³ the formation of composites with virgin PET,⁴ and "super cleaning."⁵ In contrast, chemical recycling may yield high-quality terephthalate starting materials via the chemical breakdown of tion of a hydroxyl group rather than simply the pK_a of the bases. For glycolysis with excess short-chain alkanediols, 1,8-diazabicyclo[5.4.0]undec-7-ene is the best catalyst. In contrast, TBD shows outstanding catalytic activity in depolymerizations of PET with mono-alcohols and longer-chain diols. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 1606–1611

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PET, but has the disadvantage of high energy consumption and overall higher processing cost compared to mechanical recycling. For instance, chemical recycling is leveraged as a backup system of mechanical recycling in which materials that are repeatedly recycled are chemically processed. Moreover, many groups have utilized waste PET as a feedstock for the formation of chemically depolymerized materials, such as glycolyzed products, to be used as building blocks for a variety of high-value materials.⁶

Common methods used to depolymerize PET include hydrolysis,⁷ methanolysis,⁸ and glycolysis,⁹ and most of them are conducted upon heating, under high pressure,^{7,8} with a catalyst,^{7–9} and/or use of microwave.¹⁰ Spurred by a number of recent reports, organic catalysts are now being recognized as a powerful tool for chemical recycling and depolymerization of polymers.¹¹ We recently reported¹² that a potent neutral nitrogen base, 1,5,7-triazabicyclo-[4,4,0]-dec-5-ene (TBD) showed high catalytic activity in depolymerization of PET using ethylene glycol (EG) (Scheme 1). However, a large volume of EG was required (typically, 16 mol eq. relative to an ethylene terephthalate unit) to obtain a product comprising more than 90% of a monomer *bis*(2-hydroxyethyl)terephthalate (BHET), and, in addition, the reaction proceeds only

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SCHEME 1 Glycolysis of PET.

upon heating above 150 °C; we hoped that we could improve on these experimental conditions. BHET can be used not only as a monomer for the formation of PET, but also as a building block for other functional materials.⁶ Although BHET oligomers produced from the depolymerization of PET can be used as a feedstock for the repolymerization of PET, they are undesired if they are to be used as building blocks for functional materials.

In this light, we have undertaken a study on the depolymerization of PET with different alcohols catalyzed by several nitrogen-based organocatalysts to determine the optimal catalysts for specific conditions. We have quantitatively evaluated the catalytic activity of these organocatalysts by determining the extent of BHET formation throughout the reaction. It is our hope that analogous processes involving the formation of PET by the aminolysis, alcoholysis or thiolysis of PET would benefit from these studies.

EXPERIMENTAL

Materials

Postconsumer water bottles were used as PET sources. The bottles were washed with water, dried in air at room temperature, and shredded by hand to a size of about $3-5 \text{ mm}^2$. The flakes were dried again in vacuum at 80 °C for at least 12 h prior to the depolymerization reaction. The glass transition temperature of the postconsumer PET was 77 °C, the melting point was 252 °C, and the 5% weight loss temperature was 376 °C. All other chemicals including catalysts and solvents were purchased from Sigma-Aldrich and used as received.

Measurements

¹H NMR spectra were obtained on a Bruker Avance 400 Instrument at 400 MHz. Gel permeation chromatography (GPC) was performed in tetrahydrofuran at 30 °C using a Waters chromatograph equipped with four 5 μ m Waters columns (300 mm \times 7.7 mm) connected in series with increasing pore size (10, 100, 1000, 105, and 106 Å), a Waters 410 differential refractometer for refractive index detection, and

calibrated with polystyrene standards (750 - (2 \times 10 $^{6}) g/$ mol).

General Glycolysis of PET Using an Organic Catalyst

To a 25 mL Schlenk tube containing postconsumer PET flakes (0.96 g, 5.0 mmol) was charged a mixture of EG (4.96 g, 80 mmol) and 0.50 mmol of an organic catalyst. The tube was immersed in an oil bath and heated with stirring at 190 °C. The completion of the reaction was determined by visual inspection and the time point was defined as "degradation time." When the slurry turned into a clear and homogeneous liquid, the reaction was considered to be finished. Aliquots of the crude product were taken for ¹H NMR and GPC analysis to evaluate the contents. The crude depolymerization products obtained in the above reaction consist of BHET, PET oligomers comprising mainly dimer and trimer, and excess EG. Figure 1 is a typical gel permeation chromatogram of the crude glycolysis products formed by the depolymerization reaction. Peak A corresponds to PET oligomers, peak *B* corresponds to BHET, and peak *C* corresponds to EG. Based on the area of peak A (PET oligomers) and the area of peak B (BHET), oligomer composition in the product was determined as A/(A + B).

General Depolymerization of PET Using an Organic Catalyst in the Presence of Other Alcohols

To a 25-mL Schlenk tube containing PET flakes (0.48 g, 2.5 mmol) was charged a mixture of an alcohol (40 mmol or 20 mmol) and an organic catalyst (0.25 mmol). The tube was immersed in an oil bath and heated with stirring at 190 °C. When the slurry turned into a clear and homogeneous liquid, the reaction was finished. Aliquots of the crude product were taken for ¹H NMR and GPC analysis to evaluate the content.

RESULTS AND DISCUSSION

First, we tested several commercially available nitrogen bases, including 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),



FIGURE 1 A typical gel permeation chromatography (GPC) chart of the crude glycolysis product formed in the glycolysis reaction of PET in excess EG. Peak *A* corresponds to oligomer fractions, peak *B* corresponds to BHET, and peak *C* corresponds to EG.



FIGURE 2 Various nitrogen bases screened for depolymerization of PET.

1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 4-(N,N-dimethylamino)pyridine (DMAP), 1,4-diazabicyclo[2.2.2]octane (DABCO), N-methylimidazole (NMI), and N,N-dimethylaniline (DMA) for depolymerization of PET by EG (Fig. 2). As previously reported,^{12,13} an equilibrium exists between BHET and its oligomers in the glycolysis of PET, and consequently we used 16 eq. of EG relative to PET to suppress the formation of unwanted oligomers. The reaction was carried out using PET flakes obtained from postconsumer beverage bottles (0.96 g, 5.00 mmol), EG (2.48 g, 80 mmol), and 10 mol % of a catalyst relative to PET. The catalytic activity of these nitrogen bases for glycolysis was evaluated by the completion time and the amount of oligomer generated in the crude reaction mixture which typically comprises BHET, BHET oligomers (primarily the dimer), and excess/unreacted EG (Fig. 1). As we found in the studies on the catalytic activities for ringopening polymerization (ROP) of lactide,¹⁴ the catalytic activity of all nitrogen bases we tested in this study is correlated to their basicities (pK_a) with regard to the completion time or to the oligomer composition, except for TBD (Table 1). By comparison, a more basic organic catalyst phosphazene base P2-t-Bu finished the glycolysis slightly faster than TBD, but slower than DBU (Supporting Information Table S1), presumably owing to the steric hindrance around the active center.

The reaction finished rapidly in the presence of a few strong bases (TBD, DBU, and DBN). As the reaction conditions (190 $^\circ\text{C}$, 10 mol % catalyst) did not allow us to determine the relative reactivities of these bases, we conducted further studies to understand and differentiate between the reactivities of TBD and DBU at a range of temperatures. The reaction involving DBU was complete in a reasonable time (\sim 3 h) even at 130 °C; in contrast, the reaction involving TBD was complete only after 6 hs when heated at 160 °C [Fig. 3(A)]. Thus, DBU exhibits greater catalytic activity at lower temperatures than TBD in glycolysis of PET. The completion time was also affected by the catalyst concentration: DBU is a more active catalyst at lower concentrations than TBD; for example, at 190 °C with 0.5% loading, PET degrades in 220 min in the presence of DBU, and in 325 min in the presence of TBD (Supporting Information Fig. S1). Interestingly, the higher catalytic activity of DBU reduces the amount of oligomers generated in the products. However, with TBD, 16 eq. of EG was required to reduce the oligomer generation below 10%. DBU enabled the use of less than 16 eq. of EG

to obtain the high-quality product (6.8% oligomer composition at EG/PET = 8; Fig. 3(B)), which can be important in terms of reducing the amount of reagent required in the reaction.

We then investigated the depolymerization of PET using a variety of alcohols (Table 2) in the presence of various catalytic bases. 1,3-Propanediol and 1,6-hexanediol were used as EG analogues, whereas benzyl alcohol and 1-octanol were chosen as high-boiling point mono-alcohols which are analogous to EG. Our results indicate that the alcoholysis of PET with DBU as catalyst is fastest with excess EG but slows down for longer-chain diols, and longer-chain or bulky mono-alcohols. In contrast, alcoholysis in the presence of the TBD catalyst shows higher efficiency with 1,6-hexanediol and 1-octanol than any other catalyst including DBU. Even the potent phosphazene base, P2-t-Bu, was not able to depolymerize PET as quickly as TBD.

Overall, the amidine-based organocatalysts DBU and DBN were unexpectedly found to be more active catalysts for the glycolysis of postconsumer PET using short-chain diols compared to the guanidine-based TBD—despite being weaker bases and lacking the bifunctionality of TBD. In contrast, TBD catalytically outperforms every other base studied in depolymerizations of PET with mono-alcohols and longer-chain diols.

We rationalize these experimental findings by considering how the ester and alcohol are activated by these bases during glycolysis. TBD is a bifunctional catalyst that can activate both an ester and alcohol through hydrogen bonding.¹⁶ However, as we have previously shown through computational studies,¹² excess EG can act as a cocatalyst during the glycolysis of PET, acting in concert with TBD to activate the ester carbonyl group via hydrogen bonding.¹¹ This combined activation in the presence of excess short-chain diols can be more effective than activation by the bifunctional TBD

TABLE 1 Glycolysis of PET Using Different Nitrogen Bases^a

Catalyst	Feed ^b (mol %)	p <i>K</i> _a (Acetonitrile) ^c	p <i>K</i> a (Water) ¹⁵	Deg. Time ^c (min)	Oligomer ^d (wt %)
TBD	10	26.03	NA	8	5.1
DBU	10	24.34	11.9	6.5	1.1
DBN	10	NA	11.0	7	1.5
DMAP	10	17.95	9.7	100	6.4
DABCO	10	NA	8.2	120	6.9
NMI	10	NA	7.4	300	7.4
DMA	10	11.43	5.07	2,755	7.6
No catalyst ^e	0	NA	NA	2,400	9.4

 $^{\rm a}$ Reaction was conducted using PET (0.96 g) and EG (4.98 g; 16 eq.) at 190 $^{\circ}\text{C}.$

^b Amount of catalysts added relative to PET.

^c Degradation time.

 $^{\rm d}$ Oligomer/(oligomer + BHET) \times 100: determined by GPC.

 $^{\rm e}$ Reaction was conducted using PET (0.48 g) and EG (2.48 g) at 190 $^\circ \text{C}.$



FIGURE 3 (A) Degradation time as a function of the process temperature for glycolysis of PET (0.96 g) with 16 eq. (in molar base; 4.96 g) of EG in the presence of 10 mol % catalyst. (B) Oligomer composition in the crude product as a function of EG loading ([EG]/[PET]) for glycolysis of PET (0.96 g) conducted at 190 °C with 10 mol % of a catalyst. The data points for TBD were extracted from the previous study, see Ref. 12.

catalyst alone (Fig. 4). When longer chain diols are used to degrade PET, the binding affinity of the diol cocatalysts with the ester decreases because of conformational and steric effects. As a consequence, bifunctional activation by TBD becomes more important. In contrast, as DBU is a monofunctional catalyst, it cannot compensate for the reduced interaction of the diol cocatalyst with the ester, and therefore combined activation by the DBU/long-chain diol cocatalyst system decreases.

In summary, in the absence of short-chain diols, the optimal catalytic activity in the depolymerization of PET depends on the basicity and whether the catalyst can bind the alcohol alone or binds both the ester and the alcohol. These scenarios are addressed in an in-depth computational study¹⁷ of glycolysis reactions of aromatic esters in the presence of TBD and DBU as a model for the depolymerization of PET.

TABLE 2 Depolymerization of PET Using Different Alcohol

 Reagents^a

	Feed		Feed	Rxn. Time	Oligomer ^b
Reagent	(equiv.)	Catalyst	(mol %)	(min)	(wt %)
1,3-Propanediol	16	DBU	10	15	6.3
1,3-Propanediol	16	TBD	10	20	7.7
1,6-Hexanediol	16	DBU	10	90	8.4
1,6-Hexanediol	16	TBD	10	26	7.9
Benzyl alcohol	16	DBU	10	600	NA
1-Octanol	16	DBU	10	80	NA
1-Octanol	8	DBU	5	65	NA
1-Octanol	8	TBD	5	4.5	NA
1-Octanol	8	DMAP	5	1600	NA
1-Octanol	8	P2-t-Bu	5	11	NA

^a Reactions were conducted at 190 °C using PET (0.48 g).

^b Oligomer/(oligomer + BHET) \times 100: determined by GPC.



Finally, we investigated salts formed from DBU as potential catalysts in the depolymerization of PET (Table 3). We previously reported that a salt formed from the 1:1 mixture of DBU with benzoic acid (BA) catalyzes the ROP of lactide and produces narrowly dispersed polymers with predictable molecular weight.¹⁸ The acid-base complexes based on DBU have been used in (aza)-Michael addition,19 epoxy curing,20 and urethane formation.²¹ These catalysts possess mild and controllable reactivity and stability at ambient conditions that can be exploited in the depolymerization of PET. Our computational study revealed that the adducts of DBU with weak acids such as fluoroalcohols and phenols behave as hydrogen-bonded complexes with free DBU acting as a catalyst in the active state at high temperatures, whereas adducts formed from a stronger acid such as BA or p-toluenesulfonic acid (pTSA) are more likely to exist as an ion pair of a conjugate acid and a conjugate base. The conjugate base serves as the catalyst (BA⁻ in Supporting Information Fig. S4, left), whereas the conjugate acid serves as the cocatalyst (DBUH⁺ in Supporting Information Fig. S4, left). This was supported by experimental NMR studies (Fig. 5), showing



Faster with longer-chain diol; bifunctionality becomes more important as diol becomes less able to form bidentate complex with ester. Faster with short-chain diols but slows down longer-chain diols as diol becomes less able to activate ester by forming bidentate complex.

FIGURE 4 Hydrogen bonding activation of alcohols and PET by TBD and DBU in the presence of excess alcohol as a cocatalyst.

TABLE 3	Glycolysis	of PET	With	EG	Using	DBU-Based	Salt
Catalysts	а						

Catalyst	DBU:Acid (Molar Batio)	p <i>K</i> _a of Acid (Water)	Deg. Time ^b (min)	Oligomer ^c
outaryst	nano,	(water)	(,	(*** /0)
DBU-Phenol ^d	1:1	9.95	9	3.3
DBU-Phenol ^e	1:8	9.95	11	3.5
DBU-HFA ^{e,f}	1:0.5	NA	7	4.7
DBU-BA ^d	1:1	4.2	40	7.2
DBU-BA ^e	1:2	4.2	150	7.0
DBU-BA ^e	1:8	4.2	324	8.2
DBU- <i>p</i> TSA ^{c,g}	1:1	-2.4	1120	8.1

 $^{\rm a}$ Reaction was conducted at 190 $^\circ C$ using PET (0.48 g), EG (2.48 g), and catalyst (10 mol %).

^b Degradation time.

^c Oligomer/(oligomer + BHET) \times 100: determined by GPC.

^d Preformed.

^e Formed in situ.

^f $\alpha_{,\alpha}, \alpha', \alpha'$ -Tetrakis(trifluoromethyl)-1,3-benzene dimethanol.

^g Reaction was conducted with PET (0.96 g), EG (4.98 g).

that the equimolar mixture of DBU, BA, and EG [Fig. 5(D)] shows one broad signal for exchangeable protons, indicating that in a medium with a similar dielectric constant to EG at a high temperature (acetone; $\alpha = 20.7$ at 25 °C) EG forms a conjugate base (BA⁻) through hydrogen bonding with DBU.

pTSA, which is the strongest acid, forms the weakest conjugate base, and consequently degrades PET slowest as it is the least active catalyst. Little difference was found between the activity of complexes generated *in situ* and preformed salt complexes (data not shown). As we found for the ROP of lactide, the catalytic activity appears to be dependent on the pK_a of the acid component and the molar ratio of the acid to DBU (Table 3). The DBU-BA (1:1) salt does not lose its activity when exposed to air, unlike DBU on its own (Supporting Information Table S2).

CONCLUSIONS

Several nitrogen-based organic catalysts were screened for the depolymerization of PET. In general, the catalytic activity was found to correlate with the basicity; however, DBU showed an exceptional activity—higher than the stronger bases TBD and P2-t-Bu—for glycolysis with EG or 1,3-propanediol. This lends support to the computational prediction that short-chain diols such as EG and 1,3-propanediol serve as cocatalysts which activate ester carbonyl groups (via hydrogen bonding), thereby rendering the bifunctionality of TBD to be less important. In contrast, TBD exhibited the highest activity in other alcoholysis reactions, indicating that bifunctional activation by TBD through hydrogen bonding is more significant in the absence of activation by cocatalysts. A DBU–BA in a molar ratio of 1:1, whereas being a less effective catalyst, has the advantage over DBU alone that it does



FIGURE 5 400 MHz ¹H NMR spectra of (A) EG, (B) DBU, (C) DBU+EG (1 : 1), (D) DBU-BA+EG (1 : 1), (E) DBU-BA, and (F) BA in acetone- d_6 (0.1 M).

not "age" when exposed to air. These fundamental investigations of organic catalysts will be beneficial to progress in chemical recycling of PET waste.

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