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Wang, L., Toland, J., Nelson, G., & Holbrey, J. (2020). Glycolysis of PET using 1,3-dimethylimidazolium-2-carboxylate as an organocatalyst. *ACS Sustainable Chemistry & Engineering*, *8*(35), 13362-13368. https://doi.org/10.1021/acssuschemeng.0c04108

Published in:
ACS Sustainable Chemistry & Engineering

Document Version:
Peer reviewed version

Glycolysis of PET using 1,3-dimethylimidazolium-2-carboxylate as an organocatalyst

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Abstract

The use of 1,3-dimethylimidazolium-2-carboxylate as an organocatalyst for the glycolysis of waste PET, poly(ethylene terephthalate), is reported for the first time. Post-consumer PET was completely depolymerised in less than 1 h at 180 °C with up to 60% of *bis*(2-hydroxyethyl terephthalate) (BHET) was recovered by precipitation after cooling of the reaction mixture. Under comparable conditions the basic ionic liquid, 1,3-dimethylimidazolium acetate, was a significantly less effective catalyst suggesting that catalysis occurs through formation of a nucleophilic N-heterocyclic carbene.

Keywords: Glycolysis of PET, carbene, ionic liquids

Introduction

The demand for poly(ethylene terephthalate) (PET) PET continues to grow, 33.3 million tons of PET resin were produced in 2017. The excellent tensile strength, chemical resistance, processability, thermal stability, and good barrier properties towards moisture and oxygen[4] make PET a valuable polymer for food packaging and containment and it is widely used for soft drinks and water bottles, as a general food packaging material including 'direct to oven' trays for pre-cooked meals, and as a synthetic fibre (polyester) in clothing, furnishings, carpets, and fillings.[1–3] However, stability and resistance atmospheric and biological degradation leads to persistence in the environment, although recently enzymes that can degrade PET have been identified.[5]

Chemical recycling involves depolymerisation to yield monomer or oligomeric fragments that can subsequently be reused as high purity starting materials to yield new polymer without compromising the economics or performance of products.[6,7] Hydrolysis, glycolysis or methanolysis to recover terephthalic acid or esters[8] are the most common strategies employed in chemical recycling of PET. Glycolysis (Figure 1) to *bis*(2-hydroxyethyl terephthalate) (BHET) is currently the favoured approach as BHET can by directly re-integrated into the polymerisation process, and does not generate the salt and neutralisation wastes that characterise the production of purified terephthalic acid (PTA) by hydrolysis.[9]

PET glycolysis is slow in the absence of a catalyst,[11] and a range of metal salts, most commonly zinc acetate[10,12] and more recently basic sodium salts,[13] and organocatalysts[14] such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)[15] have been reported as catalysts. Recent studies have focused on the use of ionic liquids, either including metal-salts as components[16–21] or metal-free organocatalysts,[22–27] citing degradation of PET under relatively moderate reaction conditions, simple product isolation, and use of 'green' solvents as drivers. The most interesting systems make use of 1,3-dialkylimidazolium salts with basic anions[22,26] that can avoid potential contamination of product by residual metal-containing species and draw from previous use of 1-butyl-3-methylimidazolium acetate ([C_4mim][OAc]) as a catalyst for the methanolysis and hydrolysis of polycarbonate and poly(lactic acid).[28–31] Al-Sabagh et al.[26] reported complete PET degradation

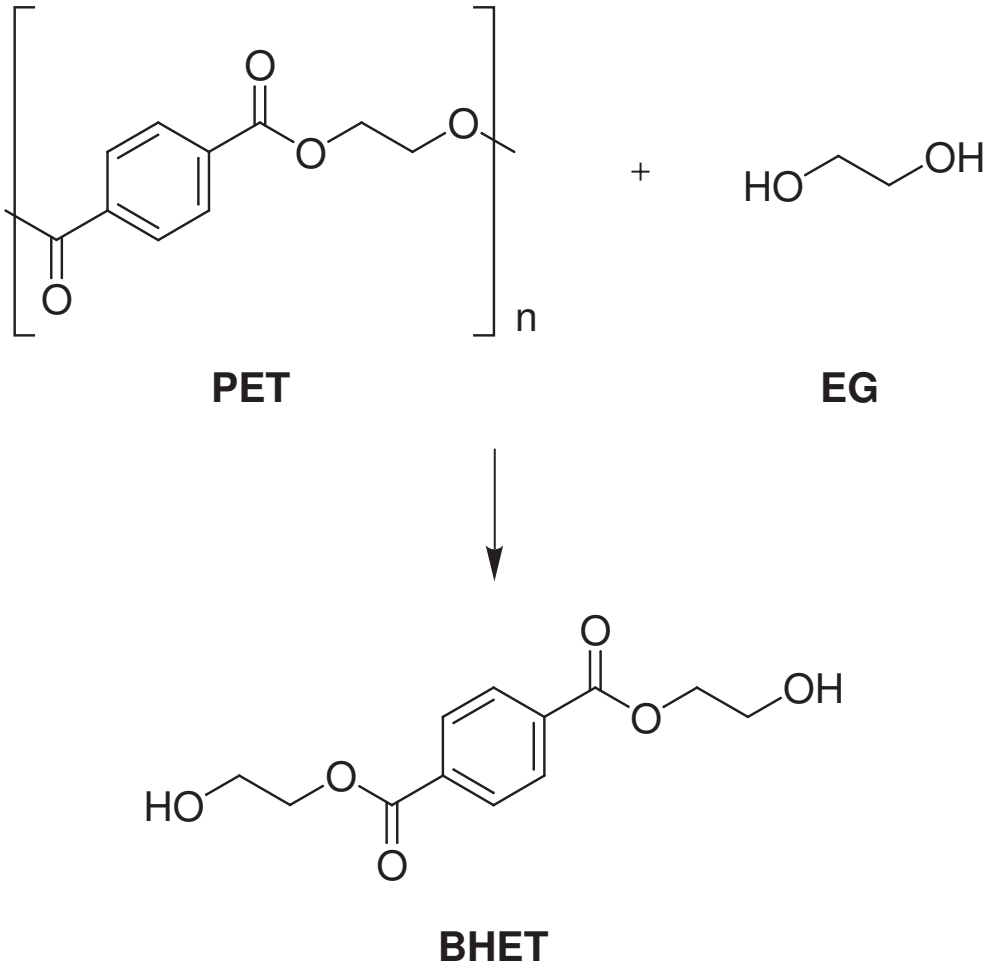

Figure 1: Schematic of the glycolysis of poly(ethylene terephthalate) (**PET**) with ethylene glycol (**EG**) to form *bis*(2-hydroxyethyl terephthalate) (**BHET**); Typical conditions are 180-250 °C, 0.5–8 h, $Zn(OAc)_2$ catalyst.[10]

(100%) using [C_4mim][OAc] as a catalyst, with a 58.2% yield of BHET under optimised conditions (1:3:20 wt ratio [C_4mim][OAc]:PET:EG, 3 h, 190 °C).

The use of [C_4mim][OAc] as a catalyst[26] is interesting in light of the well documented ability of imidazolium cations to generate N-heterocyclic imidazol-2-ylidene carbenes (NHCs)[32] by deprotonation (**1** to **2** in Fig. 2) either by the addition of stong bases, or spontaneously in ionic liquids with basic anions such as acetate,[33–35] and can lead to NHC-like chemistry in ionic liquids.[36–39]

NHCs[41] have many uses as ligands[42] and as highly basic organocatalysts for reactions including transesterification and ring-opening polymerisation of cyclic esters avoiding the use of transition metal initiators.[43–47] Glycolysis of PET using NHC catalysts has also been described as

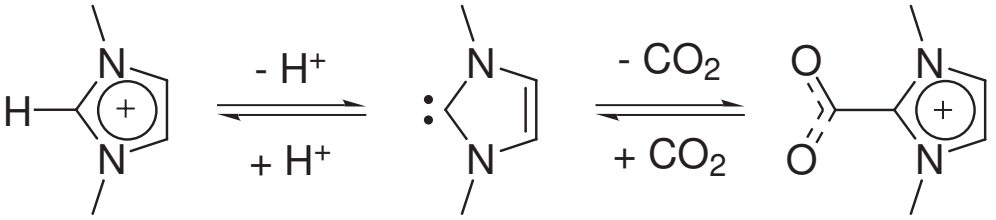

Figure 2: Schematic of relationship between 1,3-dialkylimidazolium cations (**1**) and the zwitterionic 1,3-dialkylimidazolium-2-carboxylate (**3**) as sources of imidazol-2-ylidene NHCs (**2**), after Fevre et al.[40]

a laboratory demonstration experiment[48] and highlights the potential to access lower temperature (and therefore lower energy) pathways. However the need for a strictly anhydrous, and oxygen-free, environment prevents practical application.

One approach to address these challenges from hydrolysis, while continuing the access the activity of NHCs, is to use a "masked carbene"[49,50] such as 1,3-dimethylimidazolium-2-carboxylate (**3** in Fig. 2) which was first reported[51] as a precursor to ionic liquids. 1,3-Dialkylimidazolium-2-carboxylates can be considered as NHC–CO_2 adducts and can act as NHC transfer agents[52] undergoing decarboxylation to form NHCs,[53,54] or can react with acids to generate imidazolium cations.[55] There is increasing interest in the use of 1,3-dialkylimidazolium-carboxylates as organocatalysts for a range of reactions[56,57] including CO_2 cycloaddition reactions,[58] ring-opening polymerisation of ε-caprolactone and *rac*-lactide,[40,59,60] and the preparation of cyclic carbonates from diols[37,61–63] where the tolerance of water in reaction mixtures was noted.

While 1,3-dialkylimidazolium ionic liquids, 1,3-dialkylimidazolium-2-carboxylates, and NHCs have all been used as catalysts (or pre-catalysts) for transesterification reactions, the application of 1,3-dialkylimidazolium-2-carboxylates to the degradation of polyesters has not been previously reported. In light of the number of potential pathways in which 1,3-dialkylimidazolium-2-carboxylates can act as catalysts and/or catalyst precursors,[64] we were interested in exploring whether 1,3-dimethylimidazolium-2-carboxylate could be used as a catalyst for PET glycolysis and how it would perform compared to 1,3-dialkylimidazolium acetate ionic liquid analogues.[26]

Here we report the first use of 1,3-dimethylimidazolium-2-carboxylate as an efficient and active

catalyst for the glycolysis of PET waste from consumer plastic drinks bottles, and show that it is a more effective catalyst (or catalyst pre-cursor) than 1,3-dimethylimidazolium acetate, suggesting that decarboxylation to the NHC[40] provides an additional pathway to forming active catalysts.

Experimental

Materials

PET beverage bottles were washed with water and dried before being cut into 4×4 mm squares for use. Ethylene glycol (EG) was obtained from Sigma-Aldrich and used as received. 1,3-Dimethylimidazolium-carboxylate and 1,3-dimethylimidazolium acetate were synthesised using literature procedures.[51,65] Synthesis and characterisation methods are described in the Supporting Information.

Glycolysis of PET

Glycolysis screening reactions were performed by heating (with stirring) PET, EG, and the catalyst at defined temperatures between 160–200 °C for times between 0.5–4 h.

Ethylene glycol (2–20 g) and catalyst (1,3-dimethylimidazolium-2-carboxylate or 1,3-dimethylimidazolium acetate, 0.05–0.40 g) were loaded into a 50 cm^3 round-bottom three-necked flask equipped with a thermometer and a reflux condenser, and preheated to the selected reaction temperature (160–200 °C). PET (1.0 g, from post-consumer plastic bottle cut into 4×4 mm pieces) was then added and the reaction mixture was stirred under nitrogen at reaction temperature for 0.5–4 h. After a defined reaction time, the reactor was cooled to *ca*. 60 °C and residual PET was removed by rapid vacuum filtration, washed with methanol (*ca*. 20 cm^3) and air dried. The methanolic washing was combined with the EG/BHET-rich filtrate, and then removed from the combined solutions by rotary evaporation under reduced pressure at 50 °C. The EG solution was then chilled and stored in a refrigerator overnight at 4 °C. White crystalline needles formed and

were collected by filtration, washed with cold water, and dried in air. Characterisation by ^{1}H and ^{13}C NMR and FTIR spectroscopy confirmed the formation of *bis*(hydroxyethyl) terephthalate (BHET); ^{1}H NMR (400 MHz, DMSO-D_6, δ/ppm): 8.17 (s, 4H, CH), 5.02 (s, 2H, OH), 4.39 (t, 4H, O$-CH_2$), 3.78 (t, 4H, CH_2-OH), ^{13}C NMR (101 MHz, DMSO-D_6, δ/ppm): 165.63 (2C, C=O), 134.47 (2C, *C*-C=O), 129.71 (4C, CH), 66.79 (2C, O-CH_2, 59.88 (2C, CH_2-OH. MS (+ve ion ES-MS) 255.0869/256.0903 (BHET+H^+) and 277.0688/278.0722 (BHET+Na^+).

The range of reaction temperatures, times, substrate ratios and results, and additional characterisation of BHET produced by FTIR spectroscopy, GC-MS and TGA are included in the Supporting Information. The percentage conversion of PET was calculated from the initial weight of PET W_0 and residual weight (W_1) of insoluble polymer recovered post-reaction[26] using equation (1).

$$C_{PET}(\%) = \frac{W_0 - W_1}{W_0} \times 100 \tag{1}$$

Results and Discussion

Effects of Reaction Time and Temperature

Glycolysis of waste PET from drink bottles using the zwitterionic 1,3-dimethylimidazolium-2-carboxylate as a catalyst (or catalyst-precursor) was explored, examining the effects of catalyst loading, reaction temperature and time, and comparing the results to those obtained using 1,3-dimethylimidazolium acetate as an ionic liquid analogue of the carboxylate zwitterion. The two catalysts were initially screened for PET glycolysis at 185 °C using reaction mixtures containing a 1:5:50 wt% ratio of catalyst:PET:EG, with reaction times between 0.5–4.0 h. The results are shown in figure 3. The conversion of PET to EG soluble oligomers was assessed by filtering the hot reaction solutions to recover any remaining PET which was dried and weighed.

After removal of unreacted PET, BHET was precipitated by cooling the filtered EG solution and storing at 4 °C. BHET precipitated as fine white needles, and was collected by filtration. The

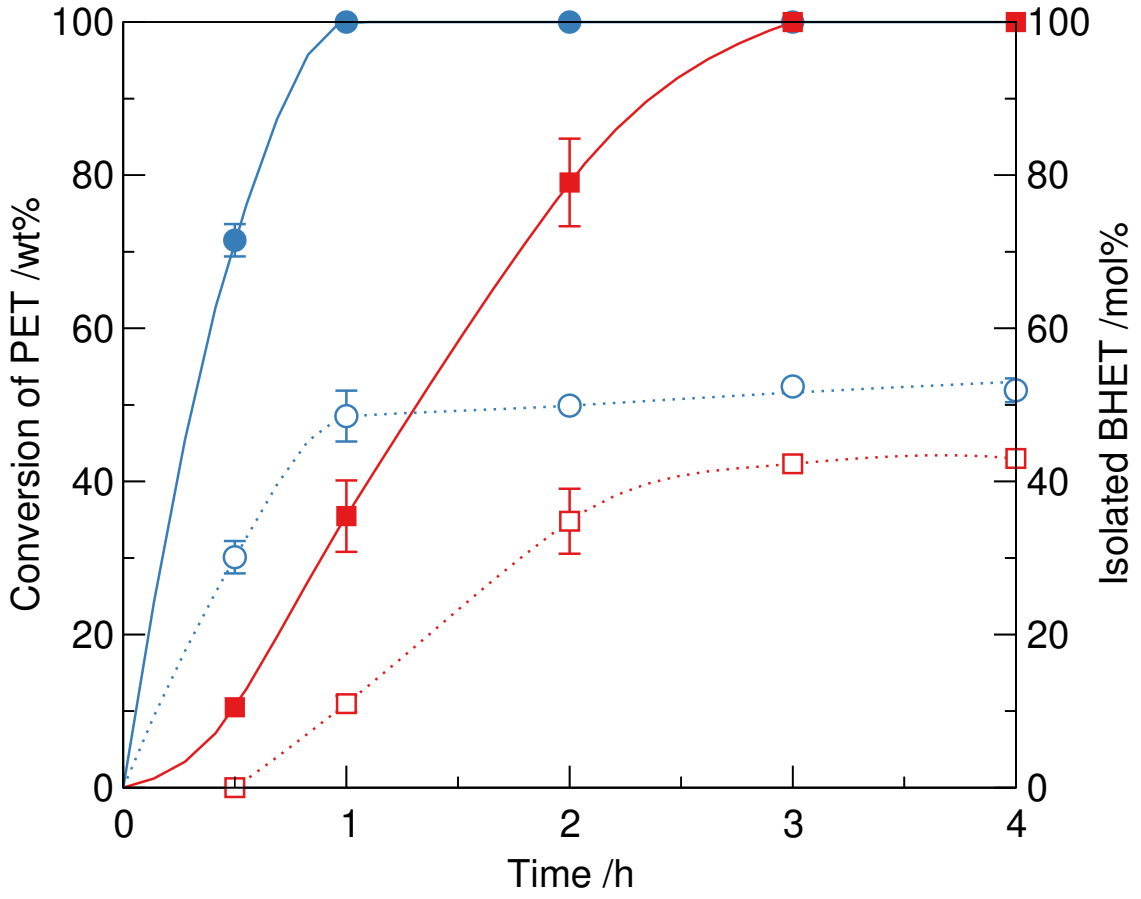

Figure 3: Effect of reaction time on PET depolymerisation and BHET isolated with 1,3-dimethylimidazolium-2-carboxylate (blue) and 1,3-dimethylimidazolium acetate (red) as catalysts. Reaction conditions; catalyst:PET:EG 1:5:50 wt ratio, reaction temperature 185 °C. Conversion of PET (wt %) shown with solid symbols and BHET isolated yield (mol %) in open symbols

isolated yield was calculated using the molar masses of recovered BHET (MW 254.24 g mol^{-1}) and the PET repeat unit (MW 192.17 g mol^{-1}) in the original PET added. HPLC analysis of the reaction mixtures pre- and post-recovery show incomplete recrystallisation of BHET, with catalyst and significant quantities of BHET remaining in the EG solution. Representative HPLC traces are shown in the Supporting Information. Because the total BHET yield was not determined in these studies, the overall conversion of PET to unisolated BHET was not quantified.

HPLC analysis of the filtrate after precipitation showed that not all BHET was recovered by this method, however this was sufficient to comparatively assess the performances of the two imidazolium derivatives as catalysts, and to compare with results using basic [C_4mim][OAc][26] and the protic [TBD][OMs][25] ionic liquids as catalysts.

Using 1,3-dimethylimidazolium acetate, moderate–good catalytic activity was obtained with PET degradation observed and formation of BHET. The extent of PET conversion increased with reaction time and complete depolymerisation (100 % conversion) was obtained after 3 h, with an isolated yield of BHET of *ca*. 40 % obtained on cooling and filtering the reaction mixtures. These results with 1,3-dimethylimidazolium acetate are largely consistent with those reported by Al-Sabagh et al.[26] using [C_4mim][OAc] where 100 % conversion with 58 % yield of BHET was reported after 3 h at 190 °C with 1:3:20 [C_4mim][OAc]:PET:EG mass ratio.

1,3-Dimethylimidazolium-2-carboxylate afforded significantly greater catalytic activity for glycolysis that 1,3-dimethylimidazolium acetate with around 2.5× greater levels of degradation of PET observed at each time point. After only 30 min over 70 % conversion of PET was achieved with complete 100 % conversion after 1 h contrasting with ca. 35% conversion after 1 h with 1,3-dimethylimidazolium acetate. Consistently higher yields of BHET (*ca*. 50 % isolated yield after 1 h) were also recovered from the reaction mixtures by filtration.

Approximate rates of conversion of PET can be estimated from the data in Figure 4, giving values of *ca*. 100% h^{-1} and *ca*. 35% h^{-1} respectively. Although not directly comparable, these ratios are similar to the relative ratios of the turnover frequencies for the cyanosilylation of benzaldehyde reported by Fevre et al.[40] with carboxylate zwitterion and imidazolium hydrogen carbonate derived catalysts (TOF/h of 30,000 and 10,000 respectively at 80 °C) which are ascribed to the relative facility of the carboxylate zwitterion to generate the NHC.

The influence of reaction temperature was then examined, using the short 1 h reaction times where, as shown in Fig. 3, 100% PET conversion was achieved at 185 °C with 1,3-dimethylimidazolium-2-carboxylate compared to *ca*. 37% conversion when 1,3-dimethylimidazolium acetate was used. The effects of temperature on the PET conversion and BHET yield obtained are shown in Fig. 4. Both PET conversion pathways follow the same profile, with greater conversion of PET obtained with increasing reaction temperature. With 1,3-dimethylimidazolium acetate, maximum conversion is obtained at reaction temperature of 195 °C, with 70 % conversion of PET and an isolated yield of BHET of *ca*. 25% after 1 h. The high activity of 1,3-dimethylimidazolium-2-

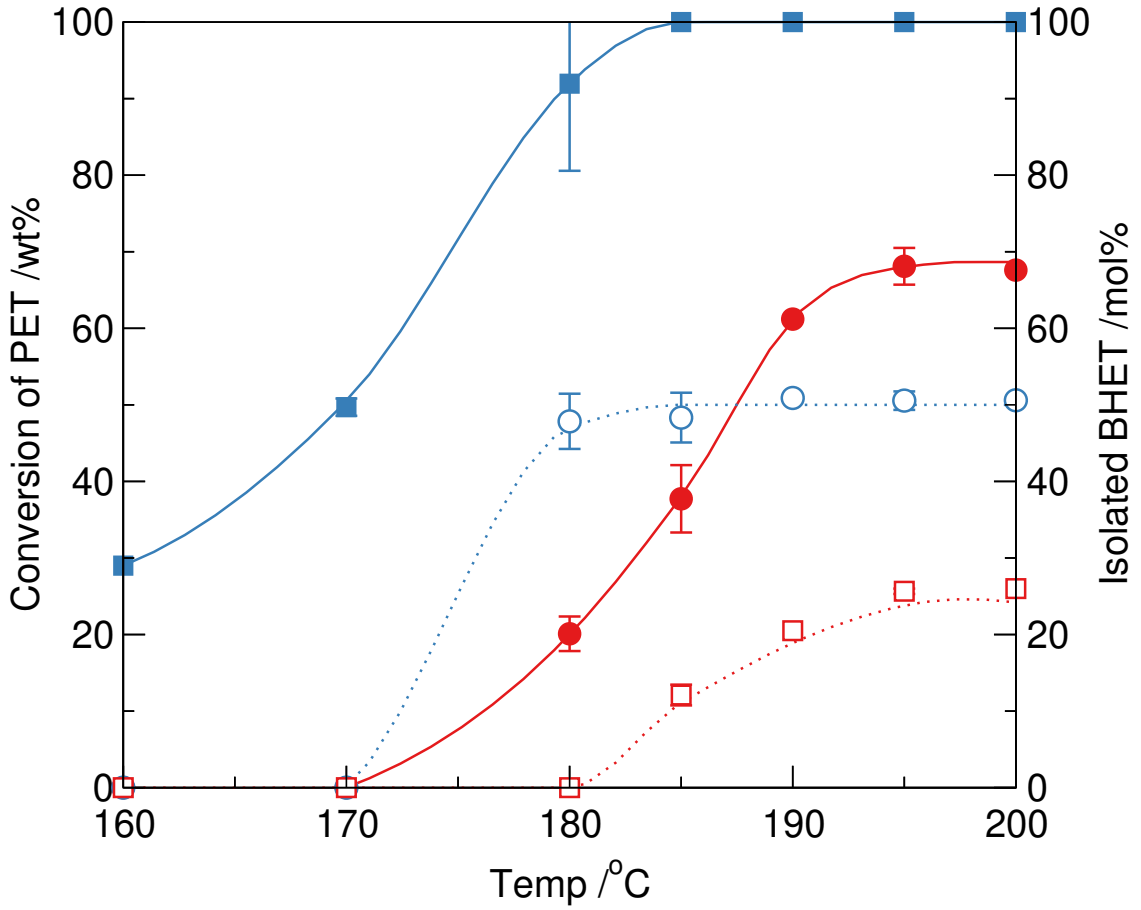

Figure 4: Effect of reaction temperature on PET depolymerisation and BHET isolated with 1,3-dimethylimidazolium-2-carboxylate blue and 1,3-dimethylimidazolium acetate red as catalysts. Reaction conditions; catalyst:PET:EG 1:5:50 wt ratio, reaction time 1 h. Conversion of PET (wt %) shown with solid symbols and BHET isolated yield (mol %) in open symbols.

carboxylate is evident from conversion profile in Fig. 4 where complete PET conversion is achieved between 180–185 °C, and at all temperatures above 180 °C, the isolated BHET yield on cooling the reaction mixtures was 50%.

For the lower temperatures examined, at 170 °C using 1,3-dimethylimidazolium-2-carboxylate the conversion of PET was reduced to *ca*. 50%, however despite this degradation of PET, no BHET was precipitated directly from the filtered reaction mixture after cooling. Similarly, at 160 °C, degradation of up to 30% of the available PET was observed. In contrast, with 1,3-dimethylimidazolium acetate, no measurable degradation of PET was observed when the reaction temperature was below 180 °C.

Effect of Reaction Component Ratios

The impact of changing the component ratios (catalyst:PET and PET:EG) were also examined (See ESI†). Although mass ratios of catalyst:PET:EG are reported here, the relative molecular masses of the two catalysts are similar (140 and 156 g mol^{-1} respectively for 1,3-dimethylimidazolium-2-carboxylate and 1,3-dimethylimidazolium acetate) and the molar ratios of catalyst:PET are similar (Table S1). As anticipated, for both catalysts, at the catalyst:PET ratio in the reaction mixtures was increased, the conversion of PET was enhanced using 1,3-dimethylimidazolium acetate, an increase in the catalyst loading from 0.05 to 0.4 mass equivalents (1:16 to 1:2 molar ratio to PET monomer) resulted in an increase in PET conversion after 1 h at 185 °C from *ca.* 10 % to *ca.* 48 %. However the yield of BHET isolated from the reaction mixtures remained low (all less than 15 %) and this value did not rise commensurately with the increase in conversion.

With the zwitterionic 1,3-dimethylimidazolium-2-carboxylate, complete conversion of PET previously found in the screening experiments, as described above, was retained as the catalyst load was reduced to 0.15 mass equivalents (1:5 molar ratio). However, when the amount of the zwitterion added was reduced to 0.1 mass equivalents (1:7 molar ratio), conversion after 1 h declined to 83±3% and was reduced further, to 23%, using a 0.05:1 mass ratio. Interestingly the isolated yield of BHET increased from 9 to 49 to 61% on increasing the catalyst to PET ratio from 1:14 to 1:4 mole ratio, with a further increase in catalyst content in the reaction mixtures, the quantity of BHET isolated decreased monotonically from 61% with 1:5 molar ratio to only 12% with 1:1.8 molar ratio catalyst:PET.

It is likely that this apparent reduction in BHET yield is due to the changes in solution composition in the post-reaction mixtures, which in this series of reactions varies from 1:200 to 1:25 mass ratio 1,3-dimethylimidazolium-2-carboxylate:EG between the lowest and highest catalyst loading. These masses correspond to a range of 1,3-dimethylimidazolium-2-carboxylate concentrations between *ca*. 0.035 and *ca*. 0.28 M, and it is likely that the high concentrations of imidazolium salts in EG enhance BHET solubility and inhibit crystallisation from the reaction mixtures.

Reducing both the catalyst and PET concentrations in the reaction mixtures by increasing

the EG content was examined under the standard screening conditions (1:5:n mass ratio catalyst:PET:EG at 185 °C over 1 h varying the EG component from $n = 25$–100). The results are shown in Table S1. With 1,3-dimethylimidazolium acetate, both PET conversion and isolated BHET yield decrease as the EG component ratio is increased and both PET and catalyst concentrations are reduced, from *ca*. 40% conversion at 1:5:25 (1:5 PET:EG) down to *ca*. 20% with an excess of EG (1:20 PET:EG). The amount of BHET that precipitated from the reaction mixtures also decreases monotonically with increasing the EG content.

In contrast, with 1,3-dimethylimidazolium-2-carboxylate, complete conversion of PET to soluble products was observed in 1 h at 185 °C across the range of PET:EG ratios examined. However, the solution composition does play a significant role in stabilising the reaction solutions and/or changing the product distributions. The yield of BHET isolated from reaction mixtures increased with increasing EG component in the reactions from 1:5:25 (1:5 PET:EG) to a maximum of *ca*. 50% in the 1:5:50 (1:10 PET:EG) system. At higher dilution with $n_{EG} > 50$, the quantity of BHET isolated from the reaction by chilling and precipitation decreased from 50% ($n_{EG} = 50$) to 20% ($n_{EG} = 100$) consistent with the solubility of BHET in EG.

Consideration of PET Conversion and BHET Yield

Glycolysis of PET to BHET monomers can also generate quantities of soluble dimeric and trimeric oligomers from scission and insertion of ethylene glycol into the polymer chains. Water formed from these transesterification reactions, if not removed, can also generate competing hydrolysis reactions to terephthalic acid.

In the studies here, the objective was to explore the impact of the catalyst source on the degradation of the PET, rather than optimisation of the isolated yield of BHET. BHET can be readily isolated in quantitative yield (of the converted materials) by addition of water, followed by collection and separation of co-precipitated dimer/trimer by repeated crystallisation/separation from hot water (see for example, Wang et al.[20]). However, the addition of water to these reaction mixtures would also quench potential NHC catalytic species anticipated to be present and so, in contrast, the

ability to isolate a proportion of the BHET formed in these reactions through a temperature swing was examined. As discussed above, after chilling filtered reaction mixtures to 4 °C, BHET precipitated with a lower isolated yields than expected by mass balance compared to the percentage degradation/conversion of PET, with the remaining BHET retained in the EG reaction solution.

Not withstanding the lower isolated yields of BHET, the potential to avoid addition of water is important in the context of examining potential routes to recycle catalysts. This is particularly relevant to NHC forming systems (see below) where an aqueous quench would revert the NHC to an imidazolium cation and make subsequent recovery of the zwitterionic pre-cursor impractical for catalyst reuse or recycling.

Acid/base or carbene-catalysis?

NHCs are highly effective organocatalysts across a range of transesterification reactions[43–47] including glycolysis of PET.[48] Furthermore the mechanism of transesterification of diols with dimethylcarbonate catalysed by 1,3-dialkylimidazolium-2-carboxylates has been explained by Naik et al.[61,62] and Stewart et al.[37] through *in situ* decarboxylation of the 1,3-dialkylimidazolium-2-carboxylates to NHCs that initiate nucleophilic attack. Lui et al.[66] have also invoked a masked-carbene mechanism for alkylation of phenols with 1,3-dialkylimidazolium-2-carboxylates.

However Al-Sabagh et al.[26] have explained glycolysis of PET in the presence of [C_4mim[OAc] through synergistic 'push-pull' interactions of PET and EG with both the Lewis acid [C_4mim]$^+$ cations and basic [OAc]$^-$ anions rather than by considering NHC generation. Intrinsic concentrations of spontaneously generated NHCs in 1,3-dialkylimidazolium acetate ionic liquids are low[36] and it seems likely that acid/base mechanisms will play a role, as it necessarily must in ionic liquids that can not form NHCs such as choline phosphate,[25,67] as well as catalysis by NHCs.

PET glycolysis is more rapid, and is activated from lower temperatures, when the 1,3-dimethylimidazolium-2-carboxylate zwitterion is used compared to the corresponding 1,3-dimethylimidazolium acetate salt. These results appear entirely consistent with the work of Fevre et al.[40,59] although the comparison here is with an acetate rather than hydrogen carbonate salt, and also to

the work from the Hedrick and coworkers[15,43,44,47,48] and Nolan and co-workers[45,46,50] that have established the general utility of N-heterocyclic carbenes as catalysts across a range of transesterification chemistries.

In the context of considering the nature of the catalytic species present, and indeed whether one or more possible active species may be present depending on the reaction conditions, it is worth considering the long-term thermal and/or chemical stability of these catalysts (or catalyst pre-cursors). Fevre et al.[40,59] compared 1,3-dialkylimidazolium-2-carboxylates and the corresponding 1,3-dialkylimidazolium hydrogen carbonates as organocatalyst precursors for benzoin condensation, transesterification, and cyanosilylation reactions. They demonstrated formation of active NHCs from both the carboxylate and basic imidazolium salts, and reported higher TOFs using the carboxylate zwitterion as the pre-catalyst compared to the equivalent imidazolium hydrogen carbonate salt. This was rationalised in terms of the ease of NHC generation from the respective precursors based, among other evidence, on the TGA profiles of comparable imidazolium-carboxylates and methylcarbonate salts have been examined. However, one should be careful extrapolating too much information from TGA data collected on pure species. Both 1,3-dialkylimidazolium salts (with a hydrogen at the C(2)-position) and 1,3-dialkylimidazolium-2-carboxylate zwitterions are unstable to thermal and base-induced deprotonation leading to NHC formation and/or decomposition. In the presence of proton donor solvents such as ethylene glycol or water, this deprotonation can be suppressed leading to significant enhancement in thermal stability.

This increased stability is, presumably, a constant feature across the wide range of ionic liquid/organic salt/deep eutectic solvents that have been explored as catalysts for PET glycolysis and related reactions under comparable conditions. However, the potential for thermal and/or chemical degradation/activation can not be neglected, as demonstrated by Welton and co-workers[35,36,68] in studies surrounding understanding the stability, or otherwise, of cellulose dissolved in ionic liquids where the intrinsic generation of NHCs within ionic liquids was demonstrated.

Examination of the lifetime and stability of *active* catalytic species, not necessarily their pre-cursors, is required and this is also needed over greater time scale than the longest (4 h) reactions

screened here in order to demonstrate the viability of immobilised organocatalysts in continuous or semi-batch reactor systems which do not require the quench/recover/recycle strategy most commonly advocated.

Conclusions

We have demonstrated, for the first time, that 1,3-dimethylimidazolium-2-carboxylate can be used as an organocatalyst (or pre-catalyst) for the glycolysis of PET. Post-consumer drinks bottle PET was completely depolymerised in 1 h at 185 °C using 1,3-dimethylimidazolium-2-carboxylate (20 mol% relative to PET monomer) at 0.75:5:50 mass ratio cat.:PET:EG, with up to 60% yield of BHET obtained directly from the reaction mixture upon chilling as a crystalline precipitate.

In comparison to the basic ionic liquid, 1,3-dimethylimidazolium acetate, the zwitterionic carbonate, 1,3-dimethylimidazolium-2-carboxylate, is significantly more effective as a catalyst (or pre-catalyst). PET degradation is initiated more rapidly, and at lower temperatures, as shown in Fig. 3 where complete PET degradation is obtained in 1 h using 1,3-dimethylimidazolium-2-carboxylate whereas with 1,3-dimethylimidazolium acetate, only *ca*. 35 % degradation was achieved after 1 h and up to 3 h is needed to obtain a comparable degree of depolymerisation.

The results using 1,3-dimethylimidazolium-2-carboxylate as a metal-free organocatalyst are comparable with the best reported transition metal–containing ionic liquids[20,21] and the enhanced reactivity compared to 1,3-dimethylimidazolium acetate is consistent with the relative facility to form NHCs[40,59] (Fig. 2) although a detailed mechanistic study has not been carried out here.

It is arguable that these catalysts can not be considered to be as 'green' or benign as zinc acetate[10] or, most particularly, sodium bicarbonate as described by López-Fonseca et al.[13] in the context of PET glycolysis. However, there is significant effort using ionic liquid catalysis to address challenges within PET glycolysis and waste recycling, and the results here demonstrate that there are still opportunities to access lower temperatures transformations through NHC formation that could lead to energy savings if transformed from batch to continuous flow conditions with

immobilised NHC catalysts.

The results described here demonstrate that the carboxylate zwitterion enables greater rates of PET glycolysis and allows lower temperatures to be used demonstrating that, if an aqueous quench can be avoided, there is potential to retain the catalyst with remaining BHET in the reactior under 'steady state concentrations'. Thus, continuous topping-up with PET/EG as they are consumed could allow development of continuous or semi-batch flow systems using immobilised carbenes, or carbene-precursors.

Acknowledgement

The authors acknowledge EPSRC and DELNI for providing PhD studentships to JT and GN respectively.

Supporting Information Available

Details of the synthesis and characterisation of the two catalysts, 1,3-dimethylimidazolium-2-carboxylate and 1,3-dimethylimidazolium acetate, the reaction conditions screened for PET glycolysis (time, temperature, composition and PET conversion (wt%) and isolated yields (mol%)) and representative characterisation data for *bis*(2-hydroxyethyl terephthalate) produced including HPLC traces from crude reaction products, and 1H NMR and FTIR spectra, GC/MS and TGA profiles of the isolated purified product are included in the supporting information.

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Synopsis

Carbene formation from 1,3-dimethylimidazolium-2-carboxylate generates superior performance in glycolysis of PET compared to corresponding basic 1,3-dimethylimidazolium acetate ionic liquid catalyst.