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Organocatalysed depolymerisation of PET in a fully sustainable cycle using thermally stable protic ionic salt

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The world's plastic production is continuously and exponentially increasing, creating millions of tons of short-lived items that end as waste and accumulate in the environment. Poly(ethylene terephthalate) (PET) provides one of the best examples as it is a non-biodegradable polymer that is mainly used as raw material for a wide range of packaging applications, making degradation of PET a subject of great interest for researchers. Herein we report a sustainable process for the chemical recycling of PET from waste to a new polymer using an innovative protic ionic salt. Using a simple solvent-free process, post-consumer PET bottles are degraded into bis(2-hydroxyethyl) terephthalate (BHET) monomer. The catalyst, formed by an equimolar quantity of triazabicyclodecene (TBD) and methanesulfonic acid (MSA), completely depolymerises PET in less than 2 h, producing 91% of highly pure BHET. Due to the unusual thermal stability of TBD:MSA salt, the catalyst can be recycled 5 times to depolymerise more PET waste. In addition, we demonstrate that the monomer obtained from the degradation reaction can be used to synthesise new PET with similar thermal properties than one produced using conventional polycondensation method. The protic ionic salt catalyst combines the excellent catalytic ability of organocatalysts with the thermal stability of metal catalysts, resisting degradation up to > 400 °C, thus for the first time presenting an industrially-relevant organocatalyst for high-temperature polymer degradation and recycling.

Introduction

Over the past century, synthetic plastics have become ubiquitous in our daily life, occupying an ever-expanding range of uses.[1] Their production has increased significantly over the past few decades from 15 to 311 million tons between 1964 and 2014, and is expected to double again by 2035.[2] Unfortunately, plastic waste management has not kept up pace and consequently, dealing with the resulting discarded plastic waste has become an urgent and global problem. Among this tremendous quantity of polymeric materials, poly(ethylene terephthalate) (PET) represents *ca.* 13% of the world's production. It is one of the most widespread and multifunctional thermoplastics and it is used for myriad of applications from food packaging and beverage bottles to synthetic fibres.[3,4]

Three different strategies can be considered to avoid plastic waste being sent to landfill: energy recovery, physical recycling and chemical recycling. As a consequence of its simplicity and low-cost, recovering energy by incineration is the most common recycling technique. However, the resulting products cannot be recovered and the process finally creates other undesirable waste products such as carbon dioxide which is released to the environment. As an alternative to incineration, pyrolysis converts waste polymers into a high calorific value fuel through pressure and heat.[5] While some plastics such as polyolefins seems to be excellent candidates for this type of recycling, in the case of PET, the generation of corrosive chemicals during the process does not make it a suitable feedstock for pyrolysis technology.[6] Physical recycling is the most practiced method for PET and involves grinding and melt-processing of plastic waste to produce new material.[7,8] This method results in structural deterioration and hence the recycled product does not share the same properties as the virgin PET. As a consequence, it is processed into lower-value products such as fibres for textile or lower grade resins and rapidly ends up as waste.[9,10]

In contrast, chemical recycling involves the de-polymerisation of polymers into monomers or oligomeric fragments that can then be re-polymerised to yield recycled polymer.[11–13] This strategy can be used to recycle PET in order to generate high purity monomer in outstanding yields that does not compromise the economics of the overall approach.[14–16] Chemical recycling of PET is conducted by the attack of different nucleophiles to the ester bond of PET[17,18] by hydrolysis,[19] methanolysis,[20] or glycolysis,[21] amongst other possible routes. As a consequence of the high chemical stability and low solubility of PET in organic solvents, the

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depolymerisation processes are generally applied in very harsh conditions and in the presence of catalysts. Organometallic catalysts such as zinc, cobalt, lead or manganese acetates, sodium/potassium sulfate, titanium phosphate, *etc.*, have dominated the field due to their high stability and activity. However, their recovery can be challenging because of the laborious separation of the catalyst from the product. [22–27] The combination of forcing reaction conditions with catalysts such these provide slow reaction rates and/or low selectivity presents significant difficulties in scaling-up to an industrially-relevant process. Several innovative solutions such as nanoparticles,[28] ionic liquids[29,30] or deep-eutectic solvents (DES)[31,32] have been recently considered. Some of these catalysts promote fast depolymerisation and/or good monomer yield. But they still present similar drawbacks: possible presence of metal in the final product, low monomer yields or challenging purification procedure.

Organocatalysts are promising “green” substitutes to classic organometallic catalysts.[33,34] Furthermore, some organic bases commonly used for transesterification reactions, have demonstrated encouraging results with monomer yields up to 78 %.[35–37] However, typically such organic compounds show poor thermal stability at temperatures that would be practical for PET recycling and as such, full or partial thermal degradation of the catalyst occurs during the depolymerisation, which hinders the perspective of reusing it for several reactions.[38] Key to the advancement of this technology is the attainment not only of PET recycling into monomer at high yields but also the ability to reuse the catalyst towards envisioning a continuous recycling process.

Herein, we report our studies into the application of a protic ionic salt, formed from triazabicyclodecene (TBD) and methanesulfonic acid (MSA), as catalyst for the high temperature depolymerisation of PET. We found that this catalyst is not only highly efficient for such a depolymerisation process but it is also extremely thermally stable, allowing its use in several recycling cycles. Using density functional theory (DFT), the molecular structure of this catalyst has been investigated to explain this extraordinary stability. Finally, we demonstrate the ability of this catalyst to re-polymerise bis(2-hydroxyethyl) terephthalate (BHET) into new PET, which demonstrates similar characteristics to virgin PET.

Experimental section

Materials

PET beverage bottles were washed with water and dried before being shredded to 4 mm squares prior to use. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), methanesulfonic acid (MSA; >99.5 %), ethylene glycol (EG) and solvents were used without any further treatment (Sigma-Aldrich). Water was distilled and deionised.

Preparation of the catalyst mixtures

Different dual catalysts were prepared by mixing TBD and MSA at molar ratios of base to acid from (3:1) to (1:3) at 60 °C for 30 minutes until obtaining a transparent and homogeneous solution. NMR characterisations demonstrated the formation of the salts, for (1:1) mixture: ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.76, (s, 2H, N-H-O), 3.28 (t, 4H, CH_2), 3.17 (t, 4H, CH_2), 2.41 (s, 3H, CH_3). 1.88 (q, 4H, CH_2). ^{13}C NMR: δ (ppm) 150.58 (s, 1C, N-C-N), 46.24 (2C, *CH₂*-CH₂-*NH*), 39.74 (2C, S-CH_3), 37.55 (2C, *CH₂*-CH₂-*N*), 20.26 (2C, *CH₂*-CH₂-*CH₂*). FTIR spectra of (1:1), (3:1) and (1:3) characterisation data are summarised in Supporting Info (Figures S4 – S8).

Characterisation of the catalysts

Nuclear magnetic resonance (NMR) spectroscopy. ^{1}H NMR spectroscopic measurements were carried out in deuterated dimethyl sulfoxide (DMSO-d_6) on a Bruker Advance 400 (400 MHz) spectrometer for crude product reaction characterisation.

Thermogravimetric Analysis (TGA) The thermal stability was analyzed by a TGAQ500 (TA instrument) under nitrogen atmosphere. Samples of 5-10 mg were heated from 40 to 600 ˚C at a rate of 10 ˚C.min^{-1}.

Differential Scanning Calorimetry (DSC). DSC measurements were performed using a DSC8500 (PerkinElmer). The instrument was calibrated with indium and tin standards. The DSC scans were performed with 4.5-5.5 mg samples at heating and cooling rates of 20 ˚C/min from -20 to 270 ˚C under a nitrogen flow of 20 ml/min. The data reported in the results section are the second heating scans.

High performance liquid chromatography (HPLC). Chromatograms of products were performed using Daicel Chiralpak IB on a Water 2487 equipped with a UV-Vis detector, measuring at 254 nm, Injected volume = 25 µL, Isocratic gradient flow = 0.5 mL/min, hexane/Isopropanol 2:1 for 30 min at 25 °C.

General procedure for the catalytic degradation of PET

In each experiment, 0.5 g of PET flakes were degraded using EG with a certain amount of catalyst. A 10 mL Schlenck flask equipped with a magnetic stirrer was used for all the reactions. The depolymerisations were carried out under atmospheric pressure at 180 °C for either a predetermined time period or until complete disappearance of any residual PET. Reagents and catalysts were loaded in the glovebox, under nitrogen atmosphere, before sealing the flask and immersion in an oil bath. When the reaction was completed, the crude product was cooled to room temperature and a large excess of distilled water was added. The resulting solution was vigorously stirred and filtered to separate ethylene glycol, catalyst and main product from oligomers and bottle additives, insoluble in water. The aqueous transparent filtrate was stored in a refrigerator at 4 °C overnight. White needle-like crystals were formed in the solution, which were then recovered by filtration before drying. ^{1}H NMR, ^{13}C NMR and FTIR spectroscopic characterisations revealed the crystals to be highly pure bis(hydroxyethyl)terephthalate (BHET) monomer (See Figures S1-S3 in the Supporting Information) with characterising data in accordance with commercially-supplied BHET. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.12, (s, 4H, CH),

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4.97 (t, 2H, OH), 4.32 (t, 4H, O-CH$_2$), 3.73 (q, 4H, CH$_2$-OH). ^{13}C NMR: δ (ppm) 165.14 (2C, C=O), 133.73 (2C, -*C*-C=O) 129.50 (4C, CH), 67.01 (2C, O-CH$_2$), 58.96 (2C, CH$_2$-OH).

The selectivity of BHET is calculated by the following equation:

$$\text{BHET yield} = \frac{\text{moles of BHET}}{\text{moles of depolymerised PET units}}$$

Bulk polymerisation of BHET

Synthesis of PET was accomplished by bulk polymerisation of BHET in the presence of 5 mol % of TBD:MSA (1:1) catalyst following a two-step self-polycondensation of BHET in the melt. BHET (2 g, 7.9 mmol) was introduced together with the catalyst into a Schlenk flask equipped with a magnetic stirrer. The reaction mixture was heated at 250-270 ˚C for 1 hour before vacuum was applied (10^{-2} bar) for 4 h at the same temperature. After completion, PET was dissolved in a mixture of chloroform and trifluoroacetic acid (8:1) and precipitated in excess of methanol to remove impurities. Finally, the polymer was collected by centrifugation and dried under vacuum. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.12, (s, 4H, CH), 4,78 (s, 4H, CH$_2$). (Yield 92%)

Computational details

All density functional theory (DFT) calculations were carried out using the Gaussian 09 suite of programs[39] and the ωB97XD functional[40] in conjunction with the 6-31+G(d,p) basis set for all atoms. To confirm that the optimised structures were minima on the potential energy surfaces, frequency calculations were carried out at the same level of theory and then used to evaluate the zero-point vibrational energy (ZPVE) and the thermal vibrational corrections at T = 298 K. The electronic energy was refined by single-point energy calculations at the ωB97XD/6-311++ G(2df,2p) level of theory.

Results and discussion

Synthesis and characterisation of the catalysts

As a consequence of the high chemical stability of PET, the depolymerisation reaction requires high temperature, above 180 °C, and the catalyst has to endure such conditions for long time periods. As such, we focussed our studies on acid-base complexes, which have already demonstrated good stability for high temperature polymerisation reactions.[41,4243] In order to increase the thermal stability of organic acid and bases and to make them suitable candidates for depolymerisation of PET at 180 °C, we synthesised a protic ionic salt, by mixing a common organic acid, here MSA, with a common organic base, here TBD. The TBD:MSA (1:1) catalyst was prepared by mixing TBD and MSA in equimolar ratio (Figure 1a). In order to confirm the formation of the protic ionic salt, the resulting mixture was characterised by ^{1}H NMR spectroscopy in DMSO-d_6. The recorded spectra for individual TBD, MSA shows the characteristic N-H proton signal of TBD as a weak, broad resonance at δ = 5.81 ppm and the O-H signal of MSA as a sharp, strong peak at δ = 14.16 ppm. In contrast, for the (1:1) mixture, these two signals disappear and a new one integrating for 2 protons appears at δ = 7.71 ppm, which demonstrates the formation of the protic ionic salt by a proton transfer from MSA to TBD (Figure 1b).

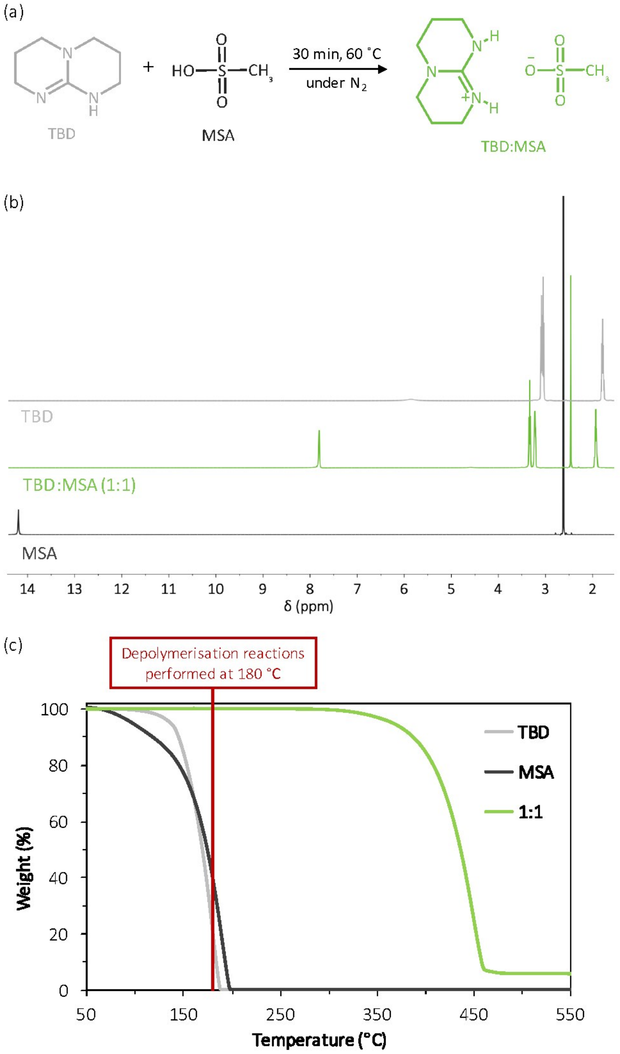

Figure 1. (a) TBD:MSA (1:1) catalyst synthesis, (b) ^{1}H NMR spectra in DMSO-d_6 (400MHz, 298 K) and (c) thermogravimetric analysis for TBD, MSA and TBD:MSA (1:1)

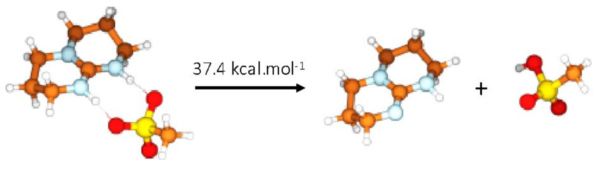

Figure 2. DFT optimised geometries of TBD, MSA and (1:1) TBD:MSA complex

In order to confirm the resistance of the catalyst to temperature, we tested the thermal stability of the catalyst by thermogravimetric analysis, TGA (Figure 1c). MSA and TBD both degrade at relatively low temperature such that 50 % of the original mass is lost at $T_{50\%}$ = 174 °C for MSA and 170 °C for TBD. In contrast, for the isolated salt (TBD:MSA (1:1)) $T_{50\%}$ = 438 °C, revealing the extraordinary high thermal stability of the protic ionic salt. To further confirm the feasibility of using the

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Scheme 1. PET depolymerisation reaction

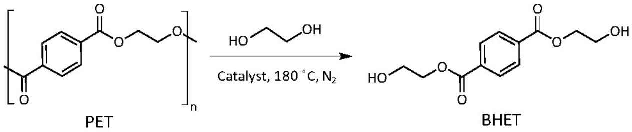

Table 1. Depolymerisation ratio of PET with different molar ratios of TBD:MSA

	TBD:MSA	PET:Catalyst:EG[a]	Time (h)	Dep ratio (%)	BHET ratio[b]
1	**-**	1:0.00:15	4	6	<0.01
2	**1:0**	1:0.25:15	4	100	0.63
3	**3:1**	1:0.25:15	4	100	0.45
4	**1:1**	1:0.25:15	4 (3*)	100	0.70 (0.71*)
5	**1:3**	1:0.25:15	4	90	0.32
6	**0:1**	1:0.25:15	4	86	0.31
7	1:1	**1:0.25:5**	10	100	0.11
8	1:1	**1:0.25:10**	3.5	100	0.59
9	1:1	**1:0.25:20**	3	100	0.72
10	1:1	**1:0.12:20**	12	100	0.27
11	1:1	**1:0.50:20**	2	100	0.91
12[c]	1:1	1:0.50:20	2	100	0.89

[a] Molecular weight of PET considered here is the molecular weight of the polymeric unit
[b] Ratio determined by ^1H NMR spectroscopy in DMSO-d_6 from the crude product using characteristic peaks of the catalysts (δ = 2.57 ppm for MSA, δ = 4.17 ppm for TBD:MSA mixtures and δ = 3.19 ppm for TBD) and characteristic peak of BHET at δ = 4.32 ppm.
[c] The experiment has been done under air.
* The experiment was repeated and stopped at the disappearance of the PET flakes to be consistent with the optimisation procedure.

TBD:MSA complex for catalytic process at high temperatures over extended time period, we studied its thermal stability at 180 °C by an isothermal TGA experiment for 18 h. At this temperature, the weight loss of TBD:MSA mixture was negligible (less than 5 wt %) while both TBD and MSA suffered a complete decomposition in less than 30 min (Figure S9). This result confirms the excellent thermal stability of TBD:MSA ionic salt at the common depolymerisation temperature of PET and hence demonstrates it potential utility for this process.

In order to gain insight into its remarkable stability, the molecular structure of the TBD:MSA ionic salt has been further investigated by means of quantum chemical calculations. Through these calculations, the acidic proton of MSA is observed to completely transfer to the basic nitrogen of TBD, thus creating an ionic pair of the protonated cation $[TBDH]^+$ and the anion MSA^- (Figure 2). Additionally, a hydrogen bond is formed between the N-H moiety of TBD and one of the oxygens of the sulfonyl group of MSA. This observation supports the ^1H NMR spectra in which the two protons corresponding to the N-H of the TBD:MSA salt are equivalent. These two cooperative interactions lead to a calculated dissociation energy of 37.4 kcal.mol^{-1}. Such a high energetic barrier explains the high decomposition temperature and hence the high stability of the TBD:MSA salt.

Catalytic activity test and optimization of depolymerisation conditions

The catalytic activities of different acid-base catalysts were evaluated (Table 1, entries 1-6). TBD, MSA, 1:1 TBD:MSA and mixtures with an excess of acid (1:3) and an excess of base (3:1) were tested to compare their catalytic activity to degrade PET in the presence of excess ethylene glycol at 180 °C. All experiments were conducted for 4 h under nitrogen atmosphere (Scheme 1). Each of catalyst systems tested demonstrated rapid depolymerisation of PET compared to the reaction without catalyst (entry 1). Analysis of the final crude products by ^1H NMR spectroscopy revealed that reactions with MSA alone or excess MSA (entries 5-6) depolymerisation was not completed after 4 h and the resultant monomer yield was not quantitative. Furthermore, additional resonances can be observed in the ^1H NMR spectra of the products from these reactions in the region between δ = 3.5 and 4.5 ppm which confirms the formation of products other than the desired BHET (Figure 3), most likely arising the formation of different oligomers consistent with the low BHET yield. HPLC chromatograms were performed to confirm the presence of products other than the desired BHET (Figures S10 and S11 for entry 5 & 6). We found that in these two cases, although the depolymerisation rate was high, HPLC analysis revealed the presence of not only BHET but also other oligomers of different length which are in good agreement with the ^1H NMR data. As the BHET oligomer ratio is highly dependent on the depolymerisation conditions,[29,44] reactions with TBD and the mixture with excess TBD (3:1) (entries 2-3) showed better efficiency with quantitative depolymerisation being complete within 4 h. Nevertheless, in the ^1H NMR spectra, the appearance of an additional triplet resonance at δ = 4.27 ppm (in addition to the triplet at δ = 4.32 ppm and the quartet at δ = 3.73 ppm from BHET) suggests formation of other species such as the dimer also occurs (Figure 3). BHET is known to exist in equilibrium with other species, in particular its dimer,[45] and

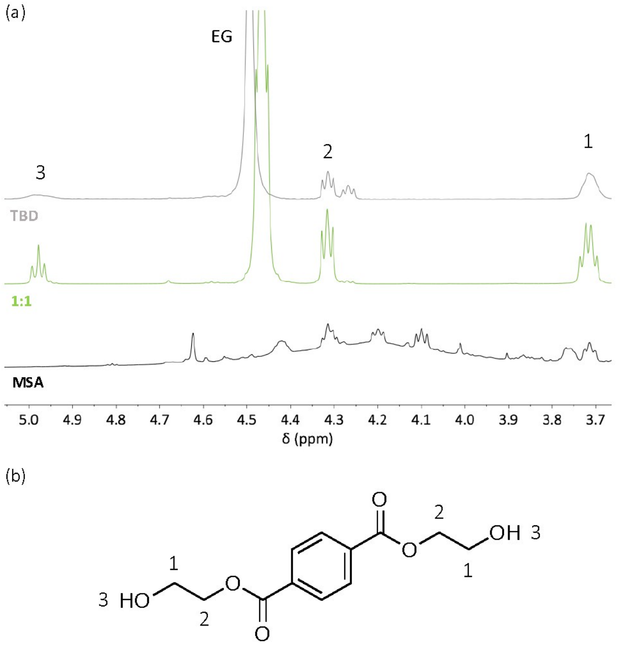

Figure 3. (a) ^1H NMR spectra of crude product of the reactions catalysed by TBD, TBD:MSA (1:1) and MSA in DMSO-d_6 (400 MHz, 298 K). Reactions conditions: PET (1 eq), catalyst (0.5 eq), EG (15 eq), 180 °C, 4 h and (b) BHET molecule

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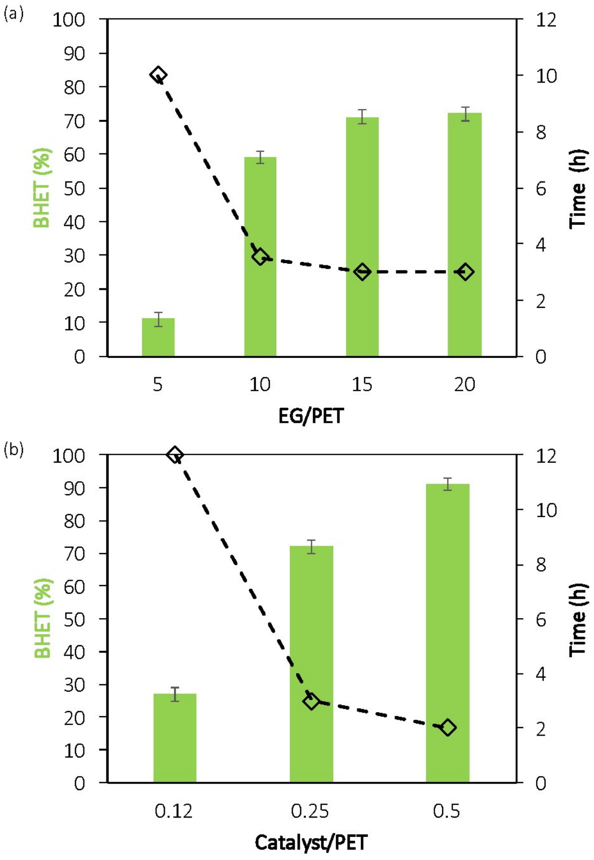

Figure 4. (a) Effect of the amount of EG on degradation time of PET (black line) and BHET yield (green bars). Reactions conditions: PET (1 eq), catalyst (0.25 eq), 180 °C. (b) Effect of the amount of catalyst on degradation time of PET (black line) and BHET yield (green bars). Reactions conditions: PET (1 eq), EG (20 eq), 180 °C.

the appearance of those species complicates the reusability of the degradation product for subsequent polymerisation. The highest yield of BHET was achieved with the 1:1 MSA:TBD mixture, reaching 70 % of BHET (Table 1, entry 4).

In order to enhance the economics of the overall approach, maximizing the BHET yield is essential. As such, different parameters that influence the depolymerisation reaction such as the EG content (entries 4,7,8 & 9) or the catalyst content (4, 10 & 11) were investigated with the TBD:MSA (1:1) mixture as catalyst (Table 1). The crude product was analysed by ^{1}H NMR spectroscopy to evaluate both the time required to complete the depolymerisation and the BHET yield. We observed that reducing the equivalents of EG below 10 eq., led to the depolymerisation being less efficient (Figure 4a). With 5 eq. EG, the time required to complete the reaction exceed 10 h and the final BHET yield was lower than when higher equivalents were used. Using 10 equivalents of EG, the reaction was complete in just 3 hours, however the BHET yield was moderate, 59 %. Using low EG/PET ratios results in a large insoluble fraction to treat during the purification process, due to the formation of PET oligomers, decreasing the final BHET yield. Increasing the EG content up to 15 eq, or above enabled BHET yields, up to 70% to be achieved in around 3 h. Above this amount, raising the EG content did not provide any significant improvement. To further optimise the BHET yield, the catalyst concentration was also varied (Figure 4b). A clear correlation is observed between the amount of catalyst and the reaction performance such that the amount of BHET increased from 27% with 0.12 eq. catalyst to 91% with 0.5 eq.. In addition, the catalyst loading also reduced substantially the time for depolymerisation from 10 h to less than 2 h. In order to evaluate the ability of TBD:MSA catalyst to work under air conditions, a reaction has been carried out without using inert atmosphere (Table 1 – entry 12). We did not observe any difference (BHET yield 89 % in 2 h) showing the potential of this process to be scaled up. We also performed the same experiment with larger scale using 5 g of PET and no significant differences were observed obtaining similar BHET yield (SI section).

These results suggest that the TBD:MSA (1:1) catalyst is a promising alternative for the chemical recycling of PET at an industrial level, as a results of the highly selective conversion to BHET as well as it's simplicity to synthesise from low-cost chemicals compare to classic metal catalysts. However, to further enhance the credentials of this catalyst system, reduction of the requirements of EG, TBD and MSA could be achieved by recycling to afford a sustainable cycle.

Recycling of the residual EG and catalyst

Considering the environmental and economical viability of the proposed process, residual reactants and catalyst need to be recycled for further PET degradation. After filtering the BHET crystals from the aqueous phase, the unreacted EG and catalyst were dried by vacuum evaporation at 60 °C before being stored in a vacuum oven at 60 °C overnight. Then, fresh PET flakes were added to the recycled system [EG + catalyst] using the same procedure. Five subsequent depolymerisation reactions have been performed for two catalytic systems, TBD:MSA (1:1) and TBD (Figure 5). In the presence of TBD:MSA (1:1), the BHET yield id observed to be constant with no loss of catalytic activity, even after 5 recycling processes. In contrast

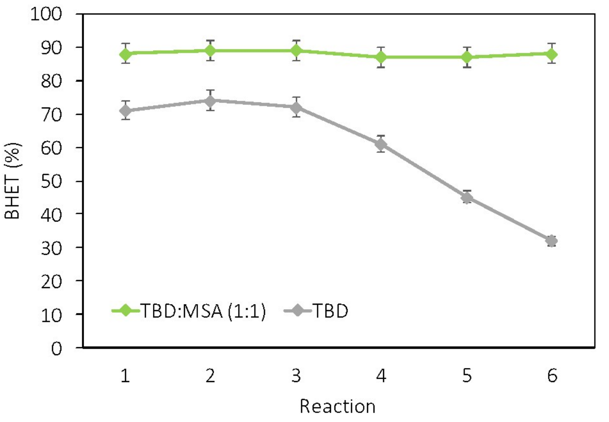

Figure 5. [Catalyst + EG] recycling. Reactions conditions: PET (1 eq), catalyst (0.5 eq), EG (20 eq), 180 °C

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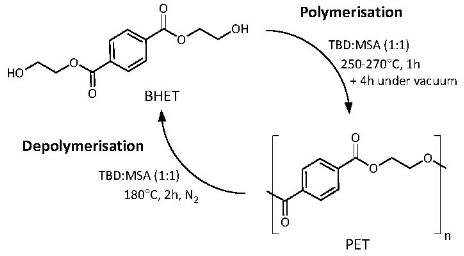
Scheme 1. PET depolymerisation reaction



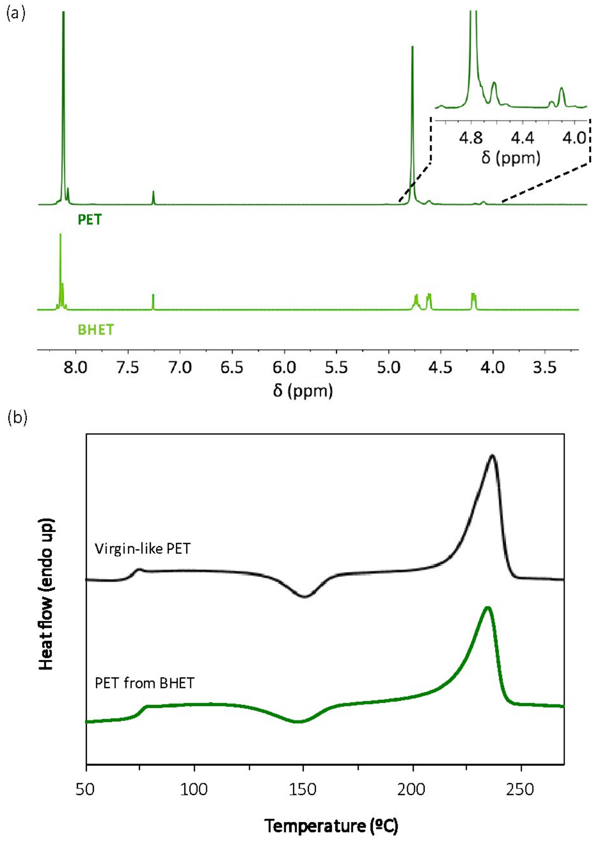


Figure 6. (a) Comparison of ^{1}H NMR spectra of PET and BHET in CDCl$_3$/TFA (400 MHz, 298 K) (b) Comparison of thermal profiles for virgin-like PET and PET polymerised from BHET with TBD:MSA (1:1) catalyst

however, the TBD-catalysed reaction has lower yields of BHET after the third reaction, so the second recycling cycle. We attribute this difference in behaviour to the unusually high thermal stability of the. TBD:MSA (1:1) catalysts. As we have previously noted, it is stable at 180 °C for more than 18 h when TBD began to display mass loss in under 30 minutes. We postulate that this stark difference in thermal stability is reflected in the ability of the TBD:MSA (1:1) catalyst to perform at high temperatures over a longer period of time. Furthermore, these results confirm that the TBD:MSA protic ionic salt is an excellent candidate for the depolymerisation of PET, not only because it can be recycled multiple times (up to 5), but also because high BHET yields could be obtained.

Polymerisation of PET with BHET from waste bottles

In order to create a simple process for the chemical recycling of PET, it is of great interest to extend this catalyst's platform from the depolymerisation to the polymerisation *via* typical polyesterification. In order to close the PET-to-PET cycle, the polymerisation of BHET was investigated using the TBD:MSA (1:1) catalyst (Scheme 2). Considering the high thermal stability of the TBD:MSA catalyst, we performed the self-condensation of BHET at 250-270 ˚C for 1 h under nitrogen atmosphere before applying vacuum for a further 4 h. The final polymer was analysed by ^{1}H NMR spectroscopy and DSC and was compared with a PET obtained in our lab with the commonly-used catalyst (titanium butoxide) and monomers (ethylene glycol and dimethyl terephthalate (DMT)). Polymerisation was confirmed with ^{1}H NMR spectroscopy by evaluating the disappearance of BHET –CH$_2$ protons at δ = 4.7 ppm and δ = 4.3 ppm and the concomitant appearance of protons assigned to PET at δ = 4.8 ppm (Figure 6a). To further confirm the formation of PET, the molecular weight was analysed by ^{1}H NMR spectroscopy using the 2-hydroxyethyl end-group protons at δ = 4.62 and 4.18 ppm[46], in both cases M_n values around 12 kDa were obtained (Figure 6a). Finally, DSC analysis confirmed that the thermal isotherm of the obtained PET is similar to the virgin-like PET, showing a thermal glass transition at around 60 ˚C, cold crystallization at 150 ˚C, and a melting transition at around 230 ˚C. With these results, the cycle is closed. Using the same catalyst, but under different conditions, we are able to polymerise a high quality PET from a monomer obtained from the depolymerisation of PET waste.

Conclusions

We have demonstrated that the TBD:MSA (1:1) mixture is a very stable protic ionic complex able to catalyse PET glycolysis in less than 2 h. The molecular structure of this catalyst was determined using DFT calculations to understand the high thermal stability of TBD:MSA mixture. Under optimised conditions, over 90% of BHET is obtained in a solvent-free reaction, easily recovered by crystallization in water. Both the reagent, used in excess, and the catalyst are easily recyclable, demonstrating same catalytic activity even after 6 reactions. In order to close the cycle, we demonstrated that this catalyst could even be used in the self-condensation of BHET to obtain new PET exhibiting good thermal and properties, similar to the virgin PET. Due to the recyclability of the chemicals employed, easy techniques used and sustainability of the protocols, the entire process could be considered for industrial perspectives.

Acknowledgements

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