SUPPORTING INFORMATION

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

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Characterisation of BHET

Figure S1. BHET $^1$H NMR in DMSO-$d_6$

Figure S2. BHET $^{13}$C NMR in DMSO-$d_6$
Figure S3. FTIR spectrum of BHET
Characterisation of catalysts

Figure S4. $^1$H NMR in DMSO-$d_6$ of TBD:MSA (1:1)

Figure S5. $^{13}$C NMR in DMSO-$d_6$ of TBD:MSA (1:1)
Figure S6. FTIR spectrum of TBD:MSA (1:1)

Figure S7. $^1$H NMR spectrum of TBD:MSA (1:3) in DMSO-$d_6$.

$^1$H NMR (400MHz, DMSO-$d_6$) $\delta$ (ppm) 13.14, (s, 2H, OH, MSA), 7.72, (s, 2H, N-H-O), 3.25 (t, 4H, CH$_2$, TBD), 3.14 (t, 4H, CH$_2$, TBD), 2.52 (s, 9H, CH$_3$, MSA). 1.85 (q, 4H, CH$_2$, TBD).

Spectra of 1:3 mixture presents both the characteristic peak of the salt at 7.71 ppm and the characteristic peak for the acidic proton of MSA over 13 ppm due to the excess of acid.
**Figure S8.** $^1$H NMR in DMSO-$d_6$ of TBD:MSA (3:1)

$^1$H NMR (400MHz, DMSO-$d_6$) δ (ppm) 6.85, (s, 2H, N-H-O) & (s, 2H, NH), 3.12 (t, 12H, CH$_2$, TBD), 3.09 (t, 12H, CH$_2$, TBD), 2.52 (s, 3H, CH$_3$, MSA). 1.85 (q, 12H, CH$_2$, TBD).

In the spectra of 3:1 mixture, only one peak appears at 6.85 ppm. Due to the high basicity of the middle, we are not able to see distinct signals but integration of the peak justifies the presence of both protons corresponding to the formation of 1:1 complex and protons expressing the N-H of the excess of TBD.
Isotherms

Figure S9. (a) Isotherms of TBD:MSA (1:1) (green line), TBD (light grey line), MSA (dark grey line) at reaction temperature, 180 °C, for 18 hours and (b) focus on the 3 first hours.
**Figure S10.** HPLC analysis of reaction 5 with MSA:TBD (3:1) as catalyst. Reaction conditions: PET (1 eq), catalyst (0.25 eq), EG (15 eq). First signal at the smallest retention time, 5.4 min, corresponds to BHET and signals between 6.3 and 17.4 min corresponds to various length’s oligomers.
Figure S11. HPLC analysis of reaction 6 with MSA as catalyst. Reaction conditions: PET (1 eq), catalyst (0.25 eq), EG (15 eq). First signal at the smallest retention time, 5.4 min, corresponds to BHET and signals between 6.3 and 17.4 min corresponds to various length’s oligomers.

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5 g of PET flakes (1 eq) were degraded using 25g of EG (20 eq) with 1.22 g of TBD:MSA (1:1) catalyst (0.5 eq). A 100 mL Schlenck flask equipped with a magnetic stirrer was used. Reagents and catalysts were loaded in the glovebox, under nitrogen atmosphere, before sealing the flask and immersion in an oil bath. The depolymerisation was carried out under atmospheric pressure at 180 °C until complete disappearance of any residual PET, after 2 hours. 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. BHET crystals were formed in the solution, which were then recovered by filtration before drying. (yield 88%)