Dual-catalytic depolymerization of polyethylene terephthalate (PET)

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Methods and Materials

General considerations

All chemicals were commercially available (purchased from Sigma-Aldrich) and used without further purification (unless otherwise stated). PET was used in the form of white pellets in all experiments. Solvents were of ACS grade or higher. 1-methyl-2-pyrrolidinone was purified by distillation under vacuum using a Schlenk line. NMR spectra (400 MHz for 1H) were recorded on a Bruker 400 spectrometer and processed using MestReNova v9.0.1 (Mestrelab Research, S.L., Santiago de Compostela, Spain). Chemical shifts were referenced to residual solvent peaks at δ = 2.50 ppm (1H).

Representative Depolymerisation reaction

For each experiment PET (0.5 g) was weighed out into a small Schlenk tube. Lewis acid and base catalysts (0.15% equiv. each compared to PET) was weighed separately, added to the Schlenk tube along with a magnetic stirrer and an accurately weighed amount of NMP. The Schlenk tube was then sealed with a rubber septum. Ethylene Glycol (EG) (20 equiv. compared to PET) was added using a syringe through the septum. The Schlenk tube was then lowered into an oil bath heated to 180 °C and allowed to stir. After 5 min the reactions had reached temperature so the nitrogen taps were closed to minimise the headspace and left stirring for 5 hours. The reactions were heated for 5 hours as most reactions appeared to complete before this time. At 5 regular time intervals during this period, a 0.1 mL sample was extracted using a syringe and transferred to a vial. To this, DMSO d6 (0.4 mL) was added while the sample was still hot, and this mixture was then transferred to an NMR tube and analysed by 1H NMR.

Comparison of the integrals of the singlet from the methyl group of NMP δ = 2.69 ppm and the singlet from the aromatic hydrogens from the depolymerisation product (BHET) δ = 8.12 ppm allowed the rate of formation of BHET to be monitored. A sample was also taken before heating began to give a t0 value. Once the reaction was complete, the Schlenk tubes were removed and the reaction mixture was allowed to cool. The mixture was washed with water to remove excess EG and remaining catalyst and the solid isolated using a Buchner funnel. The solid BHET was then dried overnight in a vacuum oven and submitted for 1H NMR dissolved in DMSO d6 (δ (ppm) 8.12, (s, 4H, CH), 4.97 (t, 2H, OH), 4.32 (t, 4H, O–CH2), 3.73 (q, 4H, CH2–OH)).
**Synthesis of MgCl₂/DMAP precatalyst**

Magnesium chloride (0.44 g) was dissolved in methanol (23 mL) in a Schlenk tube with a magnetic stirrer. DMAP (0.56 g) was dissolved in methanol (4 mL) in a vial. The dissolved DMAP was then added dropwise to MgCl₂ with stirring. The solution remained clear and was left stirring overnight. The solution had become cloudy and solvent was then removed under vacuum on the Schlenk line. A white solid was recovered and analysed by H¹ NMR then further dried in a vacuum oven overnight at 60 °C. Final yield was 76%.

**Representative procedure for recycling of the catalyst.**

A vessel was charged with PET (480 mg, 2.5 mmol, 1 equiv.), ethylene glycol (2.8 mL, 50 mmol, 20 equiv.), zinc diacetate dihydrate (69.4 mg, 0.375 mmol, 0.15 equiv.), 4-(N,N-dimethylamino)pyridine (47.5 mg, 0.375 mmol, 0.15 equiv.) and N-methyl pyrrolidone (24 µL, 0.5 equiv.) and heated to 180 °C with stirring. Aliquots of 0.1 mL were taken at t = 0, 2, and 3 h for ¹H NMR in DMSO-d₆. After 3 h the mixture was filtered hot to remove any remaining PET and oligomers then washed with hot ethylene glycol (2 mL) and water (2 mL). The white precipitate which formed on addition of water was removed by filtration and the filtrate was cooled to 4 °C for 1 h to crystallise white waxy crystals of bis(2-hydroxyethylene)terephthalate, which were separated by vacuum filtration and washing with water (3 mL). The solvent was then removed from the subsequent filtrate by vacuum distillation to recover Zn(OAc)₂•DMAP catalyst (59-82 mg, 0.19-0.27 mmol, 51-71%).

The recovered catalyst (59-82 mg, 0.15 equiv.) was then transferred to a new vessel, along with PET (246-340 mg, 1 equiv.), ethylene glycol (1.4-2.0 mL, 20 equiv.) and N-methyl pyrrolidone (0.012-0.017 cm³, 12.7-17.9 mmol, 0.1 equiv.). The mixture was then subjected to another depolymerisation kinetic study, and the catalyst was reclaimed once more (30-39 mg, 0.10-0.13 mmol, 48-51%). A third depolymerisation was completed.
**Figure S1.** Comparison of PET depolymerization with in situ added DMAP and MgCl₂ and preformed DMAP/MgCl₂ "salt".

**Figure S2.** Comparison of PET depolymerization with different oxygen-based anions showing that triflate has a clear induction period.
Figure S3. Cycling of the depolymerization of PET with Zn(OAc)$_2$ and DMAP.

Figure S4. Comparison of PET depolymerization of DMA with and without Zn(OAc)$_2$. The summation of the activity each catalyst component has been added as a dotted line for reference.
Figure S5. Comparison of PET depolymerization of imidazole with and without Zn(OAc)$_2$. The summation of the activity each catalyst component has been added as a dotted line for reference.

Figure S6. Comparison of PET depolymerization of NMI with and without Zn(OAc)$_2$. The summation of the activity each catalyst component has been added as a dotted line for reference.
**Figure S7.** Comparison of PET depolymerization of PPh$_3$ with and without Zn(OAc)$_2$. The summation of the activity each catalyst component has been added as a dotted line for reference.

**Figure S8.** Comparison of PET depolymerization of DABCO with and without Zn(OAc)$_2$. The summation of the activity each catalyst component has been added as a dotted line for reference.
Figure S9. Comparison of PET depolymerization of N(Et)$_3$ with and without Zn(OAc)$_2$. The summation of the activity each catalyst component has been added as a dotted line for reference.

Figure S10. Comparison of PET depolymerization of ABCO with and without Zn(OAc)$_2$. The summation of the activity each catalyst component has been added as a dotted line for reference.
Figure S11. Comparison of PET depolymerization of DBU with and without Zn(OAc)$_2$. The summation of the activity each catalyst component has been added as a dotted line for reference.

Figure S12. Comparison of PET depolymerization of MTBD with and without Zn(OAc)$_2$. The summation of the activity each catalyst component has been added as a dotted line for reference.
Figure S13. Comparison of PET depolymerization of TMG with and without Zn(OAc)$_2$. The summation of the activity each catalyst component has been added as a dotted line for reference.

Figure S14. Comparison of PET depolymerization of TBD with and without Zn(OAc)$_2$. The summation of the activity each catalyst component has been added as a dotted line for reference.
Figure S15. Comparison of PET depolymerization of BEMP with and without Zn(OAc)$_2$. The summation of the activity each catalyst component has been added as a dotted line for reference.