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Dual-catalytic depolymerization of polyethylene terephthalate (PET)†

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Limiting our plastic waste and finding greener, more sustainable solutions for disposal is currently an environmental priority. Polyethylene terephthalate (PET), one of the more prominent single-use plastics, has recently been under investigation for chemical recycling as a means to ameliorate the environmental impact. This work reports a dual-catalytic approach to the chemical recycling of PET, aiming to combine inexpensive, readily available Lewis acid–base pairs to exhibit cooperative catalytic activity.

Introduction

The world's production of synthetic plastics is continuously and exponentially increasing as these materials have become ubiquitous in everyday life.[1,2] This is a consequence of these materials being low cost and functional. Unfortunately, many plastics are single-use and thus waste from these materials has been building up in the environment to create a global problem. One such polymer, polyethylene terephthalate (PET) is a major part of the world's synthetic plastic production (33 million tons in 2015).[3–5] Unfortunately, the combination of the slow natural degradation of PET in the environment and poor disposal management has contributed to the global issue of plastic pollution. As PET production continues to increase, recycling strategies must also adapt.[6–11] While mechanical recycling of PET is well exploited, ultimately it leads to a deterioration in mechanical properties as a consequence of thermal degradation, contamination, and discoloration. In turn, the recycled material reduces in quality and does not perform as well as virgin PET.

Recently, chemical recycling of PET has been investigated as an innovative solution to the treatment of post-consumer PET.[12–15] Chemical recycling involves depolymerisation of the end-use plastic down to its constituent monomers that are then suitable for repolymerization (with mechanical properties comparable to the virgin material), resulting in a closed-loop cycle for the material.[16–20] Specifically, glycolysis of PET leading to bis(2-hydroxyethylene)terephthalate (BHET) has been shown to be suitable for depolymerization and repolymerization (Fig. 1).[13,21–25]

Chemical depolymerization of PET has been studied with a variety of both metal-based and organic catalysts.[4,13,14,20,25] Previously, we have shown that the depolymerization process benefits from catalyst systems composed of ionic acid–base pairs that outperformed base catalysis alone.[25,26] As such, this has led us to focus subsequent studies on the effect of combining organic bases with Lewis acidic metal complexes. The benefit of using a dual-catalytic system with a metal-based Lewis acid component is that many different variables can be tuned including Lewis acidity of the metal, size of the metal, and metal ligands/counter anions.[20,27]

Results and discussion

Previous dual-catalytic depolymerization of PET with organic salts required formation of an ionic salt precursor prior to introduction into depolymerization conditions.[25] Early investigation of PET glycolysis using 4-dimethylaminopyridine (DMAP), a popular catalyst for transesterification reactions in ester-based polymers, with readily available $MgCl_2$ and a preformed DMAP–$MgCl_2$ complex showed comparable performance (see ESI Fig. S1†). Most notably, even in these initial studies, the depolymerizations were rapid and efficient.[28] In

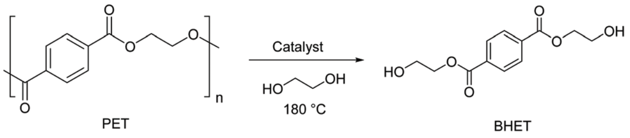

Fig. 1 Glycolysis of PET to form BHET.

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turn, all subsequent depolymerisations were run using *in situ* addition of both catalyst components. A simple screening of metal halides while retaining DMAP as base showed that metal identity has a dramatic effect on depolymerization activity (Table 1) with many metal halides affording little or no conversion (Table 1, entries 7–13). This could be due to a myriad of factors not limited to solubility, metal size, and coordination. These results are in line with similar trends seen for the dual-catalytic ROP of lactones.[29] The complexation with DMAP is likely to have a dramatic effect on the activation of the polyester backbone and subsequent nucleophilic attack needed for depolymerization. If the Lewis acid–base interaction is too strong there may not be enough "free" acid and base to enable depolymerization. Similarly, if the interaction is too weak then the catalyst components will not be stabilized and decompose under depolymerization conditions.

Conversely, comparing different halogen anions had a much smaller effect. Increasing the size of the halide from $MgCl_2$ to MgI_2 showed less than a 10% enhancement. Similar results were obtained with ZnI_2 and $ZnBr_2$. A more significant difference was observed when the anions are changed to oxygen-based moieties such as triflate (OTf) or acetate (OAc). Since magnesium is a hard metal it is expected to bind more strongly with oxygen-based ligands leading to a slight decrease in activity (Table 1, entries 16 and 17). Alternatively, zinc as a soft metal appears to have a slight increase in activity when moving from halide ligands to oxygen-based ligands. Notably, for both metals, triflate complexes show lower activity than the comparable acetate complexes. More in depth kinetic studies revealed that the triflates and halides appear to have an induction period early in the reaction (see ESI Fig. S2†). This led us to hypothesize that in some cases the metal ligands may be replaced by carboxylates that form the chain end or transesterification location in the polymer. It would stand to reason that

Table 1 Reactivity of a variety of Lewis acids paired with DMAP for the depolymerization of PET[a]

Entry	Lewis acid	Conversion after 3 hours
1	None	0.55
2	$MgCl_2$	0.62
3	$MgBr_2$	0.60
4	MgI_2	0.71
5	$ZnBr_2$	0.69
6	ZnI_2	0.54
7	$BiCl_3$	0.13
8	YCl_3	0.08
9	$AlCl_3$	—
10	$FeCl_3$	—
11	$SnCl_4$	—
12	$TiCl_4$	—
13	$Bi(OTf)_3$	—
14	$Zn(OTf)_2$	0.41
15	$Zn(OAc)_2$	0.89
16	$Mg(OTf)_2$	0.57
17	$Mg(OAc)_2$	0.68

[a] Each depolymerization was run with 0.15 equivalents of catalyst and 20 equivalents of ethylene glycol at 180 °C.

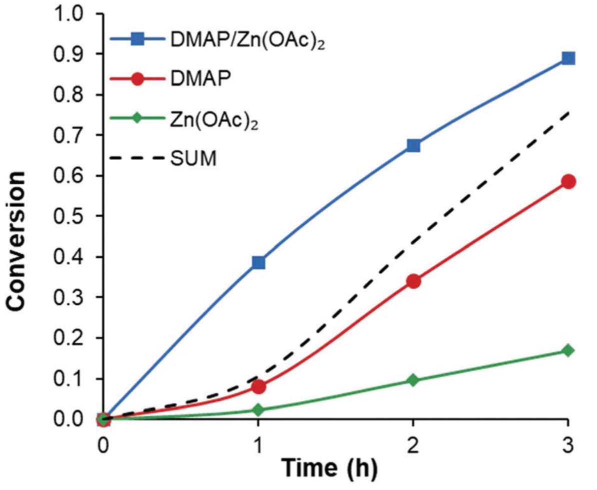

Fig. 2 Example of synergistic effect with the combination of DMAP and $Zn(OAc)_2$. Sum of both catalysts alone shown for reference.

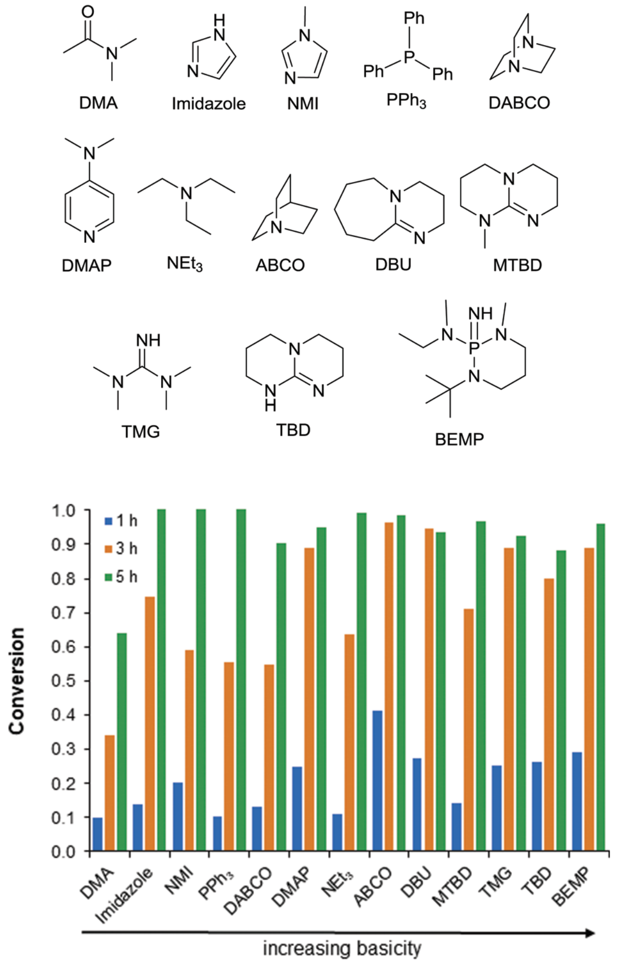

Fig. 3 Activity of $Zn(OAc)_2$ with various bases for the depolymerization of PET. Bases are ordered left-to-right by basicity.

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this exchange or formation of the active species would be more facile with metal acetate complexes. Since $Zn(OAc)_2$ showed the most promising reactivity and synergistic effect (see Fig. 2) with DMAP, it was screened with various base co-catalysts.

Combinations of $Zn(OAc)_2$ with varying bases showed a wide range of reactivity from 55% to 96% conversion at 3 h (Fig. 3). As a consequence of the complex relationship between the basicity and complexation of these bases there is not a clear trend. It appears that bases with pK_a's ranging from 9–12 are the most active. As the bases get stronger a decrease in reactivity is observed (for example TBD and BEMP). Alternatively, when the base is too weak a marked decrease in activity is observed (for example PPh_3, Fig. 3). Additionally, complexation in an equimolar relationship to the Lewis acid appears to be important. This can be seen when DABCO (two basic sites) is compared to ABCO (one basic site). A similar phenomenon has been shown to affect the temperature stability of monobasic and dibasic ionic salts. There is a clear "Goldilocks Effect" for acid–base coordination and activity.[26] Additionally, a synergistic effect is seen with all of the bases weaker than TBD and BEMP (see ESI Fig. S4–S15†). It is hypothesized that these two strong and stable bases do not benefit from the addition of the Lewis acid due to their already remarkable reactivity. Additionally, no synergistic effect is seen with the more nucleophilic bases (*i.e.* DABCO and ABCO); it is possible that these bases are operating *via* an alternative mechanism.

Currently, attempts to isolate and reuse the catalyst for subsequent depolymerizations have shown some promise (see ESI Fig. S3†). The main limitation appears to be decomposition of the catalyst components over these reaction times at high temperatures.

Conclusions

Overall, there is an apparent enhancement of depolymerization reactivity when a combination of Lewis acid and base are employed as the catalyst, similar to the organic salt systems. It is clear that tuning the strength of the acid–base interaction is the key to influencing the subsequent catalytic activity and stability. If the catalyst components bind too tightly this hinders the reactivity. However, if binding is too weak, there is no enhancement of activity or catalyst stability. Future studies will focus on fine tuning the acid–base interactions and finding a dual-catalytic system that can be recycled for many depolymerizations and ultimately lead to a closed-loop PET cycle.

Conflicts of interest

The authors have no conflict of interest to declare.

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