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## Catalytic alkaline hydrolysis of PET and BPA-PC waste in minutes at atmospheric pressure without microwaves or organic solvents†

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Rapid hydrolysis of poly(ethylene terephthalate) (PET) waste usually requires organic cosolvents, high pressures or microwave irradiation, which can increase the environmental impact/expense/operational complexity of an emerging enabling technology for more sustainable plastic recycling. Using a combination of solute-derived boiling point elevation and phase transfer catalysis, operationally facile, rapid alkaline hydrolysis of PET and poly(bisphenol A carbonate) (BPA-PC) waste – from beverage bottles/textiles and compact discs

respectively – is achievable in minutes ( $\leq 5$  min for PET and 20 min for BPA-PC) at atmospheric pressure without the need for either microwaves or organic cosolvents. Dimethyldialkylammonium halides were found to be optimal catalysts at low loadings. The rapid, one-pot catalytic hydrolysis of a waste stream of both plastics followed by ready isolation of the terephthalic acid and bis-phenol A monomer units in excellent yields (without decomposition) is possible by selective protonolysis.

### Green foundation

1. A catalytic methodology for the chemical recycling of PET and BPA-PC plastic waste by alkaline hydrolysis. This occurs on timescales comparable with the most efficient methodologies in the literature/industry, without requiring organic co-solvents, microwaves or high-pressure apparatus. This is possible through the combination of a simple and efficient (1 mol%) catalyst with boiling point elevation. The first hydrolytic rapid recycling of mixed streams of the two plastic wastes is possible – again without organic solvents.
2. The ability to quantitatively depolymerise PET in 4–5 min in minimal volumes of aqueous NaOH at atmospheric pressure without organic solvents reduces both solvent waste and the hazards associated with the containment of high-pressure reactions at scale. The short timescales at reaction temperatures  $< 150$  °C also reduce energy usage.
3. Efforts to improve catalysis and reduce the loading of NaOH closer to 2 equivalents could reduce waste further.

Poly(ethylene terephthalate) (PET) is a fossil-derived condensation polymer thermoplastic constituent of beverage bottles, food packaging and textiles. It has been reported that in 2021, the production of this material totaled 24.2 billion kg (ref. 1) and PET disposal comprised 12% of worldwide solid waste.<sup>2</sup> Despite the increasing environmental concern, if current trends continue the OECD estimates that the use of plastics is set to almost triple from 2019 to 2060.<sup>3</sup> Alongside investment in recycling infrastructure and more stringent regulatory frameworks (e.g. the EU setting minimum future levels of recycled plastic in beverage bottles<sup>4</sup>), the rapid improvement

and expansion of humanity's arsenal of recycling technologies are therefore of some urgency.

Non-destructive PET recycling methodologies can be classified as being either mechanical or chemical in nature. Mechanical recycling broadly involves cutting, washing and melting waste materials to form recycled PET flakes/pellets.<sup>5</sup> This is the most common form of PET recycling and can lead to lower quality products due to contamination and/or hydrolytic/thermal degradation (requiring the utilisation of remedial, more resource-intensive 'superclean' methodologies) and ultimate downcycling.<sup>5–7</sup> Chemical PET recycling is an emerging technology that involves solvolysis with various nucleophiles, *i.e.* aminolysis, alcoholysis, glycolysis and hydrolysis (possible under neutral, acidic or alkaline conditions).<sup>8</sup> Solvolytic PET recycling is more resource intensive and requires efficient chemistry at scale – but can regenerate pure monomers which can be either upcycled or repolymerised to

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virgin PET, thereby increasing circularity and reducing global dependence on petroleum-based plastic feedstocks.<sup>5,8</sup>

The scale of the PET recycling challenge is daunting in both volume and time domains – for instance, in 2021 on average >700 kg of PET was synthesised every second,<sup>1</sup> while the total greenhouse gas emissions associated with the PET production supply chain are the highest of the major plastic types.<sup>3,9</sup> It follows that even if an international agreement aimed at slowing production is reached, it is not difficult to foresee that future sustainability from a plastics perspective will rely in part on recycling technologies that are (a) rapid, (b) circular, (c) involving minimal waste, (d) operationally straightforward and (e) applicable in both developed and developing nations alike.

Nascent industrial processes have largely focused on catalytic methanolysis and (in particular) glycolysis.<sup>5,8,10,11</sup> The high boiling point of ethylene glycol allows glycolysis at temperatures up to 190 °C to occur at atmospheric pressure – which is advantageous in terms of rate (PET is a hydrophobic material insoluble in water and alcohol) and operational simplicity (*i.e.* avoidance of high-pressure vessels) at the process scale. The product is directly polymerisable to PET; however, an equilibrium between the product and oligomers/precursors diminishes the yield and complicates purification.<sup>11</sup>

PET hydrolysis offers advantages in terms of the use of water as a solvent and the formation of water-insoluble terephthalic acid (**1**) – a starting material for the production of PET in the petrochemical industry. Acidic,<sup>12</sup> neutral<sup>13</sup> and alkaline<sup>14</sup> hydrolysis methodologies are known. The reactions are (in a practical sense) irreversible, with outstanding product yields possible. Alkaline hydrolysis has been generally preferred in the small number of industrial processes using hydrolytic technology,<sup>11a</sup> as it can be conducted at lower temperatures, with less EG degradation and shorter reaction times – at the cost of the use of NaOH, together with mineral acids to precipitate the product. The main challenge associated with alkaline hydrolysis is the aforementioned hydrophobicity of PET, and researchers in industry and academia have attempted to circumvent this through the use of (either alone or in combination) high temperatures/pressures,<sup>15</sup> phase transfer catalysts,<sup>16</sup> organic co-solvents,<sup>17</sup> microwaves,<sup>17k,18</sup> UV-irradiation,<sup>19</sup> ultrasound<sup>20</sup> and extruders<sup>21</sup>/mechanochemistry.<sup>22</sup> All except the use of phase transfer catalysts would increase the operational complexity of the process, especially at scale.<sup>11</sup>

Representative recent advances are depicted in Fig. 1. The application of high temperatures/pressures by Karayannidis *et al.*<sup>15</sup> resulted in complete PET degradation to monomer **1** at 200 °C after 60 min (Fig. 1A). Gutiérrez-Ortiz and coworkers<sup>16d</sup> (Fig. 1B) reported the alkaline hydrolysis of PET flakes using a phosphonium ion-based phase transfer catalyst (12.5 mol%) – which allowed the reaction to proceed to a considerable extent at 80 °C over 90 min. A study from Xu's laboratory<sup>17j</sup> demonstrated efficient alkaline hydrolysis at just 35 °C in 10 min (Fig. 1C). While this level of reactivity is impressive, the methodology relies on a dichloromethane-based solvent system

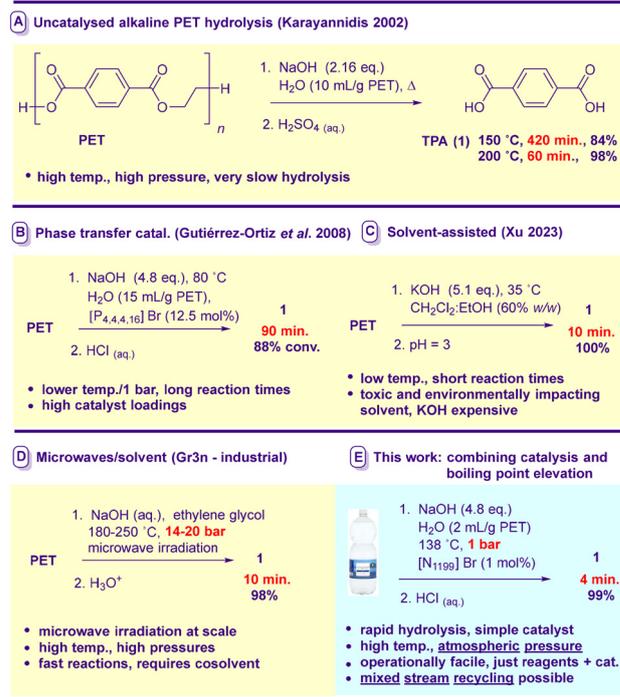


Fig. 1 Representative strategies for the alkaline hydrolysis of PET.

likely to be of toxicological<sup>23</sup> and environmental<sup>24</sup> concern at scale. Gr3n has achieved similarly rapid alkaline hydrolysis using a combination of ethylene glycol cosolvent and microwave irradiation at a high temperature and pressure (Fig. 1D).<sup>11a,18c</sup> The technology is currently at the pilot plant (60 kg PET h<sup>-1</sup>) stage; however, an agreement to build a 40 000 ton plant operational in 2027 has recently been announced.<sup>25</sup>

Given that it seems likely that future plastic recycling will have to be accomplished in the developing as well as the developed world, we were interested in the design of an operationally simple, minimal laboratory process for PET alkaline hydrolysis which still occurred on rapid timescales – ideally at atmospheric pressure without irradiation, cosolvents or mechanochemical assistance. We recently evaluated the performance of over 50 phase transfer catalysts in the hydrolysis of PET by NaOH at 90 °C.<sup>16k</sup> Catalyst-design guidelines were developed and dimethyl dialkylammonium halides emerged as an exceptional class of phase transfer agents for this process. Reactions however were prohibitively slow (1.5–3 h) for commercial use. Herein we report the unique combination of *ad hoc*-designed phase transfer catalysts (at low loadings) with alkaline aqueous solution boiling point elevation, which allows the complete hydrolysis of bottle waste PET in 4 min at 138 °C under atmospheric pressure using standard laboratory apparatus *without any cosolvent* (Fig. 1E). Extension to poly-BPA-carbonate plastic from compact disc (CD) waste and the selective isolation of monomers from an unprecedented hydrolysis of a PET/poly-(BPA carbonate) mixed-waste stream are also demonstrated.



Since it is well known that solutes increase the boiling point of aqueous solutions (sodium hydroxide is a particularly effective salt for this purpose<sup>26</sup>), the dearth of reports involving the exploitation of this phenomenon in PET alkaline hydrolysis is surprising.<sup>18e</sup> We posited that if sufficient boiling point elevation could be coupled with compatible and powerful phase-transfer catalysis, significantly accelerated depolymerisation could occur without the need for either cosolvents or high-pressure reactors. In preliminary studies we investigated the hydrolysis of PET flakes cut from waste beverage bottles purchased from a local supermarket (5 mm × 5 mm) using the same loading of NaOH as used previously (1 g NaOH/g PET, 4.8 eq.<sup>16k</sup>) but at a considerably higher concentration (*i.e.* from the more standard 10% w/v<sup>16k</sup> to ~50% w/v, Scheme 1) in the absence of catalysis.

At 90 °C after 15 min TPA (**1**) could be isolated after acidification in a low yield. However, at atmospheric pressure (non-sealed carousel glass vessel) the high hydroxide concentrations allowed hydrolysis to occur at temperatures considerably beyond 100 °C (see ESI, Table S1†). At the maximum we recorded under these conditions of 138 °C (note: the boiling temperature decreases from the maximum as the reaction progresses due to sodium hydroxide consumption and concomitant disodium terephthalate precipitation), formation of **1** was possible in 72% yield (Scheme 1, Table S1†).

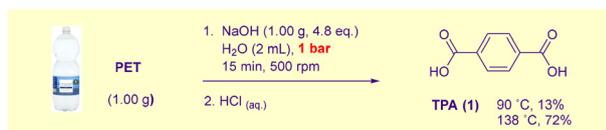
Our attention next turned to catalysis. Benzylated- and dimethyldialkylammonium halides have been identified as superior phase transfer catalyst classes for PET hydrolysis,<sup>16k</sup> so the most active members of these classes were evaluated under the reaction conditions outlined in Scheme 1 at 1 mol% loading. To both challenge the catalysts and facilitate comparisons, the reaction time was reduced to 10 min – on par with timescales associated with a microwave- and cosolvent-mediated, high-pressure current industrial process.<sup>11a,18c</sup> In the absence of a catalyst, *ca.* 50% yield is obtained (entry 1). The soluble dibutyldibenzyl ammonium salt **2** and its dihexyl analogue **3** (a highly efficacious catalyst at 90 °C under more dilute conditions<sup>16k</sup>) were largely ineffectual (entries 2 and 3). While the exchange of the bromide counterion for chloride (*i.e.* **4**, entry 4) made little difference, the presence of an extended p-system (*i.e.* **5–6**, entries 5 and 6) led to appreciable improvements in activity. Dimethyldialkylammonium salts, which are marginally superior to isomeric phase transfer catalysts under dilute conditions,<sup>16k</sup> distinguish themselves in ~50% NaOH. The diheptyl system **7** (entry 7) proved capable of significant activity, while its immediate homologues **8** and **9** mediated hydrolysis to either near or full completion (entries 8

and 9). Previously we had found **8** to be the most powerful promoter in 10% NaOH and that once higher homologues became insoluble in the reaction medium, progressively slower catalysis resulted as the catalyst chain size was increased.<sup>16k</sup> Intriguingly here **8–9** are insoluble, yet superior to the soluble **7**. Given that under these conditions catalyst insolubility was no longer a predictor of reduced activity, the higher homologues **10** and **11** were evaluated. The former species proved to be an active catalyst (entry 10), while the depolymerisation was clearly promoted more slowly by the larger **11** (entry 11). It is worth noting that the most active previously identified<sup>16k</sup> member of the *symmetrical* tetraalkylammonium halide catalyst family (*i.e.* **12**, entry 12) remains inferior to **8–10** here despite being a soluble, constitutional isomer of **10**.

To allow the relative performance of **8–10** to be more easily assessed, depolymerisation involving these catalysts was repeated with a 5 min reaction time (and an increase in the stirring speed to 1000 rpm to prevent excessive adherence of **1** to the PET flakes) – which allowed the superiority of **10** to be clearly identified (entries 13–15). Further experimentation revealed that a 4 min (note – this includes the ramp time required to heat from ambient temperature to 138 °C) reaction time is sufficient for essentially quantitative generation of **1** (entries 16 and 17). This is an unprecedented depolymerisation rate for a simple alkaline PET hydrolysis process without pressure, cosolvent or microwave irradiation. Without a catalyst, <30% yield of the product is obtained after 4 min (entry 18); however, the use of a 60% w/v NaOH solution (without altering the hydroxide loading) allows hydrolysis at 145 °C – under these conditions after 13 min the uncatalysed recycling is complete (entry 19). At these higher temperatures/concentrations, phase transfer catalysis is less effective (see ESI, Table S2†).

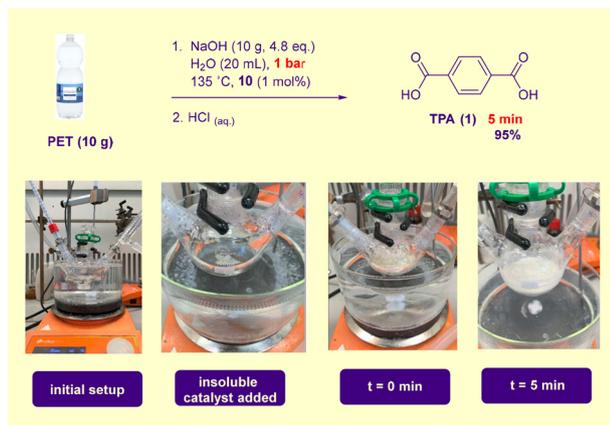
The superiority of the partially soluble **10** over the soluble **7** merits comment. Under dilute conditions, lipophilic soluble catalysts outperform insoluble homologues;<sup>16k</sup> however, the faster hydrolysis catalysed by **10** is ascribable to the physical contact with the PET flakes in the reaction vessel. PET is denser than water (1.4 g mL<sup>-1</sup>), and the phase transfer catalysts generally have densities <1 g mL<sup>-1</sup>. Under dilute conditions, insoluble phase transfer catalysts tend to accumulate at the top of the solvent, while PET sinks to the bottom, leading to reduced contact between the two even with vigorous stirring. The depolymerisation reported here occurs in 2 mL H<sub>2</sub>O per g PET. The plastic floats more easily on the denser ~50% NaOH solution alongside the insoluble catalyst, leading to improved surface contact. In addition, the solvent generally just covers the insoluble PET in the reaction vessel, so that any insoluble catalyst floating at the top of the solution remains in contact with the PET, especially at low conversions.

The depolymerisation was also carried out on a multigram scale using standard laboratory apparatus (Scheme 2). Heat transfer to a flask in an open oil bath was inferior to that associated with the carousel reactor, leading to increased ramp times. To obviate this problem (unlikely to be an issue using heated industrial reactors), PET was added to preheated aqueous NaOH. To avoid complications stemming from PET



**Scheme 1** Uncatalysed, atmospheric pressure PET alkaline hydrolysis using concentrated NaOH (50% w/v): influence of temperature.





Scheme 2 Multigram scale PET (bottle) waste hydrolysis.

addition at reflux, a marginally lower reaction temperature of 135 °C was selected. Otherwise, conditions were identical to those listed in Table 1. A 95% isolated yield of **1** was possible after 5 min. A drawback associated with this technology would be the requirement for lined reactors to avoid corrosion by the high-concentration alkaline solution. High concentration NaOH-mediated industrial PET hydrolysis processes have been described in the patent literature.<sup>11,18e</sup>

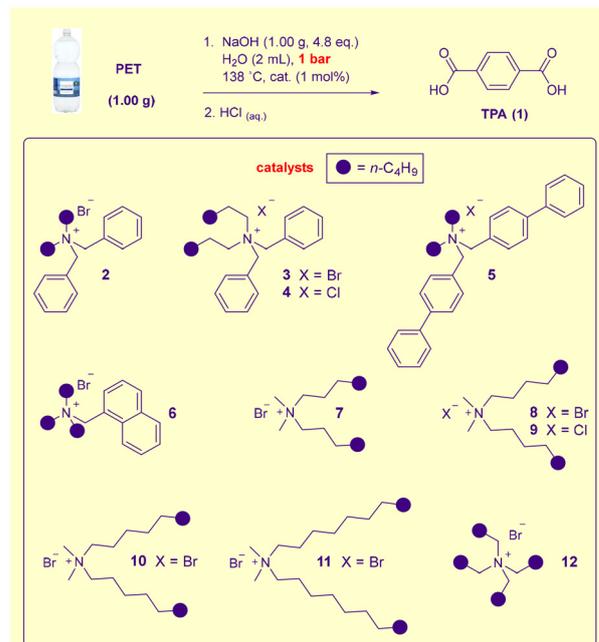
Catalyst recovery and reuse is possible in principle. After PET hydrolysis but before neutralisation, water was added to dissolve all disodium-TPA, followed by extraction of the catalyst with dichloromethane. The <sup>1</sup>H NMR spectrum of the recovered catalyst (99%) indicated that no decomposition had occurred – most likely due to the short reaction time. Reuse of the recovered catalyst in a subsequent PET hydrolysis allowed the isolation of TPA in 99.4% yield after 4 min (see the ESI†). It is clear that to be of use in an industrial process, the advantages associated with catalyst recovery would have to be balanced against the use of an organic extraction solvent (which itself would have to be recycled) – however, catalyst recovery and reuse do appear possible in principle at this juncture.

We have not recovered the ethylene glycol generated by the hydrolysis reaction by distillation – however, glycol and water do not form an azeotrope so recovery of this valuable (often overlooked) product from PET alkaline hydrolysis reaction is not problematic on an industrial scale.<sup>11b,18c,e</sup>

In terms of green chemistry metrics, the *E* factor (*E*), energy economy coefficient ( $\epsilon$ ), and environmental energy impact factor ( $\xi$ ) were calculated to be 2.09, 0.00179 C<sup>-1</sup> min<sup>-1</sup> and 1167.6 °C min respectively (see ESI†), comparable with the most sustainable values from the alkaline PET hydrolysis literature.<sup>8k,18d</sup> It is worth noting that in the calculation of these metrics, we did not factor NaCl electrolysis back to NaOH, ethylene glycol distillation or catalyst recovery – all of which are possible on a larger scale and would lead to superior process metrics overall.

Compared to the alkaline hydrolysis of PET from bottle waste, comparatively little is known regarding the corres-

Table 1 Phase transfer catalysed PET waste hydrolysis: catalyst evaluation



Entry	Cat.	Time (min)	Stirring <sup>a</sup> (rpm)	Cat. solubility <sup>b</sup>	Yield <sup>c</sup> (%)
1	None	10	500	—	51.4
2	<b>2</b>	10	500	Soluble	55.4
3	<b>3</b>	10	500	Soluble	57.8
4	<b>4</b>	10	500	Soluble	59.4
5	<b>5</b>	10	500	Insoluble solid	70.4
6	<b>6</b>	10	500	Insoluble oil	69.2
7	<b>7</b>	10	500	Soluble	89.2
8	<b>8</b>	10	500	Insoluble oil	99.9
9	<b>9</b>	10	500	Insoluble oil	98.1
10	<b>10</b>	10	500	Insoluble oil	98.5
11	<b>11</b>	10	500	Insoluble oil	58.6
12	<b>12</b>	10	500	Soluble	90.4
13	<b>8</b>	5	1000	Insoluble oil	90.2
14	<b>9</b>	5	1000	Insoluble oil	89.5
15	<b>10</b>	5	1000	Insoluble oil	99.9
16	<b>10</b>	4	1000	Insoluble oil	99.9
17	<b>10</b>	3.5	1000	Insoluble oil	96.7
18	None	4	1000	—	29.5
19 <sup>d</sup>	None	13	1000	—	99.9

<sup>a</sup> Revolutions per minute. <sup>b</sup> Refers to solubility under the reaction conditions at 138 °C. <sup>c</sup> Isolated yield. <sup>d</sup> 60% NaOH (w/v), 145 °C (the initial temperature at low conversion – the solution boiling point reduces as the hydroxide reacts due to precipitation of Na<sub>2</sub>TPA).

ponding depolymerisation of PET derived from textiles, despite textile production traditionally being the largest consumer of PET.<sup>27</sup> For example, a recent study reported >90% textile PET degradation in 3 h at 90 °C (10% NaOH), with full degradation in 24 h.<sup>28</sup> Under the previously established catalytic hydrolysis conditions (Table 2, entry 1), complete depolymerisation of PET textile waste was observed after 15 min. The longer reaction time is related to a physical issue: the more voluminous textile waste was not completely covered by the



**Table 2** Phase transfer catalysed PET (textile) hydrolysis

Entry	Time (min)	X (mL)	Yield <sup>a</sup> (%)
1	15	2	99.9
2	3	4	93.4
3	4	4	99.9

<sup>a</sup> Isolated yield.

concentrated aqueous solvent. If faster reaction times are required, the use of double the solvent provides quantitative yields in 4 min (entries 2 and 3).

We were next interested in the possibility of the rapid hydrolysis of a more challenging polymer. Poly(bisphenol A carbonate) (BPA-PC) is a high-strength hydrophobic thermoplastic used in (*inter alia*) safety goggles, headlights, computer casings, compact disks (CDs), window panes and safety paraphernalia.<sup>28</sup> Although controversial, there is concern regarding BPA-PC/BPA-PC-waste focused on the monomer constituent bis-phenol A (**13**) as an endocrine disrupting agent.<sup>29</sup> Advances in the chemical recycling of BPA-PC have proceeded along similar lines to those associated with PET,<sup>29</sup> with a major difference: BPA-PC is considerably more susceptible to the action of organic co-solvents. PET has been blended with BPA-PC to improve its resistance to organic solvents, while blending with BPA-PC can improve the impact strength and dimensional stability of PET.<sup>30</sup> Perhaps unsurprisingly, there has been a considerable focus on solvent-assisted hydrolytic depolymerisation of BPA-PC in the literature, where often com-

pletely recalcitrant base-mediated hydrolysis in water proceeds upon the addition of an organic cosolvent.<sup>31</sup> In the absence of cosolvents, hydrolysis of BPA-PC is difficult and, in addition, the product monomer **13** is prone to decomposition at high temperatures.<sup>28,32</sup> Achilles utilised microwave radiation to degrade waste BPA-PC in the presence of 1-hexadecyltrimethylammonium bromide as a phase transfer catalyst *via* alkaline hydrolysis (NaOH, 10% w/v). After 10 min at 150 °C (pressure = 4 bar), the polymer was 30% degraded, which increased to 95% degradation at 160 °C. No yield/characterisation of **13** was recorded and methanol was required to solubilise **13** and its degradation products isopropenyl phenol/*t*-butyl phenol/phenol so they could be separated from unreacted BPA-PC.<sup>33</sup>

Waste polycarbonate from CDs was pre-treated to remove the aluminum layer<sup>33</sup> cut into 2.5 mm squares and subjected to the standard hydrolysis conditions at 135 °C (Table 3). In the absence of a catalyst, BPA-PC is remarkably resistant to hydrolysis after 15 min of reaction time (entry 1). This would be attributable to the greater hydrophobicity and higher  $T_g$  (>140 °C) associated with this polymer relative to PET. Appreciable degradation occurs in the presence of 1 mol% of one of the catalysts **7**, **8** or **10**, with the dioctyl variant **8** proving superior (entries 2–4). Further optimisation allowed the formation of **13** in >90% yield after 30 min of reaction time using a 65% (w/v) NaOH solution (entries 5–8). The more concentrated solution permits the reaction at 145 °C – here depolymerisation with >90% yield requires only 20 min (entry 9).

Real-world waste streams usually comprise mixed plastic, which necessitates sorting by various means, including by density (PET = 1.4 g cm<sup>-3</sup>, BPA-PC = 1.2 g cm<sup>-3</sup>). There is therefore burgeoning interest in the chemolytic selective depolymerisation of mixed waste streams<sup>34</sup> involving the separation of 2 or more plastic types based on their relative rates of depolymerisation under a given set of conditions. Reports concerning glycolysis,<sup>35</sup> methanolysis<sup>36</sup> and reductions<sup>37</sup> have appeared.

**Table 3** Phase transfer catalysed BPA-PC (CD) hydrolysis: optimisation

Entry	Cat.	[NaOH] (% w/v)	Soln vol. <sup>a</sup> (mL)	Time (min)	Temp. <sup>b</sup> (°C)	Conversion <sup>c</sup> (%)	Yield <sup>d</sup> (%)
1	None	50	2	15	135	14.7	15.0 (14.8)
2	<b>7</b>	50	2	15	135	46.7	46.7 (46.6)
3	<b>8</b>	50	2	15	135	53.2	53.1 (53.2)
4	<b>10</b>	50	2	15	135	33.4	33.5 (33.4)
5	<b>8</b>	50	2	30	135	72.5	72.5 (72.3)
6	<b>8</b>	65	2	20	135	80.2	80.3 (80.0)
7	<b>8</b>	65	3	20	135	86.7	86.8 (86.5)
8	<b>8</b>	65	3	30	135	91.8	92.0 (91.6)
9	<b>8</b>	65	3	20	145	90.4	90.2 (90.2)

<sup>a</sup> Refers to the volume of H<sub>2</sub>O used in the sodium hydroxide solution. <sup>b</sup> Refers to the initial temperature at low conversion – the solution boiling point reduces as the hydroxide reacts due to precipitation of Na<sub>2</sub>BPA. <sup>c</sup> Calculated based on unreacted BPA-PC (see the ESI†). <sup>d</sup> Isolated yield. The value in parentheses is determined by <sup>1</sup>H NMR spectroscopy using 4-iodoanisole as an internal standard (see the ESI†).

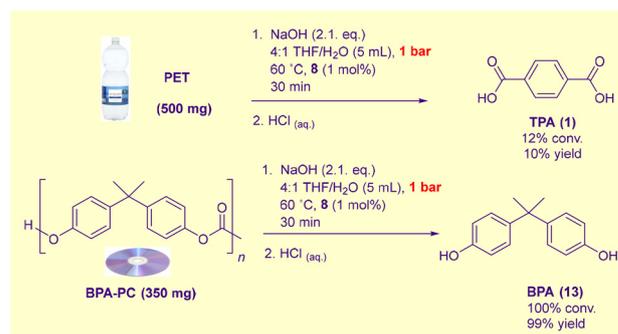


For instance, Dove *et al.*<sup>35a</sup> reported an elegant organocatalytic solution for the selective depolymerisation of BPA-PC in the presence of PET and a triol at 130 °C in under 1 h. The unreacted PET could then be removed by filtration and depolymerised at a higher temperature. Wang and coworkers<sup>36b</sup> developed an efficient ‘one pot’ depolymerisation of BPA-PC-PET by Zn(HMDS)<sub>2</sub>-catalysed methanolysis for 15 h at 100 °C involving complete destruction of both plastics followed by selective monomer isolation: washing with cold methanol allowed **13** (97%) to be separated from the soluble dimethyl terephthalate PET-derived methanolysed product (90%, which could be concentrated *in vacuo*) by filtration.

To the best of our knowledge, no hydrolytic methodology for the depolymerisation of PET-based mixed streams has been reported. Given the smooth degradation of both polymers under the concentrated conditions described above, we envisaged a ‘one pot’ catalytic alkaline hydrolysis process involving rapid depolymerisation of a BPA-PC/PET mixture to Na<sub>2</sub>-TPA and Na<sub>2</sub>-BPA, followed by pH-driven selective protonolysis to allow the sequential precipitation and isolation of the hydrophobic monomers **13** and **1**.

Accordingly, equimolar amounts of PET bottle and BPA-PC CD waste were hydrolysed catalysed by **8** (1 mol%) at 145 °C using 65% (w/v) NaOH at atmospheric pressure (Scheme 3). Cleavage of all ester and carbonate moieties was complete in 30 min. In contrast to methods involving organic solvents – where PC-PBA is the more reactive polymer<sup>35</sup> – here PET is hydrolysed first in a matter of minutes, followed by degradation of BPA-PC. Upon completion of the reaction, the addition of water and adjustment of the pH to 7.9 resulted in the precipitation of pure **13** in 90% yield, which was removed by filtration. Notably, no decomposition of **13** was observed. The filtrate was subsequently acidified to pH 2.0, allowing the precipitation of **1** in near quantitative yields. The TPA monomer contained 0.1% **13**. If required, this can be removed by washing with a small amount of ethanol (recoverable by distillation).

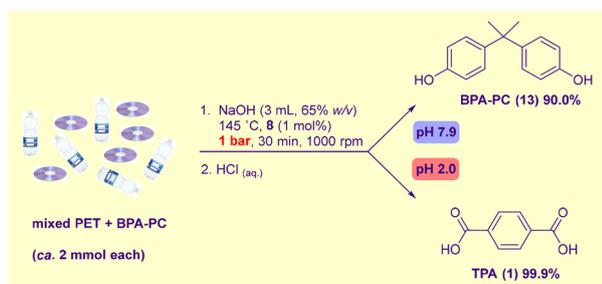
The relative reactivity of PET and BPA-PC waste under these conditions is intriguing in light of the known superior susceptibility of BPA-PC to glycolysis.<sup>35a</sup> We suspected that the switch in the order of reactivity towards alkaline hydrolysis was related to the hydrophobicity of BPA-PC in the absence of



**Scheme 4** Hydrolysis of PET and BPA-PC in a predominantly organic medium.

organic solvents. To test this hypothesis, both PET and BPA-PC waste were separately hydrolysed in the presence of minimal hydroxide in a 4 : 1 THF : H<sub>2</sub>O medium (Scheme 4). In this predominantly organic solvent, the reactivity order one would anticipate from Sardon and Dove’s study<sup>35a</sup> was restored: BPA-PC was completely hydrolysed after 30 min at 60 °C, whereas PET was largely resistant.

In summary, the rapid, operationally facile alkaline hydrolysis of PET and BPA-PC waste is possible at atmospheric pressure. The power of phase transfer catalysis has been used to magnify rate accelerations due to boiling point elevation in highly concentrated NaOH solutions of 50–65% w/v to allow the complete depolymerisation of PET in ≤5 min and BPA-PC in 20 min – timescales either similar to or shorter than those more usually associated with reactions involving either microwave irradiation or the use of organic cosolvents. The phase transfer catalysts were selected from the recently identified lipophilic dimethyldialkylammonium halide class of particular utility in chaperoning anions to the polymer surface.<sup>16k,38</sup> It is worth noting that this has been accomplished without increasing the loading of NaOH (and hence saline waste after neutralisation) relative to typical PET hydrolysis processes in the literature. In this regard, the recent electrochemical recovery of NaOH from the generated saline by Gr3N in their industrial process is an interesting avenue for future development. The first hydrolytic recycling of a mixed stream of PET and BPA-PC could be accomplished in 30 min without the involvement of bulk organic solvents in either the depolymerisation or product isolation steps. It is hoped that this operationally facile proof-of-concept hydrolysis methodology, which is devoid of complications stemming from expensive/environmentally impacting solvents, microwave irradiation or high pressures at scale, could enable the future development of globally applicable chemical recycling of hydrolytically susceptible polymer waste.



**Scheme 3** Mixed stream PET/BPA-PC waste hydrolysis and selective precipitation.

## Data availability

The data supporting this article have been included as part of the ESI.†



## Conflicts of interest

There are no conflicts to declare.

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