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## Effect of a phase transfer catalyst structure on the alkaline hydrolysis of poly(ethylene terephthalate)†

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**A systematic investigation into the factors which influence catalytic activity in 50 simple (mostly) quaternary ammonium- and phosphonium halide catalysts for the hydrolysis of poly(ethylene terephthalate) has revealed the most efficacious constitutional isomer class and the optimum properties these catalysts should possess. General guidelines for catalyst design are provided.**

It has been estimated that from 1950 to 2015,  $6.3 \times 10^{12}$  kg of plastics have been synthesised – with a recycle rate of just *ca.* 9%. Without intervention, by 2050,  $12 \times 10^{13}$  kg of these polymers will either be in landfill or out polluting the natural world;<sup>1</sup> therefore (until replacement of traditional plastics with sustainable materials is widespread) improvement in both the rate and efficiency of recycling is needed to reduce both the dependence on oil-derived virgin plastic and the contribution its synthesis/disposal makes to the current climatological and ecological emergency.

Poly(ethylene terephthalate) (PET) polyester is a major constituent in certain beverage bottles, textile fibres and food tray/pharmaceutical packaging, which in 2021 accounted for 12% of worldwide solid waste.<sup>2</sup> Of the commonly bulk-manufactured plastics, PET has the highest greenhouse gas (GHG) emissions associated with its production (up to 4.5 kg GHG per kg PET)<sup>3,4</sup> yet it is one of the most amenable for various ‘recycling’ methodologies – which can be broadly categorised as either incineration or mechanical or chemical recycling. Incineration solves the landfill problem and can recover energy from the materials but it has been determined after a recent study<sup>5</sup> by the European Commission’s Joint Research Centre that it is less preferable from a climate change impact perspective. Mechanical recycling is operationally more facile, yet amplifies existing degradation and produces recycled PET of lower value and quality unless complex, more resource

intensive superclean methodologies are utilised,<sup>3,6,7</sup> while chemical recycling *via* depolymerisation requires efficient chemical processes on large scale (frequently at high temperatures);<sup>7</sup> however it can produce pure monomers which can be repolymerised to pristine PET for any application, thereby reducing reliance on fossil fuel-derived virgin PET.<sup>3,7</sup> In addition, in the case of PET, a recent analysis found that CO<sub>2</sub> emission saving at end of life treatment is considerably lower for chemical recycling than for mechanical recycling.<sup>3</sup> Chemical recycling methodologies include (*inter alia*) aminolysis, alcoholysis, glycolysis and hydrolysis.<sup>8</sup> A particularly attractive potential PET recycling methodology is alkaline hydrolysis in the presence of a phase transfer catalyst (PTC). This has the advantages of lower reaction temperatures (typically 80–100 °C) than those required by neutral hydrolysis and less contamination by oligomers or decomposition of ethylene glycol using either neutral or acidic hydrolysis, respectively.<sup>8</sup>

While phase transfer catalysis<sup>9</sup> of alkaline PET hydrolysis to form (after acidic workup) terephthalic acid is known for over two decades,<sup>8</sup> the PTC characteristics required to bring about efficient promotion of the process are poorly understood. Attempts to elucidate a consensus model of the contributors to catalytic activity are confounded by studies using different catalysts, loadings (1–100 mol%), PET sources, particle sizes, temperatures, stirring speeds, NaOH stoichiometry, NaOH concentrations,<sup>10–17</sup> microwave-radiation<sup>18</sup> and ultrasound.<sup>19,20</sup> For instance, tetrabutylammonium iodide (TBAI) has been reported as an active catalyst in one study<sup>19</sup> at 1 mol% loading (no control experiment without a catalyst reported), while its bromide analogue has been reported as completely inactive in another study at 24 mol% loadings (conversion identical to that of the control).<sup>12</sup> Both studies used similar PET sources and very small particle sizes (*ca.* 0.25 mm), but different reaction temperatures and NaOH concentration/loadings. The latter study identified the large, water-insoluble tributylhexadecylphosphonium bromide as the optimal catalyst.<sup>12</sup>

The non-PET hydrolysis literature offers clues regarding ideal catalyst attributes but not conclusions – Herriot *et al.*<sup>21</sup>

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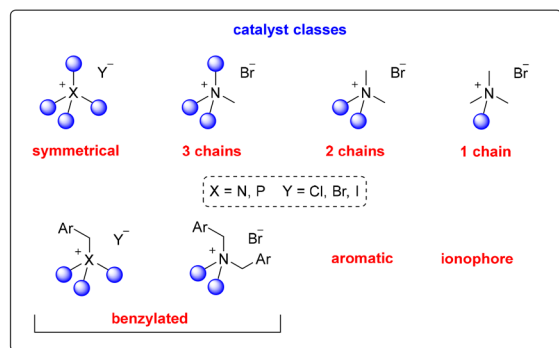
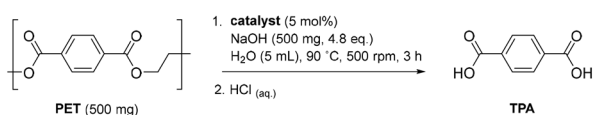
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found that larger symmetrical cations outperformed catalysts with one long chain in an  $S_N2$  reaction in benzene/water catalysed by ammonium and phosphonium PTCs, while earlier Starks<sup>9c</sup> had warned that ammonium PTCs were poor overall promoters of alkaline ester hydrolysis if the ester incorporated a long chain, including when using poly(methyl acrylate) as a substrate.

Herein we report the results of investigations aimed at shedding light on the contribution of the structural features of simple quaternary phosphonium- and ammonium-based PTCs to the catalytic activity in the alkaline hydrolysis of PET under conditions that we considered might prove a useful starting point from which a later real-world recycling process might be developed by others: *i.e.* 500 mg of PET flakes of larger size (*ca.* 5 mm square – consistent with the output from mechanical PET recycling facilities) cut from colourless water bottles purchased locally at a large supermarket chain, relatively low NaOH loadings and water usage (500 mg NaOH dissolved in 5 mL HPLC H<sub>2</sub>O – *ca.* 10 wt%, 4.8 eq.), 90 °C and 500 rpm stirring speed. Catalysts were utilised at 5 mol% loading. TPA was isolated, with high purity by NMR spectroscopy, after protonation (see the ESI<sup>†</sup>) of disodium terephthalate with HCl (aq.); however to avoid any possibility of yield data being compromised by the presence of oligomers (which could confound analysis), an internal standard (4-iodoanisole) was added after the reaction so that accurate yields could be determined by <sup>1</sup>H NMR spectroscopy. An *ad hoc* catalyst classification system to allow facile comparison of data was decided upon at the outset – catalysts were classified as being symmetrical, 3 chained (*i.e.* one methyl group), 2 chained (*i.e.* 2 methyl groups), 1 chained, benzylated, aromatic or ionophoric (generic structures not shown). The catalyst classes and standardised conditions under which they were evaluated are depicted in Scheme 1.

The investigation commenced with an examination of symmetrical catalysts (Table 1). To facilitate catalyst comparisons from a lipophilicity standpoint, only hydrocarbon substituents



**Scheme 1** Standardised conditions utilised in the PTC-catalysed alkaline PET hydrolysis and the catalyst classes employed.

**Table 1** Alkaline hydrolysis of PET catalysed by symmetrical PTCs<sup>a</sup>

Entry	Catalyst	No. of carbon atoms	Solubility under reaction conditions	Yield <sup>b</sup> (%)
1	None	0	—	4.2
2 <sup>c</sup>	None	0	—	3.9
3	<b>1</b>	4	Soluble	3.2
4	<b>2</b>	4	Soluble	3.7
5	<b>3</b>	16	Soluble	49.4
6	<b>4</b>	16	Soluble	32.2
7	<b>5</b>	16	Soluble	31.8
8	<b>6</b>	16	Soluble	30.4
9	<b>7</b>	20	Finely dispersed	67.8
10	<b>8</b>	24	Insoluble	47.1
11	<b>9</b>	32	Insoluble	37.6
12	<b>10</b>	32	Insoluble	38.8

<sup>a</sup> Reaction conditions as outlined in Scheme 1. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy using 4-iodoanisole as an internal standard. <sup>c</sup> Repeat of the experiment outlined in entry 1.

were utilised and the number of carbon atoms in each catalyst is also provided. In the absence of any PTC, very low product yields of 4% were reproducibly obtained (entries 1 and 2). Tetramethylphosphonium- and ammonium salts **1–2** (entries 3 and 4) appear to moderately inhibit hydrolysis; however the commonplace water-soluble tetrabutylphosphonium-<sup>21,22</sup> and ammonium salts **3–6** exhibited appreciable activity (entries 5–8). The more lipophilic **3** considerably outperformed its ammonium variants **4–6**, while variation of the anionic component had – as expected – little influence on the outcome once the catalyst was soluble in the reaction medium. The tetrabutyl homologue **7** exhibited interesting behaviour: it was partially soluble in the reaction medium and the undissolved portion was very finely dispersed. This catalyst promoted the reaction with considerably superior efficacy to the tetrabutyl analogue **5** (entry 9). Further chain extension led to increasing levels of insolubility (note: hereafter ‘insoluble’ is used as an *ad hoc* term meaning that the catalyst forms a discrete aggregated phase under the reaction conditions (5 mol% cat., 90 °C, 5 mL H<sub>2</sub>O, 500 mg NaOH) – this is not meant to imply that that no fraction of that catalyst is soluble in the reaction medium) and diminished yields (*i.e.* **9–10**, entries 10–12).



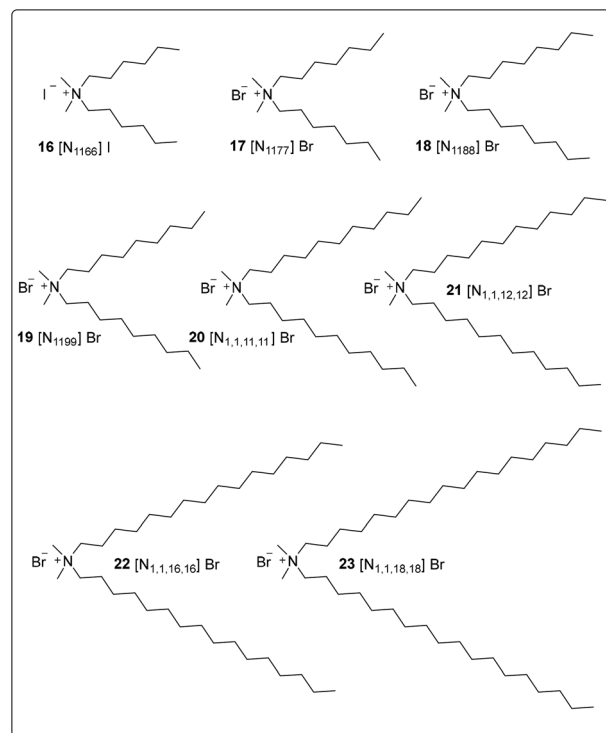
The evaluation of catalysts characterised by 3 longer chains is outlined in Table 2. The tripentylmethylammonium species **11** facilitated the formation of **2** in appreciable yield (entry 1). The partially soluble, finely dispersed homologue **12** is capable of marginally greater activity (entry 2) – however as observed earlier (*vide supra*), lipophilicity could not thereafter be increased to advantage (*i.e.* **13–15**, entries 3–5).

The two-chain catalyst class was the most useful and instructive (Table 3). The soluble catalyst **16** possesses only 14 carbon atoms, yet could facilitate hydrolysis with >40% yield (entry 1) – considerably greater than that associated with the use of the 16-carbon symmetrical material **5** (compared to Table 1, entry 7). Augmentation of each longer chain by one methylene unit (*i.e.* **17**, entry 2) resulted in a soluble catalyst with 16-carbon atoms and strikingly improved efficacy superior to that associated with any catalyst hitherto evaluated.

Most interestingly, further elongation of the 2 chains by a methylene unit (*i.e.* catalyst **18**, entry 3) resulted in a finely dispersed system and a reduction in performance. As mentioned before, once a design change led to catalyst insolubility without fine dispersion under the reaction conditions, efficacy declined and all further chain elongations resulted in decreasingly active catalysts (*i.e.* **19–23**, entries 4–8).

Single long-chain quaternary ammonium salts (Table 4) proved relatively ineffectual as catalysts, whether soluble or not (*i.e.* **24–27**, entries 1–4). Furthermore, these catalysts gave rise to emulsions which complicate the isolation of **2**. The phosphonium salts **28** and **29** are included here and mediate hydrolysis with moderate efficacy (superior to that associated with **24–27**, entries 4–6). These catalysts possess one chain longer than the others, yet their ‘small’ substituents are of 4–6 carbon

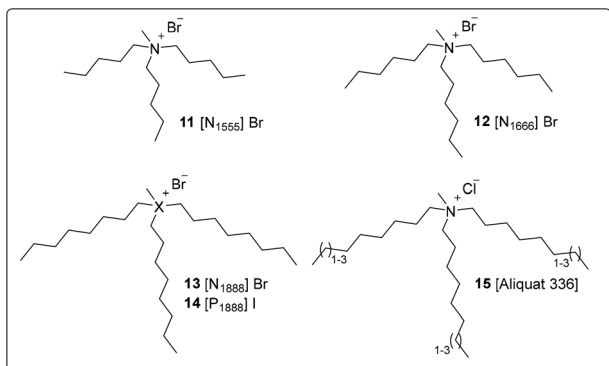
**Table 3** Alkaline hydrolysis of PET catalysed by 2-chain PTCs<sup>a</sup>



Entry	Catalyst	No. of carbon atoms	Solubility under reaction conditions	Yield <sup>b</sup> (%)
1	<b>16</b>	14	Soluble	41.1
2	<b>17</b>	16	Soluble	81.9
3	<b>18</b>	18	Finely dispersed	70.6
4	<b>19</b>	20	Insoluble	57.6
5	<b>20</b>	24	Insoluble	49.8
6	<b>21</b>	26	Insoluble	42.0
7	<b>22</b>	34	Insoluble	33.3
8	<b>23</b>	38	Insoluble	31.3

<sup>a</sup> Reaction conditions as outlined in Scheme 1. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy using 4-iodoanisole as an internal standard.

**Table 2** Alkaline hydrolysis of PET catalysed by 3-chain PTCs<sup>a</sup>



Entry	Catalyst	No. of carbon atoms	Solubility under reaction conditions	Yield <sup>b</sup> (%)
1	<b>11</b>	16	Soluble	56.4
2	<b>12</b>	19	Finely dispersed	59.0
3	<b>13</b>	25	Insoluble	55.5
4	<b>14</b>	25	Insoluble	43.7
5	<b>15</b>	25–31	Insoluble	27.6

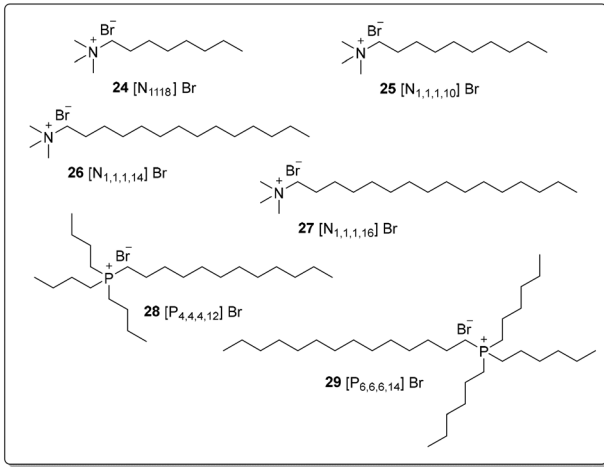
<sup>a</sup> Reaction conditions as outlined in Scheme 1. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy using 4-iodoanisole as an internal standard.

atoms in length. Hence they can be seen as a hybrid of single-chain (Table 4) and mid-sized symmetrical systems (*e.g.* **3**, Table 1) – which would correlate well with the levels of activity observed. From this perspective, the longer chain does not show greater contribution to efficacy than the shorter substituents – and it is noteworthy that adherence of the PET flakes to each other was observed in both experiments.

Catalysts incorporating benzyl (or similar) units were next examined (Table 5). These were hypothesised – *a priori* – to be of promise due to the potential for attractive  $\pi$ -stacking interactions with the polymer. Parikh *et al.*<sup>11</sup> reported that benzalkonium chloride outperformed aliphatic (albeit relatively hydrophilic) tetraalkylammonium salts in the alkaline hydrolysis of PET; however we are unaware of any systematic study regarding the influence of this group on the catalytic activity.

The small and soluble trimethylbenzyl ammonium salt **30** and its triethyl homologue **31** – the first PTC to be intensively



Table 4 Alkaline hydrolysis of PET catalysed by 1-chain PTCs<sup>a</sup>


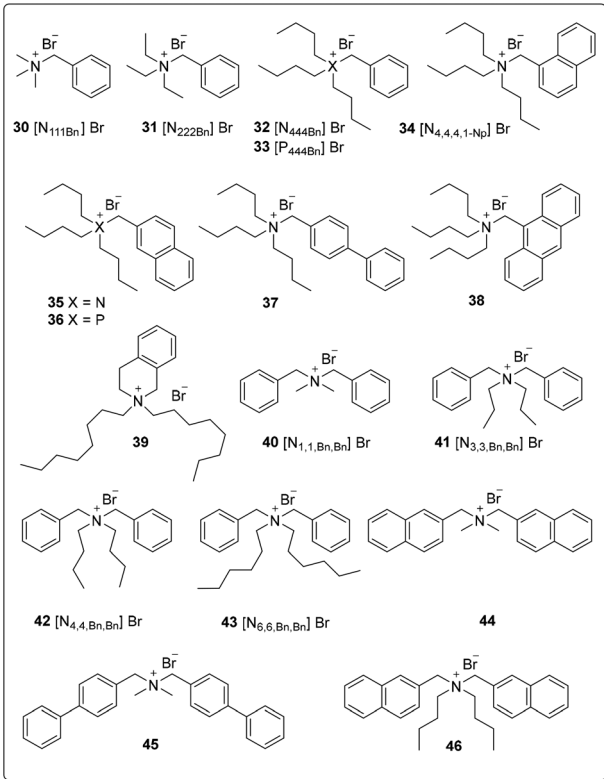
Chemical structures of 1-chain PTCs 24-29 are shown. 24 is a trimethylammonium salt with an 11-carbon chain. 25 is a trimethylammonium salt with a 13-carbon chain. 26 is a trimethylammonium salt with a 17-carbon chain. 27 is a trimethylammonium salt with a 19-carbon chain. 28 is a phosphonium salt with a 24-carbon chain. 29 is a phosphonium salt with a 32-carbon chain.

Entry	Catalyst	No. of carbon atoms	Solubility under reaction conditions	Yield <sup>b</sup> (%)
1 <sup>c</sup>	24	11	Soluble	17.1
2 <sup>c</sup>	25	13	Soluble	26.9
3 <sup>c</sup>	26	17	Soluble	32.8
4 <sup>c</sup>	27	19	Soluble	29.7
5 <sup>d</sup>	28	24	Insoluble	42.9
6 <sup>d</sup>	29	32	Insoluble	53.4

<sup>a</sup> Reaction conditions as outlined in Scheme 1. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy using 4-iodoanisole as an internal standard. <sup>c</sup> Formation of an emulsion as the reaction progressed was observed. <sup>d</sup> Severe adherence of the PET flakes to each other was observed.

studied<sup>9b,23</sup> – (entries 1 and 2) exhibited little activity under these conditions. The considerably more lipophilic ammonium salt **32** was shown to be a more suitable catalyst (entry 3), while its phosphonium variant **33** decomposed (entry 4). Extension of the  $\pi$ -system was generally advantageous (*i.e.* catalysts **34–38** entries 5 and 6) unless either a phosphonium salt (entry 7) or an anthracene unit (entry 9) was involved. An interesting phenomenon was observed here: catalysts of increasing size no longer immediately became less active when insoluble. For instance, both the insoluble naphthyl-substituted catalysts **34** and **35** show improvements compared to the soluble, benzyl analogue **32** (entries 3, 5 and 6). It is clear that the introduction of aromatic substituents changes the behaviour of these systems relative to aliphatic analogues. The dioctylisoquinolinium salt **39** (entry 10) was a moderately effective catalyst which lacked the activity of simpler systems mentioned above – so investigations along these lines were halted and attention switched to novel dibenzylated systems.

As expected, the small, soluble salt **40** did not excel as a catalyst (entry 11); however its dipropyl- and dibutyl-analogues (**41** and **42**, entries 12 and 13, respectively) showed significant improvements. Once again, the immediate penalty paid from an efficiency standpoint when catalysts in previous classes became wholly insoluble in the reaction medium is not of the same magnitude in this class of promoters – as can be seen

Table 5 Alkaline hydrolysis of PET catalysed by benzylated PTCs<sup>a</sup>


Chemical structures of benzylated PTCs 30-46 are shown. 30-34 are ammonium salts with various aromatic substituents. 35 and 36 are phosphonium salts with N and P respectively. 37-39 are phosphonium salts with various aromatic substituents. 40-46 are ammonium salts with various aromatic substituents.

Entry	Catalyst	No. of carbon atoms	Solubility under reaction conditions	Yield <sup>b</sup> (%)
1	30	10	Soluble	5.6
2	31	13	Soluble	8.8
3	32	19	Soluble	43.6
4	33 <sup>c</sup>	19	Soluble	19.7
5	34	23	Insoluble	75.9
6	35	23	Insoluble	68.7
7	36 <sup>c</sup>	23	Insoluble	14.6
8	37	25	Insoluble	57.7
9	38	27	Insoluble	19.2
10	39	25	Insoluble	40.5
11	40	16	Soluble	18.9
12	41	20	Soluble	33.4
13	42	22	Soluble	47.5
14	43 <sup>c</sup>	26	Insoluble	81.4
15	44 <sup>c</sup>	24	Insoluble	53.3
16	45	28	Soluble	39.2
17	46	30	Insoluble	60.5

<sup>a</sup> Reaction conditions as outlined in Scheme 1. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy using 4-iodoanisole as an internal standard. <sup>c</sup> Catalyst decomposition.

from the impressive performance of the insoluble **43** (entry 14). *Bis*-naphthyl/*bis*-biphenyl analogues of **40** and **42** (*i.e.* **44–46**, entries 15–17) proved to be serviceable catalysts, yet all were inferior to **43**.

The evaluation of miscellaneous systems is outlined in Table 6. The simple trimethylanilinium species **47** showed little activity (entry 1) while both pyridinium salts **48** and **49** and the tetraphenylphosphonium salt **50** decomposed (entries



Table 6 Aromatic- and ionophore-based catalysts<sup>a</sup>

Entry	Catalyst	No. of carbon atoms	Solubility under reaction conditions	Yield <sup>b</sup> (%)
1	47	9	soluble	7.0
2	48 <sup>c</sup>	6	soluble	4.1
3	49 <sup>c</sup>	13	insoluble	14.0
4	50 <sup>c</sup>	24	insoluble	6.5
5	51	10	soluble	5.3

<sup>a</sup> Reaction conditions as outlined in Scheme 1. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy using 4-iodoanisole as an internal standard. <sup>c</sup> Catalyst decomposition.

2–4). The ionophore **51** – an efficient binder of Na cations – was also inactive, which strongly indicates that effective delivery of the hydroxide anion to the PET surface is the most important for catalyst competency and not effects stemming from the metal cation.

Analysis of these data allows conclusions to be drawn, which may be useful to those interested in designing simple ammonium- or phosphonium-based catalysts for alkaline PET hydrolysis.

1. In simple aliphatic systems, catalyst performance is maximised when the catalyst is as lipophilic as possible while being either soluble or finely dispersed (cloudy solution) in the reaction medium (Fig. 1). This avoids a triphasic catalysis scenario and explains why seemingly very small structural changes to the most lipophilic soluble/finely dispersed systems can lead to dramatic losses of activity (*e.g.* compare the activities of **16** and **18** to that of **17**, and the activities of **5** and **8** to that of **7**). It may also account for the discrepancies in literature data – comparing studies using different loadings, reaction temperatures and NaOH concentrations is likely to evaluate catalysts under very different conditions *vis a vis* catalyst solubility.

2. Once an aliphatic catalyst is insoluble and aggregating under the reaction conditions, a further increase in catalyst lipophilicity is deleterious to its activity (*e.g.* compare **18** to **21** and **8** to **10**; also the more lipophilic phosphonium salt **3** is superior to the less lipophilic ammonium salt **5** (both soluble), yet the phosphonium salt **9** is marginally inferior to **10** – as both are insoluble). This would imply that either the majority of the catalysis is carried out by that mole fraction of the catalyst present in aqueous solution, or that bigger, insoluble catalysts are incrementally less able to extract hydrox-

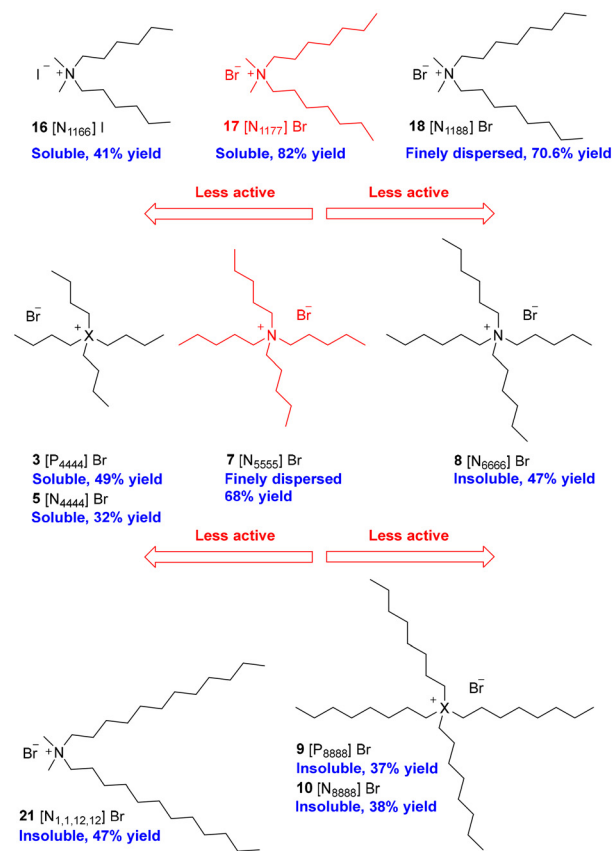


Fig. 1 Effect of increasing lipophilicity on the performance.

ide from aqueous solution into the liquid phase comprising the insoluble catalyst itself and deliver it to the surface of the also insoluble PET, or both.

3. In terms of simple aliphatic catalyst structures, a 2-chain structure is clearly a superior design template. 3-Chain systems are the next most generally favourable, followed by symmetrical systems; while one-chain systems are particularly ill-suited to the task (*e.g.* compare the activities of the 16-carbon atom, soluble ammonium catalysts **17**, **11** and **5** with both each other and the 17 carbon atom-containing catalyst **26**). We would suggest that the 2-chain systems evaluated represent an advantageous balance between being able to deliver coordinated hydroxide to the ester carbonyl being attacked (facilitated by a small hydrophilic 'head' unlikely to cause significant steric hindrance) and the ability to associate with the PET surface through van der Waals attractive forces between the hydrophobic polymer and the two long aliphatic catalyst chains.

4. Benzylated catalysts obey these rules when soluble; however the insoluble catalysts **34**, **35**, **43** and **46** aggregate under the reaction conditions, yet exhibit unexpectedly high catalytic activity. It is also interesting to note that the 16 carbon debenzylated species **40** is less active than **17**, **11** or **15**. These observations, coupled with the general improvement in catalyst performance as the  $\pi$ -system is extended (Table 5),



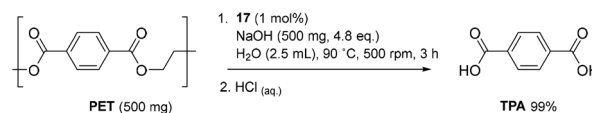
lead to the conclusion that these systems may behave differently from simple aliphatic analogues when aggregated and thus warrant further investigation.

5. Benzylated phosphonium salts are unsuitable under these reactions due to catalyst decomposition.

Conclusion 1 (*vide supra*) predicts that if the solubility of an active, soluble catalyst is reduced to the point of heterogeneity, that activity would be negatively impacted, while the opposite would be expected if an active, finely dispersed catalyst is rendered soluble. To test this, the insoluble iodide variant of the highly active, soluble catalyst **17** (*i.e.* **52**) and the soluble chloride analogue of the less active finely dispersed homologue **18** (*i.e.* **53**) were synthesised and evaluated (Table 7). The heterogeneous iodide **52** proved markedly inferior to **17** (entries 1 and 2) while the soluble, more lipophilic cation containing (than **17**) catalyst **53** accelerated the PET depolymerisation more efficiently than all other catalysts evaluated in this study (entries 3 and 4).

Finally, since the reaction is heterogeneous and the flakes relatively large (relative to powders), we reasoned that the simple adaptation of reducing the volume of water in the reaction by 50% would bring about significant improvements in efficacy – as both hydroxide/catalyst concentration would be doubled while the PET flakes would be in contact with a greater proportion of the bulk solution – and the reaction would generate less aqueous waste. Accordingly, we repeated the standard PET hydrolysis with half the volume of aqueous solvent and with only 1 mol% of the benchmark bromide catalyst **17**. The result was the isolation of TPA in near quantitative yield after 3 h (Scheme 2).

In summary, the first systematic investigation into the influence of the structure on activity in simple quaternary ammonium- and phosphonium-based catalytic systems for alkaline PET hydrolysis has revealed that catalysts incorporating 2 longer aliphatic chains and a smaller hydrophilic cation generally outperform other constitutional isomers. Optimum catalysts were as lipophilic as possible while either remaining



**Scheme 2** PET hydrolysis catalysed by **17** under concentrated conditions.

soluble under the reaction conditions or being finely dispersed. Once a catalyst is insoluble and aggregating, a further increase in lipophilicity is deleterious – as are reductions in lipophilicity if the catalyst is soluble. Benzylated catalysts exhibited interesting behaviour which may indicate that  $\pi$ -stacking can allow largely insoluble ammonium salts to possess considerable activity. After evaluation of over 50 catalytic systems, a picture emerged in which it is perhaps unwise to search for a ‘universal’ optimum catalyst for the acceleration of alkaline PET hydrolysis, but rather that the practitioner should design the catalyst and the reaction conditions together – as the solutes in the aqueous medium and the reaction temperature will alter the ability of the medium to solubilise the catalyst – with dramatic consequences regarding catalyst efficacy. While a given catalyst for one set of conditions may prove optimal, alteration of those conditions may shift the solubility equilibrium such that a larger or smaller homologue of the original catalyst may be better suited. Other factors such as the PET source and particle size are no doubt also similarly relevant. Further investigations along these lines are underway.

## Data availability

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

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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**Table 7** Manipulation of catalyst solubility and activity *via* the halide counterion<sup>a</sup>

Entry	Catalyst	No. of carbon atoms	Solubility under reaction conditions	Yield <sup>b</sup> (%)
1	<b>17</b> <sup>c</sup>	16	Soluble	81.9
2	<b>52</b>	16	Insoluble	58.4
3	<b>18</b> <sup>c</sup>	18	Finely dispersed	70.6
4	<b>53</b>	18	Soluble	88.9

<sup>a</sup> Reaction conditions as outlined in Scheme 1. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy using 4-iodoanisole as an internal standard. <sup>c</sup> Data from Table 3.



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