



Cite this: *Polym. Chem.*, 2019, **10**, 172

Organocatalysis for depolymerisation

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Polymeric materials have been accumulating in the environment for decades as a result of the linear way of consuming plastics. Unfortunately, the current approaches followed to treat such a large amount of plastic waste, mainly involving physical recycling or pyrolysis, are not efficient enough. Recently, chemical degradation has emerged as a long-term strategy towards reaching completely sustainable cycles where plastics are polymerised, depolymerised, and then re-polymerised with minimal changes in their quantity or final properties. Organocatalysts, which are promising “green” substitutes for traditional organometallic complexes, are able to catalyse depolymerisation reactions yielding highly pure small molecules that are adequate for subsequent polymerisations or other uses. Moreover, by varying several reaction parameters (e.g. solvent, temperature, concentration, co-catalyst, etc.), the depolymerisation products can be tuned in innumerable possibilities, which further evidences the versatility of depolymerisation. In this review, we highlight the recent advances made by applying organocatalysts, such as organic bases, organic acids, and ionic compounds, to chemically degrade the most commonly used commercial polymers. Indeed, organocatalysis is envisaged as a promising tool to reach a circular and environmentally friendly plastic economy.

Received 3rd September 2018,
Accepted 17th October 2018

DOI: 10.1039/c8py01284a

rsc.li/polymers

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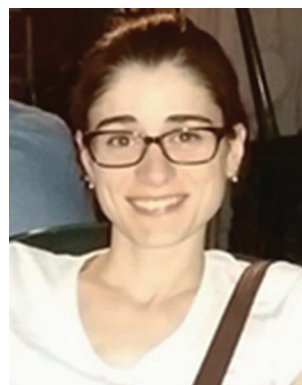
Introduction

Polymers have become ubiquitous materials in our daily life on account of their low cost production and safety combined with their remarkable functional properties. Many of the materials that we use, however, have extremely short lifetimes and are commonly limited to a single use. Consequently, plastic waste



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has been accumulating in the environment for years, and it is only very recently that this linear way of consuming plastics has raised concerns. Hence, the treatment of plastic waste, which is a global societal and environmental problem, requires innovative solutions to sort, degrade, and re-process these materials.

Despite economic and environmental incentives to promote plastic waste treatment, current alternatives are very limited. The Ellen MacArthur foundation recently suggested three different strategies for a sustainable plastic packaging economy based on (i) reusing 20% of the packaging items in the long-term; (ii) re-designing 30% of them; and (iii) recycling the remaining 50%.¹ This last category mainly concerns the most commonly used plastics, such as polyethylene (PE), polyesters, polycarbonates, or polyurethanes. Currently, only 14% of these polymers are being recycled, mostly by mechanical methods that involve grinding and re-processing of the material into low-value plastic products. The inferior properties of the resulting material compared to the initial polymer has been cited as “downcycling”, referring to loss of strength, chemical or food contamination, discoloration, or decrease in molecular weight, for example.² Another approach for treating post-consumed plastics relies on their direct conversion into high calorific value fuels through pyrolysis, a treatment that requires elevated pressure and temperature. However, this thermal degradation only postpones their unsustainable end-of-life since the resulting combustible will typically be burnt to produce energy, releasing undesirable gases into the environment. Therefore, chemical degradation, another recycling approach, represents an attractive long-term strategy to create a sustainable polymer supply chain. Recently, the chemical recycling of polymers has attracted a lot of attention among the scientific community,^{3–6} mainly driven by the current public awareness of this problem.

Chemical recycling involves transforming polymers from plastic waste into small molecules with high yield and purity.

Specifically, chemical depolymerisation either produces the initial monomers that can be subsequently re-polymerised into high quality polymers (circular economy – Fig. 1), or innovative small molecules that can be used as high added-value building blocks for creating unique polymeric materials or other chemicals (added-value plastic economy – Fig. 1). However, as a consequence of the high stability of polymeric materials, forcing conditions, such as microwave assistance,^{7–9} supercritical conditions,^{10,11} or the use of catalysts^{12–14} are usually required to enhance the efficiency of the depolymerisation reactions. In particular, stable and highly active organometallic catalysts, such as zinc or lead acetates, sodium/potassium sulphate, or titanium phosphate, which are already well-known for organic chemistry reactions, have been largely applied to depolymerisation processes. Despite their advantages, these metal-based catalysts display several drawbacks: (i) they are challenging to separate from the crude product, thus leading to lower-quality final materials; (ii) they have poor selectivity during the depolymerisation process, which results in a mixture of oligomers that are difficult to re-process; and (iii) the use of metal-based catalysts entails a high environmental and economic cost – some widely used metals risk complete disappearance in the next 100 years (e.g. zinc or silver), while others will be seriously threatened in the future if their consumption continues to increase (e.g. ruthenium, lithium, or copper).¹⁵

As an emerging alternative, organocatalysts have appeared as promising “green” substitutes for traditional organometallic complexes. While a wide range of organic catalysts are being applied in an increasing number of polymerisations,^{16–18} to date, the translation to depolymerisation processes is limited. When applied to polymer degradation, in particular to transesterification reactions, organocatalysts can promote mechanisms that lead to highly pure small molecules, which are in turn suitable for subsequent polymerisations. In many cases,



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Jeremy Demarteau received his undergraduate education in chemistry in Belgium. In 2013, he started his Ph.D. at the laboratory of CERM (Liège, Belgium). During his Ph.D. supervised by Dr Christophe Detrembleur, he investigated the controlled radical polymerization of less-activated monomers using organocobalt complexes, notably with the synthesis of block copolymers based on vinyl acetate and ethylene. In 2017, he

joined the Innovative Polymers Group of POLYMAT (San Sebastian, Spain) as a post-doctoral researcher. With Dr Harritz Sardon, he is working on the organocatalytic depolymerization of commodity polymers, such as polyesters, into valuable monomers and their use in a circular economy.



Haritz Sardon

Haritz Sardon received his Ph.D. in 2011 at the University of Basque Country under the supervision of Prof. Lourdes Irusta and Prof. M. J. Fernandez-Berridi before joining the group of Dr James Hedrick at IBM-Almaden Research Center, USA, as a post-doc. In 2014, Haritz returned to Spain with a Ministry grant and joined POLYMAT institute as junior group leader before starting his independent research career as

Associate Prof. for the University of Basque Country in 2017. His work is focused on organocatalysis for polymerization/depolymerization reactions, including step growth polymerization of polyurethanes, polycarbonates, polyesters and polyethers as well as depolymerization of commodity plastics.



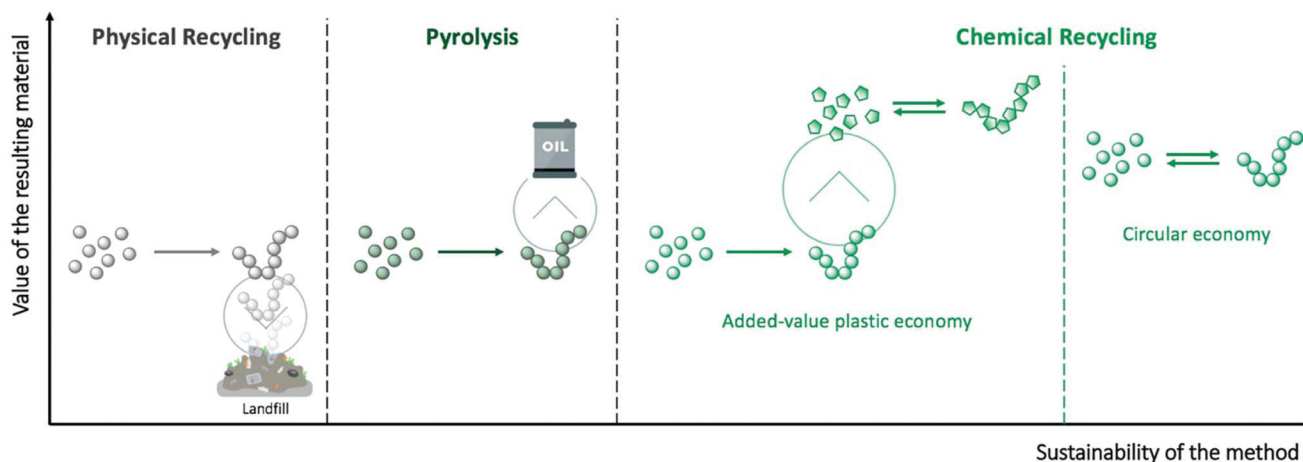


Fig. 1 The different methodologies of polymer recycling.

hydrogen-bonding interactions involved in the depolymerisation mechanism promoted by organocatalysts play an important role in controlling the catalytic activity and selectivity of the depolymerisation reaction, as well as the architecture of the resulting polymer.^{19–21} Herein, the contribution of organocatalysts to the field of chemical recycling is reviewed, outlining the advances made by using organic base, organic acid, and ionic compound catalysts, as well as comparing their performance to that displayed by typically applied organometallic catalysts.

Depolymerisation of commercial polymers

Commodity polymers, which are extensively used across a wide range of sectors including packaging, building, automotive, or

electronics, are seldom recycled. Hence, despite being a technological challenge, the design of suitable pathways for their depolymerisation is of the utmost necessity. An important aspect of such a challenge is found in the diversity of the plastic waste that requires treatment (Fig. 2). Because of the internal chemical differences among the various polymeric families, each type of polymer needs to be treated in a different way. Herein, the different organic catalysis methods that have been studied to date have been compiled to provide an overview of the progress for each class of polymers.



Andrew P. Dove

Andrew P. Dove is a Professor of Chemistry at the University of Birmingham, UK. He obtained his Ph.D. under Prof. Vernon Gibson from Imperial College London in 2003 before postdoctoral study at both Stanford University and IBM, under the supervision of Prof. Robert Waymouth and Dr James Hedrick. Andrew returned to the UK as a RCUK Fellow at the University of Warwick in 2005 before being promoted to Assistant (2006),

Associate (2009) and Full Professor (2014). Andrew moved to Birmingham in 2018. Andrew was awarded the Macro Group UK Young Researcher Medal in 2009, RSC Gibson-Fawcett Award in 2014, Biomacromolecules/Macromolecules Young Researcher Award in 2016 and RSC Norman Heatley Award in 2018.

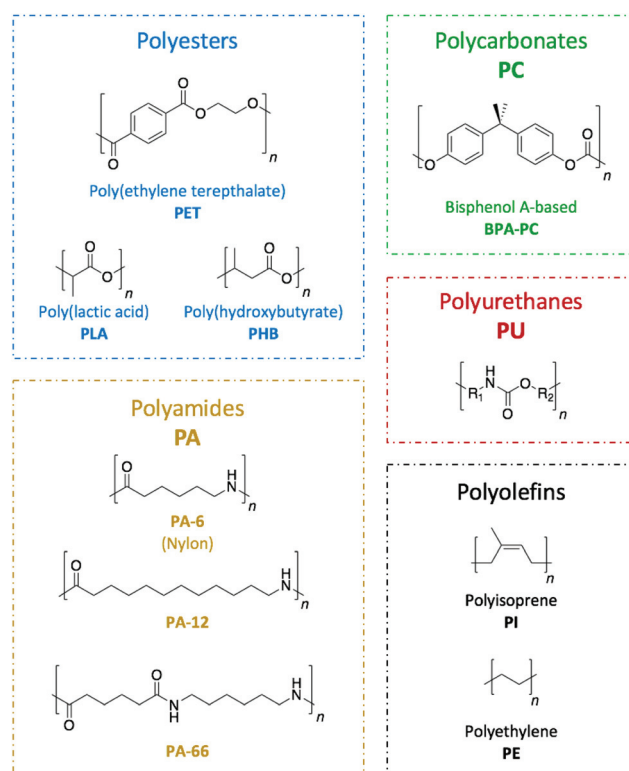


Fig. 2 Commercial polymers examined in this review.



Poly(ethylene terephthalate), PET

Poly(ethylene terephthalate) (PET) is the most commonly used thermoplastic from the polyester family (*i.e.* 13% of the world plastic production), and it is used in a large variety of applications, from clothing to food and liquid packaging. It is also the most recycled polymer in the world, with current industrial applications mainly in Europe and USA. According to the European Environment Agency (EEA), the rate of recycled PET bottles reached 57% in 2017 in Europe,²² an encouraging number only clouded by the high portion of mechanical recycling processes that lead to low-value materials, mainly fibres for carpet or clothes. As a result, PET is also one of the most studied polymers for depolymerisation, and organocatalysts have been often tested first on PET before applying them on other type of polymers.^{23–25} Hence, designing chemical recycling technologies for PET would impact the cyclic production of other polymers.

In 2011, Hedrick and co-workers reported the glycolysis of PET using a strong guanidine base, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, Fig. 3).²⁶ In a large excess of ethylene glycol (EG) (16 eq.) at 190 °C, pellets of waste PET beverage bottles degraded in 3.5 h. The major product (78% after crystallisation from water) of this reaction was bis(2-hydroxyethyl)terephthalate (BHET), a convenient monomer for the subsequent polymerisation into high quality PET (Scheme 1, I). Insoluble impurities were identified as short oligomers of PET and addi-

tives (*i.e.* isophthalic acid, diethylene glycol, and cyclohexane dimethanol). For coloured PET bottles, glycolysis took place at a slower rate with a lower BHET yield (64%). These results are comparable to those obtained when organometallic catalysts, such as acetate or alkoxide salts, are employed for this reaction.^{27,28} A complementary density functional theory (DFT) computational study demonstrated that while EG was modelled as co-activator of the depolymerisation, the system was energetically favoured, emphasising that both TBD and EG played an important role in the depolymerisation mechanism by activating the transesterification reaction *via* H-bonding.²⁹

In a subsequent work, the efficiency of a range of other nitrogen bases was investigated to establish the correlation between their basicity (pK_a) and their catalytic activity (Fig. 3).³⁰ Glycolysis appeared to be more efficient (*i.e.* more rapid with lower undesirable oligomers content) when strong bases, such as TBD, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) were used compared to bases with a lower pK_a , such as 1-methylimidazole (NMI) or dimethylaniline (DMA) (Fig. 3). Surprisingly, DBU showed higher efficiency than TBD despite its slightly lower pK_a . Moreover, the authors observed differences in reactivity by conducting an experiment using different chain-length diols, ranging from EG to 1-octanol (Scheme 1, II). For alcohols with a 4-carbon or longer chain, TBD exhibited higher catalytic activity than DBU since the bifunctional acid/base character of TBD provides a simultaneous activation of the carbonyl group of the ester and the nucleophilic group of the reactant, thus leading to a faster reaction, as computational studies revealed. In contrast, for short-chain alcohols in large excess, the diol activates the carbonyl of the polymer, undermining the bifunctionality of TBD and increasing the reaction rate.

Extension of this approach to other nucleophiles has led to the study of the aminolysis of PET to create a range of crystalline terephthalamide compounds as high added-value materials (Scheme 1, III).³¹ Moreover, the thermal and mechanical properties of such building blocks depended on the amine that was used as reagent. In a typical depolymerisation, terephthalamides were synthesised in reasonable yields at temperatures from 110 to 190 °C for 1 to 18 h, using TBD as catalyst. Again, the bifunctionality of TBD was crucial to activate the carbonyl group *via* H-bonding, making it more efficient for aminolysis than other organic bases.

The use of salt-based organocatalysts for PET depolymerisation has also received some attention. Although slower than DBU alone for depolymerising PET, DBU-based salts (specifically the organic salts DBU : benzoic acid and DBU : phenol, in a 1 : 1 molar ratio) were more stable in air-rich atmospheres, thus facilitating the depolymerisation procedure.³⁰ Similarly, we recently reported the glycolysis of PET using a thermally stable acid : base salt catalyst (Fig. 4a).³² An equimolar mixture of TBD and methane sulfonic acid (MSA) produced a very stable protic ionic salt that resists thermal degradation up to 400 °C, an uncommon property since most organic catalysts usually degrade at much lower temperatures, thus making them impractical for bulk depolymerisation processes

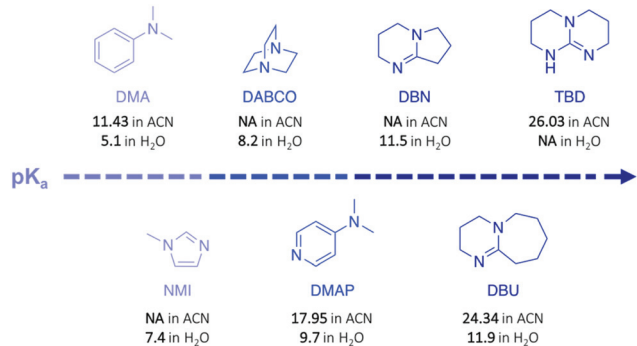
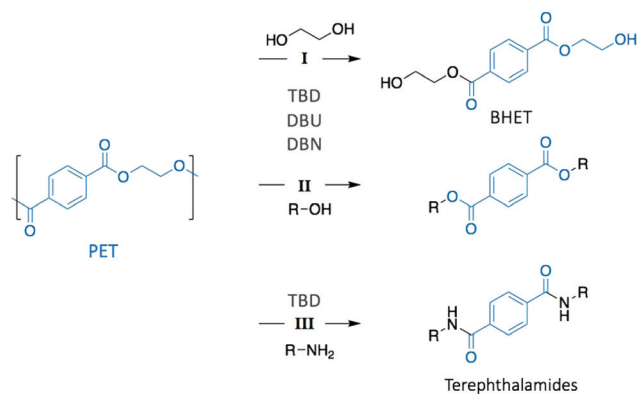


Fig. 3 Organic bases described in this review.



Scheme 1 Depolymerisation of PET through glycolysis (I), alcoholysis (II), and aminolysis (III).



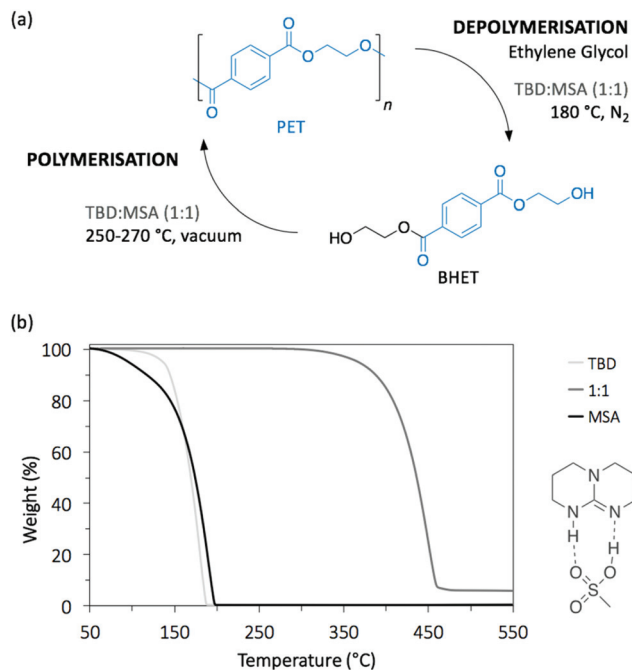


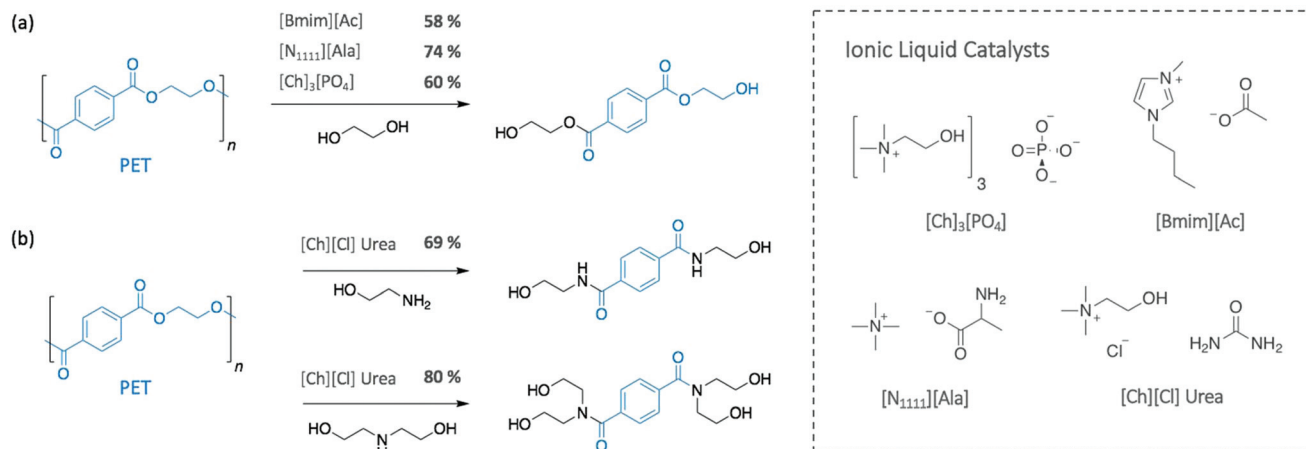
Fig. 4 (a) The depolymerisation of PET and re-polymerisation of monomeric products (BHET) using TBD:MSA (1:1) catalyst and (b) the thermogravimetric analysis (TGA) comparison between TBD:MSA (1:1) and TBD and MSA alone.

(Fig. 4b). At 180 °C, TBD:MSA (1:1) efficiently depolymerised post-consumed PET bottle waste in less than 2 h in the presence of EG. Under optimised conditions, over 90% of monomeric BHET was recovered with high purity through simple crystallisation in water. Additionally, the TBD:MSA catalyst was able to mediate the polymerisation of BHET back to PET showing comparable properties to the industrially produced one. Finally, the catalyst was recycled up to 6 times without any activity loss. Hence, TBD:MSA is proposed as an interesting catalytic platform for the industrially viable depolymerisation/polymerisation cycle of PET.

Ionic liquids (ILs) are classically defined as mixtures completely composed of ions with a melting point below 100 °C. As such, they display many similarities with the acid:base salts outlined above. The use of ILs for the depolymerisation of PET was firstly reported in 2009 by Wang *et al.* and involved imidazolium-based ILs. This family has been increasingly studied for the last couple of decades, especially as green solvents or catalysts for organic synthesis or separation techniques.^{33,34} In this work, 1-butyl-3-methylimidazolium ([Bmim]) was investigated with different anions (Cl, Br, BF₄, PF₆) as solvent for the glycolysis of PET.³⁵ Even though some of the ILs ([Bmin][Cl] and [Bmin][Br]) solubilised the polymeric material, depolymerisation required additional catalysts, such as zinc acetate, tetrabutyltitanate, or solid superacid, to be completed. The authors indicated the depolymerisation product to be an oligomeric mixture without identifying its nature or yield. Nevertheless, the possibility of recycling the IL, as well as its easy separation from the product, made the study an encouraging starting point for the use of ILs for depolymerisation.

More recently, Al-Sabagh *et al.* showed that a basic imidazolium-based IL (*i.e.* 1-butyl-3-methylimidazolium acetate [Bmim][Ac]) fully degraded PET without requiring any additional catalyst.³⁶ At 190 °C, PET depolymerised through glycolysis in 3 h giving a BHET monomeric yield of 58%, as opposed to neutral 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) or 1-butyl-3-methylimidazolium bromide ([Bmim][Br]), which did not display any catalytic activity (Scheme 2a). These results suggest that basic imidazolium ILs can promote the desired depolymerisation, while neutral ones can only be used as solvent and require the adding of a catalyst. In another approach to improve the depolymerisation of PET with neutral [Bmim][BF₄], Nunes *et al.* used supercritical ethanol (255 °C).³⁷ Under the best conditions, diethyl terephthalate, the monomer resulting from the ethanolysis of PET, was obtained at 98% yield in 45 min.

Similarly, urea-based ILs have been applied as efficient catalysts for both glycolysis and aminolysis of PET. Using EG as nucleophile and solvent at 170 °C, 73.9% of BHET was col-



Scheme 2 (a) Glycolysis and (b) aminolysis of PET using different ionic liquids as catalyst.



Table 1 Hydrolysis and methanolysis of BPA-PC using imidazolium ionic liquids

| Ref. | Reagent (R) | Catalyst (IL) | Temp. (°C) | Duration | R : IL : PC | BPA ^a (%) |
|------|-------------|---------------|------------|----------|------------------|----------------------|
| 47 | Methanol | [Bmim][Cl] | 105 | 2 h30 | 1.5 : 1 : 1 | 96 |
| 48 | Water | [Bmim][Cl] | 165 | 3 h | 10 : 1.5 : 1 | 95 |
| 49 | Methanol | [Bmim][Ac] | 90 | 3 h | 0.5 : 0.5 : 1 | 96 |
| 48 | Water | [Bmim][Ac] | 140 | 3 h | 0 : 35 : 1.5 : 1 | 96 |

^a Determined with HP liquid chromatography.

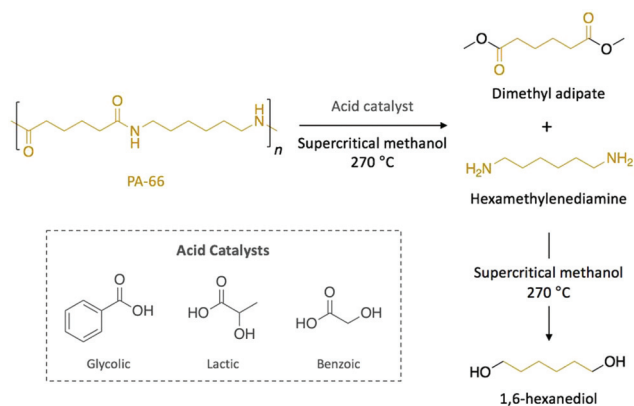
Moreover, BPA and dimethyl carbonate (DMC) were isolated in high yields (up to 96%), and the IL was reused up to 8 times with no significant decrease in the catalytic activity being observed.

Following this promising result, [Bmim][Cl] and [Bmim][Ac] were further investigated for the methanolysis and hydrolysis of BPA-PC.^{48,49} For both catalysts, the polymer fully depolymerised in 3 h with very good yields (>95%) (Table 1). Notably, higher temperature and catalyst loading were required to complete the depolymerisation by hydrolysis (*i.e.* 140 °C and 165 °C) in comparison to methanolysis (*i.e.* 90 °C and 105 °C). For [Bmim][Ac], the depolymerisation reaction through hydrolysis followed first-order kinetics with an activation energy of 228 kJ mol⁻¹, which is higher than for methanolysis (168 kJ mol⁻¹), thus validating that more forcing conditions were required to complete the depolymerisation when water was employed. Furthermore, the authors suggested that the enhanced performance of [Bmim][Ac] for catalysing the depolymerisation of BPA-PC under milder conditions is partially attributed to the better solubility of the polymer in this IL. Indeed, at 105 °C, 5 g of [Bmim][Ac] solubilised 1 g of BPA-PC, whereas, in the same quantity of [Bmim][Cl], the polymer barely swelled.

Polyamides

Polyamides are polymers that can be either found in nature (*e.g.* proteins, silk, or wool) or prepared synthetically (*e.g.* nylons, aramids, or sodium polyaspartate). They are characterised by amide bonds linking their repeating units. Most typically with respect to plastic waste, polyamides are found in the form of nylons which have several applications from biomedicine to clothing. As a consequence of their excellent mechanical strength, artificially made polyamides are widely used in textile, automotive, and transportation industries.

Typical aqueous acidic solutions (*e.g.* formic acid, hydrochloric acid, or sulfuric acid) were firstly applied as acid catalysts for the chemical degradation of discarded polyamide-6 (PA-6) waste fibres, which were completely dissolved in the concentrated solutions.⁵⁰ After different times up to 20 h, the degradation products, which displayed different molecular weight, were recovered through fractional precipitation. Interestingly, for hydrochloric acid and sulfuric acid, aminocaproic acid was the major component of the crude product and it was isolated in high purity, which eventually allowed for subsequent polymerisation. More recently, Kamimura and co-workers reported the depolymerisation of polyamide-66

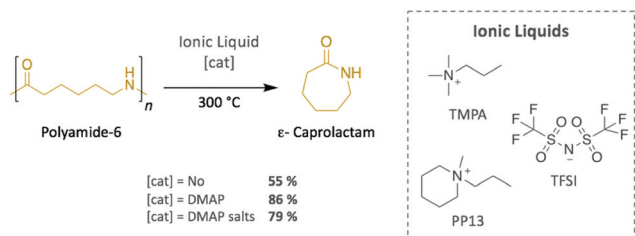


Scheme 4 Depolymerisation of PA-66 catalysed by organic acids in supercritical methanol.

(PA-66) into high-added value chemicals combining supercritical methanol as solvent and organic acids as catalysts (Scheme 4).⁵¹ Specifically, depolymerisation with 8 eq. of glycolic acid in methanol yielded 75% of dimethyl adipate and 50% of 1,6-hexanediol after 6 h of reaction at 270 °C. Other organic acids, such as lactic or benzoic acid, also catalysed the depolymerisation of PA-66 with similar yields, while esters or weaker acids provided comparable yield values for dimethyl adipate, but lower for 1,6-hexanediol. In this case, the authors proposed that the acid catalyst favoured the scission of the amide bond to yield dimethyl adipate and hexamethylenediamine before supercritical methanol promoted the subsequent degradation of the diamine into various compounds, including 1,6-hexanediol. Hence, the resulting diol, which is a monomer of interest in the polymerisation of polyesters and polyurethanes, can be obtained from commercial PA-66, thus turning this depolymerisation process into an economically viable technology.

For this family of polymers, ILs have also been applied as efficient catalytic media for the depolymerisation of PA-6 (Scheme 5). Quaternary ammonium salts, such as *N*-methyl-*N*-propylpiperidinium (PP13) and *N,N,N*-trimethyl-*N*-propylammonium (TMPA), together with bis(trifluoromethane sulphonyl)imide (TFSI) as counter anion, successfully depolymerised PA-6 into ϵ -caprolactam (43–55% in yield) in 5–6 h at 300 °C without requiring any additional catalyst.⁵² However, adding 5 wt% of DMAP improved the depolymerisation efficiency up to 86% monomeric yield. Further optimisation of the reaction conditions demonstrated the important role played by temp-





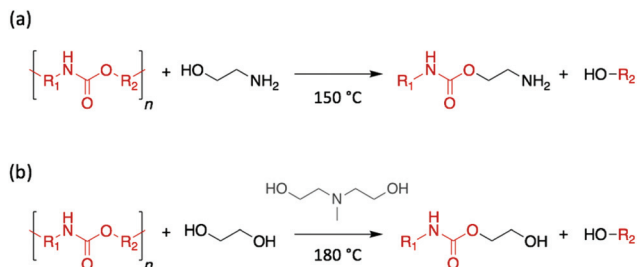
Scheme 5 Depolymerisation of PA-6 into ϵ -caprolactam using ILs as catalyst.

erature, with 7%, 55%, and 6% of the monomer being isolated at 270 °C, 330 °C, and 360 °C, respectively. For temperatures lower than 300 °C, a large portion of oligomeric polyamides were found in the crude product, which explains the poor recovery value of ϵ -caprolactam, whereas ILs decomposed at temperatures higher than 300 °C, as evidenced by the formation of *N*-methyl- and *N*-propyl lactams by-products, which prevented depolymerisation from reaching good yield values. Later, this methodology was extended to polyamide-12 (PA-12), for which the corresponding lauractam was isolated; however, the yield did not exceed 17%, most likely as a consequence of the closing of the 12-member ring being energetically disfavoured.⁵³ Furthermore, the ILs were recycled up to 5 times without losing their depolymerisation efficiency. Finally, the same research group depolymerised PA-6 in these quaternary ammonium-based ILs using DMAP salts prepared with iodine and imidazolium as counter anions.⁵⁴ This system catalysed the reaction several times, reaching up to 79% of monomer recovery; however, since their performances in terms of catalytic activity and selectivity were poorer than the ones displayed in previous experiments using DMAP alone, this catalyst was not further investigated.

Polyurethanes

Polyurethanes (PUs) are generally prepared by the condensation reaction between isocyanates and polyols. Owing to their distinctive feature to be processed as flexible foam, rigid, or elastomeric materials, PUs have found applications as diverse as insulation panels, wheels and tires, adhesives, surface coatings, sealants, synthetic fibres, or hard-plastic electronic components for the consumer goods, automotive, and construction industries. This variety of applications requires clear distinctive properties, which originate from the distinctive polymer structures obtained from the multiple combinations of polyols and isocyanates. As PU is the 6th most produced polymer in the world, with an annual production above 16 million tons in 2016, the sorting and the treatment of this polymeric material is of very special interest.⁴¹

In 1993, Xue *et al.* successfully depolymerised discarded PU rigid foams through glycolysis using diethylene glycol (DEG) as reagent and EA as catalyst. The resulting product, glycolysate, was used as additive for the further synthesis of epoxy resins.⁵⁵ However, all recent studies have reported the use of alkaline



Scheme 6 Depolymerisation of PU (a) using EA as reagent and catalyst or (b) using EG as reagent and DEA as catalyst.

salts or metal complexes as catalysts to complete the depolymerisation,^{56,57} thus suggesting that low molecular-weight glycols and alkanolamines may be unable to depolymerise PU rigid foams by themselves. The depolymerisation of PU flexible foams using alkanolamines was also reported, a year later, by Kanaya and Takahashi.⁵⁸ Contrary to the previous example, a diphenyl isocyanate-based PU was depolymerised into a pure polyether polyol using EA, without adding any further catalyst, and the authors suggested alcoholysis rather than aminolysis as the reaction mechanism involved (Scheme 6a). Similarly, in 2000, Borda *et al.* studied the glycolysis of PU flexible foams and elastomers using DEA, and EG, 1,2-propylene glycol, triethylene glycol, or low molecular weight poly(ethylene glycol) as reagents.⁵⁹ Specifically, using an equimolar quantity of EG and DEA, PU-based waste depolymerised in less than 2 h at 180 °C, and the resulting polyol phase was directly employed to synthesise an industrial adhesive mixture (Scheme 6b). In this study, although alcoholysis was assumed to be the favoured pathway, the presence of CO₂ in the gases released during the reaction suggested decarboxylation as a competing process.

More recently, the efficiency of DEA and EA to degrade PU flexible foams was compared with that displayed by metal catalysts, such as acetate metallic salts, tin oxides, or tin laurates.⁶⁰ At 200 °C, even though alkanolamines significantly enhanced the depolymerisation rate compared to the control reaction performed without adding catalyst, the highest efficiency was still obtained for a metallic catalyst, namely zinc acetate. Notably, DEA showed the same performance as barium acetate, while EA performed similarly to potassium salt. In contrast, other metallic catalysts (*i.e.* dibutyl tin dilaurate, butyl tin oxide, and hydroxy butyl tin oxide) performed extremely poorly.

In another example, the glycolysis of a thermoplastic PU elastomer (TPU) based on 4,4'-diphenylmethane diisocyanate and polyether polyol was also conducted using low-weight glycols (*i.e.* DEG or EG), and EA and lithium acetate as catalyst and co-catalyst, respectively.⁶¹ When treated with a DEG:EG:EA (9:9:2) mixture at a temperature range from 160 °C to 190 °C, the elastomeric TPU depolymerised into two distinct layers in 3 h. In the resulting crude product, the upper liquid phase contained a polyether polyol that corresponded to the starting industrial polyol used to polymerise TPU.



Polyolefins: polyisoprene and polyethylene

Polyolefins, which are produced from polymerising alkenes, can be prepared as liquid or rigid solids depending on their molecular weight and degree of crystallinity. For instance, polyethylene (PE), which is one of the most commonly used plastic with an annual production of around 80 million tons, is mainly used as a packaging item manufactured as bags, films, or bottles. Degrading polyolefins represents one of the major challenges in polymer recycling for two main reasons. Chemically, their C–C backbone is extremely stable and as such harsh conditions are usually required to afford and control the depolymerisation reaction. Furthermore, economically the production of polyolefins is a cheap and well-controlled process. Hence, chemical depolymerisations are far from competitive with their preparation using low-cost petroleum-based monomers. However, some attempts in depolymerising polyolefins have been undertaken, giving different kind of products, from a mixture of light alkanes, to novel materials, and among them, organocatalysts have been an even more rare methodology.^{62–66}

Firstly, polyisoprene-based materials, which are more accessible owing to the reactivity of the C=C double bond that remains in the polymer structure, have been depolymerised with *m*-chlorobenzoic acid,⁶⁷ phenylhrazine,⁶⁸ or potassium persulfate.⁶⁹ In all cases, the molecular weight of the polymer decreased drastically, producing telechelic oligomers as degradation products. However, among the acid catalysts explored for the depolymerisation of both natural and synthetic rubber (*i.e.* poly(*cis*-isoprene)), periodic acid (*i.e.* H₅IO₆ or HIO₄) has been the most widely studied. For instance, in 2005, Phinyocheep *et al.* reported the oxidative depolymerisation of epoxidised natural rubber (ENR) catalysed by periodic acid.⁷⁰ Indeed, periodic acid, which in an excess of water is a weak acid, releases periodate anions, which are able to cleave 1,2-difunctional compounds. Specifically, the molecular weight of ENR was reduced from 15 kg mol⁻¹ to 0.4 kg mol⁻¹ after 8 h of reaction at low temperature (30 °C). Moreover, the same process applied to natural rubber (NR) also resulted in the depolymerisation of the polymer, the molecular weight decreasing from 20 kg mol⁻¹ to 1 kg mol⁻¹ in 30 h. In the case of NR, the authors formulated that periodic acid catalyses the epoxidation of NR into ENR in the first step of the reaction, which explains the longer reaction time (30 h instead of 8 h) (Scheme 7). Subsequently, Sadaka *et al.* adapted this method to directly depolymerise ground waste tyres through an oxidative mechanism,⁷¹ which first involved the epoxidation of

the double bond of polyisoprene before cleaving the *in situ* formed oxirane (Scheme 7). As a result, a range of low molecular-weight telechelic polymers with aldehyde end-groups were obtained by controlling the quantity of periodic acid employed. Interestingly, these oligomers were then used as precursors for the synthesis of other relevant materials for the rubber industry.

While PE is one of the simplest and cheapest polymers to synthesise, its depolymerisation requires breaking the very energetically stable C–C single bond, which makes the depolymerisation of PE technologically demanding. Despite this fact, Bäckström *et al.* undertook an original initiative to recycle low density PE (LDPE) into value-added functional chemicals *via* a microwave-assisted fast and effective oxidative process.⁷² Through this approach, LDPE powder was totally degraded after just 1 h of microwave irradiation at 180 °C in relatively dilute nitric acid solution, which led to well-defined water-soluble products, such as succinic, glutaric, and adipic acids, as well as longer dicarboxylic acids, acetic acid, and propionic acid. Notably, the length of the dicarboxylic acids could be adjusted by varying the reaction conditions (*i.e.* time, temperature, and the amount of oxidizing agent). Finally, the authors validated their strategy by recycling LDPE freezer bags, which were depolymerised into dicarboxylic acids with a good yield (71%).

Finally, ILs have also been used as solvent and catalyst to depolymerise polyolefins. In 2000, Adams *et al.* described the use of chloroaluminate(III) ILs for cracking both high and low density PE (HDPE and LDPE, respectively).⁷³ At temperatures below 200 °C, the reaction led to low-volatility alkanes. However, although this catalyst is metal-based, the novelty of this example opened the way to other initiatives for polymer recycling. Indeed, more recently, waste tyres were depolymerised through metathesis in hydrophobic ILs (*i.e.* trihexyl-(tetradecyl) phosphonium chloride (Cyphos101) and *N,N*-dioctylimidazolium bromide (C₈ C₈ ImBr)), which produced low molecular weight telechelic polymers of controlled lengths.⁷⁴ These resulting oligomers, as pointed out above, are notably interesting intermediates for the synthesis of innovative polymers by metathesis.

Biodegradable polyesters

The polyester family gathers polymers containing an ester functional group in their main chain, PET being the most commonly used. However, other polymers, such as polylactide (PLA) and poly(hydroxy butyrate) (PHB) are relatively new commodity polymers and, in the case of PHB, still to make a



Scheme 7 Depolymerisation of polyisoprene using periodic acid.





Scheme 8 Depolymerisation and subsequent polymerisation of PG and PLA for the synthesis of new materials.

significant impact. Both polymers attract high interest as a consequence of their production from renewable sources and their ability to decompose in relatively mild conditions. Thus, they have been extensively investigated as decomposable materials, mainly for packaging applications. While PLA has begun to be successfully translated into these areas (with an expected PLA production growth by 300% between 2015 and 2020 in Europe, for example ref. 22), they have been also applied as polymeric scaffolds in the biomedical and biotechnological fields on account of their ready compatibility with biological systems.

For both polymers, organic bases have gained a lot of attention as catalysts for their depolymerisation. Indeed, Leibfarth *et al.* reported the efficiency of TBD to degrade PLA into valuable building blocks at room temperature (Scheme 8).⁸⁷ Similarly to what was observed for the depolymerisation of PET, degrading PLA with a range of alcohols led to a mixture of products of lactate esters and their dimers. Specifically, more than 95% of ethyl lactate was recovered with ethanol as reagent and using 2.5 mol% TBD.

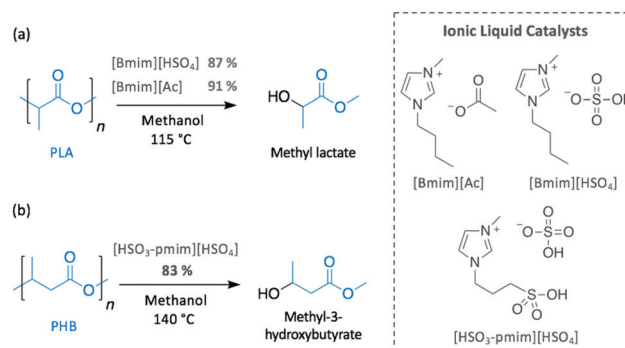
Additionally, when poly(*L*-lactide) was depolymerised with benzyl alcohol, the product retained the stereochemistry of the polymer (*i.e.* >95% of the product was *S*-benzyl lactate). Moreover, the possibility to introduce various polymerisable groups to the ester products allows new polymers to be produced by step growth methods. For instance, the monomers resulting from the depolymerisation of PLA and polyglycolide (PG) with EG and allyl alcohol were polymerised into new materials. Specifically, the diols produced using EG were condensed with succinic anhydride, while the dialkenes obtained *via* allyl alcohol were alkylated with allyl bromide before polymerising them through acyclic diene metathesis. These two different examples highlight the wide spectrum of possibilities that recycled monomers present to create new materials.

In another example, Coulembier *et al.* noticed the chemical degradation of poly(*L*-lactide) catalysed by organic bases. Specifically, the presence in the polymer of residual DBU from the polymerisation favoured its thermal degradation. Indeed,

the salt formed by the organocatalyst, DBU, and benzoic acid, which was used to quench the activity of the organic base, acted as a catalyst for the depolymerisation of poly(*L*-lactide) under high temperatures (*i.e.* melt process).⁷⁵

As described in previous sections, basic ILs have been widely investigated for the alcoholysis of oxygen-containing polymers, such as PET or BPA-PC. Similarly, the efficiency of different imidazolium ILs (*i.e.* [Bmim][Cl], [Bmim][PF₆], [Bmim][Ac] and [Bmim][HSO₄]) to catalyse the methanolysis of PLA into methyl lactate was compared (Scheme 9a).⁷⁶ Likewise PET, neutral ILs ([Bmim][Cl] and [Bmim][PF₆]) were inactive, whereas basic [Bmim][Ac] and acidic [Bmim][HSO₄] completely degraded PLA in 3 h at 115 °C, which is not a surprising result since the efficacy of acid and base catalysts for PLA depolymerisation by transesterification is well known. [Bmim][Ac] appeared to be slightly more active than its acidic homologue, reaching 96% of PLA conversion and producing methyl lactate in 91% yield.

In contrast, although acidic ILs have received much less attention, one notable work explored the efficient methanolysis of PHB into methyl 3-hydroxybutyrate (83% yield) in 3 h at 140 °C using 1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate [HSO₃-pmim][HSO₄] as catalyst (Scheme 9b).⁷⁷



Scheme 9 PLA and PHB depolymerisation using ILs.



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