Catalytic chemical depolymerisation of mixed plastic waste

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Declaration of Authorship

This thesis is submitted to the University of Birmingham in support of my application for the degree of Master of Science by research. It has been composed by myself and has not been submitted in any previous application for any degree. The work presented (including data generated and data analysis) was carried out by myself, except in the following cases which are outlined below:

Thesis summary

This thesis investigates the chemical recycling to monomer of three common use polymers. It follows a two-phased approach based upon conducting an initial depolymerisation screen, before leading on to the investigation of selective depolymerisation reactions.

Chapter 1: Provides a background into the current state of global waste plastic processing, discussing current practices and their drawbacks. The advent of chemical recycling, and chemical recycling to monomer, are then introduced, highlighting potential prospects and challenges that could be met. The second section of this chapter is an in-depth review of recent literature and current advances within the areas of chemical recycling to monomer, and selective chemical recycling, encompassing a range of polymers.

Chapter 2: Outlines the screening process undertaken to assess the reactivity of the polyesters polyethylene terephthalate (PET), and polylactic acid (PLA) and the polycarbonate bisphenol A polycarbonate (BPA-PC), to glycolysis across a range of temperatures and employing different combinations of Lewis acid and Lewis base catalysts. With the aim to uncover instances of selectivity in depolymerisation.

Chapter 3: Builds upon the experience gathered from the previous chapter, taking notable instances of selectivity, and combining them into sequential processes for mixed polymer depolymerisation studies. Investigation into alternative reaction conditions is also undertaken, to identify reactions systems that will produce value-added products.

Chapter 4: Summarises and concludes the findings from chapters 2 and 3 and discusses the possible future directions of this work.

List of abbreviations

1D	1-Dimensional
2-HEtLa	2-hydroxyethyl lactate
2-MeTHF	2-methyl tetrahydrofuran
AOMEC	2-allyloxymethyl-2-ethyltrimethylene carbonate
BHET	Bis(2-hydroxyethyl) terephthalate
BPA	Bisphenol A
BPA-PC	Bisphenol A polycarbonate
BPA-SP	Bisphenol A bis(2-hydroxyethyl) ether
CDCl$_3$	Deuterated chloroform
CRM	Chemical recycling to monomer
d	Doublet
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DMAP	4-dimethylaminopyridine
DMSO-d_6	Deuterated dimethylsulfoxide
g	Gram
g mol^{-1}	Grams per mole
h	Hour
HDPE	High-density polyethylene
IR	Infrared
LDPE	Low-density polyethylene
Mg(OAc)$_2$	Magnesium(IV) acetate tetrahydrate
MgCl$_2$	Magnesium chloride
min	Minute
mL	Millilitre
mm	Millimetre
mmol	Millimole
mmol kg^{-1}	Millimoles per kilogram

mol	Moles
mol%	Mole percent
MSA	Methanesulfonic acid
M_w	Molecular weight
NMP	N-methyl-2-pyrrolidinone
NMR	Nuclear magnetic resonance
PA	Polyamide
PCL	Polycaprolactone
PCW	Post-consumer waste
PE	Polyethylene
PET	Polyethylene terephthalate
PLA	Polylactic acid
PP	Polypropylene
PPC	Polypropylene carbonate
ppm	Parts per million
PS	Polystyrene
PU	Polyurethane
PVC	Polyvinyl chloride
q	Quartet
s	Singlet
S_N2	Nucleophilic substitution-2
T	Temperature
t	Time
t	Triplet
TBD	Triazabicyclodecene
T_d	Thermal degradation temperature
T_g	Glass transition temperature
THF	Tetrahydrofuran
T_m	Melting temperature

TMPAE	Trimethylolpropane allyl ether
TMS	Tetramethylsilane
UV	Ultraviolet
wt%	Weight percent
$Zn(OAc)_2$	Zinc(II) acetate dihydrate
δ	Chemical shift

Chapter 1: Introduction

The overwhelming presence of plastics in everyday life is undeniable. It could even be said that for most of the global population, no interaction with a plastic product (or a product containing plastic components) in a single day is almost impossible. The mainstream manufacture and use of plastics began to boom in the 1950's and since then, global production of consumer plastics has increased dramatically, from 1.5 million tonnes per year in 1950 to 322 million tonnes per year in 2016.[1, 2] Increased production means increased waste, and should current levels of plastic waste generation increase at a continuous rate, annual waste generation figures could range between 155 and 265 million tonnes by 2060, near threefold the annual waste generation figures estimated for 2015.[3]

Generally, it is estimated that 6300 million tonnes of plastic waste have cumulatively been generated since the widespread adoption of plastic commodities occurred. However, it is approximated that only 20% of this total mass has been recycled or incinerated, with the remainder entering landfill or the open environment.[4] This has serious environmental consequences, and the high percentage of waste plastics in the environment only emphasises that both current and previous recycling methods are inadequate and unable to meet the demand.

Even though developed countries have available infrastructure for recycling, a large proportion of their post-consumer waste (PCW) plastic is exported for processing around the world due to high demand. In the UK in 2017, for example, 85% of polyethylene (PE) exports were shipped to non-European countries such as Indonesia and the Philippines, which leads to further environmental cost associated with transportation.[5] When analysing contributions

to total ocean debris from the exportation of PE, Bishop *et al.* found that the UK was responsible for 29% of the total PE ocean debris found to originate in Europe.[5]

Alongside general landfill waste, a serious side-effect from the loss of waste polymer material to the environment is the formation of microplastic particles (plastic fragments less than 5mm in length).[6, 7] Microplastics shed from commodity plastics, and have been found in different environments around the world, from the deepest oceanic trenches to the summit of Mount Everest, and even the human placenta and blood stream.[8-11] Whilst the health implications are still being researched, the environmental consequences are somewhat more visible. Therefore, the implementation and discovery of novel ways to recycle plastic waste is paramount, and the chemical recycling of waste plastic to monomers and other value-added products offers one such solution.[12, 13]

As a concept, chemical recycling is the conversion of waste polymers into their parent monomers, oligomers or crude oils and gases by chemical means, which can then be utilised as a raw material for the remanufacture of commodity products.[14] Chemical recycling is at a formative stage, and the chemical recycling techniques of pyrolysis and gasification are becoming more widely used in conjunction with conventional mechanical recycling techniques. Pyrolysis is the thermolytic degradation of a material at high temperatures, generally above 500 °C, and under an inert atmosphere.[15] In the case of plastic waste, it can be pyrolyzed to produce hydrocarbon-rich oils, gases and waxes which can be used as fuel (petrol and diesel),[16] or to supplement existing petrochemical feedstock.[17] Pyrolysis conditions are easily varied, making the process highly tuneable to a range of desired products, it is also a very effective method of converting waste into energy as the products are often of high

calorific value.[18] Gasification is a similar process, however the plastic waste is reacted in an atmosphere of steam or oxygen to yield a product called syngas, or synthesis gas, which is a mixture of mainly molecular hydrogen and carbon monoxide.[19] This offers benefits over the more commonplace incineration of plastic waste as the range of gasification products is comparatively narrow, whilst energy inefficient and toxic molecules such as certain aromatics and dioxins are not produced.[20-22] Like the products of pyrolysis, syngas can be a useful source of energy as it is further reacted into synthetic natural gas, which is an important compound in energy production. However, once the polymer has undergone pyrolysis or gasification, it is unrecoverable and lost to the environment when burnt, thereby losing the inherent value of the product.

The controlled depolymerisation of waste polymers to parent monomers offer a way in which plastic waste can be reclaimed, unlike in pyrolysis and gasification methods. Therefore, chemical recycling to monomer (CRM), via depolymerisation, has potential advantages for plastic waste management, and has additional benefits over other strategies, such as mechanical recycling.[23] When a plastic is mechanically recycled, it is shredded into fibres which are then melted before extrusion into lengths, which are cut into pellets, ready for repurposing into another product.[24] Although the mechanical recycling of some PCW can be a closed-loop process, such as for poly(ethylene terephthalate) (PET) drinks bottles, where the materials are directly remoulded into the same form from recycled PCW, these new commodities are of an inferior quality to the original product, and the associated virgin polymer. This is because when a polymer is reprocessed via mechanical and thermal treatment, the individual polymer chains are degraded in a process called chain scission,[25] reducing the molecular weight and uniformity of the sample. The net effect is a reduction in

the long-range structural order present in virgin polymers which give them favourable material properties and mechanical strength, including impact and chemical resistance.[26] As a consumer product is repeatedly recycled throughout its useable life, the constant degradation of polymer chains feeds a linear 'downcycling' problem in which eventually, there are no more ways to recycle the polymer as it has become unusable as a material.[27, 28] At this point, it is released to the environment as landfill, where it is lost.

To this end, the chemical recycling of plastic waste can curtail this conventional downcycling approach by 'closing the plastic loop' and creating a veritable circular plastics economy.[29] Monomers retrieved from chemical recycling processes are able to be repolymerised into high molecular weight polymers, that are indistinguishable from the feedstock waste polymer, resulting in a true recycling step which closes the plastic loop. As an example, a polyester t-shirt made from recycled plastic bottles can be recycled into carpeting (downcycling) or undergo CRM to be repolymerised and start the cycle again (Figure 1.1).
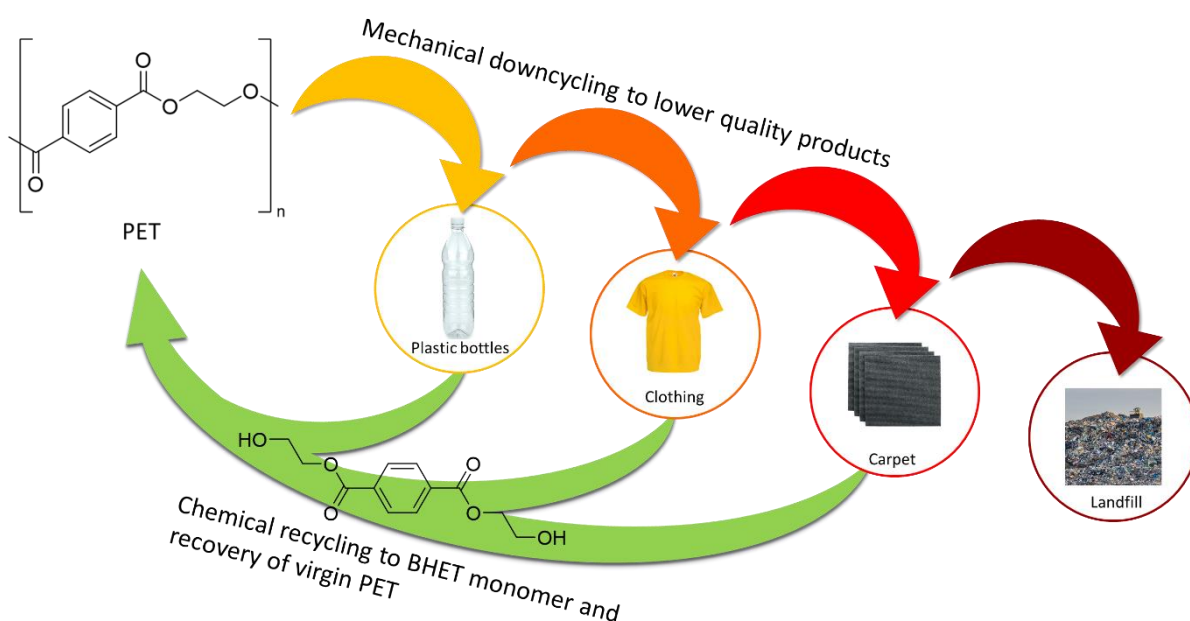
Figure 1.1: *Closing the plastic loop of PET recycling, showing that chemical recycling and upcycling is achievable after each downcycling stage. If the loop is not closed, material is lost to landfills.*

Although there are some quite clear benefits to chemical recycling over mechanical recycling, it is important that potential issues are addressed, namely cost, and implementation / accessibility. Chemical recycling by pyrolysis, gasification, and CRM, are energy intensive processes, and require large quantities of chemicals (solvents, catalysts) to function. Over time, these costs will build as reactants would need to be replaced in order to keep the working conditions optimal. Furthermore, with little existing infrastructure the expenses needed to implement national chemical recycling schemes would be massive as new processing plants would need to be constructed. Furthermore, access to mechanical recycling services is offered by all UK local authorities, and mechanical recycling infrastructure is widespread across the country.[30] Whereas, developing chemical recycling technology is still very much a privatised industry with many companies focussing on individual pilot solutions, with only recent years seeing chemical recycling firms band together to form associations for the faster development of innovative chemical recycling technology.[31] With these considerations in mind, it could be suggested that Chemical recycling techniques would be better employed in conjunction with existing recycling infrastructure, rather than setting off to outright replace it.

Chemical recycling of plastic waste has also formed the basis for an emerging method of PCW recycling, mixed plastic recycling via selective co-depolymerisation. This process takes CRM via depolymerisation and combines it with orthogonal chemistry, creating reaction pathways that are purely selective to one polymer within a mixture or blend of others. At present, standard recycling procedure is to sort PCW plastics by composition (i.e., polycarbonates are separated from polyesters) prior to mechanical processing, which are then individually processed. However, pre-sorting waste will inherently possess a degree of error, leading to

plastics being incorrectly sorted and entering the wrong recycling stream and thus causing contamination. For example, high density polyethylene (HDPE) is widely recycled, whereas low density polyethylene (LDPE) is not, despite their chemical similarities. This is a result of structural differences, HDPE possess a linear non-branching backbone which allows for tight, uniform chain packing and results in desirable physical properties such as hardness, high impact resistance, and chemical resistance. LDPE on the other hand, comprises of short, highly branched chains that pack poorly, making it flexible and soft, lowering its tensile strength (Figure 1.2). Therefore, if LDPE were to enter a HDPE recycling stream, issues would arise as the quality of the recycled HDPE would be compromised (reduced hardness, higher flexibility) due to the inability of chains to uniformly pack.[32] Likewise, the separation of PE and polypropylene (PP) is challenging as mechanically they are very similar (and therefore hard to separate by density) and find use in comparable applications. They are immiscible in molten and solid phases, and so impurities derived from interfacial tension where the two polymers meet will arise. This reduces mechanical properties such as impact resistance and tensile strength, and can even compromise the structural soundness of the resultant commodity.[33] Similarly, carbonyl group containing plastics, such as polyesters and polycarbonates, are also hard to distinguish visually, requiring techniques such as infra-red (IR) sensing to distinguish them.[34] Furthermore, chain scission occurs more readily in carbonyl plastics during recycling rather than in plastics such as PE or PP, this is due to the increased reactivity of the carbon-heteroatom bond compared to non-functionalised backbones of polyolefins.[35] Therefore, degradation products are often of poorer quality, as more random chain scissions occur. The application of CRM processes can therefore be beneficial in these situations as product quality is maintained.

High Density Polyethylene
T_m (°C): 130 – 140
Tensile strength at break (MPa): 30 – 40
Young's modulus (GPa): 0.5 – 1.1

Low Density Polyethylene
T_m (°C): 100 – 120
Tensile strength at break (MPa): 10 – 20
Young's modulus (GPa): 0.13 – 0.3
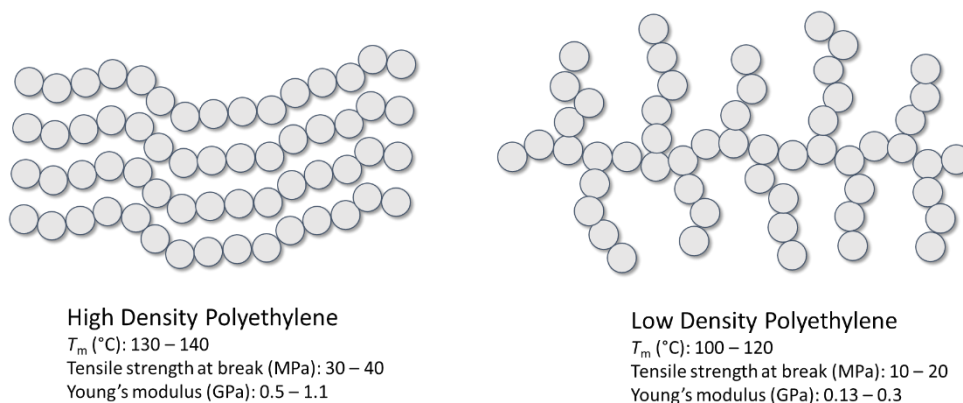
Figure 1.2: A comparison of HDPE with LDPE, showing how the linear nature of HDPE allows for tight packing of chains, whereas the branching nature of LDPE does not. The resultant differences in thermal and mechanical properties have also been shown. Backbone structures have been simplified.

By exploiting the interaction between plastics, solvents, and catalysts, selective co-depolymerisation could eliminate the pre-sorting step and the resulting error, whilst allowing each component of a plastic mixture to be chemically recycled to their respective monomers individually and sequentially. This methodology has been reported in 1976, when a mixture of polystyrene (PS), poly(vinyl chloride) (PVC) and polyolefin (HDPE and LDPE) was separated based on the interactions of each polymer with different solvents.[36] Furthermore, chemical recycling allows for the recovery of monomers while separating impurities, such as additives, dyes and fillers, that can produce unfavourable odour or colour and impact the recyclability of the material.[37] This is something that mechanical recycling has struggled with, as a single polymer type with multiple uses will contain a range of different additives, all of which have a chance of being retained in the resultant recyclate as mechanical recycling does not allow for the separation of additives and contaminants found in PCW, thus compromising product properties and quality.[38]

In order to facilitate and optimise chemical recycling, catalyst systems can be employed to enable large reductions in both working temperatures and timescales, as well as enhance product yield. In this sense, organocatalysts have attracted increasing attention recently and

offer an alternative replacement to metal inorganic catalysts, which usually incur high energy and resource cost, requiring high temperatures to become catalytically activate, as well as the need for the metal to be mined from the earth to retrieve them. Over time this will create environmental challenges, as many common-use metal catalysts have low natural abundancies, resulting in veins drying up quickly.[39-42]

Organocatalysts, as their name would suggest, are catalytic species that solely comprise of organic atoms such as carbon, nitrogen, sulphur, oxygen and hydrogen.[43] Although the use of small organic compounds as catalysts has been fairly well documented in recent literature, widespread acknowledgement and advances in their usage were not made until the early 2000's. This is somewhat surprising, considering the host of benefits they can offer over inorganic catalysts, such as insensitivity to air and moisture (negating the need for dry and inert reaction conditions), low cost of production due to their general ease of synthesis, and typically low or non-toxicity (making them far more environmentally considerate).[44] Furthermore, some organocatalytic species, such as D/L-Proline, possess natural enantiopurity which allows the facile instigation of asymmetric catalysis, and therefore formation of chiral reaction products.[45, 46]

Organocatalysts can also be combined to form dual catalyst complexes and species (Figure 1.3). These species, which are generally a combination of a Lewis acid and Lewis base, can activate both parts of the respective electrophile and nucleophile in the reaction. This results in greatly improved reaction performance, which is superior to the sum of both catalysts individually and is known as a synergistic effect.[47] Synergy is also observed in a class of catalysts that lies between metal-based, and purely organic catalysts, called organometallic

catalysts. These catalysts are typically metal salts, such as acetates, sulphates or phosphates comprising of earth abundant metals, such as zinc or sodium.[48] Although an environmental cost is still incurred, their performance as a consequence of synergistic effects is far improved compared to solely metal-based catalysts, making them of great interest for depolymerisation.
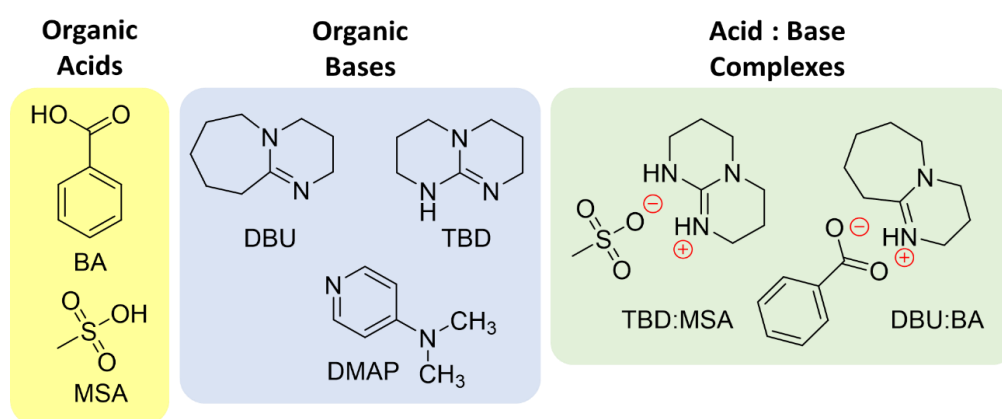
Figure 1.3: *Examples of common organocatalysts, benzoic acid (BA), methane sulfonic acid (MSA), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), triazabicyclodecene (TBD) and 4-dimethylamino pyridine (DMAP), and dual organocatalyst complexes.*

1.1 Current advances in chemical recycling of plastic waste

By volume, the majority of plastics produced in the world are of the PE, PP and PVC types.[23] These polyolefins consist of solely carbon backbones with different degrees of branching and in the case of PVC, a singular chlorine atom in the repeat unit. This presents an issue, in which when compared to the 'polar plastics' (that is those which comprise a functionalised backbone, such as carbonyl containing polyesters, polycarbonates, polyurethanes and polyamides), there are stark reactivity differences which ultimately dictate the ability of these polymers to undergo facile chemical recycling.

Carbonyl containing plastics undergo CRM through nucleophilic attack of the carbonyl carbon, which cleaves the polymer chain. Therefore, the chemical recyclability of polymers is

fundamentally directed by a couple of factors, such as hydrogen bonding, stability of functional groups, solubility, and others.

Polyamides, for example, have been generally challenging to chemically recycle in mild conditions due to the extensive hydrogen bonding networks formed between chains, and the high stability of the amide group, owing to the strong electron donating character of the amine nitrogen. This renders them irresponsive to hydrolysis, only until harsh conditions are applied. In a similar fashion, PET, and poly(bisphenol A carbonate) (BPA-PC) will also rely on the respective reactivities of ester and carbonate functional groups to be depolymerised. Oxygen is less electron donating than nitrogen, and so carbonates and esters are more susceptible to nucleophilic attack than amides, however the presence of a second oxygen in the carbonate group increases the deactivating effect experienced by the carbonyl carbon. Furthermore, the resonance structures of these functionalities are also highly important, amides are more able to form stable resonance structures than esters due to the ability of the amide nitrogen to better accommodate a positive charge. Therefore, a general assumption for polymer reactivity can be observed: polyamide < polycarbonate < polyester (Figure 1.4). However, this is not a definite rule, as the overall stability of a functional group can be altered by factors such as external pH and attached 'R-' groups.[49, 50]
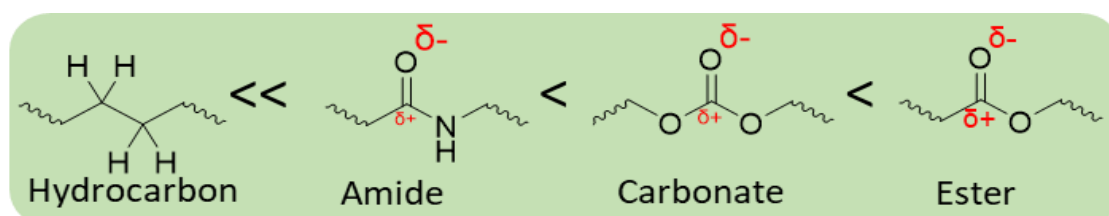
Figure 1.4: Reactivity trend of hydrocarbon, amide, carbonate, and ester functionalities, with implied dipole moments to show activation of the carbonyl carbon to nucleophilic attack as reactivity increases.

Herein, current advances in the chemical recycling of several polar plastics: polyesters (poly(ethylene terephthalate) and poly(lactic acid)), polycarbonates (poly(bisphenol A carbonate)), polyamides and polyurethanes will be discussed. This will be followed by outlining current research into selective co-depolymerisation in mixed polymer degradation reactions.

1.1.1 Poly(ethylene terephthalate) (PET)

PET is one the world's most used plastics and as such, a large fraction of waste-plastic recycling research has been focussed on the degradation of PET. It is regularly synthesised via two primary polycondensation methods, the esterification of terephthalic acid with ethylene glycol, or the transesterification of dimethyl terephthalate with ethylene glycol.[51] Chemical recycling of PET by methods such as hydrolysis,[52] glycolysis[53] and aminolysis[54] has already seen widespread coverage (Scheme 1.1). The terephthalate products of hydrolysis and glycolysis can also be used to resynthesise PET, whilst the terephthalamides produced by aminolysis, are applicable in the synthesis of value-added materials. However, much of the PET depolymerisation research has involved the use of metal-based catalyst systems and only the most recent advances have reported the use of 'greener' organo- and organometallic catalyst alternatives, which can result in higher yields/conversions while applying milder temperatures when compared to metallic catalyst systems.
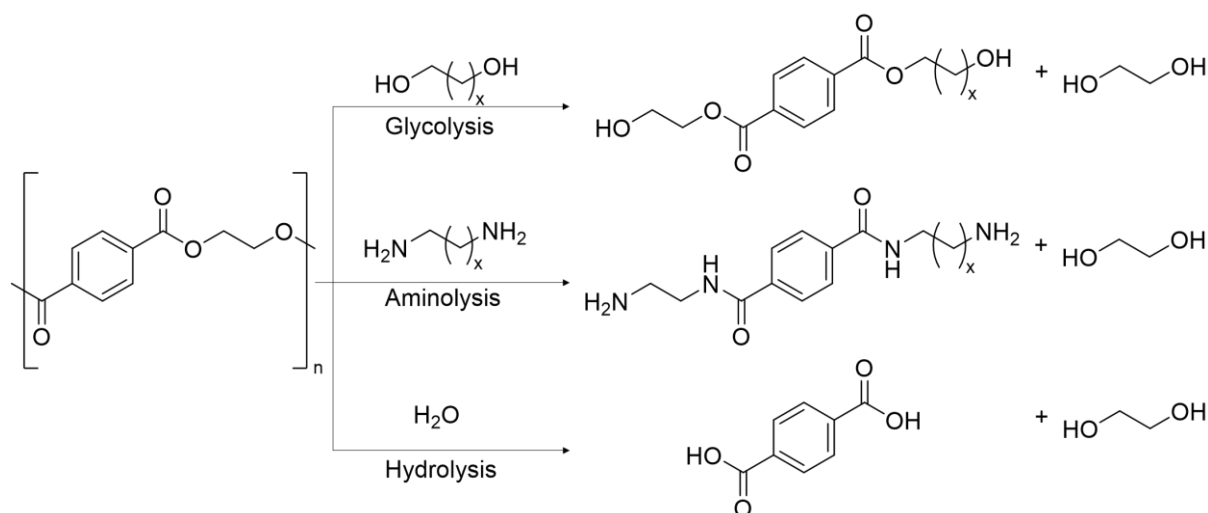
Scheme 1.1: *Depolymerisation reactions of PET via glycolysis, aminolysis and hydrolysis.*

The screening of several nitrogen-based organocatalysts in the depolymerisation of PET by mono- and di-alcohols was reported by Fukushima *et al.* in 2013.[55] Seven catalysts were evaluated for their effectiveness in a glycolysis reaction at 190 °C at 10 mol% catalyst loading. Strong bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) were better able to depolymerise PET, with only $1.1 - 1.5$ wt% of residual oligomers observed after $6.5 - 7$ min of reaction, compared to 7.6 wt% observed for the weak base dimethylacetamide (DMA) after 46 h. Monofunctional bases such as DBU and DBN displayed superior ability when catalysing reactions employing short-chain diols as solvents, whereas triazabicyclodecene (TBD) was more active in reactions utilising long-chain diols. The authors surmised that reactions with DBU and DBN, short chain diols are able to activate carbonyl groups in the ester moieties in the polymer backbone, effectively acting as cocatalysts. In this specific case, the bifunctionality of TBD does not cause any benefit, however, when longer chain diols, or monofunctional alcohols are present, bifunctionality enables the activation of the ester group in the polymer backbone to attack

from the incoming nucleophile highlighting the relationship between catalytic performance and solvent choice (Figure 1.5).
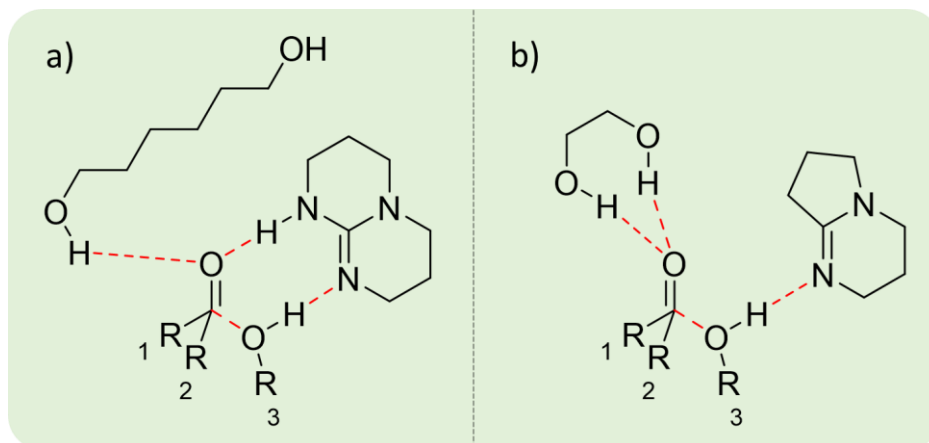
Figure 1.5: *Interactions between diols and catalysts based on chain length: (a) TBD bifunctionality allows for faster reactions with longer chain diols and (b) monofunctional bases such as DBN allow for faster reactions with short chain diols.*

In 2018, Jehanno *et al.* reported the use of a novel protic ionic salt catalyst, which was formed by the equimolar combination of TBD and methanesulfonic acid (MSA), for the efficient glycolysis of PET at 180 °C.[56] The catalyst displayed remarkable thermal stability, with a thermal degradation temperature at 50% weight loss ($T_{50\%}$) of 438 °C, which was higher than TBD and MSA alone (170 °C and 174 °C, respectively). A stoichiometric 1:1 ratio of TBD:MSA was found to be optimal for high reaction rate and monomer yield (91% under air conditions and 89% under a nitrogen atmosphere), with the complete depolymerisation of PET to bis(2-hydroxyethyl) terephthalate (BHET) achieved in 2 h when using ethylene glycol. Similar results were observed when the reaction was scaled up to the 5 g scale. Alongside the better thermal stability of TBD:MSA, the dual catalyst is synergistic, producing higher yields of BHET and less side-products compared to each catalyst individually. The catalyst was also found to be reusable over 5 cycles with no noticeable change in activity, whereas TBD lost activity after 2 cycles. The self-condensation of BHET recovered from waste plastic bottles was also facilitated

by using the TBD:MSA system, and a new PET polymer with comparable thermal properties and molecular weight to those of virgin PET was produced, thus closing the depolymerisation – repolymerisation cycle.

Demarteau *et al.* used the same catalyst in the formation of diol-terephthalamide synthons from PET and several aminoalcohols, that can be further used in the synthesis of value-added polyester-amides.[57] Similarly to the work of Jehanno *et al.* reported in 2018, the authors confirmed that the catalytic activity of TBD:MSA was superior when compared to TBD alone and to a 1,8-diazabicyclo[5.4.0]undec-7-ene: benzoic acid (DBU:BA) system. In this regard, TBD:MSA was able to fully convert PET and ethanolamine (EA) into bis(2-hydroxyethyl) terephthalamide (BHETA) in 8 min at 180 °C, whereas 10 to 12 min were required to convert the substrates when using TBD alone and DBU:BA, respectively. The recyclability of TBD:MSA was investigated, and it was found that no significant change in PET conversion or BHETA yield was observed after 5 reaction cycles.

The same group has also employed TBD:MSA as an organocatalyst in the production of imidazolium-based self-supported elastomeric ionenes from waste commodity polymers, such as PET.[58] These molecules are highly valuable due to their wide applicability in organic synthesis, however their current production involves toxic reagents. The authors reported the depolymerisation of PET in conjunction with 1-(3-aminopropyl) imidazole (API) or 1-(3-aminopropyl)-2-methyl-1H-imidazole (2Me-API) to form ionenes after 90 min of reaction at 180 °C in yields higher than 80%.

Most recently, the implementation of acid-base dual-catalyst systems was reported by Delle Chiaie *et al.* in the glycolysis of PET at 180 °C. [59] Several Lewis acids (metal halides, triflates

and acetates) were paired with the simple Lewis base 4-dimethylaminopyridine (DMAP), and screened for activity and synergistic effect. The authors found that zinc or magnesium-based Lewis acids afforded the highest activity, whilst metal acetates generally outperformed metal halides and triflates. Overall, zinc acetate was found to be the best performing Lewis acid when paired with DMAP, converting 89% of PET to BHET in 3 h. To further optimise the process, zinc acetate was paired with 13 different bases, featuring a range of basicity, from dimethylacetamide (DMA, pKa = -0.19) to a phosphazene base (BEMP, pKa = 27.6), and after 3 h there was a range of conversion from 55% to 96%, with more basic molecules generally exhibiting higher conversion. In general, full conversion was observed after 5 hours for most of the tested bases and the work demonstrated the ability of various acid-base combinations to effectively influence the activity and stability of PET depolymerisation.

Aside from amidine- or guanidine- based organocatalysts, such as DBU and TBD), 'masked carbenes' like 1,3-dimethylimidazolium-2-carboxylate (1,3-DMI-2-C) have also been employed in the glycolysis of PET.[60] Wang and co-workers compared the activity of 1,3-DMI-2-C and its ionic liquid analogue 1,3-dimethyllimidazolium acetate (1,3-DMIA) in the depolymerisation of PET (Figure 1.6). It was found that whilst increasing temperature and catalyst loading benefitted both catalysts, 1,3-DMI-2-C was superior to 1,3-DMIA across all investigated conditions and BHET was recovered in 50% yield. For 1,3-DMI-2-C (20 wt%), complete conversion of PET to BHET occurred within 1 h at 185-200 °C, while longer times were required when the reaction was conducted at temperatures lower than 185 °C. [61]
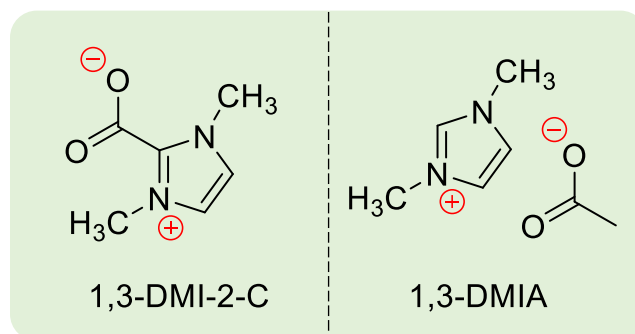
Figure 1.6: The 'masked carbene' catalysts employed by Wang et al.

In 2021, a process for the instantaneous hydrolysis of PET was displayed by Rubio Arias and co-workers.[62] The authors showed that PET could be quantitatively converted to either terephthalic acid (TPA) or dimethyl terephthalate (DMT), and ethylene glycol with microwave assistance under basic conditions (KOH in methanol) in short reaction times (TPA: 1 minute at 120 °C or 4 minutes at 100 °C; DMT: 4 minutes at 80 °C). Selectivity to TPA or DMT is determined by temperature; hydrolysis to TPA is preferential at higher temperatures, whilst methanolysis to DMT is more favourable at lower temperatures. This outcome presents a series of advantages over other previously reported strategies, including the rapid conversion of PET to tailorable products and the absence of oligomers or side products at the end of the reaction.

Whilst most efforts to depolymerise PET are focussed on CRM processes, Chen *et al.* demonstrated the synthesis of aromatic polyamide copolymers from chemically recycled PET via glycolysis and aminolysis.[63] PET was first depolymerised to BHET and low molecular weight oligomers using zinc acetate in ethylene glycol (reflux, 6 h). Following purification of the recovered BHET and oligomers, an aminolysis step, using hexamethylene diamine (HMDA), converted the BHET and oligomers to bis(6-aminohexyl) terephthalamide (BAHT), which acts as a building block in the copolymer. BAHT was combined with adipic acid (AA) to make a BAHT-AA salt (65 °C for 6 h). The final copolymers were synthesised from this BAHT-AA salt, a

polyamide 66 (PA66) salt and deionised water in a melt polycondensation process under a nitrogen atmosphere (280 °C for 1 h, followed by 295 °C for 3.5 h). The solid copolymers were then finely smashed and subjected to a solid step polymerization (230 °C, 6 h, nitrogen) to increase the relative viscosity of the new copolymer. To this end, various PA66 copolymers were synthesised, each with different levels of aromatic content. Copolymers with more aromatic moieties possessed greater renewable content, due to having a higher ratio of BAHT blocks within the chain. The synthesised copolymers presented good thermal properties, rapid crystallisation ability and physical properties comparable to, or better than, unaltered PA66.

The chemical upcycling of PET, by glycolysis and aminolysis, catalysed by half-salen zinc complexes, was demonstrated by Jones *et al.* in 2022.[64] The authors found that at 180 °C, with 8 wt% catalyst loading, a 48 % yield of BHET could be recovered from waste PET glycolysis after 1.5 h, whilst a PET thin-film could be completely depolymerised in 1 h, using 4 wt% catalyst, yielding BHET at 61%. The catalyst employed was noted to perform better than zinc acetate dihydrate, a common benchmark catalyst for PET glycolysis, under the same conditions. Following this, the authors used the zinc-salen catalysts in the aminolysis of PET, to produce terephthalamides that could be employed in the synthesis of polyester-amides. Ethylene diamine and ethanolamine were reacted with PET at 110 °C-120 °C, with 8 wt% catalyst, producing good yields of terephthalamides within 1 – 2 h. The resultant polyester-amides had notable thermal properties, displaying glass transition temperatures (T_g) values as high as 126 °C.

1.1.2 Polycarbonates (PC)

Polycarbonates have found extremely widespread use, including engineering and electrical components (owing to their insulating and heat resistant properties), safety applications (owing to their respective light weights and impact resistance), glass substitutes due to high optical transparency and more recently as materials for biomedical applications. The most common polycarbonate, BPA-PC is synthesised from the polyaddition of bisphenol A (BPA) monomers and phosgene, which is a highly toxic gas. Alongside chemical recycling, more sustainable methods that reduce or fully remove the usage of phosgene are being investigated, such as the copolymerisation of carbon dioxide with epoxides or the ring-opening polymerisation of cyclic carbonates.[65] The chemical recycling of BPA-PC is a very promising and widely researched method, in which BPA-PC is depolymerised into Bisphenol A (BPA) and a linear (or cyclic) carbonate, which can then be repolymerised into BPA-PC. However, BPA is an endocrine system disruptor, more specifically a xenoestrogen,[66] and therefore there is a pressing need to develop 'BPA free' plastics for home use and food storage solutions. By varying the nucleophile employed in the chemical recycling process, a wide range of carbonates can be isolated from BPA-PC, which can then be repolymerised to meet the demand for BPA-free plastics (Scheme 1.2).
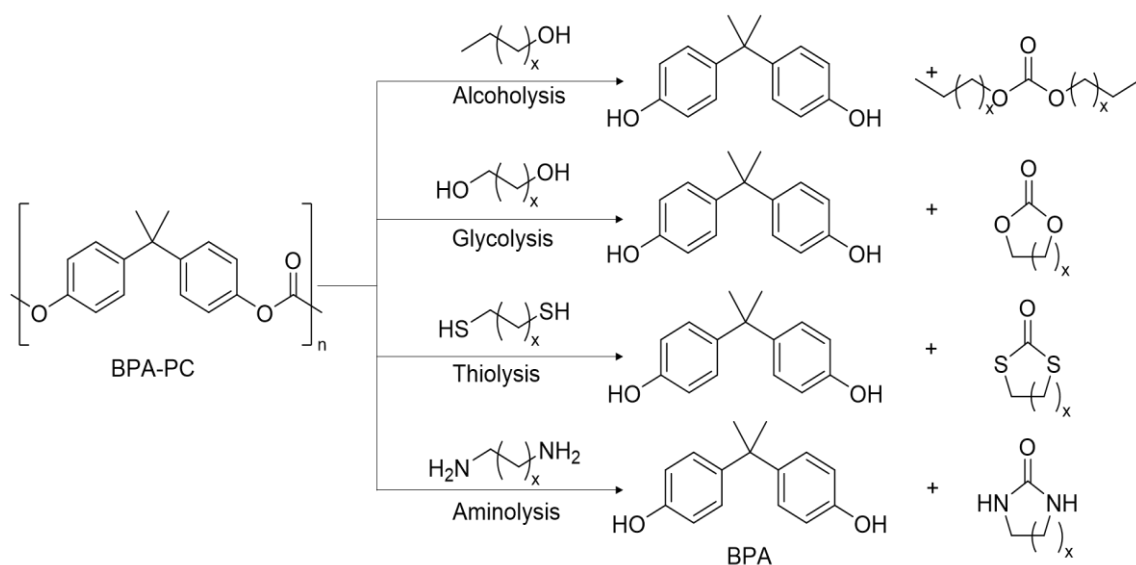
Scheme 1.2: *Examples of the transesterification reactions and products afforded by BPA-PC chemical recycling.*

Quaranta *et al.* previously reported both the solvent-free alcoholysis and glycolysis of BPA-PC under mild conditions using the organocatalyst DBU.[67, 68] The alcoholysis and glycolysis of BPA-PC produced dimethyl carbonate (DMC) and cyclic carbonates respectively, which are important feedstocks to replace phosgene in carbonylation reactions, as they are classified as non-toxic.[69, 70] Alcoholysis and glycolysis reactions proceeded solvent-free, with DBU showing activity in methanol, ethanol and 1,2-propane diol. In both cases, complete conversion was achieved in 30 min at low catalyst loadings (1 mol% for glycolysis and 10 mol% for alcoholysis), however higher temperatures were required for glycolysis (180 °C versus 100 °C). DBU catalysed alcoholysis afforded quantitative BPA and DMC yield in less than ¼ of the reaction time observed for other common organocatalysts, such as 1,4-diazabicyclo[2.2.2]octane (DABCO) and DMAP. Furthermore, near quantitative yields of DMC were still observed when the catalyst (recovered as a BPA:DBU adduct) was recycled and reused up to 7 times.

TBD was also employed to investigate the solvent-free alcoholysis of BPA-PC in mild conditions.[71] In order to avoid the use of auxiliary solvents, DMC (one of the degradation

products) was used to solubilise BPA-PC, additionally simplifying product separation at the end of the reaction. Compared to several other catalyst classes (such as organic acids, organic bases, alkali metals and transition metals) in 2-methyltetrahydrofuran (2-MeTHF), TBD was the only catalyst able to produce quantitative yields of BPA and DMC without producing major yields of mono-methylated and di-methylated side-products, showing its higher activity and stability during the conversion process. Full conversion was observed after 12 h at room temperature when using 2-MeTHF, shorter times were observed for the reaction in DMC using the same catalyst concentration and excess of MeOH (6 h at 50 °C and 2 h at 75 °C). Furthermore, BPA was recovered in a 96% yield from a recycled pair of safety goggles, highlighting the ability of TBD to successfully catalyse the depolymerisation of commodity plastics containing additives. TBD was also shown to be highly recyclable as a catalyst, maintaining comparable activity after 5 successive cycles. However, if the catalyst was not recovered and more BPA-PC was simply added to the reaction vessel (similar to a flow chemistry process), activity decreased noticeably between the cycles. The authors attributed this behaviour to the increased conversion of active TBD into its less catalytically active conjugate acid, for each successive addition of BPA-PC therefore lowering the concentration of active catalyst.

Jehanno *et al.* described the synthesis of value-added cyclic carbonates from PCW polycarbonates.[72] Based on their previous work,[56] the authors used the TBD:MSA catalytic system to isolate different 5-membered cyclic carbonates in 90-96% yields and depolymerisation times ranging from 5 min to 3 h. This was achieved at temperatures ranging from 90 °C to 160 °C and 15 mol% of TBD:MSA under nitrogen. Additionally, 6-membered cyclic carbonates were also formed from their respective diols in moderate to high yields (35-

97%) and low reaction times (1-4 h), with the side chain functionality of each diol preserved. It was found that bulkier side chains produced greater yields of cyclic carbonate and the authors suggested that these groups reduce the ability of the carbonate functionality to ring-opening, and so ring-closure is favoured overall due to the torsion experienced by the polymer backbone.

More recently, the same group reported the formation of short-chain aliphatic carbonates, which display ionic conductivity, from chemically recycled polycarbonate.[73] To this end, glycolysis reactions were performed using TBD:MSA (15 mol%) at 160°C to convert BPA-PC into BPA and their respective linear carbonate-diol products. Nucleophiles with different chain lengths were used (from 1,3-propane diol to 1,5-pentane diol) to isolate the respective products in good yields (64 – 67%) and short reaction times (0.75 – 2 h). However, when 1,4-butane diol was used, low product yield (4%) was observed after 24h, the authors attributed this to the decomposition of the formed carbonate by an intra-molecular backbiting reaction. Finally, the successfully recovered carbonate-diols were copolymerised by polycondensation with DMC, catalysed by DMAP to afford aliphatic polycarbonates. These carbonates were then tested for their ability to act as solid polymer electrolytes (SPEs). Upon analysis for ionic conductivity, the copolymers displayed higher values than those previously reported for high-performance SPEs. These results are important as the recycled copolymers have the potential to improve the performance of solid-state lithium batteries, highlighting the ability of chemical recycling to make useful value-added compounds.

The chemical recycling of BPA-PC by diaminolysis as a route to obtain isocyanate free polyurethanes has also been previously reported.[74] BPA-PC was reacted with both aliphatic

(1,6-diaminohexane, 4,7,10-trioxa-1,13-tridecanediamine, *m*-xylenediamine and *p*-xylenediamine), and aromatic diamines (4,4'-diaminodiphenylmethane and 2,4-diaminotoluene) at 120 °C in THF. The reactions employing aliphatic diamines proceeded without the need for a catalyst, whereas reactions using aromatic diamines required the presence of DBU or sodium hydroxide (NaOH) (10.5 – 20.3 mol%) to afford suitable conversion. Aliphatic diamines produced high yields of both BPA (83% – 86%) and their respective polyurethane (PU) (78% – 99%) in times varying between 2 and 12 h. On the other hand, longer times (7-27 h) were required for aromatic diamines to reach similar yield (83% – 95% BPA; 87% – 94% PU). Furthermore, the newly furnished polyurethanes each displayed good thermal stability (T_d= 212 °C– 270 °C), with maximum rates of degradation ($T_{d\ Max}$) between 323 °C and 366 °C, suggesting the ability of these polyurethanes to be conventionally processed. This work shows both the ability to produce value-added products from waste polycarbonate, and the design of isocyanate-free polyurethanes in a one-pot fashion.

Ionic liquids have found good utility as catalysts for the depolymerisation of BPA-PC due to their initial ease of production, low environmental impact, and high activity.[75-78] Recent examples include Lewis acidic ionic liquids formed by 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) in conjunction with Iron trichloride ($FeCl_3$), DBU-based ionic liquids formed with acetate, propanoate and lactate anions, and novel succinimide-based ionic liquids. In all these cases, high conversion of BPA-PC was achieved under mild reaction conditions (70 °C – 140 °C) and short reaction times (2 – 3 h). Furthermore, each catalyst was found to be highly active in low to moderate loadings (5.0 – 30.0 mol %) and could be reused in up to 6 cycles without loss in activity.

The same group has also presented the application of deep-eutectic solvents (DESs), based on choline chloride, as catalysts for BPA-PC methanolysis under mild conditions.[79] Near quantitative conversion of BPA-PC and yields of BPA were achieved with the choline chloride: urea (1:2) (ChCl:2Urea) catalyst species, in 2.5 h at 130 °C and 10 wt% loading. The authors found that whilst all choline chloride: urea DESs investigated (1:1 – 1:4) displayed a synergistic effect, ChCl:2Urea was the most active and economical. This was further displayed when the catalyst system was found to be reusable, catalysing the depolymerisation of BPA-PC in no less than 5 cycles, with little depreciation in catalytic performance observed between each successive cycle.

Nacci *et al.* employed an ionic liquid, tetrabutylammonium chloride (NBu_4Cl), as the base in Lewis acid – Lewis base catalyst complex, with nanostructured zinc oxide (ZnO-NPs), for the depolymerisation of BPA-PC.[80] Complete depolymerisation, with quantitative BPA yield, was achieved after 7 h at 100 °C with a 5 mol % catalyst loading using excess 1,2-propanediol. Several other nucleophiles were also successfully employed, including water, other alcohols (and polyols), amines (and polyamines) and aminols. The ability of this reaction to proceed with a wide range of nucleophiles creates the benefit of a wide variety value-added products alongside BPA, such as cyclic carbonates, cyclic ureas and 2-oxazolidinone (which can be used to reform polycarbonates), urea-formaldehyde resins, and polyurethanes, respectively. Furthermore, the glycerolysis reaction produces BPA and glycerol carbonate, which means that two industrial waste products can be entirely converted into valuable products (glycerol carbonate is both a fuel additive and industrial solvent) in one-step. Finally, the authors report that the catalyst was reusable in up to 5 cycles of use, with no observable loss in activity.

In 2021, Jung *et al.* reported the upcycling of BPA-PC using hydroxamic acid nucleophiles to synthetically valuable 1,4,2-dioxazol-5-ones and BPA.[81] Quantitative yields of dioxazolones were achieved in 4 h at 30 °C, by employing the organocatalyst TBD (2 mol%) in 2-MeTHF. Different organobases and hydroxamic acids were investigated, and it was observed that higher basicity of the catalyst increased overall conversion of BPA-PC, whereas less electron withdrawing groups and longer conjugated moieties on the hydroxamic acid were more favourable. This process was further completed on a gram scale using real-life commodities in the form of CDs. In addition to this, a green synthetic process for aryl amides was developed in the one-pot depolymerisation of BPA-PC to the relevant dioxazolone, followed by the ruthenium catalysed C-H amidation of the dioxazolone. Overall, this process is environmentally beneficial because BPA-PC acts as a replacement for both phosgene and non-green carbodiimidazole carbonylation agents previously used in this synthesis.

Huang and co-workers have recently reported the synthesis of thermoplastic polyurethane elastomers from the upcycling of BPA-PC.[82] BPA-PC was depolymerised to phenolic carbamate derivatives and BPA, using ethylene diamine (EDA, 1.02 equiv) as nucleophile in catalyst free conditions under nitrogen at 65 °C. These EDA-based carbamate monomers were then polymerised with isocyanates in a two-step polymerisation, to form the thermoplastic polyurethane product. The synthesised polymers were found to be robust, as well as re-processable, with properties comparable to thermoplastic polyurethanes made from pristine raw materials.

The chemical upcycling of the polycarbonates BPA-PC and PPC, by methanolysis and glycolysis, catalysed by half-salen zinc complexes, was recently demonstrated by Jones *et al.*[64] The

authors reported that, when using 4 wt% catalyst at 50 °C, with 2-MeTHF as auxiliary solvent, the methanolysis of BPA-PC to BPA and DMC could be achieved in 1 h, yielding BPA at 88 %. These results are much superior compared to zinc acetate dihydrate, which was observed to be barely active at this working temperature. BPA-PC glycolysis to different cyclic carbonates was also demonstrated, with good yields of product (48% – 78%) achieved, at temperatures as low as 75 °C, with a 2.2 mol% catalyst loading in 1 h. BPA was recovered between 96% and 99% under all circumstances. The zinc catalysts were then employed in the methanolysis of PPC, which was converted to PC, a green solvent, in 1.5 h at 50 °C, yielding PC at 58%. The authors believed this to be the first example of PPC methanolysis that produces good yields of product at low temperature.

1.1.3 Poly(lactic acid) (PLA)

PLA is a polyester bioplastic formed from the condensation of lactic acid, which can be obtained from the fermentation of crops, or by the ring-opening polymerisation of lactide. Due to this more environmentally conscious production method, increasing attention has been devoted to PLA as a common-use polymer.[83] Yet, the biodegradable nature of PLA has proven to have become somewhat of a crutch for its more justified release into the environment, in the understanding that it will eventually break down. However, its degradation rate is strongly related to environmental factors and can vary widely (ranging from months to years).[84] In addition, biodegradability serves to obscure potential toxicity problems associated with bioplastics. A study conducted by Zimmermann *et al.* found that bioplastics are no less toxic than conventional plastics, such as PE and PET, and that whilst they may present some sustainability benefits, the same benefits do not extend to

fundamental chemical hazards.[85] Furthermore, the composting (biodegradation) of PLA produces a considerable loss in value, as the ultimate degradation products are carbon dioxide and water.[86] The value held in recovered material is huge as it can aid the reformation of original biopolymers (in a time when the life-cycle of many bioplastics is linear and single-usage), and reduce demand for farmland in the process as less crops need to be grown. Since PLA has a polyester backbone, its depolymerisation occurs in a similar way to PET and BPA-PC. Thus, chemical recycling is becoming an attractive approach to processing PLA waste material (Scheme 1.3).
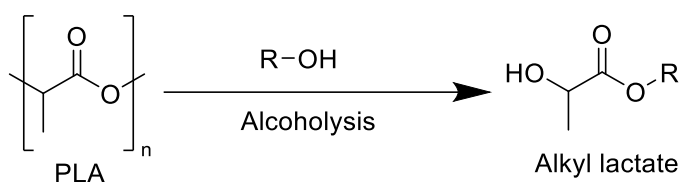
Scheme 1.3: *A large focus of current PLA CRM research is via alcoholysis processes, affording akyl lactates.*

Recently, the chemical recycling of PLA using tetramethylammonium carbonate (TMAC) as transesterification catalyst was reported.[87] Alongside PLA ,the authors found that TMAC was also a suitable catalyst for the depolymerisation of several different polymer types. Conditions for the conversion of PLA into methyl lactate (Me-La) were mild (50 °C), with low catalyst loadings (0.5 – 2 mol%) in methanol, with THF present as an auxiliary solvent. Whilst lower catalyst loadings (0.5 mol%) were able to facilitate the complete depolymerisation of PLA, product selectivity for Me-La was poorer than when higher loadings (2 mol%) were employed (83% versus 100%). Furthermore, 'green' solvent alternatives to THF were employed, including ethyl acetate (EtOAc), 2-MeTHF, acetone, acetonitrile, DMC and cyclopentyl methyl ether (CPME). These alternative solvents were able to effectively solubilise PLA (except for CPME) and promote depolymerisation to Me-La, with EtOAc and 2-MeTHF proving to be the

most promising (yielding Me-LA in 100% and 93%, respectively). The transformation is also achievable under solvent-free conditions, with quantitative conversion to Me-La observed in 10 min at 100 °C (0.5 mol% TMAC).

The same group also reported the use of a zinc(II) complex as catalyst for the methanolysis of waste PLA to Me-La under mild conditions.[88] Reactions proceeded under a nitrogen atmosphere from 70 °C to 110 °C, with 8 wt% of catalyst loading and THF as an auxiliary solvent. Objects such as a toy, a cup and a 3D printed object were used for the study, and each commodity exhibited varying levels of conversion, selectivity, and yield within a given time. Depolymerisation of the cup reached 90% conversion after 1 h at 70 °C, whereas 55% conversion was observed for the toy in the same conditions. Despite these varied results, the work demonstrated the feasibility of chemical recycling of waste PLA commodities and offering an interesting approach for future industrial applications.

Another recent example of PLA alcoholysis by a zinc-based catalyst in mild conditions was reported by Lamberti et al.[89] For this work, ethanolysis, propanolysis and butanolysis of PLA at different temperatures (50 °C – 130 °C) was achieved when catalysed by either a zinc ethylenediamine Schiff-based complex ($Zn(1)_2$) or a zinc propylenediamine Schiff-based complex ($Zn(2)_2$) (8 wt% of each) in an excess of THF and under nitrogen (Figure 1.7). The final products (consisting of alkyl-lactates) were recovered in good yields; however, propyl and butyl lactates (Pr-La, Bu-La) were recovered in lower yields than ethyl lactate (Et-La) due to increased steric hinderance produced by the longer-chain alcohols. As expected, increasing temperature improved both rate and yield of reactions, however the effect on catalytic performance was less straightforward. $Zn(1)_2$ showed all-round better performance as

temperature increased, whereas Zn(2)$_2$ was most active at 50 °C, producing a higher yield of Et-La in less than one third the time required by Zn(1)$_2$. Zn(2)$_2$ also displayed a further ability to facilitate conversion, albeit minimal, of PLA below 0 °C, which is a remarkable benchmark in the field. Ultimately, this work shows that alcoholysis of PLA on a multi-gram scale by different alcohols is possible under mild conditions in suitable times, and that the more industrially useful Et-La is accessible in high quantity at low temperatures, therefore providing a great opportunity for reduced operational costs.
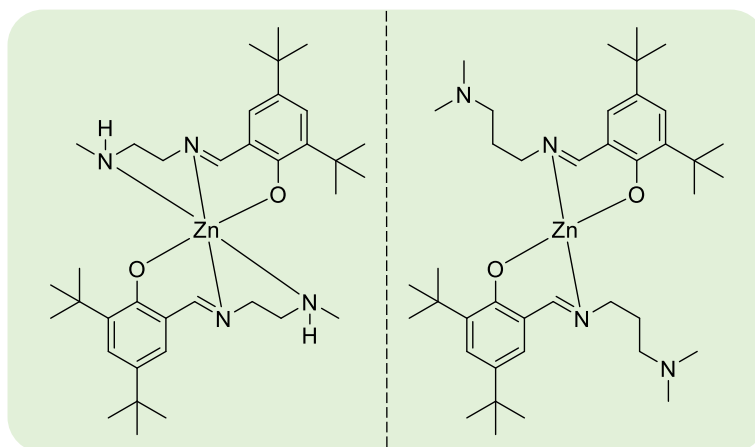
Figure 1.7: *Zinc ethylenediamine Schiff-based complex (Zn(1)$_2$) (Left) and zinc propylenediamine Schiff-based complex (Zn(2)$_2$) (Right).*

The formation of lactide-based polyurethanes from the products of chemically recycled PLA by alcoholysis was reported by Nim *et al.*[90] PLA was depolymerised in 10 minutes using either ethylene glycol, propane-1,3-diol or butane-1,4-diol, facilitated by the addition of tetrabutyl orthotitanate (TBT, 2 wt%) at 240 °C, with microwave assistance. PLA to diol ratios from 1:1 to 4:1 wt/wt were investigated, and the products of alcoholysis were used as starting polyols for the preparation of lactide based polyurethanes, alongside hexamethylene diisocyanate (HDI) and a chain extender. The polymers synthesised were found to have properties which would make them useful in single-component materials or adhesives.

More recently, Tian and co-workers displayed the facile ammonolysis of PLA to alanine.[91] The reaction was catalysed by a ruthenium/titanium dioxide catalyst in ammonia solution at 140 °C. Within 32 h, it was observed that 94% of PLA was converted selectively to alanine in 77% yield. The ammonolysis was found to proceed via the complete conversion of PLA to lactamide in 10 minutes, before the slower conversion of lactamide to ammonium lactate and then alanine. Catalyst free conditions were also investigated; however, it was found that formation of alanine was not possible under these conditions.

Most recently in 2021, Lamberti *et al.* reported the alcoholysis of PLA facilitated by a synergistic dual catalyst system.[92] High selectivity (72%) and yield (72%) of methyl lactate was achieved in 1 h at 130 °C when using the dual catalytic combination of zinc acetate and DMAP (5 wt% of each). The authors investigated different ratios of zinc acetate:DMAP from 3:1 to 1:3 and found that a 50:50 mixture of both provided the greatest catalytic and synergistic affect.

1.2 Other polar plastics: Polyamide (PA) and Polyurethane (PU)

1.2.1 Polyamides (PA)

Polyamides are a commonplace polymer found in routine products from textiles and clothes to ropes and medical sutures. This wide ranging presence is owed to their high strength and relative durability, due to the extensive presence of hydrogen bonding between polymer chains (Figure 1.8).[93] Furthermore, the relatively high stability of the amide bond (compared to carbonates or esters) has made chemical recycling approaches, especially hydrolysis-type reactions, more challenging. For example, in 2011 Kamimura *et al.* reported the depolymerisation of nylon 6,6 using ionic liquid catalysts.[94] However, this was only achievable

when high temperatures (300 °C) and long reaction times were employed (*ca.* 6 h), as a consequence of the high stability of polyamides towards hydrolysis. Therefore, much of the current polyamide recycling is still focussed on mechanical and/or high temperature melt reprocessing, which leads to deterioration of mechanical properties and ultimately lower value of the end-products.[95]
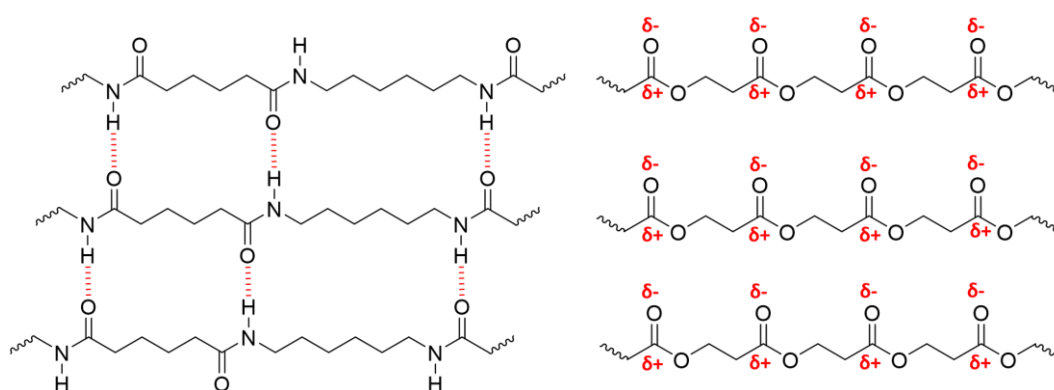
Figure 1.8: *The hydrogen bonding network (hashed bonds) in polyamides (left) makes their degradation more difficult compared to polyesters (right), which are bonded together by weaker dipole-dipole interactions.*

More recently, however, Kumar and co-workers presented a novel hydrogenation method to chemically recycle PA in milder conditions using a ruthenium pincer catalyst that was previously reported for the hydrogenation of small molecules like esters and amides (Figure 1.9).[96] The depolymerisation reaction was carried out at 150 °C under a pressurised hydrogen atmosphere (70 bar) in dimethyl sulfoxide (DMSO), which acted as a plasticiser. A range of various nylon polymers (with both aliphatic and/or aromatic backbones) and polyurethanes were at least partially depolymerised to diols and diamines in the corresponding conditions. The maximum conversion of nylon 6 was observed after 48 h of reaction (80%), whilst a two-step hydrogenation reaction was able to convert 99% of a nylon 6 sample in 5 days. To demonstrate a closed-loop cycle, an aromatic polyamide of molecular weight (M_w) 1500 g mol⁻¹ was hydrogenated, and the recovered monomers and oligomers were successfully

repolymerised into a new polyamide with a molecular weight of 1600 g mol^{-1} after 48 h of reaction. Whilst this method is still under refinement, it shows that chemical recycling of nylons of various types can be achieved in more environmentally friendly conditions than previously reported in literature.
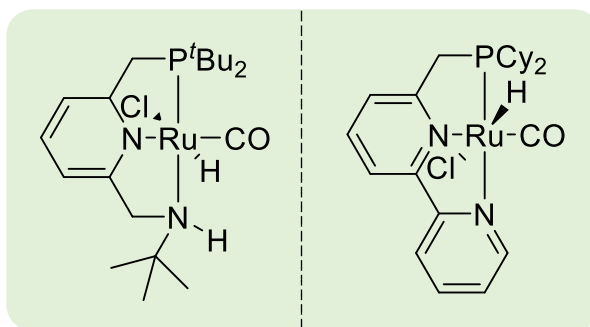
Figure 1.9: *The Ru pincer complexes employed by Kumar (Left) and Schaub (Right).*

The employment of ruthenium pincer catalysts in the depolymerisation of both polyamide and polyurethane samples by hydrogenation was also reported by Schaub *et al* (Figure 1.9).[97] Similar to previous work by Kumar and co-workers,[96] a pressurised hydrogen atmosphere (50 – 100 bar) was used with the addition of KO^{t}Bu (4 mol%) as a basic additive to enhance catalytic ability, THF as a solvent and 1 mol% of catalyst. Among the four low molecular weight PA 6,6 samples tested (two with an excess of amine end-groups and two with and excess of carboxylic end-groups), those with an excess of amine moieties were able to be depolymerised, whereas no conversion was observed for those with an excess of carboxylic end-groups. The first basic PA, 'PA-1' (M_w 8240 g mol^{-1}, amine end-groups 1748 mmol kg^{-1}), was successfully depolymerised in 20 h at 200 °C under a hydrogen atmosphere pressure of 100 bar to produce diamine and diol in yields of 78% and 62%, respectively. The second basic PA, 'PA-2' (M_w 8750 g mol^{-1}, amine end-groups 1482 mmol kg^{-1}), required milder conditions (120 °C, 50 bar hydrogen atmosphere) and produced lower amounts of diamine and diol products (62% and 37%, respectively). A technical-grade polyamide 6,6 sample was also

investigated, and its full conversion to diol and diamine products achieved after 50 h in the conditions used for depolymerisation of PA-1, however product yields were low. Commercial PU foam and a commodity PU sponge were both converted in the same conditions on a 10 g scale, yielding polyol and diamine products within 30 h. Despite the environmental and economic drawbacks presented by employing higher reaction temperatures and pressurised reaction atmospheres, this work further solidifies that chemical recycling of both PA and PU is feasible in large scale reactions.

1.2.2 Polyurethanes (PU)

The controlled chemical recycling of polyurethane (PU) is not yet fully feasible, and the large combination of different amines and isocyanates that can be used to synthesise PU only strengthens the complexity of their degradation, as polymers with different physical properties can be obtained (plastics, elastomers and hard or soft foams). Furthermore, the isocyanate monomers required to form PU are highly reactive, which renders them easily hydrolysable and even self-reactive bonds (e.g., forming cyclic species).[98-100]

In addition, within the urethane unit, competition between the cleavage of the C-N versus C-O bond leads to large variations of depolymerisation products.[101] Despite the current challenges associated with closing the PU loop, chemical recycling to polyol products has been investigated. Also, the development of non-isocyanate polyurethanes is also gaining traction, such as those synthesised by the ring-opening addition of cyclic carbonates with amines (Scheme 1.4).[102]
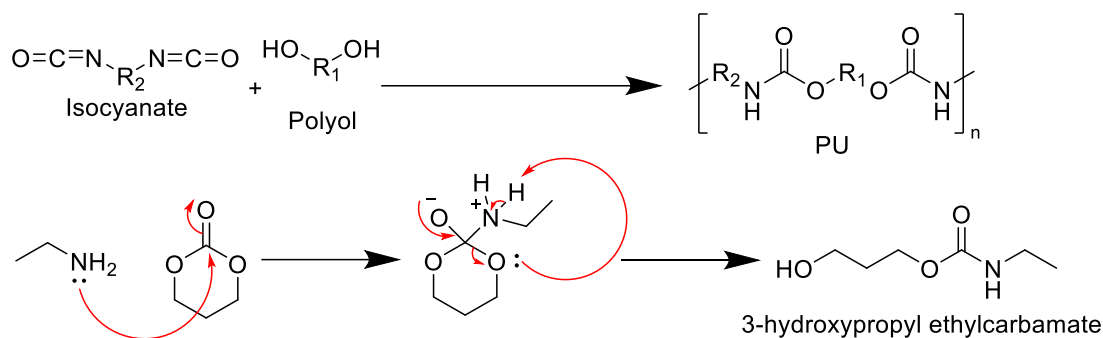
Scheme 1.4: *A traditional method of polyurethane formation, from isocyanates and polyols (Top) compared to an isocyanate free urethane synthesis between an amine (ethanamine) and a cyclic carbonate (trimethylene carbonate) (Bottom).*

Earlier works showed that catalysts normally used for polyurethane synthesis, such as stannous octoate, are suitable for the depolymerisation of flexible polyurethane under glycolysis conditions.[103] Furthermore, in 2013, dos Santos *et al.* reported the usage of several different catalysts for the glycolysis of PU and zinc acetate showed to be the most promising.[104]

In 2019, the metal-catalysed glycolysis of PET and PU was reported by Esquer and co-workers.[105] In this work, both flexible and rigid PU foams were successfully depolymerised by a number of metal-based catalysts, and the most promising results were obtained when $FeCl_3 \cdot 6H_2O$ was used to recover the polyol from flexible PU (96% yield after 1 h at 200 °C). Similar yields were obtained for the iron-catalysed depolymerisation of rigid PU foam, however the reaction required 5 h to complete at the same temperature due to more extensive internal crosslinking found in rigid PU foams. The oxidation state of the metal was determined to influence overall catalytic activity, with high oxidation state metals performing better than their low oxidation state counterparts.

More recently, the solvent-free acidic hydrolysis of scrap flexible polyurethane foams was reported using succinic acid under mild conditions.[106] Degradation of a mixture of polyurethane foams (densities 23 – 30 kg m^{-3}) was possible in 5 hours at 195 °C, and the

resultant recycled polyol products were able to be used to partially substitute (up to 30%) conventional polyols in the synthesis of new rigid polyurethane foams.

A two-stage glycolysis/hydrolysis process for the chemical recycling of polyurethanes was developed by Zahedifar *et al*. in 2021.[107] Dicarbamates and short-chain model polyurethanes were synthesised from phenyl diisocyanate, phenyl isocyanate, 1-hexanol and 1,6-hexanediol. The dicarbamate and polyurethane models were subjected to glycolysis in ethylene glycol under an argon atmosphere for 2 h, with 10 wt% of sodium acetate as catalyst, at either 190 °C (PU) or 170 °C (dicarbamates). After precipitation, the products underwent a microwave-assisted (800 W) hydrolysis reaction (pH 11) using sodium hydroxide at 200 °C for 90 minutes under a 40-bar atmosphere of air. Overall, the glycolysis step produced alcohols and diols and the hydrolysis step produced isocyanate-based amines, alcohols, and polyols.

Most recently, Gausas and co-workers demonstrated the catalysed hydrogenation of various polyurethanes, using and iridium MACHO catalyst under basic conditions and isopropyl alcohol (IPA) as a green solvent.[108] Virgin and end-of-life polyurethane samples (flexible solid and foam, rigid solid and foam), were converted to aniline and polyol fractions in good yields at temperatures ranging from 150 °C to 180 °C when the catalyst Ir-^{iPr}MACHO (2 wt%) was used in combination with potassium tertbutoxide (KO^{t}Bu, 2 eq) under hydrogen atmosphere (30 bar).

1.3 Selective Co-depolymerisation

Interest to explore 'selective' or 'co-depolymerisation' of mixed-plastic waste is growing. This approach generally entails the selective and sequential degradation of a range of polymer types, in the same reaction vessel, with each depolymerisation facilitated by a change in

reaction conditions (Figure 1.10). There are several apparent benefits related to selective chemical recycling of mixed-plastic waste, such as the ability of chemical recycling to produce high-value pure monomers, which are able to be repolymerised into new polymers with equivalent properties to their pre-commodity form.[48] In addition to this, the pre-sorting of plastic waste that is usually encountered in plastic recycling of any kind can be bypassed, with the individual polymers separated at the product stage during a one-pot reaction, thus improving physical material and economic value recovery, as well as eliminating the issue of recycling stream contamination, which is a challenge to tackle due to many plastics sharing physical properties and appearances.
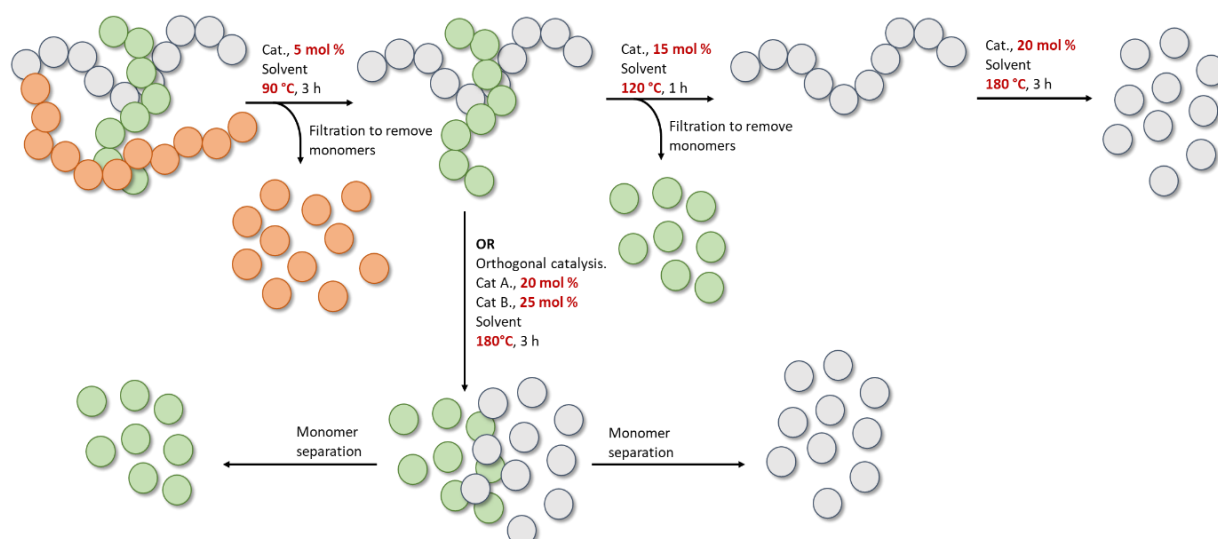
Figure 1.10: *An example of the selective depolymerisation of 3 different generic polymers (in orange, blue and green), triggered by a change in reaction conditions or by employing orthogonal catalysis, in which depolymerisations are carried out simultaneously but using catalysts that are selective to each polymer.*

An earlier example of selective depolymerisation was reported by Carné Sánchez and Collinson in 2011, when the authors reported the selective depolymerisation of PLA in a mixture of PLA and PET.[109] The methanolysis reaction was catalysed by zinc acetate, converting 90% of the PLA to yield 65% of Me-La whilst PET was stable and unreacted under the reported conditions. Me-La could be removed from the reaction by filtration, and the

remaining PET could be sequentially depolymerised by glycolysis, also catalysed by zinc acetate. The differences in the reactivity of both polymers could be related to solubility, nature of the polymer backbone, polymer architecture and interaction with the catalyst. Although the reason for these differences is not fully understood yet, this work demonstrates that different polyesters can be orthogonally reacted.

In 2015, Feghali and Cantat investigated the selective degradation of PET in mixed plastic reactions whilst describing the hydrosilylation of polyethers, polyesters and polycarbonates.[110] The reactions were carried out at ambient temperature using a Lewis acid organocatalyst $B(C_6F_5)_3$ and the triethylsilane (Et_3SiH), The mixed samples were composed of PET with PLA, PET with PS, and PET with PS and PVC. PET was selectively depolymerised from a PET-PLA mixture after 3 h, producing two disilylethers in moderate yields (51% – 62%), while PLA was unaffected at the respective conditions. However, when the equivalents of Et_3SiH were approximately doubled, and catalyst loading was increased 5-fold, both PET and PLA were degraded into bis(triethylsilyloxy) alkanes after 16 h (Scheme 1.5). Following this, the authors found that PET could be selectively depolymerised from a mixture with PS, also achieving disilylethers in 66% to 69% yields. Finally, PET was selectively depolymerised in a reaction consisting of PET, PS and PVC to produce disilylethers (61% to 65% yield) while PS and PVC remained intact. Whilst PLA, PS and PVC were not recovered like PET, it is important to note that their presence had no influence on the depolymerisation efficiency of PET.
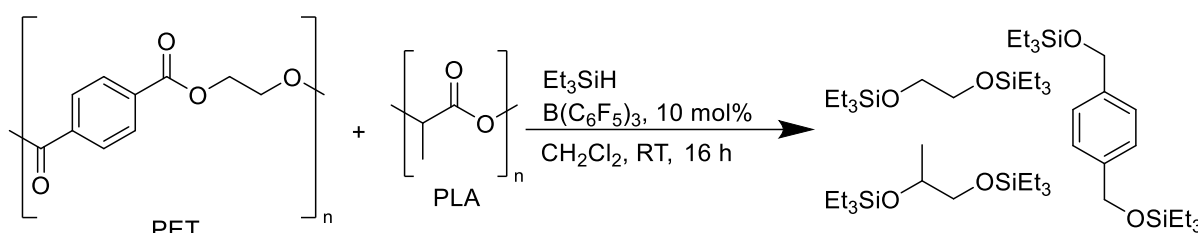
Scheme 1.5: *Reaction of PET and PLA in ambient conditions to produce bis(triethylsiloxy) alkanes.*

The controlled selective hydrogenolysis of polyester mixtures, triggered by a change in temperature or solvent, was presented by Westhues *et al.* in 2018.[111] By employing a ruthenium complex, [Ru(triphos-xyl)tmm] (triphos-xyl=1,1,1-tri(bis(3,5-dimethylphenyl) phosphinomethyl)ethane, tmm = trimethylenemethane), with bis(trifluoromethanesulfonyl) imide (HNTf2) as cocatalyst, the selective sequential depolymerisation of PLA and PET was achieved (0.5 mol% catalyst, 16 h, 100 bar H_2) in 1,4-dioxane or 1,2-propanediol. Both PET and PLA were fully converted (into 1,4-benzenedimethanol and ethylene glycol and 1,2-propanediol, respectively) in 1,4-dioxane at 140 °C. Selectivity to PET decreased when lowering the temperature, so that PLA was fully degraded at 45 °C while PET was unreacted. PET was removed by filtration and its degradation completed at either 120 °C or 140 °C. When 1,2-propanediol was used, PLA could be selectively depolymerised at 140 °C with no degradation of PET observed (not soluble in 1,2-propanediol). Following PLA depolymerisation, PET was filtered off and its degradation achieved in 1,4-dioxane at 120 – 140 °C. This work highlights how solvent choice and temperature can affect the depolymerisation characteristics of two similar types of plastics, and therefore lead to selective depolymerisation.

More recently in 2018, following an in-depth investigation of the activity of Brookhart's Iridium (III) hydrosilylation catalyst in the hydrosilylation of several common waste plastics, Monsigny and co-workers utilised the observed differences in reactivity of the polymers to

carry out selective depolymerisations.[112, 113] The first of which was the depolymerisation of poly(propylene carbonate) (PPC) in the presence of PLA with Et_3SiH (Scheme 1.6). At 65 °C, PPC (which was insoluble in the chlorobenzene solvent employed) was reduced into silylated propylene glycol, whilst PLA (which is soluble in chlorobenzene) was unreacted, this is contrary to prior investigations in which both polymers were individually degradable under these conditions. Further to this, a mixed reaction containing PVC and PLA displayed similar results, with PVC being dechlorinated to PE and chlorotriethylsilane (Et_3SiCl) at 110 °C and leaving PLA unreacted which is, again, unusual due to prior observations of PLA degradation at much lower temperatures. These observations are of great importance because it shows that the choice of catalyst has the potential to flip the usual order of reactivity for reduction of functional groups.
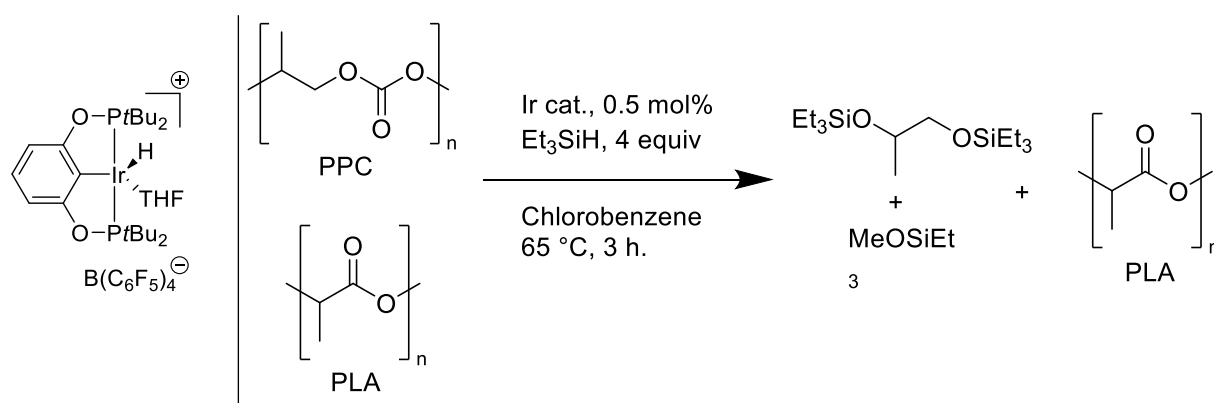
Scheme 1.6: *Brookhart's Ir(III) catalyst that was employed (Left). Selective depolymerisation of PPC in the presence of PLA at 65 °C (Right).*

Another recent study outlined the depolymerisation of several waste plastics, facilitated by a dioxomolybdenum catalyst, $MoO_2Cl_2(H_2O)_2$ in conjunction with hydrosiloxane PMHS.[114] The authors described the selective depolymerisation of PCL, PLA and PET in chlorobenzene at 110 °C over the course of 24 h. In this reaction, PCL was fully converted into 1,6-hexanediol, PLA was transformed to propane gas and PET was unreactive. This work is significant due to being

the simultaneous depolymerisation of three plastics, followed by the facile separation of each reaction product.

Most recently, Sardon and co-workers reported the thermally controlled sequential depolymerisation of both PET and BPA-PC in a mixed plastic reaction, catalysed by organocatalyst complex TBD:MSA (15 – 50 mol%).[115] In ethylene glycol (EG) at 130 °C, BPA-PC was converted into BPA (95% yield) and ethylene carbonate in 10 h whilst in the presence of PET, only a small amount of BHET was formed (2% yield). Lengthening the reaction to 48 h decreased yields of BPA (79%) and increased yields of side-product carbonates (from 8% after 10 h to 22% after 48 h). Again, PET was mostly unreacted under these conditions, with only a 7% yield of BHET observed. A subsequent reaction at 180°C showed the depolymerisation of BPA-PC to BPA (96% yield) after 20 min, followed by the depolymerisation of PET to BHET (88% yield) after 31 h. However, as observed previously, prolonging the reaction had negative effects of BPA yield. Furthermore, increasing the loading of catalyst from 15 to 50 mol % was detrimental and increased the yield of the formed carbonates. To improve the selectivity to BPA, the authors postulated that the use of a substituted nucleophile, the 1,3-diol trimethylolpropane allyl ether diol (TMPAE), would provide more favourable depolymerisation kinetics for selective degradation of BPA-PC. The resulting depolymerisation at 130 °C, with 15 mol % catalyst, was able to achieve 98% conversion to BPA (88% yield) after 3 hours, with no difference in yield of 2-allyloxymethyl-2-ethyltrimethylene carbonate (AOMEC) side products and most importantly, no evidence of PET degradation. The above conditions were further applied to commodity PET and BPA-PC mixtures: PET and BPA-PC blends, and PET and BPA-PC powder. In all cases, conversion to BPA and AOMEC was high (>95%) with little to no evidence of BHET formation in times between 6 and 24 h. The

employment of TMAD is also useful due to the ability of the alkene functionality on the side chain to undergo post-polymerisation functionalisation reactions, for further production of functional materials. This work is highly important as it is an early example of a true sequential depolymerisation, in which solvents and catalysts are not changed and each depolymerisation is separated by a kinetic change.

1.4 Summary

To summarise, the chemical recycling of plastic waste by catalysed depolymerisation is fast becoming a potential solution to the global waste plastic problem. The successful degradation of many plastic commodities has been presented, often with high selectivity to value-added products, and under more economically and environmentally conscious conditions, creating multiple angles for future development. This has been facilitated by the employment of highly active organocatalysts, which display high degrees of recyclability and product selectivity. Chemical recycling of both PET and PC has been somewhat more investigated, and therefore so has the formation of value-added materials from the re-polymerisation of their respective recovered monomers. The creation of value-added materials from PLA by chemical recycling is also noteworthy, as it presents a diversion away from the linear life cycle that bioplastics generally live, which ends in tremendous loss of material value to the compost heap. New ways to chemically recycle PA waste in mild, more favourable, conditions than traditional pyrolysis techniques have been achieved at the proof-of-concept level, creating a new avenue for PA waste processing. Due to the sheer variety of PU formulations available, CRM of waste PU is more complex, however several different rigid and soft foams have been depolymerised successfully on up to the 10 g scale, with larger scale achieved in industrial settings.

Selective co-depolymerisation, whilst being far more niche at current is also an area of growing promise. Even though mixed-plastics chemical recycling is still a growing area, it has the potential to be transformational. The ability to recycle a variety of mixed plastic wastes selectively and systematically, when stimulated by a change in reaction conditions, holds a huge opportunity to greatly streamline current plastic recycling processes. The overall process can become more efficient, economically viable and environmentally friendly, whilst maintaining high and uncompromised product purity. However, despite massive prospect for growth, current research is still fairly limited in scope, generally presenting the depolymerisation of one polymer in the presence of another that is unreactive in the chosen conditions, rather than both polymers being sequentially reacted. In the cases of both singular and mixed polymer chemical recycling there is still a long way to go before large-scale implementation is achievable. It is important to show that these methods work on the bench-scale, however it needs to be ensured that this research is translatable to the pilot-scale and ultimately the plant-scale, on which it will ultimately be employed. Despite these hurdles, large strides are certainly being made in the right directions to achieve CRM on the large scale.

This thesis aims to explore selective depolymerisation in mixtures of polyesters and polycarbonates, employing different combinations of single and dual Lewis acid and Lewis base catalyst systems, temperature, and nucleophiles to tailor depolymerisation to a variety of different outcomes. Depolymerisation of individual polymers across a range of reaction conditions, to act as a screening process, is discussed in Chapter 2. Selective depolymerisation processes, built upon data gathered in the screen are investigated and discussed in Chapter 3.

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Chapter 2: Depolymerisation study – Screening catalyst systems with respect to temperature and polymer

2.1 Introduction

Chemical recycling to monomer (CRM) is the process in which a waste polymer material is chemically broken down into its constituent monomers, and when compared to present day recycling processes used for plastic waste, it offers several benefits. CRM enables the reconstruction of the original virgin-quality polymer materials, or even upcycled polymer-based products from any point in the lifecycle of a plastic material; this is referred to as closing the plastics loop.[1] This contrasts greatly to the techniques currently employed to manage plastic waste, in which the mechanical processes of shredding, heating and extrusion facilitate a decrease in the quality of recycled polymer materials; this is known as linear downcycling and is a result of chain-scission reactions splitting the polymer backbone into shorter segments.[2] Inherently this means that as a polymer material is repeatedly recycled, the integrity of the polymer chains that make up the material decline, until eventually they lose the characteristics that enable them to be used in the manufacture of new plastic commodities and so are lost to landfill as waste. CRM is unaffected by chain-scission, as all the polymer chain segments can still be broken down into monomers, this means that in theory, no plastic material should be lost to landfill. Variants of chemical recycling processes are already used around the world, as waste plastic is thermally converted directly into energy (liquid, solid and gas forms), waxes and naphtha by pyrolysis, or into 'syngas'- synthetic gas, by gasification.[3, 4] Whilst these two processes are effective at completely converting waste plastic into useful products, there is a large loss in material value as there is no way to reclaim polymer material or monomers which could be remanufactured and therefore, the plastic loop is not closed.

As with many industrial processes, catalysts can be applied in CRM to improve reaction efficiency and reduce the costs associated with the high energy. More frequently, organo- and organometallic catalysts are being studied in CRM reactions. These catalysts either employ metals that are naturally abundant (such as zinc, sodium, or magnesium) compared to common industry catalysts based on rare-earth metals such as ruthenium or iridium, or do not rely on metals at all and are formed from organic molecules, such as Lewis acids and Lewis bases.[5, 6] Another benefit to organo- / organometallic catalysts is that in several cases they are used to produce selectivity between products in a reaction, for example through chemoselective or stereoselective means.[7, 8] With that in mind, it can be suggested that these catalysts could potentially exhibit selectivity when applied to the depolymerisation of plastics, preferentially enabling the breakdown of one polymer type over another in the same mixture.

The catalyst mediated depolymerisation of heteroatom containing plastics to monomers is not one single process; there are multiple different ways and reaction systems that can be used to depolymerise plastics. A large proportion of research focus has been on polyethylene terephthalate (PET) as this polyester is used in many applications that we encounter in our day-to-day lives. Despite the focus on PET, chemical recycling studies have also been conducted on several other heteroatom containing plastics, such as the polyesters polylactic acid (PLA) and polycaprolactone (PCL), the polycarbonates bisphenol A polycarbonate (BPA-PC) and polypropylene carbonate (PPC), and polyamides and polyurethanes.[6, 9-15] This work aims to both broaden the scope of depolymerisation routes for several common usage polymers, by investigating a range of organic and organometallic

catalysts employed over a range of reaction temperatures; but also highlight instances of catalytic selectivity, in which a catalyst is active with one polymer type, but not another.

2.2 Results and discussion

In this chapter, the screening of single-catalyst and dual-catalyst systems for the chemical recycling of PET, PLA and BPA-PC was investigated.

2.2.1 Screening for catalytic selectivity

The starting point for the screening process was derived from previous work carried out by our group, in which different combinations of Lewis acid and organic base pairs were employed to facilitate the glycolysis of PET.[16] Therefore, the initial catalyst systems studied were the Lewis acid zinc(II) acetate dihydrate (Zn(OAc)$_2$), the organic base DMAP and then the two combined as a dual-catalyst system. These catalysts were chosen as our previous work found them to be the overall best performing catalysts in a range of different Lewis acids and bases. The scope was then expanded with the introduction of the alternative acids and bases to be investigated, magnesium(IV) acetate tetrahydrate (Mg(OAc)$_2$), magnesium chloride (MgCl$_2$) and imidazole respectively. However, rather than being solely focussed on the glycolysis of PET, the aim was also to investigate the glycolysis of both PLA and BPA-PC, and any differences in depolymerisation kinetics that could be exploited in a selective mixed-plastic depolymerisation reaction. PLA and BPA-PC were chosen as they, like PET are common usage everyday plastics, which serve a wide variety of commodities. They also possess ester and carbonate functionalities, which render them susceptible to CRM. To mimic industrial conditions, all three polymers were employed in reactions as pellets.

Glycolysis reactions of PET, PLA and BPA-PC proceed *via* a transesterification reaction, in which a nucleophile, in this case ethylene glycol, attacks the carbonyl of either the ester or carbonate functionality within the polymer chain in a S_N2 fashion (Scheme 2.1).[17] Lewis acid and Lewis base catalysts can be applied to this process to improve the kinetics by stabilising different parts of the interacting molecules. Lewis acids stabilise the electrophilic component by coordinating to the carbonyl through the metal centre, whilst Lewis bases coordinate to the incoming nucleophile, lowering the energy barrier for the nucleophilic substitution. In a dual catalytic system, it is possible for the acidic and basic components to complement each other in a way which means that the produced reaction kinetics are greater than the sum of the reaction kinetics observed when both catalysts are applied individually, we describe this interaction as a synergistic effect.[18]
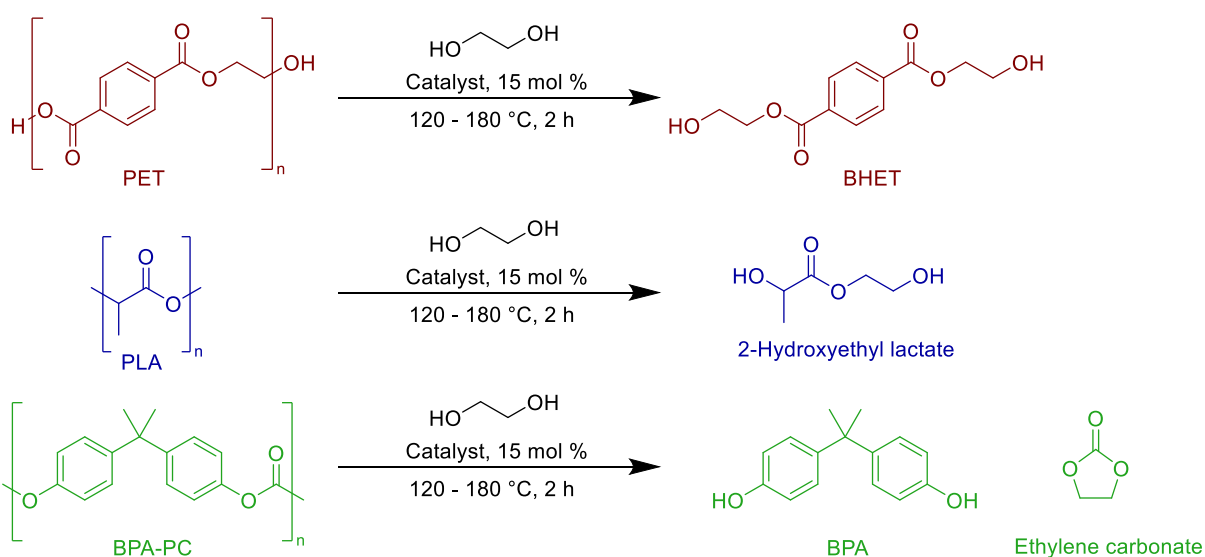
Scheme 2.1: *One-step glycolysis of PET, PLA and BPA-PC to their respective products using ethylene glycol.*

The initial conditions for depolymerisation reactions were kept consistent with the previous work, reactions were conducted at 180 °C for 2 h, with a catalyst loading of 15 mol % for each acid and base component, in an excess of ethylene glycol. For all cases, catalytic ability

was measured by assessing the percent of conversion of each polymer to their respective monomer within a defined timeframe (2 h). This was achieved by removing a small aliquot of reaction mixture at regular time points during the reaction, these aliquots were analysed by ^{1}H NMR spectroscopy, and the peaks relating to each respective monomer were integrated against the peak corresponding to the internal standard *N*-methyl-2-pyrrolidinone (NMP, 10 mol % present in each reaction).

PET conversion was calculated by integrating the singlet peak relating to the 4 aromatic protons within bis-2(hydroxyethyl terephthalate) (BHET) arising at δ = 8.10 ppm with respect to that of NMP, which arises at δ = 2.71 ppm. An example of the NMR spectra produced during a PET depolymerisation reaction are shown below (Figure 2.1).
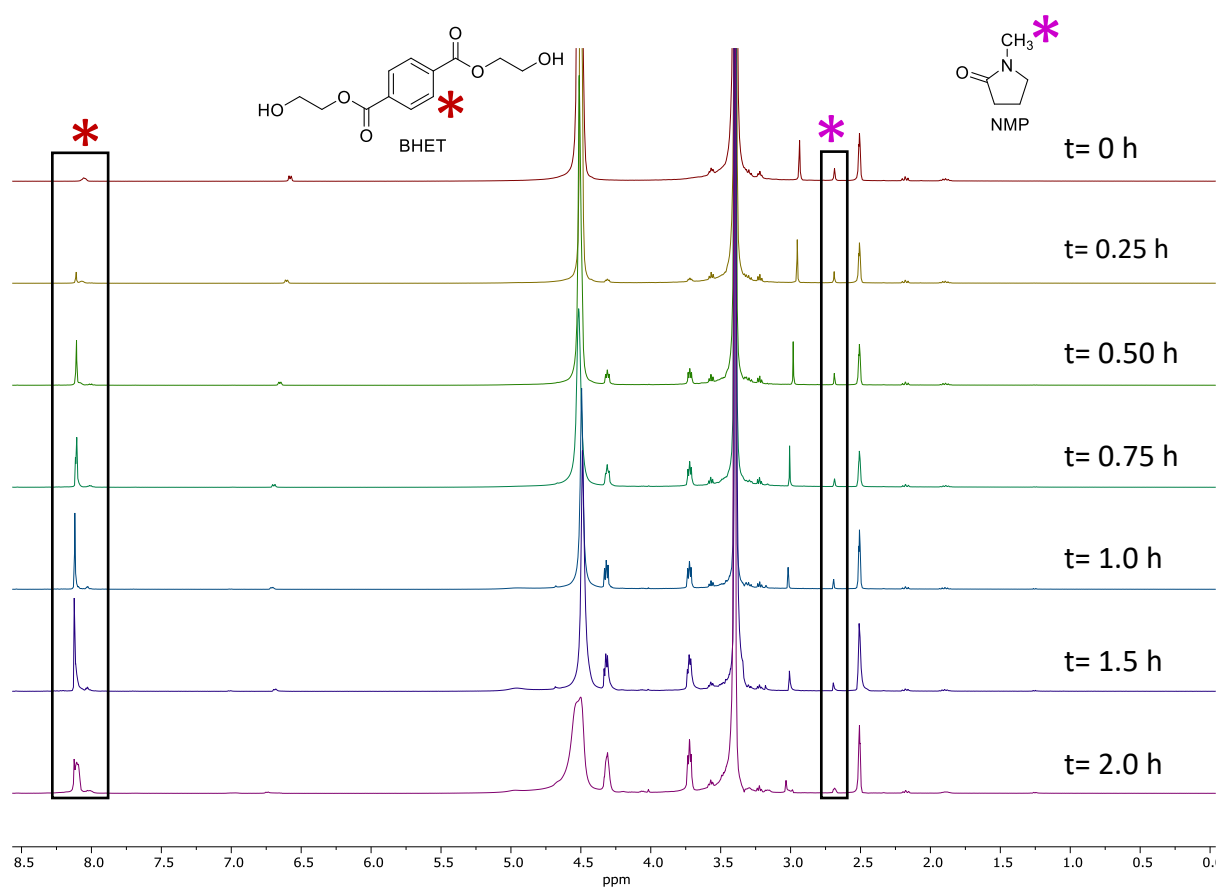
Figure 2.1: Stacked ¹H NMR (DMSO-d₆, 400 MHz, 298 K) spectra of a PET glycolysis reactions from t = 0 h to t = 2 h, using MgCl₂ / DMAP as catalyst system, showing the peaks used to measure conversion to BHET, alongside that of NMP which was used as an internal standard.

These spectra were then used to create conversion / time plots, to visualise the rate of conversion from polymer to product. The plot corresponding to Figure 2.1 is shown below (Figure 2.2).

PET conversion- 180 °C
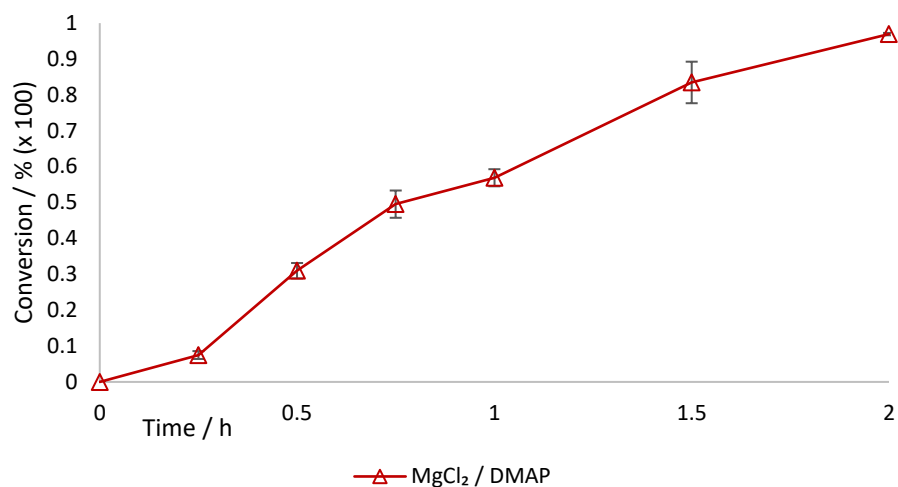
Figure 2.2: Conversion / Time plot for the depolymerisation of PET at 180 °C, using the MgCl₂ / DMAP dual catalyst system, showing conversion to BHET.

Likewise, PLA conversion was calculated using the doublet peak arising at δ = 1.24 ppm, which relates to the methyl group present in 2-hydroxyethyl lactate (2-HEtLa). As above, an example of the spectra recorded, and the resultant conversion / time plot are shown below (Figure 2.3, 2.4).
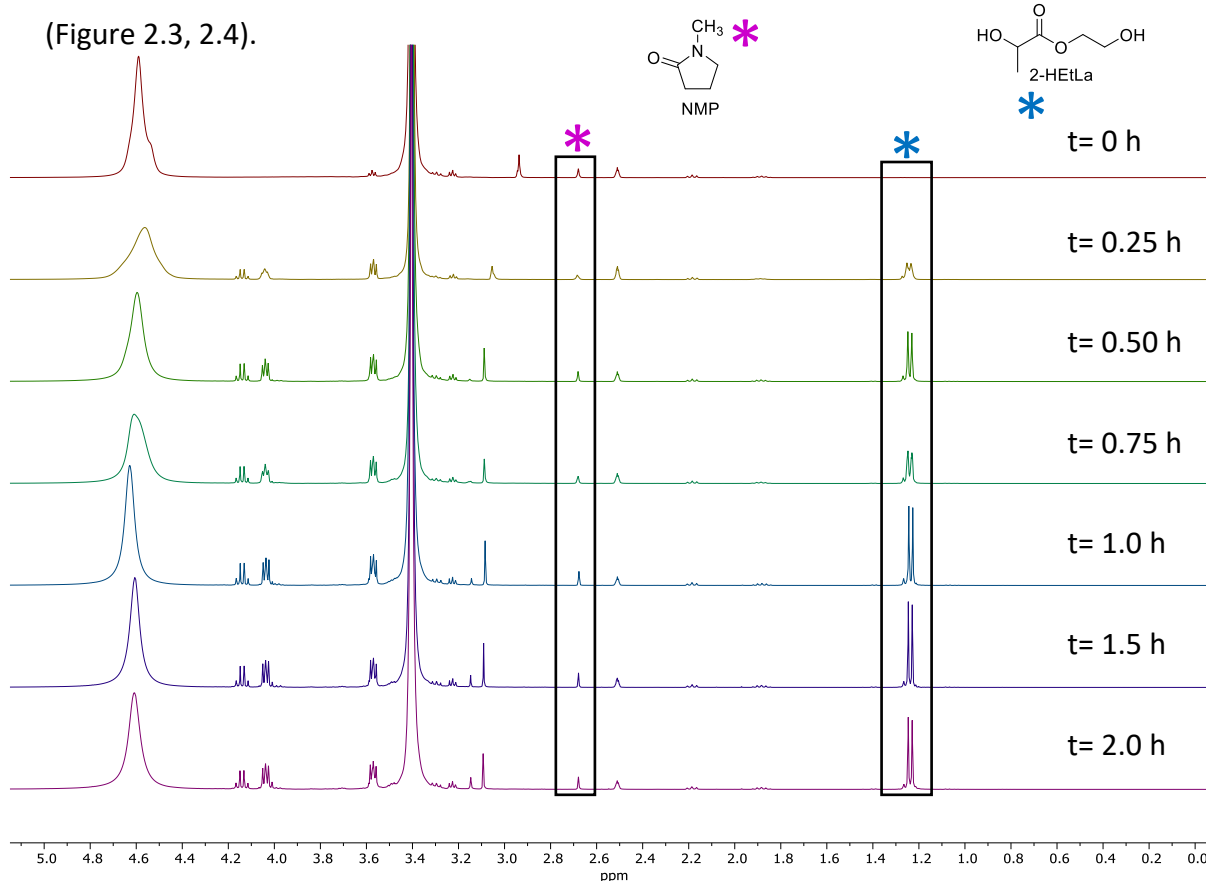
Figure 2.3: Stacked ¹H NMR (DMSO-d₆, 400 MHz, 298 K) spectra of a PLA glycolysis reactions from t = 0 h to t = 2 h, using MgCl₂ / DMAP as catalyst system, showing the peaks used to measure conversion to 2-HEtLa, alongside that of NMP which was used as an internal standard.

PLA conversion- 180 °C
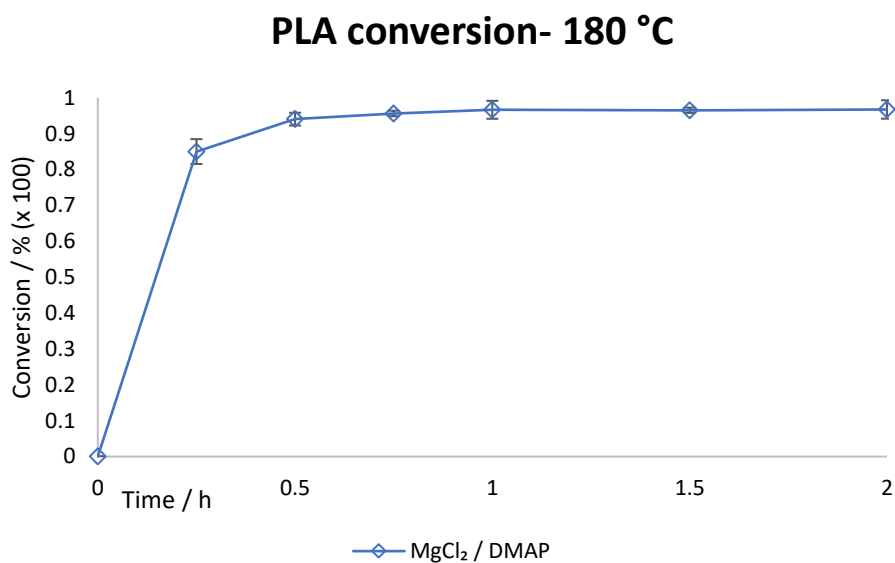
Figure 2.4: *Conversion / Time plot for the depolymerisation of PLA at 180 °C, using the MgCl₂ / DMAP dual catalyst system, showing conversion to 2-HEtLa.*

Finally, BPA-PC conversion was calculated by averaging the integration of the two doublet peaks found at δ = 6.95 ppm and δ = 6.65 ppm respectively, which correspond to the aromatic protons of the product bisphenol A (BPA). An example ^{1}H NMR spectra and the respective conversion / time plot is shown below (Figure 2.5, 2.6). During the depolymerisation screening process, which will be discussed in detail later in this chapter, it was noticed that in some cases of BPA-PC depolymerisation a side-product, bisphenol A bis(2-hydroxyethyl) ether (BPA-SP), was formed, evidenced by two doublet peaks arising at δ = 7.06 ppm and δ = 6.78 ppm. Formation of this side product negatively affected conversion of BPA-PC into the target monomer of bisphenol A (BPA), therefore the formation of BPA-SP was also monitored, as an ideal catalyst system would solely promote the depolymerisation of BPA-PC to BPA. Total conversion of BPA-PC is taken as the sum of the average integral corresponding to BPA and the average of the integrals corresponding to BPA-SP.
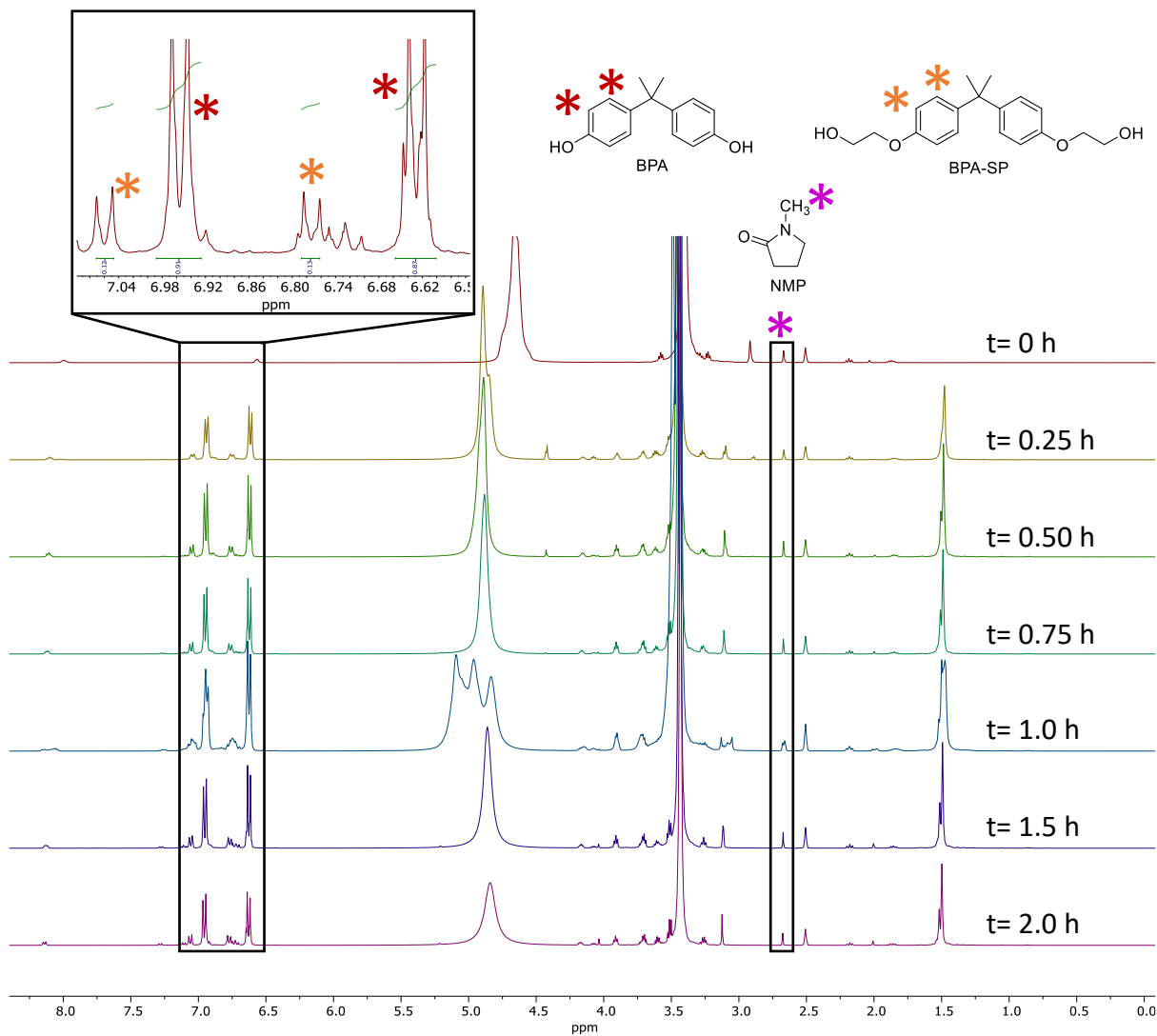
Figure 2.5: *^{1}H NMR (DMSO-d$_6$, 400 MHz, 298 K) spectrum of a BPA-PC glycolysis reaction from t = 0 h to t = 2 h, using MgCl$_2$ / DMAP as catalyst system, showing the peaks that correspond to product BPA and side product BPA-b2Hee (BPA-SP), alongside that of NMP, which was used as an internal standard.*
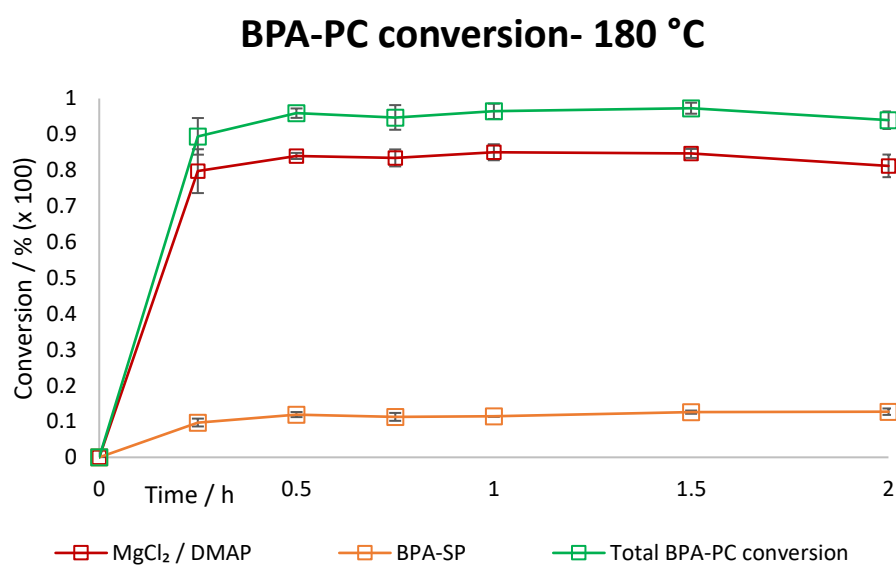
Figure 2.6: *Conversion / Time plot for the depolymerisation of BPA-PC at 180 °C, using the MgCl$_2$ / DMAP dual catalyst system, showing conversion to BPA, side-product (BPA-SP), and the total conversion of BPA-PC.*

The purpose of the devised screen was to investigate whether varying the catalyst system can influence the depolymerisation kinetics of polymers, to the degree that instances of selectivity to a certain polymer over another arise. The aim of the screening process was to provide a library of depolymerisation kinetics for PET, PLA, and BPA-PC, that could then be used to design a three-step process in which each step results in the selective depolymerisation of one of these polymers over the other two, when in a mixed reaction. The screening process was divided into several sections, between plastic type, dual and single catalyst systems, and temperature.

The single catalyst systems to be investigated were applied in the glycolysis reactions of PET, PLA, and BPA-PC at 180 °C, 150 °C and 120 °C, catalyst loading was 15 mol % with respect to the polymer pellets, and reactions were conducted in an excess of ethylene glycol with NMP present as an internal standard for 2 h. The resultant data can be found below for Lewis acids (Table 2.1) and Lewis bases (Table 2.2).

Entry	Catalyst system	Temperature (°C)	Final average Conversion (%)			Conversion to (%)	
			PET	PLA	BPA-PC	BPA	BPA-SP
1		180	83	97	95	86	9
2	Zn(OAc)$_2$	150	0	99	92	90	2
3		120	0	22	0	0	0
4		180	62	97	94	87	7
5	Mg(OAc)$_2$	150	5	85	83	79	4
6		120	0	13	1	1	0
7		180	18	99	98	91	7
8	MgCl$_2$	150	0	97	0	0	0
9		120	0	0	0	0	0

Table 2.1: *Conversion data for PET, PLA, and BPA-PC glycolysis, using different Lewis acids as single catalyst systems at 180 °C, 150 °C and 120 °C. *Total BPA-PC conversion is broken down into conversion to BPA and side-product (BPA-SP). Key data have been highlighted: red- best overall performance, green- best selectivity.*

All three Lewis acids investigated showed some promise at enabling the depolymerisation of PET, PLA, and BPA-PC, especially at elevated temperature. Overall, the best performing was Zn(OAc)$_2$ (Table 2.1, entry 1), which facilitated the complete / near complete conversion of all three polymers at 180 °C, and then proceeded to maintain higher levels of conversion compared to Mg(OAc)$_2$ and MgCl$_2$ as the temperature was reduced. Below 180 °C, PET conversion completely stalled, perhaps due to its natural chemical resistance and semi-crystalline structure rendering nucleophilic attack less facile at reduced temperature, whereas PLA and BPA-PC conversion was still achievable. However, at 150 °C and below, BPA-PC conversion levels began to decrease also. BPA-SP formation was generally low across all conditions evaluated, with the highest level being measured with Zn(OAc)$_2$ as catalyst at 180 °C (Table 2.1, entry 1). At 120 °C, we found that conversion of all 3 polymers was very poor in all cases. However, during the conductance of this section of the screen, we observed an instance of selectivity that could potentially be exploited in a selective depolymerisation setting. At 150 °C, whilst employing MgCl$_2$ as catalyst, the near quantitative conversion of PLA was observed, whilst neither PET nor BPA-PC displayed any conversion whatsoever within the 2 h period (Table 2.1, entry 8), the full data set for MgCl$_2$

catalysed reactions are shown below (Figure 2.7). These conditions are highly selective towards PLA, making them applicable in a selective depolymerisation process.
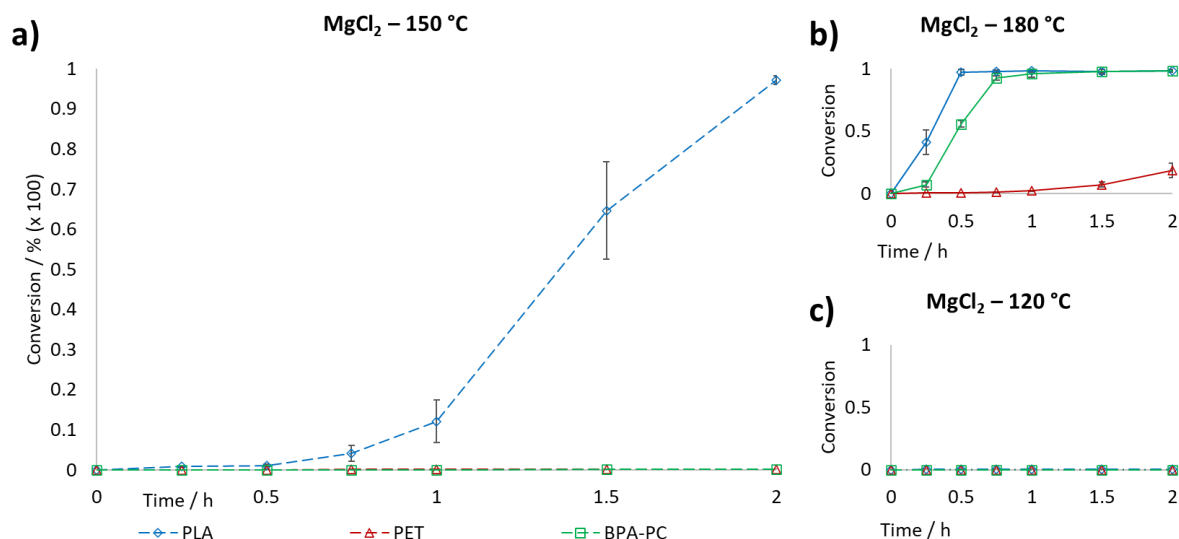
Figure 2.7: Conversion / Time plot for PET (red), PLA (blue) and BPA-PC (green) glycolysis, using MgCl₂ (15 mol %) as catalyst system at 150 °C (a), 180 °C (b) and 120 °C (c).

Entry	Catalyst system	Temperature (°C)	Final average Conversion (%)			Conversion to (%)	
			PET	PLA	BPA-PC	BPA	BPA-SP
10	DMAP	180	94	88	89	47	42
11		150	30	99.6	98	70	28
12		120	0	99.1	67	56	11
13	Imid	180	17	94	96	66	30
14		150	1	90	68	59	9
15		120	0	0	0	0	0

Table 2.2: Conversion data for PET, PLA, and BPA-PC glycolysis, using different Lewis bases as single catalyst systems at 180 °C, 150 °C and 120 °C. Total BPA-PC conversion is broken down into conversion to BPA and side-product (BPA-SP). Key data have been highlighted: red- best overall performance.

The single Lewis bases produced similar results to the Lewis acids, in that higher conversion of each polymer were reached with greater reaction temperature. However, in the case of PET, when imidazole was employed as the catalyst, the achieved conversion was low in all cases. This is especially noticed at 180 °C, where final PLA and BPA-PC conversions were 94%

and 96% respectively, whilst only 17% conversion of PET was recorded (Table 2.2, entry 13).

High BPA-PC conversion levels were compounded by the issue of much greater proportions of BPA-SP being formed, with a near 50% formation of BPA-SP produced when DMAP was employed as catalyst at 180 °C (Table 2.2, entry 10). PLA was again found to be amenable to depolymerisation across most of the conditions tested, with complete conversion being achievable at 120 °C when DMAP is employed as catalyst; this is the only example of complete conversion of a polymer being achieved at 120 °C in this screen (Table 2.2, entry 12).

The next sections of the screen focussed on dual catalyst systems, pairing the Lewis acids investigated with imidazole (Table 2.3) and DMAP (Table 2.4).

Entry	Catalyst system	Temperature (°C)	Final average Conversion (%)			Conversion to (%)	
			PET	PLA	BPA-PC	BPA	BPA-SP
16		180	82	91	94	66	28
17	$Zn(OAc)_2$ / Imid	150	9	94	95	82	13
18		120	0	33	2	2	0
19		180	71	94	95	80	15
20	$Mg(OAc)_2$ / Imid	150	6	86	88	82	6
21		120	0	13	6	6	0
22		180	69	99.5	96	85	11
23	$MgCl_2$ / Imid	150	3	99	99	95	4
24		120	0	8	8	8	0

Table 2.3: *Conversion data for PET, PLA, and BPA-PC glycolysis, using different Lewis acids paired with imidazole as the Lewis base component in a dual catalyst system at 180 °C, 150 °C and 120 °C. Total BPA-PC conversion is broken down into conversion to BPA and BPA-side product (BPA-SP). Key data have been highlighted: red- best overall performance, green- best selectivity.*

Like previous observations, high levels of PLA depolymerisation are achievable above 120 °C regardless of the catalyst system employed.

With respect to PET, similarly to what was observed when imidazole was applied as a single catalyst system, at 150 °C and below, conversion drops off dramatically when imidazole is paired in a dual catalyst system. However, in contrast to previous results, at 180 °C a moderate conversion of 69% is achieved within 2 h when imidazole is paired with $MgCl_2$ (Table 2.3, entry 22). This figure is far greater than the conversion levels measured when both catalysts were employed individually, suggesting that this system is synergistic in effect.

This synergic effect is also noticed in BPA-PC depolymerisation facilitated by $MgCl_2$ / imidazole. At 150 °C, when both catalysts are individually used, $MgCl_2$ does not enable any level of BPA-PC conversion (Table 2.1, entry 8), and the glycolysis reaction catalysed by imidazole reaches 68% within 2 h (Table 2.2, entry 14). However, employment of the dual catalyst system results in 99% conversion of BPA-PC, with only minimal conversion to BPA-SP over BPA (Table 2.3, entry 23). This high level of conversion, alongside the very poor conversion of PET under the same conditions makes this system a good candidate for a selective depolymerisation process (Figure 2.8). Other, less significant synergistic effects were noted for the combinations of $Zn(OAc)_2$ / imidazole and $MgCl_2$ / imidazole at 120 °C. The former system displayed synergy in the conversion of PLA to 2-HEtLa, facilitating a conversion of 33% in 2 h, compared to 22% for $Zn(OAc)_2$ and 0% for imidazole individually, whilst the latter exhibited a synergistic effect for both PLA and BPA-PC conversion, with each reaction reaching 8% conversion with the dual catalyst system, in comparison to no observed conversion when using each catalyst singly.
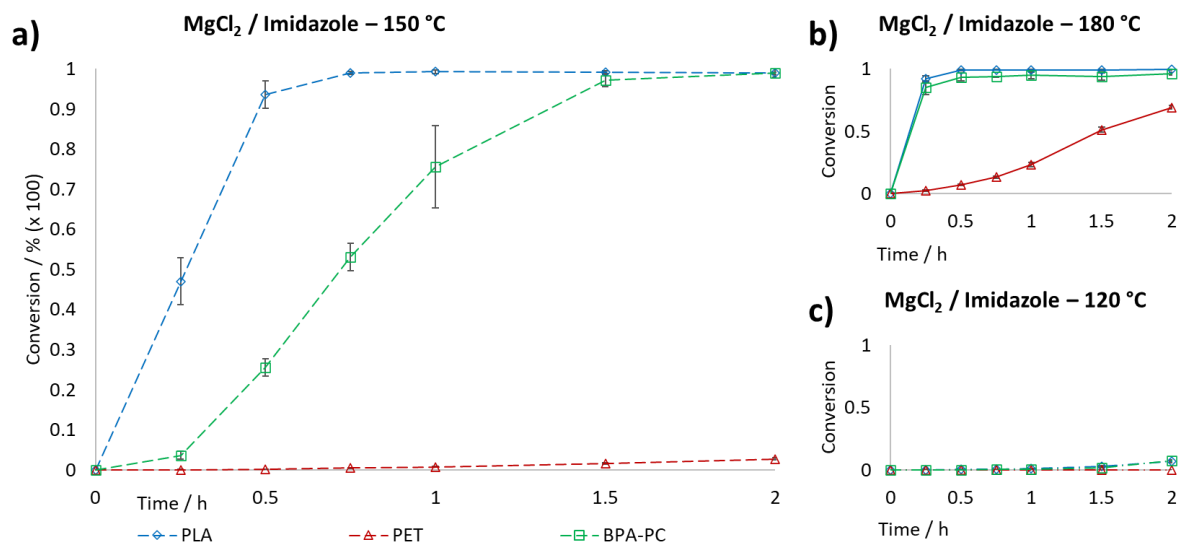
Figure 2.8: Conversion / Time plot for PET (red), PLA (blue) and BPA-PC (green) glycolysis, using $MgCl_2$ / imidazole (15 mol %) as catalyst system at 150 °C (a), 180 °C (b) and 120 °C (c).

Entry	Catalyst system	Temperature (°C)	PET	PLA	BPA-PC	BPA	BPA-SP
25	Zn(OAc)$_2$/ DMAP	180	98	96	98	62	36
26		150	36	96	97	74	23
27		120	1	73	54	54	0
28	Mg(OAc)$_2$/ DMAP	180	66	92	97	77	20
29		150	20	88	97	87	10
30		120	0	55	37	36	1
31	MgCl$_2$ / DMAP	180	97	97	94	81	13
32		150	18	99	93	82	11
33		120	0	70	58	57	1

Table 2.4: Conversion data for PET, PLA, and BPA-PC glycolysis, using different Lewis acids paired with DMAP as the Lewis base component in a dual catalyst system at 180 °C, 150 °C and 120 °C. Total BPA-PC conversion is broken down into conversion to BPA and side-product (BPA-SP). Key data have been highlighted: red- best overall performance.

Dual catalyst combinations of Lewis acids with DMAP did not display discrete selectivity in polymer degradation. Near quantitative PLA and BPA-PC depolymerisation was observed in all cases at 150 °C and above, however increased temperature also served to increase the ratio of BPA-SP forming from BPA-PC depolymerisation.

PET depolymerisation responded in a similar fashion to that when single catalyst systems were employed, in which final conversion figures achieved were highly influenced by the reaction temperature, with lower temperature severely restricting and even halting entirely conversion to BHET. The system previously identified by our group as an excellent dual catalyst system for the glycolysis of PET, Zn(OAc)$_2$ / DMAP, was again found to be the most reliable combination investigated at 180 °C (Table 2.4, entry 25; Figure 2.9). Furthermore, noticeable synergy was not observed for any combination of Lewis acid paired with DMAP in a dual catalyst system. This could be attributable to the high activity of DMAP as a catalytic species shrouding any potential benefits of a second catalyst.
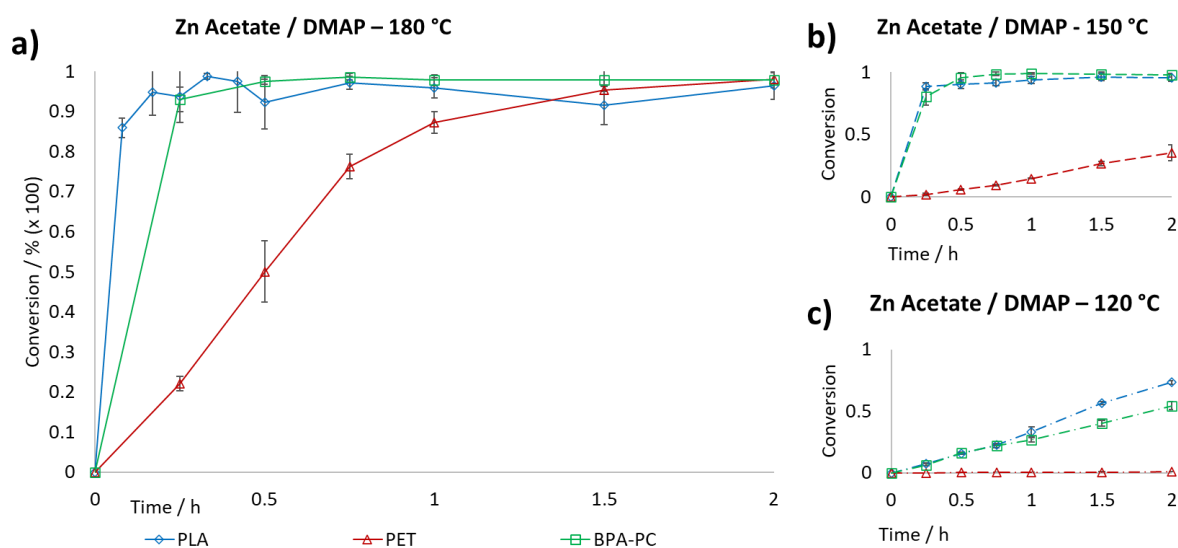
Figure 2.9: *Conversion / Time plot for PET (red), PLA (blue) and BPA-PC (green) glycolysis, using Zn acetate / DMAP (15 mol %) as catalyst system at 180 °C (a), 150 °C (b) and 120 °C (c).*

2.3 Summary

With the completion of the screening process, a comprehensive library of kinetic data was obtained from which we could identify instances of depolymerisation selectivity that could be taken forward to build a sequential depolymerisation process involving all three

polymers. Furthermore, a few instances of synergy in dual catalyst systems have been identified, one of which has the potential to display selectivity. PET depolymerisation was most successful at 180 °C, with zinc acetate, DMAP and their respective dual system proving to facilitate best conversion to BHET. BPA-PC conversion was found to be more complex because the formation of BPA-SP as a side product greatly affected conversion of BPA-PC to BPA, however the most promising system was found to be the synergic combination of MgCl$_2$ / imidazole at 150 °C. PLA conversion to 2-HEtLa was near quantitative for all catalyst systems at both 180 °C and 150 °C, although only one system was found to be suitable for any further progression with selective depolymerisation. The suitable catalyst systems identified will be employed in investigations into selective depolymerisation in the next chapter.

2.4 Experimental

2.4.1 Materials

The chemicals used in the screening process are as follows, they were used without further purification. PET, PLA, and BPA-PC granules (3 mm) were purchased from Goodfellow, ethylene glycol (anhydrous), NMP, zinc acetate dihydrate, magnesium acetate tetrahydrate, magnesium chloride and imidazole were purchased from Sigma Aldrich and DMAP was bought from Acros Organics, deuterated DMSO was purchased from Apollo Scientific.

2.4.2 Instrumentation

Nuclear Magnetic Resonance (NMR) Spectroscopy

All ^{1}H NMR spectra were recorded on either a Bruker AVIII 400 MHz spectrometer or a Bruker AVANCE NEO 400 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to the residual solvent signal of deuterated dimethyl sulfoxide (DMSO-d_6, ^{1}H: quintet, δ = 2.50 ppm, ^{13}C: septet, δ = 39.51 ppm).

2.4.3 Experimental procedure

A general procedure was followed for all glycolysis reactions and all reactions were completed in triplicate, to allow for conversion levels to be averaged. Reactions were carried out in triplicate in 20 mL scintillation vials equipped with magnetic stirrers, each vial was charged with the catalyst(s) (0.375 mmol, 15 mol % of each), ethylene glycol (50 mmol, 2000 mol %) and the internal standard NMP (0.25 mmol, 10 mol %). The vials were sealed and placed within a heating block at the working temperature, whilst stirring at 500 rpm, for 15 minutes to solubilise the catalysts and allow the solvent to reach temperature. After 15 minutes, an aliquot (0.2 mL) was removed from the reaction mixture to act as a t0 for ^{1}H NMR spectroscopic analysis, pelletised polymer (2.5 mmol) was then added, the vials were resealed, and a timer set. Further aliquots for ^{1}H NMR spectroscopy were taken at t = 0.25 h, 0.5 h, 0.75 h, 1 h, 1.5 h and 2 h, all aliquots taken for ^{1}H NMR spectroscopy were dissolved in DMSO-d_6. At t = 2 h, the vials were removed from the heating block, the magnetic stirrers were removed, and the sealed vials were placed in the fridge overnight to cool down pending further work up.

2.4.4 Calculation of polymer conversion from ^{1}H NMR spectra

The final polymer conversion is calculated from the integration of the relevant product peaks with respect to the set integration value of NMP. The integration value to which NMP is set varies with respect to the number of protons present in each of the chosen environments within the products, following the formula $(3/y) \times 0.1$, where 3 is the number of protons in the NMP reference environment, y= no. of protons in product environment (BHET= 4, BPA= 4, 2-HEtla= 3) and 0.1 is the no. of equivalents of NMP with respect to equivalents of starting polymer, this gives NMP settings of 0.075 for PET and BPA-PC conversion and 0.1 for PLA conversion.

However, due to the removal of aliquots of reaction mixture during the process of the depolymerisation, a small quantity of NMP will be removed each time, thus decreasing the ratio of NMP to polymer in the reaction. Therefore, to counter this, an adjustment must be applied to the integration values of the relevant product peaks upon each removal of an aliquot until the point at which the polymer pellets are fully solubilised in the reaction solvent (at this point polymer and NMP will be removed and so the ratio is set from here onwards).

NMP adjustment is calculated by considering the reduction in NMP concentration as aliquots are removed, with respect to the initial concentration of NMP in the reaction mixture. Initial molarity of NMP is taken as $moles\ NMP \div total\ volume\ of\ solution$, which equals 8.88×10^{-5} mol mL^{-1}. The decrease in NMP concentration, and hence the adjustment factor, is determined by the total volume of solution with respect to the initial molarity of NMP, decrease in NMP molarity is cumulative. The cumulative percentage of NMP removed in

aliquots is then calculated, with respect to initial concentration of NMP and this produces

the adjustment factors for each aliquot (Table 2.5). Examples of the process of calculating

final polymer conversion is shown below (table 2.6, 2.7).

Aliquot	Total solution volume [a] (mL)	Aliquot NMP concentration [b] (mol mL^{-1})	Cumulative NMP concentration removed (mol mL^{-1})	Cumulative NMP concentration removed [c] (%)	NMP concentration remaining (%)	Adjustment factor
0	2.8	N/A	0	0	100	1
1	2.8	3.17×10^{-6}	3.17×10^{-6}	3.57	96.43	0.964
2	2.7	3.29×10^{-6}	6.46×10^{-6}	7.27	92.73	0.927
3	2.6	3.42×10^{-6}	9.88×10^{-6}	11.13	88.87	0.889
4	2.5	3.55×10^{-6}	1.34×10^{-5}	15.09	84.91	0.849
5	2.4	3.7×10^{-6}	1.71×10^{-5}	19.26	80.74	0.807
6	2.3	3.86×10^{-6}	2.10×10^{-5}	23.65	76.35	0.764

Table 2.7: Calculation of NMP adjustment factors. a) To 1 decimal place, b) Aliquot NMP concentration is taken as: initial NMP molarity / (Total solution volume x 10), c) Taken as: (cumulative NMP concentration removed / initial NMP concentration) x 100.

Aliquot	Reaction time (h)	Integration	Multiplier	Conversion (Integration x multiplier)	Conversion (%)
1	0	0	1	0	0
2	0.25	0.045	0.964	0.043	4
3	0.5	0.112	0.927	0.104	10
4	0.75	0.215	0.889	0.191	19
5	1	0.432	0.849	0.366	37
6	1.5	0.740	0.807	0.597	60
7	2	0.924	0.764	0.706	71

Table 2.6: Calculating final polymer conversion from 1H NMR spectra integration data and adjustment due to the removal of aliquots of reaction mixture. Reaction system is PET depolymerisation at 180 °C, using Mg Acetate / imidazole as catalyst. In this case, PET was insoluble throughout the reaction.

Aliquot	Reaction time (h)	Integration	Multiplier	Conversion (Integration x multiplier)	Conversion (%)
1	0	0.000	1	0.000	0
2	0.25	0.882	0.964	0.850	85
3	0.5	1.015	0.927	0.941	94
4	0.75	1.032	0.927	0.956	96
5	1	1.043	0.927	0.967	97
6	1.5	1.041	0.927	0.965	97
7	2	1.044	0.927	0.967	97

Table 2.5: Calculating final polymer conversion from 1H NMR spectra integration data and adjustment due to the removal of aliquots of reaction mixture. Reaction system is PLA depolymerisation at 180 °C, using MgCl2 / DMAP as catalyst. In this case, PLA fully solubilises between t = 0.25 h and 0.5 h. Therefore, after t = 0.5 h, the multiplier is set.

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Chapter 3: Devising a three-stage sequential selective depolymerisation process

3.1 Introduction

The need for selective chemical recycling to monomer has arisen due to efficiency limitations associated with state-of-the-art mechanical recycling processes. The sorting of consumer plastic waste into discrete plastic types for recycling is an imperfect, multi-step process. Each of the incorporated steps, from human sorting to density separation and even infrared sorting, possess an inherent level of error. Over time, this error will compound, and contaminate plastic waste streams.[1] Furthermore, many plastic commodities that are responsive to mechanical recycling also contain additives within their formulation, which can be carried through to the final recycled product. When left to reside in the recycled product, these additives can pose serious health risks to consumers and further compromise recycled product quality. Commonly employed additives, such as phthalate esters that are used as plasticisers, have been found to leach into the environment or accumulate within human bodies, sometimes leading to endocrine system disruption.[2-4] Others have been found to detrimentally enhance the degradation of plastics, as they convert into compounds such as pro-oxidants during the mechanical recycling process. Thus, many challenges remain that hinder modern plastics recycling.

Selective chemical recycling to monomer seeks to address many of the limitations associated with plastic waste stream complexity and mechanical recycling by exploiting reactivity differences between distinct plastic types. By carefully adjusting reaction conditions to orthogonally react different polymer classes, one can tailor the route of depolymerisation to sequentially recycle mixed plastic feeds and remove additives.

Alongside orthogonality, selective chemical recycling offers several other benefits over mechanical recycling. Due to the shredding and melt processes used to mechanically recycle plastic waste (and the resultant chain scission reactions that occur), the quality of the recycled product is greatly reduced in comparison to the virgin plastic that enters the system.[5, 6] As plastic commodities are further recycled, the quality continuously degrades until the material has poor properties and is essentially waste. This process is referred to as linear downcycling, and in most cases will lead to landfill and the overall loss of polymer material. Conversely, chemical recycling can be applied to waste plastic and plastic commodities at any stage in their lifecycles.[7] This enables the formation of a circular plastic economy, where virgin quality polymer products are reproduced from the recycling of any late-life plastic.[8] Furthermore, the formation of recycling products can be tailored by using different solvents, producing value-added products, and creating an upcycling effect.[9-13]

By exploiting the chemical reactivity differences that arise between polymer types, we can facilitate selective depolymerisation and eliminate the need for costly separation or sorting steps. Furthermore, pure monomers and other products can be more easily obtained with less risk of contamination from external additives. There have been recent advances in the selective chemical recycling plastics, however these trials focus on two plastics in a one-step process, in which one plastic depolymerises in the presence of another material which remains unreacted.[14-16] An efficient, multi-step process that features the complete depolymerisation of two or more polymers in series has yet to be demonstrated. This work establishes a proof-of-concept, sequential depolymerisation process for a mixture containing 3 distinct plastics – PLA, PET, and BPA-PC.

3.2 Results and discussion

In this chapter, the suitable systems previously identified in the screening process (Chapter 2) will be employed in a multi-stage selective depolymerisation process using a mixture of PLA, PET, and BPA-PC. Further investigation into the use of alternative solvents, to modify the depolymerised products, is also discussed.

3.2.1 Testing and proof of concept

In an ideal scenario, chemical recycling by selective depolymerisation to monomer is envisioned as a 'one-pot' process in which all plastics are mixed during the reaction. Each polymer would then be sequentially depolymerised in an orthogonal manner to allow for isolation of pure products, corresponding to each initial polymer, without further modification of reaction conditions (Figure 3.1).
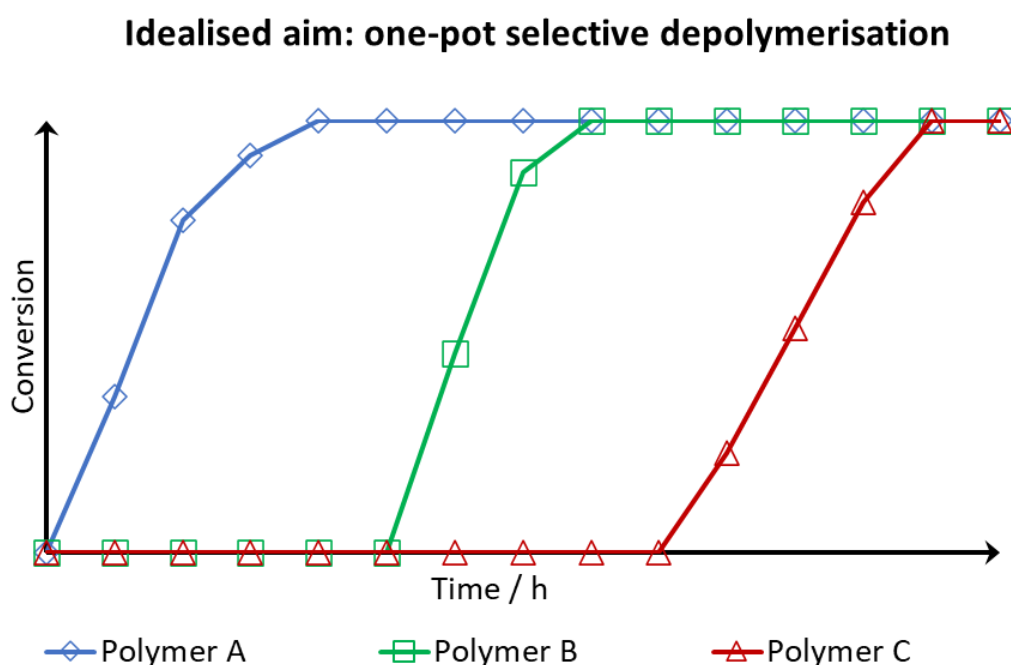
Figure 3.1: *An ideal process for the one-pot selective depolymerisation of mixed plastics.*

Building from reaction selectivity data that were reported in chapter 2, a three-stage process for the sequential and selective depolymerisation reaction of PLA, PET, and BPA-PC was designed. The three stages identified through the screening process are as follows:

- Stage 1 will be catalysed by $MgCl_2$ at 150 °C and will selectively depolymerise PLA in the presence of PET and BPA-PC, which will remain unreacted;

- Stage 2 will be catalysed by the $MgCl_2$ / imidazole dual catalyst system at 150 °C and is selective to BPA-PC in a mixture with PET;

- Stage 3 is to be catalysed by $Zn(OAc)_2$ / DMAP at 180 °C and will depolymerise the remaining PET.

As with the previous screening tests, reaction kinetics and overall polymer conversion were determined by ^1H NMR spectroscopy. As described in chapter 2, PET conversion was calculated using the singlet resonance relating to the 4 aromatic protons within BHET arising at δ = 8.10 ppm, PLA conversion was calculated using the doublet signal arising at δ = 1.24 ppm, which relates to the methyl group present in 2-hydroxyethyl lactate (2-HEtLa), finally BPA-PC conversion was calculated by averaging the integration of the two doublet peaks found at δ = 6.95 ppm and δ = 6.65 ppm respectively, which correspond to the aromatic protons of BPA. These peaks were all integrated with respect to NMP, which was employed as an internal standard as in chapter 2.

Before a complete demonstration of the designed process could be performed, the results observed for each individual depolymerisation in the screening studies (See Chapter 2) were

repeated in order to ensure that they were reproducible when other polymers were also present. A complete summary of the trials can be found below (Table 3.1).

Entry	Reaction stage	Catalyst	Temp (°C)	Time (h)	PLA Average Conversion (%)	BPA-PC Average Conversion (%)	PET Average Conversion (%)
1	1	$MgCl_2$	150	2	28	N/A	0
2	1	$MgCl_2$	150	2	21	1	N/A
3	1	$MgCl_2$	150	4	98	2	N/A
4	1	$MgCl_2$	150	4	98	2	0
5	2	$MgCl_2$/ imidazole	150	2	N/A	99	5
6	3	$Zn(Ac)_2$ / DMAP	180	2	N/A	N/A	99

Table 3.1: The respective conversions of PLA, BPA-PC and PET during trial stages of a planned three-stage selective depolymerisation process to show proof-of-concept. These stages were carried out discretely, with fresh polymer pellets used in each reaction.

We began trials of the first stage with only dual polymer reactions, combining PLA with either BPA-PC or PET. As expected from the data gathered in the screening stage, BPA-PC and PET showed no, or very minor, evidence of glycolysis occurring when under the conditions employed for the first stage. However, contrary to what we had anticipated from the screening data, PLA depolymerisation kinetics were sensitive to the BPA-PC or PET that were present in the reaction mixture. Independently, PLA was quantitatively converted within 2 h under the working conditions, however in a mixture with either PET or BPA-PC, conversion levels of < 30% were recorded within 2 h (Table 3.1, entries 1, 2). Closer inspection of the reaction mixture during the 2 h period revealed that as the PLA pellets were solubilising, the insoluble BPA-PC or PET pellets were becoming entangled within the PLA pellets that had swollen together. This impacted the homogeneity of the reaction mixture as polymer pellets were unable to be stirred or solubilised, thus slowing the reaction

kinetics and therefore the conversion levels of the mixed depolymerisation. This issue was solved by increasing the reaction time to 4 h (Table 3.1, entry 3). This timeframe allowed the degradation of the PLA pellets, and subsequently enabled near complete conversion of PLA to 2-HEtLa (Table 3.1, entry 3), without inducing significant conversion of BPA-PC into BPA. Next, PET was also incorporated into the mixed plastic reaction and near quantitative, orthogonal depolymerisation of PLA to 2-HEtLa was observed in the presence of both BPA-PC and PET (Table 3.1, entry 4). Furthermore, trials of the second stage in which BPA-PC is selectively depolymerised over PET, and the third and final stage, which is the sole depolymerisation of PET, proceeded efficiently as anticipated. However, a small degree of PET conversion was also observed during the BPA-PC depolymerisation stage (Table 3.1, entries 5, 6).

3.2.2 Demonstration of a complete selective depolymerisation process

Following these trials, we proceeded to carry out a complete sequential and selective depolymerisation process. In this process the polymer pellets used in stage 1 would be used subsequently in each following stage to mimic these processes in industrial settings, with washing and weighing steps in between (unlike in the trials, where fresh pellets were used for each stage of the reaction). After each step in the reaction, unreacted polymer pellets were removed, and each respective product recovered, before recombination in the subsequent step.

By employing the adjusted conditions (4 h reaction time), the first stage was carried out to afford 99% conversion of PLA to 2-HEtLa, with no evidence of BPA or BHET formation from the depolymerisation of their respective polymers (Figure 3.2). The residual PET and BPA-PC pellets were recovered, washed in ethylene glycol, dried, and then weighed, whilst 2-HEtLa was isolated from the reaction mixture. The remaining BPA-PC and PET pellets swelled during this first stage, resulting from plasticisation with ethylene glycol into the polymer matrix. Although the polymer pellets gained mass overall, the mass of PET and BPA-PC was assumed to be unchanged since no degradation had occurred. Therefore, we did not need to adjust molar ratios of reactants in subsequent steps.
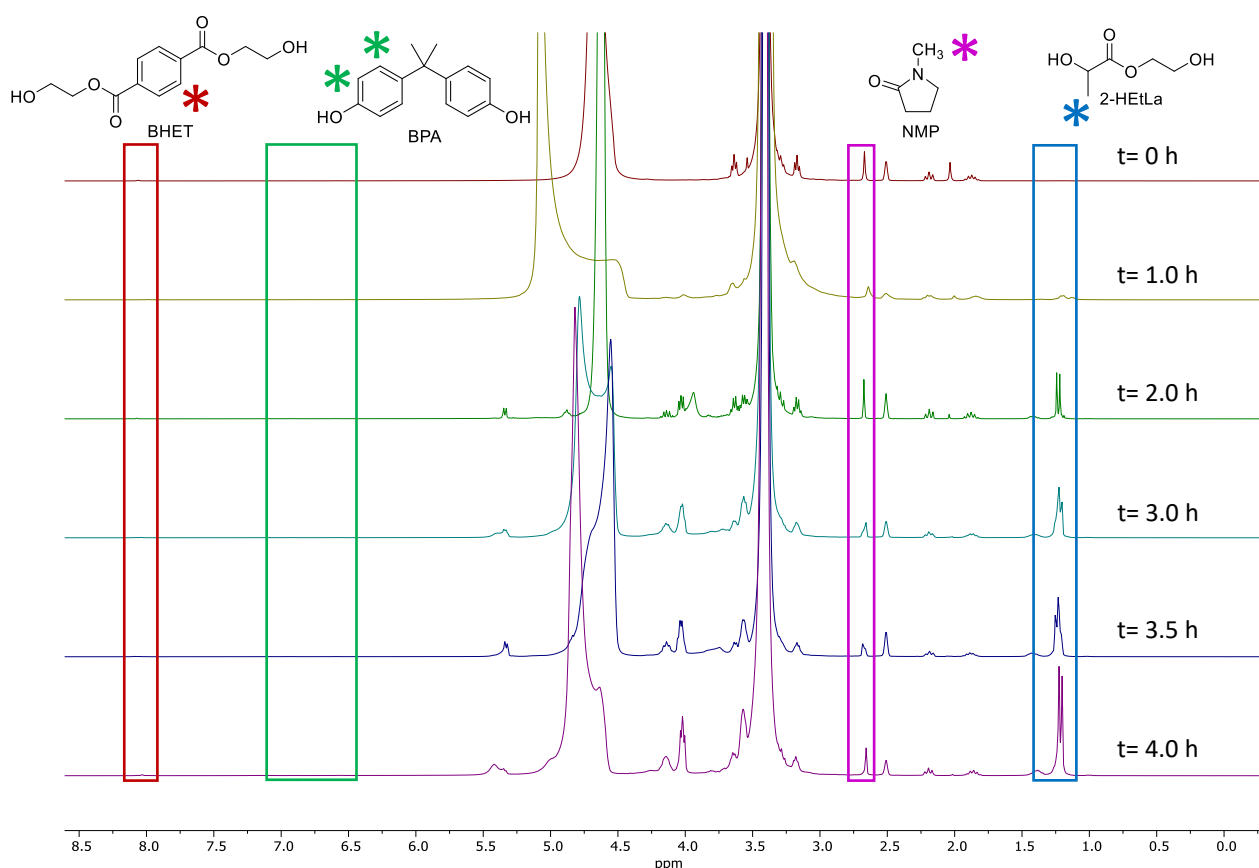
Figure 3.2: Stacked ^1H NMR (DMSO-d_6, 400 MHz, 298 K) spectra for stage 1 of mixed plastic depolymerisation process, from t = 0 h to t = 4 h, using MgCl$_2$ as catalyst system at 150 °C, showing the selectivity towards depolymerisation of PLA over PET and BPA-PC. NMP was used as an internal standard, as in chapter 2.

In the second stage, the washed BPA-PC and PET were recombined before being added to the pre-heated reaction mixture. However, unlike in previous tests, complete visual disappearance of BPA-PC did not occur within the 2 h period, so the reaction time was also increased to 4 h during this second stage. It is possible that the observed swelling of the BPA-PC pellets at the end of the previous stage was a contributing factor to the slower depolymerisation seen in the second stage, as less efficient stirring hindered the ability of the reaction to homogenise. After 4 h, near complete (93%) conversion of BPA-PC to BPA was reached, although a small level of PET conversion (6%) was also observed, likely due to the prolonged reaction period (Figure 3.3).
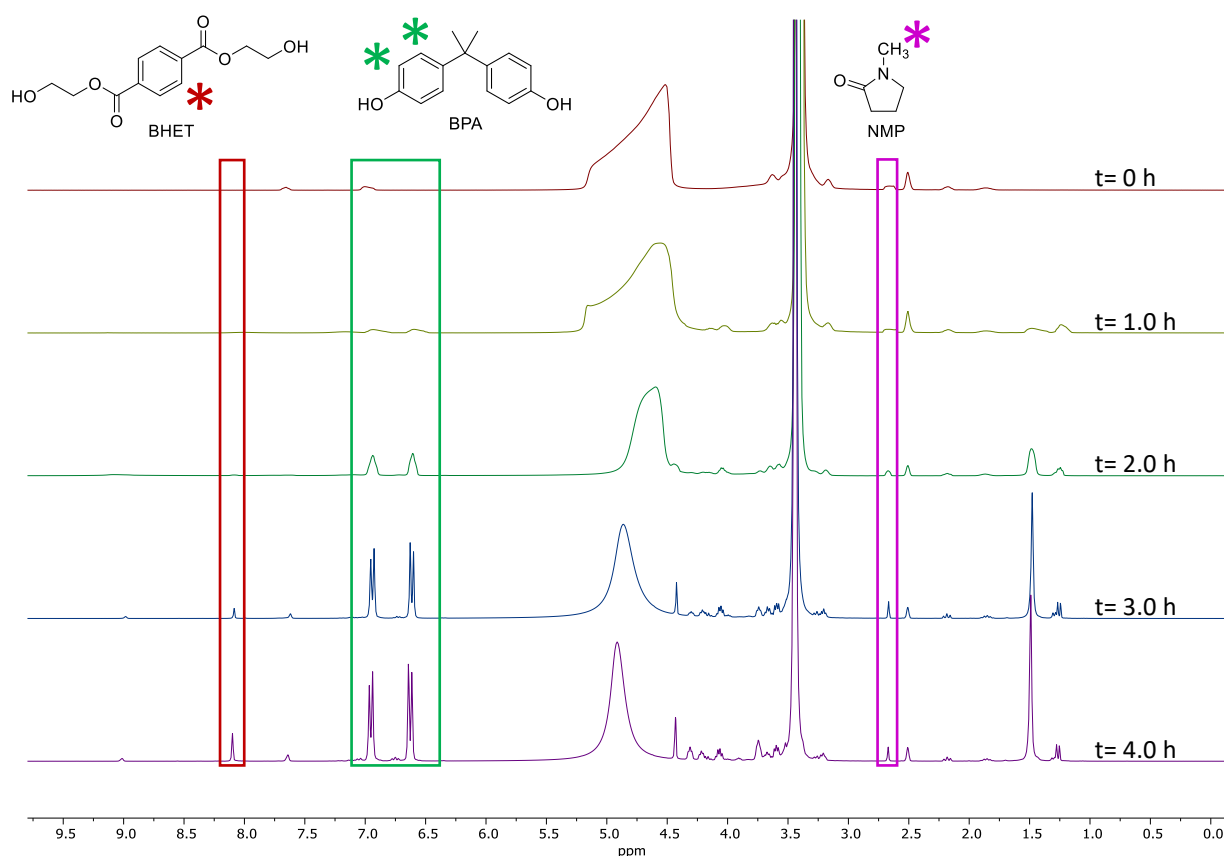
Figure 3.3: *Stacked ^{1}H NMR (DMSO-d$_6$, 400 MHz, 298 K) spectra for stage 2 of mixed plastic depolymerisation process, from t = 0 h to t = 4 h, using MgCl$_2$ / imidazole as catalyst system at 150 °C, showing the selectivity towards depolymerisation of BPA-PC over PET. NMP was used as an internal standard, as in chapter 2.*

As with after the first stage, the residual PET pellets were recovered washed, dried, and weighed before being used for stage 3. The final stage proceeded efficiently, and near quantitative (98%) conversion of PET to BHET was observed after 2 h, despite the PET pellets being present during the two prior depolymerisation stages (Figure 3.4).
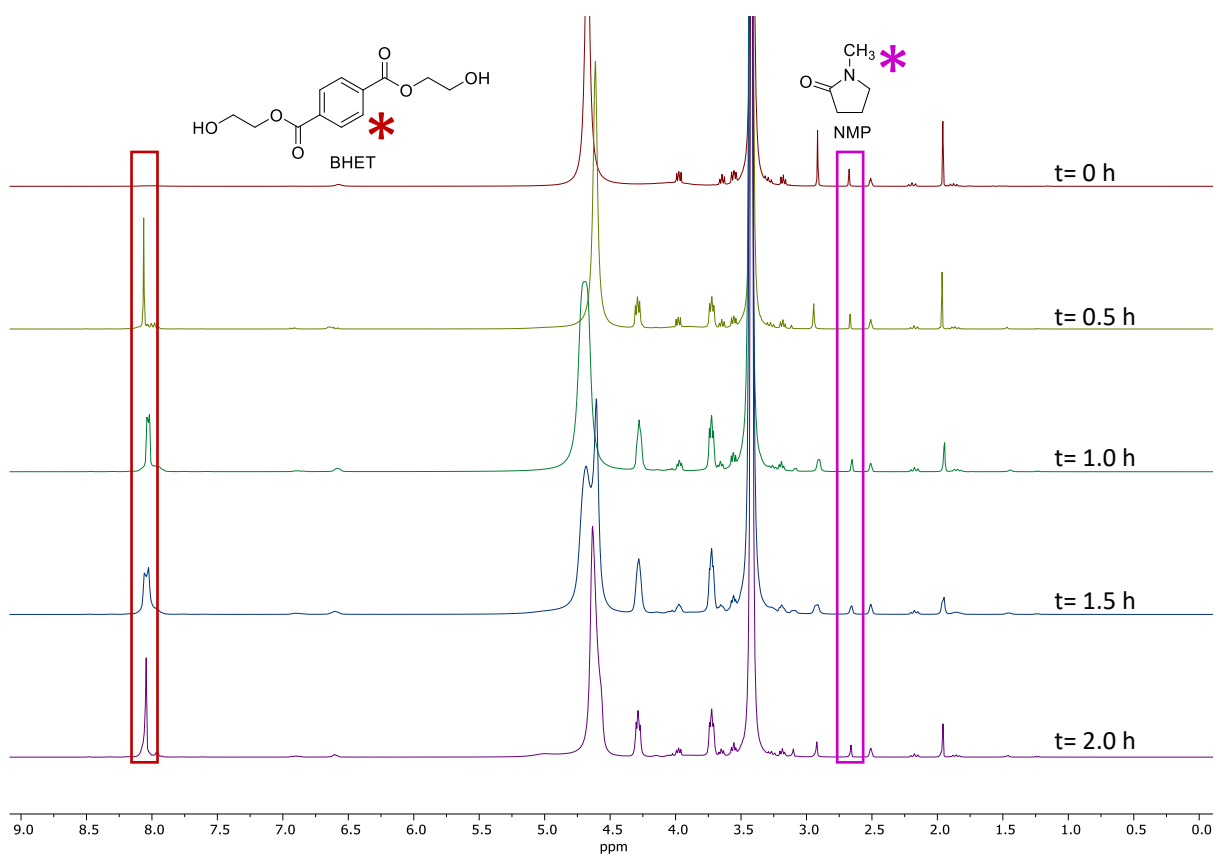

Figure 3.4: *Stacked ^{1}H NMR (DMSO-d$_6$, 400 MHz, 298 K) spectra for stage 3 of mixed plastic depolymerisation process, from t = 0 h to t = 2 h, using Zn(Ac)$_2$ / DMAP as catalyst system at 180 °C, showing the depolymerisation of PET. The minor peaks visible at δ = 6.5 − 7 ppm relate to DMAP. NMP was used as an internal standard, as in chapter 2.*

The overall time / conversion plots for this complete three-stage process can be found below (Figure 3.5).
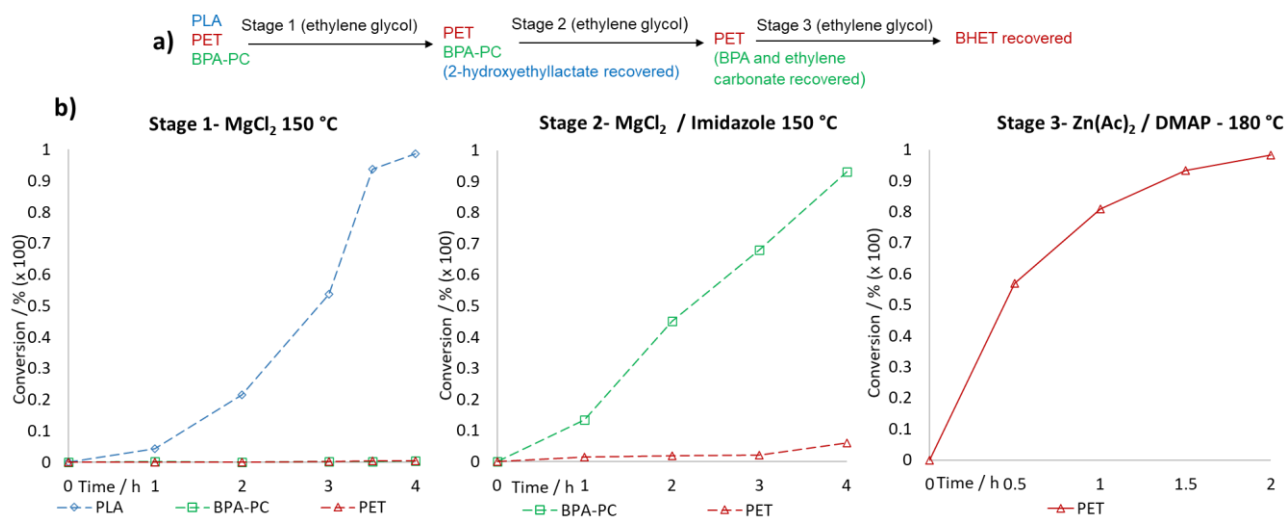
Figure 3.5: *Straight-through process 1 using ethylene glycol as solvent throughout. a) An outline of each stage of the process. After each reaction the polymer pellets to be taken to the next stage are washed before re-use; reaction products are worked-up separately, b) Conversion / Time plots of each respective depolymerisation reaction.*

Following each stage, the reaction mixture was left in a fridge overnight to cool down before recovery of each respective product occurred. 2-HEtLa was recovered by flash column chromatography in a 22% yield. BPA and ethylene carbonate were recovered in the same manor in 20% and 29% yield respectively. Recovery of BHET, in a 27 % yield, was achieved by precipitation in water before filtering and drying the crystals on a Büchner funnel.

The successful demonstration of a straight-through, mixed-plastic process signified a proof-of-concept for our proposed sequential depolymerisation route. Next, different nucleophiles (solvents) were screened in various stages to investigate if value-added or functional products could be produced and isolated from the sequential depolymerisation reactions.

3.2.3 Alternative nucleophile trials

Following the success of the three-stage glycolysis process, we investigated alternative nucleophiles to ethylene glycol for the first and second stages, which would produce comparable selectivity under the same conditions as outlined above and lead to value-added products.

We considered several options for nucleophiles and decided on high-boiling point primary alcohols. Importantly, the primary alcohols could not conflict with the ^{1}H NMR spectra signal of the PLA depolymerisation product (for stage 1) and would have a boiling point greater than 150 °C, so that they could be employed in at least two of the three stages. For stage 1, primary alcohols 1-octanol and 1-hexanol, 1,4-butanediol, and naturally occurring monoterpenoid alcohols, geraniol and nerol, were screened. For stage 2, a recent publication by Jehanno *et al.* provided inspiration for the alternative nucleophile, trimethylolpropane allyl ether diol (TMPAE).[10] The cyclic carbonate produced from this reaction, 2-allyloxymethyl-2-ethyltrimethylene carbonate (AOMEC), is a value-added molecule as it possesses a reactive allyl functionality. Upon ring-opening polymerisation of the cyclic carbonate, this will form a pendant arm that can be further reacted, such as in thiol-ene chemistry, which can lead to cross-linking reactions and therefore multiple improvements and adjustments to polymer properties. These solvents were trialled in mixed polymer reactions under the conditions stated for the first stage and second stages (Table 3.2).

Entry	Solvent	Reaction stage	Catalyst	Temp (°C)	Time (h)	PLA Average Conversion (%)	BPA-PC Average Conversion (%)	PET Average Conversion (%)
1	Ethylene glycol	1	MgCl$_2$	150	4	99	0	0
2	Ethylene glycol	2	MgCl$_2$ / imidazole	150	4	N/A	93	6
3	TMPAE*	2	MgCl$_2$ / imidazole	150	2	N/A	99	0
4	Geraniol	1	MgCl$_2$	150	6	96	15	0
5	Nerol	1	MgCl$_2$	150	6	68	23	1
6	1,4-butanediol	1	MgCl$_2$	150	5	98	8	0
7	1-hexanol	1	MgCl$_2$	150	1	99	6	0
8	1-octanol	1	MgCl$_2$	150	5	99	78	0

Table 3.2: The alternative solvents investigated for use in stages 1 and 2 of the depolymerisation process. Entries 1 and 2 are the conversion figures achieved in the first two stages of the straight-through glycolysis process.

Looking at stage 2, and previous results (Chapter 2, tables 2.1 – 2.4), a dual BPA-PC and PET system is simpler to selectively depolymerise than a PLA/BPA-PC mixture, due to the high susceptibility to glycolysis of both species. Similarly to the glycolysis process, a trial depolymerisation showed that complete conversion of BPA-PC was achieved in within 2 h when TMPAE was employed as solvent. (Table 3.2, entry 3). However, unlike in the glycolysis process, BPA-PC was solely depolymerised to BPA and AOMEC, with no evidence of side product formation (Chapter 2, table 2.3, entry 23). BPA-PC and PET conversion was determined via ^{1}H NMR spectroscopy, in the same manner as the glycolysis reactions.

Following the trial depolymerisation reactions, TMPAE was applied as the second solvent in another straight-through process which proceeded without hindrance or modification. BPA-PC reached 99% conversion in 2 h, whilst PET was unreacted (Figure 3.6).
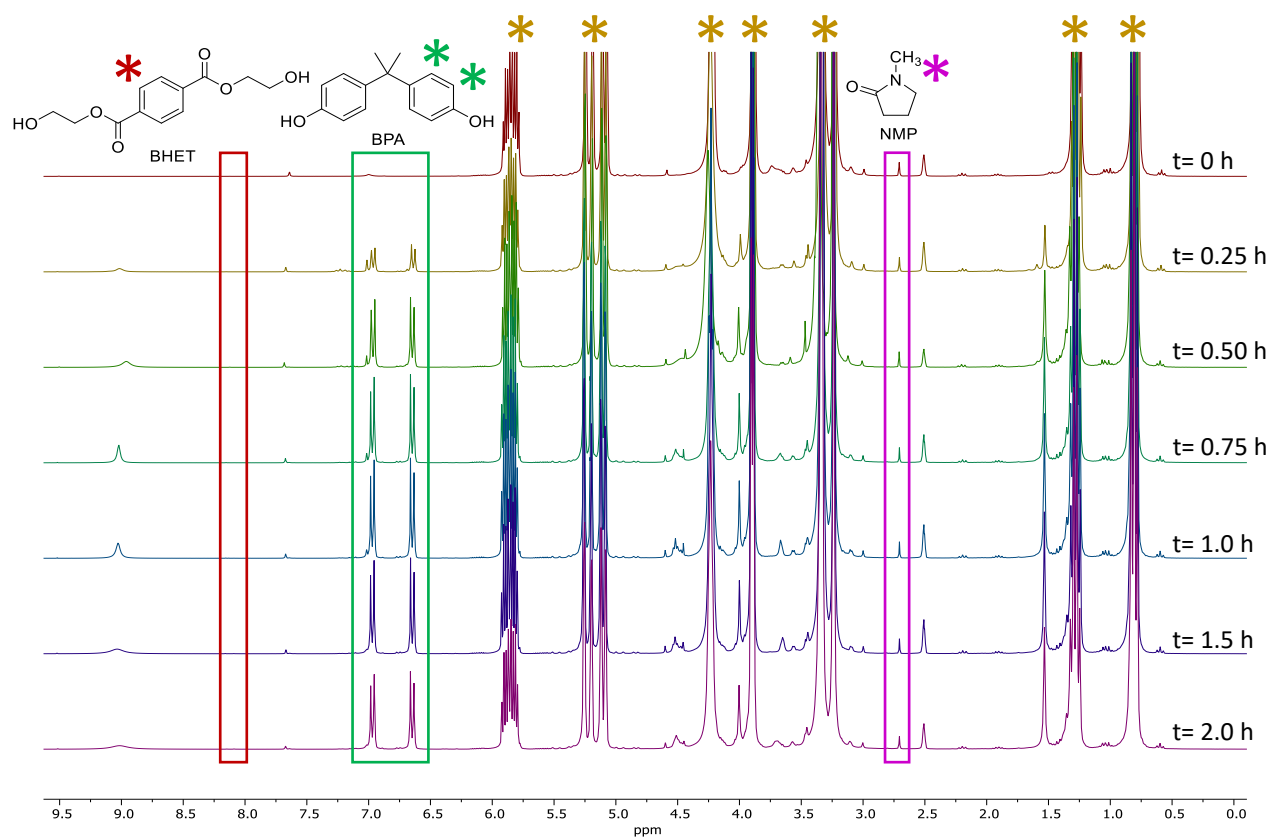
Figure 3.6: *Stacked ^1H NMR (DMSO-d$_6$, 400 MHz, 298 K) spectra of a BPA-PC alcoholysis reaction, using TMPAE, from t = 0 h to t = 2 h, using MgCl$_2$ / imidazole as catalyst system, showing the peaks used to measure conversion to BPA, alongside that of NMP which was used as an internal standard, as in chapter 2. TMPAE peaks are marked in gold.*

AOMEC was recovered from the second stage reaction mixture by flash column chromatography in a 11% yield. Furthermore, from the first stage 2-HEtLa was recovered as a white powder in a 26% yield; and from the third stage BHET was recovered as white crystals in a 25% yield. A complete summary of the process can be seen below (Figure 3.7)
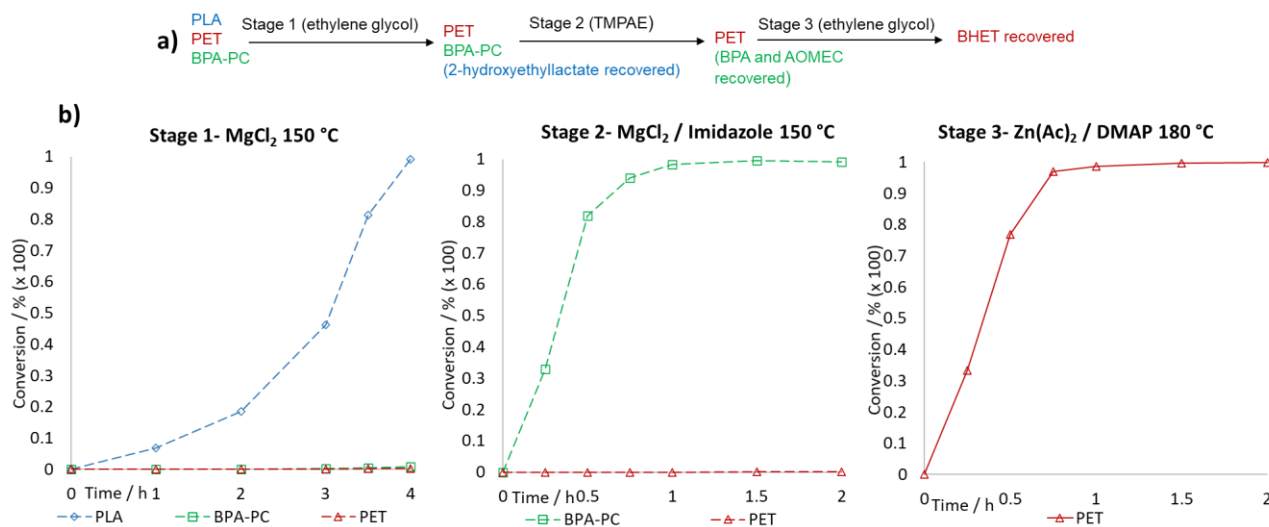
Figure 3.7: *Straight-through process 2, employing TMPAE as an alternative solvent in the second stage. a) An outline of each stage of the process. After each reaction the polymer pellets to be taken to the next stage are washed before re-use; reaction products are worked-up separately, b) Conversion / Time plots of each respective depolymerisation reaction.*

Following the success using TMPAE as an alternative solvent for the second stage, other nucleophiles were also investigated for the first stage (Table 3.2, entries 4-8). In all cases, PET conversion was not observed. However, as anticipated, finding a clear selectivity difference between PLA and BPA-PC was more challenging. The most promising alternative nucleophile was 1-hexanol, which resulted in complete conversion (99%) of PLA in 1 h and only a minimal conversion (6%) of BPA-PC. Alcoholysis of PLA with 1-hexanol produces hexyl lactate, a flavouring compound found naturally in wines following fermentation, but which can also be applied as a food additive.[17, 18] In addition to these uses, hexyl lactate has been shown to be employed as a starting material for the synthesis of higher poly(alkyl lactate acrylate)s, which can act as viscosity modifiers in bio-derived lubricating oils.[19, 20]

When 1-hexanol was used as solvent, PLA conversion was monitored using the signal at δ = 4.02 ppm, which corresponds to the single methine proton of the hexyllactate product.

In a final selective depolymerisation process, we applied 1-hexanol into the first stage instead of ethylene glycol. Within 1 h, complete visual degradation of PLA had occurred and so the reaction was stopped, and the residual BPA-PC and PET pellets prepared for stage 2 by being washed in TMPAE and then dried. Quantitative conversion (99.7%) of PLA to hexyllactate was achieved, however a small degree conversion (4%) of BPA-PC was also noted. Furthermore, there is evidence to suggest a hexanol substituted BPA derivative was formed alongside BPA, in a similar fashion to when BPA-SP formation was observed during BPA-PC depolymerisation screening (Figure 3.8; see Chapter 2, Figure 2.5, 2.6).
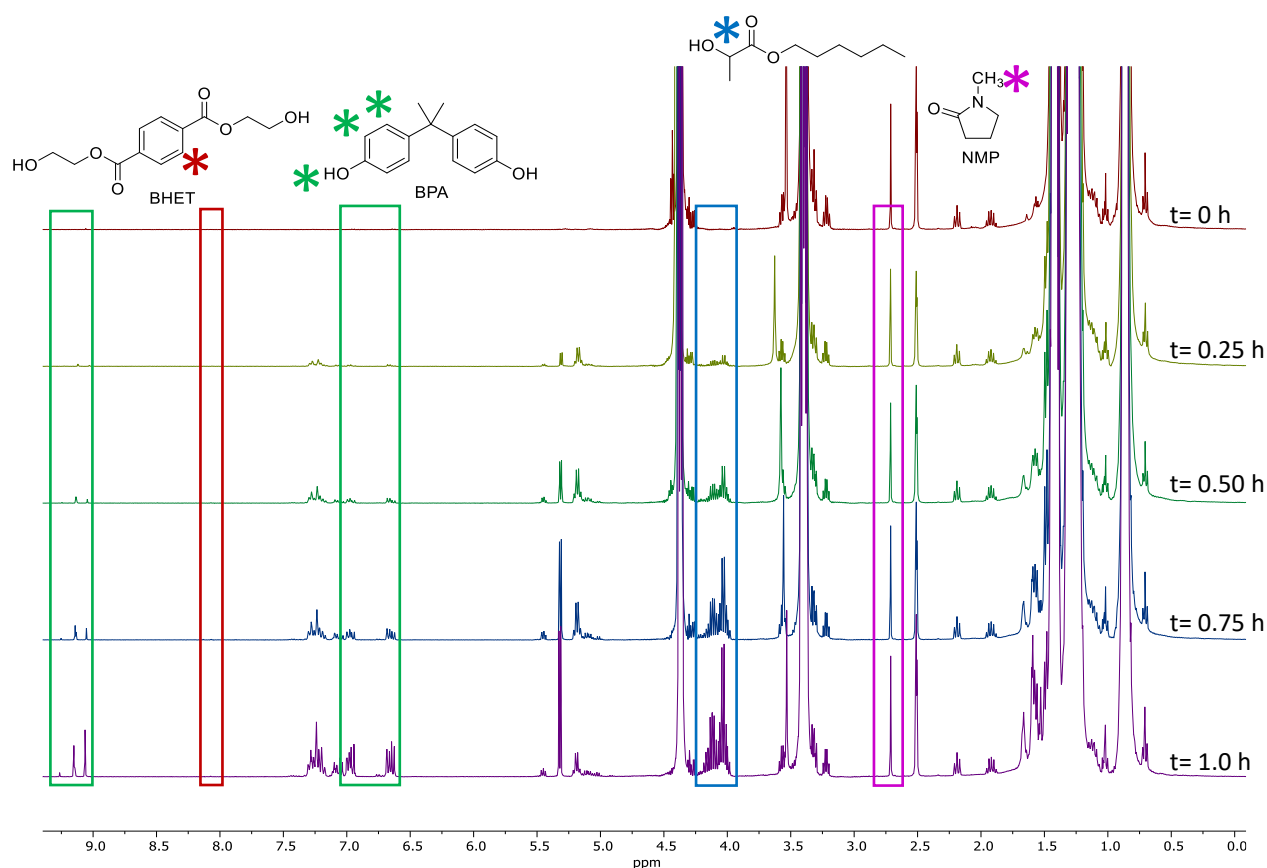
Figure 3.8: Stacked ^1H NMR spectra (DMSO-d_6, 400 MHz, 298 K) of a PLA alcoholysis reaction, using 1-hexanol, from t = 0 h to t = 1 h, using MgCl$_2$ as catalyst system, showing the peaks used to measure conversion to hexyllactate, alongside that of NMP which was used as an internal standard, as in chapter 2. Multiple phenolic peaks at δ = 9.0 - 9.1 ppm, suggest formation of mono-hexanol substituted BPA derivative.

The second stage was carried out in the same fashion to previous experiments. Quantitative conversion (99%) of BPA-PC to BPA and AOMEC was achieved, whilst no conversion of PET to

BHET occurred. The residual PET pellets were recovered, washed in ethylene glycol, and then

dried, for stage 3 of the process. By this point, the PET pellets were noticeably more

deformed than in previous experiments, with surface cracks and visible wear. However,

quantitative conversion (99%) of PET to BHET was still achieved in 2 h. A complete overview

of this process is shown below (Figure 3.9)
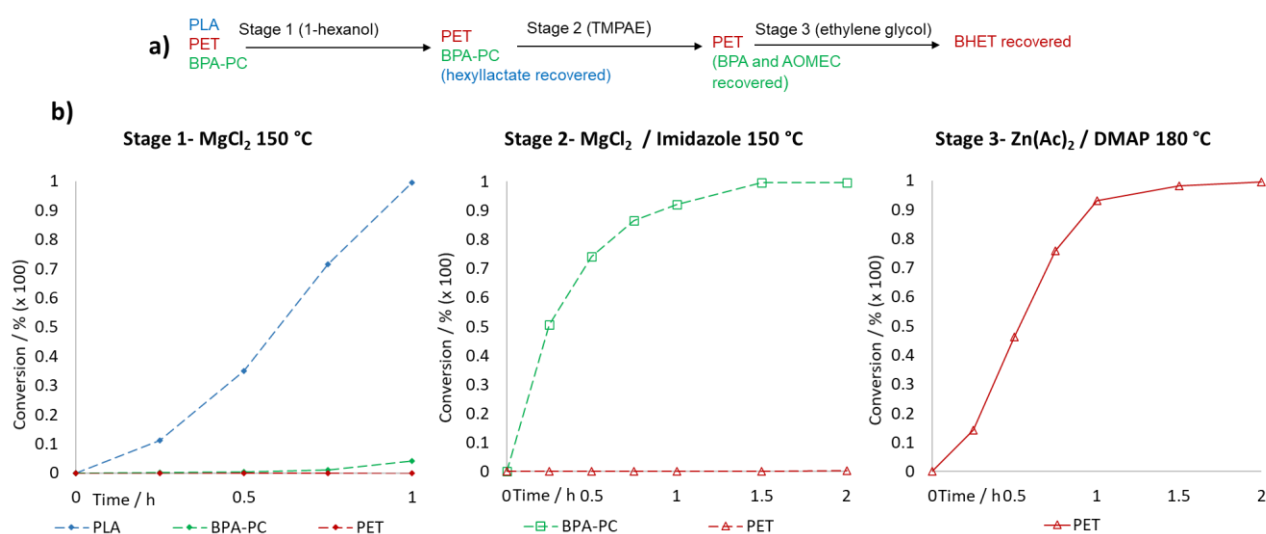
Figure 3.9: *Straight-through process 3, employing both 1-hexanol and TMPAE as alternative solvents in the first and second stages. a) An outline of each stage of the process, after each reaction the polymer pellets to be taken to the next stage are washed before re-use; reaction products are worked-up separately, b) Conversion / Time plots of each respective depolymerisation reaction.*

Product recovery was attempted after each stage, BHET was recovered as white crystals in a

49% yield, a trace mass of AOMEC was recovered in a 1% yield and hexyl lactate was

recovered as mixed fractions, with need for further purification steps. A full summary table

of product yields from the three straight-through process can be found below (Table 3.3).

Due to the presence of NMP in the reaction, to act as internal standard, the conversion

figures of polymer to product are also equivalent to the crude yield of product prior to

isolation. Therefore, yield has been broken down into both crude and isolated.

Entry	Reaction stage	Reaction Route	Product	Polymer	Solvent	Crude yield* (%)	Isolated yield (%)
1	1	1	2-HEtLa	PLA	Ethylene glycol	99	22
2	1	2	2-HEtLa	PLA	Ethylene glycol	99.2	26
3	1	3	hexyllactate	PLA	1-hexanol	96	N/A
4	2	1	BPA	BPA-PC	Ethylene glycol	93	20
5	2	1	Ethylene carbonate	BPA-PC	Ethylene glycol	93	29
6	2	2	AOMEC	BPA-PC	TMPAE	99.2	11
7	2	3	AOMEC	BPA-PC	TMPAE	99.7	1
8	3	1	BHET	PET	Ethylene glycol	98	27
9	3	2	BHET	PET	Ethylene glycol	99.8	25
10	3	3	BHET	PET	Ethylene glycol	99.3	49

Table 3.3: *Crude and isolated yields of each reaction product recovered after each stage of a selective depolymerisation process. *Due to the use of an internal standard in depolymerisation reactions, final polymer conversion is equal to crude yield.*

3.3 Summary

In summary, we successfully demonstrated three distinct routes for selective depolymerisation among PLA, BPA-PC and PET mixtures. Two of the devised routes introduced alternative nucleophiles, which enabled the formation of value-added products during the first (PLA depolymerisation) and second stages (BPA-PC depolymerisation). Product recovery and isolation after each step was achieved with varying degrees of success (ranging from poor to moderate yield) although high conversions were noted in all instances. Nearly all respective depolymerisation products were isolated in high purity, however for those that evaded purification attempts the expected product ^{1}H NMR spectra signals could still be identified in mixed fractions. The ability to employ a range of nucleophiles creates the opportunity to build a modular system, which can be uniquely tailored across a range of circumstances and situations, resulting in bespoke value-added products. However, to leverage selective chemical recycling to monomer, and give it a watershed moment, several

outstanding challenges need to be addressed. Whilst we have shown that a selective depolymerisation process can be conducted on the bench scale, ultimately, it needs to be reproducible on the pilot scale for it to even be considered industrially viable. Thus, the main areas for improvement are scalability, further nucleophile variation, and process development to enhance the recovery of depolymerisation products. Other areas of development include moving towards the idealised system (Figure 3.1), in which the process is truly one-pot where multiple polymers react orthogonally and simultaneously.

3.4 Experimental

3.4.1 Materials

The chemicals used in the screening process are as follows, they were used without further purification. PET, PLA, and BPA-PC granules (3 mm) were purchased from Goodfellow, ethylene glycol (anhydrous), trimethylolpropane allyl ether (TMPAE), 1-octanol, nerol, *N*-methyl-2-pyrrolidinone (NMP), zinc acetate dihydrate, magnesium chloride and imidazole were purchased from Sigma Aldrich. Geraniol, 1-hexanol and DMAP were bought from Acros Organics, deuterated DMSO was purchased from Apollo Scientific.

3.4.2 Instrumentation

Nuclear Magnetic Resonance (NMR) Spectroscopy

All ^{1}H NMR spectra were recorded on either a Bruker AVIII 400 MHz spectrometer or a Bruker AVANCE NEO 400 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to the residual solvent signals of deuterated dimethyl

sulfoxide (DMSO-d_6, ^{1}H: quintet, δ = 2.50 ppm, ^{13}C: septet, δ = 39.51 ppm) or deuterated chloroform (CDCl$_3$, ^{1}H: singlet, δ = 7.26 ppm, ^{13}C: triplet, δ = 77.2 ppm).

3.4.3 Experimental procedure

The same procedure was followed for all alternative solvent trials and selective depolymerisation processes. All trial reactions were completed in triplicate, for reproducibility and to allow for conversion levels to be averaged, and full processes were run in singlet based on the data gathered in the trials.

Selective depolymerisation and alternative solvent trials

All reactions were carried out in triplicate in 20 mL scintillation vials equipped with magnetic stirrers. Each vial was charged with the catalyst(s) (0.375 mmol, 15 mol % of each), solvent (50 mmol, 2000 mol %) and the internal standard NMP (0.25 mmol, 10 mol %). The vials were sealed and placed within a heating block at the working temperature (120 – 180 °C), whilst stirring at 500 rpm, for 15 min to solubilise the catalysts and allow the reaction mixture temperature to stabilise. After 15 minutes, an aliquot (0.1 mL) was removed from the reaction mixture to act as a t0 for NMR spectroscopy analysis, pelletised polymer (2.5 mmol of each) was then added, the vials were resealed, and a timer set. Aliquots were further removed for NMR spectroscopy analysis at regular intervals for 1-6 h depending on solvent chosen. At reaction end, the vials were removed from the heating block, the magnetic stirrers removed, and the sealed vials were placed in the fridge overnight to cool pending further work up.

Three-stage depolymerisation processes

Stage 1 – Selective depolymerisation of PLA by glycolysis and alcoholysis

A 20 mL scintillation vial with a magnetic stirrer bead was charged with magnesium chloride (0.375 mmol, 15 mol %), ethylene glycol or 1-hexanol (50 mmol, 2000 mol %) and the internal standard NMP (0.25 mmol, 10 mol %). The vial was sealed and placed within a heating block at 150 °C, whilst stirring at 500 rpm, for 15 minutes to solubilise the catalyst and allow the reaction mixture temperature to stabilise. After 15 minutes, an aliquot (0.1 ml) was removed from the reaction mixture to act as a t0 for NMR spectroscopy analysis, pelletised PLA, BPA-PC and PET (2.5 mmol of each) were then added, the vial was resealed, and a timer set. Further aliquots for NMR spectroscopy analysis were taken at t = 1 h, 2 h, 3 h, 3.5 h and 4 h for ethylene glycol and 0.25 h, 0.5 h, 0.75 h and 1 h for 1-hexanol. All aliquots taken for ^{1}H NMR spectroscopy analysis were dissolved in DMSO-d_6. At reaction end, the vial was removed from the heating block and the magnetic stirrer removed. Unreacted PET and BPA-PC pellets were removed from the reaction mixture, washed with ethylene glycol or TMPAE, dried, and then weighed before usage in the following stage. The vial containing the reaction mixture was sealed and placed in the fridge to cool down overnight, prior to recovery of 2-HEtLa or hexyllactate. 2-HEtLa was recovered by flash column chromatography using acetone as eluent. Following the combining of fractions and removal of excess solvent, 2-HEtLa was isolated as a white powder (^{1}H NMR, 400 MHz, CDCl$_3$) δ = 4.33 – 4.27 (q, 2H), 4.26 – 4.22 (q, 1H), 3.83 – 3.79 (t, 2H), 3.69 – 3.67 (s, 2H), 1.41 – 1.38 (d, 3H). Hexyllactate was recovered as mixed fractions using the same process, and so further purification is required.

Stage 2 – Selective depolymerisation of BPA-PC by glycolysis and alcoholysis

A 20 mL scintillation vial with a magnetic stirrer bead was charged with magnesium chloride and imidazole (0.375 mmol, 15 mol % of each), ethylene glycol or TMPAE (50 mmol, 2000 mol %) and the internal standard NMP (0.25 mmol, 10 mol %). The vial was sealed and placed within a heating block at 150 °C, whilst stirring at 500 rpm, for 15 minutes to solubilise the catalyst allow the reaction mixture temperature to stabilise. After 15 minutes, an aliquot (0.1 ml) was removed from the reaction mixture to act as a t0 for NMR spectroscopy analysis, pelletised BPA-PC and PET from the previous stage were then added, the vial was resealed, and a timer set. Further aliquots for NMR spectroscopy analysis were taken at t = 1 h, 2 h, 3 h and 4 h for ethylene glycol and 0.25 h, 0.5 h, 0.75 h, 1 h, 1.5 h and 2 h for TMPAE. All aliquots taken for ^{1}H NMR spectroscopy analysis were dissolved in DMSO-d_6. At reaction end, the vial was removed from the heating block and the magnetic stirrer removed. Unreacted PET pellets were removed from the reaction mixture, washed with ethylene glycol, dried, and then weighed before usage in the following stage. The vial containing the reaction mixture was sealed and placed in the fridge to cool down overnight, prior to recovery of BPA, ethylene carbonate or AOMEC. BPA and ethylene carbonate were recovered from the depolymerisation using ethylene glycol as solvent by column chromatography using an automatic column, with 60:40 hexane: ethyl acetate as eluent system. BPA eluted first and was isolated as a white powder following the combining of fractions and removal of excess solvent (^{1}H NMR, 400 MHz, DMSO-d_6) δ = 9.15 – 9.13 (s, 2H), 7.01 – 6.95 (d, 4H), 6.66 – 6.61 (d, 4H), 1.55 – 1.52 (s, 6H). Ethylene carbonate was recovered second, also as a white powder following the same process. (^{1}H NMR, 400 MHz, DMSO-d_6) δ = 4.50 – 4.44 (m, 4H).

AOMEC was recovered from the depolymerisation using TMPAE as solvent by column chromatography under the same process as outlined above. It eluted from the column first and was isolated as a white powder following removal of excess solvent under vacuum (^{1}H NMR, 400 MHz, DMSO-d_6) δ = 5.94 – 5.78 (m, 1H), 5.28 – 5.10 (m, 2H), 4.02 – 3.95 (m, 4H), 3.93 – 3.86 (d, 2H), 3.34 – 3.33 (s, 2H), 1.35 – 1.27 (q, 2H), 0.84 – 0.76 (t, 3H). BPA was recovered within mixed fractions following the elution of AOMEC.

Stage 3 – Depolymerisation of PET by glycolysis

A 20 mL scintillation vial with a magnetic stirrer bead was charged with zinc acetate dihydrate and DMAP (0.375 mmol, 15 mol % of each), ethylene glycol (50 mmol, 2000 mol %) and the internal standard NMP (0.25 mmol, 10 mol %). The vial was sealed and placed within a heating block at 180 °C, whilst stirring at 500 rpm, for 15 minutes to solubilise the catalyst allow the reaction mixture temperature to stabilise. After 15 minutes, an aliquot (0.1 ml) was removed from the reaction mixture to act as a t0 for NMR spectroscopy analysis, pelletised PET from the previous stage were then added, the vial was resealed, and a timer set. Further aliquots for NMR spectroscopy analysis were taken at t = 0.25 h, 0.5 h, 0.75 h, 1 h, 1.5 h and 2 h. All aliquots taken for ^{1}H NMR spectroscopy analysis were dissolved in DMSO-d_6. At t = 2h, the vial was removed from the heating block and the magnetic stirrer removed. Cold deionised water was added to the reaction vial to precipitate BHET, before the vial was sealed and placed in the fridge overnight to cool. Once cooled, BHET was recovered as white, needle like crystals using vacuum filtration (^{1}H NMR, 400 MHz, DMSO-d_6) δ = 8.15 – 8.12 (s, 4H), 5.00 – 4.95 (t, 2H), 4.35 – 4.30 (t, 4H), 3.76 – 3.70 (q, 4H).

3.4.4 Calculation of polymer conversion from ^{1}H NMR spectra

The final figure of achieved polymer conversion is directly linked to the integration of the relevant product peaks with respect to the integration of NMP. The integration value to which NMP is set varies with respect to the number of protons present in each of the chosen environments within the products, following the formula $(x/y) \times 0.1$, where x = no. of protons in NMP environment (= 3), y = no. of protons in product environment (BHET= 4, BPA= 4, 2-HEtla= 3, hexyllactate= 1), and 0.1 is the no. of equivalents of NMP with respect to equivalents of polymer repeat unit, this gives NMP integrals of 0.075 for PET and BPA-PC conversion and 0.1 or 0.3 for PLA conversion, depending on what the reaction product is. To calculate the conversion of PET and BPA-PC during stage 1 reactions, in which the integral of NMP is set to that of the relevant PLA product environment, the integration of each the environments of BHET and BPA that are used must be adjusted to align them with the setting of NMP. This adjustment is simple to make and comprises of multiplying the integrations of both BHET and BPA by 0.75 when 2-HEtLa is the product of PLA depolymerisation, or by 0.25 when hexyllactate is the product of a PLA depolymerisation.

However, due to the removal of aliquots of reaction mixture during the process of the depolymerisation, a small amount of NMP will be removed each time, thus decreasing the ratio of NMP to polymer in the reaction. Therefore, to counter this, an adjustment must be applied to the integration values of the relevant product peaks upon each removal of an aliquot, until the point at which the polymer pellets are fully solubilised in the reaction solvent (at this point polymer and NMP will be removed and so the ratio is set from here onwards).

NMP adjustment is calculated by considering the reduction in NMP concentration as aliquots are removed, with respect to the initial concentration of NMP in the reaction mixture. Initial molarity of NMP is taken as moles NMP ÷ total volume of solution, which equals 8.88×10^{-5} mol mL^{-1}. The decrease in NMP concentration, and hence the adjustment factor, is determined by the total volume of solution with respect to the initial molarity of NMP, decrease in NMP molarity is cumulative. The cumulative percentage of NMP removed in aliquots is then calculated, with respect to initial concentration of NMP and this produces the adjustment factors for each aliquot (Table 3.4)

Aliquot	Total solution volume [a] (mL)	Aliquot NMP concentration [b] (mol mL^{-1})	Cumulative NMP concentration removed (mol mL^{-1})	Cumulative NMP concentration removed [c] (%)	NMP concentration remaining (%)	Adjustment factor
0	2.8	N/A	0	0	100	1
1	2.8	3.17×10^{-6}	3.17×10^{-6}	3.57	96.43	0.964
2	2.7	3.29×10^{-6}	6.46×10^{-6}	7.27	92.73	0.927
3	2.6	3.42×10^{-6}	9.88×10^{-6}	11.13	88.87	0.889
4	2.5	3.55×10^{-6}	1.34×10^{-5}	15.09	84.91	0.849
5	2.4	3.7×10^{-6}	1.71×10^{-5}	19.26	80.74	0.807
6	2.3	3.86×10^{-6}	2.10×10^{-5}	23.65	76.35	0.764

Table 3.4: Calculation of NMP adjustment factors. a) To 1 decimal place, b) Aliquot NMP concentration is taken as: initial NMP molarity / (Total solution volume x 10), c) Taken as: (cumulative NMP concentration removed / initial NMP concentration) x 100.

Further to this, in stage 1 reactions where all three polymers are present, the integration values corresponding to BPA-PC and PET conversion must be further adjusted so that they are aligned with the set integration value of NMP, which corresponds to PLA conversion. This adjustment is simple to make and comprises of multiplying the integrations of both BHET and BPA by 0.75 when 2-HEtLa is the product of PLA depolymerisation, or by 0.25 when hexyllactate is the product of PLA depolymerisation. Examples of the process of calculating final polymer conversion in mixed polymer reactions is shown below (Table 3.5, 3.6, 3.7).

Aliquot	Reaction time (h)	PLA integration	PLA multiplier	PLA conversion (integration x multiplier)	PLA conversion (%)	BPA-PC integration	BPA-PC adjusted integration (x0.75)	BPA-PC multiplier	BPA-PC conversion (adjusted integration x multiplier)	BPA-PC conversion (%)	PET integration	PET adjusted integration (x0.75)	PET multiplier	PET conversion (adjusted integration x multiplier)	PET conversion (%)
0	0	0	1	0	0	0	0	1	0	0	0	0	1	0	0
1	1	0.045	0.964	0.04338	4	0.002	0.0015	0.964	0.001446	0	0.001	0.00075	0.964	0.000723	0
2	2	0.232	0.927	0.215064	22	0.001	0.00075	0.927	0.000695	0	0	0	0.927	0	0
3	3	0.605	0.889	0.537845	54	0.002	0.0015	0.889	0.001334	0	0.002	0.0015	0.889	0.001334	0
4	3.5	1.104	0.849	0.937296	94	0.004	0.001	0.849	0.002547	0	0.007	0.00525	0.849	0.004457	0
5	4	1.161	0.849	0.985689	99	0.006	0.0045	0.807	0.003632	0	0.006	0.0045	0.807	0.003632	0

Table 3.5: *The process for calculating conversion figures following a Route 1, stage 1 depolymerisation reaction. PLA, BPA-PC and PET, ethylene glycol as solvent, MgCl2, 150 °C, 4 h.*

Aliquot	Reaction time (h)	PLA integration	PLA multiplier	PLA conversion (integration x multiplier)	PLA conversion (%)	BPA-PC integration	BPA-PC adjusted integration (x0.25)	BPA-PC multiplier	BPA-PC conversion (adjusted integration x multiplier)	BPA-PC conversion (%)	PET integration	PET adjusted integration (x0.25)	PET multiplier	PET conversion (adjusted integration x multiplier)	PET conversion (%)
0	0	0	1	0	0	0	0	1	0	0	0	0	1	0	0
1	0.25	0.132	0.964	0.127	13	0.003	0.00075	0.964	0.000723	0	0	0.00075	0.964	0	0
2	0.5	0.392	0.927	0.363	36	0.016	0.004	0.927	0.003708	0	0.001	0.00025	0.927	0.000232	0
3	0.75	0.819	0.889	0.728	73	0.048	0.012	0.889	0.010668	1	0.001	0.00025	0.889	0.000222	0
4	1	1.122	0.889	0.997	99.7	0.191	0.04775	0.849	0.04054	4	0.001	0.00025	0.849	0.000212	0

Table 3.6: The process for calculating conversion figures following a Route 3, stage 1 depolymerisation reaction. PLA, BPA-PC and PET, 1-hexanol as solvent, MgCl2, 150 °C, 1 h.

Aliquot	Reaction time (h)	BPA-PC integration	BPA-PC multiplier	BPA-PC conversion (integration x multiplier)	BPA-PC conversion (%)	PET integration	PET multiplier	PET conversion (integration x multiplier)	PET conversion (%)
0	0	0	1	0	0	0	1	0	0
1	1	0.139	0.964	0.133966	11	0.015	0.964	0.01446	1
2	2	0.487	0.927	0.451449	45	0.019	0.927	0.017613	2
3	3	0.765	0.889	0.68085	68	0.024	0.889	0.021336	2
4	4	01.098	0.849	0.932202	93	0.071	0.849	0.060279	6

Table 3.7: *The process for calculating conversion figures following a Route 1, stage 2 depolymerisation reaction. BPA-PC and PET, ethylene glycol as solvent, MgCl2 / Imidazole,150 °C, 4 h. The calculations for when TMPAE are solvent are the same as for when ethylene glycol is solvent.*

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Chapter 4: Conclusions and future directions

4.1 Conclusions

This work has successfully demonstrated the selective depolymerisation of mixed plastics on a bench-scale by using an operationally simple 3-stage sequence. This was achieved by identifying and exploiting reactivity differences among three carbonyl-containing plastics: PET, PLA, and BPA-PC. Several catalyst systems, including single and/or dual combinations of Lewis acids and Lewis bases, were screened for each plastic across a temperature range of 120 °C – 180 °C. This data afforded distinct reactions conditions (choice of catalyst and temperature) where each plastic would be expected to depolymerize orthogonally among one another. For example, PET depolymerisation was best achieved when more forcing conditions (180 °C, dual catalyst) were employed, owing to the high hydrolytic stability and robust physical properties of PET. In comparison, PLA, which is both less physically resilient and hydrolytically stable, was much more amenable to depolymerisation at reduced temperatures using either single or dual catalyst systems. Additionally, occasions where selectivity was not observed, but quantitative conversion of two or more polymers occurred, provided useful reaction condition data that could be applied to one-component chemical recycling systems. By applying optimized depolymerization conditions for each plastic, sequential and selective depolymerisation among PET, PLA and BPA-PC was successfully executed using multiple solvents such as ethylene glycol, 1-hexanol and TMPAE. This led to the isolation of chemically diverse degradation products, some of which are considered value-added chemicals or monomers. The crude yields of depolymerisation products were found to be near quantitative in all cases, although the isolated yields varied greatly due to purification challenges.

4.2 Future directions

Despite our successful proof-of-concept demonstration for mixed plastics depolymerisation, there are still several limitations and areas for improvement. An immediate area to address is the poor isolated yields of the depolymerisation products. Specifically, alternative purification strategies that avoid chromatography and tedious separations should be pursued. In addition to this, a suitable method for the recovery of hexyllactate needs to be devised. Any synthetic protocol must initially be high yielding, reliable, and cost-effective to be truly viable for further development or mainstream usage. Furthermore, it is important to consider that any future applicability in industry will be dictated by the scalability of the bench-top process that we investigated. For the purposes of this exploratory work, we worked on a small reaction scale (< 1 g polymer). However, translation to pilot or industry scales would require increasing to 100 g or kg scale and beyond. An important initial step toward such an aim would be to scale the reaction by an order of magnitude, i.e., to 10 g scale. Scaling reactions often provides advantages in process efficiencies, including purification, since mass-transfer losses can be exacerbated on small scales. Thus, similar benefits could be anticipated when scaling our established depolymerisation process.

Further efforts could focus on broadening the reaction parameters. For example, non-metal organic acid catalysts could be screened individually or even paired with the organobase catalysts that were already investigated. Solvents possessing greater functional group diversity could also be explored to yield additional high value depolymerisation products. Finally, our study was restricted to carbonyl-containing plastics (PET, PLA, and BPA-PC). However, other plastics such as polyurethanes also possess significant recycling challenges.

We began an exploratory screening study into the depolymerisation characteristics of a dicarbamate polyurethane mimic using our established reaction conditions. The model polyurethane molecule was assessed under standard depolymerisation conditions (180 °C) with various catalysts. Initial results were inconclusive, the complex degradation behaviour of urethanes proved too challenging to dissect in this situation. Mixed reaction products were observed across the assessment screening, although none were successfully isolated. Further experiments were warranted to seek ways of improving the selectivity and efficiency of model polyurethane degradation before screening polyurethanes occurs.