

Efficient and Selective Organocatalytic Depolymerisation under milder conditions

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Summary

For almost a century, plastics have become one of the most widely employed materials for producing products daily used, both for common and high added value applications. This is largely due to the various properties that can be obtained from their ease of processing into objects compared to other materials such as glass or metals. As a result, global plastic production has exponentially increased in the past decades, reaching 390 million tons in 2021, and this growing is expected to continue until at least 2060. Due to its high production, a huge amount of plastic waste is generated, which, if it is not properly disposed of, contaminates the environment, where it takes centuries to degrade. Plastic contamination is a worldwide problem that requires new methods for collecting, separating, and recycling these materials. Currently, this problem is gaining a lot of attention not only because of the pollution it generates but also due to its potential effects on human health from the ingestion of small plastic particles known as microplastics.

Chemical recycling allows for recovering molecules of sufficient purity for obtaining through polymerisation materials of virgin quality, which means that theoretically, infinite recycling loops could be performed. In contrast, traditional recycling methodologies are not able to perform a circular economy approach. On one hand mechanical recycling can be just applied for a material in a finite number of loops before its properties decrease (downcycling). On the other hand, pyrolysis enables the recovery of energy by converting plastics into fuel, but the subsequent emission of global warming gases arises environmental concerns. However, despite its promising potential, chemical recycling still faces significant challenges that hinder its implementation at industrial scale. Among these challenges are the use of harsh reaction conditions, such as high temperatures, which prevent the development of energy-efficient and economically viable reactions. Additionally, many examples reported in the literature involve the use of toxic metallic catalysts that are difficult to separate from the products and could accumulate in the materials during successive recycling processes. In contrast to this, organocatalysts are a very promising and less toxic alternative. Unlike conventional organic reactions with small molecules, their application in the field of depolymerisation still needs further study to understand and optimise the chemical reactions (catalytic mechanism, solvent effects, etc.). In addition, organocatalysts typically lack high thermal resistance, and therefore, the development of low-temperature processes could allow for their reuse multiple times.

To put the topic in context, **Chapter 1** introduces the advances that have been reported in chemical recycling, highlighting the recent literature and the challenges that need to be faced for achieving efficient depolymerisation reactions. First the plastic production and projections are explained showing the need of finding alternative recycling pathways. Chemical recycling is explained in terms of advantages and disadvantages in comparison with conventional recycling pathways. Additionally, since this thesis is focused on the use of organocatalyst for depolymerisation the existing literature is summarised, and the remaining challenges in the area regarding efficiency and scale-up are explained.

Chapter 2 is focused on the depolymerisation of PUs through aminolysis. The initial results obtained with hexamethylenediamine as a nucleophile and solvent revealed that a temperature in the range of 130-190 °C was necessary to achieve excellent depolymerisation rates. Due to its ability to withstand these temperatures and its superior catalytic activity, TBD:MSA was considered the most suitable catalyst. However, it was observed that primary amines broke the C-O and C-N bonds of the urethane group indiscriminately, releasing 1,8-octanediol and urea as products. In contrast, it was demonstrated that secondary amines such as 2-(methylamino)ethan-1-ol selectively broke the C-O bond, yielding potentially dynamic substituted ureas. Furthermore, this reaction was investigated on commercial polyurethane foams, capable of depolymerising thermoset materials in short periods of time allowing for the recovery of the polyol.

Chapter 3 explores the depolymerisation of BPA-PC combining the use of imidazole as catalyst and 1-methylimidazole as solvent. Imidazole is a catalyst capable of depolymerising polycarbonate at exceptionally low temperatures, *i.e.* 50 °C, in short reaction times. The low reaction temperature along with the selectivity of imidazole allowed for the formation of six-membered cyclic carbonates, including TMC. It was also demonstrated by means of ¹H NMR spectroscopy that the catalytic mechanism of imidazole was mediated by the formation of covalent intermediates. Additionally, the method was adapted to the synthesis of other cyclic molecules while using a range of nucleophiles (diols, thiols and amines) and it was tested on contaminated real samples.

In **Chapter 4** the depolymerisation of PET was investigated. Initially 1-methylimidazole was used as solvent and TBD as catalyst due to its good performance in model reactions with DMT. Despite of being able to carry out the depolymerisation at low temperatures (100 °C) compared to the reported literature, it was discovered that during the depolymerisation reaction the TBD was protonated throughout the reaction, thus being inactivated by the formation of a salt. The addition of a strong

sterically hindered base such as tBuOK allowed to protect TBD, improving the reaction yield by avoiding the poisoning of the catalyst.

To conclude, **Chapter 5** encompasses the conclusions reached in this thesis. The achieved objectives, such as the depolymerisation of PUs, BPA-PC, and PET through organocatalysis, are highlighted, with a focus on the selectivity and efficiency of the chemical reactions. Furthermore, future studies that could be conducted based on the results obtained are explained, with the aim of facilitating the industrial application of chemical recycling. Finally, a perspective on the future of chemical recycling is provided, which, despite still facing significant challenges, holds great potential.

Resumen

Desde hace aproximadamente 100 años, los plásticos se han convertido en uno de los materiales más usados para la producción de productos de uso cotidiano tanto de bajo como de alto valor añadido. Esto se debe en gran parte a las diversas propiedades que se pueden obtener a partir de los diferentes polímeros y a su fácil procesado en objetos en comparación con otros materiales como el vidrio o los metales. Como resultado, la producción mundial de plástico ha aumentado de forma exponencial en las últimas décadas llegando a los 390 millones de toneladas en 2021 y se espera que esta tendencia se mantenga hasta, al menos, 2060. Como consecuencia de su alta producción, también producen una gran cantidad de desechos plásticos, los cuales, si no son correctamente desechados, contaminan el medioambiente y tardan décadas en ser degradados. La contaminación producida por los plásticos es un problema a nivel mundial que necesita nuevos métodos para recolectar, separar, y reciclar este tipo de materiales. En la actualidad este problema está cobrando una gran importancia debido no solo a la contaminación que produce sino también por sus potenciales efectos en la salud humana que pudieran tener la ingesta de pequeñas partículas de plástico conocidas como microplásticos.

El reciclaje químico permite obtener moléculas en una pureza suficiente para ser polimerizadas otra vez en un material con propiedades iguales al virgen. Idealmente, se podrían realizar infinitos reciclados. En cambio, las metodologías de reciclado tradicionales no son capaces de aplicar un enfoque de economía circular. Por una parte, el reciclaje mecánico solo se puede aplicar a un material en un número limitado de ciclos antes de que las propiedades del material se deterioren (Downcycling). Por otra parte, el reciclado por pirólisis permite recuperar energía al convertir plástico en combustible, pero su combustión implica problemas medioambientales al liberar gases de efecto invernadero. Sin embargo, a pesar de su prometedor potencial, el reciclaje químico aun presenta importantes retos que impiden su implementación a escala industrial. Entre ellos destacan, el uso de condiciones de reacción severas, por ejemplo, altas temperaturas que impiden desarrollar reacciones energéticamente eficientes y económicamente viables. Además, muchos de los ejemplos reportados en la literatura implican el uso de catalizadores metálicos tóxicos que son difíciles de separar de los productos y podrían acumularse en los materiales durante sucesivos reciclados. A diferencia de estos, los organocatalizadores son una alternativa muy prometedora y menos tóxica. A diferencia de las reacciones orgánicas convencionales con moléculas pequeñas, su aplicación en el ámbito de la despolimerización todavía debe estudiarse más a fondo para entender y optimizar las reacciones químicas (mecanismo catalítico, efecto de los disolventes...). Además, los organocatalizadores

típicamente carecen de una alta resistencia térmica y por lo tanto el desarrollo de procesos a baja temperatura podría permitir reutilizarlos múltiples veces.

Para poner el tema en contexto, el **Capítulo 1** presenta los avances que se han realizado en el reciclaje químico, destacando la literatura reciente y los desafíos que deben afrontarse para lograr reacciones de despolimerización eficientes. En primer lugar, se explican la producción y las perspectivas de reciclaje del plástico, mostrando la necesidad de encontrar vías de reciclaje alternativas. Se explica el reciclaje químico en términos de ventajas y desventajas en comparación con los procedimientos de reciclaje convencionales. Además, dado que esta tesis se centra en el uso de organocatalizadores para las reacciones de despolimerización, se resume la literatura existente y se explican los desafíos restantes en el área en cuanto a eficiencia y escalado.

En el **Capítulo 2** se investigó la despolimerización de poliuretanos mediante aminólisis. Los primeros resultados obtenidos con hexametilendiamina como nucleófilo y disolvente revelaron que era necesaria una temperatura de entre 130-190 °C para conseguir porcentajes razonables de despolimerización. Por su capacidad para soportar estas temperaturas y por su superior actividad catalítica se consideró que la sal protica compuesta por la base 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) y el ácido metanosulfónico (MSA), TBD:MSA era el catalizador más adecuado. Sin embargo, se observó que las aminas primarias rompían los enlaces C-O y C-N del grupo uretano indistintamente liberando el 1,8-octanodiol junto a una urea como sub-productos. En cambio, se demostró que las aminas secundarias como la 2-(metilamino)etan-1-ol rompían el enlace C-O de forma selectiva dando lugar a ureas sustituidas potencialmente dinámicas. Además, esta reacción se probó con espumas de poliuretano de formulaciones comerciales siendo capaces de despolimerizar, los materiales termoestables en cortos periodos de tiempo y recuperar el polioliol del que están compuestos con propiedades idénticas a las del reactivo de partida permitiendo su reciclaje.

El **Capítulo 3** explora la despolimerización de policarbonato de bisfenol A (BPA-PC) usando una combinación de imidazol como catalizador y 1-metilimidazol como disolvente. El imidazol es un catalizador capaz de despolimerizar el policarbonato a temperaturas excepcionalmente bajas, hasta 50 °C en cortos tiempos de reacción. Las bajas temperaturas de reacción junto a la selectividad del imidazol permitieron obtener carbonatos cíclicos de 6 miembros incluido el trimetilen carbonato (TMC). Además, se demostró mediante $^1\text{H-RMN}$ que el mecanismo catalítico del imidazol era covalente. Finalmente, se aplicó el método desarrollado a muestras comerciales con impurezas demostrando la versatilidad de nuestra reacción.

En el **Capítulo 4** se investigó la despolimerización del tereftalato de polietileno (PET). Inicialmente se usó 1-metilimidazol como disolvente y TBD como catalizador debido a su buen rendimiento en reacciones modelo con dimetil tereftalato (DMT). A pesar de poder realizar la despolimerización a temperaturas relativamente bajas (100 °C) se descubrió que en la reacción de despolimerización el TBD se iba protonando a lo largo de la reacción inactivándose así a bajas temperaturas debido a la formación de la sal TBD:TPA. La adición de una base fuerte estéricamente impedida como el tert-butoxido de potasio permitía proteger al TBD de ser protonado mejorando el rendimiento de la reacción. Finalmente se probó el método con muestras que contenían impurezas para demostrar que la reacción tenía el mismo rendimiento.

Para finalizar, el **Capítulo 5** engloba las conclusiones alcanzadas en esta tesis. Se destacan los objetivos cumplidos como la despolimerización de PUs, BPA-PC y PET mediante organocatalisis centrándose en la selectividad y eficiencia de las reacciones. Además, se explican futuros estudios que se podrían realizar basándose en los resultados obtenidos con la finalidad de facilitar la aplicación industrial del reciclaje químico. Por último, se ofrece una perspectiva del futuro del reciclaje químico, el cual, a pesar de tener aun grandes retos, presenta un gran potencial.

List of abbreviations

ATR	Attenuated total reflectance
BA	Benzoic acid
BAETA	N ¹ ,N ⁴ -bis(2-aminoethyl)terephthalamide
BHET	Bis(hydroxyethyl)terephthalate
BHEU	1,3-Bis(2-hydroxyethyl)urea
BPA	Bisphenol A
BPA-PC	Bisphenol A-based polycarbonate
CHCl ₃	Chloroform
DABCO	1,4-Diazabicyclo[2.2.2]octane
DAT	2,4-Diaminotoluene
DBN	1,5-Diazabicyclo [4.3.0]non-5-ene
DBU	1,8-Diazabicyclo(5.4.0)undec-7-ene
DFT	Density functional theory
DCM	Dichloromethane
DMAP	4-Dimethylaminopyridine
DMC	Dimethyl carbonate
DMSO	Dimethyl sulfoxide
DMT	Dimethyl terephthalate
DSC	Differential scanning calorimetry
EG	Ethylene glycol
FTIR	Fourier-transform infrared spectroscopy
GPC	Gel permeation chromatography
HSP	Hansen Solubility Parameters
IPDA	Isophorone diamine
IPDI	Isophorone diisocyanate
IPDI-PU	PU synthesised with Isophorone diisocyanate and 1,8-octanediol
K ₂ CO ₃	Potassium carbonate
MALDI-TOF	Matrix-assisted laser desorption/ionisation time-of-flight
Me-TBD	7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene
MSA	Methanesulfonic acid
NIPU	Non-isocyanate polyurethane
NMR	Nuclear magnetic resonance
PA	Polyamide
PE	Polyethylene
PET	Poly(ethylene terephthalate)
PG	Polyglycolide
PHB	Poly(3-hydroxybutyrate)

PLA	Poly(lactic acid)
PTMC	Poly(trimethylene carbonate)
p-TSA	p-Toluenesulfonic acid
PP	Polypropylene
PU	Polyurethane
RED	Relative Energy Difference
ROP	Ring opening Polymerisation
rPET	recycled Poly(ethylene terephthalate)
TBD	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
tBuOH	Tert-butanol
tBuOK	Potassium tert-butoxide
TDI	Toluene diisocyanate
TDI-PU	PU synthesised with Toluene diisocyanate and 1,8-octanediol
TEA	Triethylamine
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TPA	Terephthalic acid
TMC	Trimethylene carbonate
TMG	1,1,3,3-Tetramethylguanidine

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CHAPTER 1

Introduction

1.1 Plastic production and environmental concerns

1.1.1 Overview of the situation

In the last decades the production of plastic has been constantly increasing due to their adequate properties for a wide range of applications, from short life items to advanced engineering materials. Therefore, enormous quantities of plastic waste which requires adequate collection, sorting and treatment are generated daily. The worldwide production of plastics has been increasing over the past decades for reaching 390 million tons in 2021.¹ (Figure 1.1)

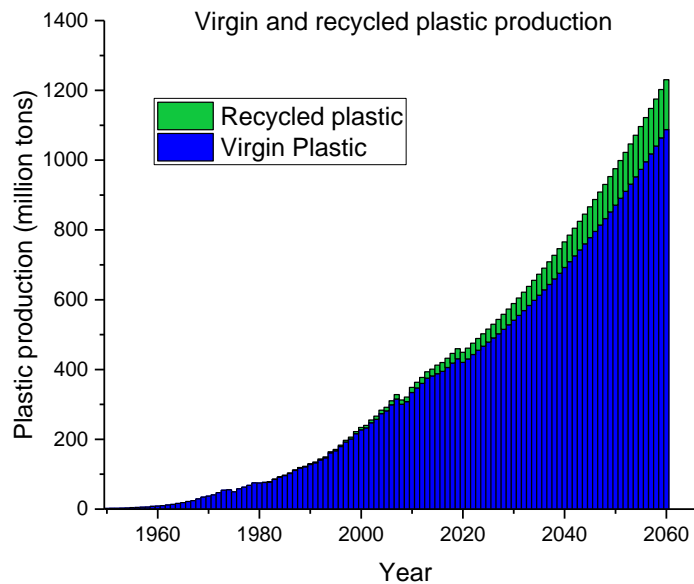


Figure 1.1. Global plastic production since 1950 and predictions for the next decades up to 2060.

From one side, this tendency is going to continue over the following decades. According to the predictions of the OECD, considering the upcoming economic and population growing, the plastic production is expected to almost triple by 2060 with more than 1000 million tons of plastics manufactured. Although efforts have been made recently on research and development, the recycling of polymeric-based materials into new objects remains an important challenge because of the mismanagement of the huge quantities disposed.^{2,3} Moreover, despite of the recent regulations implemented by governments to reduce the plastic contamination, it is projected that by 2060 not only more plastic is going to be produced but also leakage is going to increase with more than 11

million tons of plastic entering the oceans annually. From another side, projections estimate an increase of the recycled plastic of barely 20% by 2060 while 50% should remain landfilled, a similar value to the one reported in 2019.⁴ (Figure 1.2) For all these reasons, the need for developing strategies to counter the current and future plastic contamination is urgent and the implementation at large scale of technologies capable of process and recycle large quantities of plastics should be a priority for the plastic industry.^{4,5}

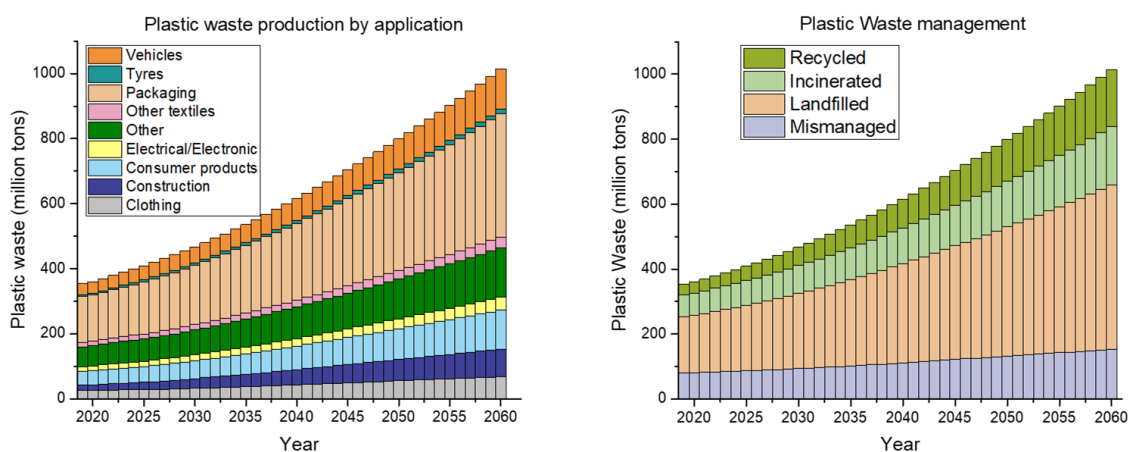


Figure 1.2. Prediction on the plastic waste production from 2020 to 2060, sorted by **A.** application and **B.** disposal management strategy.⁴

Currently, the industrial alternatives to landfilling plastics are almost exclusively energy recovery, which consists in burning plastic waste to release heat which is converted into electrical energy, or mechanical recycling. At the European level, numbers for 2021 reflect this repartition with 23% of recovered plastics sent to landfill, 42% burned for energy recovery and 35% recycled from which more than 99% is mechanically recycled.⁶

1.2 Plastic waste treatment routes

1.2.1 Mechanical recycling

Mechanical recycling implies the trituration and melting of the material for its reshape into new items.⁷ While this approach is straightforward to implement industrially, and economically profitable, the obtained material is of inferior quality because of the scission and degradation of the polymer chains occurring during the process. This negative aspect, commonly called *downcycling*, remains the

principal issue of mechanical recycling which limits the number of possible recycling loops for a given product.⁸ (Figure 1.3)

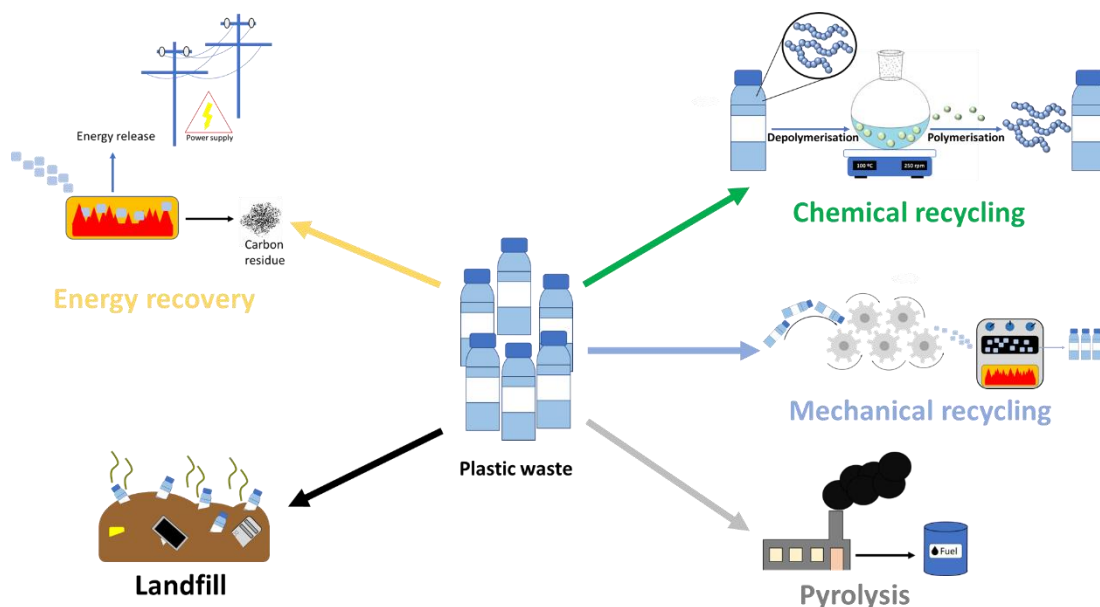


Figure 1.3. Currently applied plastic management procedures.

1.2.2 Thermochemical recycling

Thermochemical recycling, mainly pyrolysis and gasification consist in the obtention of combustible or fuel through the treatment of the plastic wastes at very high temperatures in an oxygen-free environment.^{9,10} Up to now, these processes have been only scarcely implemented industrially, mainly because of the low economic profitability. Additionally, the generation of global warming gases such as CO₂ as well as the release of toxic gases arise several environmental concerns. Thermochemical recycling methodologies are specifically unsuitable for oxygen- and nitrogen- containing polymers because of the generation of toxic and corrosive compounds that significantly decrease the quality of the recycled material while damaging the overall installation. For example, the pyrolysis of PET yields high contents of BA which is corrosive and decreases the obtained fuel quality and applicability.^{9,11}

1.2.3 Chemical recycling

As an alternative, chemical or molecular recycling, also called depolymerisation, is arising as a more sustainable and possibly more selective alternative. Chemical recycling consists in the cleavage of the chemical bonds main chain of the polymeric materials in order to recover well-defined small molecules or oligomers.¹² Depolymerisation allows to obtain small molecules which can be employed as

monomers for the synthesis of the starting material or another polymer with identical or superior properties compared to the virgin material, avoiding downcycling.¹³ Theoretically, infinite recycling loops can be achieved, allowing for the implementation of a fully circular approach for the production of plastic materials.^{13–15}

Depending on the reactants employed, a large portfolio of molecules with different functionalities and properties can be designed using discarded plastics as feedstock. In this case, the depolymerisation of a plastic into an innovative molecule or material can be called *upcycling* since wastes are transformed into enhanced properties products. This approach does not only offer the possibility of converting waste polymers into new materials for advanced applications but also in some cases can solve the economic viability issues related with molecular recycling.¹⁶ Upcycling is a very interesting alternative as it enables the valorisation of polymeric residues, converting contaminating wastes into attractive synthetic precursors with huge potential.^{17–19}

1.3 Organocatalysis for depolymerisation

The polymers exceptional chemical and thermal stability render these materials challenging for depolymerisation.²⁰ Their lack of reactivity calls for harsh reaction conditions to intervene in the process which makes the catalyst selection critical to for the reaction to be completed.²¹ A catalyst is a molecule which possesses the ability to increase the reaction rate through its interaction with the reactant(s) by lowering the activation energy that must be overcome to yield the desired products.²² For recycling, the increase of reaction rates and decrease of operating temperature is key for developing industrially scalable procedures.

Industrially, most employed catalyst are organometallic compounds. They usually operates at low catalytic loads, possess high thermal resistance and high catalytic activity.^{23,24} However, their metallic nature arise many concerns for chemical degradation of polymers which includes lack of selectivity, difficult purification and high prices. Catalysts such as zinc acetate or titanium butoxide have been successfully applied for the polymerisation of many materials but for depolymerisation processes they show a remarkable lack of selectivity which led to oligomers formation and side reactions, preventing from obtaining the targeted molecule(s) in good yields while complicating the purification procedure.^{25–27} Moreover, some of the metals employed as catalysts could endure shortages on a mid-long-term basis. Organocatalysts have emerged in the past decade as a possibly more sustainable to

organometallic counterparts for many applications including chemical recycling.^{28,29} Organocatalysts usually exhibit a high selectivity and lower toxicity, which renders them a preferable choice, even more for applications in which the plastic is in close contact with human or the environment (*i.e.* food packaging, cosmetics, biomedicine, furniture, coatings...).³⁰ Moreover, recent studies have shown the great efficiency of several organocatalysts for depolymerisation. They can be classified according their chemical structure being usually divided into three different groups, *i.e.* organic bases, organic acids and ionic compounds.¹²

1.3.1 Organic bases

Organic bases are molecules containing into their chemical structure atoms with lone electron pairs allowing for the activation of other molecules mainly, but not exclusively, through the protonation of the atom bearing this lone pair. For many organic bases, this atom is a nitrogen and the resulting compound's basicity depends on the molecule structure.³¹ Above the most employed organic bases, guanidines, amidines, phosphazenes, alkylamines, derivatives of imidazole or pyridine have been intensively studied for both polymerisation and depolymerisation reactions.^{28,32–34} Most commonly employed amidines include DBN and DBU which have been mainly reported for the synthesis of organic molecules and polymerisation reactions while there are few examples related with depolymerisation.^{35,36} Guanidines, which are usually slightly more basic than amidines, have also been extensively investigated.^{37–39} (Figure 1.4) The most remarkable examples of this family include TMG, 1,4,6-triazabicyclo[3.3.0]oct-4-ene (TBO) and TBD which different activities has been studied revealing that the molecular structure of guanidine's has a great impact on its catalytic properties.^{28,40}

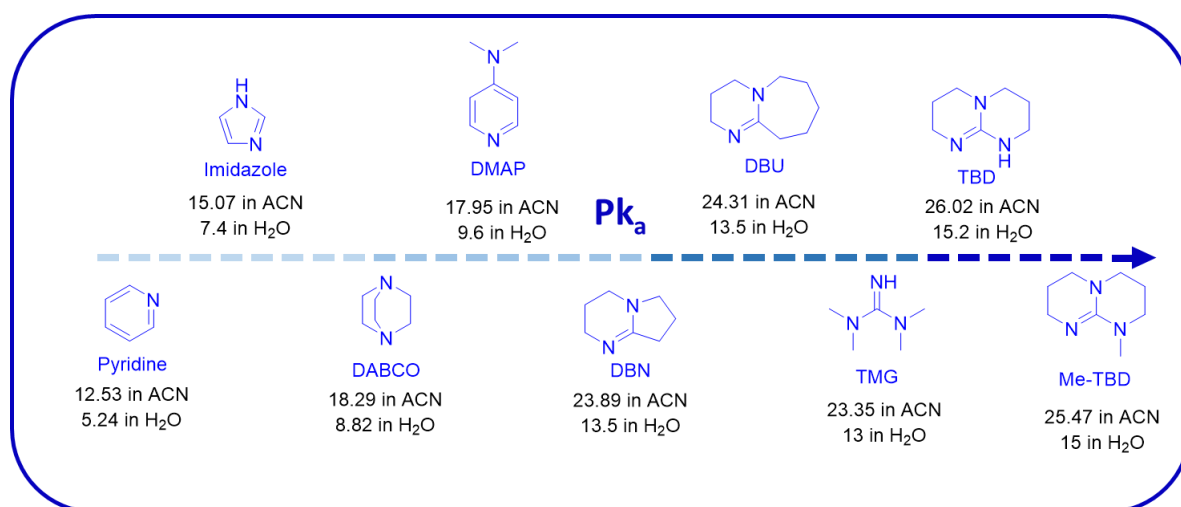
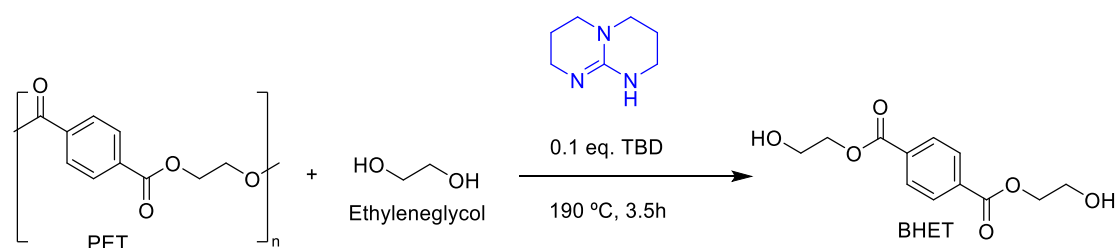


Figure 1.4. Organic bases employed as catalysts ordered from lower to higher pK_a.³¹

In 2011, Hedrick and co-workers published the first organocatalytic depolymerisation of PET using an organic base. Bottle-grade PET was degraded in 3.5 h using EG in excess (16 eq.) at 190 °C mediated by TBD.⁴¹ (**Scheme 1.1**) The reaction led to the recovery of BHET in good yields (78%) after crystallisation in water overnight at 8 °C, which is comparable with previously reported organometallic catalysts such as zinc acetate or titanium butoxide. The proposed reaction mechanism was supported by density functional theory (DFT) calculations which demonstrated that TBD interactions with EG were critical to accelerate the transesterification reaction.



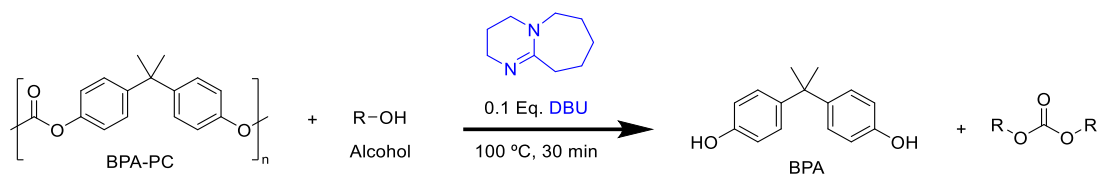
Scheme 1.1. PET glycolysis catalysed by TBD.

Consequent to this pioneer work, a wide range of organic bases were screened for the depolymerisation of PET through glycolysis and alcoholysis under analogous conditions.³⁶ The results revealed that strong bases such as TBD, DBU or DBN yield higher BHET contents than weaker bases like 4-(Dimethylamino)pyridine (DMAP), 1,4-Diazabicyclo[2.2.2]octane (DABCO) or imidazole. A general tendency was found demonstrating that higher pK_a were correlated with superior catalytic activity and the cyclic amidine DBU together with the already studied guanidine TBD were proven to be the most efficient organic bases. Overall, the elucidation of the impact of catalyst basicity on the polymer degradation guided subsequent works in the field.

On the light of these promising results, similar processes were developed for the depolymerisation of other commodity polymers. A representative example is the alcoholysis of PLA using TBD as catalyst. Reaction were performed in DCM, in the presence of 0.01 eq. of TBD and 1.5 eq. of an alcohol, different functional molecules were obtained in high yield in minutes.⁴²

In a more recent work, organic bases were employed for the alcoholysis of BPA-PC to recover BPA and the corresponding carbonate.⁴³ The most efficient depolymerisation reaction was catalysed by 0.1 eq. of DBU at moderate temperatures (100 °C). Methanolysis was completed in 30 min producing DMC and BPA. (**Scheme 1.2**) In comparison with other organic bases such as DMAP or DABCO, DBU provided faster reaction and higher selectivity. Furthermore, the catalyst was reused for further

depolymerisations by adding more polymer after reaction completion observing no lack of activity or selectivity after 5 runs.



Scheme 1.2. BPA-PC depolymerisation through alcoholysis employing DBU as catalyst to obtain BPA and linear carbonates.

1.3.2 Organic acids

Organic acids are compounds containing an acidic functional group which interacts as hydrogen donor to electrophiles for increasing partial positive charge. In general, the activity of such organocatalysts is strongly correlated with their pK_a , acids presenting superior acidity (*i.e.* lower pK_a) performing better.⁴⁴ Among the most studied organic acids, molecules containing carboxylic acids, sulfonic acids and urea or thiourea have been increasingly studied as catalysts since a couple of decades.^{45,46} For instance, acetic acid, or BA with pK_a value of 4.19 have been widely studied for reaction that require mild activation such as aminolysis of cyclic carbonates for the production of PUs.^{47,48} In contrast, more hindered reactions such as esterification require stronger activation and usually are carried out in presence of acids with lower pK_a such as MSA or *p*-TSA which values are -1.9 and -2.8 respectively.^{12,45,49,50} (Figure 1.5) Finally, ureas and thioureas, despite of their relatively low acidity in comparison with previously mentioned acids, have demonstrated an outstanding behaviour for certain reactions such as the ring opening polymerisation (ROP) of lactide in solution but have not been explored for depolymerisation reactions.^{46,51,52}

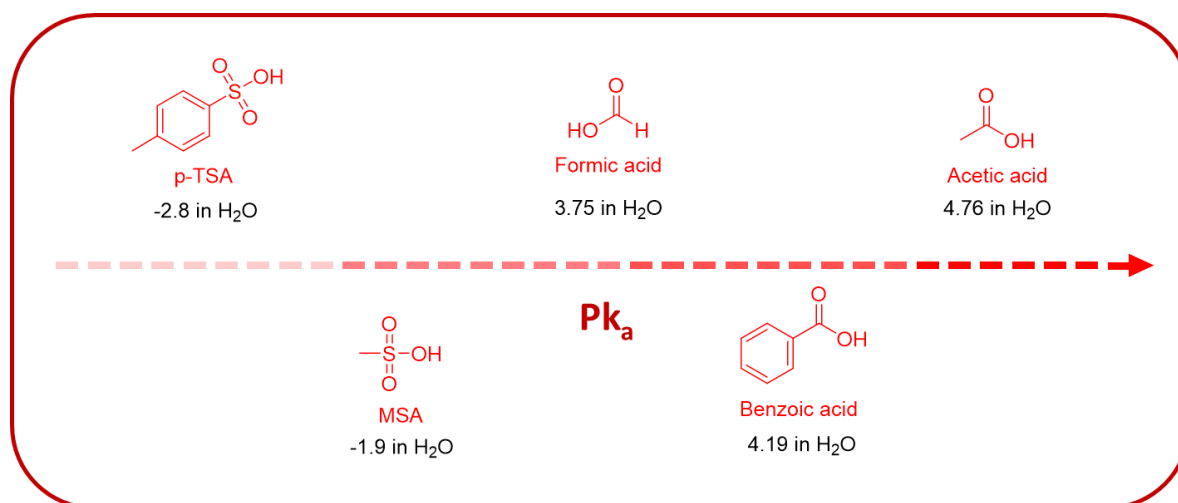
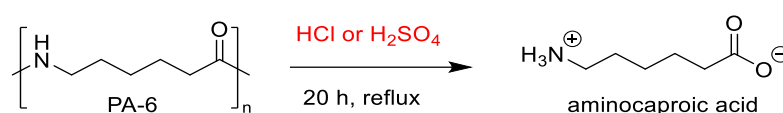


Figure 1.5. Commonly employed organic acids as catalyst ordered from lower to higher pK_a .

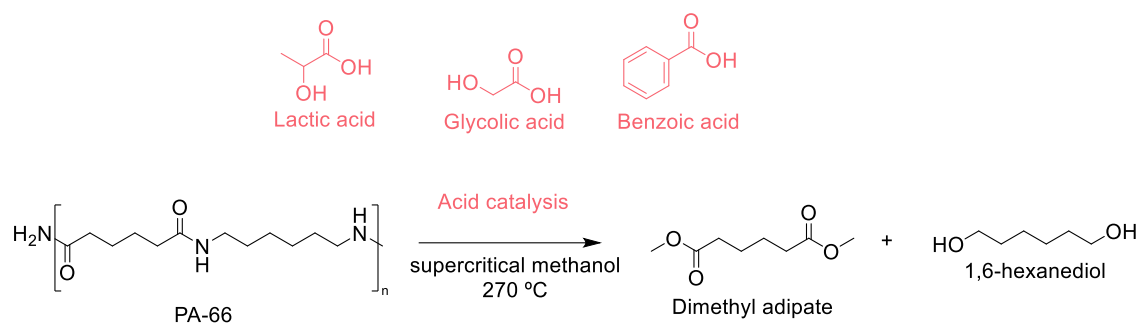
While organic bases have been widely studied for depolymerisation reactions, acids remain relatively underexplored since only a few examples can be found on literature. One of the first studies in which an acid was employed for depolymerisation was focused on the degradation of Polyamide-6 (PA-6) fibres through dissolution in concentrated formic acid.⁵³ (**Scheme 1.3**) After the reaction completion samples were taken and their molecular weight were analysed. A drastic reduction of molecular weight was observed after 20 h, from 12000 to 580 $g \cdot mol^{-1}$. It is more, while hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) were employed, up to 94% yield of aminocaproic acid was isolated in high purity. The recovery of this monomer enables the repolymerisation of aminocaproic acid into PA-6 demonstrating the potential of this methodology to recycle this material.



Scheme 1.3. Polyamide-6 depolymerisation reaction in presence of strong acids to recover aminocaproic acid.

In subsequent years, polyamide-66 (PA-66) was depolymerised by a treatment with supercritical methanol, at 270 °C after 6 h, in the presence of glycolic acid.⁵⁴ (**Scheme 1.4**) In this process, the dicarboxylic acid moiety of PA-66 endures an esterification reaction which leads to the release of dimethyl adipate and 1,6-hexanediol with rather good selectivity. As the authors demonstrated, hydroxy acids were more efficient than their ester counterparts on the formation of dimethyl adipate (75% yield). Furthermore, when ester or carbonates such as methyl formate or DMC were employed as catalyst, negligible conversion of 1,6-hexanediol was founded. Both products have a large market

on the synthesis of polyester or PUs and this synthesis from PA-66 wastes highlights the potential of depolymerisation to convert plastic residues into valuable materials.



Scheme 1.4. Depolymerisation of PA-66 by methanol under supercritical conditions using organic acids as catalyst.

More recently, PA-6 was depolymerised by a hydrothermal method in the presence of different sulfonic acids and tetra-butylammonium bromide as catalyst and phase transfer catalyst, respectively.⁵⁵ The authors reported the optimisation of this method focusing their attention on the degradation of PA-6 rather than on the formation of highly pure products. MSA was the best performing catalyst at low temperatures while the aromatic *p*-TSA and benzene sulfonic acid (BSA) performed better at high temperature, both having rate determining step at 100 °C. The thermodynamic behaviour of the reaction was studied revealing positive entropy and Gibbs free energy values demonstrating that the depolymerisation is not occurring spontaneously.

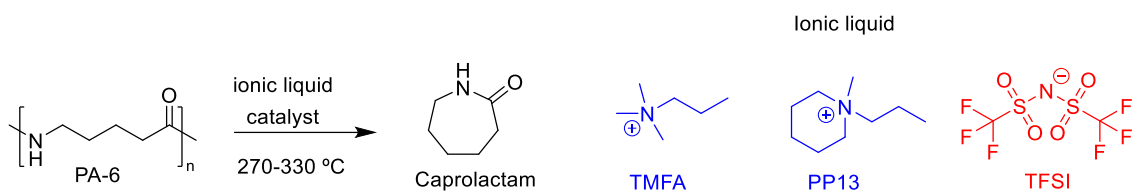
In a recent work *p*-TSA also catalysed the alcoholysis of PLA and PHB under harsh pressures. Alcohols including methanol or ethanol were loaded in 4:1 ratio (regarding the repetitive unit of the polymer) along with 1% (molar) of *p*-TSA prior to heat the reaction at 151 °C. The pressure during the reaction ranged between 7 and 15 bar. PLA was reacting faster than PHB. However, with methanol conversions superior to 90% were achieved in less than 2 h for both materials while ethanolysis was completed in 4 h providing slightly lower yields (70% and 80% for PLA and PHB, respectively). The reaction products were obtained in high purity.

1.3.3 Ionic compounds

Ionic compounds, specifically ionic liquids have also been widely explored for the chemical recycling of polymers. Ionic liquids are defined as mixtures which are only composed of ions with a melting temperature below 100 °C.⁵⁶ These compounds have been employed as special solvent, sometimes considered more sustainable, for enhancing the catalytic properties or the miscibility of a system while

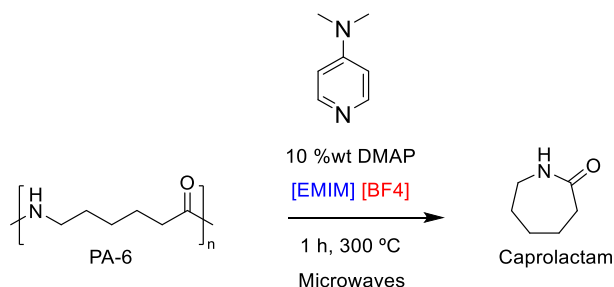
avoiding the use of volatile organic compounds.^{57,58} More recently they have been also employed as catalyst or co-catalyst for depolymerisation reactions. Because of their organic nature, organocatalysts are highly sensitive to thermal degradation which limits their utilisation in many industrial processes.²³ This drawback can be counterbalanced while ionic mixtures are employed because of their superior resistance to harsh thermal conditions. Recently, they have been proposed as alternative to common organocatalysts for reactions carried out at elevated temperatures.^{59,60} The strong ionic bonds present in these structures are responsible for the high thermal resistance as many examples report in literature.^{23,26,61} This is especially relevant for depolymerisation reactions since the chemical scission of many plastics requires harsh conditions to overcome their high chemical inertness. This high thermal stability sometimes also leads to possible recyclability of the catalyst as the unchanged ionic compounds can be recovered at the end of the process for further reactions.^{59,62} Even though the mechanism can vary depending on the chemical structure of the catalyst, it has been often hypothesised that a dual action mechanism is at state, in which the cation is interacting with the electrophile while the anion activates the nucleophile for facilitating the reaction.^{63–65} Therefore, their high thermal resistance, potential recyclability and remarkable catalytic activity make them interesting candidates for enabling and accelerating the chemical treatment of polymeric wastes.

The use of Ionic liquids as both catalyst and solvent has been first explored for the depolymerisation of PA-6. As a representative example, *N*-methyl-*N*-propylpiperidinium (PP13) and *N,N,N*-trimethyl-*N*-propyl ammonium cations in conjunction with bis(trifluoromethane sulphonyl)imide (TFSI) as counter anion were used for depolymerising PA-6 in 5 to 6 h at 300 °C.⁶⁶ (**Scheme 1.5**) ϵ -caprolactam was obtained in moderate yields, 43-55% depending on the conditions applied. However, it was demonstrated that the addition of 5% wt of DMAP as co-catalyst considerably improved the product yield, *i.e.* 86%. The operating temperature was proven to be a critical parameter, barely 7% of monomer was recovered when the reaction was carried out at 270 °C while 55% was achieved at 330 °C but only 6% with further increase to 360 °C. Authors claim that the equilibrium between PA-6 and the ϵ -caprolactam is very sensitive to temperature, below 300 °C the crude is mainly composed of PA-6 oligomers while superior temperatures reach to the formation of *N*-methyl- and *N*-propyl-lactams, probably due to the decomposition of the ionic liquid, which limits the maximum conversion into ϵ -caprolactam.



Scheme 1.5. PA-6 depolymerisation using ionic liquids to promote the cyclisation into caprolactam.

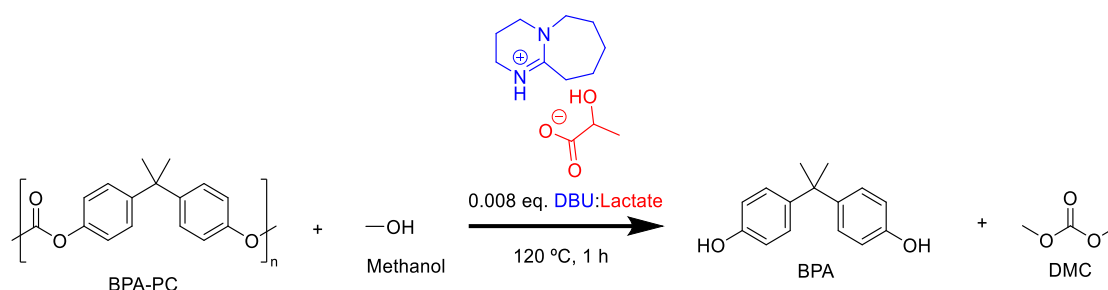
In a variation of the previous study, PA-6 was depolymerised under microwave irradiation employing the hydrophilic ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]) at 300 °C.⁶² (**Scheme 1.6**) This work assesses the effectiveness of DMAP for catalysing the depolymerisation of PA-6 since the addition of 10 wt% of the organic base increases the yield from 36 to 55%. The use of microwave irradiation allowed to decrease the reaction times to 1 h while maintaining the reaction temperature. According to the authors, the process is highly selective since no by-products were observed by ¹H NMR spectroscopy. Remarkably the ionic liquid did not suffer any degradation during the reaction at the conditions employed opening the avenue to be reused on subsequent reactions. Moreover, the recovery of ionic liquid was performed by simple liquid-liquid extractions with ethyl acetate and water. This approach highlights the capabilities of this ionic liquid to degrade polyamides at high temperatures.



Scheme 1.6. PA-6 depolymerisation into caprolactam using [EMIM][BF₄] ionic liquid and DMAP as catalyst.

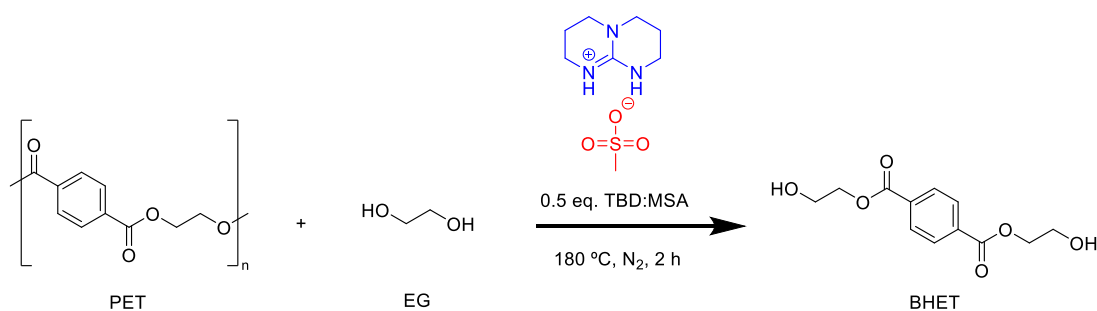
The use of ionic liquids as reaction media on polymer chemical degradations is not limited to polyamides. They have been successfully employed for the methanolysis of BPA-PC in the absence of additional solvent or catalyst.⁶⁷ (**Scheme 1.7**) Several ionic liquids formed by the reaction of a variety of amines with weak acids such as acetic, propionic and lactic acids, were screened at 120 °C. After 1 h of reaction and using 5 eq. of methanol and 0.8 mol% of catalyst, HDBU-lactate was the most promising ionic liquid considering that it led to full depolymerisation with an excellent BPA yield > 98%. To further assess the ionic liquid viability, six reaction cycles were performed employing the same

catalyst without observing any decrease in the reaction yield or selectivity. Nevertheless, a plausible interaction between lactate anion interacts and methanol through the carboxylate and hydroxyl group was studied by means of FTIR and ^1H NMR spectroscopy and their impact on the catalytic performance for BPA-PC depolymerisation was hypothesised.



Scheme 1.7. BPA-PC methanolysis catalysed by HDBU:lactate to yield DMC and BPA.

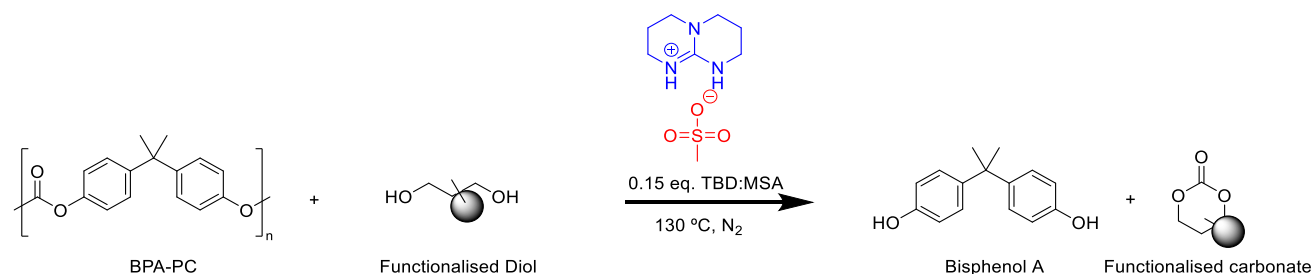
Ionic compounds based on acid-base have been also reported as great alternatives for depolymerisation. The equimolar mixture of TBD and MSA (*i.e.* TBD:MSA (1:1)) is catalysing the depolymerisation of PET at $180\text{ }^\circ\text{C}$ in 2 h in the presence of 20 eq. of EG.⁵⁹ (**Scheme 1.8**) The exceptional thermal resistance of TBD:MSA (1:1) was demonstrated by means of thermogravimetric analysis (TGA), demonstrating the stability of the compound up to $400\text{ }^\circ\text{C}$. High purity BHET was recovered by precipitation and crystallisation prior to be repolymerised into PET employing TBD:MSA as catalyst at $250\text{--}270\text{ }^\circ\text{C}$ under vacuum. This approach allows for the recycling of PET in a circular way in which TBD:MSA can be employed as an effective catalyst for both depolymerisation and polymerisation reactions in a closed loop fashion.



Scheme 1.8. PET glycolysis mediated by TBD:MSA to obtain BHET.

In an upcycling approach the synthesis of cyclic carbonates through BPA-PC depolymerisation as a source of carbonyl groups has been reported.^{68,69} The procedure involves the reaction of a wide variety of diols to depolymerise BPA-PC BPA and a wide range of 6-member cyclic carbonate containing

different functionalities. (**Scheme 1.9**) However, among the wide range of the possible carbonates, the unsubstituted TMC was not obtained. It is hypothesised that despite of the effectiveness and selectivity of TBD:MSA, TMC was too reactive under the employed conditions (130 °C and nucleophile excess).



Scheme 1.9. BPA-PC depolymerisation into 6-membered cyclic carbonates catalysed by TBD:MSA.

1.4 Towards efficient depolymerisation for commodity polymers

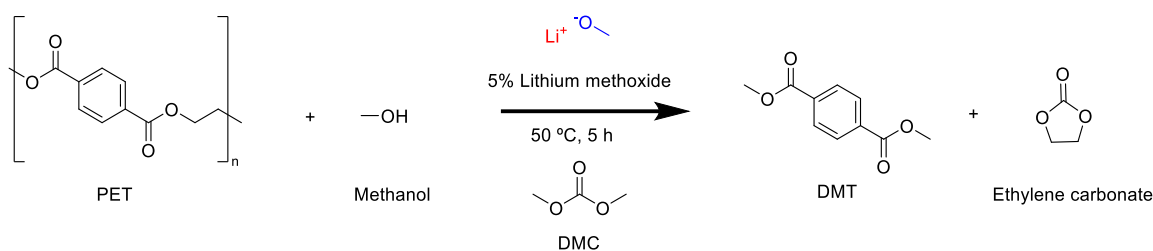
On the last decade, investigation has been very active on the chemical recycling of plastics. Pioneer articles were solely focused on studying the polymer degradation over time through the monitoring of parameters such as molecular weight. Following studies were more specific on aiming to get complete depolymerisation towards well-defined molecules which could be re-used as monomers for further polymerisations.⁷⁰ However, most of these works require harsh reaction conditions including pressure, high temperatures, strong and expensive catalysts or even supercritical conditions or microwaves. As environmental concern raises globally, the scientific community has been further involved in developing more efficient and sustainable procedures for the recycling of plastics. One of the most critical parameters is the reaction temperature which can suppose a tremendous energetic input demanding for alternatives under milder conditions.^{14,18,71}

To do so, the distinct parameters of the reaction play a key role and must be optimised. On one hand the nature of the catalyst is critical for improving efficiency and selectivity.^{12,72} On another hand, the availability of the reacting groups of the nucleophile attacking the polymer can considerably influence the performances of the reactions but also the type of products obtained. Most chemical depolymerisation occur in heterogeneous phase in which polymer pellets are degraded on the surface which leads to exaggerated reaction times. In fact, polymers are macromolecular chains of repetitive

units that form unique 3D conformations containing crystalline and amorphous domains responsible for strong physical interactions between their chains (hydrogen bonding, Van der Waals forces...). This complex physical behaviour is responsible for their chemical inertness which renders many of them highly insoluble in most common solvents.^{73,74} In fact, polymer crystallinity has been demonstrated to have a big impact on depolymerisation reaction on some polymers such as PET.⁷⁵ Currently, solvolysis employing chemicals with appropriate interaction with a given polymer is under investigation since an adequate solvent allow for the polymer to swell.^{76–78}

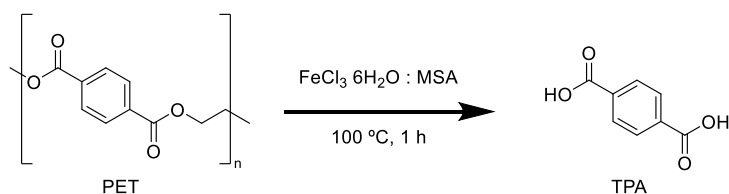
Recently the scientific community has focused its attention on selecting the solvent to achieve depolymerisation reactions under mild conditions. As a matter of proof, Cho *et al.* performed PET glycolysis into BHET employing anisole as co-solvent along with EG.⁷⁹ This reaction was catalysed by sodium or potassium acetate yielding up to 86% of BHET. Owing to the employment of anisole as co-solvent the reaction temperature could be reduced to 153 °C from the widely reported >180 °C in just 2 h. Moreover, Anisole is considered a green solvent which does not arise health concerns and its recycling capabilities after depolymerisation reactions make it suitable for scale-up. A mechanistic kinetic model was developed to describe the reaction and gain insights into the underlying mechanism. It was concluded that anisole contributes to the reaction. The results obtained with ¹H NMR spectroscopy supports that PET oligomers exhibit intermolecular interactions with anisole ether group that could enhance PET conversion into BHET. Therefore, the co-solvent was not only facilitating the dissolution of the PET chains but was also favouring the formation of BHET.

In another example, DMC is employed as solvent to perform PET methanolysis to synthesise DMT under mild conditions.⁸⁰ The reaction was carried out at 50 °C for 5 h using lithium methoxide as catalyst (5 mol %). (**Scheme 1.10**) The huge decrease on reaction temperature comparing with previous examples reported on literature was occurring mainly through two effects. On one hand, DMC partially solubilises PET, to greater extent than alcohols such as methanol or EG. On the other hand, DMC reactions with the released EG to form ethylene carbonate displace the equilibria towards the formation of DMT. This approach enables to drastically reduce the reaction temperatures opening the avenue for more energetically efficient depolymerisation procedures while demonstrating an innovative approach to shift the equilibria towards the formation of DMT.



Scheme 1.10. PET methanolysis using DMC as solvent to quench the released EG and promote the equilibria towards the formation of DMT.

In a novel approach Rollo *et al.* studied the depolymerisation of bottle grade PET under mild conditions by using Lewis/Brønsted acidic deep eutectic solvent.⁸¹ (**Scheme 1.11**) The use of deep eutectic solvents which properties can be easily tuned open new ways to improve the performance of depolymerisation systems. In this work, the eutectic solvent was synthesised by mixing iron trichloride hexahydrate with organic acids such as MSA, *p*-TSA acid monohydrate or acetic acid among others. The best results were obtained for the equimolar mixture of iron trichloride and MSA which were able to hydrolyse PET into TPA, up to 98% yield at 100 °C in just 1 h at atmospheric pressure. The analysis of the recovered product by ¹H NMR spectroscopy and FTIR showed that the produced TPA had a high purity and was suitable to be repolymerised.



Scheme 1.11. PET hydrolysis catalysed by FeCl₃:6H₂O:MSA deep eutectic solvent.

Finally, to further optimize the solvent impact to achieve efficient depolymerisation procedures not only experimental works are being carried out but also theoretical ones based on computational calculations. For example, in order to find suitable solvent for PET depolymerisation at low temperatures a MATLAB software named HSP-TPT was developed to evaluate the PET dissolving capabilities of commonly employed molecules in function of temperature.⁸² The solubility parameters of 13 solvents were evaluated at different temperatures. The results were plotted in a polymer-solvent solubility diagram that provided valuable information about relative energy difference (RED) in function of temperature. Furthermore, the developed software can predict the optimum temperature range for dissolving PET and the theoretical results were validated with the reported experiments on

literature. These simulations are emerging as very powerful tools that provide interesting information about the solvation mechanism and have the potential to lead to the discovery of more compatible solvent-polymer system that can ultimately lead to more efficient depolymerisation reactions in the close future.

1.5 Approach and objectives of the thesis

The main purpose of this thesis is the designing of novel efficient depolymerisation procedures with the objective of obtaining both the initial monomers in a circular approach and innovative molecules which could be used as synthons for further polymerisations with added value properties.

In **Chapter 2**, the depolymerisation of a wide range of PUs by organocatalysis mediated aminolysis will be studied with the aim of selectively dissociate the carbamate bond to synthesise substituted ureas which can potentially use for the creation of dynamic materials. Different organocatalysts will be screened including superbases and acid-base mixtures. The importance of the use of secondary amines for the selective cleavage of carbamates is going to be demonstrated. The impact of the aromatic-aliphatic nature is studied and the crosslinked PU foams degradation into well-defined ureas and a polyol which had identical properties in comparison with the virgin one.

BPA-PC is a common plastic waste which mechanical recycling arise several concerns due to the loss of its characteristic optical properties such as transparency. In **Chapter 3**, a thermally efficient procedure for the chemical upcycling of BPA-PC into 6-membered cyclic carbonates and especially TMC will be developed. This methodology can perform BPA-PC degradation in short times at just 50 °C. Its high efficiency relies on a new covalent catalysis mechanism based on imidazole and the effect of solvent to penetrate the material avoiding limiting the reaction to the pellets surface. Finally, this method will be tested on samples collected form plastic waste containing impurities.

PET, the most investigated commodity polymer for chemical depolymerisation due to its high market and large plastic waste share. **Chapter 4** will be focused on the depolymerisation of this material by glycolysis. In a first part, the effect of the interaction of TBD with TPA will be investigated in a basic solvent showing that the formation of TPA during the reaction will quench TBD forming a less active complex that will hinder the reaction continuation. After the assessing of this effect the impact of the protection of TBD on its free base form by a hindered alkoxide on the reaction evolution will be

studied. As a consequence of the results, a new methodology involving low temperatures (100 °C) was developed and tested in many samples collected from plastic waste.

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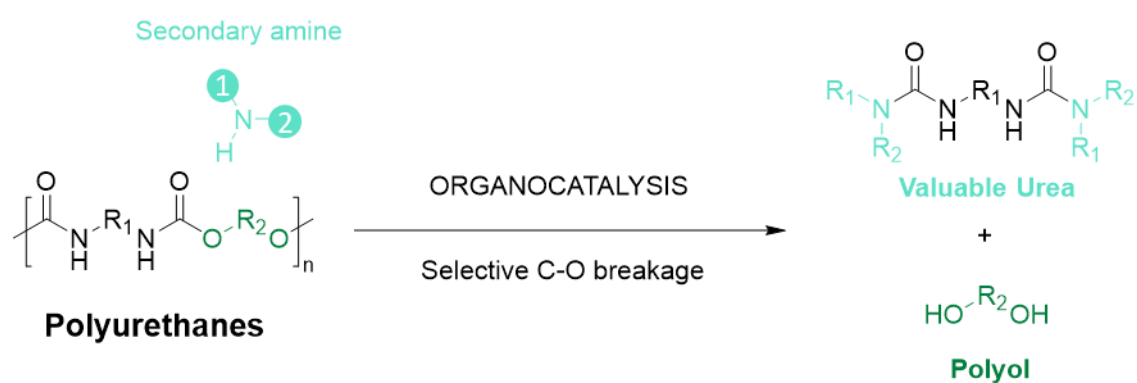
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CHAPTER 2

Selective Polyurethane depolymerisation by aminolysis



2.1 Introduction

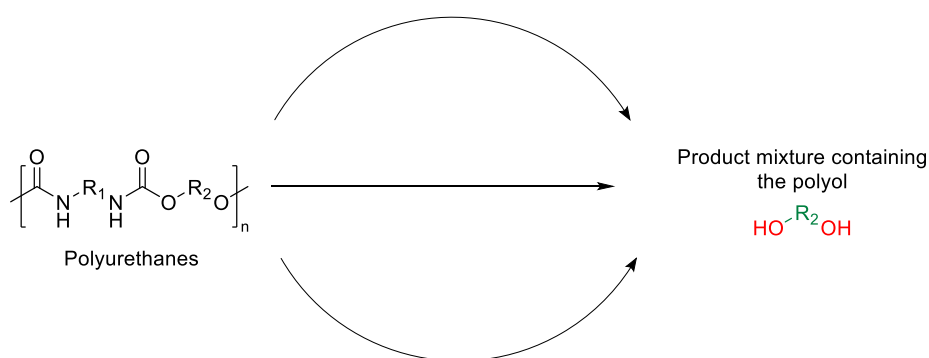
Polyurethanes (PUs) constitute one of the most important families of polymers, with more than 20 million tons produced in 2019, making them the 6th most produced polymer globally.¹ This versatile family of materials can be processed as rigid foams, flexible foams, or elastomers, which are important materials for very diverse applications.² Flexible PUs are the materials of choice for insulation panels, tires and synthetic fibres, while rigid foams are converted into electronic components for consumer goods and the automotive and construction industries. Elastomeric PUs are preferred for coatings, adhesives, surfactants and elastomers (the so-called CASE applications). Depending on the final material targeted, a PU can be thermoset or thermoplastic, but all types are generally prepared from an isocyanate and a polyol addition reaction. Considering the enormous scale of PU production, appropriate end-of-life management of these polymers is critical from an environmental point of view. End-of-life options are also important from a financial viewpoint as the PU industry represents more than US\$ 56 B globally (in 2020) and is projected to reach US\$ 82 B by 2028.³ As a result, the improvement of recycling options for PUs is being increasingly called for by leading organisations such as the European Isocyanate and Polyol Producers Association (ISOPA), the European association of flexible polyurethane foam blocks manufacturers (EuroPUR) and the Centre for the Polyurethane Industry (CPI) are inciting to their recycling.⁴⁻⁶

The various potential combinations of polyols and isocyanates leads to a myriad of distinctive structures which are key to the use of PUs in such a large range of applications. At the same time, it complicates the recycling process which is affected by physical factors, such as the density of the material or its physical form (*e.g.* foam, powder or laminate), as well as the nature of the isocyanate (aromatic or aliphatic) and the nature of the polyol (polyester or polyether). Initial attempts at recycling PUs were based on mechanical recycling as it is the easiest and most straightforward technology to recycle plastics.^{7,8} However, as PUs are mostly produced as thermosets, they cannot be recycled using conventional mechanical methods (*e.g.* regrinding, powdering or compression moulding), which renders chemical recycling a useful alternative

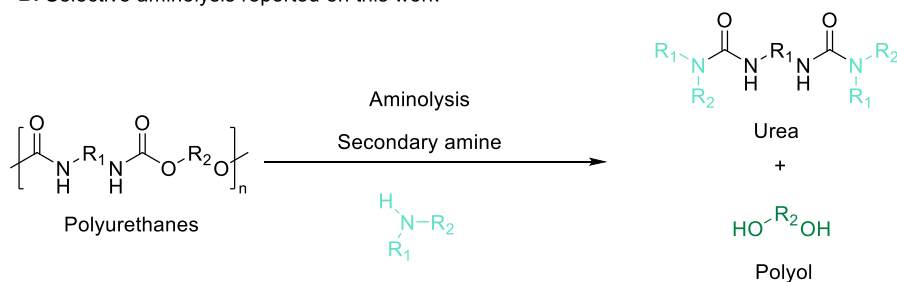
Despite the numerous examples in the literature describing chemical recycling of commodity polymers,⁹⁻¹³ the depolymerisation of PUs remains relatively unexplored.^{1,14} Only a limited number of examples are available in the literature which includes hydrolysis,¹⁵ glycolysis,^{16,17} methanolysis,^{18,19} other types of alcoholysis,²⁰ or aminolysis²¹. (**Scheme 2.1 A.**) One of the main issues with solvolysis

reactions is that harsh conditions are required for the reaction to be completed in a reasonable amount of time, including high pressures, high temperatures and/or the use of toxic catalysts. Moreover, most of these depolymerisations consist of unselective cleavages along the PU chain, and even if the depolymerisation is successful and the PU is cleaved into smaller pieces, the final product is generally a non-selective mixture from which only the polyol fragments can eventually be valorised. Although it was the first method to be explored for the depolymerisation of flexible PU foams, hydrolysis was rapidly discarded as an option because of the high pressures and temperatures required.^{22,23} The methanolysis process suffers from similar issues as the reactions are typically conducted at temperatures > 200 °C, which requires the use of supercritical methanol.^{18,19} Glycolysis has been the most studied process and various catalysts including alkaline salts^{24,25} and organometallic complexes^{26–28} have been employed. For both types of catalysis, the products obtained are rarely selective, and the amine(s) and polyol(s) formed prevents the possibility of recovering the carbamate function.

A. Unselective depolymerisation reported on previous works



B. Selective aminolysis reported on this work



Scheme 2.1 **A.** Common depolymerisation pathways resulting in a mixture of molecules containing polyol(s) and **B.** selective depolymerisation through aminolysis proposed in this study.

More recent initiatives have demonstrated alternative routes to extract value from PU wastes, such as through hydrogenolysis,^{29–31} acidolysis^{32,33} or transcarbamoylation³⁴. Hydrogenolysis is limited to the recovery of the polyol and the amine constituents of the PU (the carbonyl fragment is lost during the reaction). Acidolysis allows for the preservation of the urethane group, but the non-selectivity of the reaction leads to side reactions, resulting in a mixture of distinct molecules or oligomers. The transcarbamoylation reaction, which consists in the conversion of a carbamate in another carbamate, is limited to only a few available reagents.

The low price and high availability of amines means that aminolysis reactions are more easily compatible with industrialisation. Aminolysis can be performed with aliphatic amines, ammonia or alkanolamines (*e.g.* ethanolamine, diethyl amine, dibutylamine, etc.) at atmospheric pressure and lower temperatures than glycolysis to yield polyamines, carbamates and polyols.¹⁴ Pioneering work involving aminoalcohols (ethanolamine and diethanolamine mainly) has suggested that alcoholysis was occurring over aminolysis, the amine only working as a co-catalyst.^{35–37} Other publications have coupled alcoholysis with aminolysis for obtaining polyols of higher quality from extrusion of the recycled material, using diethanolamine as a “decomposing agent” rather than as a nucleophile.^{38,39} Only a very limited number of examples have been reported where an amine is solely used as nucleophile. For example, diethylenetriamine coupled with sodium hydroxide (NaOH) has been reported as a catalyst for depolymerising rigid PUs,⁴⁰ and butylamine without catalysts at high temperatures has been used to depolymerise elastomeric PUs.⁴¹ However, these reactions also lead to unselective rupture along the polymer backbone and also cause re-arrangements along the polymeric chain. As a result, again only, the initial polyol can be recovered in these systems.

In this chapter a depolymerisation study was led on both aliphatic and aromatic PUs prepared from two of the most widely industrially used isocyanates –IPDI and TDI – and 1,8-octanediol for obtaining representative PUs, *i.e.* IPDI-PU and TDI-PU. Both materials were depolymerised by aminolysis in the presence of different types of organocatalyst to assess the polyurethane dissociation process and the recovery of the products. The method developed allows to chemically deconstruct PUs in a controlled manner by the selective cleavage of the C-O bond of the urethane function. (**Scheme 2.1 B.**) This route not only leads to the recovery of the initial polyol but also generates a di-urea, which permits the preservation of the valuable carbonyl, and allows for subsequent polymerisation into PU-like

materials. Finally, commercial PU foams were degraded by the optimised methodology demonstrating that this chemical recycling route able not only to recycle very distinct types of PUs.

2.2 Aminolysis of model aliphatic PU with hexamethylene diamine

As a model for screening the reaction's parameters, the depolymerisation of IPDI-PU was investigated with hexamethylene diamine as nucleophile. The aliphatic IPDI-PU was selected because of the lower reactivity (and thus, higher reaction times) compared to the aromatic TDI-PU, which allowed us to follow the reaction with greater ease.⁴² Hexamethylene diamine was chosen because of the easily traceable protons in the ¹H NMR spectra. All experiments were conducted in bulk in a 100 mL flask equipped with a magnetic stirrer under nitrogen atmosphere. A large excess of nucleophile, *i.e.* 10 eq., was used corresponding to the minimum quantity required to immerse the PU. The crude product was analysed by ¹H NMR spectroscopy, in DMSO-*d*₆ for 24 h, to evaluate the depolymerisation rate (*i.e.* the formation of 1,8-octanediol) over time.

Different parameters influencing the depolymerisation reaction such as the temperature and the catalyst content were investigated with TBD:MSA as catalyst. TBD:MSA has already been proven to accelerate both polymerisation and depolymerisation reactions performed at elevated temperatures (with proven thermal stability up to 400 °C), which renders the organic acid:base mixture a suitable candidate for the present study.^{9,43,44} The results shown in **Figure 2.1 A.** suggest that the reaction is highly temperature-dependent. At 130 °C the yield did not exceed 40% after 24 h, while complete depolymerisation was afforded at the same time at 160 °C and in 2 h at 190 °C. (**Figure 2.1 B.**) However, at this temperature, increased reaction times led to the decrease of the characteristic signal's intensity of 1,8-octanediol in the ¹H NMR spectra ($\delta = 3.37$ ppm), which suggests the presence of side reactions. Concomitantly, the intensity of the signal corresponding to the methyl group of IPDA also decreased ($\delta = 2.15$ ppm), which corroborates that undesirable reactions occur between the formed diol and the diamine.

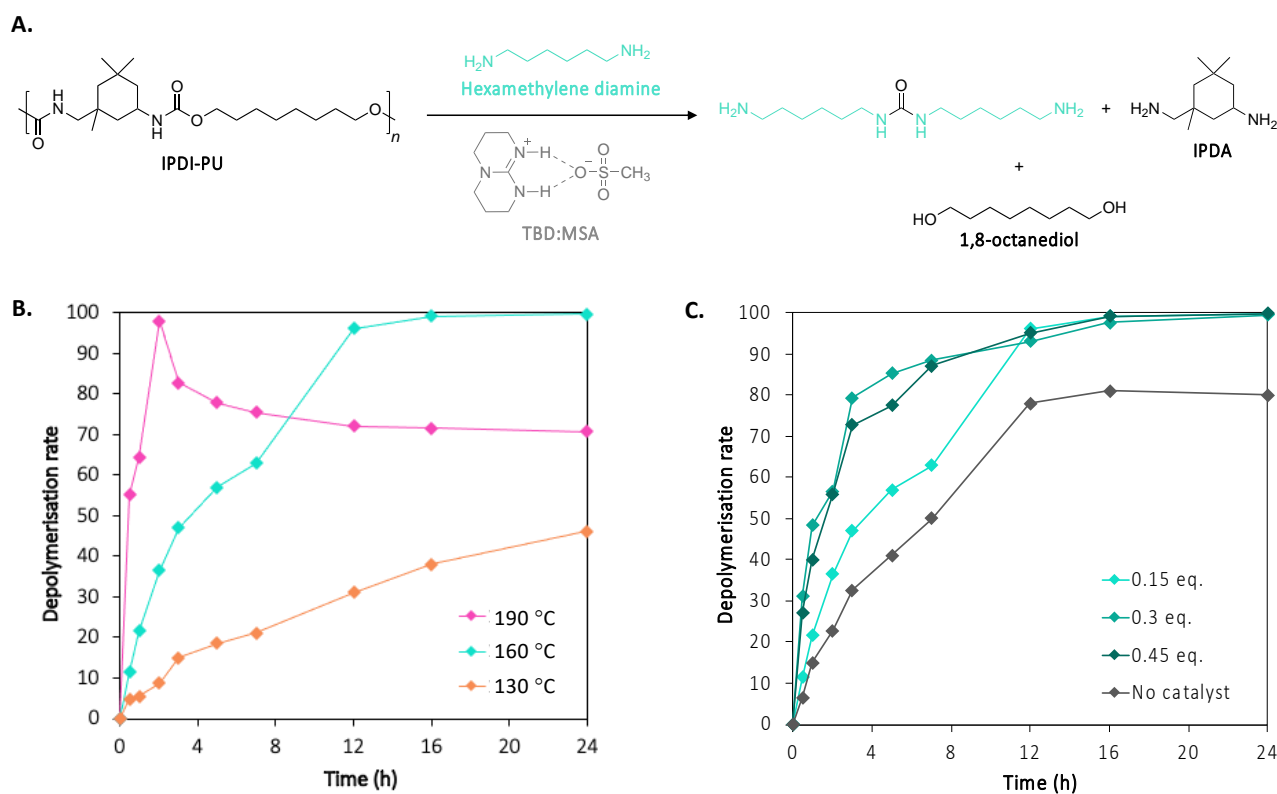


Figure 2.1 A. Reaction scheme for the depolymerisation of IPDI-PU with hexamethylene diamine. Kinetic plots of the reaction **B.** at 130, 160 and 190 °C with 0.15 eq. of TBD:MSA and **C.** at 160 °C with 0, 0.15 eq., 0.30 eq., and 0.45 eq. of TBD:MSA. The kinetic was followed by ^1H NMR spectroscopy in DMSO-d_6 using the characteristic signal of 1,8-octanediol ($\delta = 3.37$ ppm). Reaction conditions: IPDI-PU (1 eq.), hexamethylene diamine (10 eq.), N_2 .

Different loadings of TBD:MSA were also investigated to evaluate the catalytic activity of the organic mixture. (**Figure 2.1 C.**) The uncatalysed depolymerisation reached a maximum extent of depolymerisation of 80% after 12 h, reaching a plateau at 24 h. When 0.3 or 0.45 eq. of catalyst were used, the reactions rapidly reached around 85% of conversion (7 h), while the reaction performed with 0.15 eq. of catalyst exhibited lower rates of depolymerisation, with only 63% conversion at the same reaction time. Ultimately, after 16 h of reaction the three reactions reached completion without further undesirable side-reactions. Therefore, moderate quantities of catalyst are sufficient to efficiently mediate IPDI-PU depolymerisations.

The results above show that the complete aminolysis of IPDI-PU with hexamethylene diamine can be achieved in less than 24 h assuming use of the appropriate temperature and catalyst. However, using hexamethylene diamine, the depolymerisation of IPDI-PU led to three major identified products in the ^1H NMR spectra, 1,8-octanediol, IPDA and a linear urea formed through the double nucleophilic attack of the amine on the urethane, the 1,3-bis(6-aminohexyl)urea. (**Figure 2.1 A.**) The presence of these

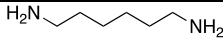
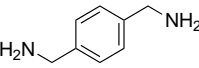
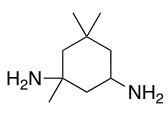
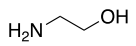
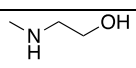
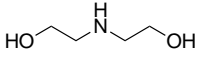
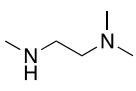

products suggests that the nucleophilic attack of the urethane carbonyl group breaks both C-N and C-O bonds, demonstrating the non-selectivity of the depolymerisation performed with hexamethylene diamine.

2.3 Screening of amines for the depolymerisation of PUs

Different amines, *i.e.* primary and secondary, were screened for the depolymerisation of IPDI-PU. The main objective was to try to avoid the nucleophilic attack on the C-N bond of the urethane and to promote the selective depolymerisation through C-O bond breaking. This would lead to a di-urea or di-urethane segment which can be homopolymerised to synthesise a new PU with no need for isocyanates. The screening of the nucleophiles was primarily performed on the model aliphatic PU (IPDI-PU) by comparing the depolymerisation using different nucleophiles. The reactions were performed at 160 °C with 0.15 eq. of TBD:MSA and 10 eq. of the nucleophile for 7 h under a nitrogen atmosphere (**Table 2.1**). The depolymerisation reactions were monitored by ¹H NMR spectroscopy in DMSO-*d*₆, for 24 h.

In addition to the use of hexamethylene diamine as described previously, an aromatic, a cyclic aliphatic diamine and an aminoalcohol were investigated as nucleophiles for the depolymerisation of IPDI-PU. All reactions demonstrated similar efficiency with conversion exceeding 95% in less than 7 h. However, similar to the reaction performed with hexamethylene diamine, IPDA and the corresponding linear urea were obtained together with 1,8-octanediol, demonstrating an unselective urethane bond cleavage. (**Table 2.1**– entries 2 to 5).

Table 2.1. Depolymerisation of IPDI-PU catalysed by TBD:MSA with different amines. *Reaction conditions: IPDI-PU (1 eq.), amine (10 eq.), catalyst (0.15 eq.), at 160 °C, 7 h, N₂.*

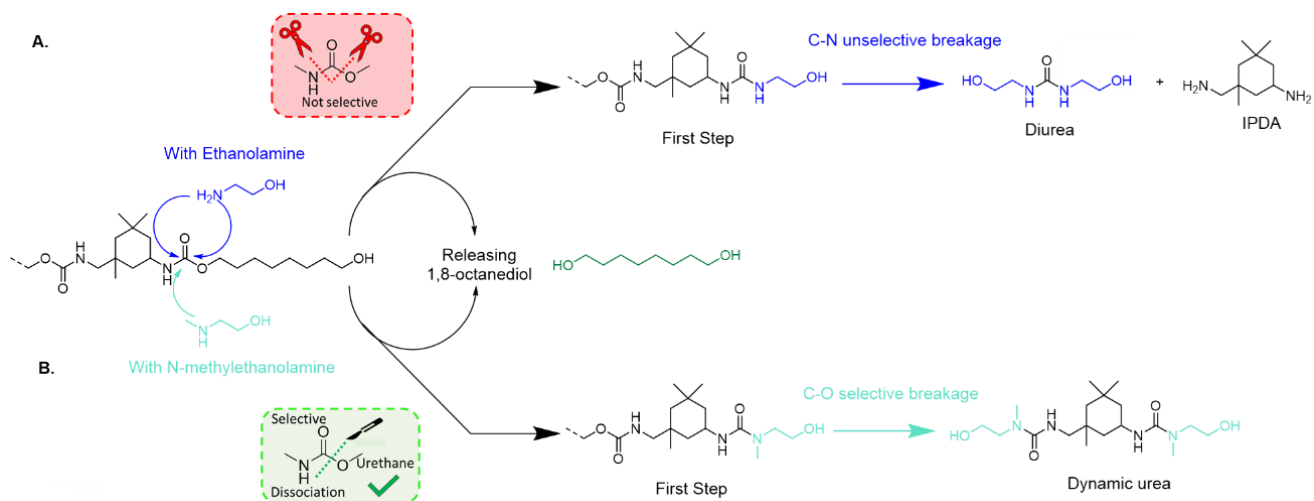
	Amine	Dep. Rate (%) ^a	IPDA (%) ^b	Di-urea (%) ^c
1	 Hexamethylene diamine	63	61	-
2	 1,4-phenylenedimethanamine	96	54 ^b	-
3	 IPDA	>98	95	-
4	 Ethanolamine	95	92	-
5	 2-(methylamino)ethan-1-ol	>98	-	87
6	 Diethanolamine	>98	-	N.A ^e
7	 <i>N,N,N</i> -trimethylethane-1,2-diamine	75	-	63
8	 Morpholine	>98	-	86

Different ratios were determined by ¹H NMR spectroscopy in DMSO-d₆ from the crude product using the characteristic signals of ^a1,8-octanediol ($\delta = 3.37$ ppm), ^bIPDA ($\delta = 2.15$ ppm) and ^cthe different characteristic signals for the di-ureas. ^dThe poor solubility of the crude product in the deuterated solvent for this reaction could have led to an underestimation of this value. ^eThe eventual cross-linking of the obtained urea has led to difficulties while determining the content of product.

After unsuccessful attempts to achieve the desired di-urea from the depolymerisation with primary amines, secondary amines were investigated as nucleophile. It was hypothesised that the higher steric hindrance of the secondary amines compared to primary amines could play a key role on the selective deconstruction of the carbamate group, allowing for the breaking of the C-O bond while leaving the C-N bond untouched. The aminolysis of IPDI-PU with different secondary amines including 2-(methylamino)ethan-1-ol, diethanolamine, *N,N,N*-trimethylethane-1,2-diamine and morpholine was investigated. (Table 2.1– entries 5 to 8) The depolymerisation was efficient when employing the aminoalcohol with 87% conversion obtained in 7 h. No characteristic signals of IPDA were observed in

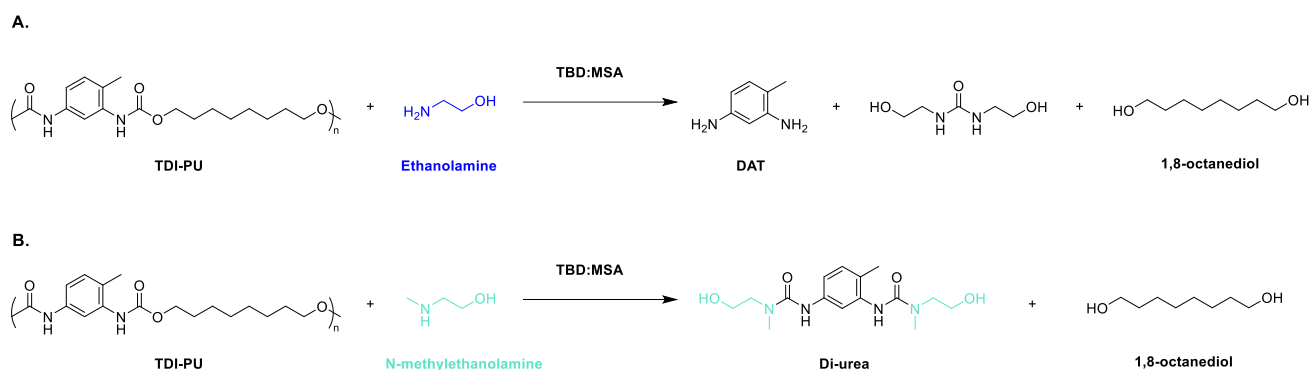
the $^1\text{H-NMR}$ spectra along with the expected increase of the singlet at $\delta = 2.80$ ppm corresponding to the $-\text{CH}_3$ group attached to the tertiary nitrogen of the substituted urea. To further confirm the absence of the urethane group and the presence of urea group the depolymerisation was followed by FTIR spectroscopy. As expected, while the urethane band centred at 1710 cm^{-1} decreased, a new band attributed to urea group appeared at 1630 cm^{-1} . Finally, the crude product was analysed by HPLC-MS. The obtained chromatogram corroborates the presence of the di-urea obtained from the selective breakage of the C-O bond, *e.g.* a signal at m/z of 373.36 corresponding to the di-urea as well as a signal at m/z of 272.24 corresponding to the mono-urea obtained from the fragmentation of the molecule. The HPLC-MS spectrum of the pure di-urea exhibits the same characteristic signal of the mono-urea which can be attributed to the well reported dynamic character of hindered ureas.⁴² No signal characteristic of IPDA can be observed in the chromatogram, confirming unequivocally its absence and the selectivity of the method.

Diethanolamine reacted rapidly and proceeded to full conversion in less than 7 h but the obtained urea became crosslinked at such high temperatures, which rendered the evaluation of the urea content in the crude product impossible. *N,N,N*-trimethylethane-1,2-diamine only reached 75% of depolymerisation conversion while the yield of urea was about 63% after 7 h. Longer times would have been necessary for completion of the depolymerisation. Finally, morpholine presented similar results to 2-(methylamino)ethan-1-ol, reaching complete conversion and 86% of urea after 7 h. Therefore, while primary amines promote both the C-O and C-N breakage (**Scheme 2.2 A.**), secondary amines exhibit an interesting selectivity that allows degradation of the PU through the unique cleavage of the C-O bond (**Scheme 2.2 B.**). The reaction with 2-(methylamino)ethan-1-ol is of particular interest as it provides a hydroxyl-terminated di-urea which can be employed as monomer for further polymerisations.



Scheme 2.2. Two possible routes for the depolymerisation of IPDI-PU using primary or secondary amine and the resulting products obtained. **A.** unselective C-O and C-N cleavage and **B.** selective C-O dissociation.

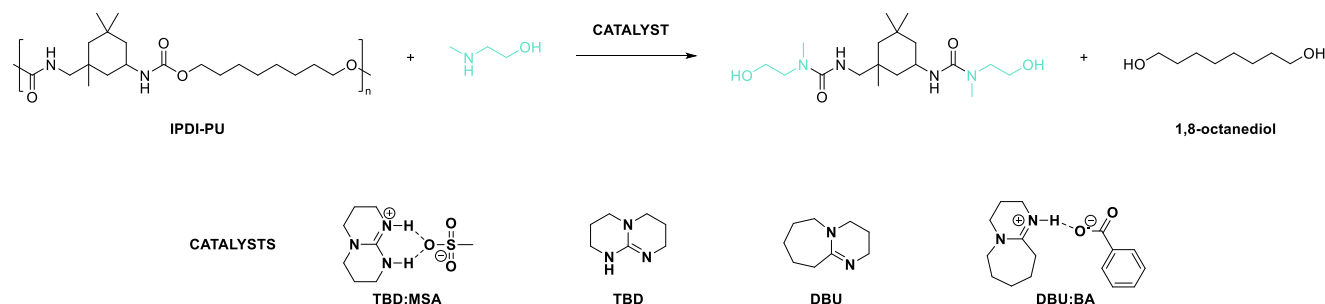
To compare the behaviour of primary and secondary amines in the depolymerisation of aromatic PUs, ethanolamine and 2-(methylamino)ethan-1-ol were used as nucleophiles for the chemical depolymerisation of TDI-PU. Shorter reaction times were observed, with completion reached in less than 1 h in both cases. Similar to what was encountered for IPDI-PU, a lack of selectivity was observed when a primary amine was used as nucleophile. For the depolymerisation performed with aminoethanol, DAT, 1,3-bis(2-hydroxyethyl)urea and 1,8-octanediol were identified as major products of the reaction in the ^1H NMR spectra. (**Scheme 2.3 A.**) However, when using 2-(methylamino)ethan-1-ol and despite the superior reactivity of aromatic PUs, only 1,8-octanediol and the corresponding di-urea were observed, confirming that a selective C-O bond cleavage is occurring. (**Scheme 2.3 B.**) The extent of depolymerisation increased to 96% after only 40 min, demonstrating the efficiency of the methodology for selective PU depolymerisation. This process is even more critical for aromatic PUs since it prevents the release of DAT, which is considered a cancerogenic chemical.



Scheme 2.3. Reaction scheme for the depolymerisation of TDI-PU with **A.** ethanolamine and **B.** 2-(methylamino)ethan-1-ol used as nucleophile. Reaction conditions: TDI-PU (1 eq.), nucleophile (10 eq.), TBD:MSA (0.15 eq.), 40 min, N_2 .

2.4 Optimisation of the reaction parameters with (methylamino)ethan-1-ol

Different conditions were investigated to optimise the depolymerisation process when a secondary amine is used. Different organocatalysts including DBU, TBD, or DBU:BA as well as different temperatures were investigated to determine the impact of these parameters on the selective C-O bond cleavage. All reactions were monitored by ^1H NMR spectroscopy in $\text{DMSO-}d_6$, for 24 h. (Scheme 2.4)



Scheme 2.4. Reaction scheme for the depolymerisation of IPDI-PU with 2-(methylamino)ethan-1-ol catalysed by a series of organocatalysts. Reaction conditions: IPDI-PU (1 eq.), 2-(methylamino)ethan-1-ol (10 eq.), catalyst (0.15 eq.), 7 h, N_2 .

All catalysed reactions performed better than the depolymerisation without catalyst. The depolymerisation yield reached 94 to 97% for all the catalysed reactions while the uncatalysed depolymerisation only reached 54% conversion after 7 h. The performance of the four catalysts were quite similar in terms of degradation of the polymer, but DBU, DBU:BA and TBD presented lower conversion into the di-urea molecule (77%, 79% and 81% respectively), as compared to TBD:MSA, *i.e.* 87%. (Figure 2.2 A.) Interestingly, the product of all reactions – including the uncatalysed depolymerisation – was the di-urea segment, suggesting that the selective breakage of the PU chain is governed by the nature of the nucleophile employed and not by the catalyst.

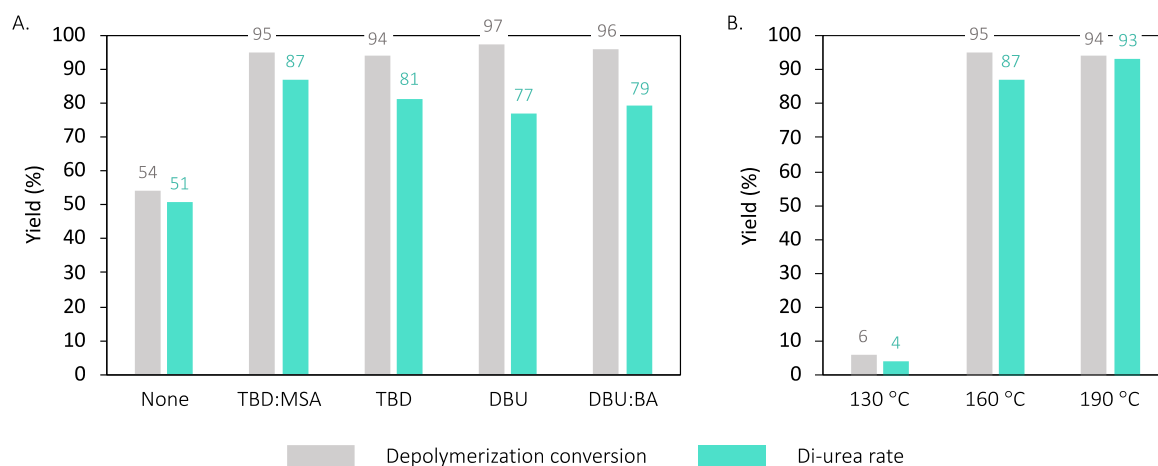


Figure 2.2. Depolymerisation reactions of IPDI-PU with 2-(methylamino)ethan-1-ol catalysed **A.** by a series of organocatalysts at 160 °C and **B.** at different temperatures with TBD:MSA. Reaction conditions: IPDI-PU (1 eq.), 2-(methylamino)ethan-1-ol (10 eq.), catalyst (0.15 eq.), 7 h. (Ratio determined by ^1H NMR spectroscopy in $\text{DMSO-}d_6$ from the crude product using the characteristic signals of 1,8-octanediol ($\delta = 3.37$) and Di-urea ($\delta = 2.81$)).

The reaction was also performed at different temperatures, *i.e.* 130, 160 and 190 °C, as it was previously noticed that temperature was the most significant parameter. (**Figure 2.2 B.**) Surprisingly, the reaction at 130 °C performed extremely poorly. In contrast, reactions at 160 and 190 °C exhibited very similar behaviours, reaching a maximum depolymerisation conversions of 95 and 94%, respectively. It can however be noted that the di-urea ratio is slightly higher when the reaction is performed at 190 °C, 93% vs 87% at 160 °C.

2.5 Depolymerisation of commercial PU foams

It has been shown that the use of 2-(methylamino)ethan-1-ol as nucleophile and TBD:MSA as catalyst lead to good depolymerisation when using thermoplastic PUs. To confirm that this observation can be extended to alternative types of PUs, the viability of the present depolymerisation method was evaluated on crosslinked PU foam, using a commercial-like foam synthesised from TDI, glycerol and a trifunctional commercial polyol. (**Figure 2.3 A.**) The depolymerisation experiment was performed at 160 °C, with 0.15 eq. of catalyst for 7 h. The synthesised foam demonstrated complete depolymerisation after only 5 min. (**Figure 2.3 B.**) The ^1H NMR spectra of the crude product of this reaction revealed that also in this case, selective breakage occurred, alike the examples with the synthesised IPDI-PU and TDI-PU. Interestingly the depolymerisation of the cross-linked TDI based PU foam seems to be much faster than the corresponding reaction previously performed on TDI-PU (5 min vs 40 min). MALDI-TOF analysis performed on the precipitated polyol obtained from the

depolymerisation crude product demonstrated no degradation, either in the structure or on the molecular weight. This could be explained by the higher specific surface area of the foam material in the case of the cross-linked material, which increases the surface contact of the foam with the reaction media and consequently the availability of the urethane groups to react. Regardless of the crosslinked nature of the foam the reaction was carried out rapidly, demonstrating the effectiveness of the method.

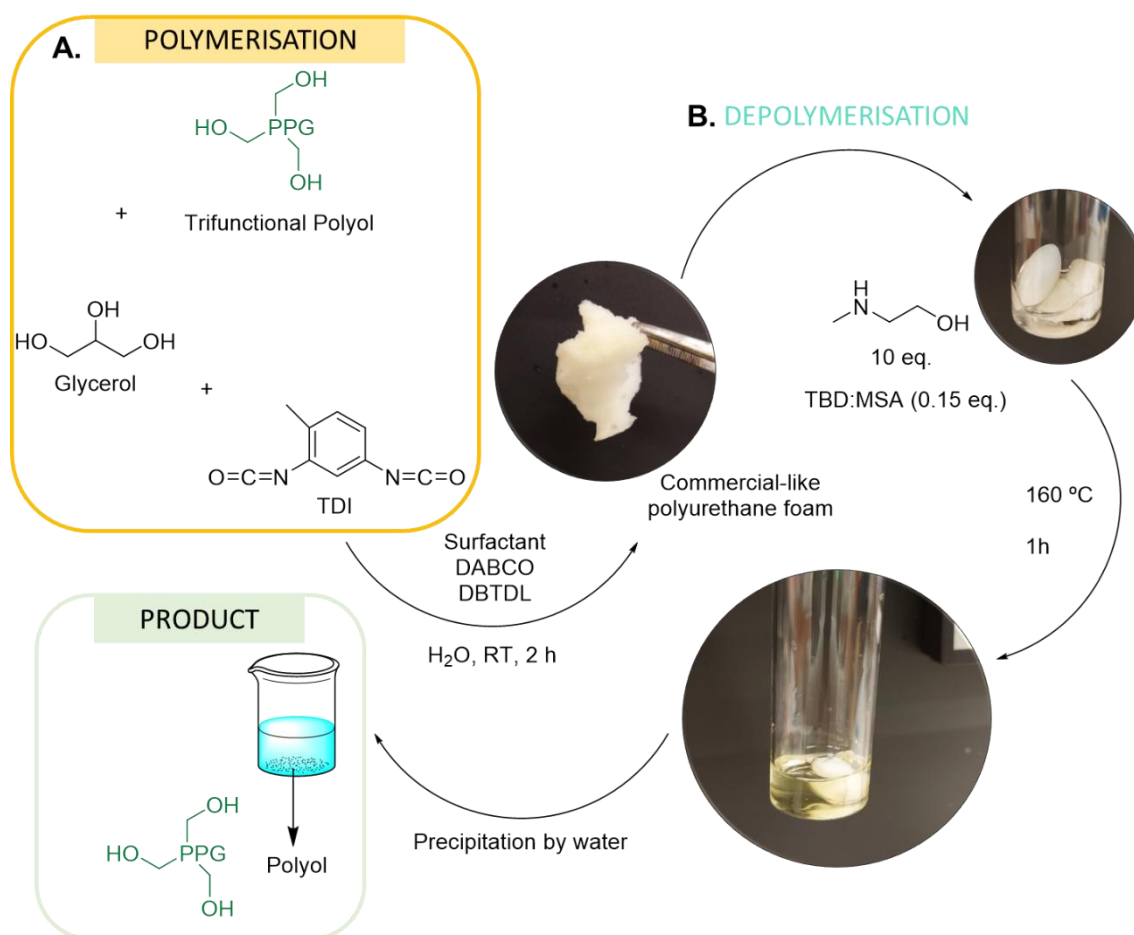



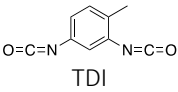
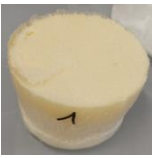
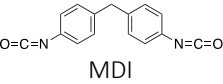


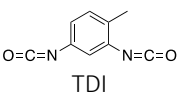


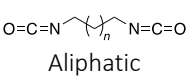

Figure 2.3 A. Synthesis scheme of the commercial-like PU foam and B. its depolymerisation employing 2-(methylamino)ethan-1-ol as nucleophile and TBD:MSA as catalyst, at 160 °C.

Finally, four different commercial PU foams were investigated for their selective depolymerisation with 2-(methylamino)ethan-1-ol under the same conditions as previously. (Table 2.2) CPU-F1, which was identified as a crosslinked rigid PU foam based on TDI and an unidentified polyol did not undergo any depolymerisation. After 7 h of reaction, the foam was still intact in the medium with no sign of degradation. On the contrary, the reaction performed on CPU-F2, which is a flexible PU foam based on aromatic MDI and a trifunctional polyol, led to the complete depolymerisation of the material in 30

min. In the ^1H NMR spectra, the doublet corresponding to the di-urea at $\delta = 2.76\text{-}2.82$ ppm can be identified. However, because of the numerous additives and the lack of data on the composition of the foam, a yield cannot be calculated. Here also, the reaction is even faster than when the model aromatic PU was employed. This again suggests that the higher specific surface area of the flexible foam facilitates depolymerisation.

CPU-F3 and **CPU-F4** presented a very similar behaviour, regardless of the aliphatic nature of **CPU-F4**. After 3 h, a homogeneous solution containing the insoluble inorganic particles was obtained. The characteristic signal of the di-urea can also be observed in the ^1H NMR spectra of the crude products, highlighting the selectivity of the process.

Table 2.2. Description of the different foams investigated and screened data for their depolymerisation.

Entry	Foam	Isocyanate	Polyol	Additives	Time	Dep.	Di-urea
1	 CPU-F1	 TDI	N.A	Carbon black	7 h	N.A no	no
2	 CPU-F2	 MDI	Trifunctional	Silicon surfactants	30 min	 yes	yes
3	 CPU-F3	 TDI	Trifunctional	Titanium dioxide, silicates	3 h	 yes	yes
4	 CPU-F4	 Aliphatic	Trifunctional	Titanium, barium or tin oxides, silicates	3 h	 yes	yes

These results demonstrate that this procedure can be applied to commercial samples, which makes it a suitable procedure for recycling PU waste. However, it should be highlighted that controlling the

additive composition of a material is essential at the recycling stage. Flame-retardants, antioxidants, curing agents, UV-stabilisers and much more constitute a long list of chemicals incorporated in small quantities in formulations which are difficult to detect but can disturb the recycling process. In order to efficiently convert discarded PU into a valuable feedstock, more transparency in the composition of the formulations and more eco-design while formulating the materials is necessary.

2.6 Conclusion

In this chapter, the organocatalytic depolymerisation of PUs has been explored with the aim of selectively cleaving the C-O bond of the urethane function. The aminolysis of the PUs, both aliphatic and aromatic, demonstrated high conversion rates with different amines as nucleophile in a process where the nucleophile is employed in excess, under nitrogen atmosphere, and catalysed by an acid:base catalyst, TBD:MSA. The study has demonstrated that while primary amines unselectively break the C-O and the C-N bonds, providing an amine and urea, secondary amines allow for selective cleavage of the of the C-O moiety to obtain the di-urea compound in high yields. This prevents the release of toxic amines and leads to monomers which can be employed for further synthesis of innovative materials. Furthermore, we found that this process could also be implemented for the depolymerisation of PU foams, which due to their crosslinked character are impractical for mechanical recycling and are a major contributor to the plastic waste problem. In this work we have demonstrated started that selectivity is crucial on depolymerisation processes. However still high temperatures were required to produce the polymer degradation limiting its industrial viability. In next chapters attempts to reduce reaction temperature will be made by facilitating the chemical reaction using adequate solvents.

2.7 Materials and methods

Materials

Reagents and solvents. IPDI, TDI, 1,8-octanediol, hexamethylene diamine, ethylene diamine, - (methylamino)ethan-1-ol, ethanolamine, IPDA, diethanolamine, *p*-xylene diamine, *N,N,N*-trimethylethane-1,2-diamine, morpholine, 1,5,7- TBD, DBU, BA, MSA, glycerol and Desmopan were purchased from Sigma Aldrich or Fisher Scientific. Solvents (technical grade) were purchased from Scharlab. Deuterated DMSO (DMSO-*d*₆) was purchased from Eurisotop. All materials were used without further purification.

Commercial PU foams. All foams are post-industrial PU waste which was provided by the University of Burgos and the technological centre GAIKER. **CPU-F1** is based on TDI and contained carbon black as additive, no further information was provided by the supplier. (FTIR spectroscopy was not possible to perform because of the high carbon black content) **CPU-F2** is based on methylene diphenyl diisocyanate (MDI) and was synthesised by Universidad de Burgos (University of Burgos) with water and a trifunctional polyol as crosslinker along with a silicon-based surfactant, under standard production parameters in the polyurethane industry. No further information was available. **CPU-F3** is based on TDI and a trifunctional polyol, it contains 1.2% of inorganic fillers including 0.4 % of titanium dioxide and silicates (0.8 %). The thermal analysis shows a maximum degradation temperature of 349 °C and a *T_g* of 78 °C. **CPU-F4** was synthesised from a trifunctional polyol and an aliphatic isocyanate, it contained 9.3 % of inorganic fillers including titanium, barium, and tin compounds, as well as some silicates. According to the data provided by the supplier it possesses a maximum degradation temperature of 393 °C and a *T_g* of 66 °C.

Experimental procedures

Synthesis of IPDI-PU

In a typical procedure, 5.00 g isophorone diisocyanate (IPDI) (22.5 mmol) was introduced in a single neck round bottom flask. A solution of 1,8-octanediol was prepared by dissolving 3.27 g (22.7 mmol) of 1,8-octanediol in 15 ml of dry THF and this solution was loaded into an addition funnel. The reaction was carried out under nitrogen atmosphere (to prevent the formation of urea moieties), at 80 °C for 24 h and under magnetic stirring. The solvent was evaporated to obtain a white powder which was

dried overnight. ^1H NMR and FTIR spectroscopy as well as GPC were performed, and the recorded data were used to characterise the product. $M_w = 7250 \text{ g}\cdot\text{mol}^{-1}$.

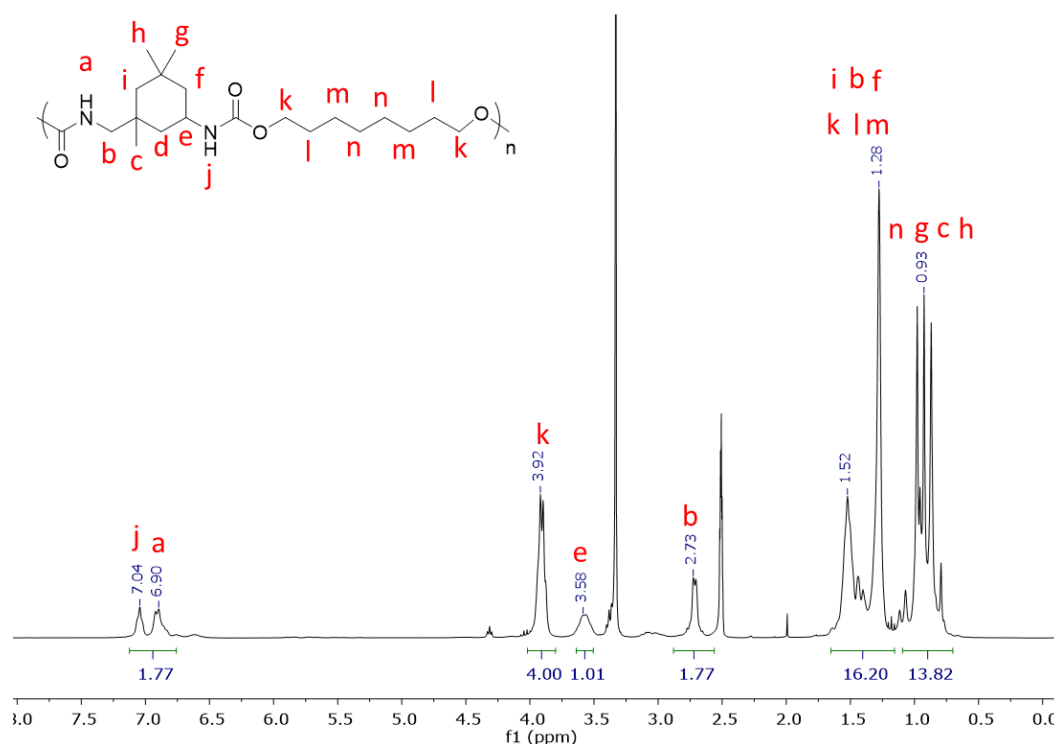


Figure 2.4. ^1H NMR spectrum of IPDI-PU in $\text{DMSO-}d_6$ (300 MHz, 298 K) synthesised from IPDI technical grade (mixture of isomers and 1,8-octanediol).

^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ (ppm) 7.05 (s, 1H, NH), 6.90 (s, 1H, NH), 3.90 (t, 4H, O- CH_2), 3.61 (t, 1H, NH-CH), 2.72 (t, 2H, CH_2 -NH), 1.52-1.25 (m, 18H, aliphatic CH_2 - CH_2), 1.12, 1.07-0.79 (m, 9H, CH_3 - CH_2).

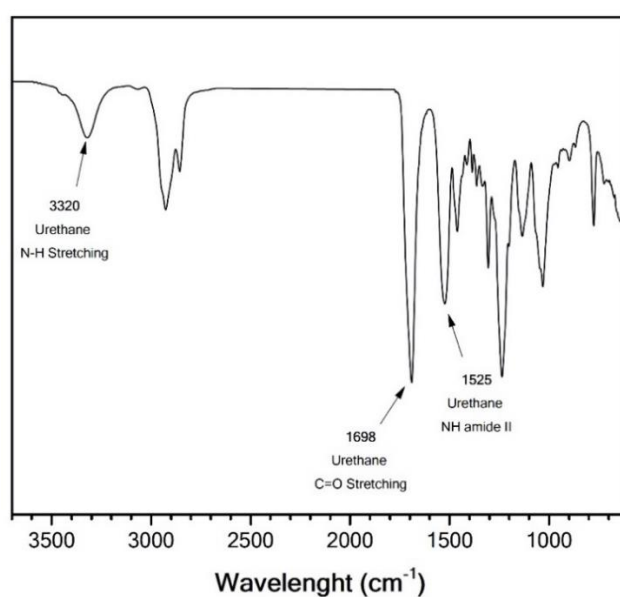


Figure 2.5. FTIR spectrum of IPDI-PU.

FTIR 3320cm^{-1} urethane NH stretching, 1698cm^{-1} urethane C=O stretching, 1525 cm^{-1} urethane NH amide II stretching.

Synthesis of TDI-PU

In a typical procedure, 5.00 g TDI (28.8 mmol) was introduced in a single neck round bottom flask. A solution of 1,8-octanediol was prepared by dissolving 4.24 g (28.9 mmol) of 1,8-octanediol in 20 ml of dry DMF and this solution was loaded into an addition funnel. The reaction was carried out under a nitrogen atmosphere (to prevent the formation of urea moieties), at $60\text{ }^{\circ}\text{C}$ for 24 h and under magnetic stirring. The solvent was evaporated to obtain a white powder which was dried overnight. ^1H NMR and FTIR spectroscopy as well as GPC were performed, and the recorded data were used to characterise the product. $M_w = 7600\text{ g}\cdot\text{mol}^{-1}$.

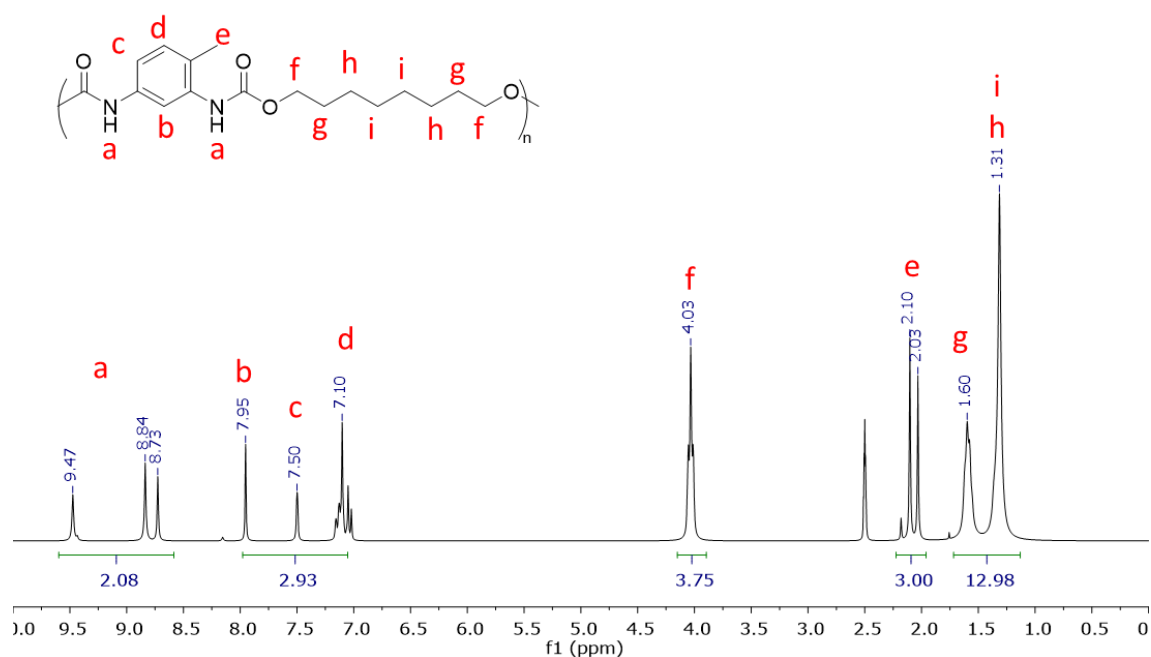


Figure 2.6. TDI-PU ^1H NMR spectrum recorded in $\text{DMSO}-d_6$.

^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ (ppm) 8.84 (s, 1H, NH), 8.73 (s, 1H, NH), 7.50 (s, 1H, NH), 7.10, 7.05, 7.03 (m, 4H, aromatic CH-CH), 4.04 (t, 4H, O- CH_2), 2.11, 2.04 (t, 3H, $\text{CH}_3\text{-C}$), 1.60-1.32 (t, 12H, $\text{CH}_2\text{-CH}_2$).

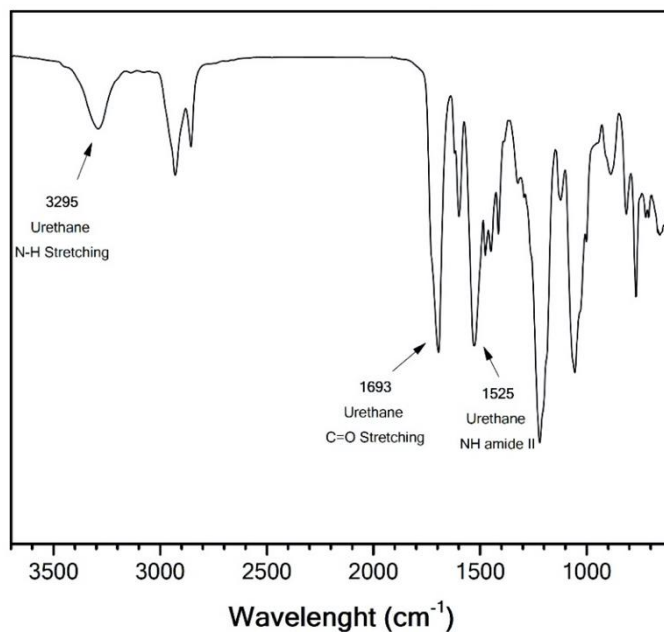


Figure 2.7. FTIR spectrum of TDI-PU.

FTIR 3295cm^{-1} urethane NH stretching, 1693cm^{-1} urethane C=O stretching, 1525cm^{-1} urethane NH amide II stretching.

General procedure for PU depolymerisation reactions

In a typical experiment, 1.00 g of PU (4.48 mmol, 1 eq.) was degraded using the nucleophile in excess (10 eq.) with a certain amount of catalyst (from 0.15 to 0.45 eq.). A 25 mL round bottom flask equipped with a magnetic stirrer was used for every reaction. The depolymerisations were carried out under atmospheric pressure and a nitrogen atmosphere at 130, 160 or 190 °C for 7 h. Reagents and catalyst were previously loaded in the glovebox before sealing the flask which was then immersed in an oil bath. At different reaction times an aliquot of the crude product was taken and dissolved in DMSO- d_6 in order to be analysed by means of ^1H NMR spectroscopy for identification of the products and determination of both the depolymerisation rate and the different products' yields.

Synthesis of commercial-like PU foam

In a typical procedure 0.88 g (9.6 mmol) of glycerol, 15.5 g (4.13 mmol) of desmopan 4042BT trifunctional polyol and 0.045 g (2.5 mmol) of water were mixed in a beaker along with 0.10 g of Tegostab B8110 as surfactant, 0.15 g (1.34 mmol) of DABCO and 0.04 g (0.063 mmol) of DBTDL. 4 g (23 mmol) of TDI was then added and under stirring until foam formation.

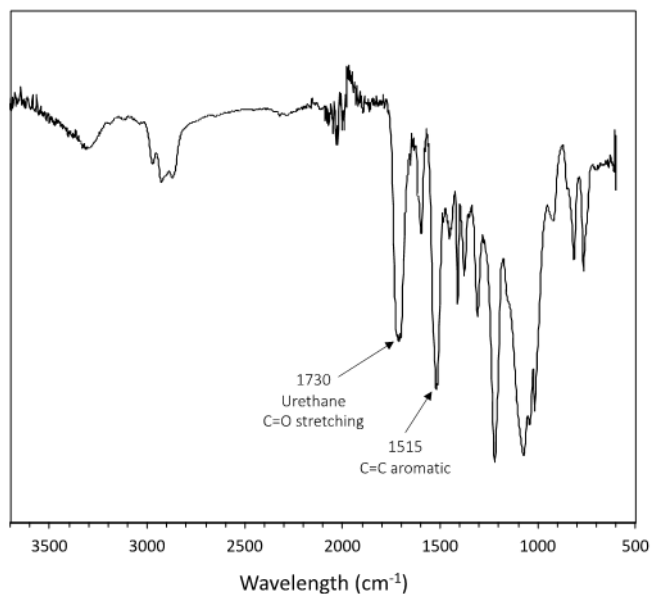


Figure 2.8. FTIR spectra of the commercial-like foam.

Synthesis of TBD:MSA

In a typical procedure, a 100 ml Schlenk flask was dried in an oven at 100°C overnight before being transferred into the glovebox. The organocatalyst was prepared in the Schlenk flask within the glovebox by adding TBD (1 g, 7.18 mmol) followed by the addition of MSA (0.466 ml, 7.18 mmol). During the mixing process, acidic vapours were observed in the Schlenk flask. Subsequently, a magnetic stir bar was introduced into the flask, and the mixture was stirred magnetically for 5 minutes. Following this, 60 ml of dry acetone was added to the flask, which was then sealed with a rubber cap. The Schlenk flask was removed from the glovebox and placed in a pre-heated oil bath at 55°C. If necessary, a needle was introduced through the septum to prevent overpressure. After complete solubilisation of the catalyst, agitation and heating were discontinued. The Schlenk flask was subsequently transferred to a refrigerator at +5°C for 72 hours to promote the precipitation of the product. White to slightly yellowish needles were obtained, filtered, and washed with acetone before being dried under vacuum and stored in a desiccator (1.55 g, yield = 92%).

Synthesis of DBU:BA

A flame dried flask was transferred into a glovebox. Then the flask is charged with BA (1.0 g, 8.18 mmol), ether (20 mL) and it was stirred under magnetic agitation until its complete dissolution. To the stirred solution, DBU (1.2 g, 8.18 mmol) was slowly added and instantly a white precipitate was formed. Once the addition of DBU is complete, the mixture stirring was continued for 3 h more. The precipitate, 2.0 g (91%) of a white powder was washed with more ether and isolated by decantation.

References

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**Los capítulos 3 y 4 están sujetos a
confidencialidad por el autor**

CHAPTER 5

Conclusion and perspectives

In this thesis, various approaches to chemically recycle commodity polymers were investigated. Two different methods were applied, depending on the specific polymer. On one hand, upcycling was performed to obtain high-value molecules from plastic waste, with a particular focus on achieving product purity through selective pathways. On the other hand, after observing the high temperatures required for PU depolymerisation, efforts were made to design low-temperature processes for economically feasible depolymerisation pathways aimed at recycling plastic waste.

To achieve these objectives, depolymerisation reactions, which typically require harsh conditions, needed to be carefully catalysed using efficient and selective molecules. In this thesis, our focus was on studying the application of organocatalysis, a type of molecule that has shown significant potential for polymer degradation in recent years. Additionally, organocatalysts present fewer health concerns compared to their organometallic counterparts, making them a more environmentally friendly alternative.

The depolymerisation of commonly used plastics was considered, and this thesis began with the aim of depolymerising polyurethanes (PUs). These materials find wide applications in our daily lives, from adhesives to foams and engineering applications. However, the chemical breakdown of these materials remains challenging due to the high temperatures required to break the urethane linkages and the complex chemical structure of the resulting products related to the carbamate moiety.

To address this challenge, we demonstrated that PUs can be degraded by amines within a temperature range of 130 to 190 °C. However, primary amines led to the cleavage of both C-N and C-O bonds of the carbamate linkage, resulting in the release of diols and ureas with unclear applications. In contrast, secondary amines, such as *N*-(methylamino)ethan-1-ol, selectively broke the C-O bond while leaving the C-N bond intact, forming substituted dynamic ureas with potential applications in the production of dynamic materials. These reactions were catalysed by TBD:MSA, an ionic protic salt capable of withstanding the high temperatures required for the reactions, unlike other organic bases like TBD or DBU. The developed methodology was applied to a variety of polyurethane foams, leading to the recovery of a polyol with an identical molecular structure compared to the virgin material, as confirmed by MALDI-TOF analysis. This method allows polyurethanes to be depolymerised through aminolysis, yielding dynamic molecules for enhanced applications and recyclable polyols, thus enabling the valorisation of PU waste.

Subsequently, BPA-PC was depolymerised using diols to obtain six-membered cyclic carbonates. This part of the research focused on obtaining TMC, a highly valuable molecule that had not been previously synthesised via depolymerisation due to its high reactivity. To address the instability of the product, a novel procedure involving highly efficient covalent catalysis was developed to perform the depolymerisation at low temperature. The combination of a suitable solvent, such as 1-methylimidazole, which swells and partially dissolves BPA-PC, along with imidazole or similar compounds, allowed for the depolymerisation of polycarbonate at temperatures as low as 50 °C. Under these conditions, the tendency of TMC to undergo ring opening was minimised, making its recovery possible. This new catalytic mechanism was thoroughly characterised using ^1H NMR, which revealed the intermediates involved. Additionally, other nucleophiles were employed, resulting in a wide range of six-membered carbonates, ureas, and dithiocarbonates, showcasing the versatility of this approach in efficiently converting plastic waste into various valuable chemical products.

Building on the knowledge gained from BPA-PC, PET glycolysis was investigated with the goal of reducing the high temperatures typically required in existing processes. Similar to the previous case, 1-methylimidazole was used as a solvent, and TBD was studied as a catalyst. PET was successfully converted at 100 °C, but it required up to 0.5 equivalents of TBD. The inactivation of TBD occurred due to the formation of a salt with terephthalic acid during the reaction. The addition of a strong, hindered base such as tBuOK prevented the formation of the salt, thus maintaining TBD in its free base form and achieving the same yield with significantly less TBD. After confirming the effectiveness of the TBD and tBuOK combination and the importance of using 1-methylimidazole, a broad screening of PET containing different impurities was performed revealing that similar BHET conversion were achieved with all of them.

In summary, by leveraging organocatalysis and efficient and selective depolymerisation processes, we have successfully upcycled PU and BPA-PC into valuable building blocks that can be polymerised in subsequent steps. After assessing the high temperatures required for PU depolymerisation using diamines as nucleophile we decided to develop low temperature processes for BPA-PC. Owing to the synergic effect of imidazole and optimal solvent reaction temperatures could be drastically reduced comparing with existing examples on literature. This reduction does not only facilitate the scale up to industrial scale but also permits the obtention of highly reactive molecules such as TMC. For PET, we have depolymerised it into BHET, a monomer with the potential to pave the way for a circular economy

approach to this material. In the final stage, successful reactions with contaminants commonly found in plastic waste have been addressed, confirming the applicability of the developed processes to real plastic waste streams. These results open new perspectives for energetically and economically more feasible chemical recycling of commodity polymers, and based on the current studies, further research avenues can be envisioned.

Future works:

1 Depolymerise other commodity polymers containing electrophile groups, such as esters or amides, using the approach described in this thesis. For example, PLA and aliphatic carbonates can be depolymerised through a transesterification reaction employing TBD and imidazole combination. Preliminary experiments have been conducted, showing that these reactions work, but further work is needed to provide a complete description of the reactions. Ideally, the aim would be to obtain lactide or cyclic carbonates, which would contribute to a circular economy approach for these materials. While the formation of these compounds was observed, isolating the products in high yields remains challenging. Additionally, successful preliminary attempts to degrade polyamides have been made, yielding notable quantities of caprolactam and upcycling products.

2 Improve the ease of product isolation procedures. While TMC, several ureas, BPA, BHET, and their corresponding dimers and trimers were obtained relatively easily, without the need for industrially unfeasible chromatographic columns, there is still a need to develop isolation procedures that are easy to scale up from an industrial perspective, which may not always align with laboratory-scale requirements.

3 The selection of solvents for depolymerising specific polymers has been demonstrated to be of key importance in achieving low-temperature processes that save energy and costs. For example, this approach has been successfully applied to the depolymerisation of BPA-PC and PET, but there is still room for further research. Currently, we are focused on explaining the underlying interactions of solvents with polymers during the reaction.

4 Develop new synthetic pathways to obtain organocatalysts in a facile and environmentally friendly manner, without using toxic and dangerous reagents. Organocatalysts have been shown to be an efficient approach to degrade plastics into well-defined building blocks. However, their implementation at an industrial scale is very limited, partly due to their relatively high cost and the

generally more complicated and tedious synthetic routes required compared to organometallic counterparts. Additionally, they often require lower catalytic loads to perform the reaction. The development of alternative procedures for producing organocatalysts could facilitate their use on an industrial scale. In fact, a project aimed at achieving this goal has been developed, demonstrating that amidine and guanidine protic salts can be obtained in a variety of structures in a simple and cost-effective manner. The products obtained included TBD:MSA and benzimidazole, two of the catalysts employed in this work. This project will be completed, and a publication will be written in the near future.

5 Study the possibility of performing the depolymerisation reaction through heterogeneous catalysis. While this thesis focuses on homogeneous catalysis, from an industrial perspective, heterogeneous catalysis offers several advantages, such as the elimination of isolation steps to recover the catalyst. To achieve this, the choice of solvent would be critical, as the migration of the polymer chains to the heterogeneous catalyst surface would significantly enhance reaction yields and efficiency.

Nowadays, there is significant attention on the plastic waste problem from industry, governments, and citizens. The fact that most plastic is currently produced from limited resources, its accumulation in the environment for decades due to slow degradation, and the unknown effects on health caused by microplastic particles are concerning the global population. However, the widespread use of plastics, owing to their advantages over other materials, has made them indispensable in our daily lives in the form of countless plastic items. To address the issues arising from plastics, several strategies are under research.

On one hand, the synthesis of biobased and biodegradable polymers presents a very interesting and promising long-term alternative to reduce our dependence on petroleum for producing these materials and to decrease the accumulation of plastic waste. However, this field still requires extensive research and is not expected to transform the industry as quickly as needed to address plastic-related problems.

On the contrary, plastic recycling is currently implemented in many countries around the world and is the most realistic approach in the short to mid-term. The strategies currently applied for polymer recycling are not perfect, and significant quantities of plastic are still discarded because they cannot be used for further applications due to downcycling. As an alternative, chemical recycling can ideally implement an economically circular approach to plastics including the one that cannot be further

treated by mechanical means. Both approaches may be employed simultaneously due to the low cost of mechanical treatment and the ability to of chemical recycling to treat the plastics that cannot be further processed mechanically. Additionally, plastics can be upcycled into chemicals for high-value applications, which has garnered the interest of companies changing the view of plastic waste from useless rubbish to chemical synthetic precursors.

Plastic recycling still requires further study and improvement to tackle the challenge of treating the constantly increasing amounts of plastic waste produced every year. However, the growing attention and action on this topic underscore the immense importance of plastic recycling both currently and in the future.

CHAPTER 6

Appendix

Characterisation methods

Nuclear Magnetic Resonance (NMR) spectroscopy

^1H and ^{13}C Nuclear Magnetic Resonance (NMR). ^1H NMR spectroscopic measurements were carried out on a Bruker Avance 300 (300 MHz) spectrometer using deuterated DMSO (DMSO-d_6) or chloroform (CDCl_3) as solvent. Experimental conditions were as follows unless other conditions are specified: for ^1H NMR spectroscopy, 10 mg of sample; 3 s acquisition time; 1 s delay time; 8.5 μs pulse; spectral width 5000 Hz and 32 scans; b) for ^{13}C NMR spectroscopy: 40 mg; 3 s acquisition time; 4 s delay time; 5.5 μs pulse; spectral width 18800 Hz and scans vary in a range between 500-10000 scans.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transformation infrared spectra (FT-IR). FT-IR spectra were obtained by FT-IR spectrophotometer (Nicolet 6700 FT-IR, Thermo Scientific Inc., USA) using attenuated total reflectance (ATR) technique (Golden Gate, spectra Tech). Spectra were recorded between 4000-525 cm^{-1} with a spectrum resolution of 4 cm^{-1} . All spectra were averaged over 10 scans.

High-Performance Liquid Chromatography – Mass Spectra (HPLC-MS)

Experiments were performed in waters Alliance HPLC-QDA employing a C18 5-micron column with an injection volume of 50 μL using a mixture of 90 % water, 10 % of acetonitrile, and 0.1 % of trifluoroacetic acid running for 60 min ($F = 0.5 \text{ mL}$). Each compound present in the mixture was analysed separately to confirm their behaviour and characteristic signals on the mass spectra and were compared with the crude reaction mixture.

Gas permeation Chromatography (GPC).

GPC analysis (Agilent PL-GPC 50) were performed using a Shodex GPC HFIP-803 ($300 \times 8.0 \text{ mm}^2$) with THF as the eluent, with a flow rate of 1 $\text{mL}\cdot\text{min}^{-1}$ with polystyrene standards.

Differential Scanning Calorimetry (DSC)

The thermal behaviour of the polymers was determined using a DSC 8500 (PerkinElmer). Unless other conditions are specified, experiments were carried out at heating and cooling rates of 20°C/min from -60 to 150°C and 20°C/min from 40 to 300°C under a nitrogen. Flow of 20 mL/min, employing samples of 4.5-5.5 mg. The instrument was calibrated with indium and tin standards.

Chapter 2 PU depolymerisation

FTIR spectra for commercial and commercial-like foams employed in this study.

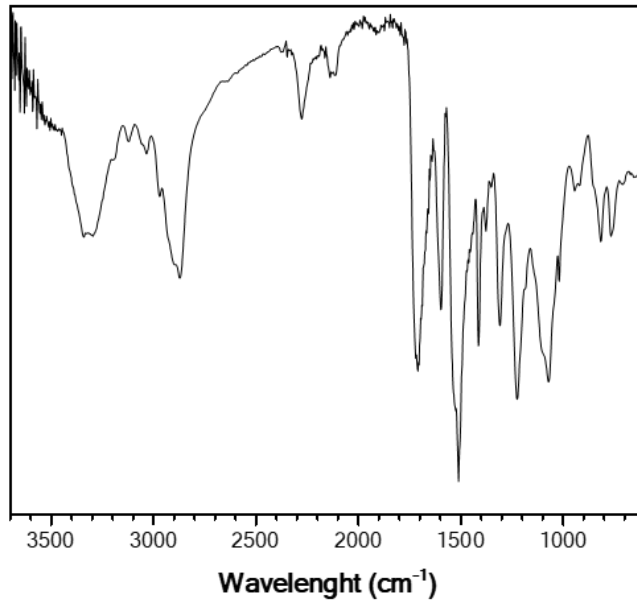


Figure S.2.1. FTIR spectrum of CPU-F2.

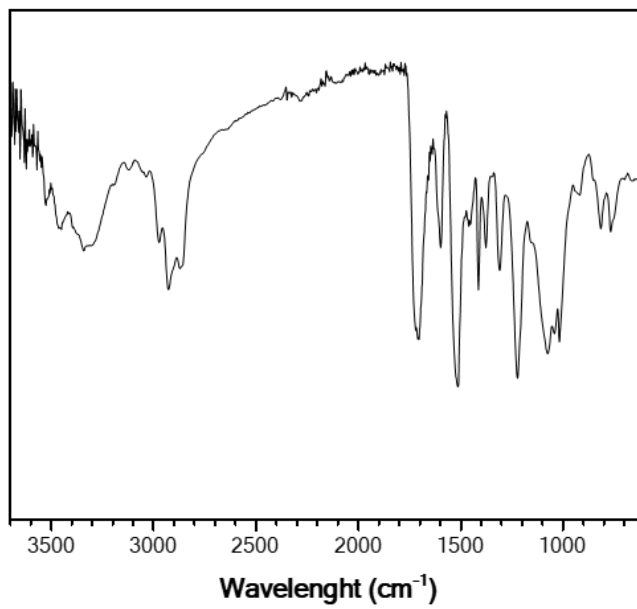


Figure S.2.2. FTIR spectrum of CPU-F3.

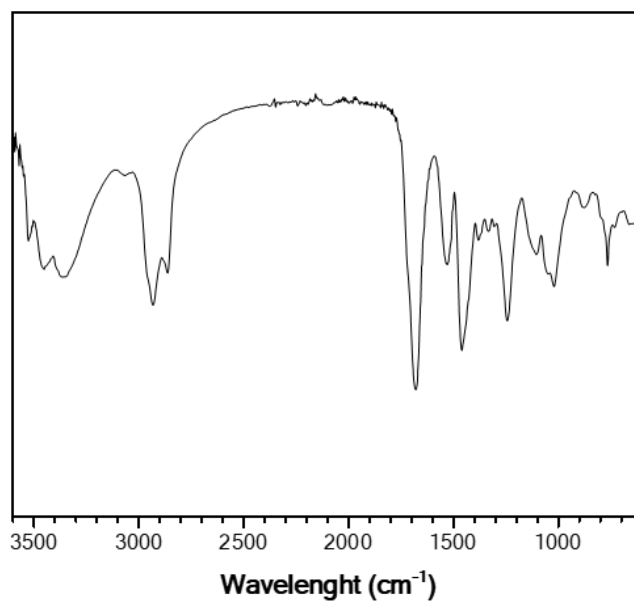


Figure S.2.3. FTIR spectrum of CPU-F4.

Catalyst characterisation

TBD:MSA

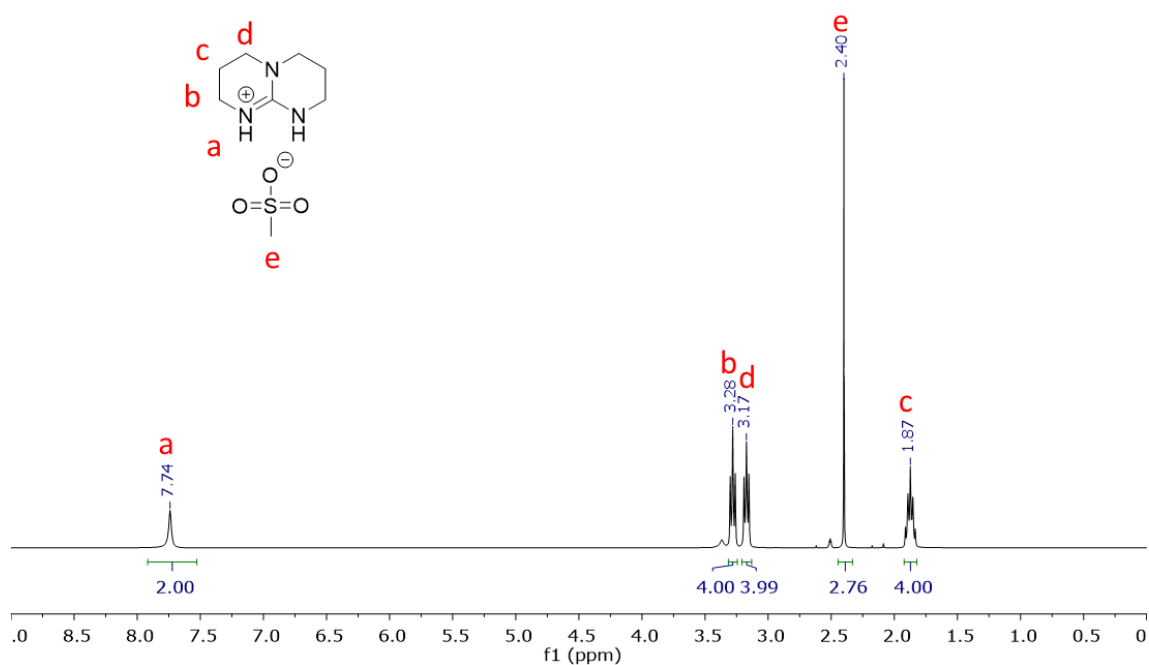


Figure S.2.4. ^1H NMR spectrum of TBD:MSA in $\text{DMSO-}d_6$.

^1H NMR (300 MHz, $\text{DMSO-}d_6$, 298K) δ (ppm) 7.73 (s, 2H), 3.28 (t, 4H, $J = 6.0$ Hz, 2H), 3.17 (t, 4H), 2.39 (s, 3H), 1.87 (q, 4H, $J = 5.9$ Hz).

DBU

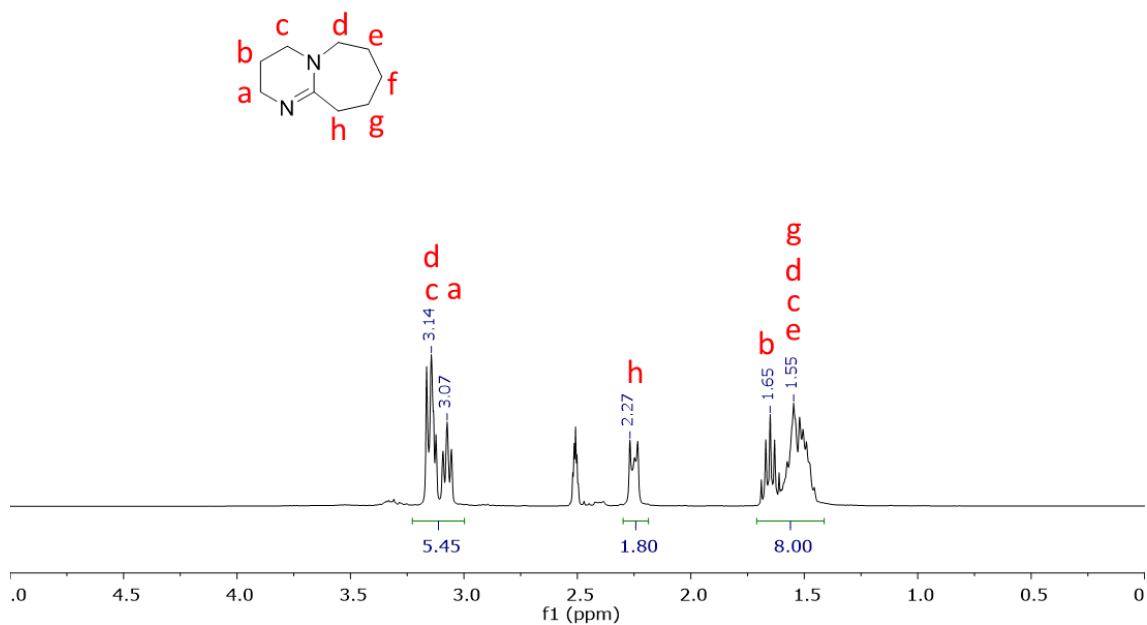


Figure S.2.5 ¹H NMR spectrum of DBU in DMSO-*d*₆ of DBU in its free base form.

¹H NMR (300 MHz, DMSO-*d*₆, 298K) δ(ppm) 3.14 (t, 4H), 3.07 (t, 2H, J = 5.6 Hz), 2.27(m, 2H), 1.65 (q, 2H, J = 5.9 Hz), 1.55 (m, 6H, J = 19.5, 9.5 Hz).

DBU:BA

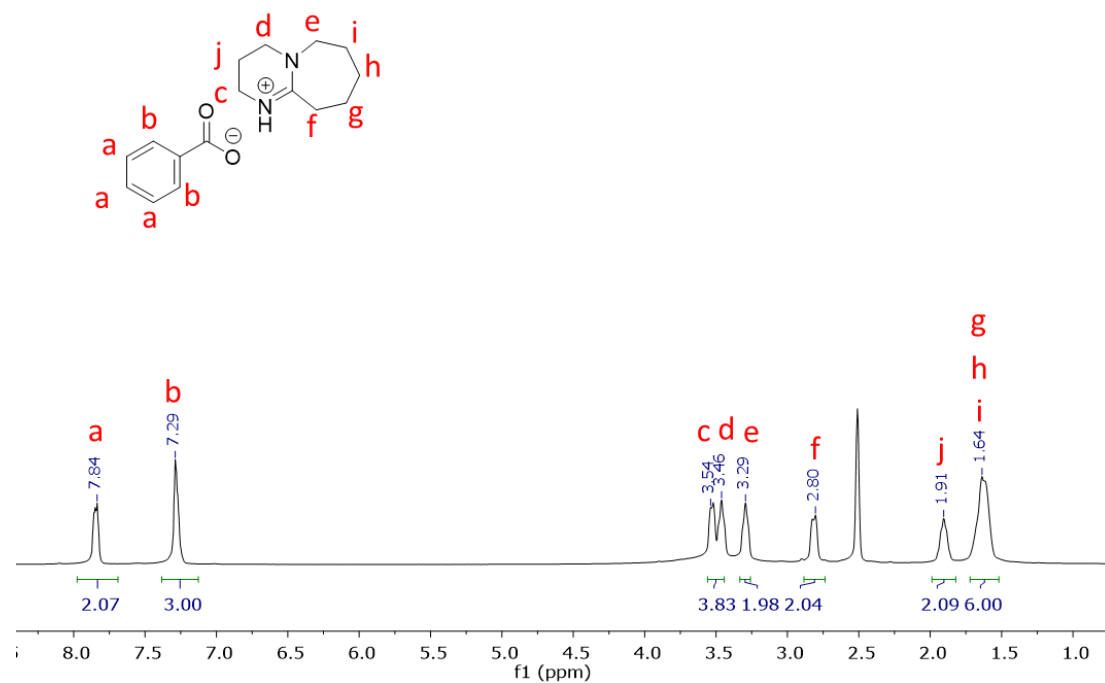
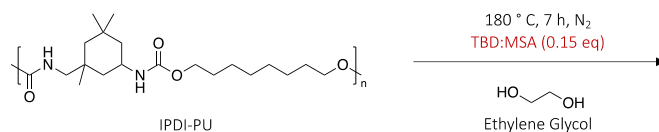


Figure S.2.6. ¹H NMR spectrum of DBU:BA in DMSO-*d*₆.

¹H NMR (300 MHz, DMSO-*d*₆, 298K) δ(ppm) 7.84 (m, 2H, CH), 7.29 (m, 3H, CH), 3.54-3.46 (dd, 4H, CH₂), 3.29 (t, 2H, CH₂), 2.80 (t, 2H, CH₂), 1.91 (q, 2H, CH₂), 1.64 (q, 6H, CH₂).

PU depolymerisation reactions

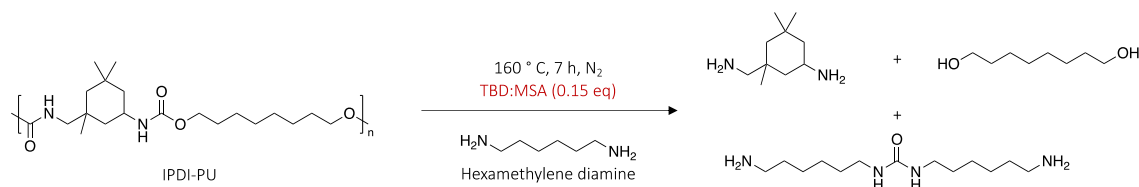
Depolymerisation of IPDI-PU with EG



Scheme S.2.1. Depolymerisation of IPDI-PU with EG at 180 °C with 0.15 eq. of TBD:MSA.

1.00 g of PU (4.48 mmol, 1 eq.) are degraded with EG (44.8 mmol, 10 eq.) with TBD:MSA (0.672 mmol, 0.15 eq.) in a 25 mL round bottom flask equipped with a magnetic stirrer. The depolymerisation is carried out under atmospheric pressure and nitrogen atmosphere at 180 °C for 7 h.

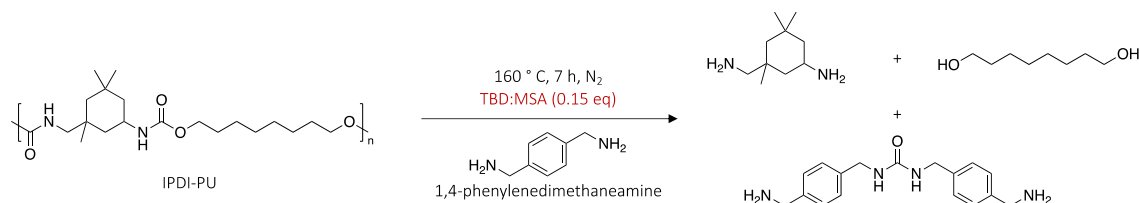
Depolymerisation of IPDI-PU with hexamethylene diamine



Scheme S.2.2. Depolymerisation of IPDI-PU with hexamethylene diamine at 160 °C with 0.15 eq. of TBD:MSA.

1.00 g of PU (4.48 mmol, 1 eq.) are degraded with hexamethylene diamine (44.8 mmol, 10 eq.) with TBD:MSA (0.672 mmol, 0.15 eq.) in a 25 mL round bottom flask equipped with a magnetic stirrer. The depolymerisation is carried out under atmospheric pressure and nitrogen atmosphere at 160 °C for 7 h.

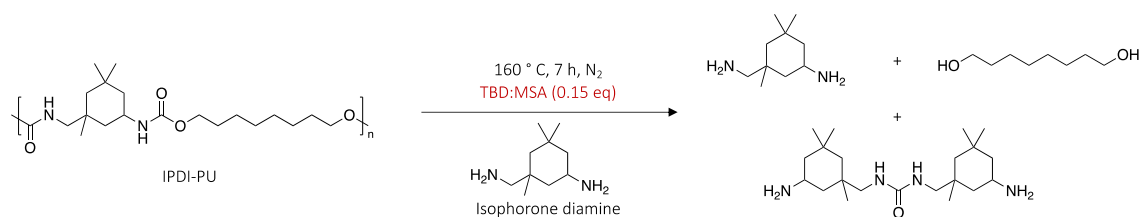
Depolymerisation of IPDI-PU with 1,4-phenylenedimethanamine



Scheme S.2.3. Depolymerisation of IPDI-PU with 1,4-phenylenedimethanamine at 160 °C with 0.15 eq. of TBD:MSA.

1.00 g of PU (4.48 mmol, 1 eq.) are degraded with 1,4-phenylenedimethanamine (44.8 mmol, 10 eq.) with TBD:MSA (0.672 mmol, 0.15 eq.) in a 25 mL round bottom flask equipped with a magnetic stirrer. The depolymerisation is carried out under atmospheric pressure and nitrogen atmosphere at 160 °C for 7 h.

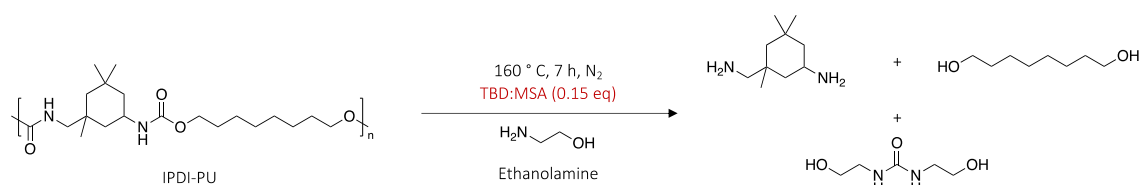
Depolymerisation of IPDI-PU with IPDA



Scheme S.2.4. Depolymerisation of IPDI-PU with IPDA at 160 °C with 0.15 eq. of TBD:MSA.

1.00 g of PU (4.48 mmol, 1 eq.) are degraded with IPDA (44.8 mmol, 10 eq.) with TBD:MSA (0.672 mmol, 0.15 eq.) in a 25 mL round bottom flask equipped with a magnetic stirrer. The depolymerisation is carried out under atmospheric pressure and nitrogen atmosphere at 160 °C for 7 h.

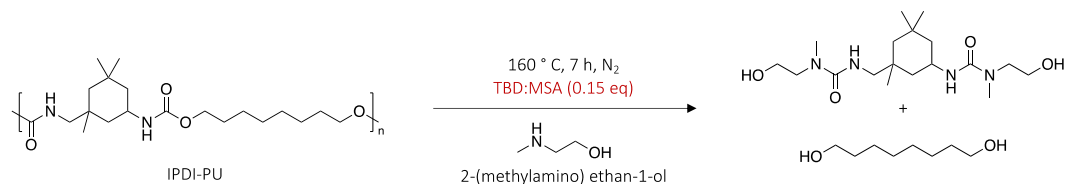
Depolymerisation of IPDI-PU with ethanolamine



Scheme S.2.5. Depolymerisation of IPDI-PU with ethanolamine at 160 °C with 0.15 eq. of TBD:MSA.

1.00 g of PU (4.48 mmol, 1 eq.) are degraded with ethanolamine (44.8 mmol, 10 eq.) with TBD:MSA (0.672 mmol, 0.15 eq.) in a 25 mL round bottom flask equipped with a magnetic stirrer. The depolymerisation is carried out under atmospheric pressure and nitrogen atmosphere at 160 °C for 7 h.

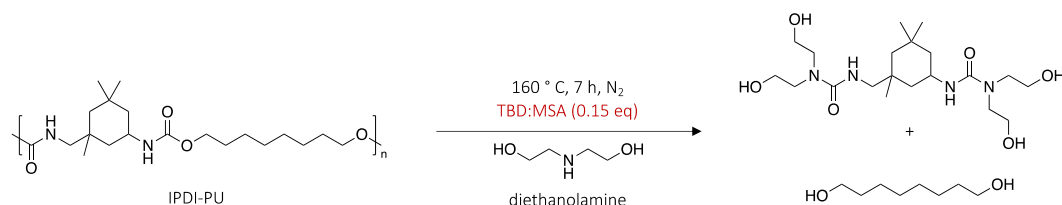
Depolymerisation of IPDI-PU with 2-(methylamino) ethan-1-ol



Scheme S.2.6. Depolymerisation of IPDI-PU with ethanolamine at 160 °C with 0.15 eq. of TBD:MSA.

1.00 g of PU (4.48 mmol, 1 eq.) are degraded with 2-(methylamino) ethan-1-ol (44.8 mmol, 10 eq.) with TBD:MSA (0.672 mmol, 0.15 eq.) in a 25 mL round bottom flask equipped with a magnetic stirrer. The depolymerisation is carried out under atmospheric pressure and nitrogen atmosphere at 160 °C for 7 h.

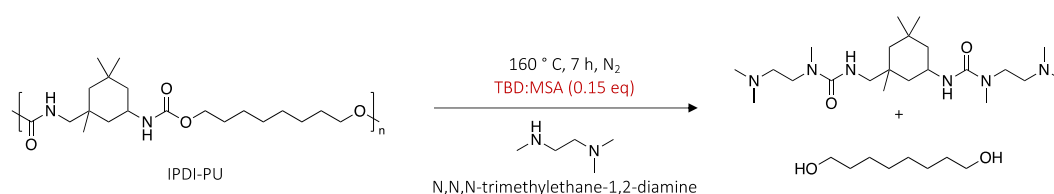
Depolymerisation of IPDI-PU with diethanolamine



Scheme S.2.7. Depolymerisation of IPDI-PU with diethanolamine at 160 °C with 0.15 eq. of TBD:MSA.

1.00 g of PU (4.48 mmol, 1 eq.) are degraded with diethanolamine (44.8 mmol, 10 eq.) with TBD:MSA (0.672 mmol, 0.15 eq.) in a 25 mL round bottom flask equipped with a magnetic stirrer. The depolymerisation is carried out under atmospheric pressure and nitrogen atmosphere at 160 °C for 7 h.

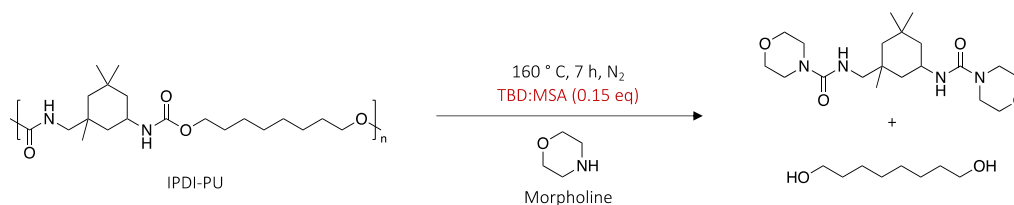
Depolymerisation of IPDI-PU with N,N,N-trimethylethane-1,2-diamine



Scheme S.2.8. Depolymerisation of IPDI-PU with N,N,N-trimethylethane-1,2-diamine at 160 °C with 0.15 eq. of TBD:MSA.

1.00 g of PU (4.48 mmol, 1 eq.) are degraded with N,N,N-trimethylethane-1,2-diamine (44.8 mmol, 10 eq.) with TBD:MSA (0.672 mmol, 0.15 eq.) in a 25 mL round bottom flask equipped with a magnetic stirrer. The depolymerisation is carried out under atmospheric pressure and nitrogen atmosphere at 160 °C for 7 h.

Depolymerisation of IPDI-PU with morpholine

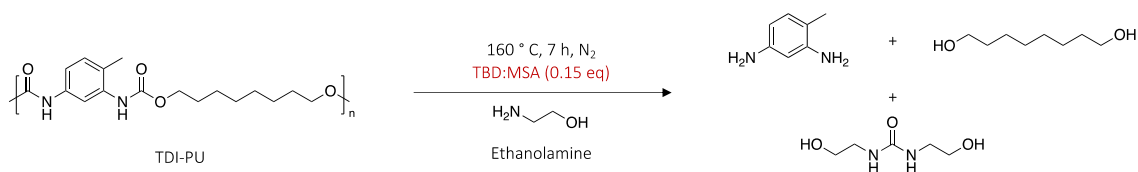


Scheme S.2.9. Depolymerisation of IPDI-PU with morpholine at 160 °C with 0.15 eq. of TBD:MSA.

1.00 g of PU (4.48 mmol, 1 eq.) are degraded with morpholine (44.8 mmol, 10 eq.) with TBD:MSA (0.672 mmol, 0.15 eq.) in a 25 mL round bottom flask equipped with a magnetic stirrer. The

depolymerisation is carried out under atmospheric pressure and nitrogen atmosphere at 160 °C for 7 h.

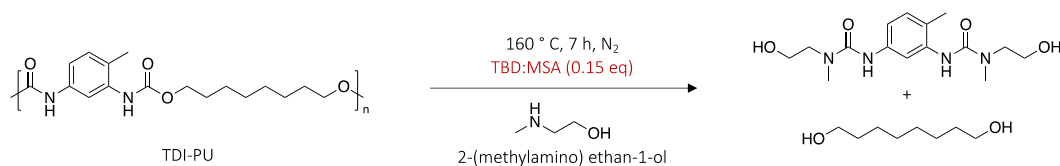
Depolymerisation of TDI-PU with ethanolamine



Scheme S.2.10. Depolymerisation of TDI-PU with ethanolamine at 160 °C with 0.15 eq. of TBD:MSA.

1.00 g of PU (3.13 mmol, 1 eq.) are degraded with ethanolamine (31.3 mmol, 10 eq.) with TBD:MSA (0.468 mmol, 0.15 eq.) in a 25 mL round bottom flask equipped with a magnetic stirrer. The depolymerisation is carried out under atmospheric pressure and nitrogen atmosphere at 160 °C for 7 h.

Depolymerisation of IPDI-PU with 2-(methylamino) ethan-1-ol



Scheme S.2.11. Depolymerisation of TDI-PU with ethanolamine at 160 °C with 0.15 eq. of TBD:MSA.

1.00 g of PU (3.13 mmol, 1 eq.) are degraded with 2-(methylamino) ethan-1-ol (31.3 mmol, 10 eq.) with TBD:MSA (0.468 mmol, 0.15 eq.) in a 25 mL round bottom flask equipped with a magnetic stirrer. The depolymerisation is carried out under atmospheric pressure and nitrogen atmosphere at 160 °C for 7 h.

Products characterisation by means of $^1\text{H-NMR}$

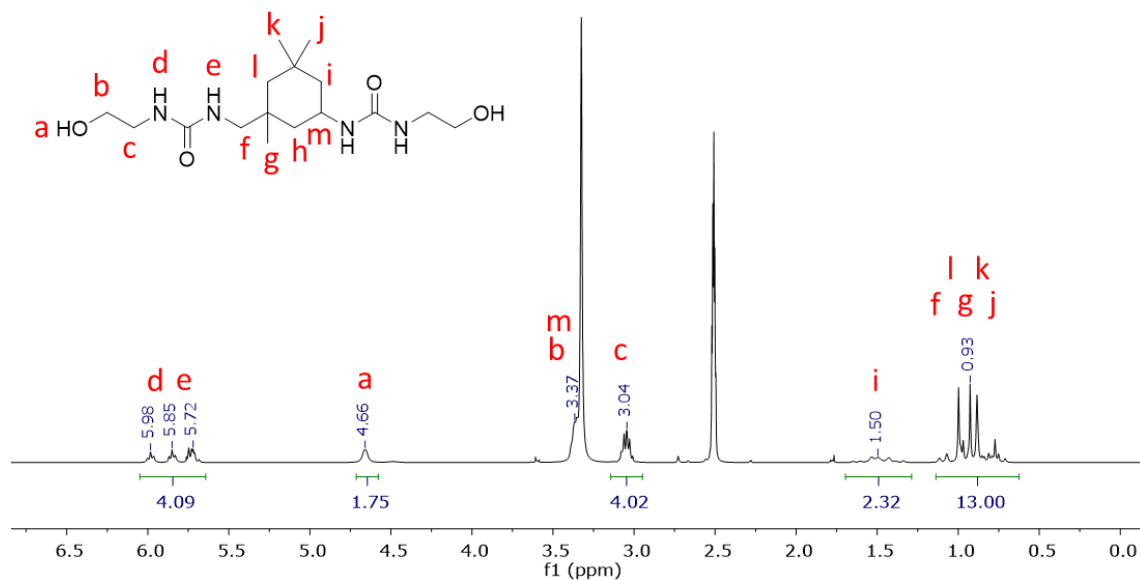


Figure S.2.7. $^1\text{H-NMR}$ spectrum for the di-urea resulting from the depolymerisation of IPDI-PU with ethanolamine as nucleophile. (300 MHz, DMSO- d_6) δ 6.07 – 5.64 (m, 4H), 4.66 (s, 2H), 3.05 (td, J = 5.9, 4.5 Hz, 4H), 1.65 – 1.31 (m, 2H), 1.16 – 0.66 (m, 13H).

$^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 5.98 (t, J = 5.9 Hz, 1H), 5.85 (t, J = 5.7 Hz, 1H), 5.80 – 5.67 (m, 2H), 4.66 (s, 2H), 3.05 (td, J = 5.9, 4.5 Hz, 4H), 1.70 – 1.29 (m, 2H), 1.16 – 0.63 (m, 13H).

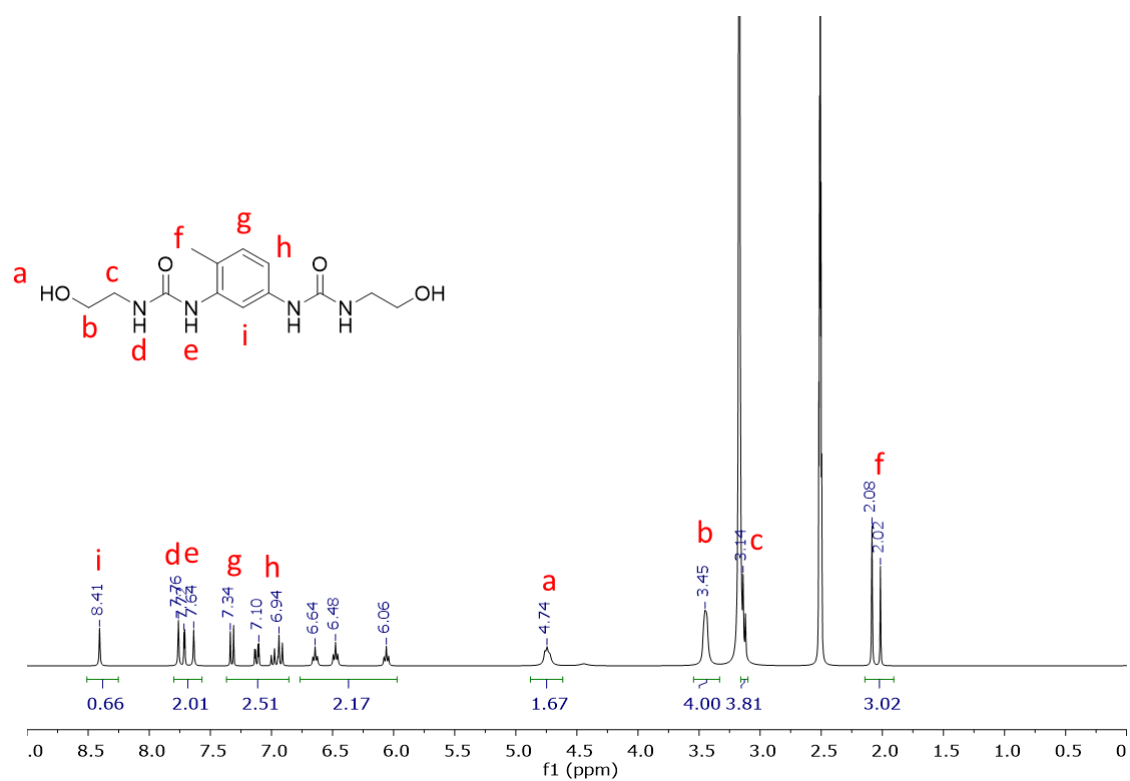


Figure S.2.8. ¹H-NMR spectrum for the di-urea resulting from the depolymerisation of TDI-PU with ethanolamine as nucleophile. (300 MHz, DMSO-*d*₆) δ 7.85 – 7.54 (m, 2H), 7.39 – 6.87 (m, 2H), 6.73 – 5.90 (m, 1H), 4.74 (t, *J* = 6.2 Hz, 1H), 3.52 – 3.42 (m, 4H), 2.05 (d, *J* = 20.7 Hz, 3H).

¹H NMR (300 MHz, DMSO-*d*₆) δ 8.41 (s, 1H), 7.76 (s, 1H), 7.71-7.64 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 10.4 Hz, 1H), 6.96 (dd, *J* = 19.1, 8.2 Hz, 1H), 6.64 (t, *J* = 5.4 Hz, 1H), 6.48 (t, *J* = 5.5 Hz, 1H), 6.06 (t, *J* = 5.6 Hz, 1H), 4.84 – 4.61 (m, 2H), 3.44 (s, 4H), 3.14 (t, 4H), 2.08-2.02 (2 s, 3H).

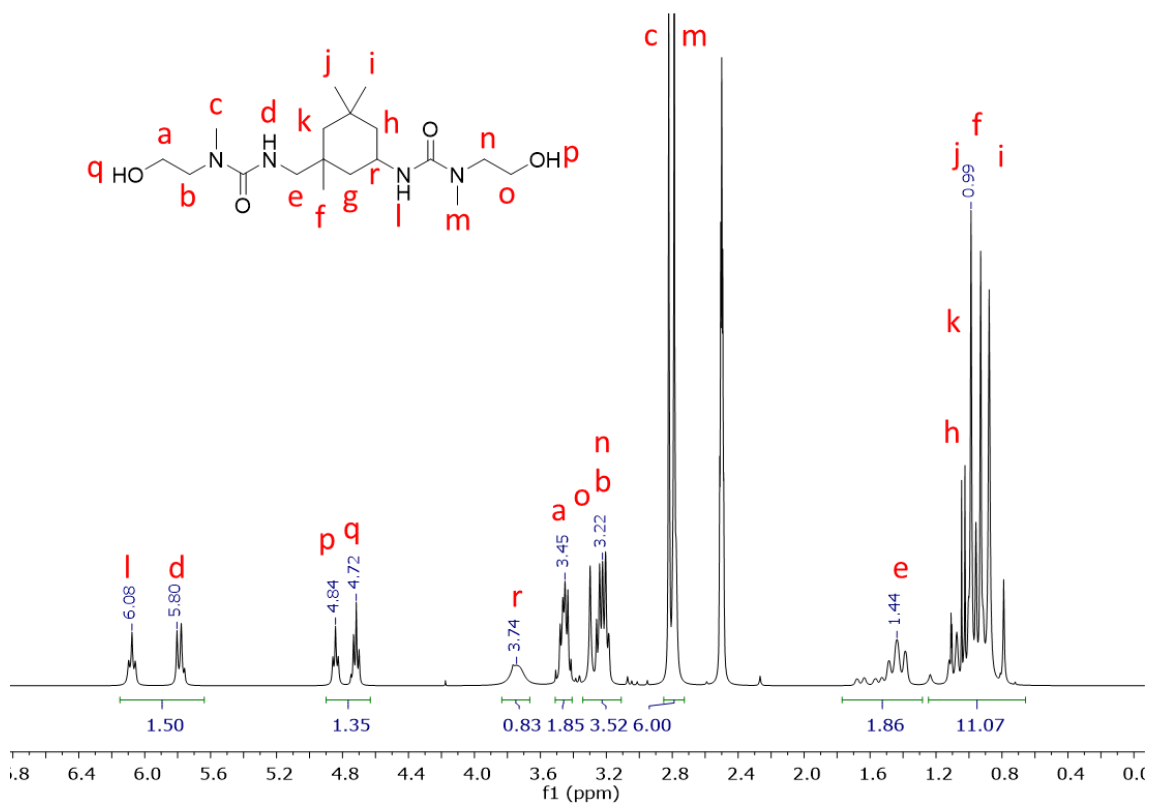


Figure S.2.9. ¹H-NMR spectrum for the di-urea resulting from the depolymerisation of IPDI-PU (mixture of isomers) with 2-(methylamino)ethan-1-ol as nucleophile.

¹H NMR (300 MHz, DMSO-d₆) δ 6.08 (t, J = 6.1 Hz, 1H), 5.80 (d, J = 7.6 Hz, 1H), 4.84 (t, J = 4.9 Hz, 1H), 4.72 (t, J = 5.0 Hz, 1H), 3.74 (m, 1H), 3.45 (dt, J = 10.7, 5.3 Hz, 2H), 3.22 (dt, J = 10.9, 5.4 Hz, 4H), 2.85 – 2.76 (2 s, 3H), 1.52 – 1.35 (m, 2H), 1.15 – 0.82 (m, 11H).

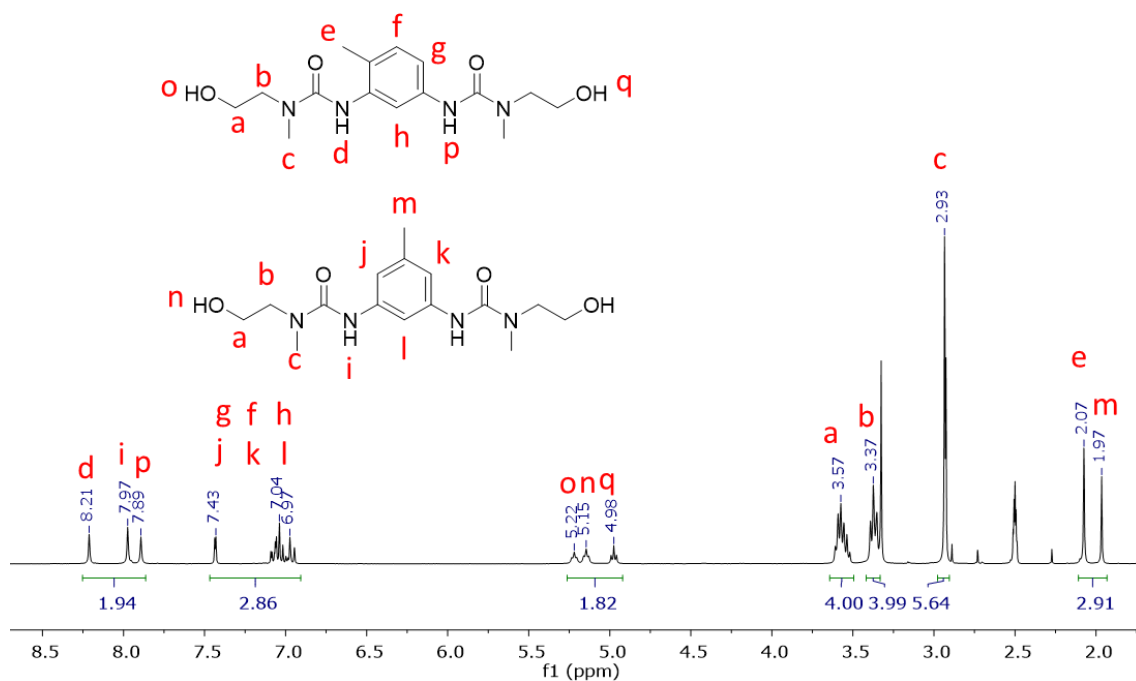


Figure S.2.10. ^1H -NMR spectrum for the di-urea resulting from the depolymerisation of TDI-PU with 2-(methylamino)ethan-1-ol as nucleophile (mixture of isomers).

^1H NMR (300 MHz, DMSO-d_6) δ 8.21 (s, 1H), 7.97-7.89 (s, 1H), 7.43 (d, $J = 2.2$ Hz, 1H), 7.13 – 6.90 (m, 2H), 5.18 (d, $J = 22.1$ Hz, 1H), 4.98 (t, 1H), 3.56 (dq, $J = 10.9, 5.3$ Hz, 4H), 3.37 (t, $J = 5.9$ Hz, 4H), 2.93 (d, $J = 2.6$ Hz, 6H), 2.07-1.97 (s, 3H).

Kinetics followed by ^1H NMR spectroscopy

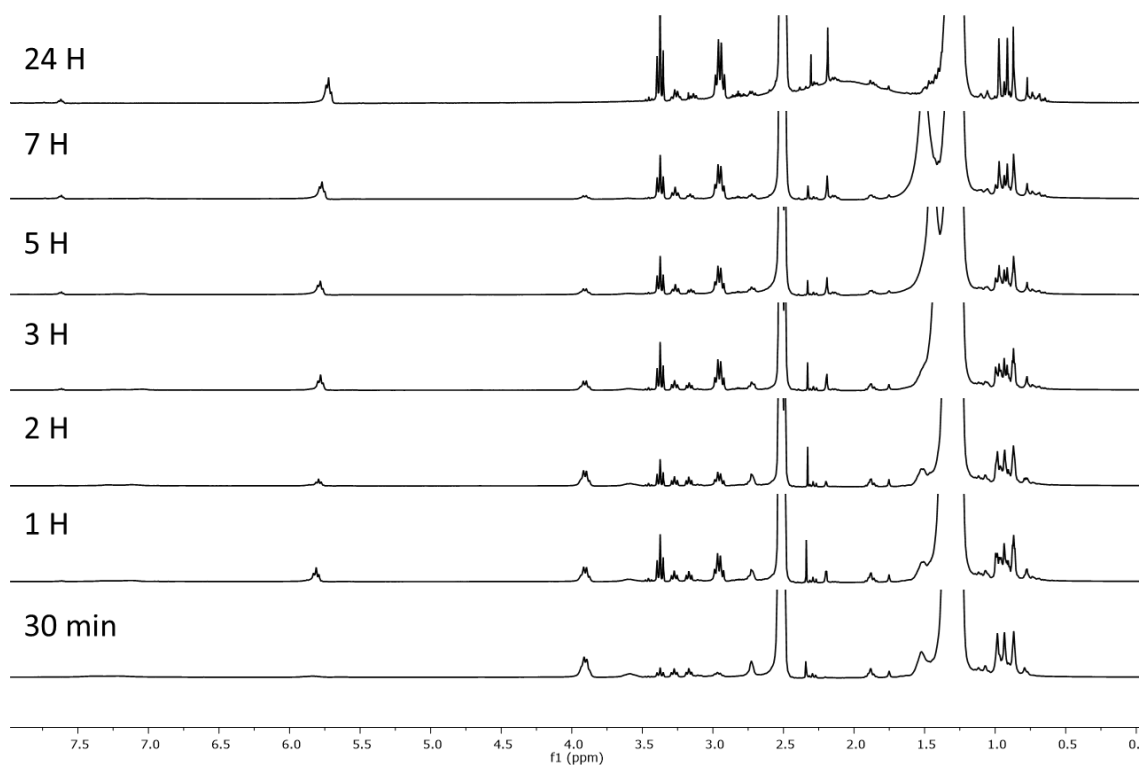


Figure S.2.11. Stacked ^1H NMR spectra for the kinetics of IPDI-PU depolymerisation with hexamethylenediamine as nucleophile with TBD:MSA as catalyst at 160 °C. (DMSO- d_6 , 300 MHz, 298 K)

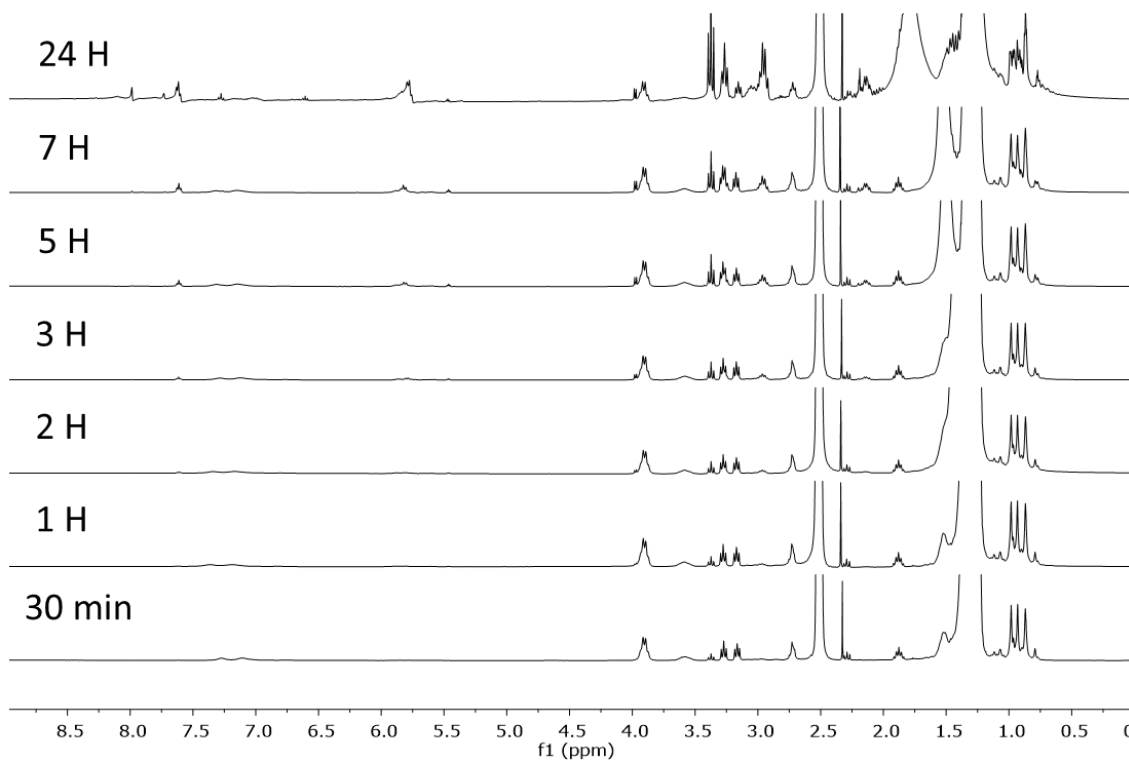


Figure S.2.12. Stacked ^1H NMR spectra for the kinetics of IPDI-PU depolymerisation with hexamethylenediamine as nucleophile with TBD:MSA as catalyst at 130 °C. (DMSO- d_6 , 300 MHz, 298 K)

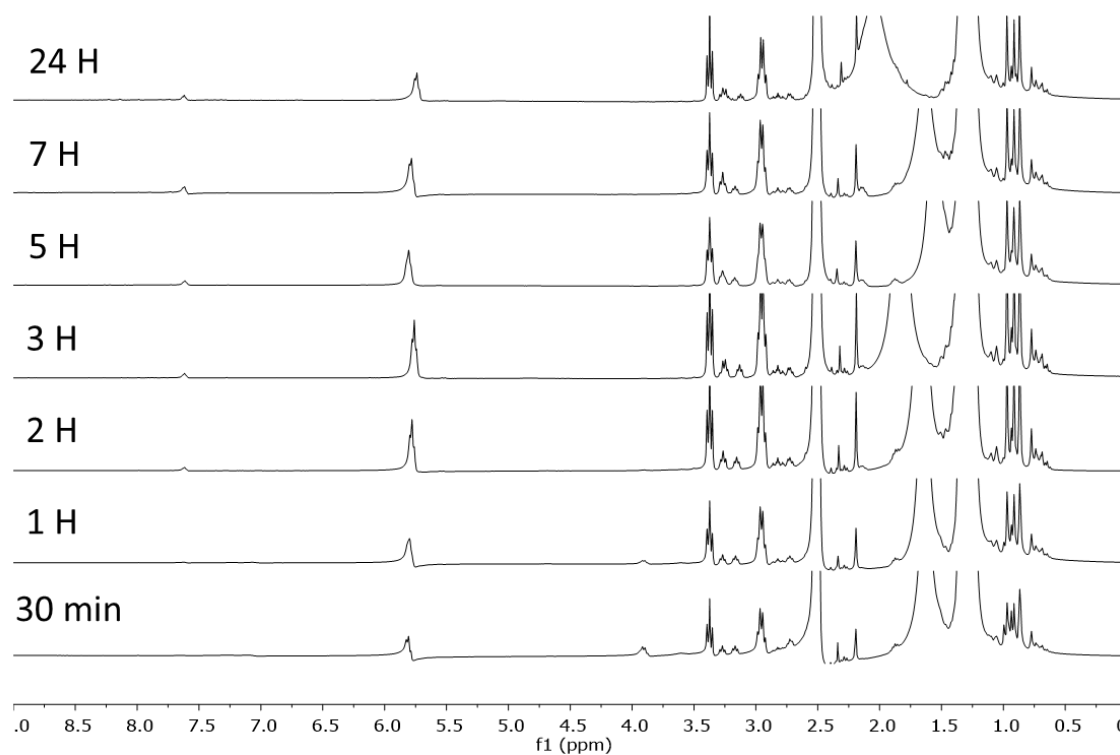


Figure S.2.13. Stacked ^1H NMR spectra for the kinetics of IPDI-PU depolymerisation with hexamethylenediamine as nucleophile with TBD:MSA as catalyst at 190 °C. (DMSO- d_6 , 300 MHz, 298 K)

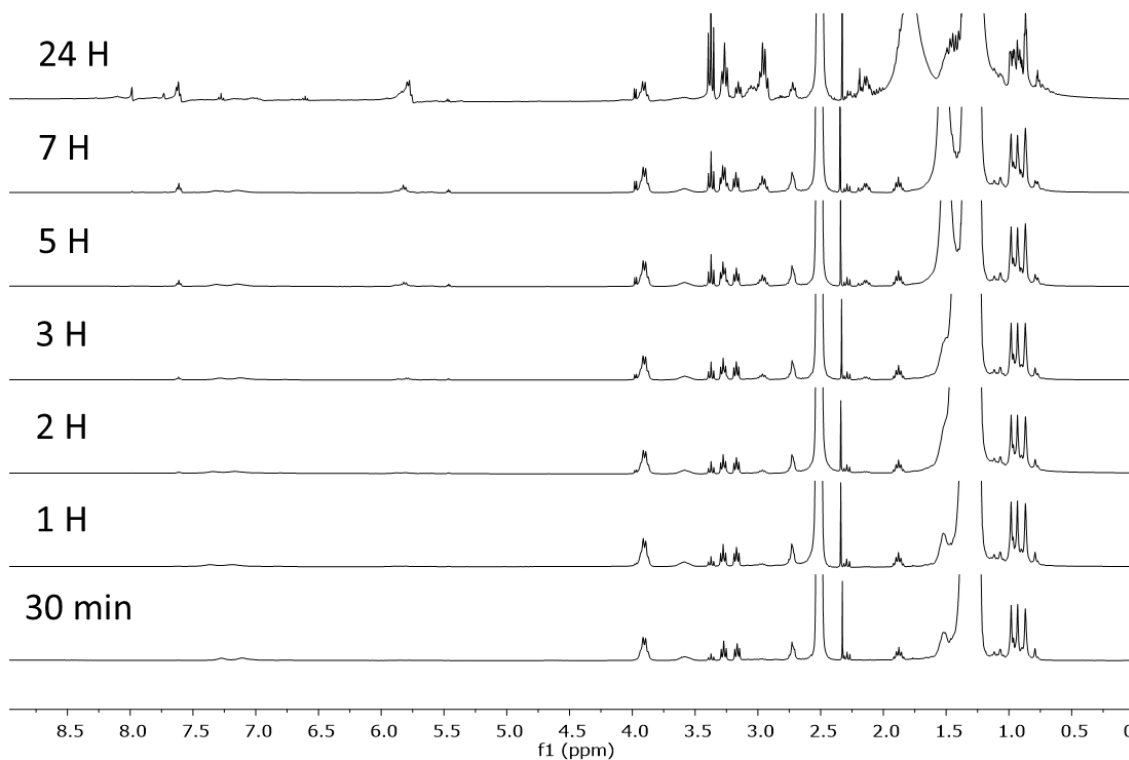


Figure S.2.14. Stacked ^1H NMR spectra for the kinetics of IPDI-PU depolymerisation with hexamethylenediamine as nucleophile with 0.3 eq. of TBD:MSA as catalyst at 130 °C. (DMSO- d_6 , 300 MHz, 298 K)

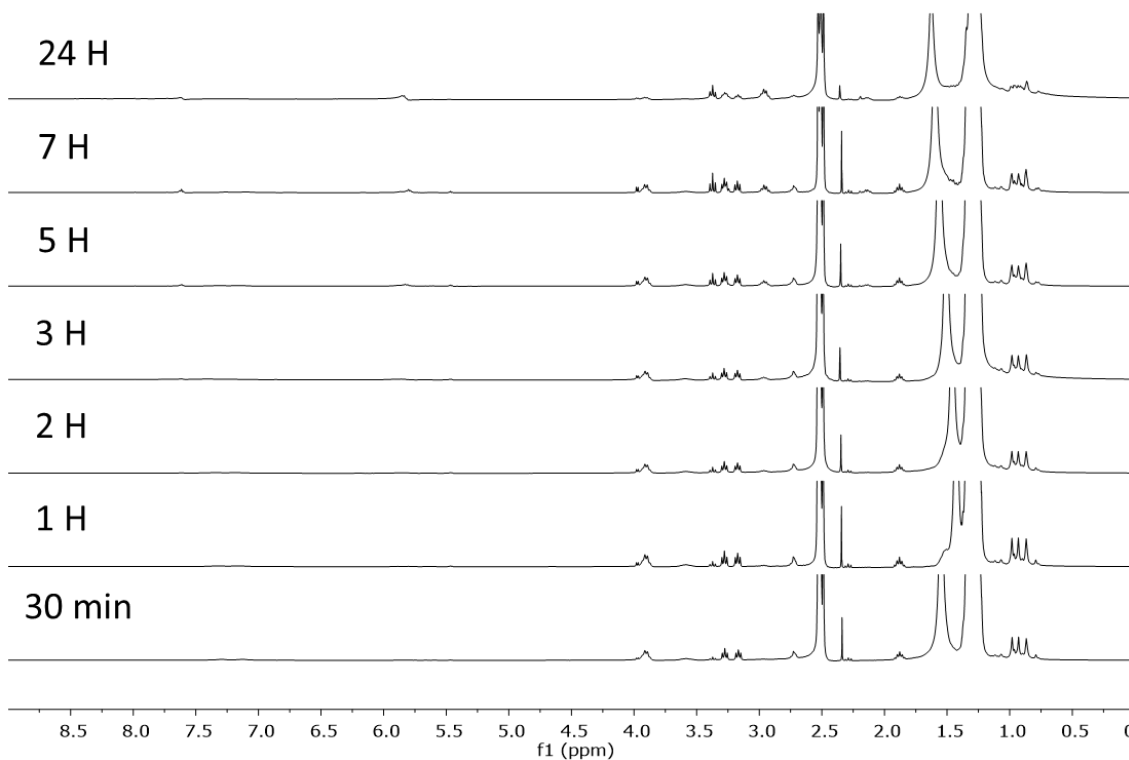


Figure S.2.15. Stacked ^1H NMR spectra for the kinetics of IPDI-PU depolymerisation with hexamethylenediamine as nucleophile with 0.45 eq. of TBD:MSA as catalyst at 130 °C. (DMSO- d_6 , 300 MHz, 298 K)

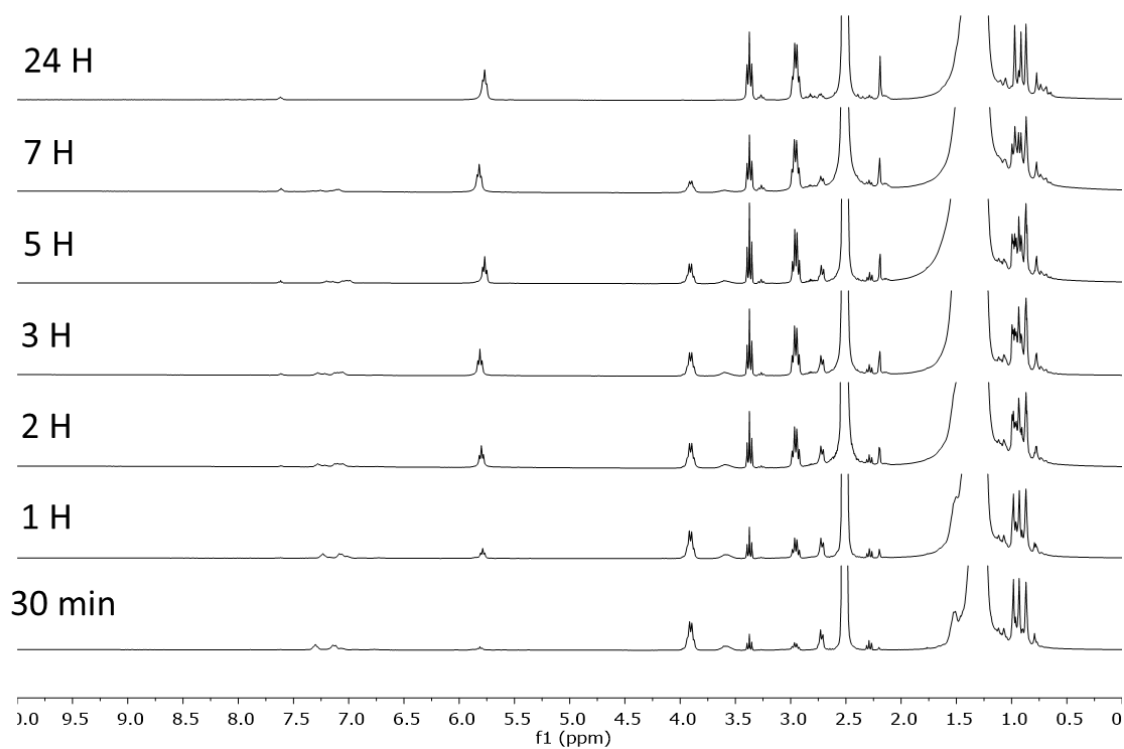


Figure S.2.16. Stacked ^1H NMR spectra for the kinetics of IPDI-PU depolymerisation with hexamethylenediamine as nucleophile without catalyst at 160 °C. (DMSO- d_6 , 300 MHz, 298 K)

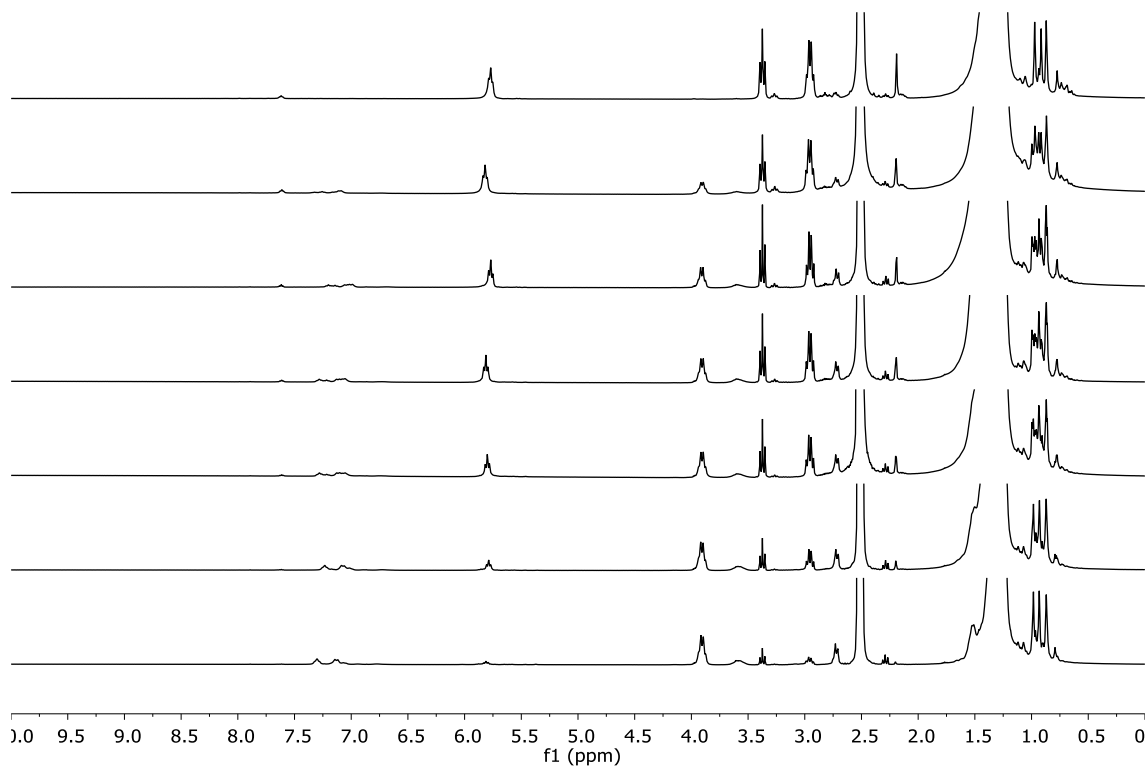


Figure S.2.17. Stacked ^1H NMR spectra for the kinetics of IPDI-PU depolymerisation with hexamethylenediamine as nucleophile without catalyst at 160 °C. (DMSO- d_6 , 300 MHz, 298 K)

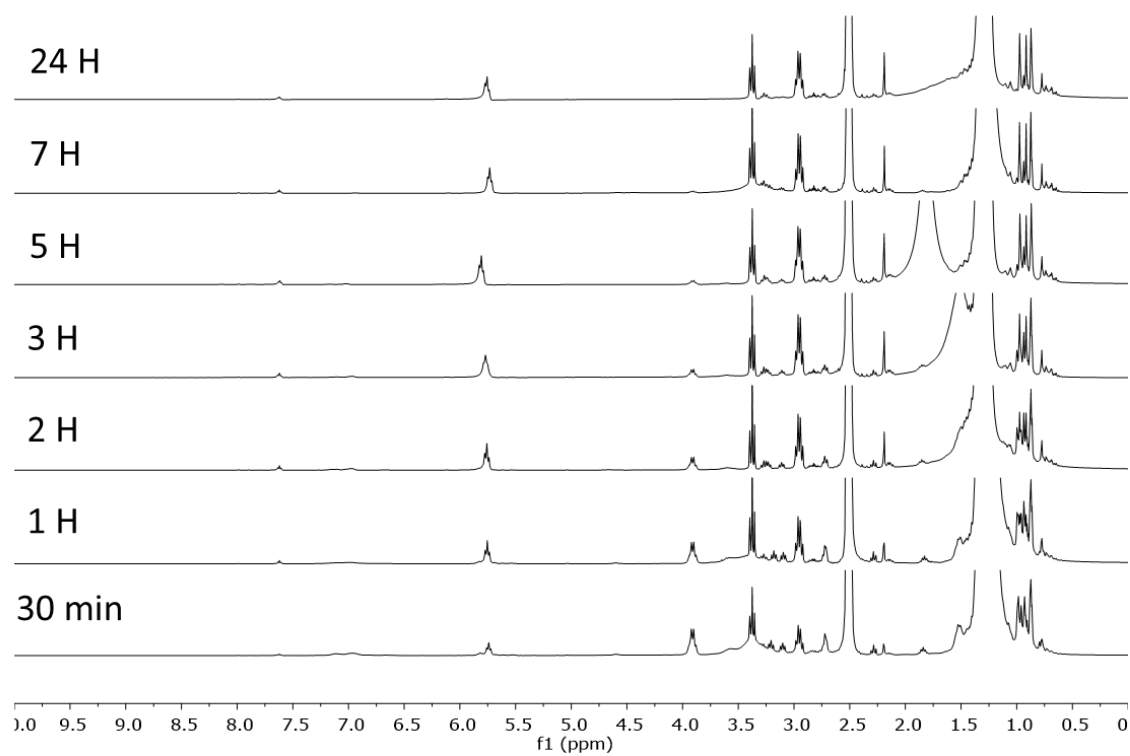


Figure S.2.18. Stacked ^1H NMR spectra for the kinetics of IPDI-PU depolymerisation with hexamethylenediamine as nucleophile with TBD as catalyst at 160 °C. (DMSO- d_6 , 300 MHz, 298 K)

Additional reaction kinetics plots followed by means of $^1\text{H-NMR}$

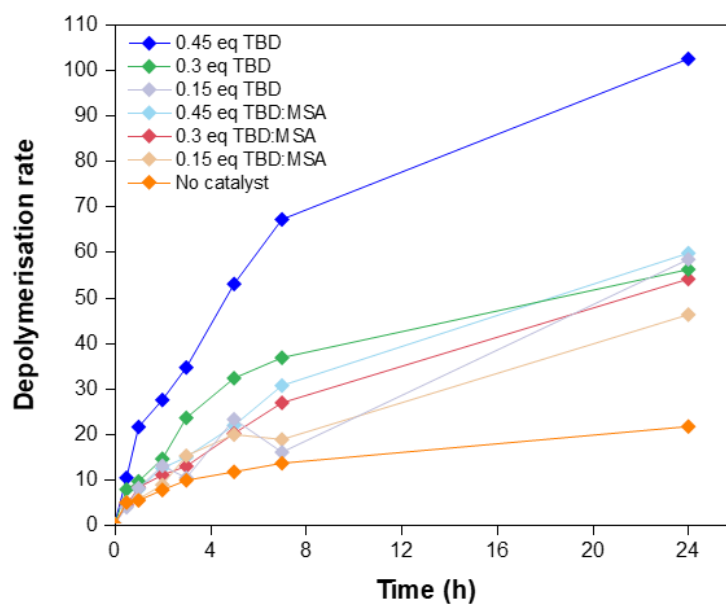


Figure S.2.19 Kinetic plots for the depolymerisation of IPDI-PU with hexamethylene diamine with different catalysts content and without catalyst at 130 °C.

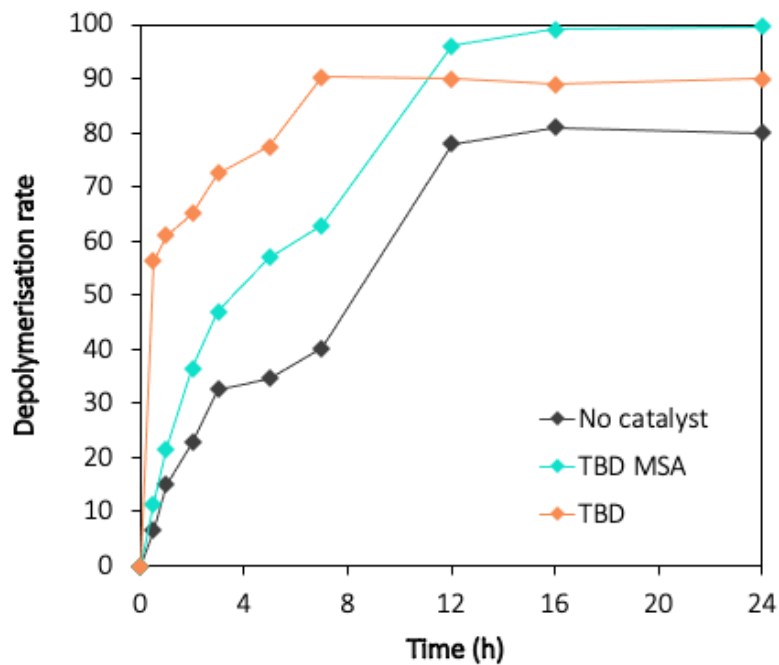


Figure S.2.20. Kinetic plots for the depolymerisation of IPDI-PU with hexamethylene diamine with different catalysts and without catalyst. Reaction conditions: IPDI-PU (1 eq.), hexamethylene diamine (10 eq.), 24 h, 160 °C.

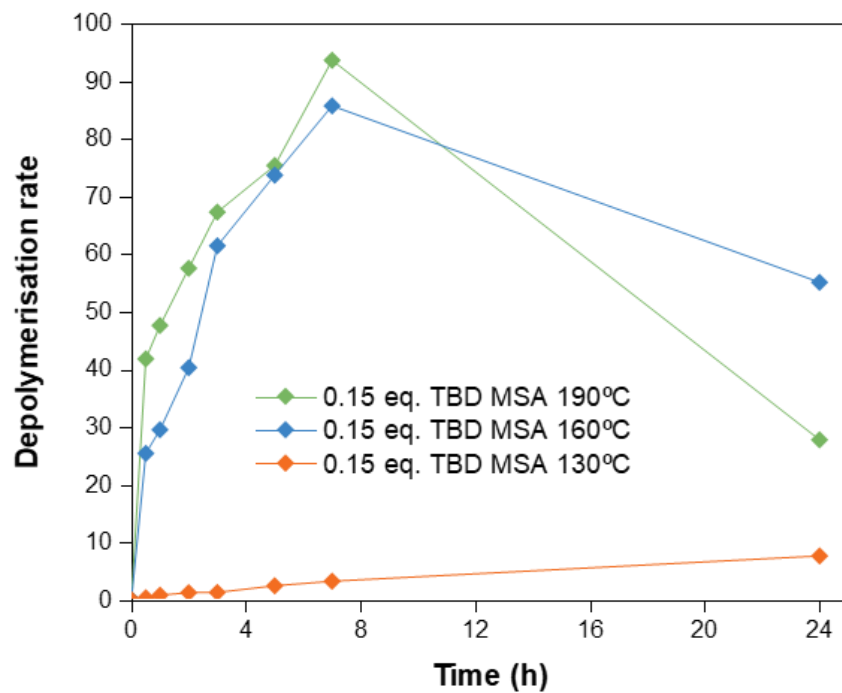


Figure S.2.21. Kinetic plots for the depolymerisation of IPDI-PU with 2-(methylamino)ethanol with TBD:MSA as catalysts at different temperatures.

¹H NMR spectra of the crude products for the depolymerisation of IPDI-PU with different amines

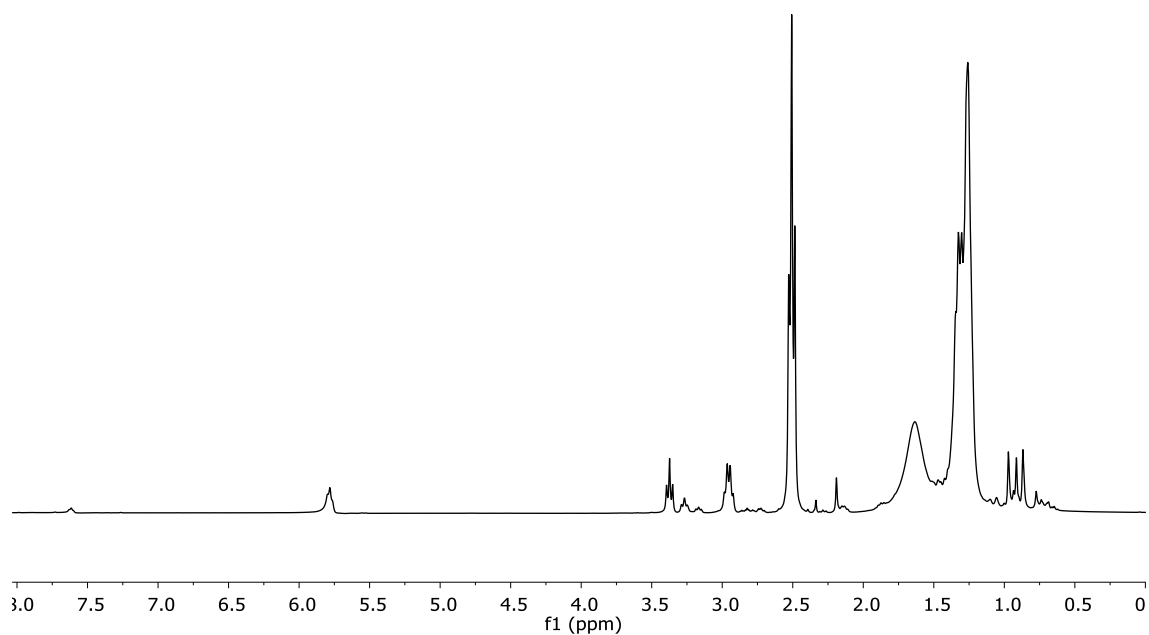


Figure S.2.22. ^1H NMR spectra in $\text{DMSO-}d_6$ of the crude product resulting from the depolymerisation of IPDI-PU with hexamethylene diamine as nucleophile. ($\text{DMSO-}d_6$, 300 MHz, 298 K)

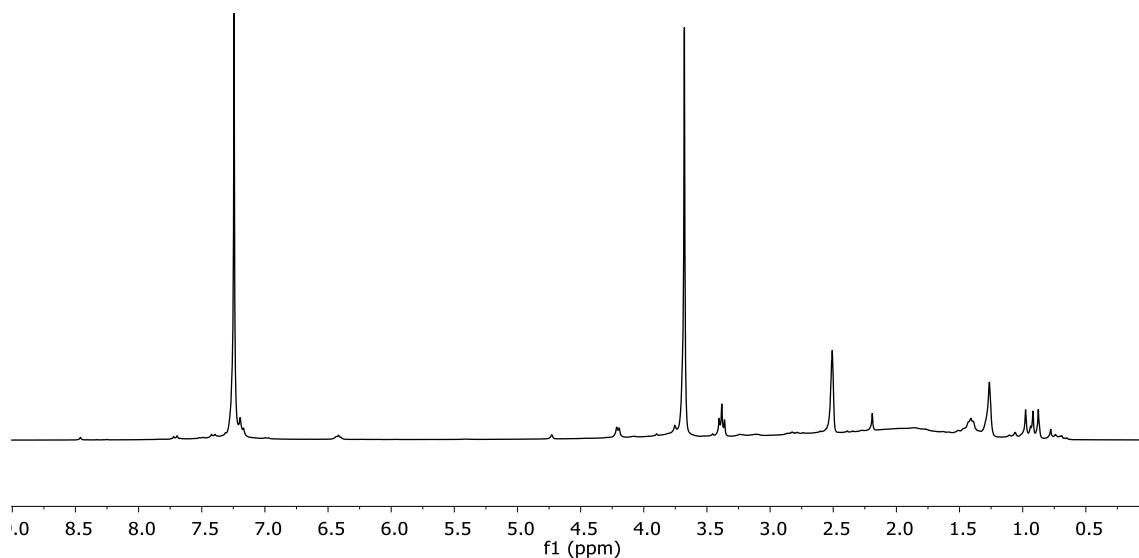


Figure S.2.23. ^1H NMR spectra in $\text{DMSO-}d_6$ of the crude product resulting from the depolymerisation of IPDI-PU with 1,4-phenylenedimethanamine as nucleophile. ($\text{DMSO-}d_6$, 300 MHz, 298 K)

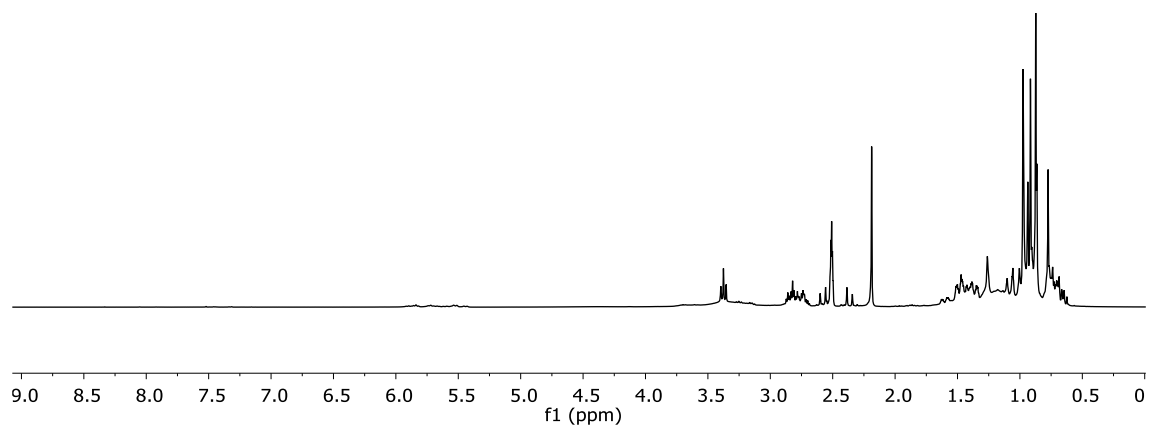


Figure S.2.24. ^1H NMR spectra in $\text{DMSO-}d_6$ of the crude product resulting from the depolymerisation of IPDI-PU with IPDA as nucleophile. ($\text{DMSO-}d_6$, 300 MHz, 298 K)

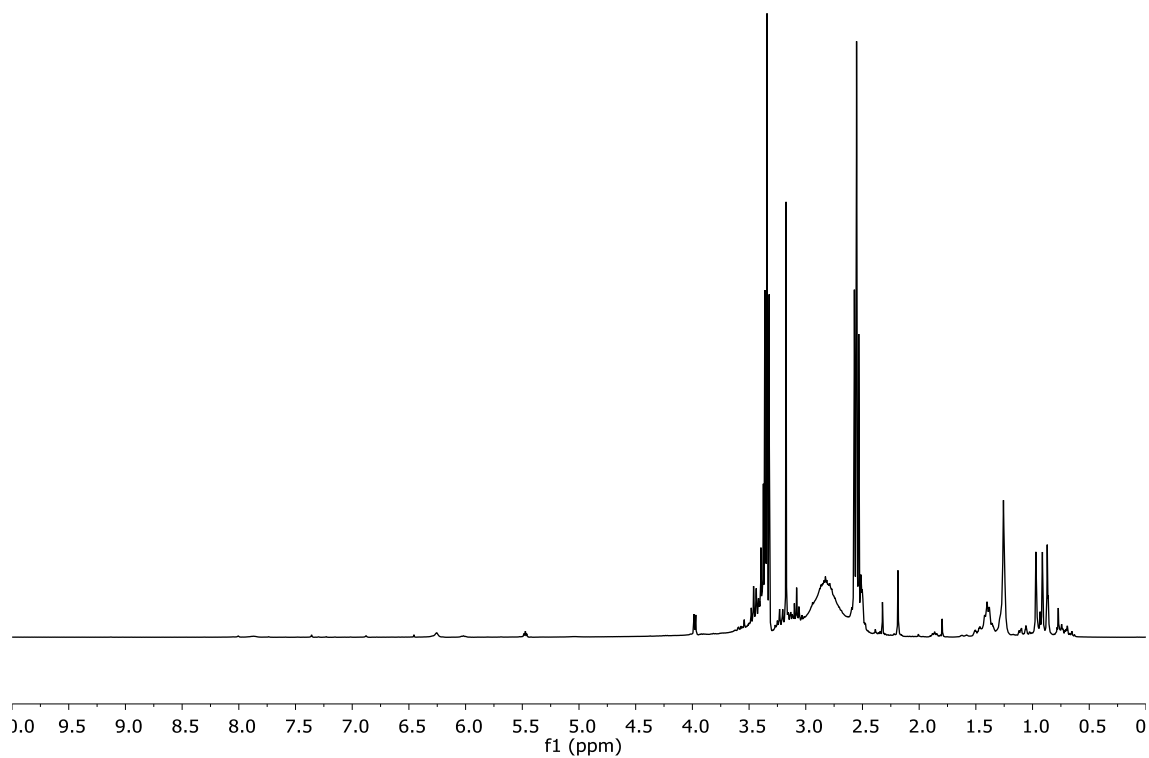


Figure S.2.25. ¹H NMR spectra in DMSO-*d*₆ of the crude product resulting from the depolymerisation of IPDI-PU with ethanolamine as nucleophile. (DMSO-*d*₆, 300 MHz, 298 K)

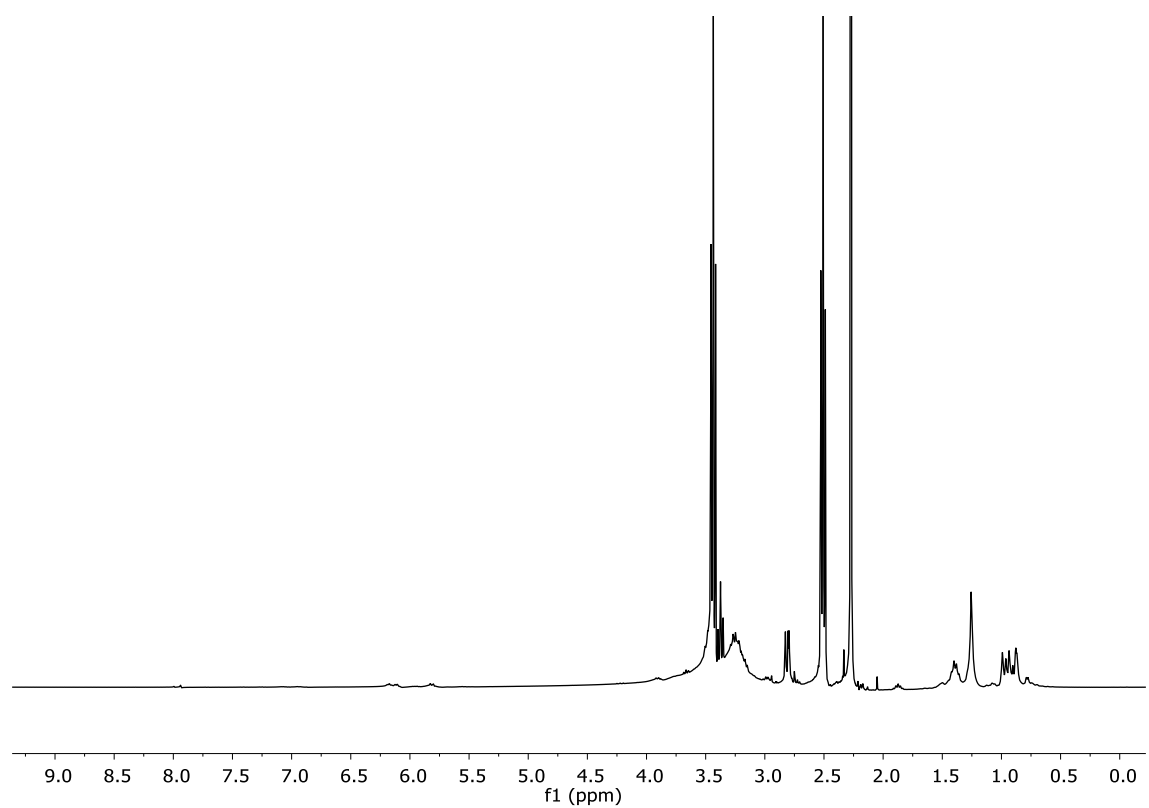


Figure S.2.26. ¹H NMR spectra in DMSO-*d*₆ of the crude product resulting from the depolymerisation of IPDI-PU with 2-(methylamino)ethan-1-ol as nucleophile. (DMSO-*d*₆, 300 MHz, 298 K)

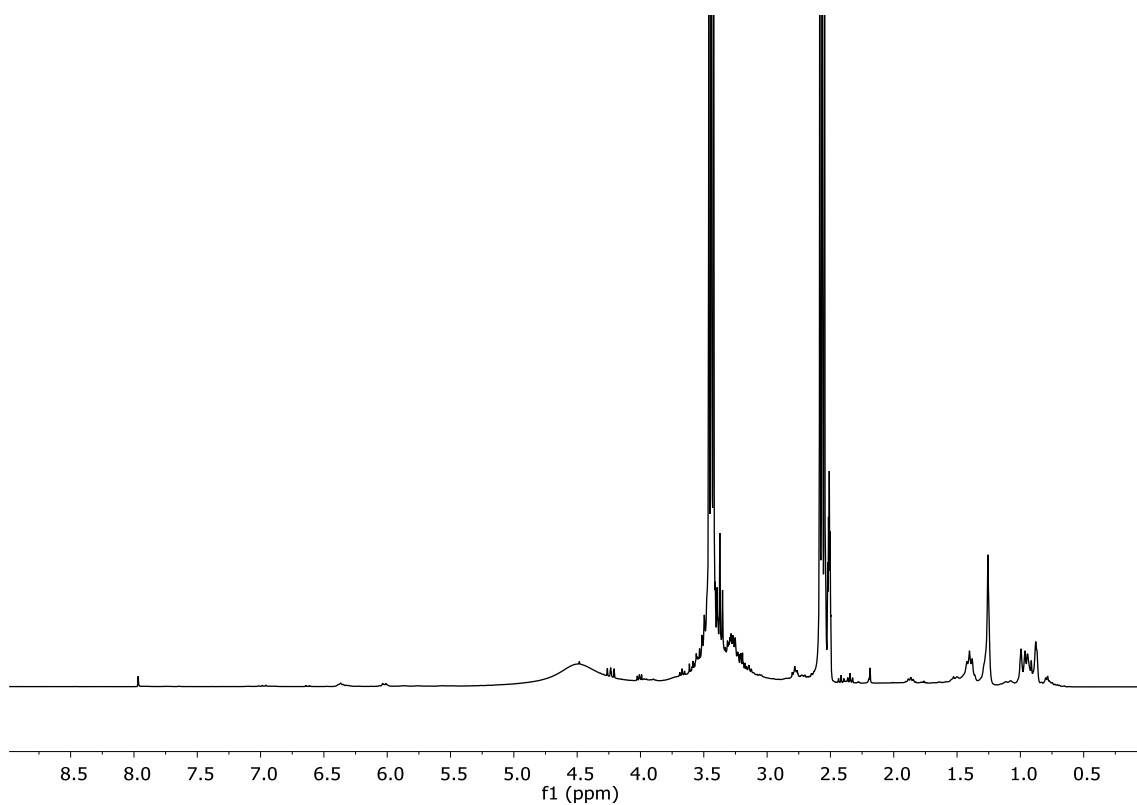


Figure S.2.27. ^1H NMR spectra in $\text{DMSO-}d_6$ of the crude product resulting from the depolymerisation of IPDI-PU with diethanolamine as nucleophile. ($\text{DMSO-}d_6$, 300 MHz, 298 K)

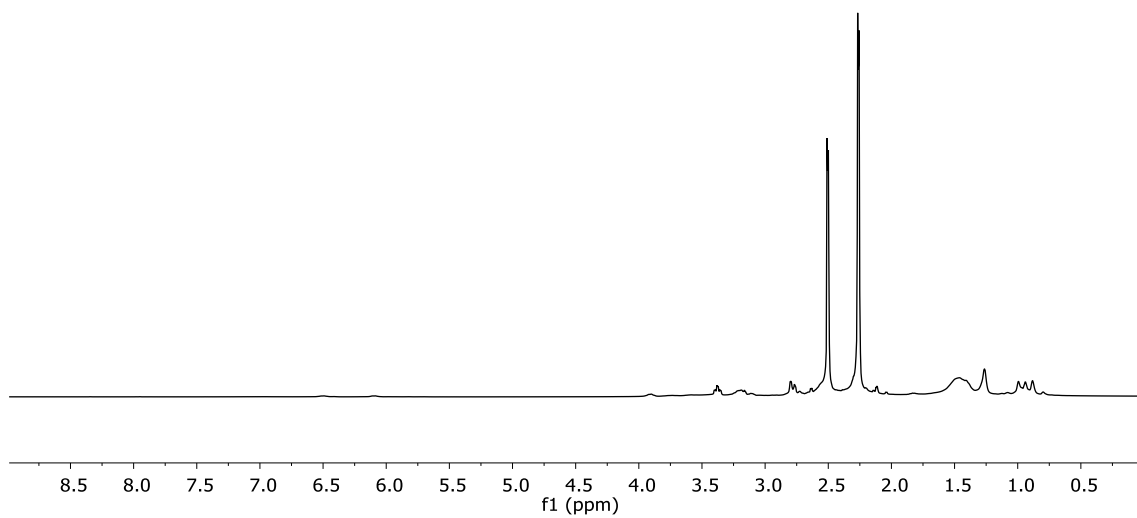


Figure S.2.28. ^1H NMR spectra in $\text{DMSO-}d_6$ of the crude product resulting from the depolymerisation of IPDI-PU with N,N,N -trimethylethane-1,2-diamine as nucleophile. ($\text{DMSO-}d_6$, 300 MHz, 298 K)

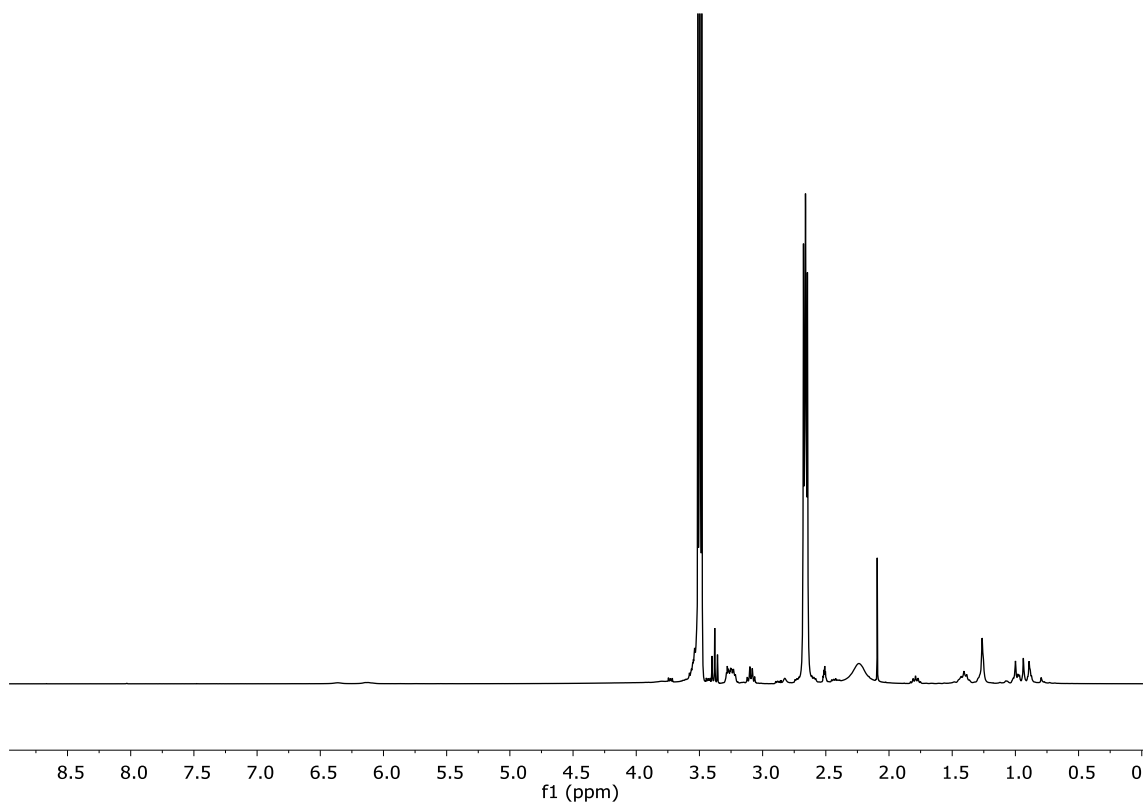


Figure S.2.29. ^1H NMR spectra in $\text{DMSO-}d_6$ of the crude product resulting from the depolymerisation of IPDI-PU with morpholine as nucleophile. ($\text{DMSO-}d_6$, 300 MHz, 298 K)

FTIR spectroscopy analysis for the reaction with 2-(methylamino)ethanol

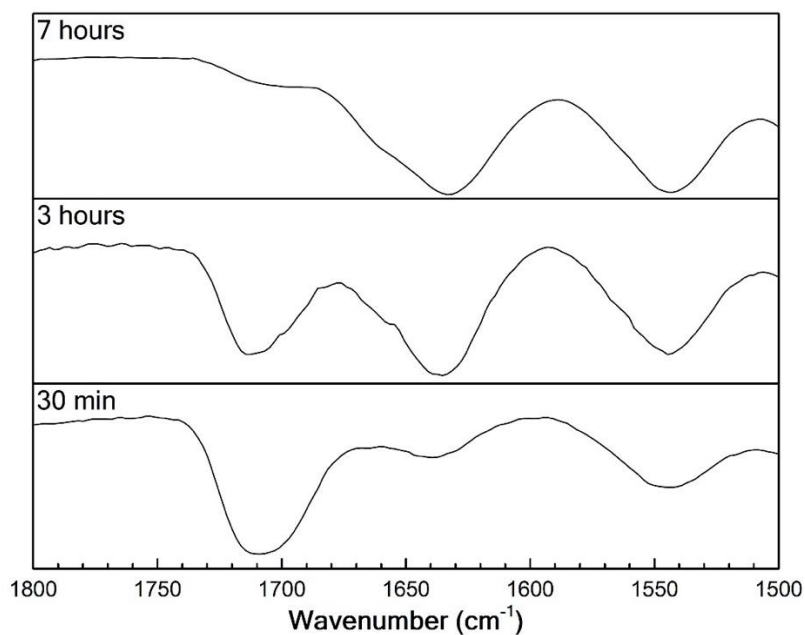


Figure S.2.30. Kinetics for the depolymerisation of IPDI-PU with 2-(methylamino)ethan-1-ol as nucleophile.

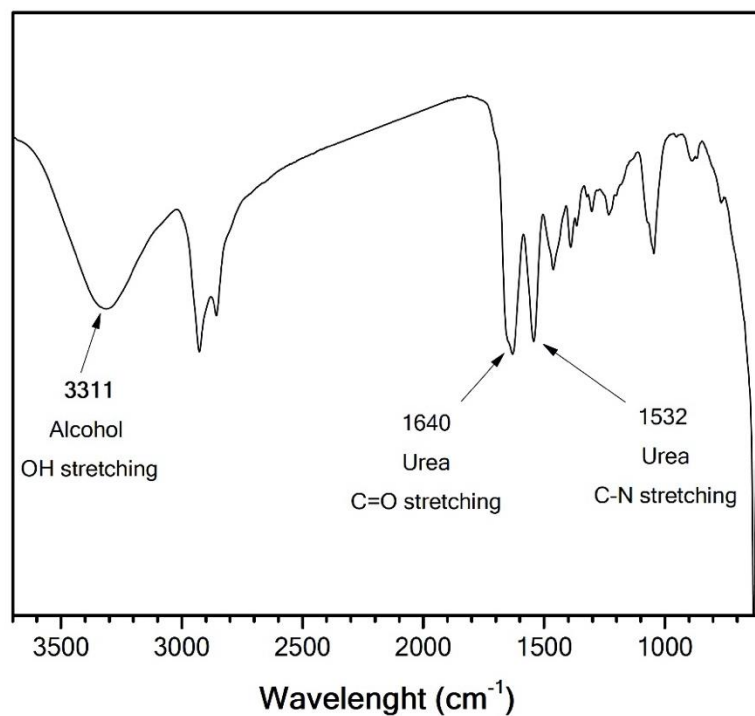


Figure S.2.31. FTIR spectra of the crude product resulting from the depolymerisation of IPDI-PU with 2-(methylamino)ethan-1-ol as nucleophile.

HPLC-MS analysis for the reaction with 2-(methylamino)ethan-1-ol

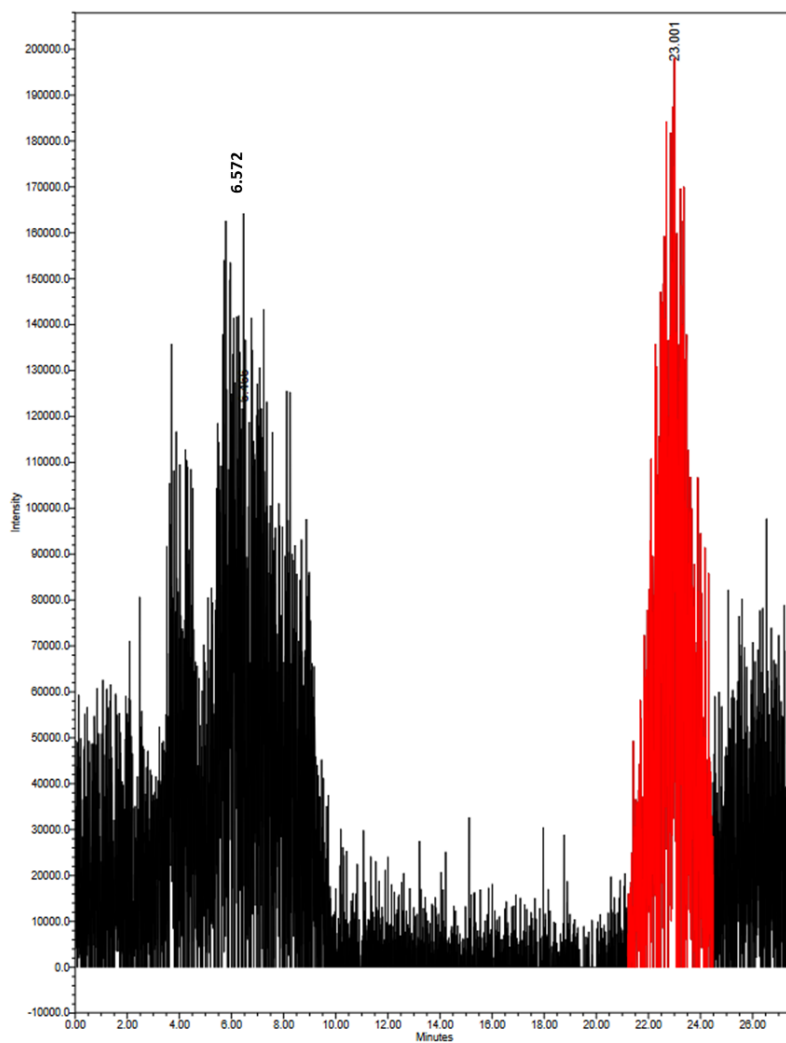


Figure S.2.32. HPLC-MS complete chromatogram. Two main signals can be observed at 6.572 min and 23 min.

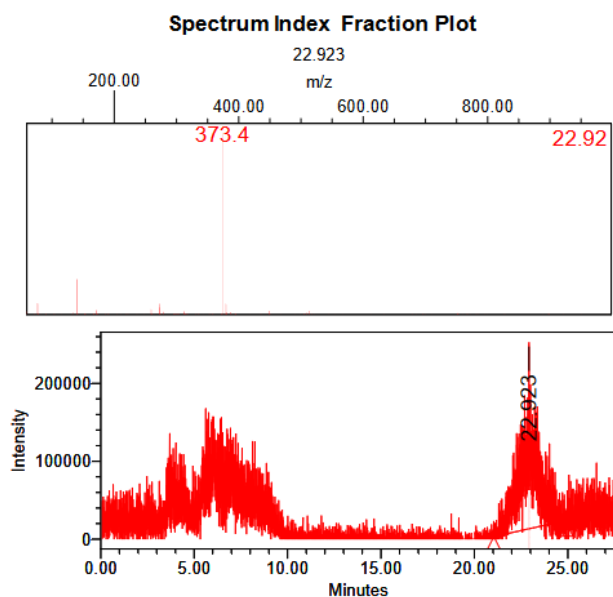


Figure S.2.33. Spectrum index fraction plot and auto-scaled chromatogram showing the expected di-urea product (373.4 m/z) on the crude product of the reaction at 22.923 min retention time.

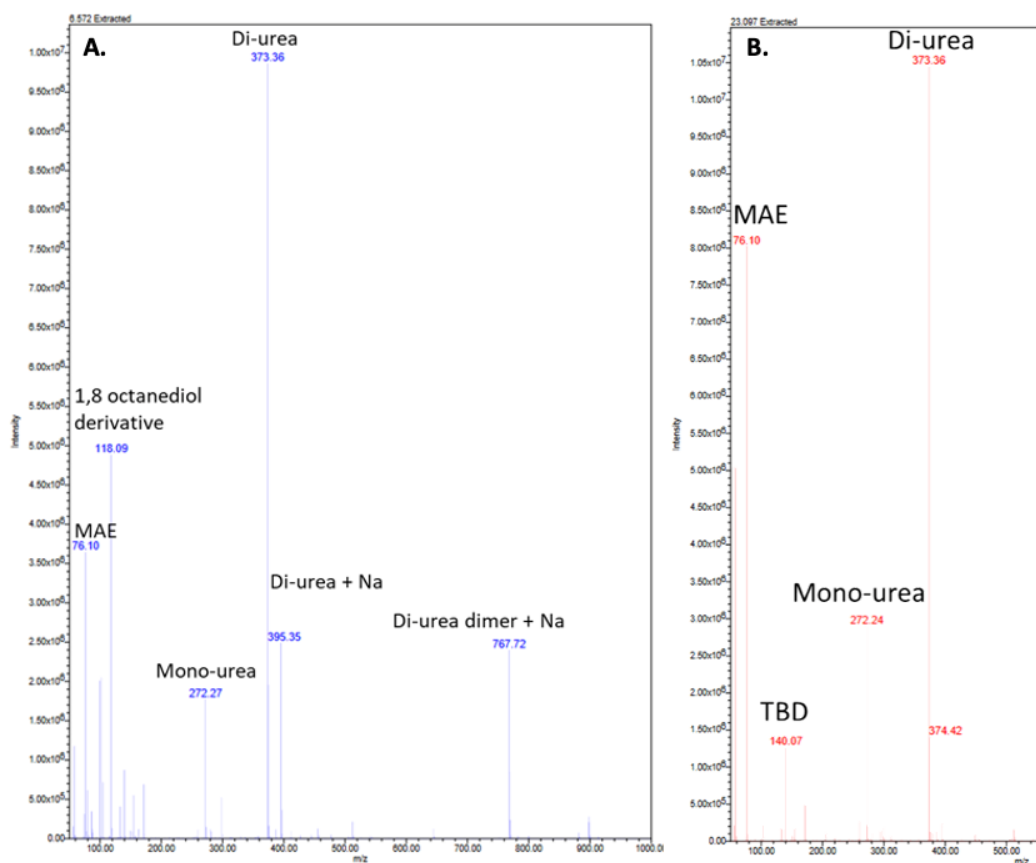


Figure S.2.34. Mass spectra **A.** at 6.572 min retention time and **B.** at 23.067 min of retention time.

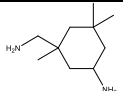
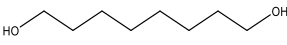
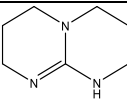
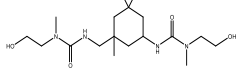
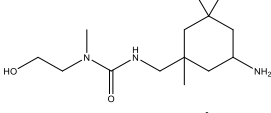
A. In this chromatogram, the signal characteristic of the 2-(methylamino)ethanol (MAE) can be observed at 76.10 m/z, the di-urea at 373.36 m/z, the di-urea with sodium at 395.35 m/z and the corresponding dimer with sodium at 767.72 m/z, are clearly observed. Different signals from the

fragmentation of some of the products are also observed. A signal at 272.27 m/z is identified as corresponding to the mono-urea which was confirmed to appear because of fragmentation during the analysis since this signal is also present in the spectrum of the lone di-urea. A signal at 118.09 m/z corresponds to the fragmentation of 1,8-octanediol which can be observed in the spectrum of the crude product of the reaction and the spectrum of the commercial product. Interestingly, the expected signal at 146 m/z does not appear, neither for the crude product nor for the commercial product. It can be because of the harsh ionisation conditions applied on the mass spectrometer, the 1,8-octanediol could be fragmented to give heptanol.

B. The characteristic signal of 2-(methylamino)ethanol (MAE) (76.10 m/z) can be identified as well as the signal for TBD (at 140.07 m/z) and for the di-urea product (373.36 m/z) and the corresponding fragmentation into mono-urea (272.24 m/z).

The chromatogram of the lone IPDA presents two characteristic signals (at 170 m/z and at 340 m/z, corresponding to the dimer) which cannot be identified in none of these chromatograms of the crude product of the reaction, which clearly attests that no IPDA was obtained from the depolymerisation IPDI-PU with 2-(methylamino)ethanol.

Table S1. Different products identified in the crude product by HPLC-MS and their corresponding m/z.

Molecule	Observed?	Fragmentation product	m/z
 IPDA	No	N.A	170.18
 1,8-octanediol	Yes (only fragmentation product)	Heptanol	146 (1,8-octanediol) heptanol (116.09)
 TBD	Yes	N.A	140.01
 Di-urea product	Yes	Mono-urea	373.36
 Mono-urea product	Yes	Product of the fragmentation of the di-urea	272.24

^1H NMR spectra of the crude products for the depolymerisations of TDI-PU

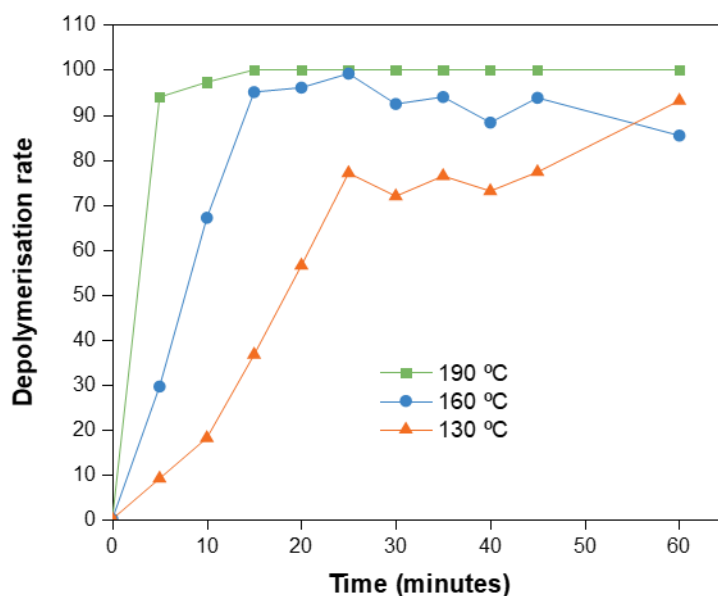


Figure S.2.35 Plot of TDI PU depolymerisation reactions by hexamethylenediamine using 0.15 eq. TBD:MSA as catalyst at different temperatures.

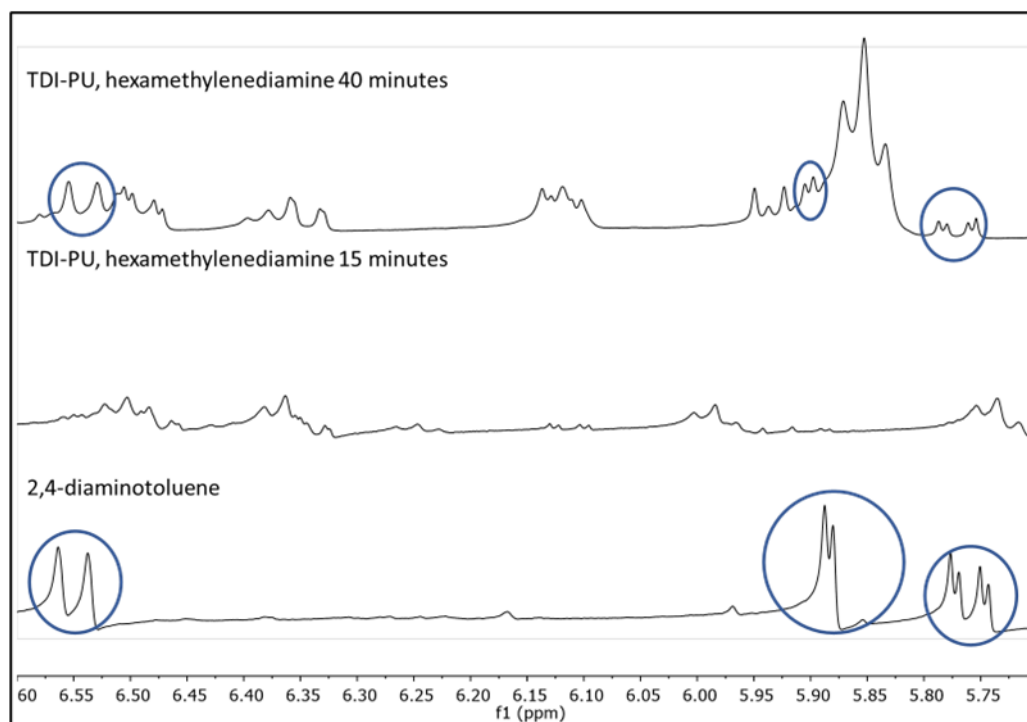


Figure S.2.36 ^1H -NMR spectra of pure 2,4-diaminotoluene and TDI-PU depolymerisation reaction carried out using TBD:MSA as catalyst 160 °C.

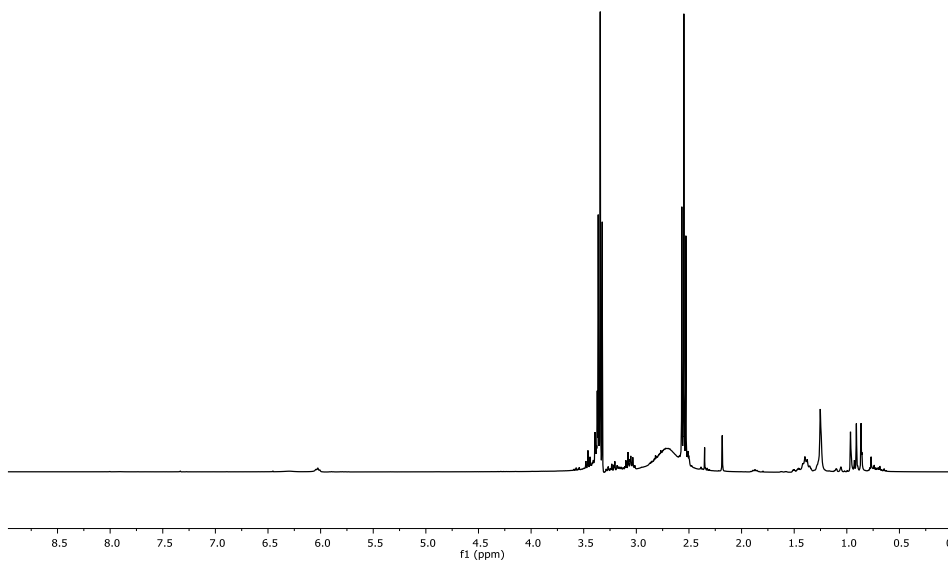


Figure S.2.37. ¹H NMR spectra in DMSO-*d*₆ of the crude product resulting from the depolymerisation of IPDI-PU with ethanolamine as nucleophile. (DMSO-*d*₆, 300 MHz, 298 K)

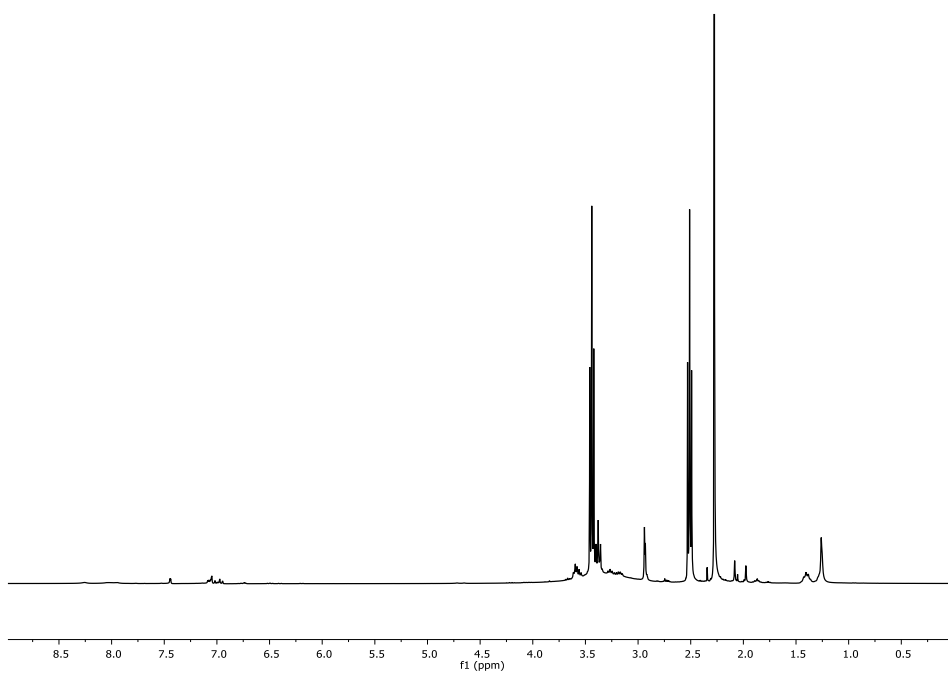


Figure S.2.38. ¹H NMR spectra in DMSO-*d*₆ of the crude product resulting from the depolymerisation of TDI-PU with 2-(methylamino)ethan-1-ol as nucleophile. (DMSO-*d*₆, 300 MHz, 298 K)

^1H NMR spectra of the crude products for the depolymerisation of IPDI-PU with 2-(methylamino)ethan-1-ol with different catalysts and various temperatures

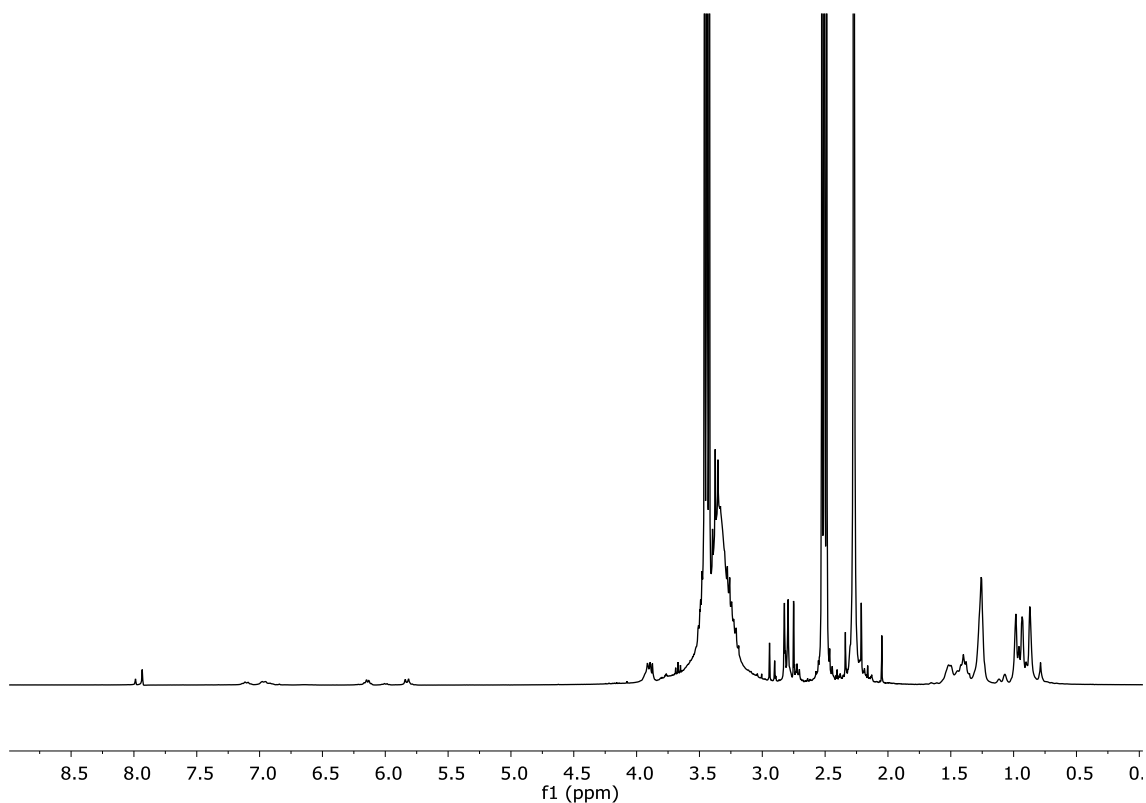


Figure S.2.39. ^1H NMR spectra in $\text{DMSO-}d_6$ of the crude product resulting from the depolymerisation of IPDI-PU with 2-(methylamino)ethan-1-ol as nucleophile without catalyst. ($\text{DMSO-}d_6$, 300 MHz, 298 K)

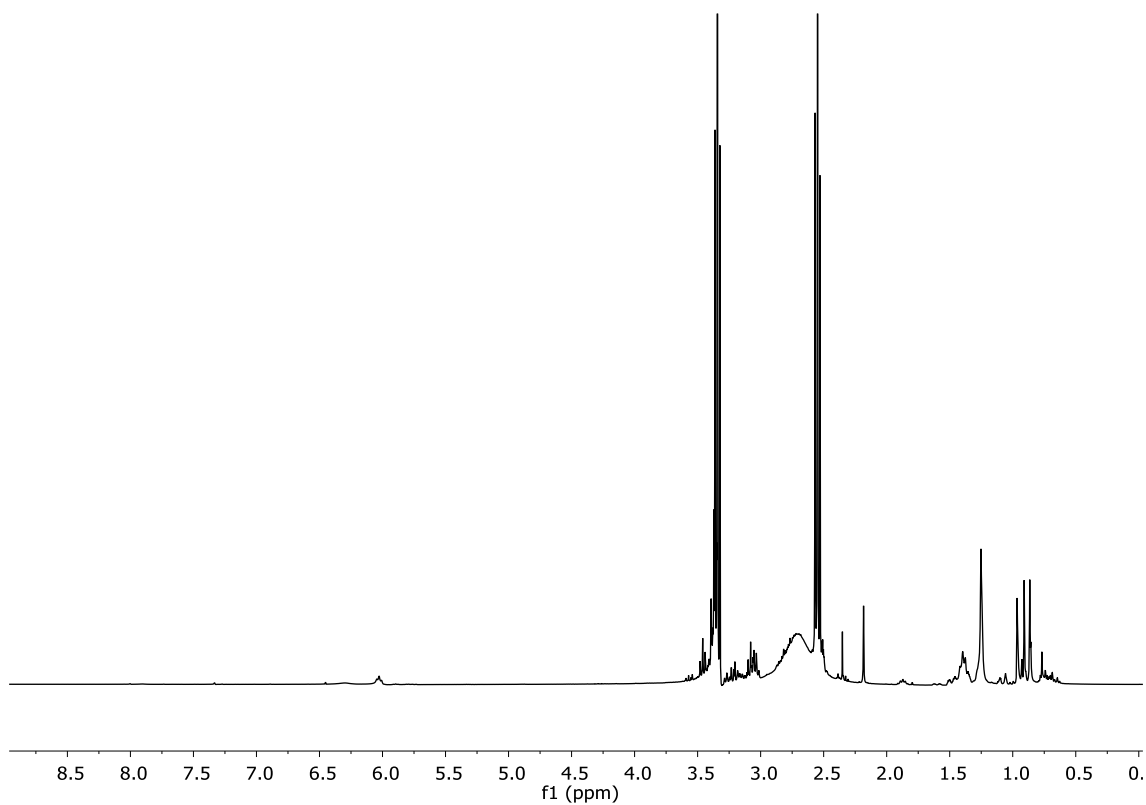


Figure S.2.40. ^1H NMR spectra in $\text{DMSO-}d_6$ of the crude product resulting from the depolymerisation of IPDI-PU with 2-(methylamino)ethan-1-ol as nucleophile with TBD:MSA. ($\text{DMSO-}d_6$, 300 MHz, 298 K)

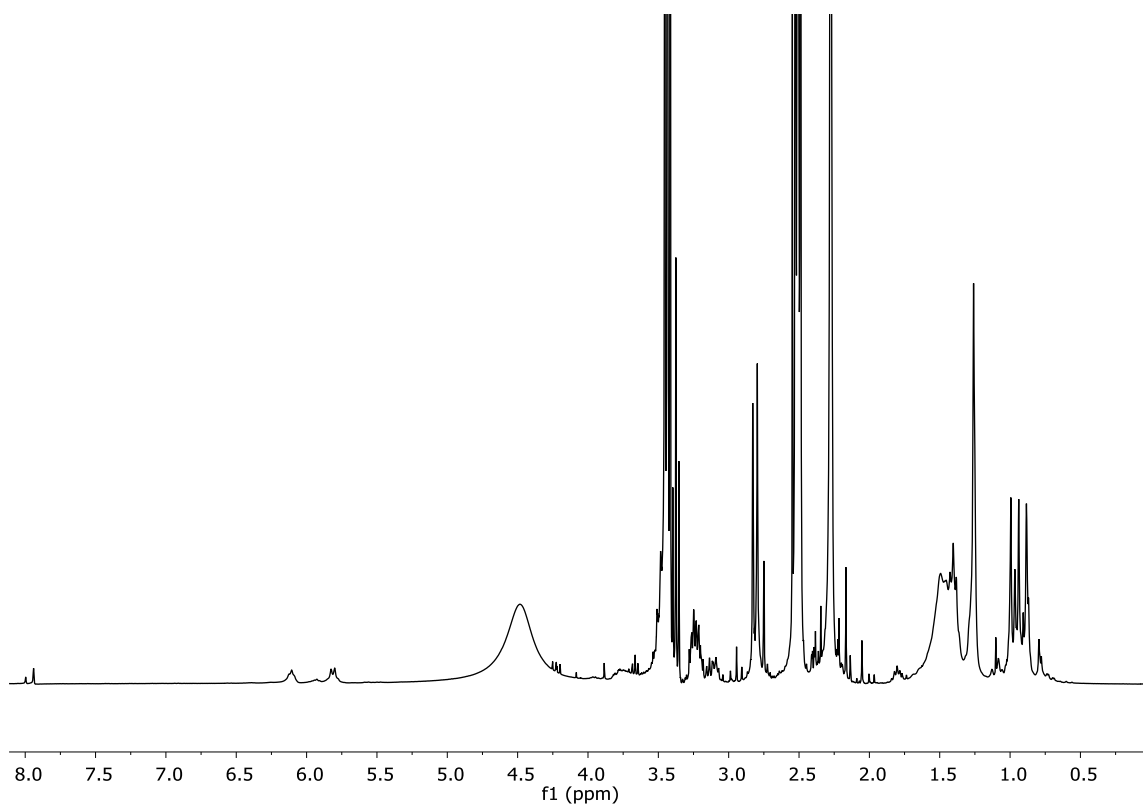


Figure S.2.41. ^1H NMR spectra in $\text{DMSO-}d_6$ of the crude product resulting from the depolymerisation of IPDI-PU with 2-(methylamino)ethan-1-ol as nucleophile with TBD. ($\text{DMSO-}d_6$, 300 MHz, 298 K)

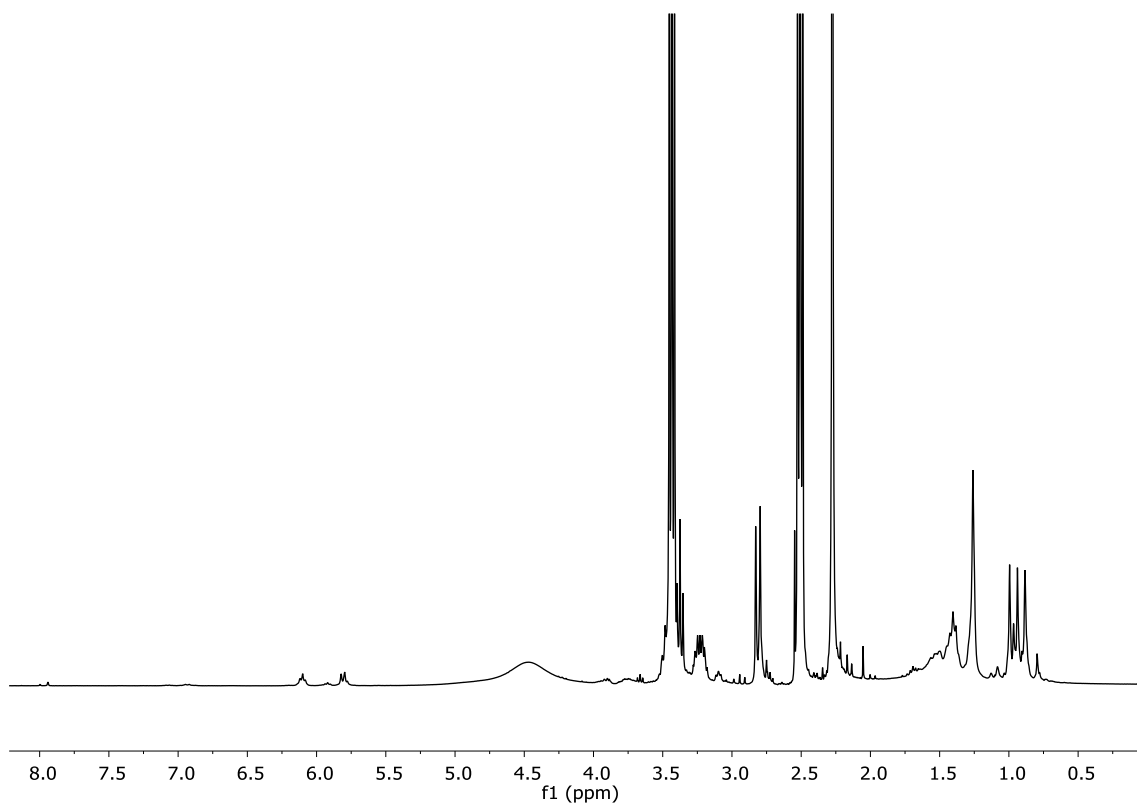


Figure S.2.42. ^1H NMR spectra in $\text{DMSO-}d_6$ of the crude product resulting from the depolymerisation of IPDI-PU with 2-(methylamino)ethan-1-ol as nucleophile with DBU. ($\text{DMSO-}d_6$, 300 MHz, 298 K)

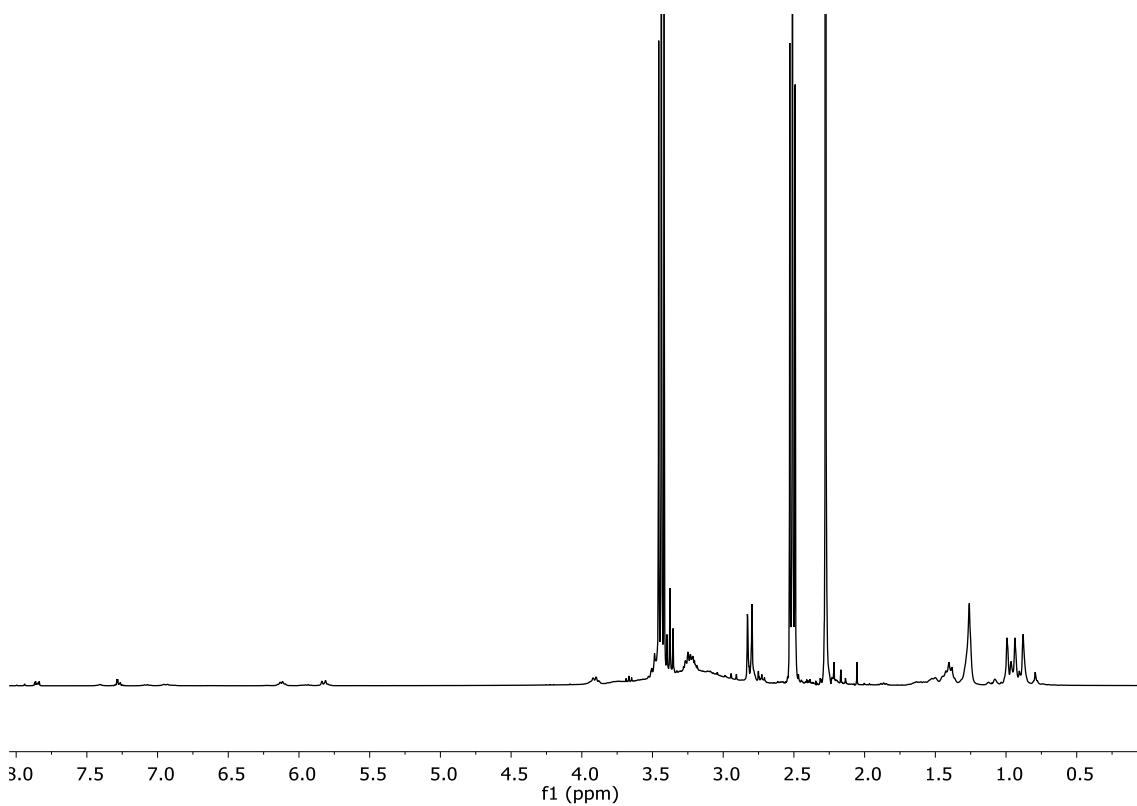


Figure S.2.43. ^1H NMR spectra in $\text{DMSO-}d_6$ of the crude product resulting from the depolymerisation of IPDI-PU with 2-(methylamino)ethan-1-ol as nucleophile with DBU:BA. ($\text{DMSO-}d_6$, 300 MHz, 298 K)

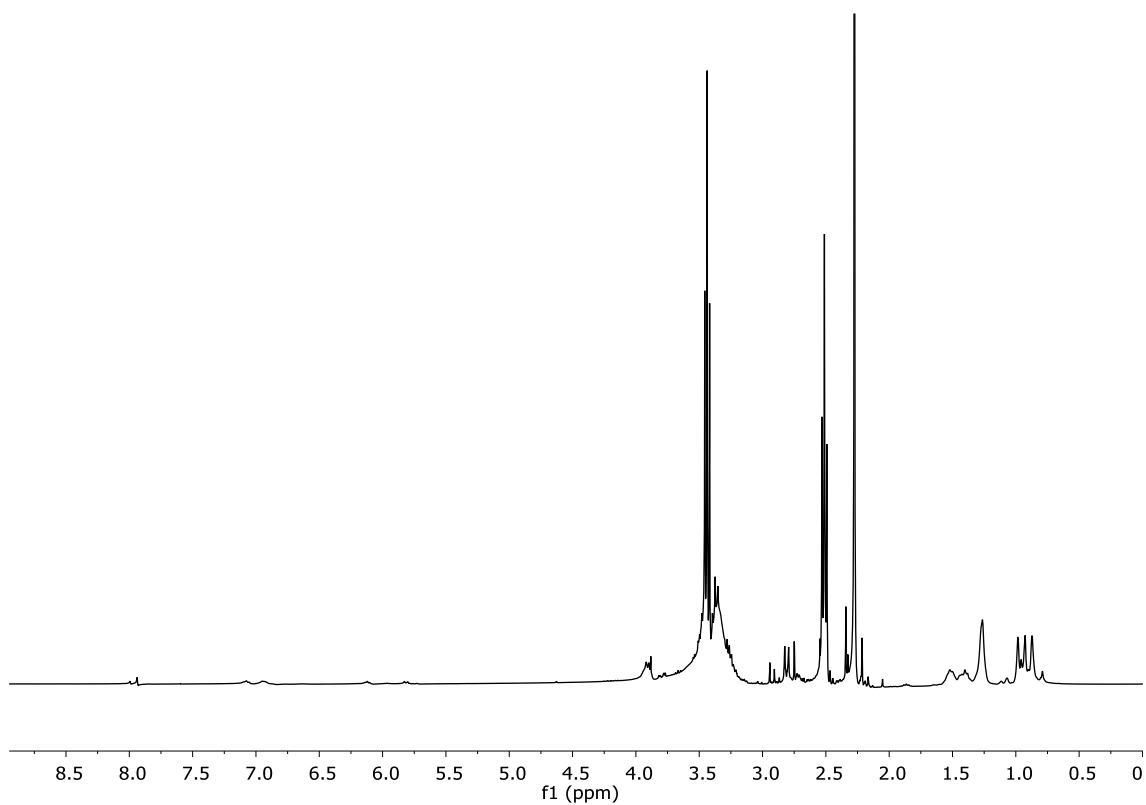


Figure S.2.44. ^1H NMR spectra in $\text{DMSO-}d_6$ of the crude product resulting from the depolymerisation of IPDI-PU with 2-(methylamino)ethan-1-ol as nucleophile at 130 °C. ($\text{DMSO-}d_6$, 300 MHz, 298 K)

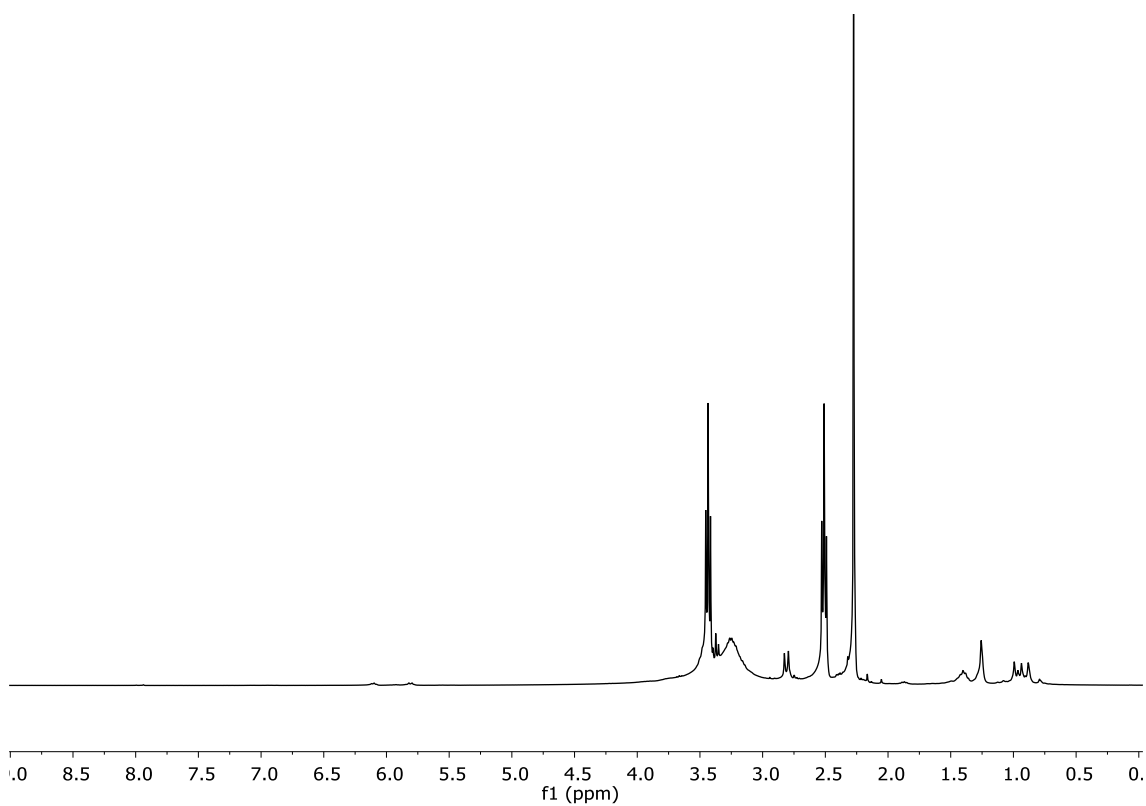


Figure S.2.45. ^1H NMR spectra in $\text{DMSO-}d_6$ of the crude product resulting from the depolymerisation of IPDI-PU with 2-(methylamino)ethan-1-ol as nucleophile at 190 °C. ($\text{DMSO-}d_6$, 300 MHz, 298 K)

MALDI analysis of the recovered polyol after PU foam depolymerisation

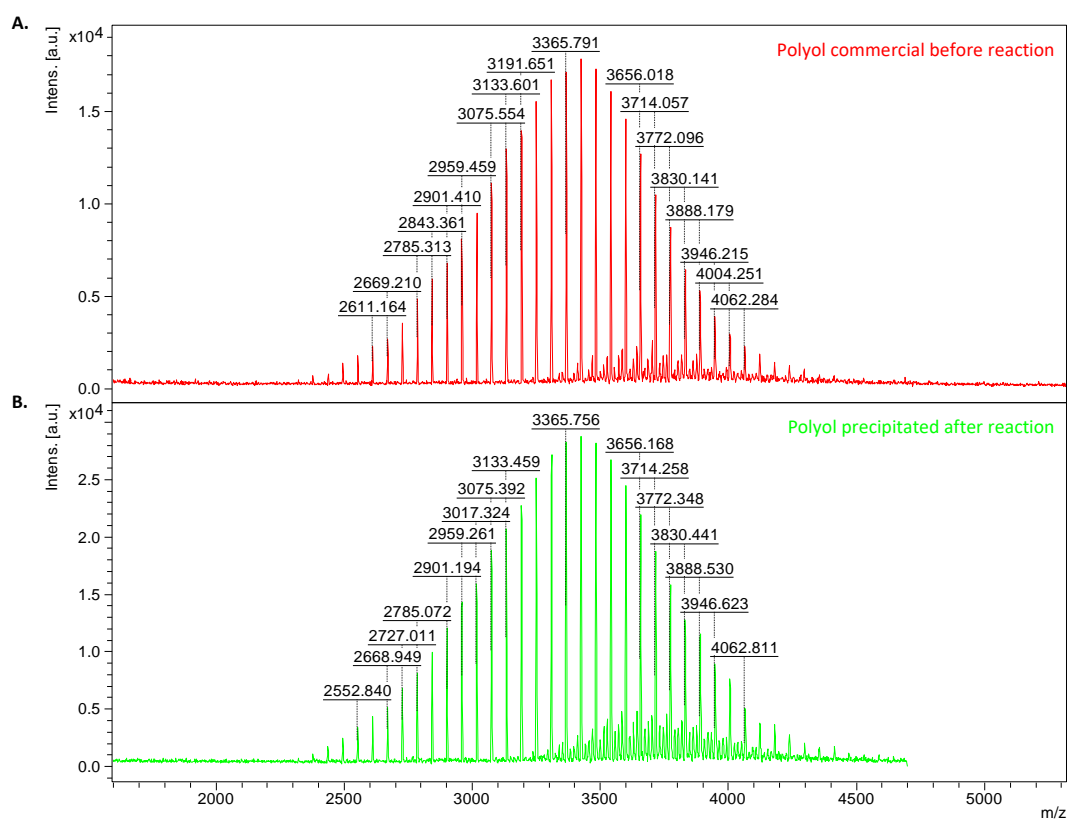


Figure S.2.46. MALDI analysis of the polyol **A.** before the polymerisation and **B.** the recovered polyol after depolymerisation and purification.

^1H NMR spectra of the crude products for the depolymerisations of the commercial foams

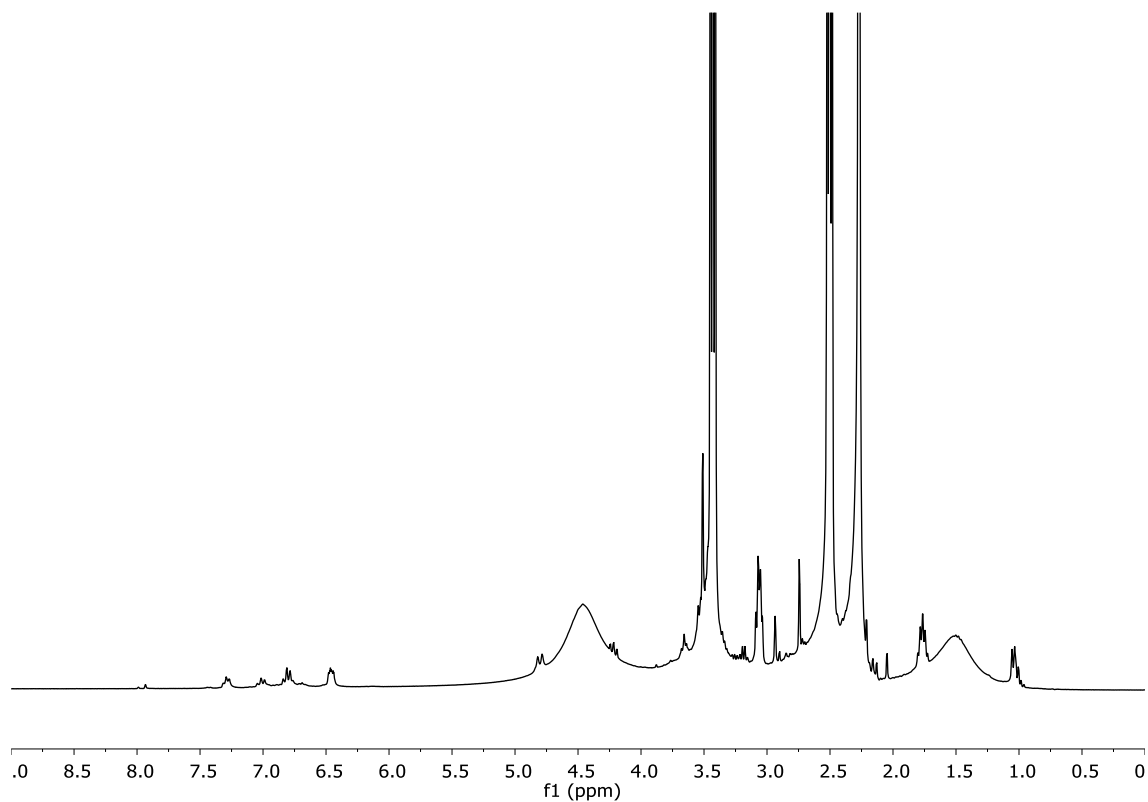


Figure S.2.47. ^1H NMR spectrum of depolymerised CPU-F2 crude product. The di-urea characteristic signal can be identified at $\delta = 2.94$ ppm. (DMSO- d_6 , 300 MHz, 298 K)

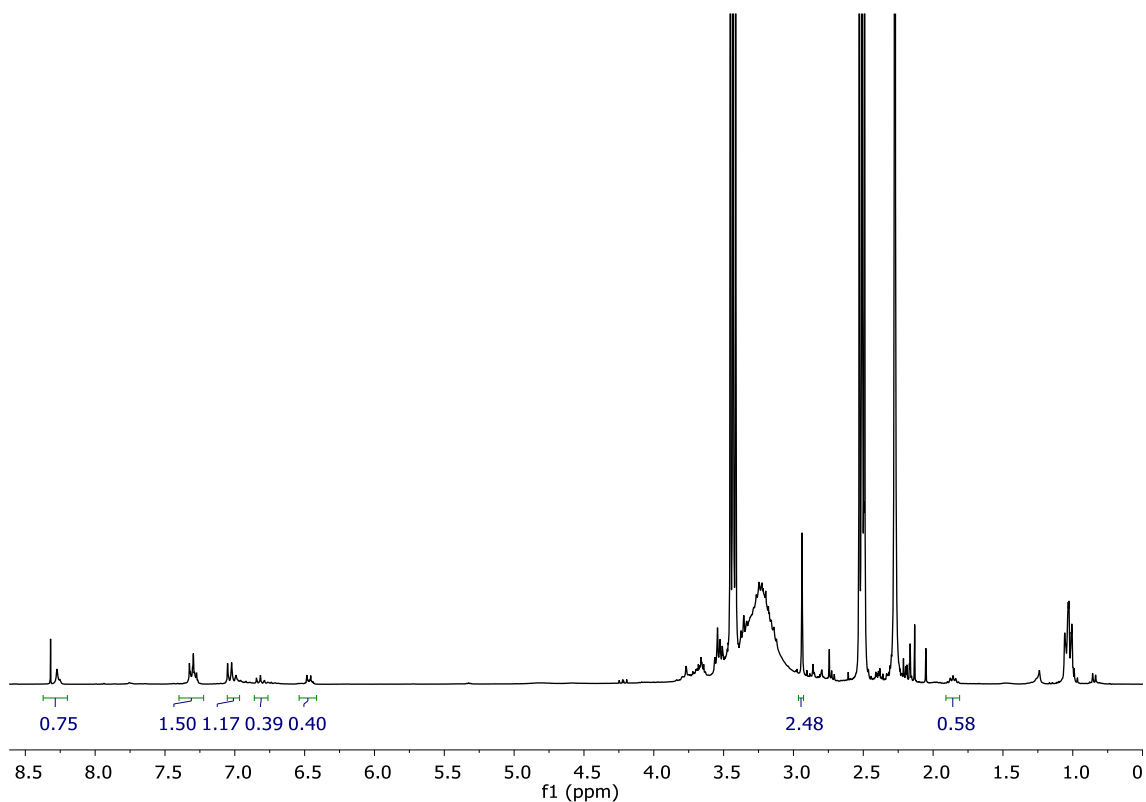


Figure S.2.48. ^1H NMR spectrum of depolymerised CPU-F3 crude product. The di-urea characteristic signal can be identified at $\delta = 2.94$ ppm. (DMSO- d_6 , 300 MHz, 298 K)

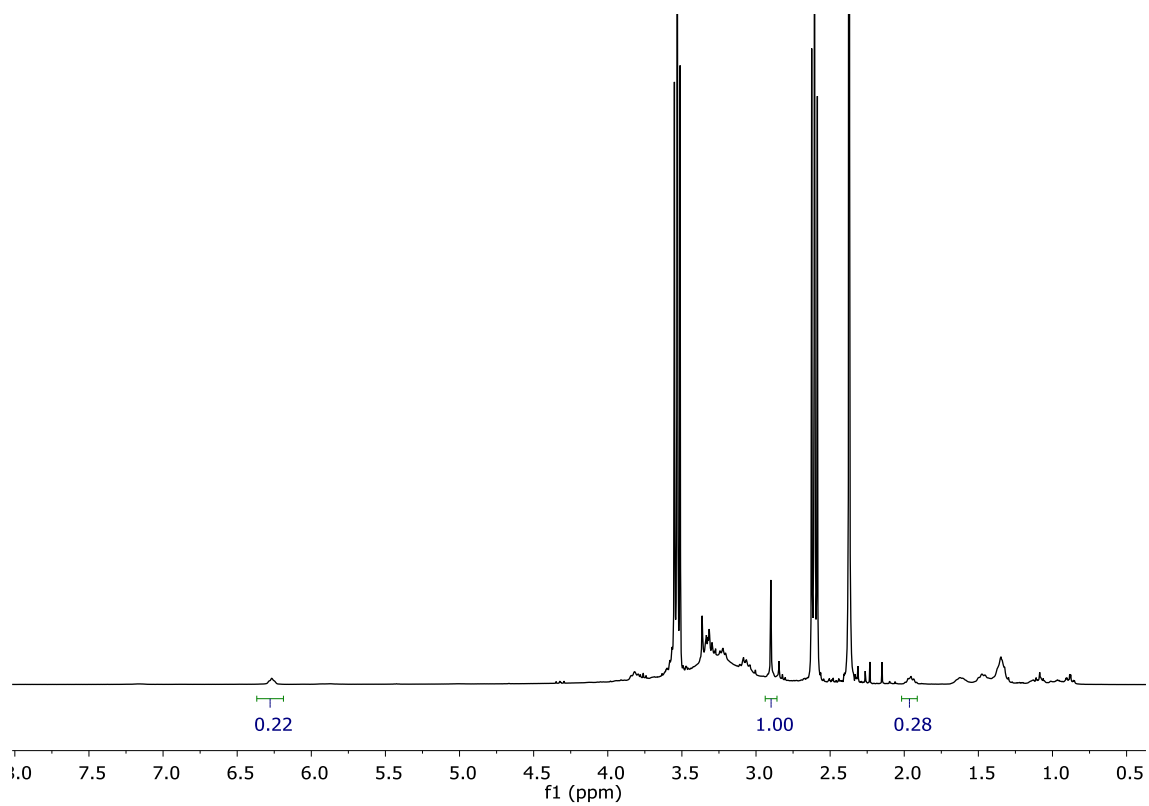


Figure S.2.49. ^1H NMR spectrum of depolymerised CPU-F4 crude product. The di-urea characteristic signal can be identified at $\delta = 2.94$ ppm. (DMSO- d_6 , 300 MHz, 298 K)

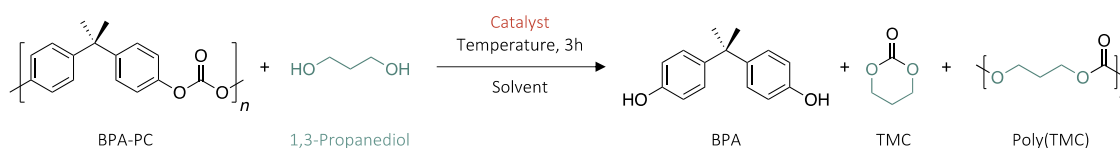
Chapter 3 BPA-PC Depolymerisation

Chemical Reagents

1,3-propanediol (98%), butane-1,3-diol (99,5%), Di(trimethylolpropane) (97%) Trimethylolpropane allyl ether, 2,2-dimethylpropane-1,3-diol (99%), 2,2-diethylpropane-1,3-diol (99%) 2-methyl-2-propylpropane-1,3-diol (98%), 2,2-Bis(hydroxymethyl) propionic acid (98%) ethylene diamine (99%) anhydrous EG (99,8%), glycerol (99%), ethanedithiol (98%), 1-methylimidazole, imidazole (99%), benzimidazole (98%), benzotriazole (99%) and 1,2,4-triazole (98%) were purchased from Sigma Aldrich. Deuterated solvents such as CDCl_3 and $\text{DMSO-}d_6$ were purchased from Eurisotop. Commonly employed solvents such as THF, CHCl_3 , DCM, toluene and methanol were purchased in HPLC grade from Sigma Aldrich or Fisher Scientific. All materials were used without further purification. BPA-PC pellets were purchased from Idemitsu Chemical Europe (TARFLON IV1900R).

Experimental procedures

General procedure for the depolymerisation reactions



Scheme S.3.1. BPA-PC depolymerisation reaction by 1,3-propanediol to obtain TMC.

In a typical reaction, BPA-PC pellets (1 g, 3.9 mmol, 1 eq.) 1,3-propanediol (1.05, 1.25, 1.5 or 1.75 eq.), catalyst (0, 0.5, 1 and 2 eq.) and solvent (2.5, 5, 10 or 20 eq.) and were loaded into a 25 ml vial along with an oval magnetic stirrer. The mixture was introduced in an oil bath pre-heated at the desired temperature (40, 50, 60 or 90 °C). To monitor the conversion, DMF was added to the reaction media (0.5 eq.) and aliquots were taken at certain intervals as well as after completion of the reaction to be analysed by means of ^1H NMR spectroscopy. The depolymerisation yield was calculated through the integration of the characteristic aromatic signals of BPA, *i.e.* δ (ppm) 6.98 (d, 4H) and 6.67 (d, 4H), compared to DMF standard.

Procedure for the purification of TMC

The depolymerisation of BPA-PC (1 g, 3.9 mmol, 1 eq.) was performed in 10 eq. of 1-Methylimidazole (3.2 g, 39 mmol), with 1.05 eq. of 1,3-propanediol (0.30 g, 3.9 mmol) as nucleophile and 1 eq. of imidazole as catalyst (0.27 g, 3.9 mmol) at 50 °C. After 3 h of reaction and following the isolation method already described by Hedrick and co-workers¹, the crude product is dissolved in a large excess of DCM and passed through an acidic resin (*i.e.* Amberlyst 15) for retaining the catalyst (imidazole) and the solvent (1-methylimidazole) by forming the corresponding acid:base salt. The column was refrigerated below 45 °C to compensate the heat created through the exothermic formation of the salts. The solution is then concentrated by means of rota-evaporation and TMC is precipitated in diisopropyl ether for eliminating BPA before re-crystallisation in DCM. White crystals are obtained (0,13 g, 1,25 mmol, 32% yield) and analysed through ¹H and ¹³C NMR spectroscopy.

¹H NMR (300 MHz, DMSO-*d*₆, 298K) δ (ppm) 4.39 (t, 2H, CH₂), 2,03 (q, 4H, CH₂).

¹³C NMR (300 MHz, DMSO-*d*₆, 298K) δ (ppm) 152.9 (s, 1C, C=O), 77.6 (s, 2C, CH₂-O), 14.8 (s, 1C, CH₂-CH₂).

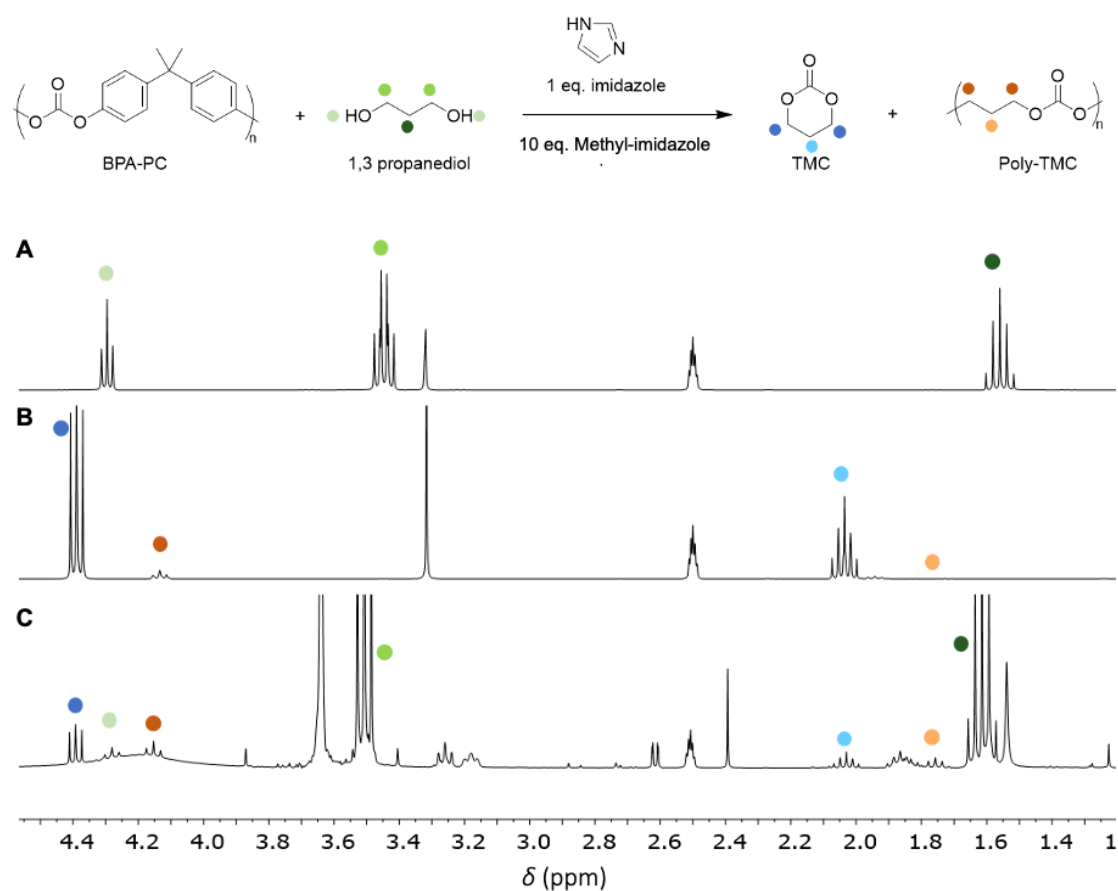


Figure S.3.1. ^1H NMR spectra and assignment of **A.** the reactant, 1,3-propanediol, **B.** the products formed, TMC and PTMC, and **C.** the crude of the depolymerisation reaction.

^1H NMR (300 MHz, $\text{DMSO-}d_6$, 298K) TMC δ (ppm): 4.40 (t, $J = 11.3$ Hz, 4H), 2.04 (m, $J = 5.7$ Hz, 2H).

^1H NMR (300 MHz, $\text{DMSO-}d_6$, 298K) PTMC δ (ppm): 4.16 (m, $J = 7.9, 3.9, 2.1$ Hz, 4H), 1.80 – 1.72 (m, 2H).

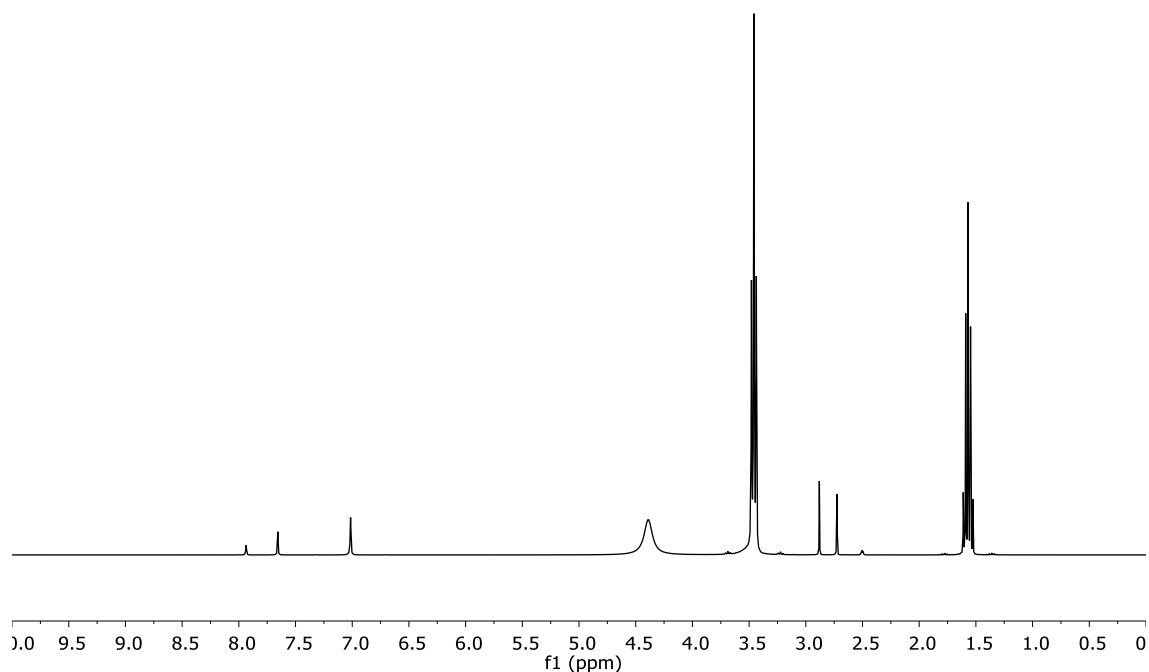


Figure S.3.2. ^1H NMR spectra of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 10 eq. of 1,3-propanediol as nucleophile, in bulk, after 3 h at 50 °C. No conversion was observed.

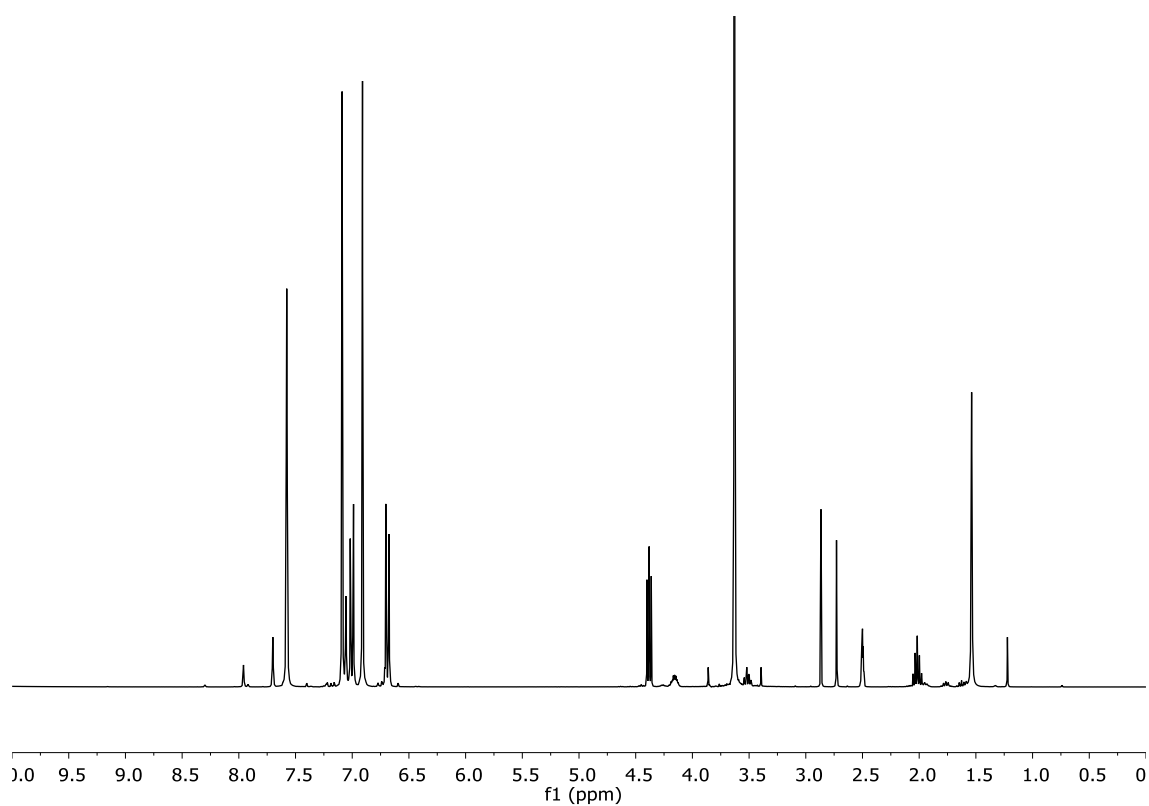


Figure S.3.3. ^1H NMR spectra of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-methylimidazole as solvent, after 3 h at 50 °C.

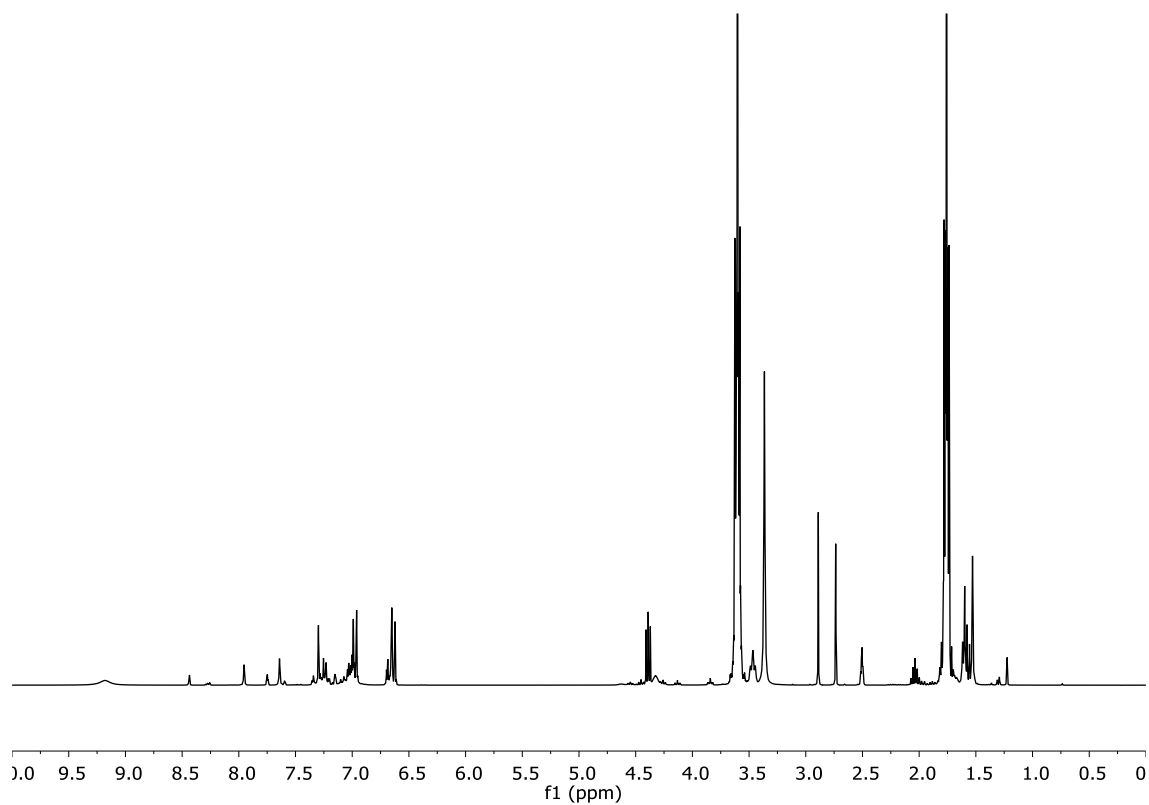


Figure S.3.4. ^1H NMR spectra of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of THF as solvent, after 3 h at 50 °C.

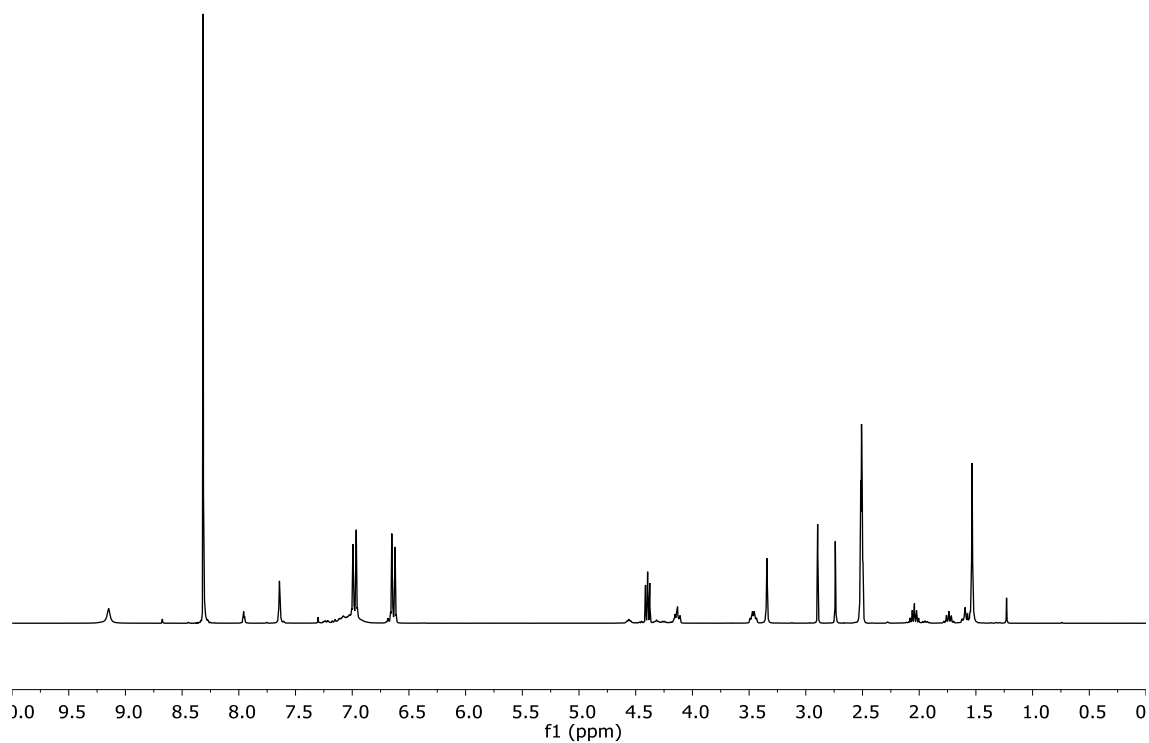


Figure S.3.5. ^1H NMR spectra of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1 eq. of 1,3-propanediol as nucleophile and 10 eq. of CHCl_3 as solvent, after 3 h at 50 °C.

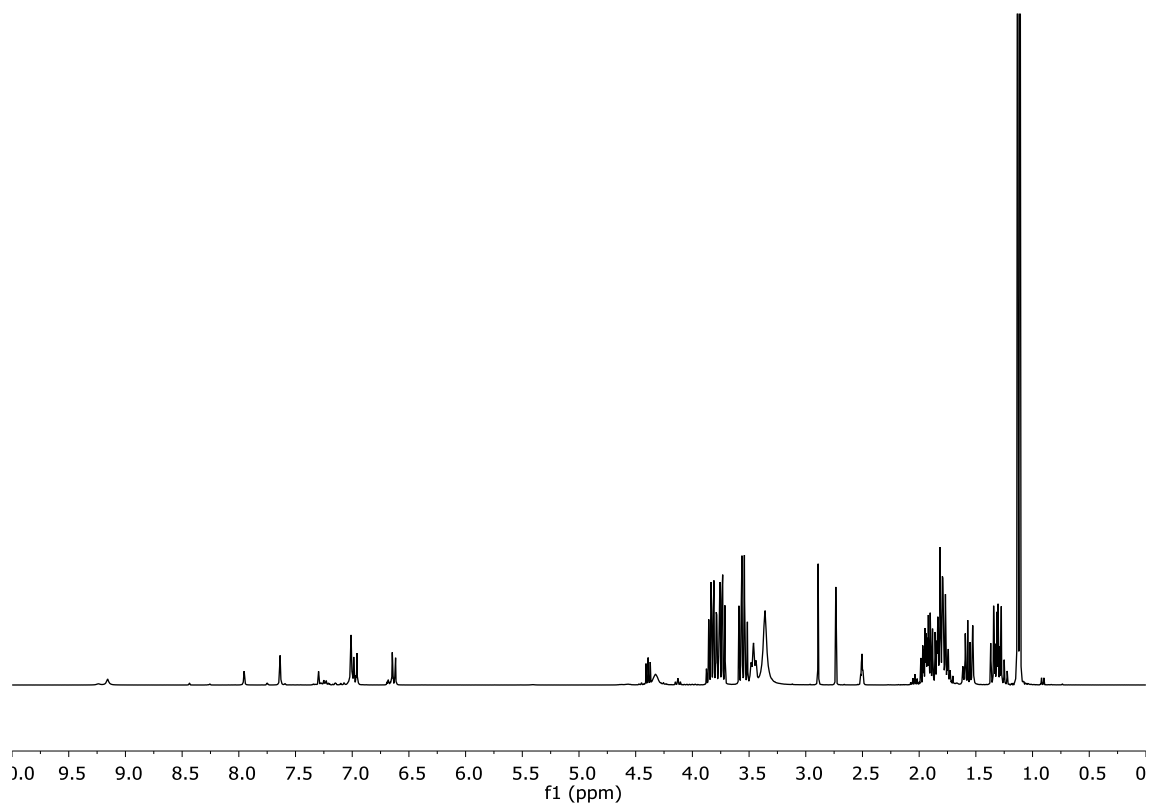


Figure S.3.6. ^1H NMR spectra of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 2-Methyltetrahydrofuran as solvent, after 3 h at 50 °C.

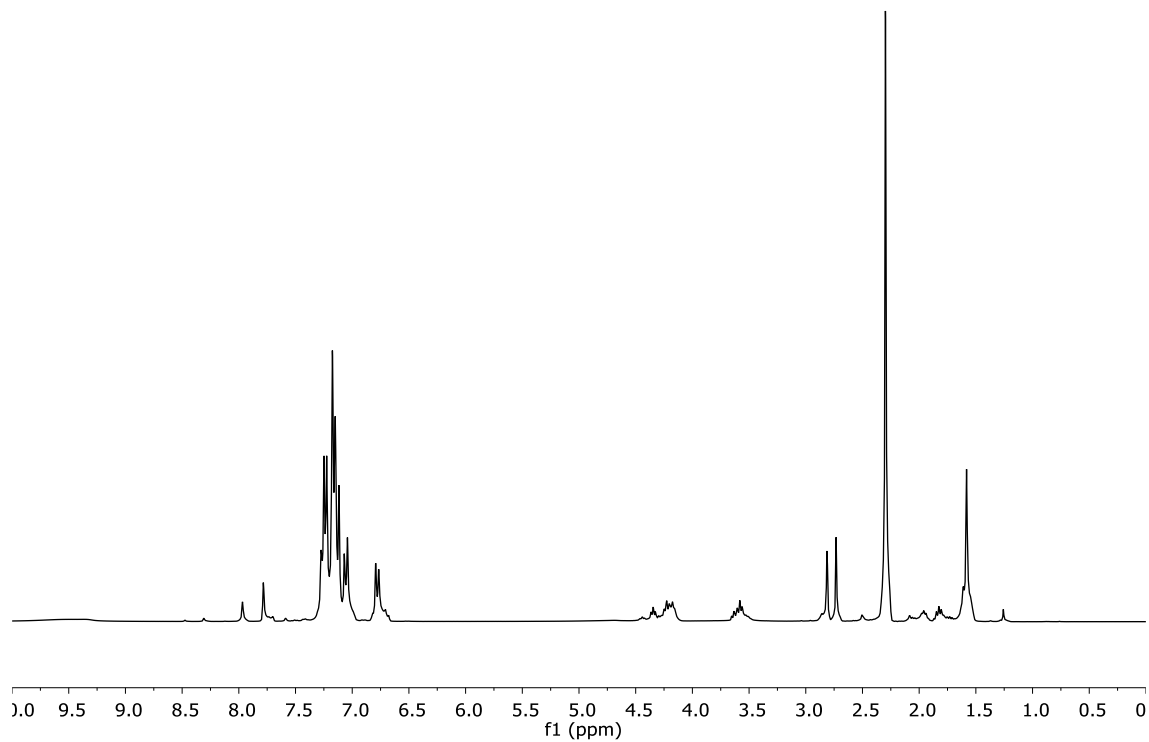


Figure S.3.7. ^1H NMR spectra of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of toluene as solvent, after 3 h at 50 °C.

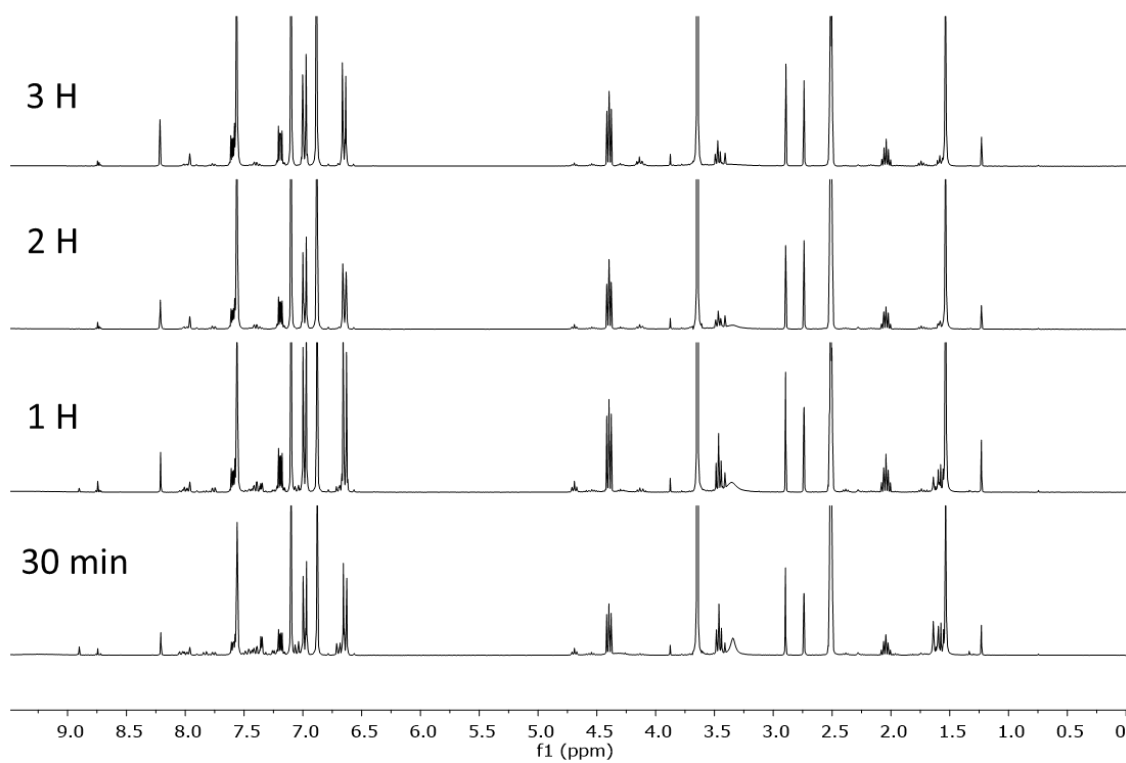


Figure S.3.8. Kinetics of the depolymerisation of BPA-PC monitored through ^1H NMR spectroscopy carried out with 1 eq. of benzimidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

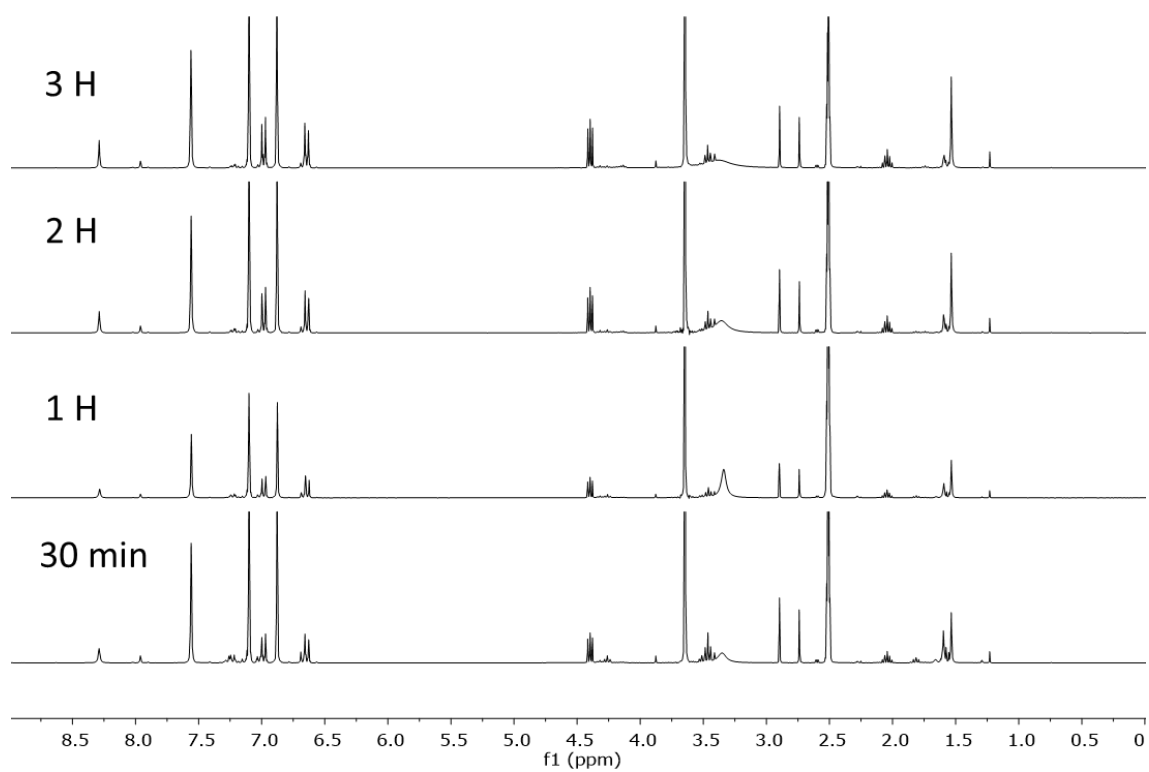


Figure S.3.9. Kinetics of the depolymerisation of BPA-PC monitored through ^1H NMR spectroscopy carried out with 1 eq. of triazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

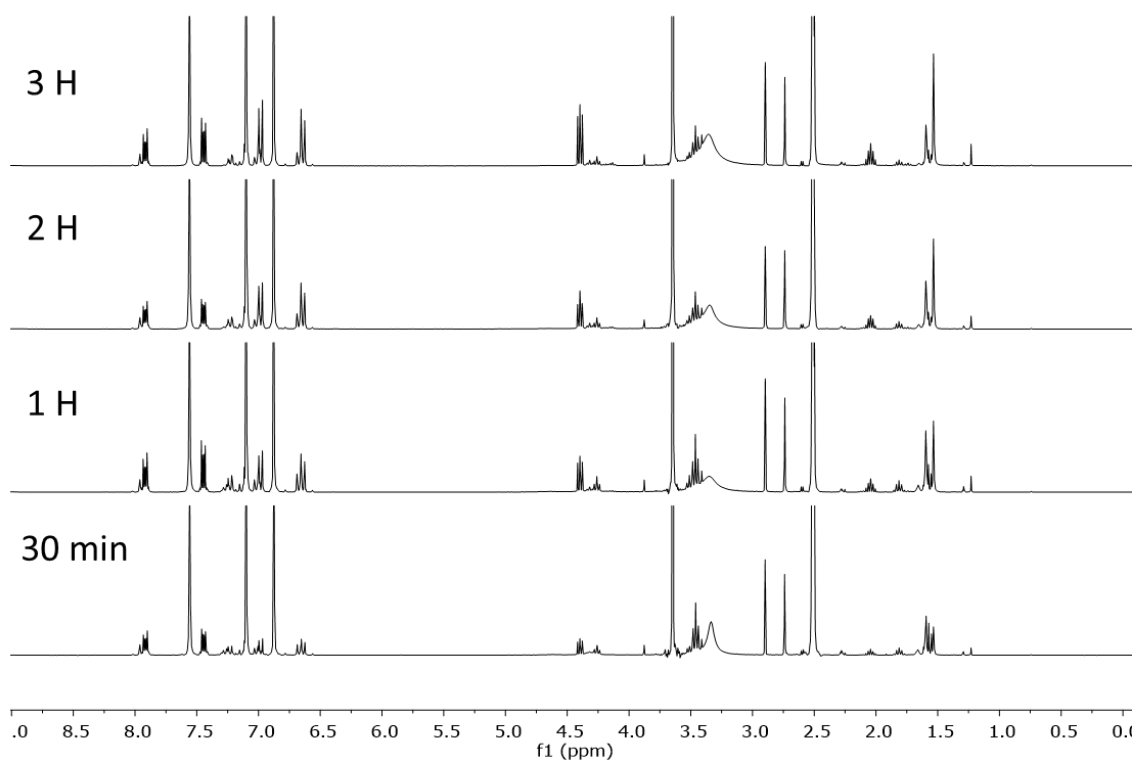


Figure S.3.10. Kinetics of the depolymerisation of BPA-PC monitored through ¹H NMR spectroscopy carried out with 1 eq. of benzotriazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

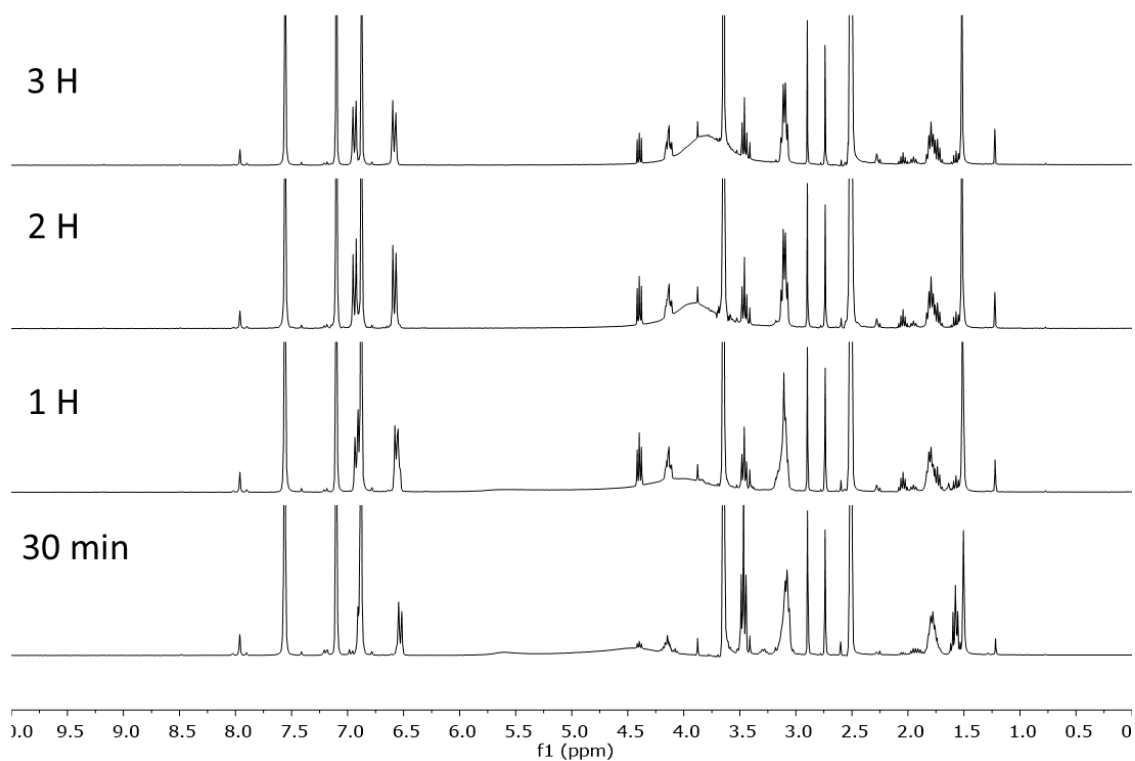


Figure S.3.11. Kinetics of the depolymerisation of BPA-PC monitored through ¹H NMR spectroscopy carried out with 1 eq. of TBD as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

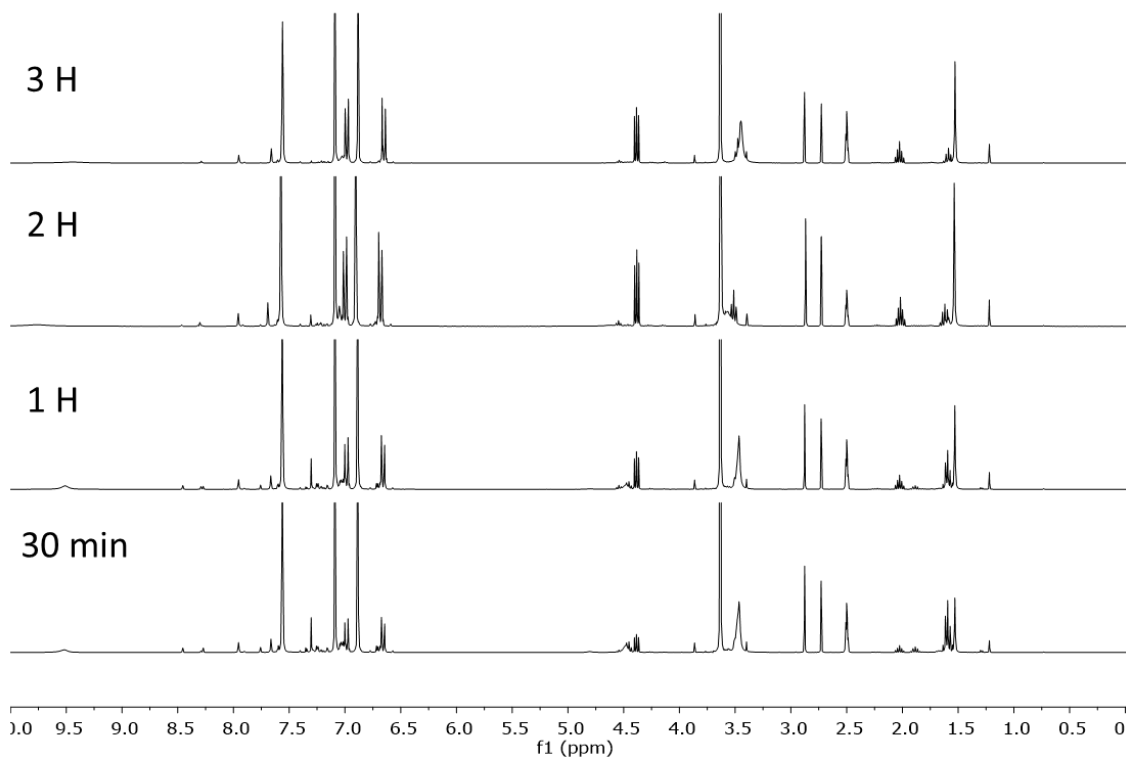


Figure S.3.12. Kinetics of the depolymerisation of BPA-PC monitored through ^1H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 40°C .

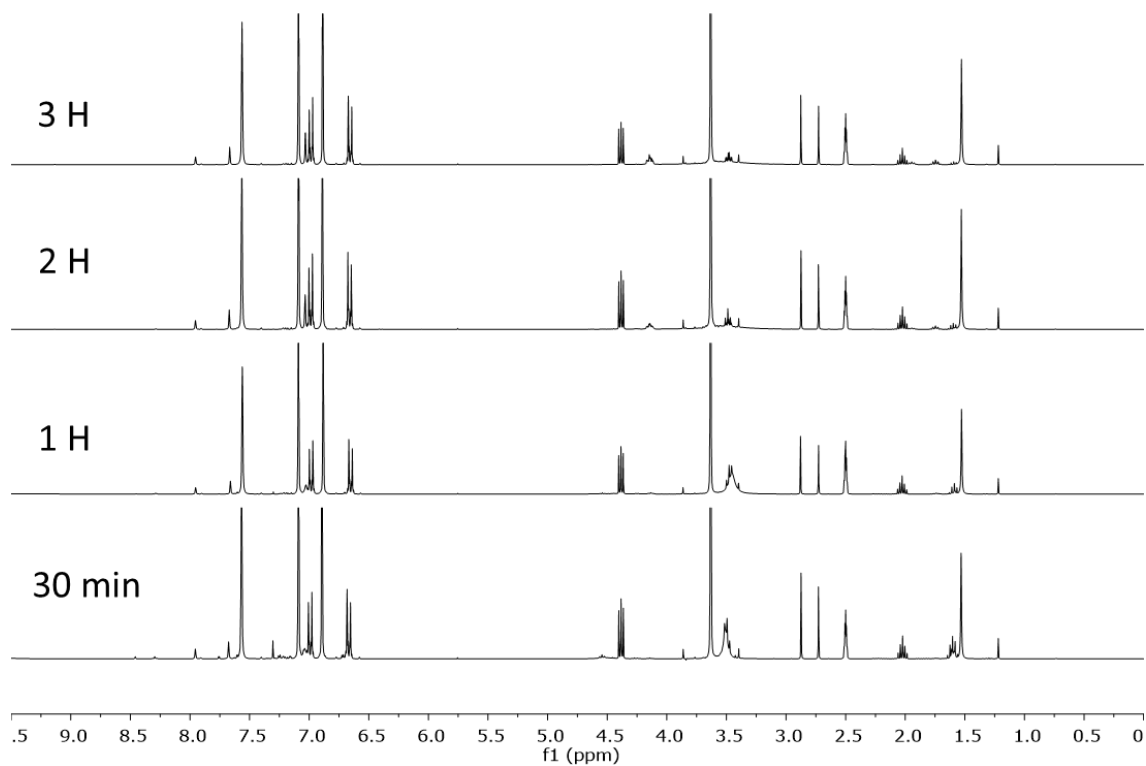


Figure S.3.13. Kinetics of the depolymerisation of BPA-PC monitored through ¹H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 60 °C.

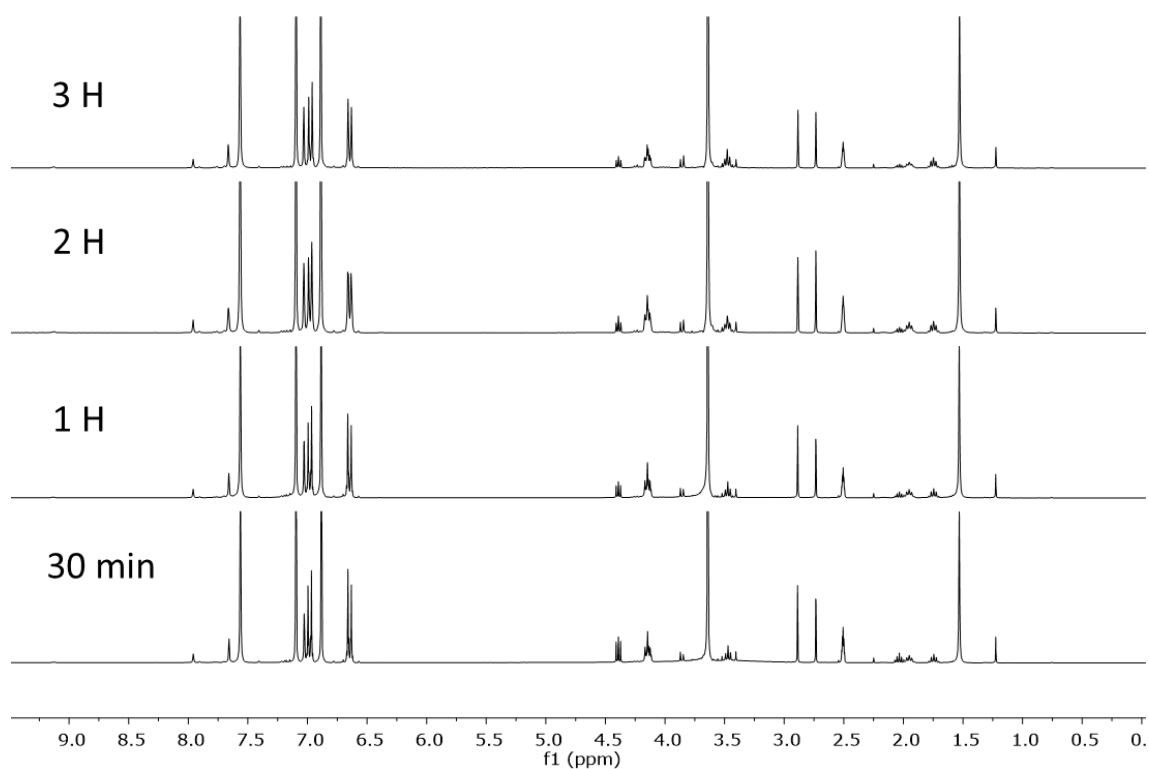


Figure S.3.14. Kinetics of the depolymerisation of BPA-PC monitored through ^1H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 90 °C.

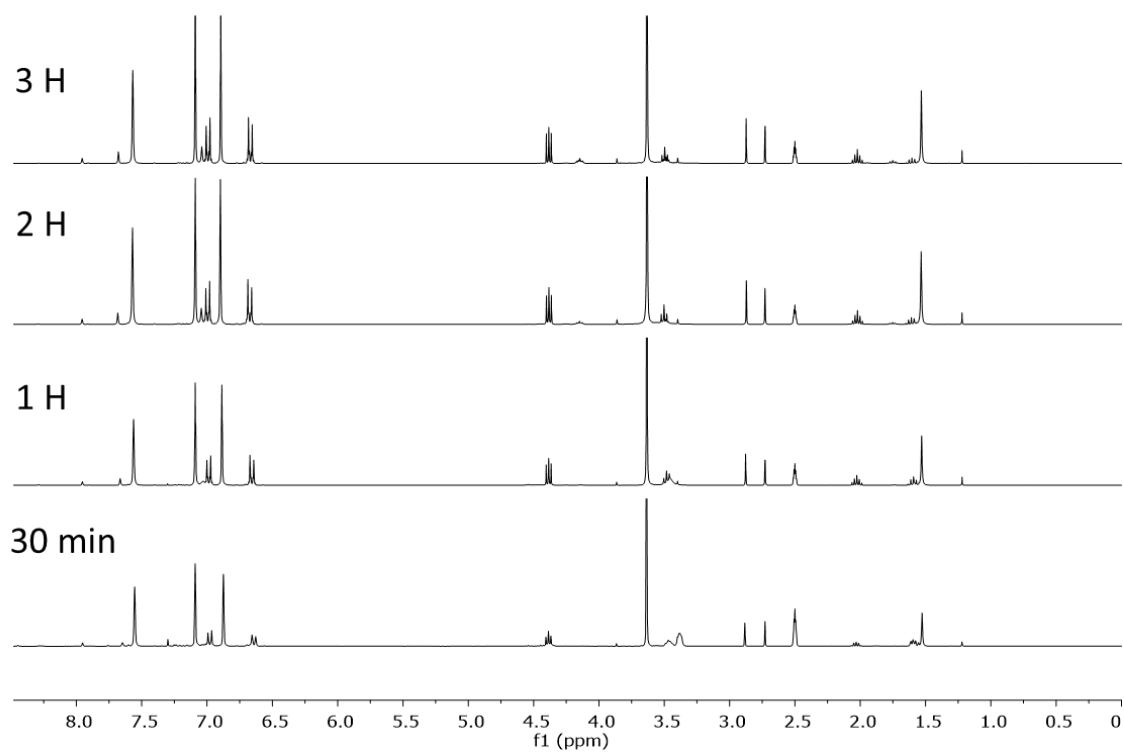


Figure S.3.15. Kinetics of the depolymerisation of BPA-PC monitored through ^1H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.25 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

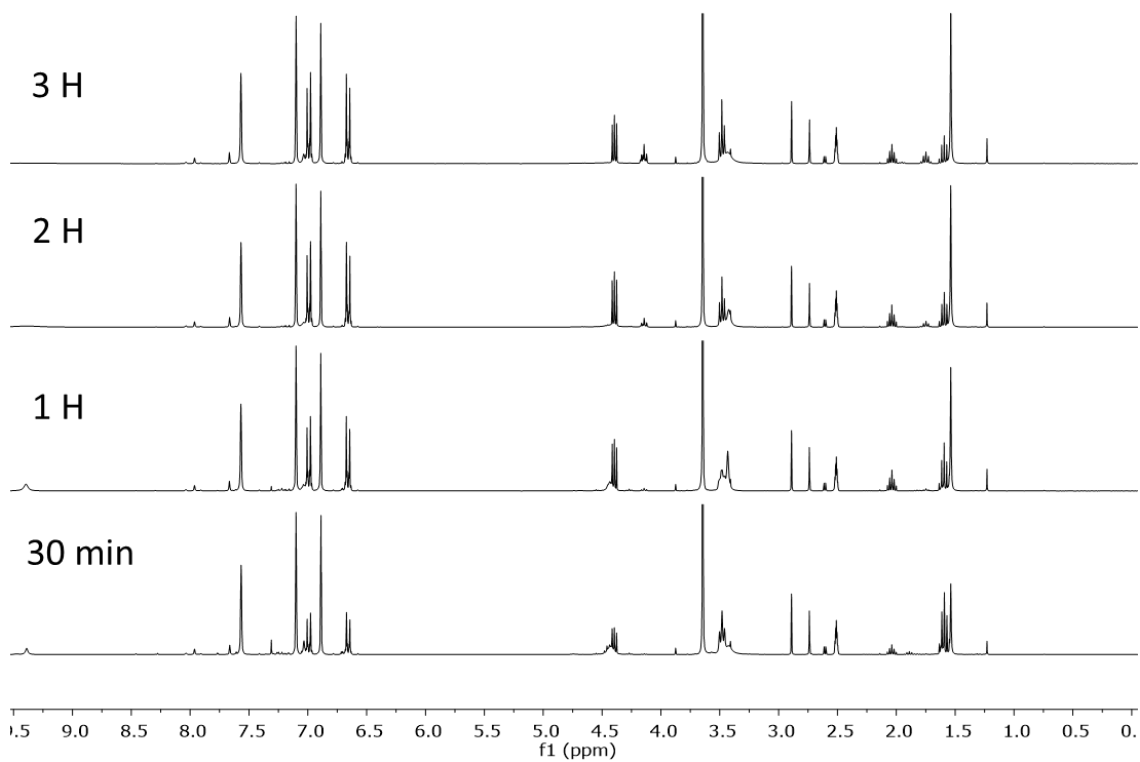


Figure S.3.16. Kinetics of the depolymerisation of BPA-PC monitored through ^1H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.5 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

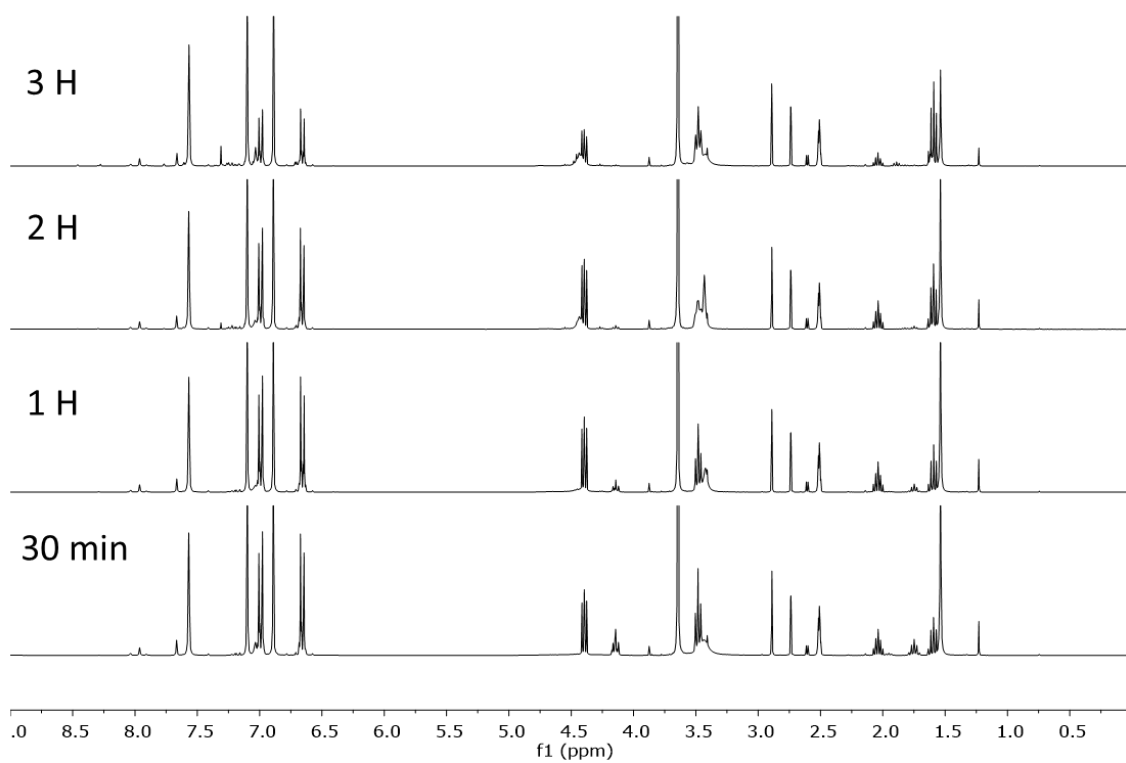


Figure S.3.17. Kinetics of the depolymerisation of BPA-PC monitored through ^1H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.75 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

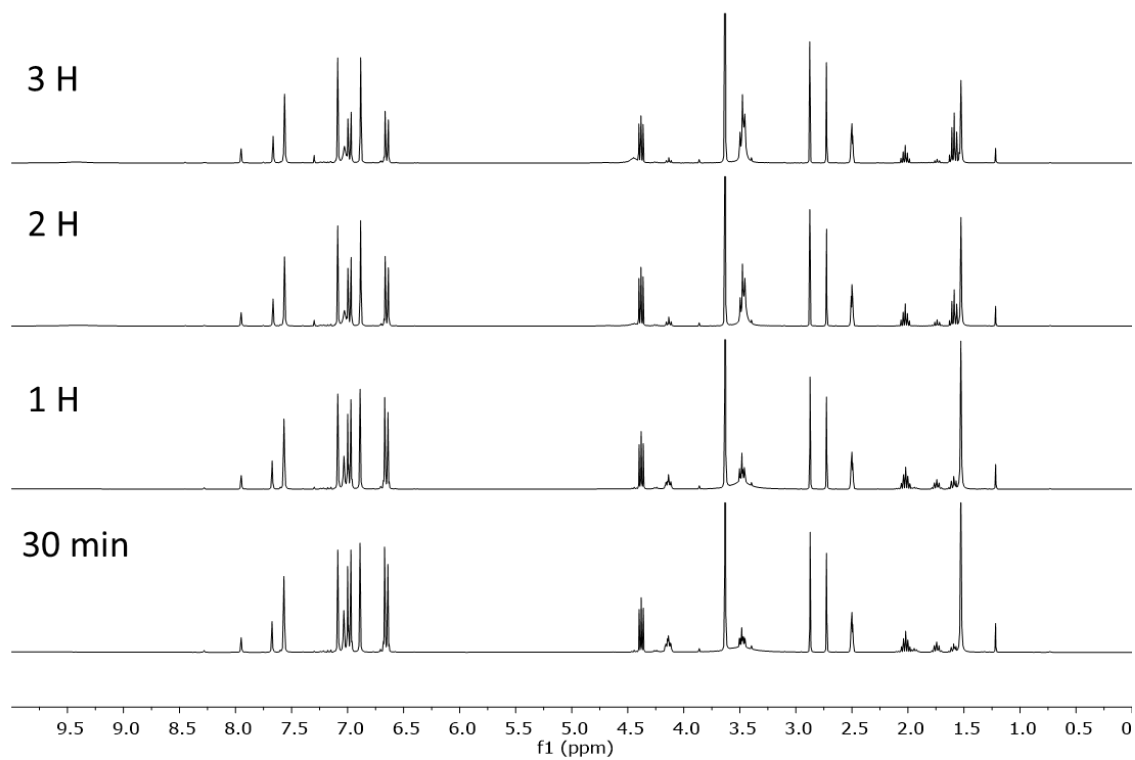


Figure S.3.18. Kinetics of the depolymerisation of BPA-PC monitored through ^1H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 2.5 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

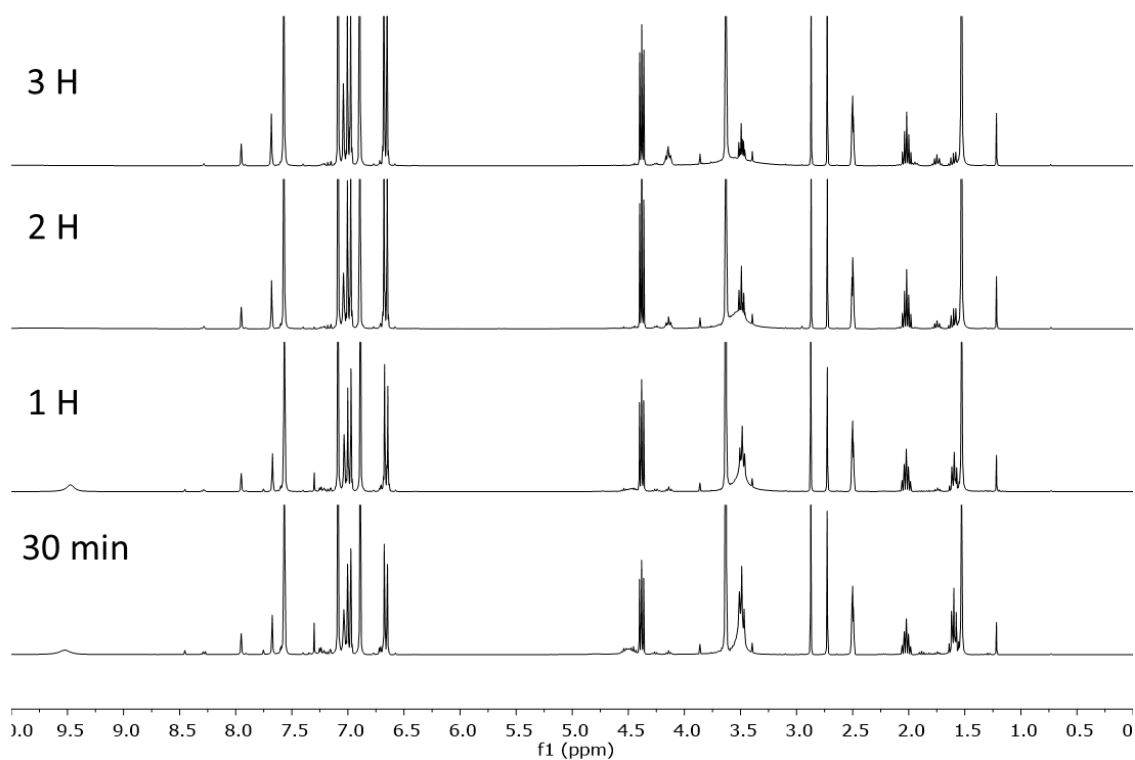


Figure S.3.19. Kinetics of the depolymerisation of BPA-PC monitored through ^1H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 5 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

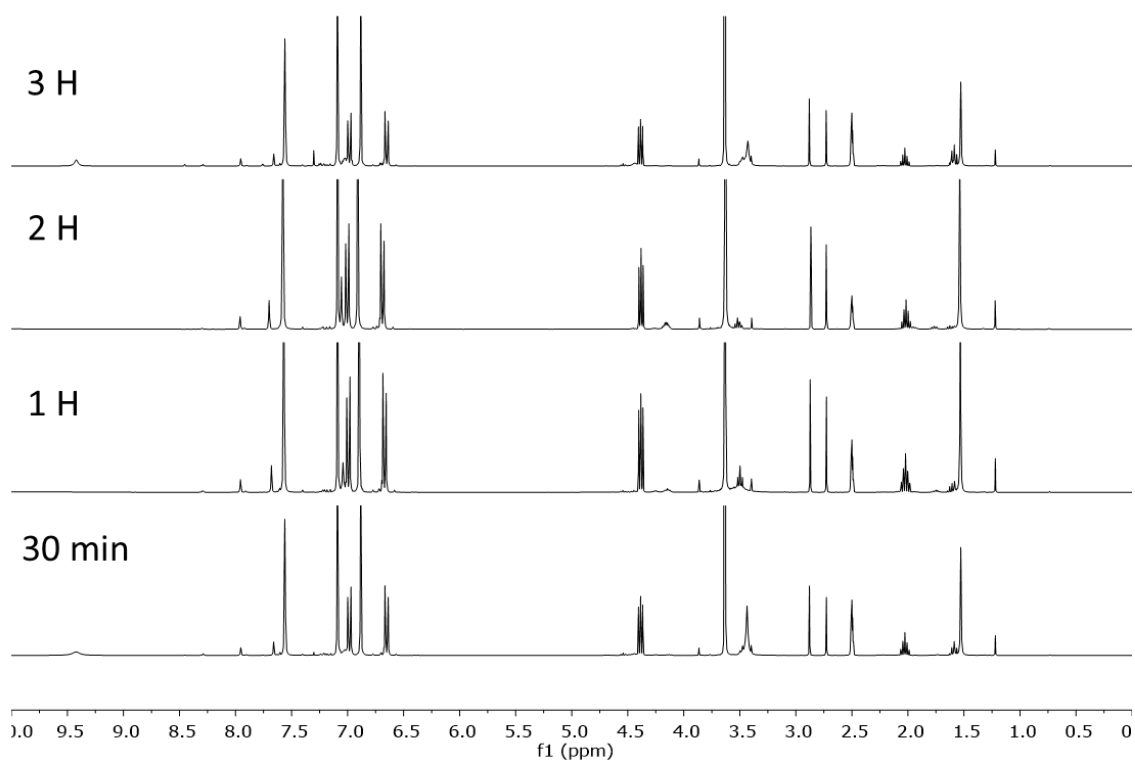


Figure S.3.20. Kinetics of the depolymerisation of BPA-PC monitored through ¹H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 20 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

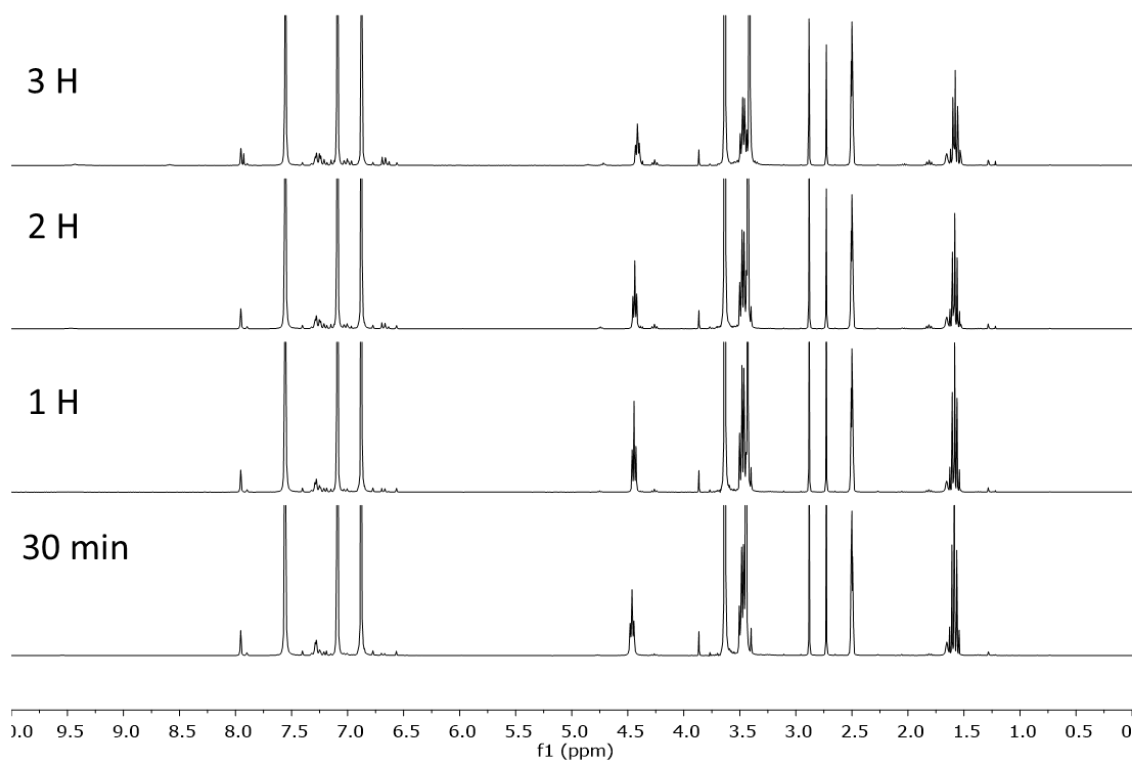


Figure S.3.21. Kinetics of the depolymerisation of BPA-PC monitored through ¹H NMR spectroscopy carried out without catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

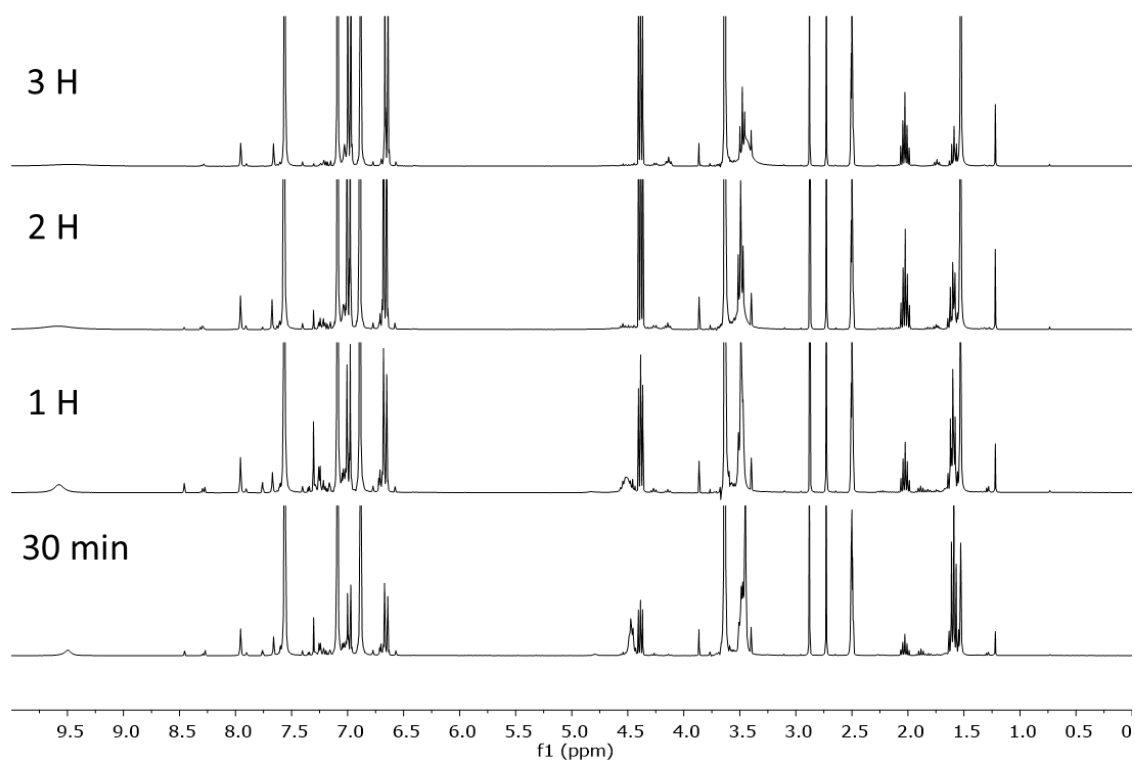


Figure S.3.22. Kinetics of the depolymerisation of BPA-PC monitored through ^1H NMR spectroscopy carried out with 0.5 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

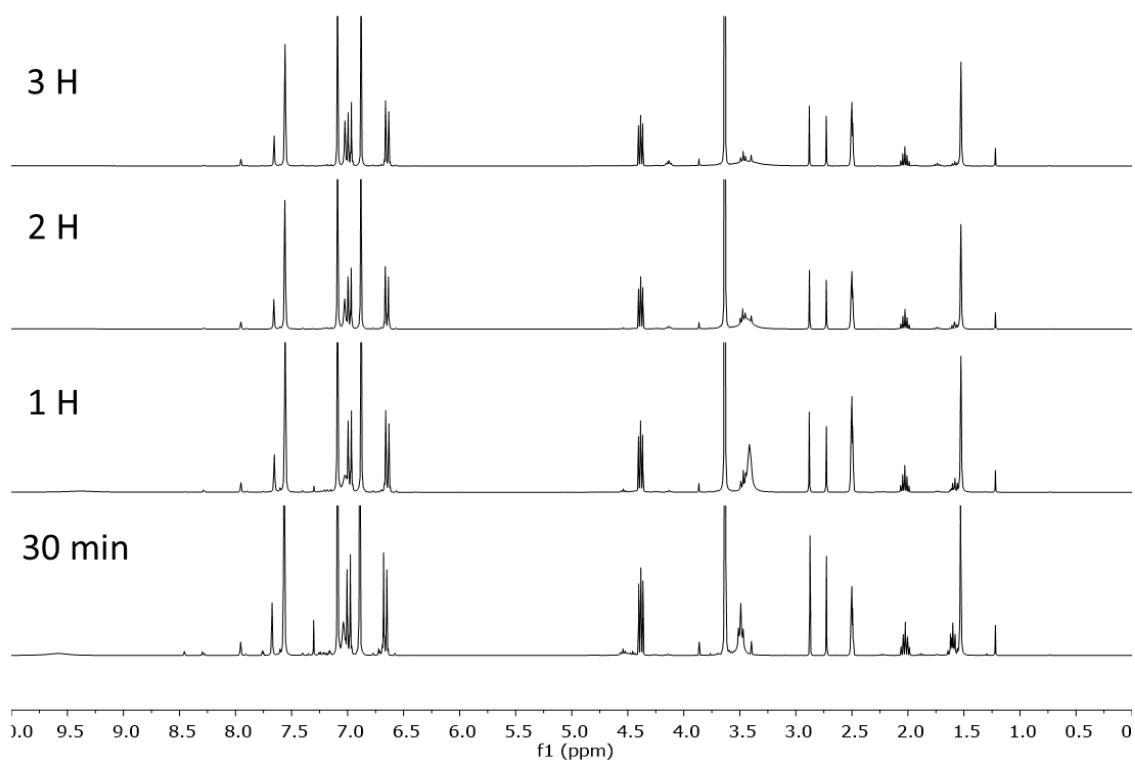


Figure S.3.23. Kinetics of the depolymerisation of BPA-PC monitored through ^1H NMR spectroscopy carried out with 2 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

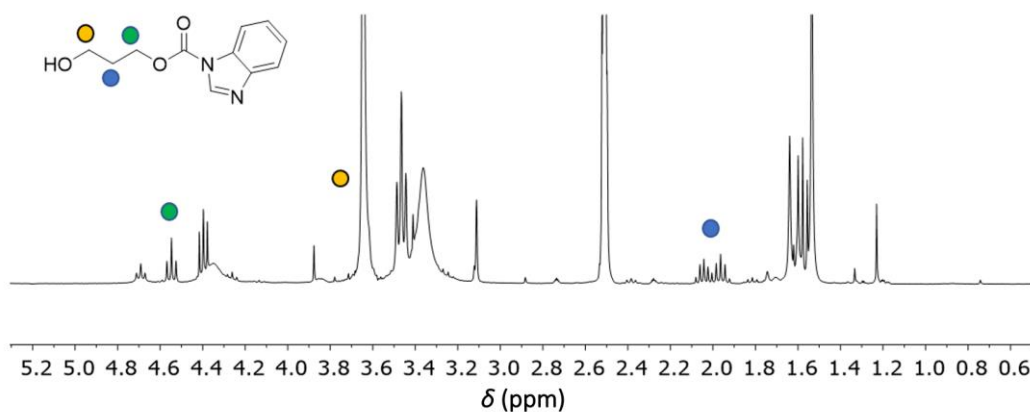


Figure S.3.24. ^1H NMR spectrum of the crude product of model reaction 2, 20 min after the addition of 1,3-propanediol. Reaction conditions: 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

^1H NMR (300 MHz, $\text{DMSO-}d_6$, 298K) TMC δ (ppm): δ 4.55 (t, 2H, $J = 6.4$ Hz), 3.65 (t, 2H) 1.96 (m, 2H, $J = 6.2$ Hz).

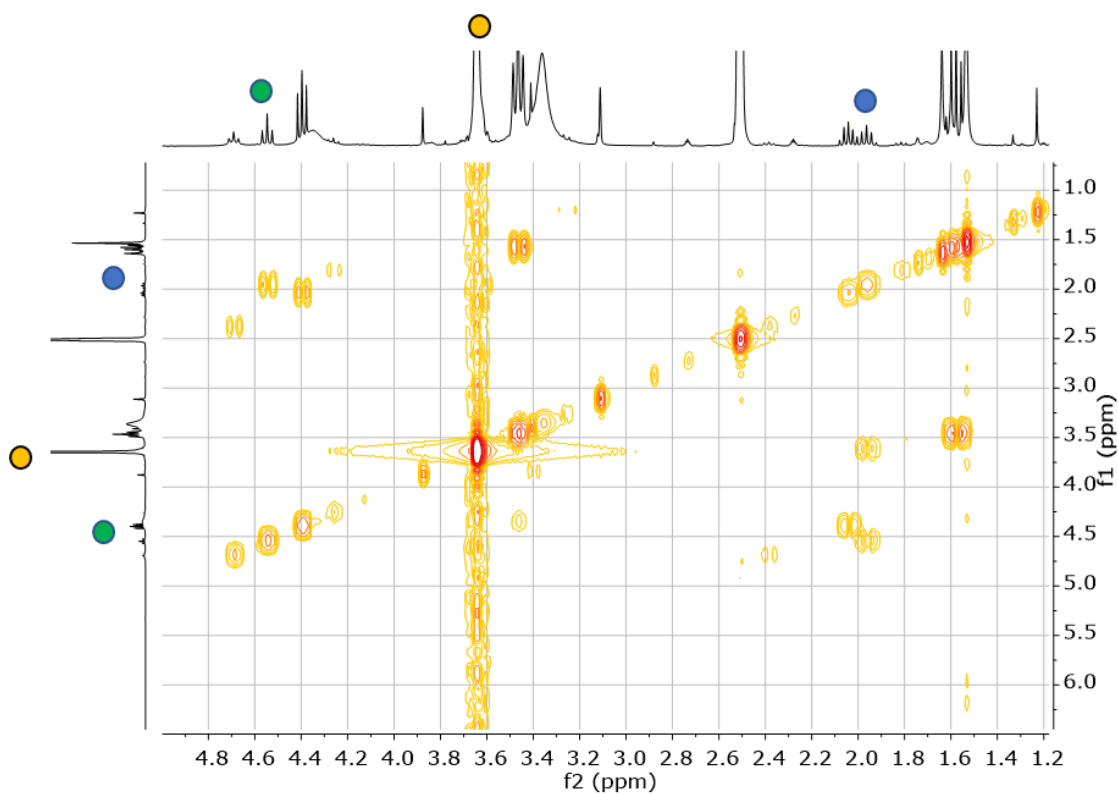


Figure S.3.25. ^1H - ^1H COSY NMR spectrum of the model reaction 2 after addition of 1,3-propanediol after 20 min of reaction. Reaction conditions: 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

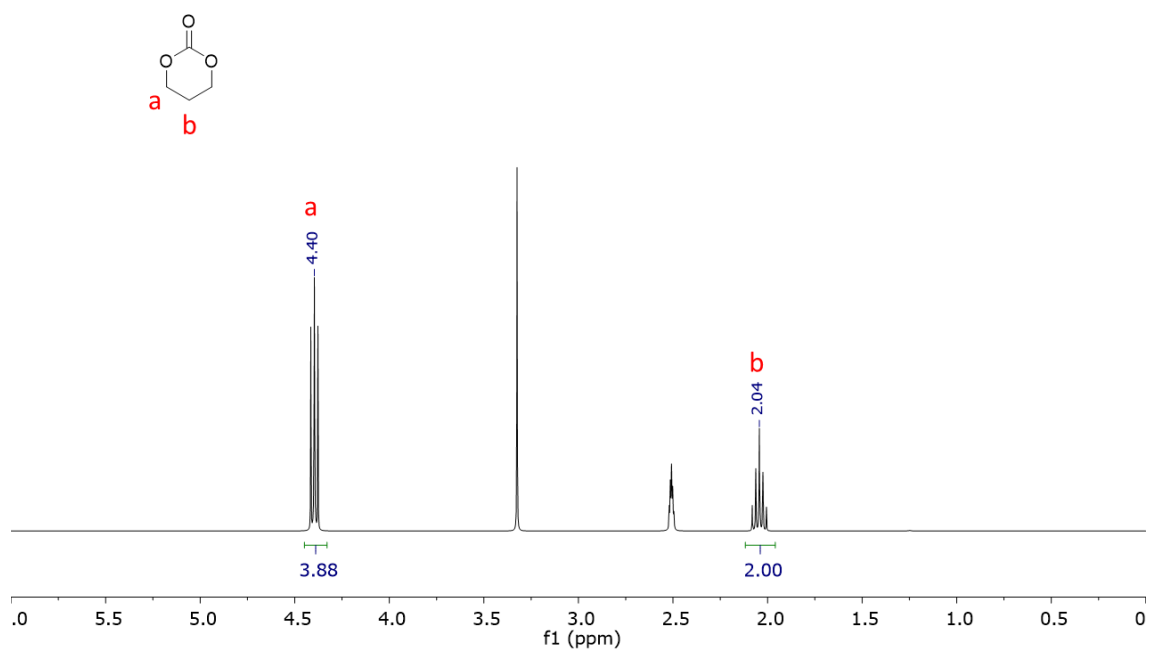


Figure S.3.26. ¹H NMR spectrum of the recovered TMC from BPA-PC depolymerisation carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3 propanediol as nucleophile and 10 eq. of 1-methylimidazole as solvent at 50 °C after an ionic exchange column with dry Amberlyst A 15 hydrogen form.

¹H NMR (300 MHz, DMSO-d₆, 298K) δ (ppm) 4.40 (t, 4H), 2.04 (p, *J* = 5.7 Hz, 2H).

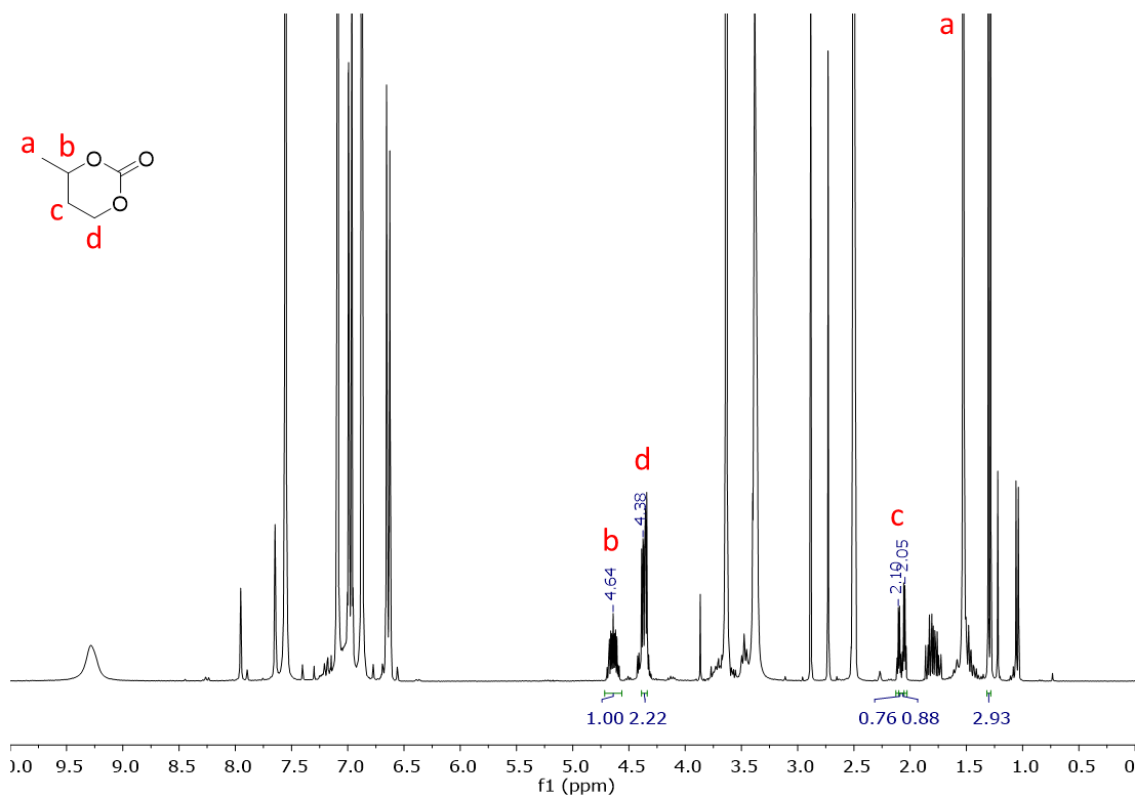


Figure S.3.27. ¹H NMR spectrum of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-butanediol as nucleophile and 10 eq. of 1-methylimidazole as solvent, after 3 h at 50 °C.

¹H NMR (300 MHz, DMSO-d₆, 298K) δ (ppm) 4.64 (m, 1H, CH, J = 6.2, 4.0, 3.3 Hz), 4.38 (m, 2H, CH₂, J = 4.4 Hz), 1.79 (m, 2H, CH₂), 1.30 (d, 6H, CH₃, J = 6.3 Hz).

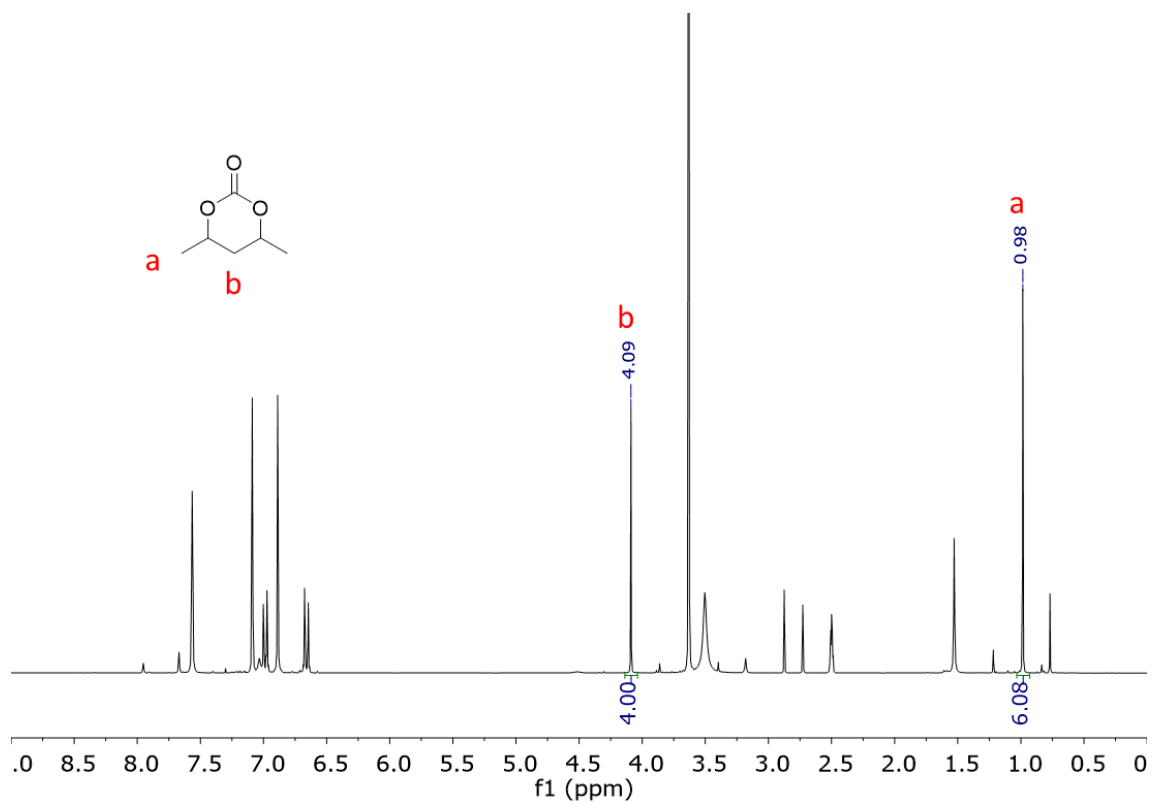


Figure S.3.28. ^1H NMR spectrum of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 2,2-dimethyl propanediol as nucleophile and 10 eq. of 1-methylimidazole as solvent, after 3 h at 50 °C.

^1H NMR (300 MHz, $\text{DMSO}-d_6$, 298K) δ (ppm) 4.09 (s, 4H, CH_2), 0.98 (s, 6H, CH_3).

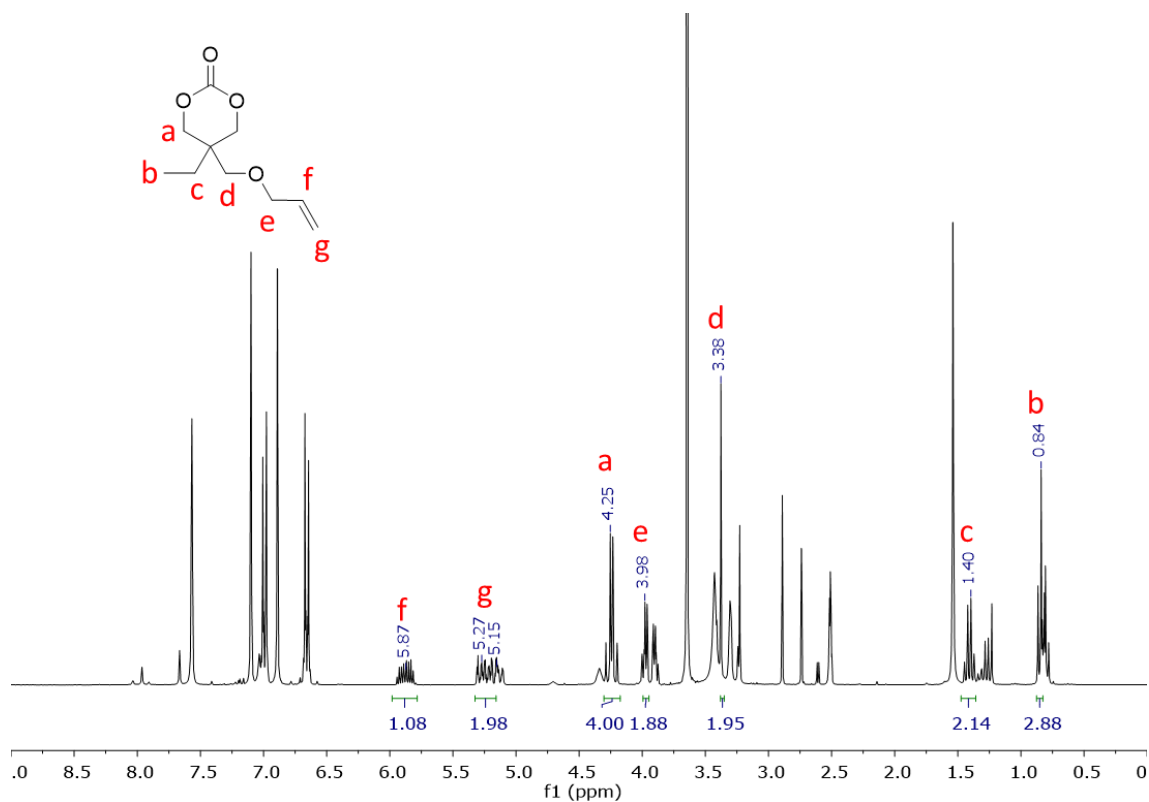


Figure S.3.29. ¹H NMR spectrum of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of trimethylolpropane allyl ether as nucleophile and 10 eq. of 1-methylimidazole as solvent, after 3 h at 50 °C.

¹H NMR (300 MHz, DMSO-*d*₆, 298K) δ (ppm) 5.94 – 5.79 (m, 1H, J = 17.3, 10.5, 5.3 Hz, CH=CH₂), 5.27 – 5.11 (m, 2H, CH=CH₂, J = 33.3, 15.7, 10.4, 1.7 Hz), 4.23 (q, 2H, O-CH₂-C-CH₂-O), 4.00 (m, 2H, O-CH₂-C-CH₂-O, J = 5.4, 1.5 Hz), 3.98 (s, 2H, O-CH₂-CH), 1.39 (m, 2H, CH₂-CH₃, J = 7.6 Hz), 0.84 (m, 6H, CH₂-CH₃, J = 7.1, 2.3 Hz).

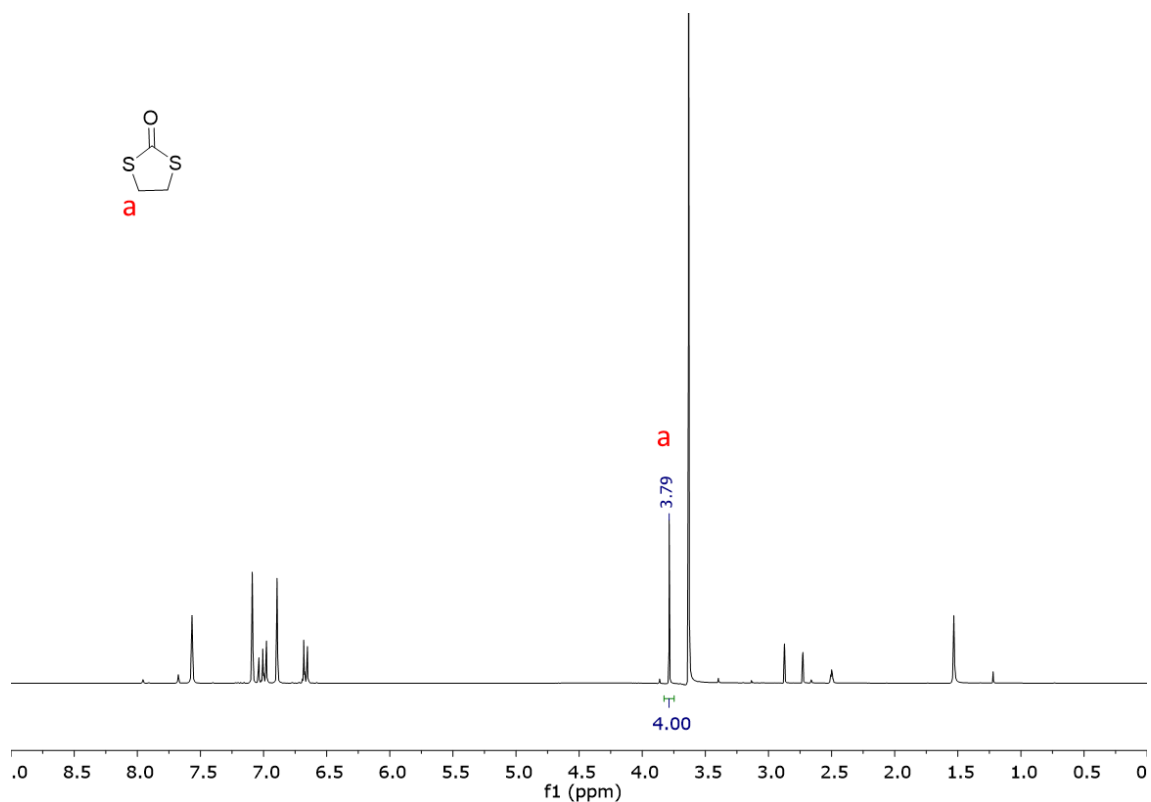


Figure S.3.30. ^1H NMR spectrum of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of ethanedithiol as nucleophile and 10 eq. of 1-methylimidazole as solvent, after 3 h at 50 °C.

^1H NMR (300 MHz, $\text{DMSO}-d_6$, 298K) δ (ppm) 3.77 (s, 4H, $J = 6.8$ Hz, CH_2).

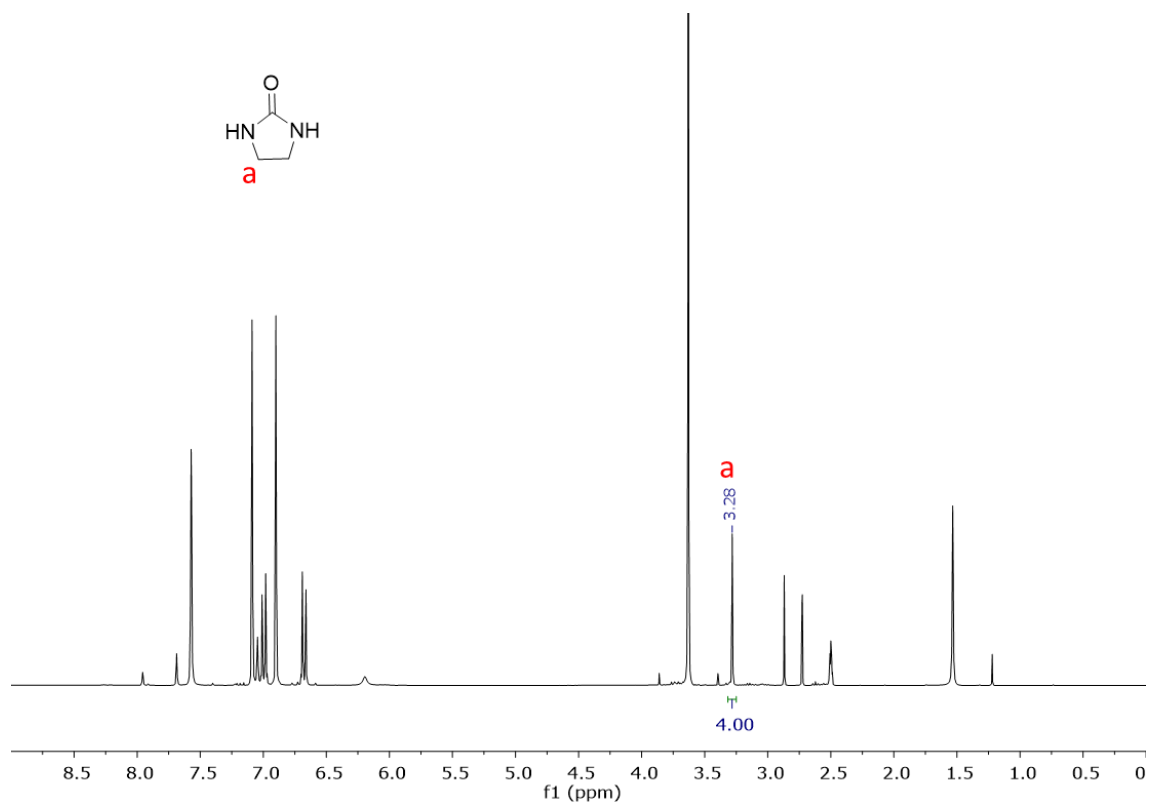


Figure S.3.31. ¹H NMR spectrum of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of ethylenediamine as nucleophile and 10 eq. of 1-methylimidazole as solvent, after 3 h at 50 °C.

¹H NMR (300 MHz, DMSO-*d*₆, 298K) δ (ppm) 3.27 (s, 4H, J = 5.2 Hz, CH₂).

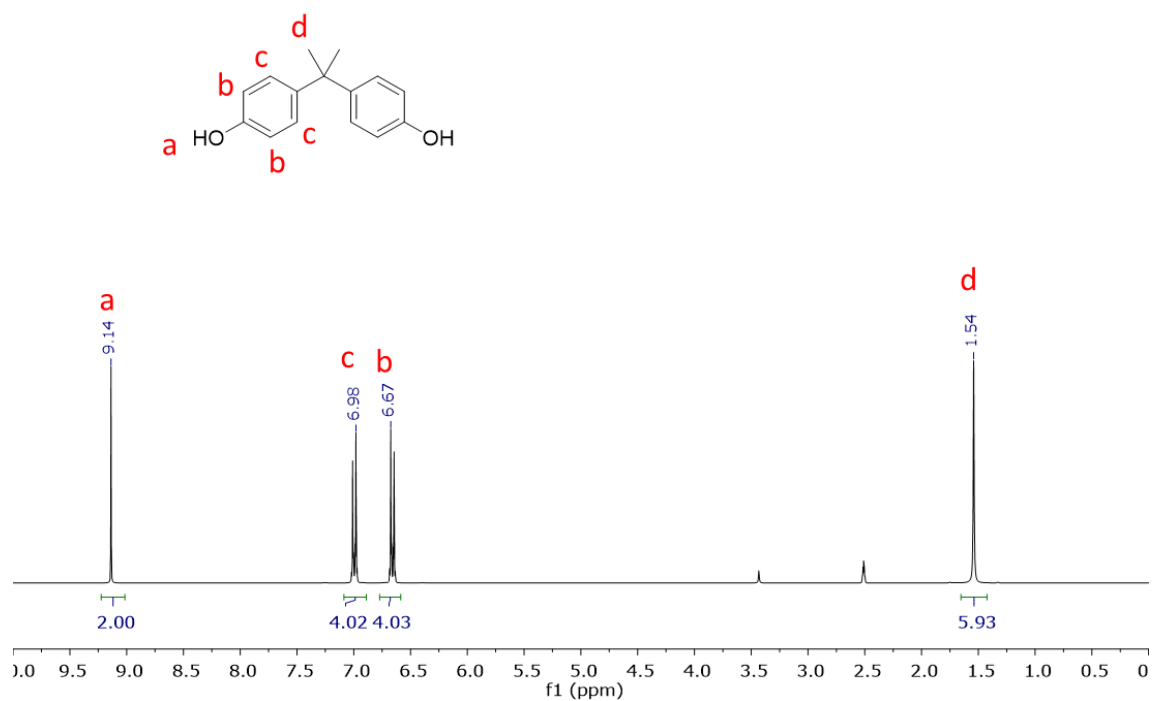


Figure S.3.32. ^1H NMR spectrum of the commercial BPA.

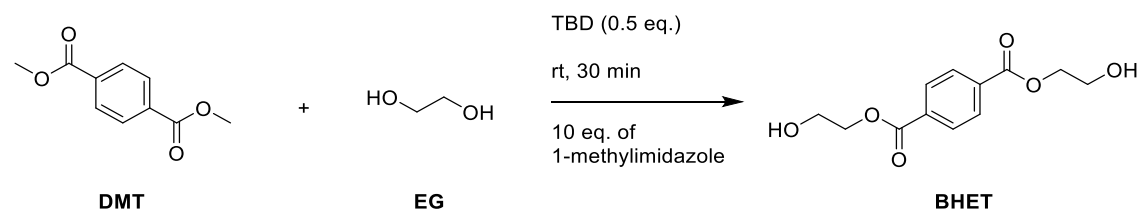
^1H NMR (300 MHz, $\text{DMSO-}d_6$, 298K) δ (ppm) 9.14 (s, 2H), 7.00 (d, $J = 8.8$ Hz, 4H), 6.66 (d, $J = 8.8$ Hz, 4H), 1.54 (s, 6H).

Chapter 4 PET Depolymerisation

PET depolymerisation using 1-methylimidazole as solvent

Model reactions

DMT reaction with EG



Scheme S.4.1. Model reaction scheme of DMT transesterification with EG catalysed by TBD to form BHET.

DMT (0.5 g, 2.57 mmol) was reacted with EG (0.32 g, 5.14 mmol) using 0.2 eq. TBD as catalyst (0.1 g, 1.23 mmol) in the presence of 1-methylimidazole as solvent (2,11 g, 25,7 mmol) at room temperature for 30 minutes in normal atmosphere. After reaction completion an aliquot was taken and analysed by means of ^1H NMR in deuterated DMSO.

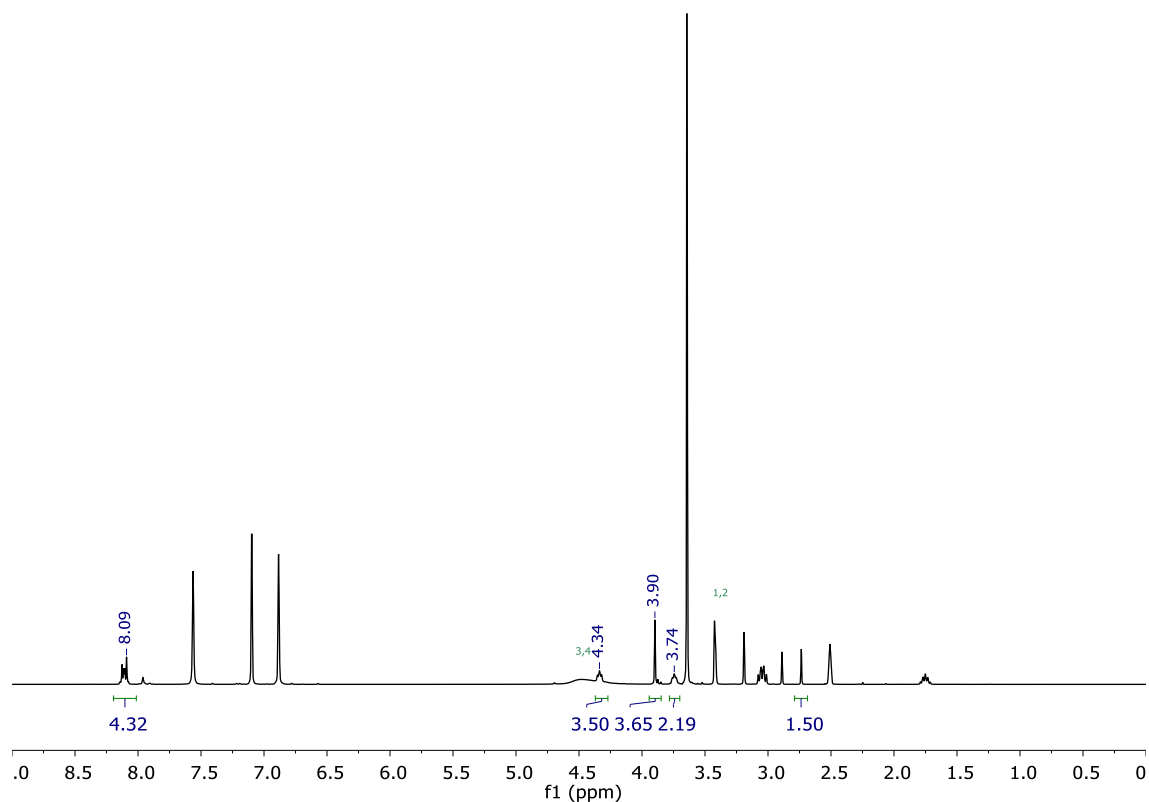
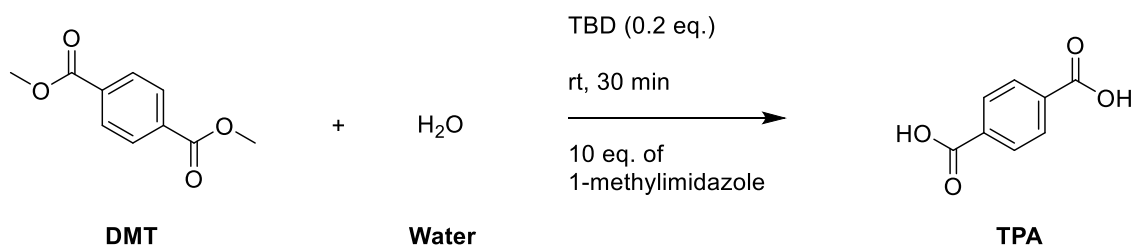


Figure S.4.1. DMT reaction with EG at room temperature in the presence of 0.2 eq. of TBD and 10 eq. of 1-methylimidazole as solvent. An equilibrium between DMT and the so formed BHET is observed close to 50% proportion of both compounds.

DMT reaction with water



Scheme S.4.2. Model reaction scheme of DMT transesterification with water catalysed by TBD to form TPA.

DMT (0.5 g, 2.57 mmol) was reacted with water (0.092 g, 5.14 mmol) using 0.2 eq. TBD as catalyst (0.072 g, 0.51 mmol) in the presence of 1-methylimidazole as solvent (2.11 g, 25.7 mmol) at room temperature for 30 minutes in normal atmosphere. After reaction completion an aliquot was taken and analysed by means of ¹H NMR in deuterated DMSO.

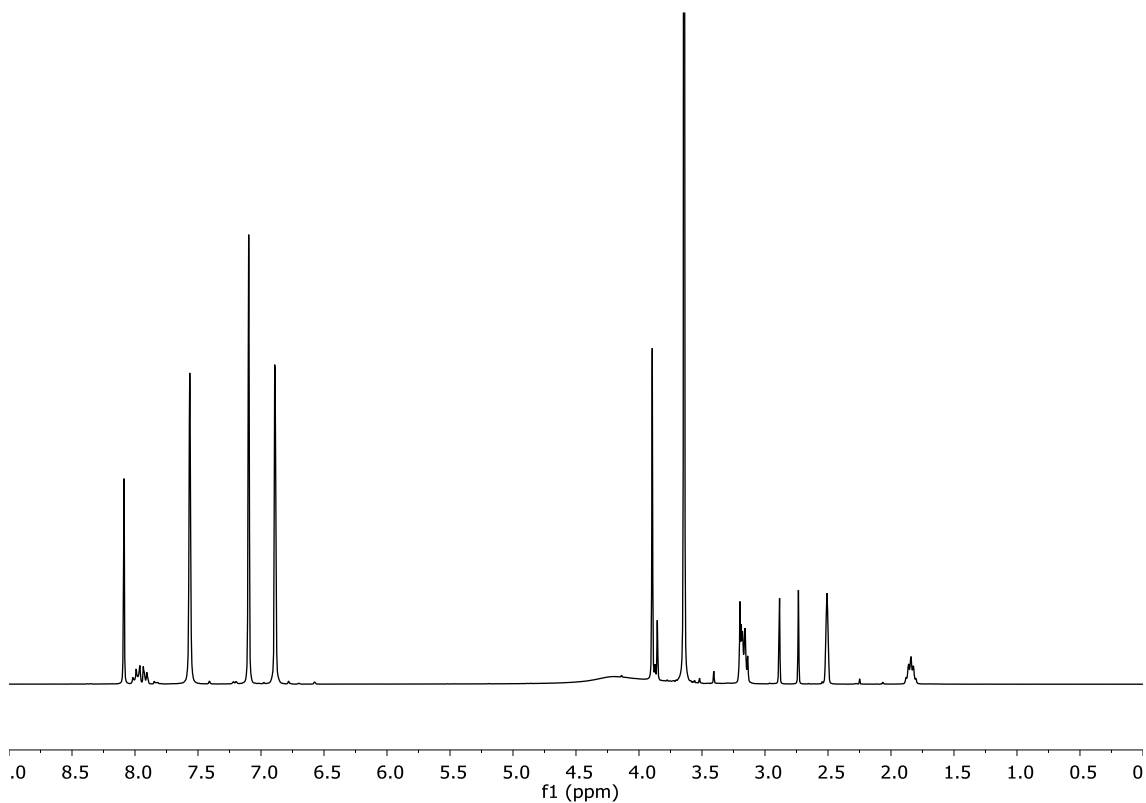
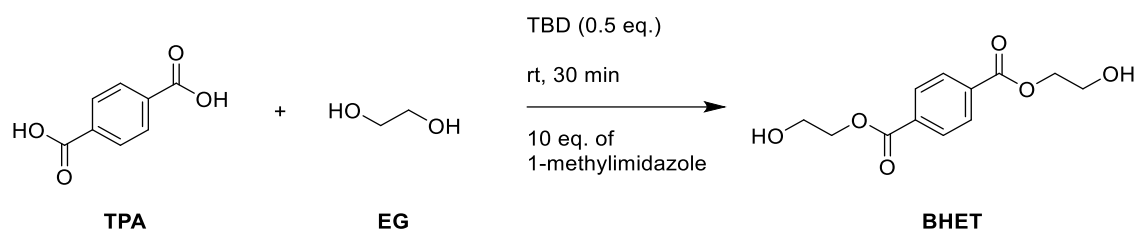


Figure S.4.2. DMT reaction with water at room temperature in the presence of 0.2 eq. of TBD and 10 eq. of 1-methylimidazole as solvent. No TPA was observed.

TPA esterification with EG catalysed by TBD



Scheme S.4.3. Model reaction scheme of TPA esterification with EG catalysed by TBD to form BHET.

TPA (0.5 g, 3.01 mmol) was reacted with EG (0.37 g, 6.01 mmol) using 0.5 eq. TBD as catalyst (0.212 g, 1.5 mmol) in the presence of 1-methylimidazole as solvent (2.33 g, 30.1 mmol) at room temperature for 1 hour in normal atmosphere. After 10 minutes and after reaction completion samples were taken and analysed by means of ^1H NMR in deuterated DMSO.

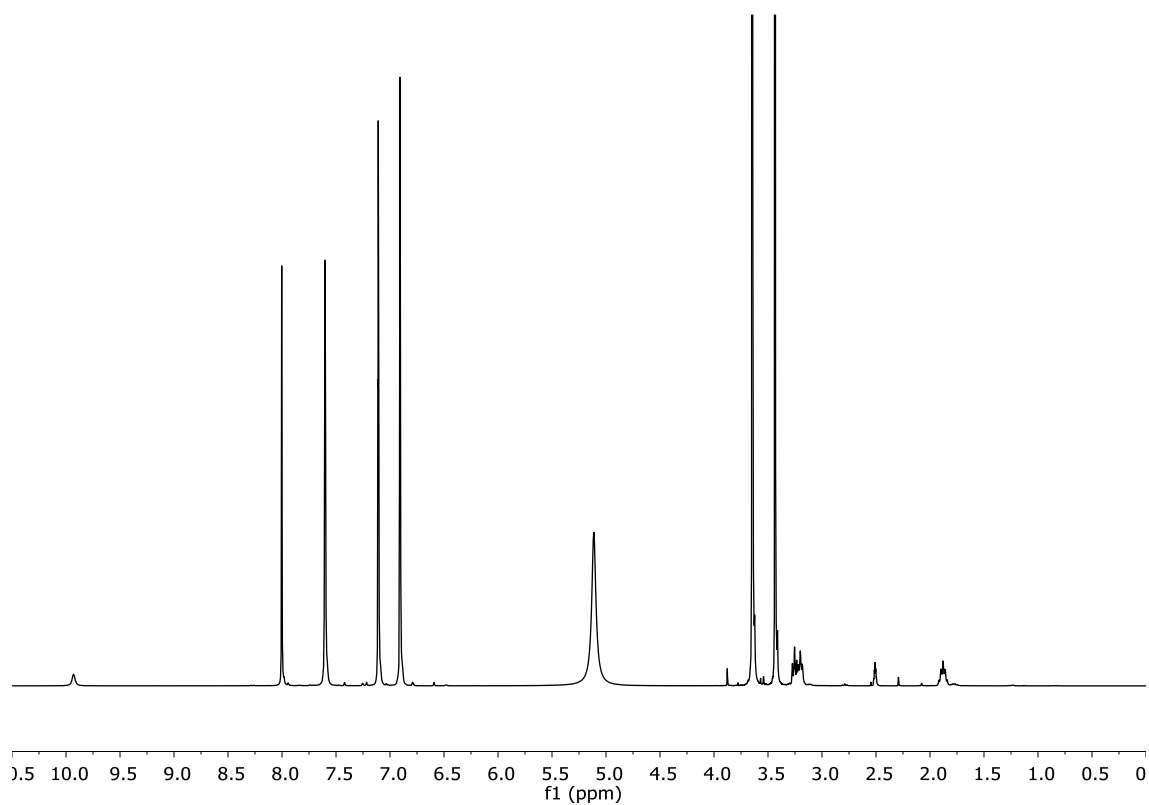


Figure S.4.3. TPA reaction with EG at room temperature in the presence of 0.5 eq. of TBD and 10 eq. of 1-methylimidazole as solvent. No esterification was observed.

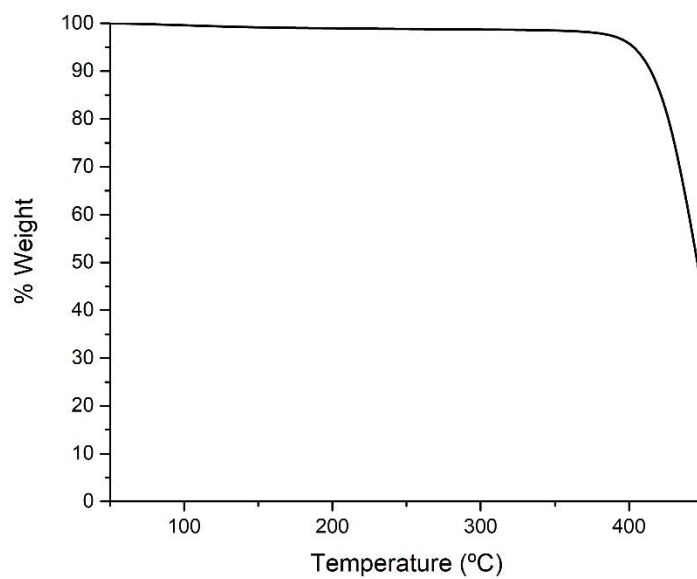


Figure S.4.4. TGA of bottle grade PET employed for depolymerisation reactions. No weight loss related with water traces could be observed.

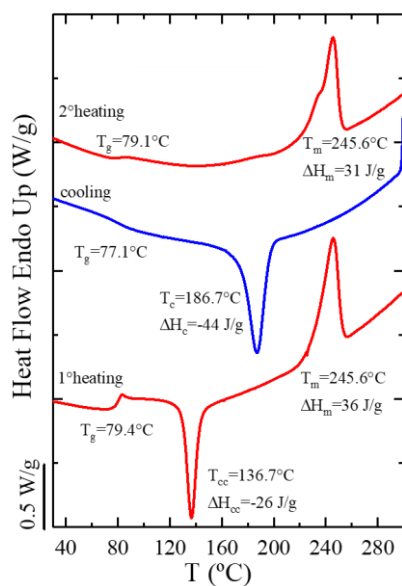


Figure S.4.5. DSC thermogram of bottle grade PET. According to the results the crystallinity degree of this PET was 7.4 % calculate from the first heating rate.

Kinetics varying catalysts type and loading

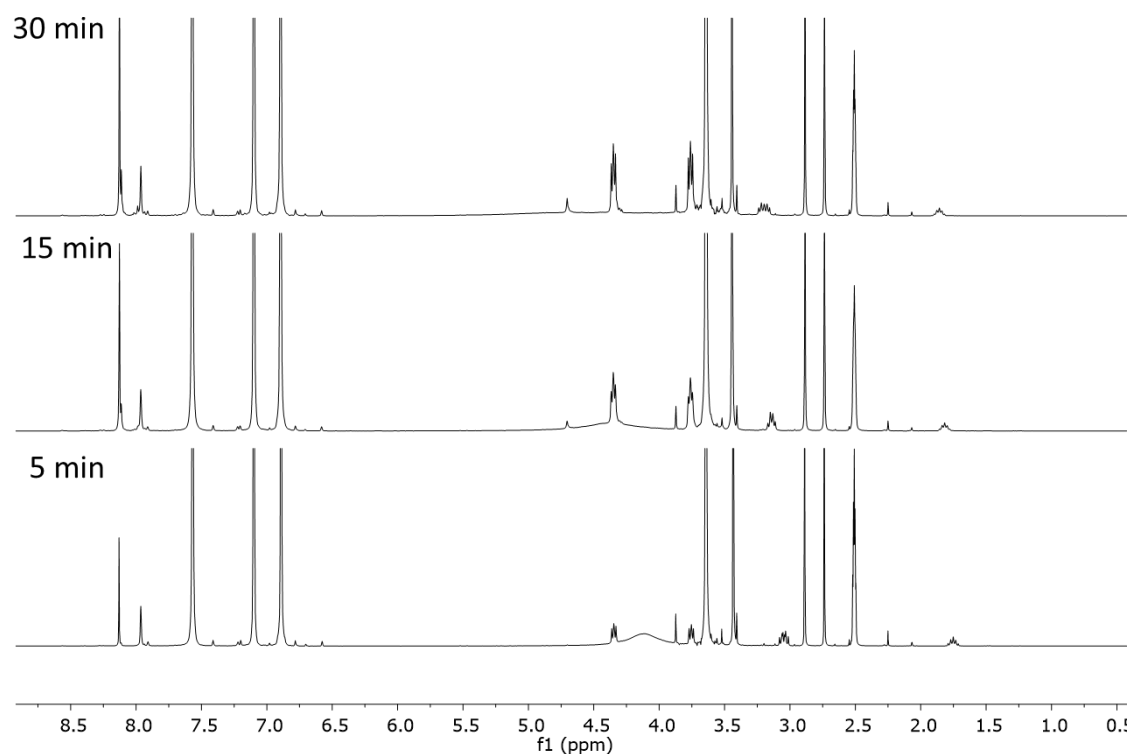


Figure S.4.6. Kinetics of the depolymerisation of PET monitored through ^1H NMR spectroscopy carried out with 0.1 eq. of TBD as catalyst, 2 eq. EG as nucleophile and 10 eq. of 1-Methylimidazole as solvent, at 100 °C.

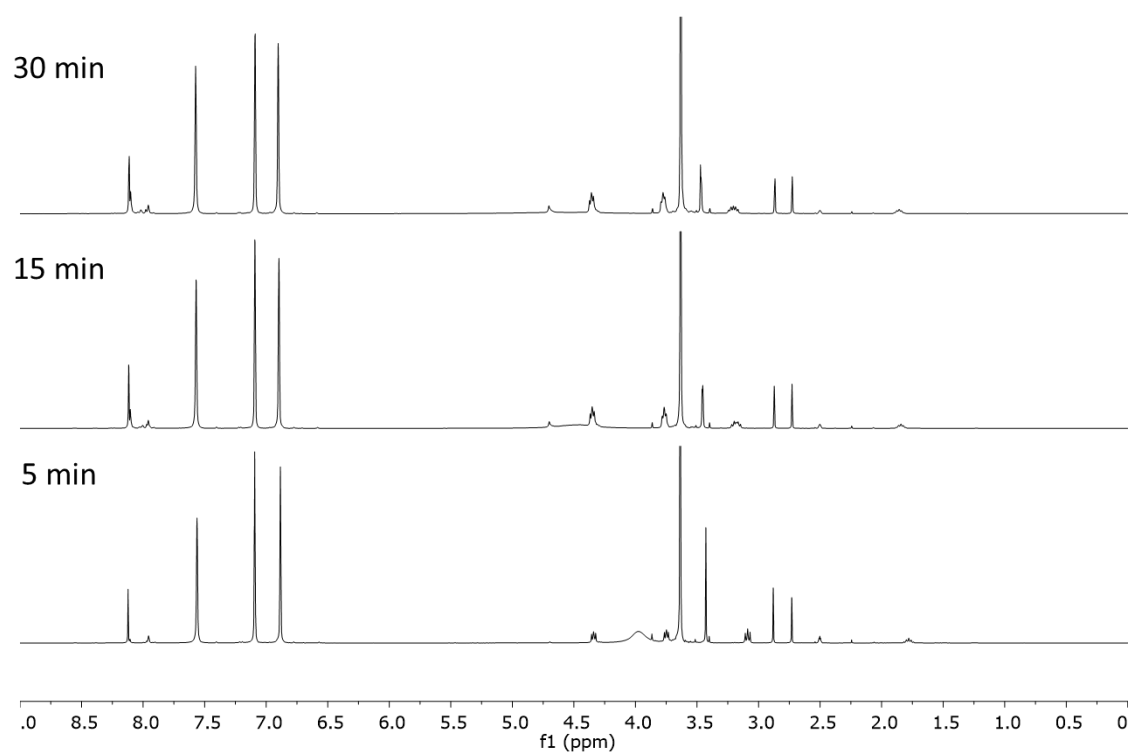


Figure S.4.7. Kinetics of the depolymerisation of PET monitored through ^1H NMR spectroscopy carried out with 0.2 eq. of TBD as catalyst, 2 eq. EG as nucleophile and 10 eq. of 1-Methylimidazole as solvent, at 100 °C.

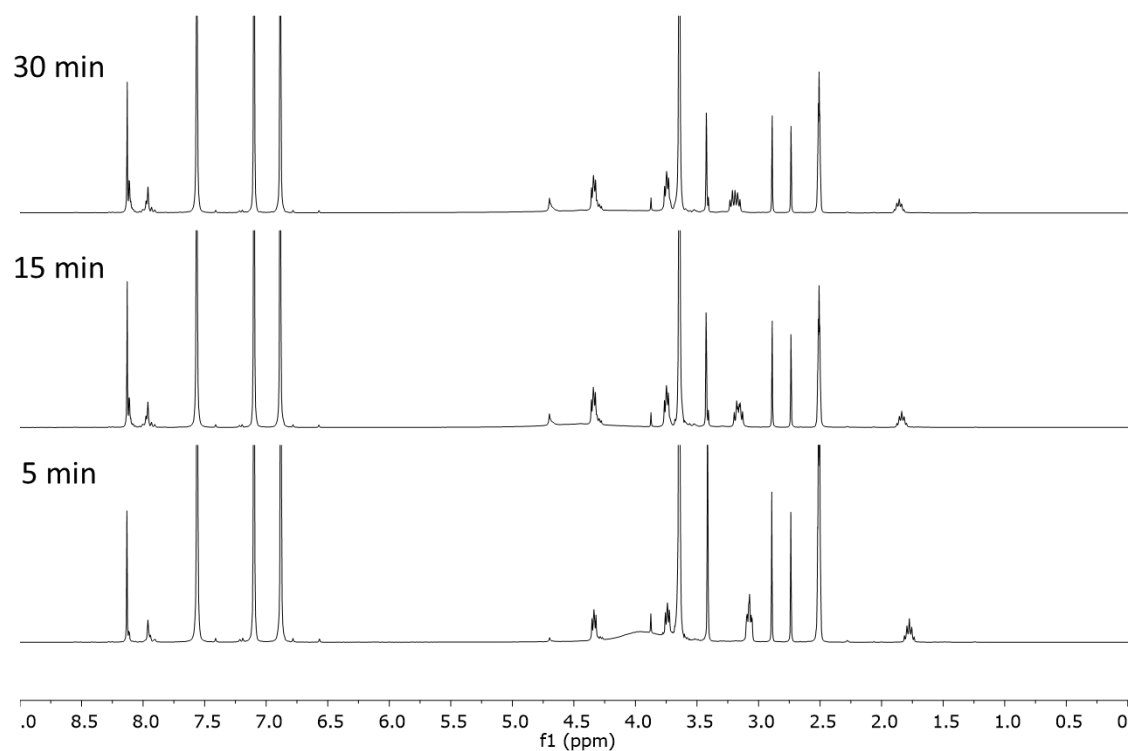


Figure S.4.8. Kinetics of the depolymerisation of PET monitored through ^1H NMR spectroscopy carried out with 1 eq. of 0.3 eq. TBD as catalyst, 2 eq. EG as nucleophile and 10 eq. of 1-Methylimidazole as solvent, at 100 °C.

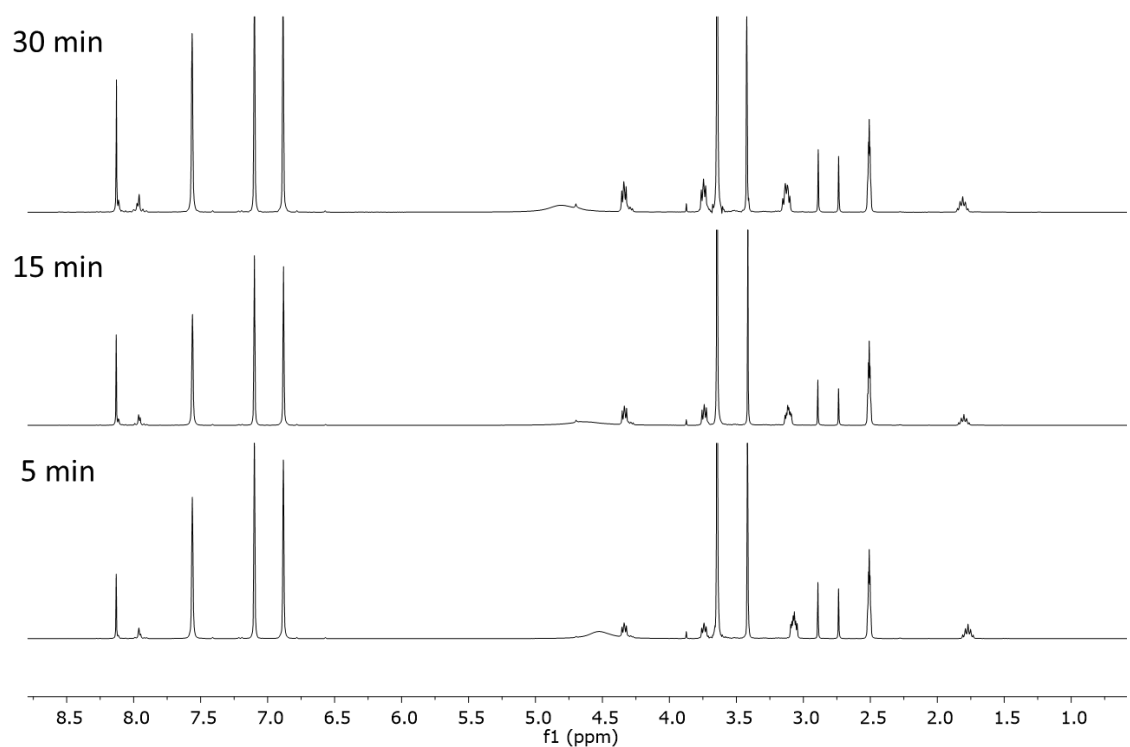


Figure S.4.9. Kinetics of the depolymerisation of PET monitored through ^1H NMR spectroscopy carried out with 0.5 eq. of TBD as catalyst, 2 eq. EG as nucleophile and 10 eq. of 1-Methylimidazole as solvent, at 100 °C.

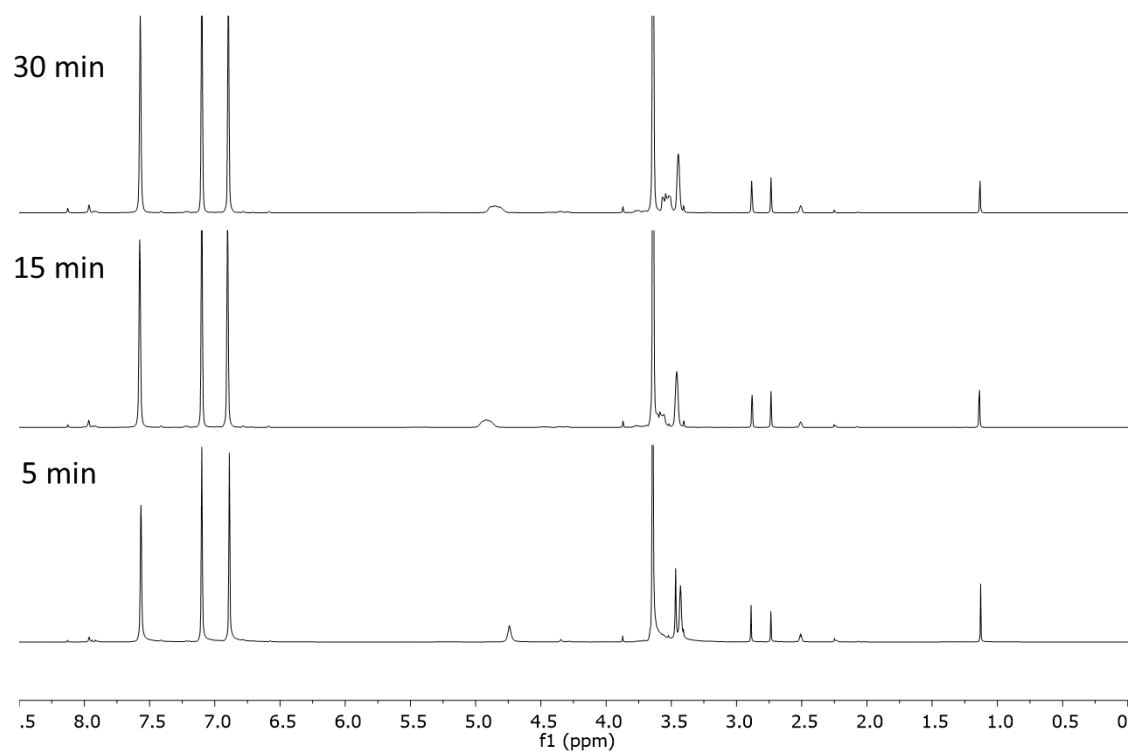


Figure S.4.10. Kinetics of the depolymerisation of PET monitored through ¹H NMR spectroscopy carried out with 0.2 eq. of tBuOK as catalyst, 2 eq. EG as nucleophile and 10 eq. of 1-Methylimidazole as solvent, at 100 °C.

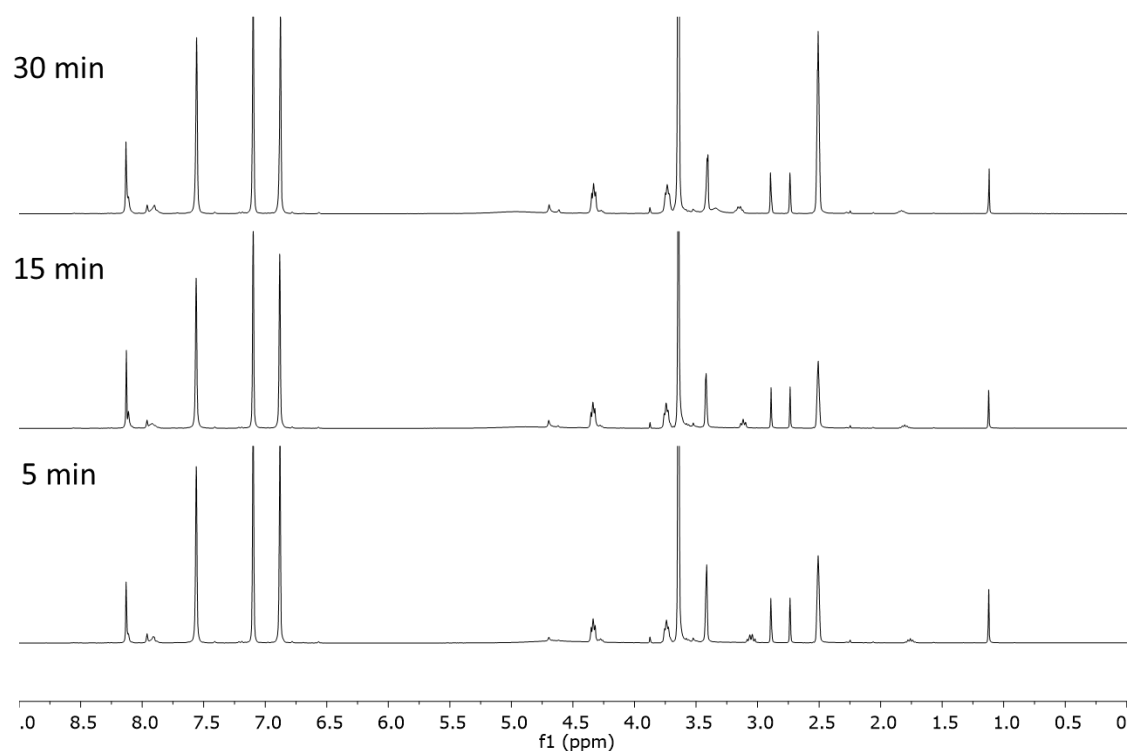


Figure S.4.11. Kinetics of the depolymerisation of PET monitored through ¹H NMR spectroscopy carried out with 0.1 eq. of TBD and 0.2 eq. of tBuOK as catalyst, 2 eq. EG as nucleophile and 10 eq. of 1-Methylimidazole as solvent, at 100 °C.

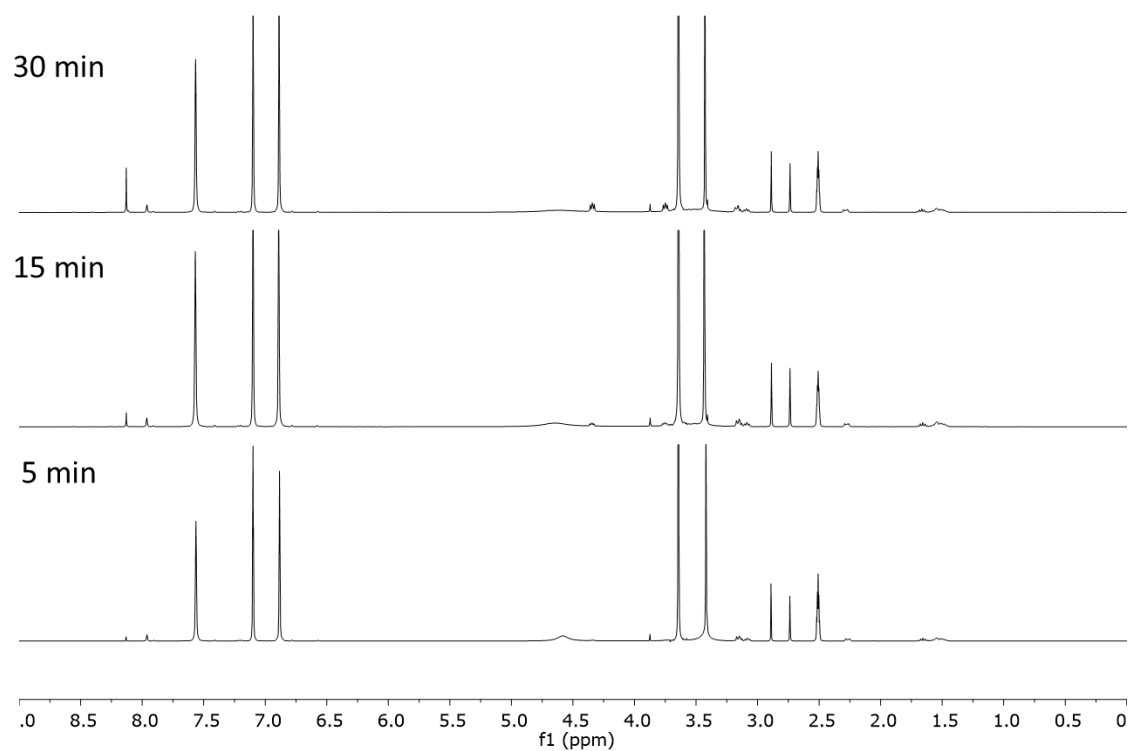


Figure S.4.12. Kinetics of the depolymerisation of PET monitored through ^1H NMR spectroscopy carried out with 0.2 eq. of DBU as catalyst, 2 eq. EG as nucleophile and 10 eq. of 1-Methylimidazole as solvent, at 100 °C.

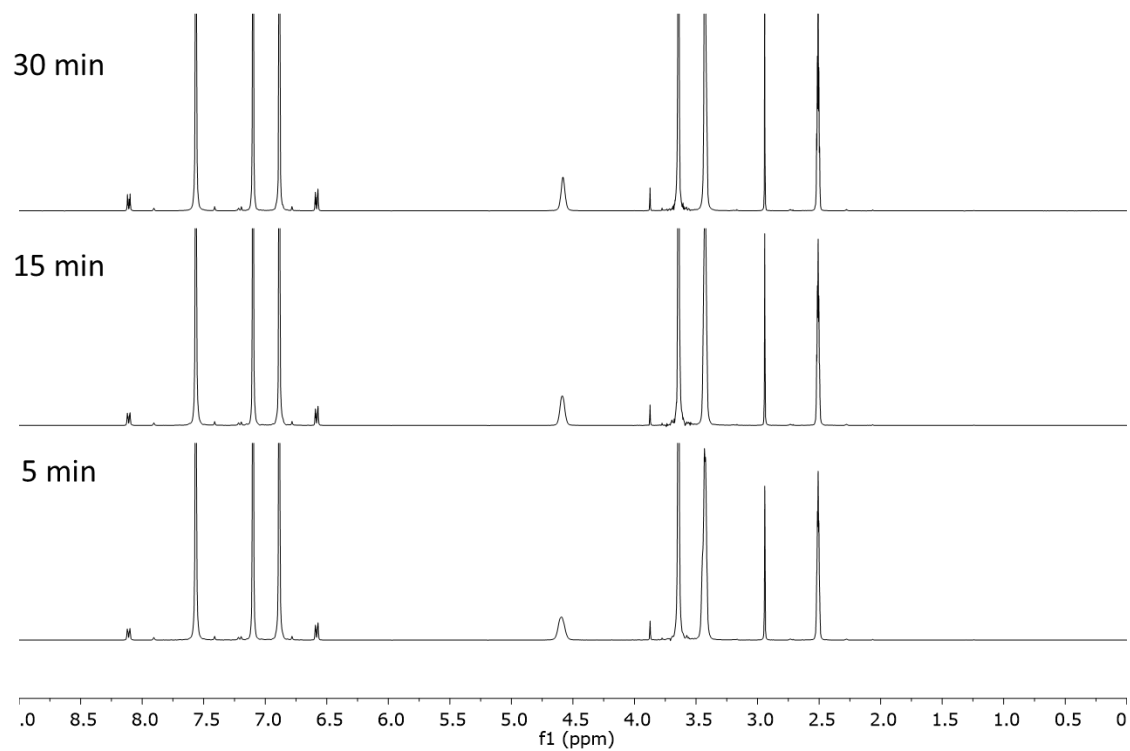


Figure S.4.13. Kinetics of the depolymerisation of PET monitored through ^1H NMR spectroscopy carried out with 0.2 eq. of DMAP as catalyst, 2 eq. EG as nucleophile and 10 eq. of 1-Methylimidazole as solvent, at 100 °C.

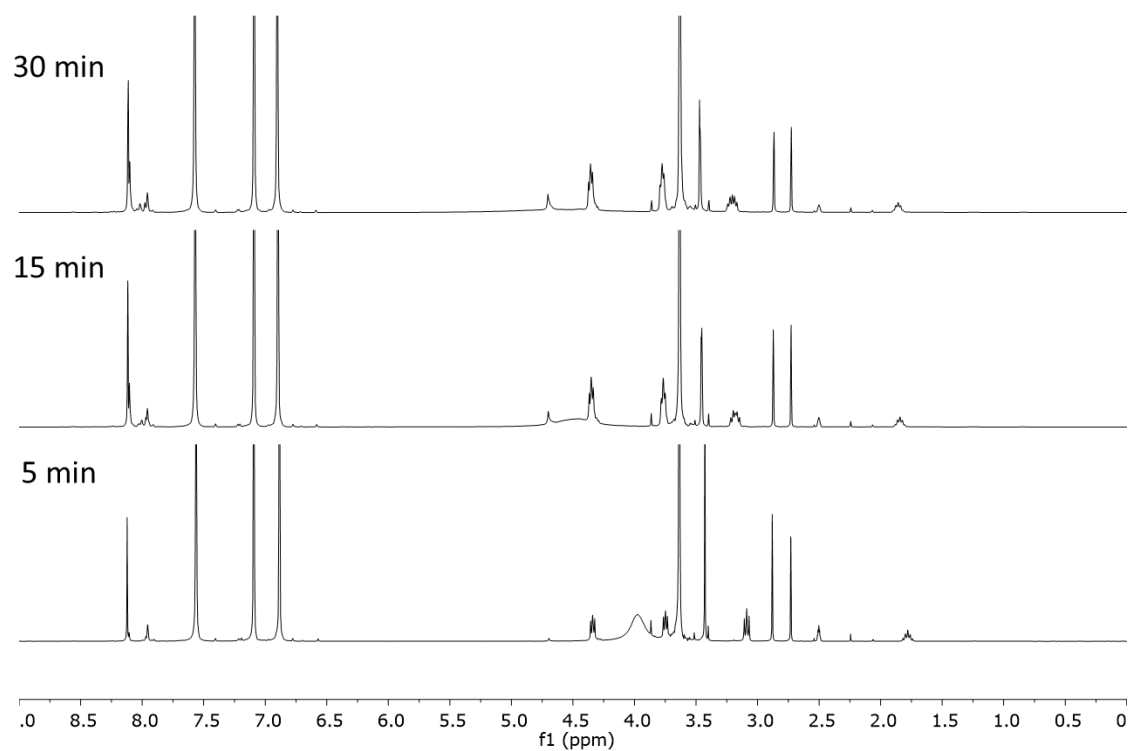


Figure S.4.14. Kinetics of the depolymerisation of PET monitored through ^1H NMR spectroscopy carried out with 0.2 eq. of TBD as catalyst, 2 eq. EG as nucleophile and 10 eq. of 1-Methylimidazole as solvent, at 100 °C.

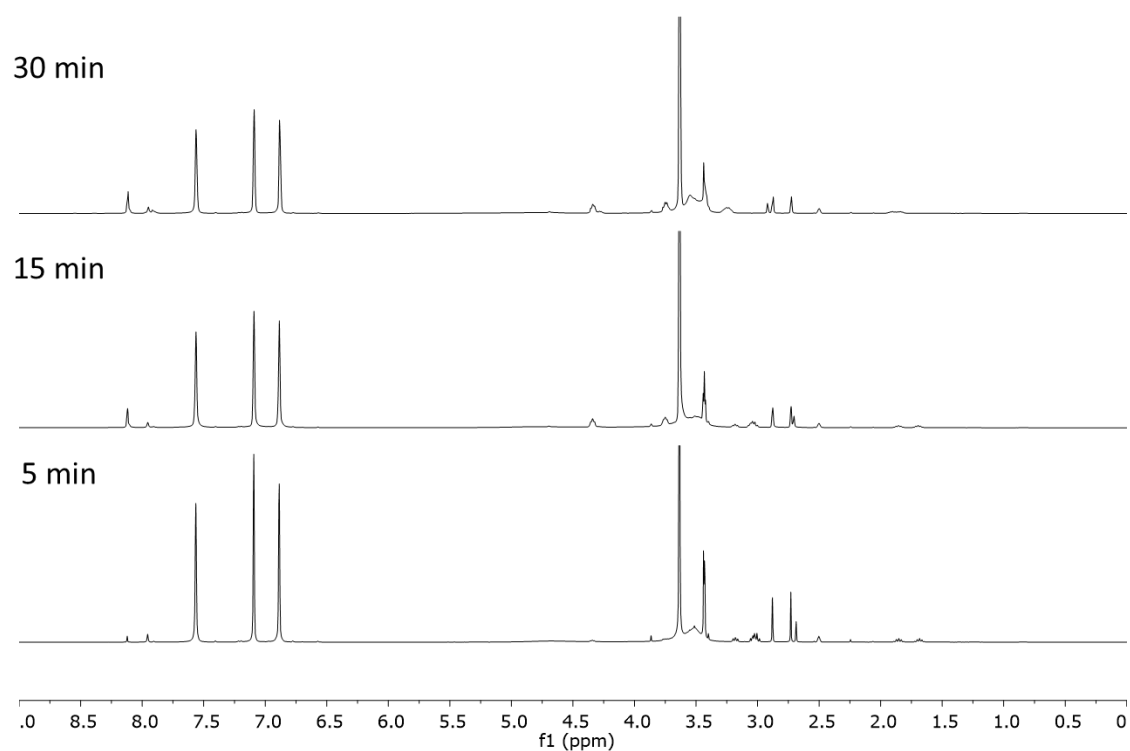


Figure S.4.15. Kinetics of the depolymerisation of PET monitored through ^1H NMR spectroscopy carried out with 0.2 eq. of Me-TBD as catalyst, 2 eq. EG as nucleophile and 10 eq. of 1-Methylimidazole as solvent, at 100 °C.

DOSY NMR experiment of PET reaction with TBD in the presence of 1-methylimidazole

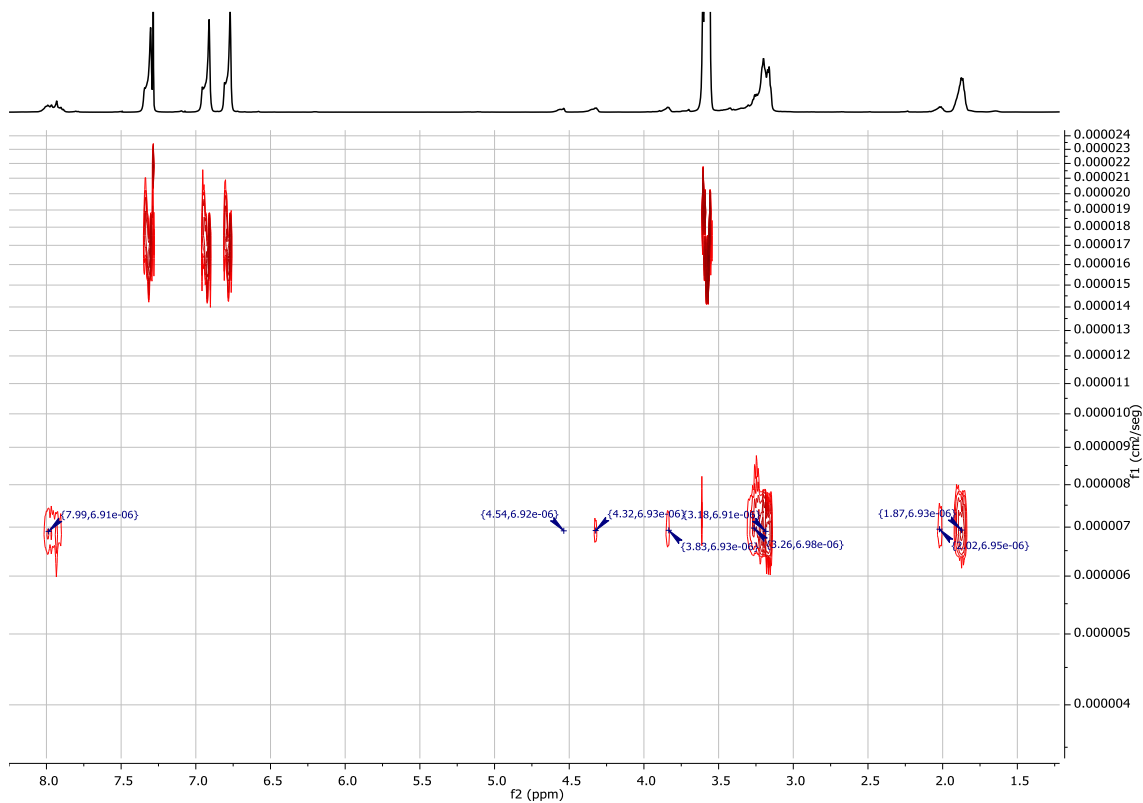


Figure S.4.16. DOSY-NMR experiment performed in CDCl₃ of a reaction of PET in the presence of 1 eq. TBD and 10 eq. of 1-Methylimidazole as solvent. TBD and PET showed the same diffusion coefficient.

PET depolymerisation reactions in the presence of different water content

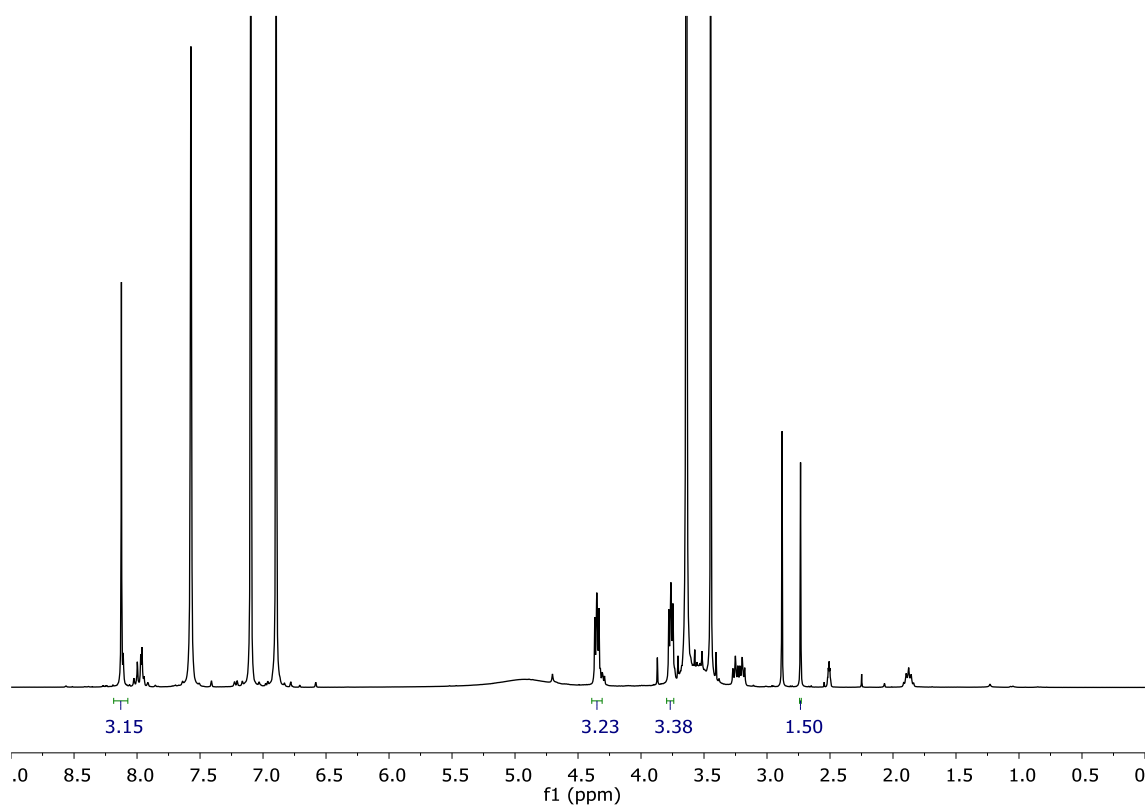


Figure S.4.17. ^1H NMR spectrum of PET glycolysis depolymerisation by 2 eq. of EG using of 0.2 eq. of TBD as catalyst in 10 eq. of dry 1-methylimidazole as solvent in the absence of water. BHET conversion was evaluated by comparing the area of the corresponding signals with the ones of 0.5 eq. DMF added as internal standard.

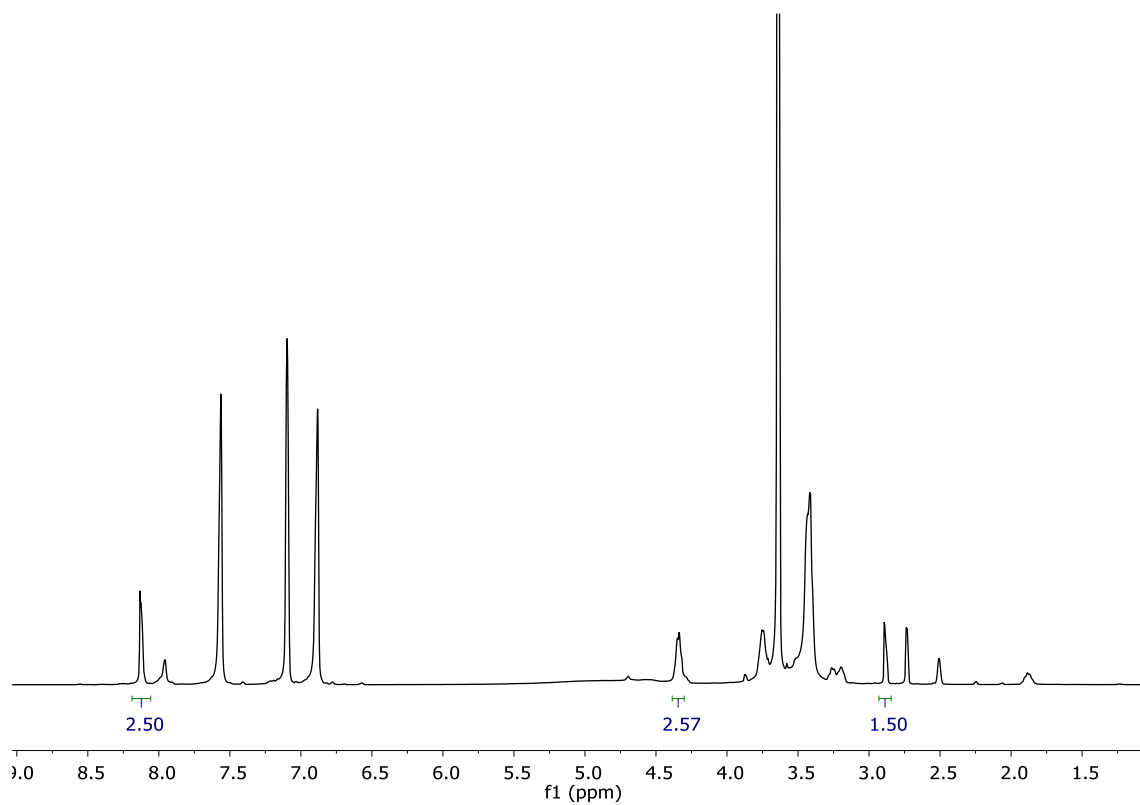


Figure S.4.18. ¹H NMR spectrum of PET glycolysis depolymerisation by 2 eq. of EG using of 0.2 eq. of TBD as catalyst in 10 eq. of dry 1-methylimidazole as solvent in the presence of 0.5 eq. of water.

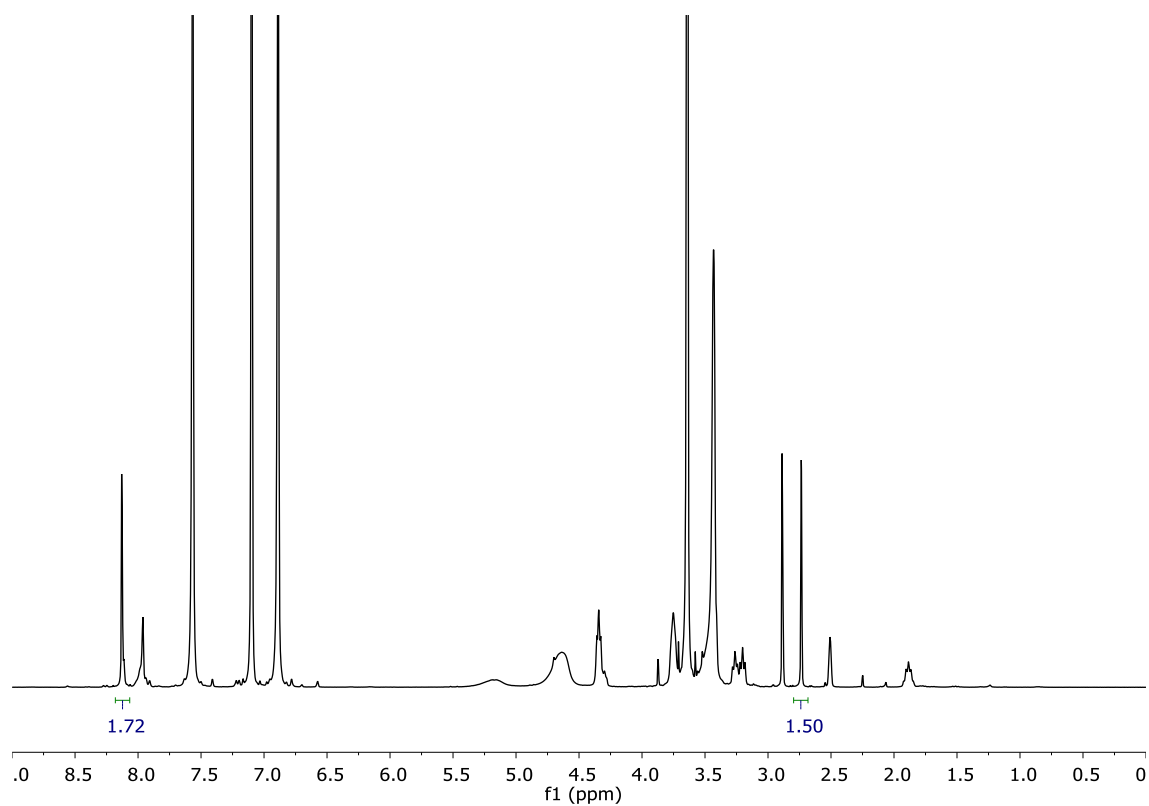


Figure S.4.19. ¹H NMR spectrum of PET glycolysis depolymerisation by 2 eq. of EG using of 0.2 eq. of TBD as catalyst in 10 eq. of dry 1-methylimidazole as solvent in the presence of 1 eq. of water.

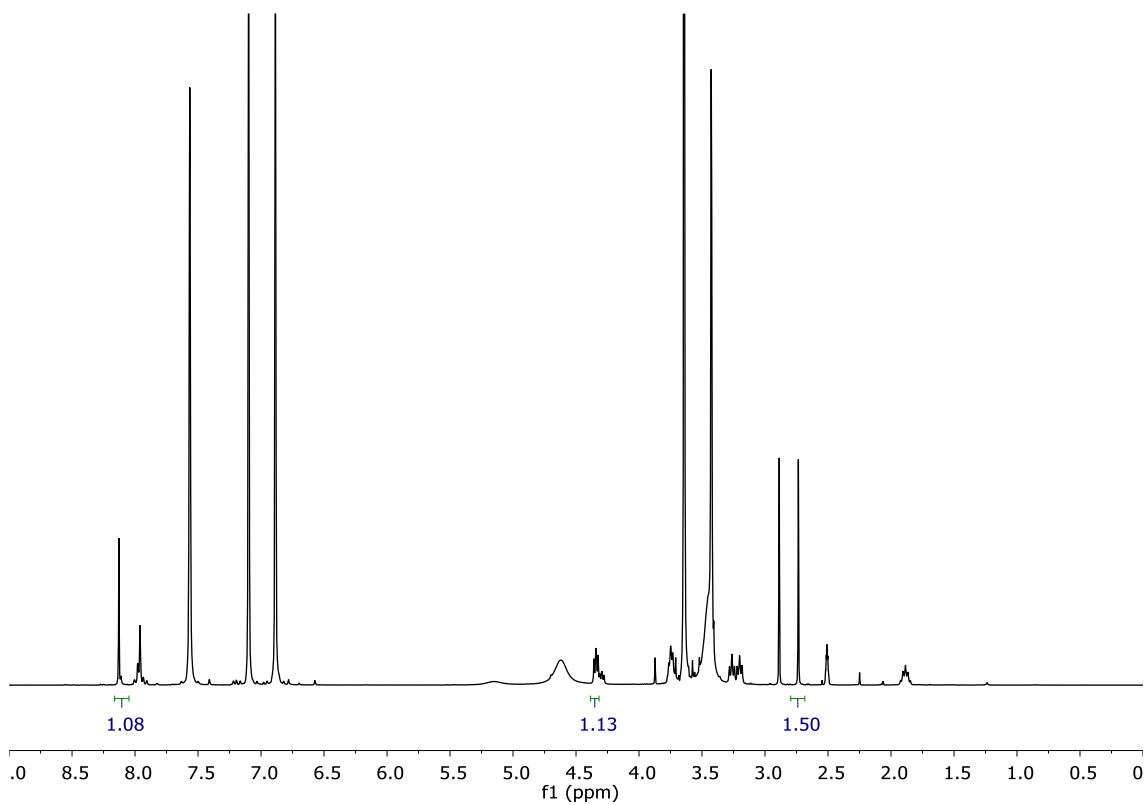


Figure S.4.20. ¹H NMR spectrum of PET glycolysis depolymerisation by 2 eq. of EG using of 0.2 eq. of TBD as catalyst in 10 eq. of dry 1-methylimidazole as solvent in the presence of 3 eq. of water.

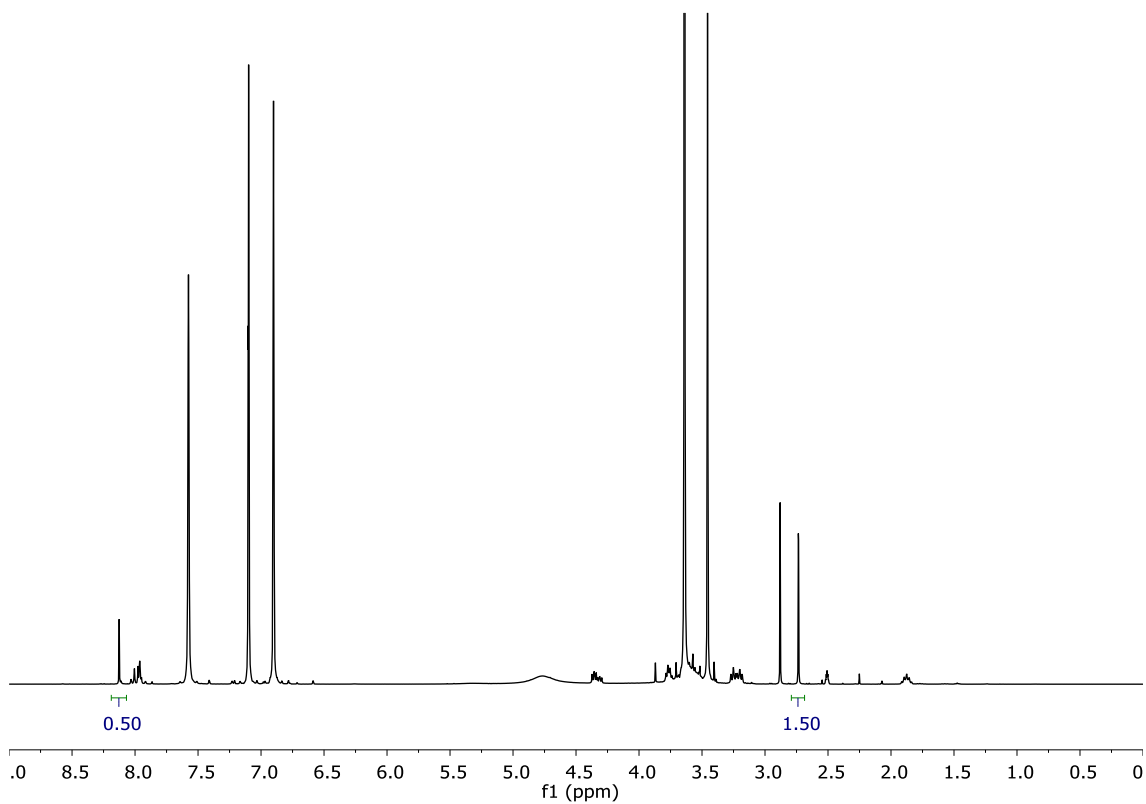


Figure S.4.21. ¹H NMR spectrum of PET glycolysis depolymerisation by 2 eq. of EG using of 0.2 eq. of TBD as catalyst in 10 eq. of dry 1-methylimidazole as solvent in the presence of 5 eq. of water.

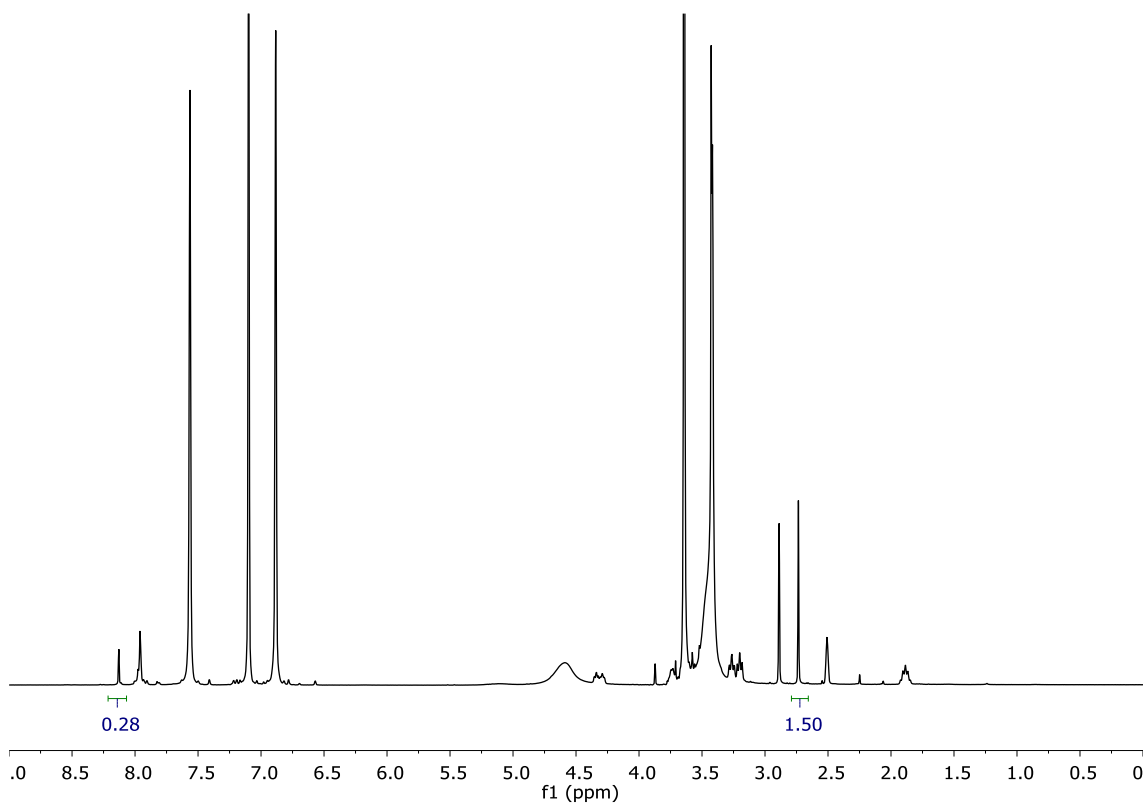


Figure S.4.22. ^1H NMR spectrum of PET glycolysis depolymerisation by 2 eq. of EG using of 0.2 eq. of TBD as catalyst in 10 eq. of dry 1-methylimidazole as solvent in the presence of 10 eq. of water.

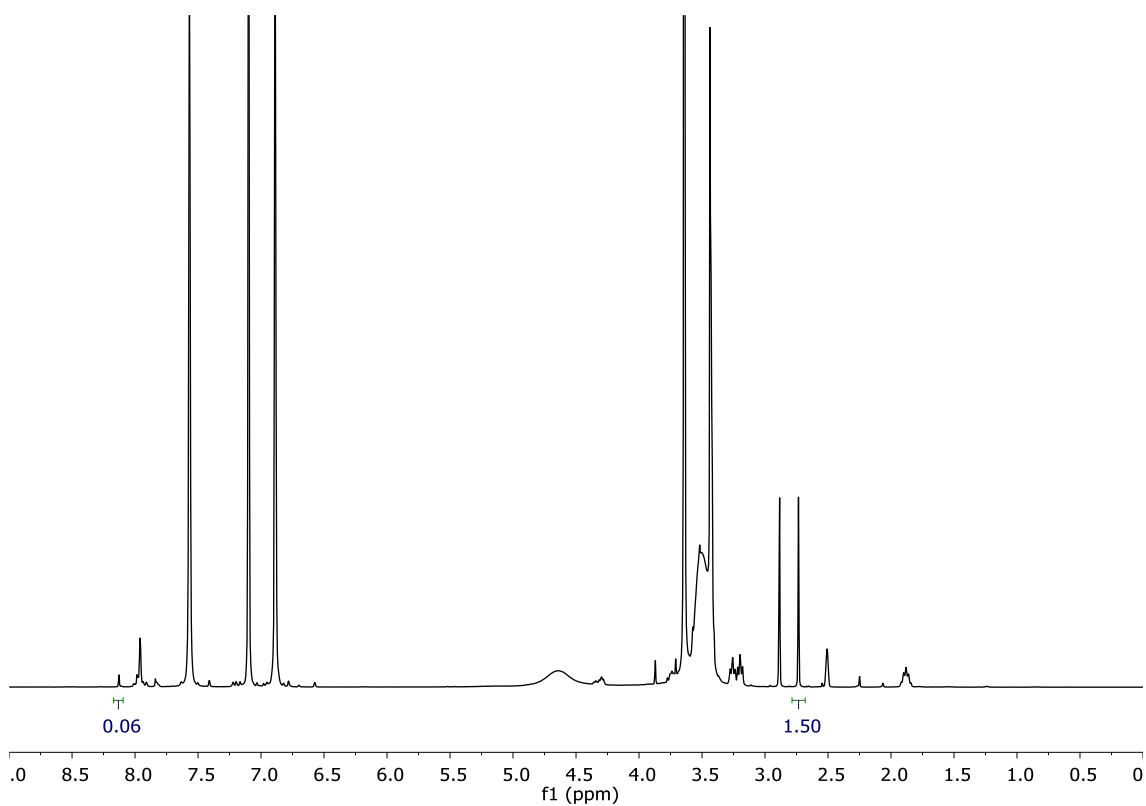


Figure S.4.23. ^1H NMR spectrum of PET glycolysis depolymerisation by 2 eq. of EG using of 0.2 eq. of TBD as catalyst in 10 eq. of dry 1-methylimidazole as solvent in the presence of 20 eq. of water.

¹H NMR spectra of TBD, protonated TBD with TPA in 1:1 and 1:2 molar ratio and BHET product

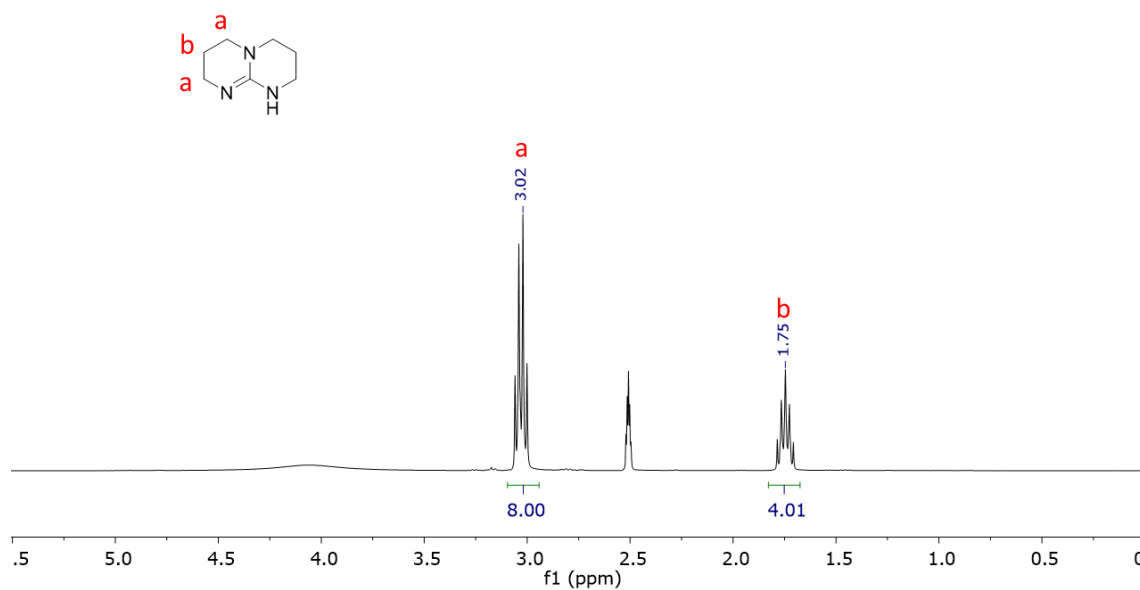


Figure S.4.24. ¹H NMR spectrum of pure TBD in its free base form.

¹H NMR (300 MHz, DMSO-d₆:298 K) δ 3.03 (q, J = 5.8 Hz, 8H), 1.83 – 1.67 (m, 4H).

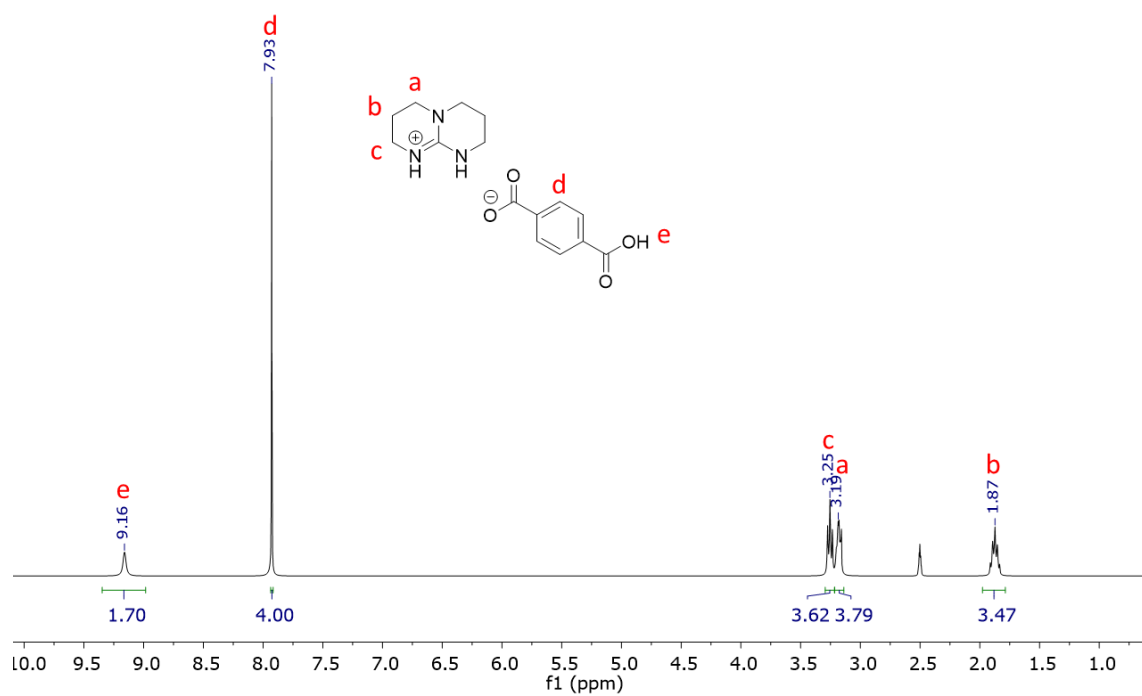


Figure S.4.25. ¹H NMR spectrum of TBD:TPA 1:1 mol ratio recorded in-DMSO-d₆.

¹H NMR (300 MHz, DMSO-d₆, 298 K) δ 9.16 (s, 2H), 7.93 (s, 4H), 3.25 (t, J = 5.9 Hz, 4H), 3.21 – 3.14 (t, J = 5.9 Hz, 4H), 1.87 (q, J = 5.9 Hz, 4H).

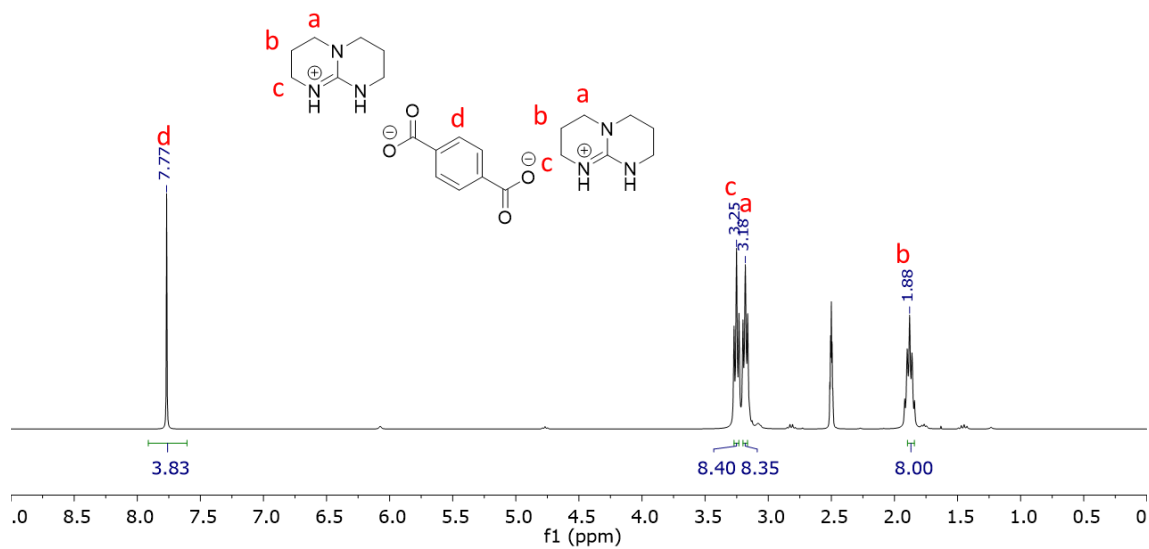


Figure S.4.26. ¹H NMR spectrum of TBD:TPA 1:2 mol ratio recorded in DMSO-d₆.

¹H NMR (300 MHz, DMSO-d₆; 298 K) δ 7.77 (s, 4H), 3.25 (t, $J = 5.9$ Hz, 4H), 3.21 – 3.16 (t, 4H), 1.88 (q, $J = 5.9$ Hz, 4H).

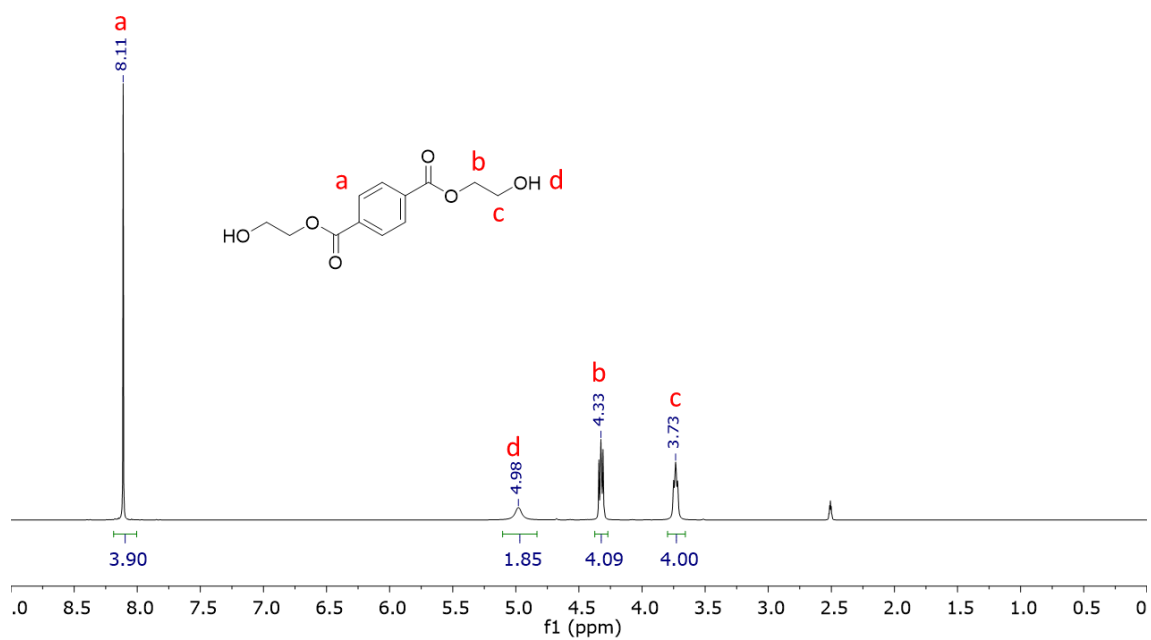


Figure S.4.27. ¹H NMR spectrum of obtained BHET product.

¹H NMR (300 MHz, DMSO-d₆, 298 K) δ 8.11(s, 4H), 4.98(s, 2H), 4.33(t, 4H), 3.73(t, 4H).