New trends in the synthesis of polyesters: from catalyst design to chemical recycling

PhD Thesis

presented by

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Summary

Polyesters have demonstrated to be interesting materials to approach the sustainability target that is proposed by the United Nations in the field of "Sustainable Development Goals". A key reason for their choice is not only their ability to biodegrade under appropriate conditions but also their potential to be chemically recycled as well as their potential to be prepared from biomass. Although this polymer conceivably could be obtained from biomass and several efforts have been made to increase their recyclability, most of the polyesters produced industrially are petroleum-based and the synthetic methods employed are not green enough considering the Sustainable Development Goals as during their synthesis transition metals and energy-intensive processes are employed.

Taking advantage of the possibilities that this polymer family offers this work addresses some of the challenges that are still needed to increase the sustainability of polyester materials and synthesis processes.

To put the topic in context, Chapter 1 introduces the advances that have been done in polyester synthesis highlighting the recent literature and the challenges that need to be faced for sustainable polyester obtaining. First, polyesters and different routes for their synthesis have been described and afterward, the three challenges that are approached in this thesis are furtherly explained. On one side, the use of naturally occurring catalysts, from the other side, the transition from petroleum-based monomers to biobased monomers, and finally, the preparation of polyesters in mild conditions.

Chapter 2 proposes an interesting naturally occurring catalyst for ring-opening polymerization of L-lactide at industrially reliable conditions. Different natural catalysts

have been investigated for the synthesis of polylactide at high reaction temperatures in bulk, concluding that taurine is a highly efficient catalyst, comparable to commonly used catalysts. Due to its good results, it was furtherly characterized in order to understand its catalytic mechanism. Moreover, the toxicity of the synthesized materials was tested. In addition, taurine was used for the ring-opening polymerization of some other monomers, such as cyclic amides and cyclic carbonates.

In Chapters 3 and 4 an advance towards the implementation of biobased monomers and polymers is done. In Chapter 3 polyethylene furanoate (PEF) is introduced as a biobased alternative to petroleum-based polyethylene terephthalate (PET), as it has good properties that could be competitive with PET for some applications. In order to make it suitable for industrial implementation, a closed-loop recycling process was studied as a sustainable end-of-life assessment by the use of a thermally stable organocatalyst. In Chapter 4, an end-of-life option of polyhydroxybutyrate has been described, a polymer synthesized naturally by microorganisms. Through the hydrolytic depolymerization of it, interesting β-hydroxy acid monomers have been obtained using a facile method. The depolymerization process was optimized by the use of taurine as the catalyst reducing up to 2 % the side products formed during the process.

Focusing on the last challenge proposed in this thesis, a room temperature step-growth polymerization method for the synthesis of polyester is presented in Chapter 5. For that, first, the synthesis of a novel reactive spiro-dilactone was carried out by a three-step synthetic route. Afterward, the polymerization of the synthesized dilactone together with a diol was performed, obtaining interesting polyesters by polyaddition reaction at room temperature employing DBU as an organocatalyst. In order to extend the scope of this promising room temperature step-growth polymerization method,

some other nucleophiles were tried including diamines and dithiols, for the synthesis of polyamides and polythioesters.

To conclude, Chapter 6 encompasses the conclusions attained in this thesis, facing three challenges for more sustainable polyester materials and synthetic methods. Furthermore, a perspective for the implementation of these methods for industrial processes is offered, disclosing that there is the need to continue exploring sustainable procedures to create a more environmentally and cost-effective society.

Resumen

Los poliésteres han demostrado ser un material interesante para la misión de sostenibilidad que propone Naciones Unidas en el ámbito de los "Objetivos de Desarrollo Sostenible". Una de las razones fundamentales de su elección para este fin no es sólo su capacidad de biodegradación en condiciones adecuadas, sino también su potencial de reciclaje junto con su potencial de ser preparado a partir de biomasa. Aunque este polímero podría obtenerse a partir de la biomasa y se han realizado varios esfuerzos para aumentar su reciclabilidad, la mayoría de los poliésteres producidos industrialmente están basados en el petróleo y los métodos sintéticos empleados no son lo suficientemente ecológicos teniendo en cuenta los Objetivos de Desarrollo Sostenible, ya que durante su síntesis se emplean metales de transición y procesos intensivos en energía.

Aprovechando las posibilidades que ofrece esta familia de polímeros, este trabajo aborda algunos de los retos que aún son necesarios para aumentar la sostenibilidad de los materiales y procesos de síntesis del poliéster.

Para contextualizar el tema, el Capítulo 1 introduce los avances que se han realizado en la síntesis de poliésteres destacando la literatura reciente y los retos que hay que afrontar para la obtención de un poliéster sostenible. En primer lugar, se han descrito los poliésteres y las diferentes rutas para su síntesis y, posteriormente, se explican los tres retos que se abordan en esta tesis. Por un lado, el uso de catalizadores naturales, por otro, la transición de los monómeros derivados del petróleo a monómeros de origen biológico y, por último, la preparación de poliésteres en condiciones suaves.

El Capítulo 2 propone un interesante catalizador de origen natural para la polimerización de apertura de anillo de L-lactida en condiciones industrialmente fiables.

Se han investigado diferentes catalizadores naturales para la síntesis de polilactida a altas temperaturas de reacción en masa, concluyendo que la taurina es un catalizador altamente eficiente, comparable a los catalizadores comúnmente utilizados. Debido a sus buenos resultados, se caracterizó aún más para entender su mecanismo catalítico, junto con la toxicidad de los materiales sintetizados. Además, la taurina se utilizó para la polimerización de apertura de anillo de algunos otros monómeros, tales como, amidas cíclicas y carbonatos cíclicos.

En los Capítulos 3 y 4 se realiza un avance hacia la aplicación de monómeros y polímeros de base biológica. En el Capítulo 3 se presenta el furanoato de polietileno (PEF) como una alternativa de biobasada al tereftalato de polietileno (PET) basado en el petróleo, ya que tiene buenas propiedades que podrían ser competitivas con el PET para algunas aplicaciones. Con el fin de hacerlo apto para su aplicación industrial, se estudió el proceso de reciclado de ciclo cerrado como una evaluación sostenible del fin de vida mediante el uso de un organocatalizador térmicamente estable. En el Capítulo 4 se ha descrito una opción de fin de vida del polihidroxibutirato, un polímero sintetizado naturalmente por microorganismos. Mediante la despolimerización hidrolítica del mismo se han obtenido interesantes monómeros de β-hidroxiácidos utilizando un método sencillo. El proceso de despolimerización se optimizó mediante el uso de taurina como catalizador reduciendo hasta un 2 % los productos secundarios formados durante el proceso.

Centrándonos en el último reto propuesto en esta tesis, en el Capítulo 5 se presenta un método de polimerización por etapas a temperatura ambiente para la síntesis de poliéster. Para ello, se procedió con la síntesis de una nueva espiro-dilactona reactiva mediante una ruta sintética de tres pasos. Posteriormente, se llevó a cabo la polimerización de la dilactona sintetizada junto con un diol, obteniéndose interesantes poliésteres por reacción de poliadición a temperatura ambiente empleando DBU como

organocatalizador. Para ampliar el alcance de este prometedor método de polimerización por etapas a temperatura ambiente, se probaron otros nucleófilos, incluyendo diaminas y ditioles, para la síntesis de poliamidas y poliésteres.

Para finalizar, el Capítulo 6 engloba las conclusiones alcanzadas en esta tesis, afrontando tres retos para conseguir materiales y métodos sintéticos de poliéster más sostenibles. Además, se ofrece una perspectiva para la implementación de estos métodos para los procesos industriales, revelando que existe la necesidad de seguir explorando en los procedimientos sostenibles con el fin de crear una sociedad más ecológica y económicamente rentable.

List of abbreviations

AcOH	acetic acid
BA	benzoic acid
BHEF	bis(2-hydroxyethyl)-furan-2,5-dicarboxylate
BHET	bis(2-hydroxyethyl) terephthalate
BINAP-Ru	ruthenium 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
bio-EG	biobased ethylene glycol
bio-PET	biobased polyethylene terephthalate
CA	crotonic acid
$CDCl_3$	deuterated chloroform
C-ML	methyl-3-methyl-5-methylene-2-oxotetrahydrofuran-3-carboxylate
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	diazabicyclo[5.4.0]undec-7-ene
DMAP	4-dimethylaminopyridine
DMT	dimethyl terephthalate
DP	degree of polymerization
DSC	differential scanning calorimetry
D_2O	deuterium oxide
E	Young's modulus
E_a	activation energy
EG	ethylene glycol
E1	unimolecular elimination
E1cB	elimination unimolecular conjugate base
FDCA	furan-2,5-dicarboxylic acid
FTIR	fourier transform infrared spectroscopy
GHG	greenhouse gas

HBA	3-hydroxybutyric acid
HCl	hydrochloric acid
HHA	hydroxyhexanoic acid
HMF	5-hydroxymethylfurfural
HVA	hydroxyvaleric acid
H_2SO_4	sulfuric acid
LDPE	low-density polyethylene
LP	limonene permeability
MALDI-TOF	matrix assisted laser desorption ionization - time of flight
MMF	5-methoxy methyl furfural
M_n	number average molecular weight
MP	melt polycondensation
MSA	methanesulfonic acid
MT	million tone
MW	molecular weight
M_w	weight average molecular weight
NADH	reduced nicotinamide adenine dinucleotide
NaOH	sodium hydroxide
NMR	nuclear magnetic resonance
OP	oxygen permeability
PBAT	poly(butylene adipate-co-terephthalate)
PBS	polybutylene terephthalate
PCL	polycaprolactone
PE	polyethylene
PEF	polyethylene furanoate
PET	polyethylene terephthalate
PHB	polyhydroxybutyrate

PHBH	poly(hydroxybutyrate-co-hydroxyhexanoate)
PHBV	poly(hydroxybutyrate-co-hydroxyvalerate)
PLA	polylactide
PLA-b-PCL	polylactide-co-polycaprolactone block copolymer
PP	polypropylene
pTSA	p-toluenesulfonic acid
PT6HP-co-PγBL	poly(*trans*-hexahydrophthalide)-co-(γ-butyrolactone)
RH	relative humidity
ROP	ring-opening polymerization
RT	room temperature
S-DL	3,8-dimethylene-2,7-dioxaspiro[4.4]nonane-1,6-dione
SEC	size exclusion chromatography
SSP	solid-state polycondensation
TBD	1,5,7-triazabicyclo[4.4.0]dec-5-ene
T_{deg}	degradation temperature
TDT	heat deflection temperature
T_g	glass transition temperature
TGA	thermogravimetric analysis
T_m	melting temperature
TPA	terephthalic acid
$T_{5\%}$	onset temperature of degradation measured at a mass loss of 5%
VST	Vicat softening point
WVP	water vapor permeability
ΔH_m	melting enthalpy
σ_y	tensile strength at yield
σ_{max}	maximum tensile strength

$Đ$	dispersity
ε_b	elongation at break
ε_y	elongation at yield
X_c	degree of crystallinity

Table of content

Chapter 1

Introduction

Plastics are the largest synthetic consumer product in the world, with an annual production that reached 359 million metric tons in 2018[1]. Plastics are the material of choice for applications as diverse as packaging, construction materials, electronics, biomedical devices, and energy storage because of their lightweight, low cost, easy processability, and diverse properties. At the molecular level, plastics are long chains in which the properties of the material are dictated by the movement and arrangement of these chains. Indeed, the properties are not only adjusted with different monomer identities but also molecular weight distribution and crystallinity are key factors for the final use of these plastics in diverse applications. Despite these considerable advantages, the end-of-life management of plastic waste has not advanced at a rate proportionate to their production; the resulting accumulation of plastic waste that does not degrade negatively affects the environment not only due to the large plastic volumes but also due to the recent concerns of microplastic presence into the environment.

Even though there is a growing concern about the unsustainable use of plastics and it seems that society is doing an effort to reduce virgin plastic consumption by about 10 MT since 2017[1]; plastic production is expected to continue to be large. Therefore, solutions must be provided after the end of life of these plastics finishes, and sustainable polymers must be designed and produced besides legacy plastics. Sustainable polymers are defined as plastic materials that fulfill the need of the consumers without causing harmful effects on the environment, health and economy[2]. To do so the designed polymers must prioritize a) the use of renewable feedstock, b)

reduction of the use of organic solvents emission of greenhouse gases and waste during their production, and c) Facile end of life of produced plastics.

The European Union's Environmental Commission is working hard to implement policies and specific programs to increase the sustainability of commercial plastic with a special effort aiming to enhance the circularity of polymeric products and reduce current landfilling rates. Indeed, the European Union is leading the transition from current linear plastic production to a more circular plastic production by using waste plastic as a high-quality source for making new plastics[3].

However, the journey just has begun as still 23.4 % of the collected plastic was landfilled in 2020, 42 % was used for energy recovery and the rest was recycled, 34.6 %[1]. The tendency seems promising, as has been observed an increase of 117 % in recycling and a decrease of 46 % in landfilled waste since 2006[1]. Unfortunately, the plastics currently recycled are almost universally mechanically recombined and limitations in sorting techniques means that additives, contaminants, mis-sorted polymers, or multilayer products found in plastic waste streams lead to significant deterioration of properties during and after reprocessing.

Consequently, while mechanical recycling enables the reuse of plastics, mechanical recycling is a finite recycling process as eventually materials are used in a less property demanding application, as the recycling process compromises the properties of the material. Alternatively, chemical recycling, has the potential of providing the polymer with endless recycling cycles as it offers the possibility to depolymerize the plastic to some intermediates that could be used either to polymerize back the same plastic with virgin-like properties (recycling) or to use them for another value-added purposes (upcycling)[4].

In terms of chemical recycling strategies, synthetic polymers could be categorized as polymers linked by C–C bonds and polymers with C–N and C–O inter-monomer linkages[5]. Depolymerization reactions for polymers that contain heteroatom backbones linked by C–O and C–N bonds (for example, PET, polyamides, and polyurethanes) typically exhibit relatively low reaction barriers and near-neutral reaction free energies compared with polyolefins, as C–O or C–N bonds are typically more labile than C–C or C–H bonds[5]. Indeed, some of the largest produced polymers such as polyethylene (PE) or polypropylene (PP) are challenging to depolymerize into virgin-like materials. Therefore, these plastics have been used as energy recovery materials, as they generate high quantities of energy in the incineration process.

In the case of polymers with heteroatom backbones, the C-O and C-N bonds are more labile than C-C and C-H bonds, making easier their cleavage[5]. Normally, the depolymerization reaction is carried out by the use of a nucleophile that reacts with the carbonyl group causing the scission of the chain. Heteroatom polymers could be depolymerized by solvolysis process, which could be more specifically hydrolysis, alcoholysis or aminolysis, or by thermal depolymerization.

Solvolysis is a depolymerization method where the solvent acts as a nucleophile to carry substitution or elimination reactions[6]. The use of this method enables the depolymerization of the polymer into monomers that enable the resynthesis of the same polymer, but also the synthesis of different monomers from the initial one that potentially could be used in high value-added applications[7]. Thermal depolymerization instead, consist of the depolymerization of a polymer into monomers by the use of the temperature[6]. This process does not use any reactant; however, in some cases, a catalyst is added to enhance the depolymerization process. Among the different

polymers investigated one of the polymer families that could meet the sustainable goals without compromising the material properties is the family of polyesters.

Polyesters were firstly discovered in 1926 in the laboratories of DuPont, USA, by Wallace Carothers. Together with polyester Carothers also synthetized for the first-time polyamides, stating the based for polycondensation reactions. In the case of polyesters, he found out that the combination of carboxylic diacids and diols was giving synthetic fibers, creating a promising material with properties that were never seen before. He also explored the reversible nature of these polymers, which was a problem to obtain high molecular weight chains (Figure 1.1)[8].

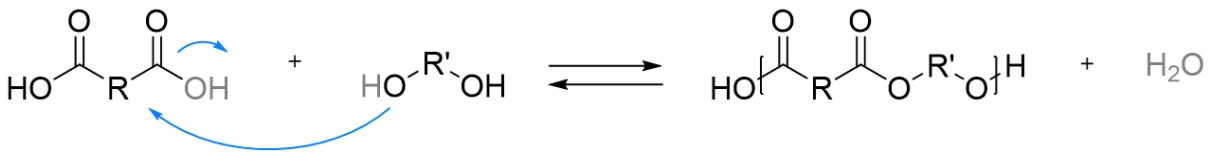


Figure 1.1. Reaction scheme of the polyester synthesis discovered by Carothers.

Since the pioneering work of Carothers, polyesters have been broadly studied by many researchers, such as polyethylene terephthalate in 1941 by the British scientist John Whinfield and James Dickson. Polyesters of very diverse properties have been created and therefore they are the materials of choice in multiple applications, such as biomedicine, packaging, construction, electronics, textile and automotive industry (Figure 1.2)[8].

Figure 1.2. Main applications of polyesters.

Polyesters could be prepared by step-growth and chain-growth polymerization, being the main difference between both of them the relation that they have towards the molecular weight. The step-growth polymerization begins with the synthesis of dimers from monomer and increases the size until high molecular weight polymers are obtained. High molecular weights are reached by the combination of oligomers of different lengths and that is why they are obtained at high conversion rates (Figure 1.3,

green line)[9]. As mentioned before, Carothers stated the principles of polycondensation reaction, together with the conversion dependence with the degree of polymerization (equation 1).

$$X_{n,\ step-growth} = \frac{2}{2-\rho f_{avg}} \qquad (1)$$

Where X_n is the degree of polymerization, ρ conversion and f_{avg} represents the average functionality of the system.

However, the synthesis of high molecular weight polymers by this polymerization method requires some needs: a) monomer functionality (f) of 2.0, stoichiometry between the functional groups of 1.0, reduction of side reactions, high reaction conversions (99.9 %) and efficient removal of condensates[9].

In the case of chain-growth polymerization, the polymerization starts by an initiation step where a reactive intermediate is formed. Afterward, the propagation step takes place by the reaction of the reactive intermediate with a monomer, transferring the reactive center to the end of the chain. The molecular weight increases by the addition of a monomer to the chain and not by the combination of different chains, which makes the dispersities to be low. In this case, the molecular weight increases at the beginning of the reaction (Figure 1.3, orange line)[9].

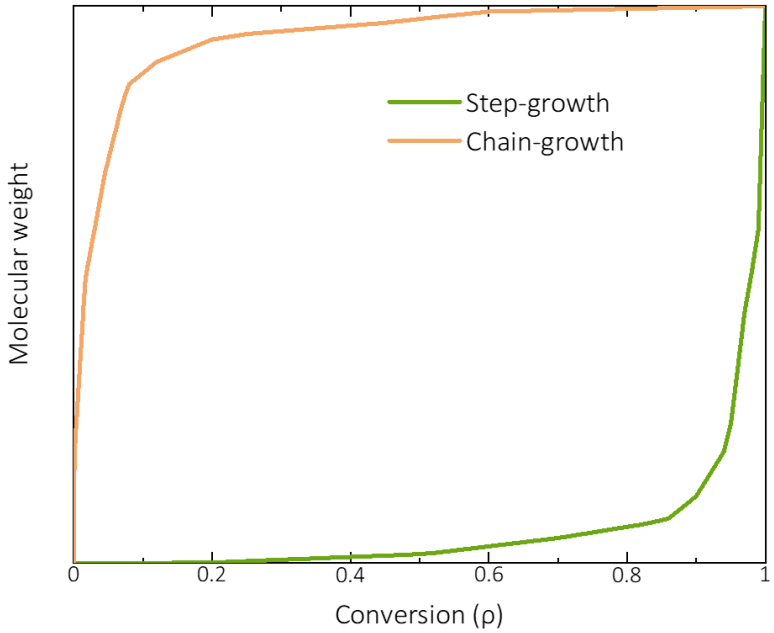


Figure 1.3. Molecular weight vs conversion in different polymerization mechanisms: step-growth and chain-growth.

In the case where chain-growth polymerization is used for the synthesis of polyester, the ring-opening polymerization (ROP) of cyclic esters is the pathway employed (Figure 1.4)[10–12].

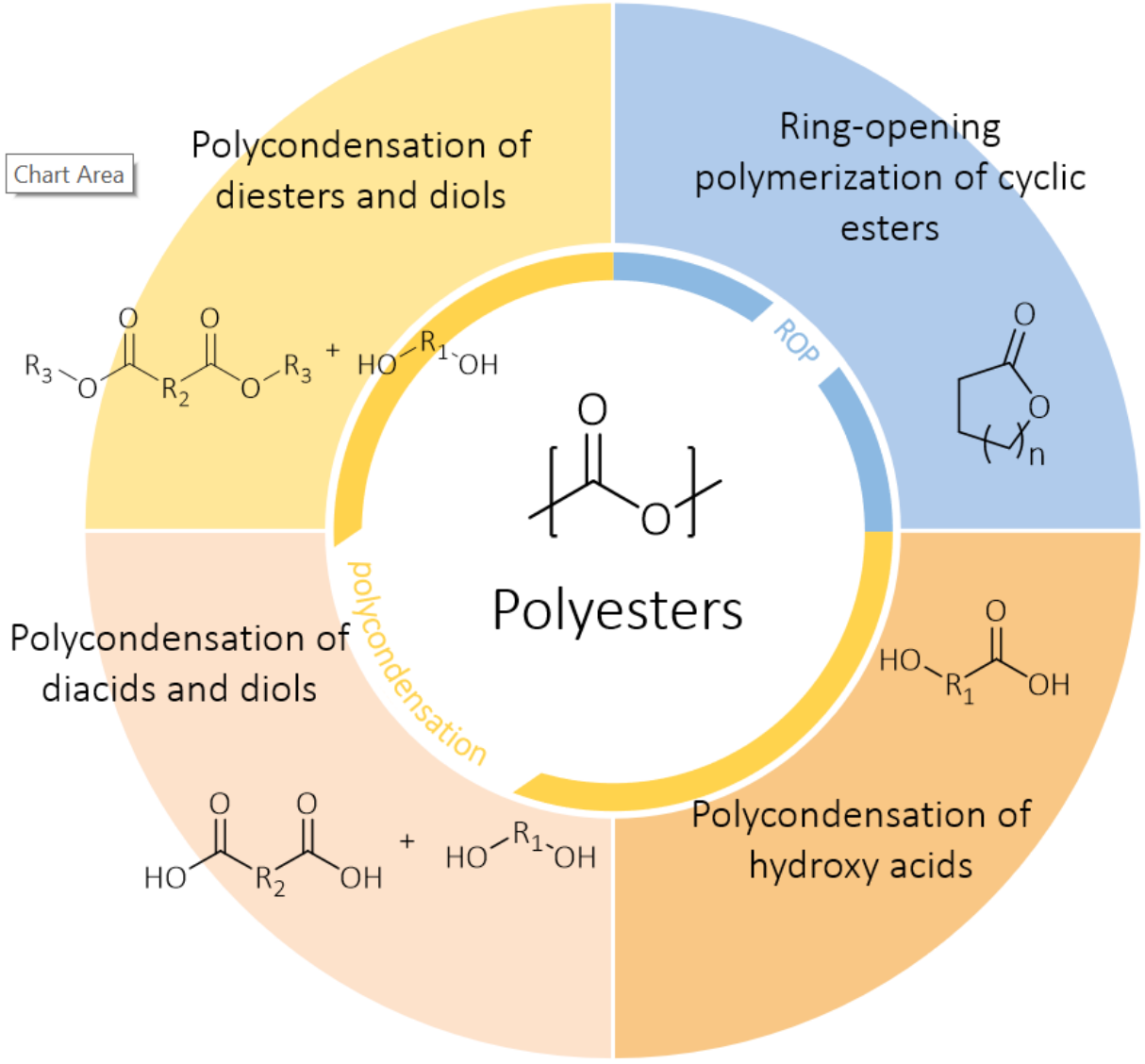


Figure 1.4. Graphical representation of the main synthesis methods for the synthesis of polyesters.

The polymerization of cyclic monomers by ROP has attracted great attention since it is a simple method to obtain high-molecular-weight (MW) polyesters. ROP follows chain-growth kinetics since the monomer is added to the active chain end and the polymerization can proceed by acyl-oxygen or alkyl-oxygen scission (Figure 1.5)[13]. The acyl-oxygen scission is given when the nucleophile attacks the carbonyl group of the ester and therefore, ester cleavage takes place, when the nucleophile attacks the alkyl group next to the oxygen instead, a cleavage between the alkyl and oxygen group is

given, forming an acid group at the end of the chain. A wide range of polyesters has been synthesized by ROP such as polylactide (PLA) and polycaprolactone (PCL). The main advantage of this polymerization route is related to its ability to obtain well-defined polymers with narrow dispersities and high MWs. Nevertheless, as cyclic monomers are required to perform the polymerization, the polymerization is limited to monomers able to be polymerizable by means of ROP[10–12,14–16]. Moreover, in many cases, the preparation of the cyclic monomer is not straightforward and complex multi-step synthesis is required to obtain the desired cyclic structures.

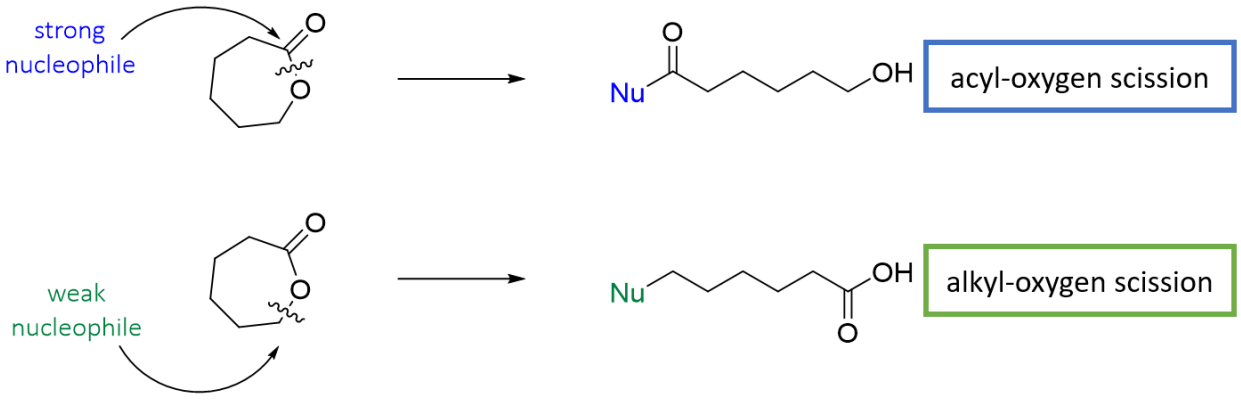


Figure 1.5. Chain-growth via acyl-oxygen and alkyl-oxygen scission.

Besides chain-growth polymerization, polyesters can also be prepared using the step-growth polymerization approach. In step-growth polymerization, three main methods could be used: polycondensation of diacids and diols, polycondensation of diesters and diols, and the self-condensation of hydroxy acids (Figure 1.4). Thus, the polycondensation of diacids or diesters with diols represents the most investigated and industrially relevant route for the production of polyesters. The main advantage of this method is based on the fact that there is a wide range of these monomers available that provide access to a plethora of new polyesters, without the need of additional cyclization steps, making the process more economically affordable and less time

consuming than ROP. However, it also has some disadvantages. For instance, this process requires harsh polymerization conditions, such as high temperatures, vacuum to remove condensate, and exquisite control of the stoichiometry to achieve high MWs[9–12].

Polyesters can also be obtained by the self-polycondensation of hydroxy acids. The main advantage of this method in comparison with the conventional step-growth polymerization of diacids and diols or diesters and diols lies in the fact that there is no need to control the stoichiometry. Consequently, with an appropriate setup in terms of polymerization conditions, that is, good control of temperature, a high-performance catalyst, and vacuum, high MWs can be obtained[17].

As described before polyesters are ideal polymers for depolymerization as the ester linkage could be easily triggered by nucleophiles. Depending on the polyester, different approaches could be employed, the depolymerization by solvolysis or the depolymerization to the cyclic ester monomer. Jehanno et al. depolymerized PET by glycolysis, where an ethylene glycol monomer attacks the ester bond of the polymer, creating the break of the linkage[18]. Therefore, bis(2-hydroxyethyl) terephthalate (BHET) monomer is formed, which will enable the repolymerization of PET in a closed-loop recycling process or an upcycling approach. Sangroniz et al. used a different strategy for the chemical depolymerization of poly(*trans*-hexahydrophthalide)-co-(γ-butyrolactone) (PT6HP-co-PγBL) copolyester[19]. In this case, the monomers that were used for the synthesis of the copolymer were cyclic esters and therefore, the chemical depolymerization into the cyclic esters could be achieved. For that purpose, $ZnCl_2$ catalyst was used in 2 mol % amount using toluene as solvent at 120 °C and in 60 h reaction time, obtaining the initial cyclic esters, *trans*-hexahydrophthalide and γ-butyrolactone.

Many research projects are focused on the development of new polyesters, with a huge improvement in the production these polyesters in a more environmentally friendly manner[20]. The mission "Sustainable Development Goals" impulse by the United Nations, among the 17 objectives that it has, there is one strongly linked with plastics, the target number 12 "ensure sustainable consumption and production patterns"[21]. This target will encourage society to the sustainable management and efficient use of natural sources and the reduction of waste through prevention, reduction, recycling and reuse, among others.

1.1. Nature inspired catalysts

While some polyesters could be prepared at room temperature in solution by ring-opening polymerization, no matter the synthesis route employed for the synthesis of polyesters, high temperatures are required for the industrial polymerization reactions, between 150 and 300 °C, requiring a high thermal stability catalyst[22]. Industrially metal catalysts, such as tin (II) octoate, titanium (IV) tetrabutoxide, and aluminum and zinc complexes are used. They show high selectivity together with effectiveness and the quantities required are low, with few ppm-s. However, the problem with metal catalysts is that they imply a high environmental and economic cost, according to some predictions some metals could be in danger of disappearance in the following decades, such as cobalt and magnesium[23]. In addition, some of them are toxic and as it is not possible to remove them by purification step from the material, due to their coordination abilities, they remain stacked in the polymer causing problems especially for biomedicine and electronic applications, together with difficulties in the recycling process[24].

Organocatalysis has emerged as an effective catalytic system for the synthesis of polyesters, as they show versatility, high selectivity and there is the possibility of

removing them from the reaction media by a purification step[9,25,26]. However, common organic acids and bases, such as methanesulfonic acid (MSA), triazabicyclodecene (TBD), diazabicyclo[5.4.0]undec-7-ene (DBU) and 4-dimethylaminopyridine (DMAP), normally show low thermal stabilities (50-110 °C) being unsuitable for polyesters polymerization[18,27]. In an attempt to overcome the low thermal stability issue, stoichiometric and non-stoichiometric acid-base mixtures have been studied. It was observed that the proton transfer between the acid and the base increases considerably the stability of the compounds, as an example, TBD:MSA, DBU:BA and DMAP:MSA salts, are much more stable than their respective counterparts, reaching thermal stabilities of 300 °C in some cases[27–29]. These catalysts have been seen that are highly suitable for polymerization reactions of polyesters, by ROP, for the polymerization of L-lactide and also by polycondensation reactions, for the synthesis of PET, using dimethyl terephthalate (DMT) and ethylene glycol (EG) as monomers[30]. As mentioned before, one of the advantages of organocatalysis is the possibility of removing them from the reaction media, to avoid any damaging effects on the environment and living organisms. However, the need for a purification procedure implies an extra step in the production system, increasing considerably the cost of the process, in combination with the high prices of the acid and bases. Due to that, nontoxic organocatalyst could be the most promising alternative, in order not to have the requirement to remove them from the media after the reaction, as it would not cause any harmful effect.

It is highly known that enzymes could also catalyze polymerization reactions and functionalization reactions in an effective way. The advantage over the chemical synthesis is the sustainability of the catalyst, together with their specificity and lack of harsh conditions for the polymerization process[31]. However, when the polymerization reaction requires extreme conditions, such as incorrect pH conditions or temperatures

above 40-50 °C, the enzymes would suffer a decrease in their activity or denaturalization, not catalyzing the reaction. While several attemps have been focused on engineering enzymes to trigger chemical reactions at high temperatures, their use in industrial processes is still under investigation. Besides enzymes, amino acids, have demonstrated that they are very resistant to temperature, with degradation temperatures of above 200 °C in most of the cases studied[32,33].

Although amino acids have not been widely used to catalyze polymeric reactions, some authors have used them as precursors for their catalysts. For instance, Sanchez-Sanchez et al. investigated densely substitute L-proline and combined it with DBU to promote ROP of rac-lactide of high stereocontrol[34]. He et al. also synthesized PLA by using amino acid complexes with tin and obtaining high molecular, well-controlled polymers[35]. While these complexes have shown great performance, their high cost makes them impractical for polymer production processes, and the use of amino acids as received will be much more interesting from an industrial perspective. Due to the presence of acid and base groups in their structure, it is expected that amino acids could be highly thermally stable and efficient catalyst for polymerization of polyesters. In addition, as they are present in the human body, it is believed that they will not be toxic or have low toxicity, avoiding the need for purification of the synthesized materials.

1.2. From petroleum-based to biobased monomers

Most industrially relevant polymers are petroleum-based; monomers are refined from the petroleum and used for the polymerizations. The refining process employs harsh conditions, such as high temperatures and pressures, and in addition, harmful gases are released into the atmosphere, methane and carbon dioxide among others, which are responsible for climate change. To try to change this trend biobased polymers have emerged and started gaining industrial interest, especially for single-use applications.

These polymers could be naturally synthesized, normally by the microorganism, or the monomers used for their preparation are found in nature, for instance, polylactic acid (PLA), a well-known polyester belonging to this second group, as lactic acid could be found in plants and sour milk. In addition, PLA also belongs to the group of biodegradable materials, giving an extra value to this polymer[36].

Biodegradable polymers are the materials that undergo deterioration and completely degrade when they are exposed to microorganisms to result in natural byproducts, such as gases (CO_2, N_2), water and biomass[37]. This process is highly interesting from the sustainability point of view, as the polymer will go back to the land after finishing its useful life period and reduce the waste amount that needs to be treated. The source of biodegradable polymers could be diverse, not matter if they belong to the biobased polymers group or the petroleum-based polymers group (Figure 1.6)[38].

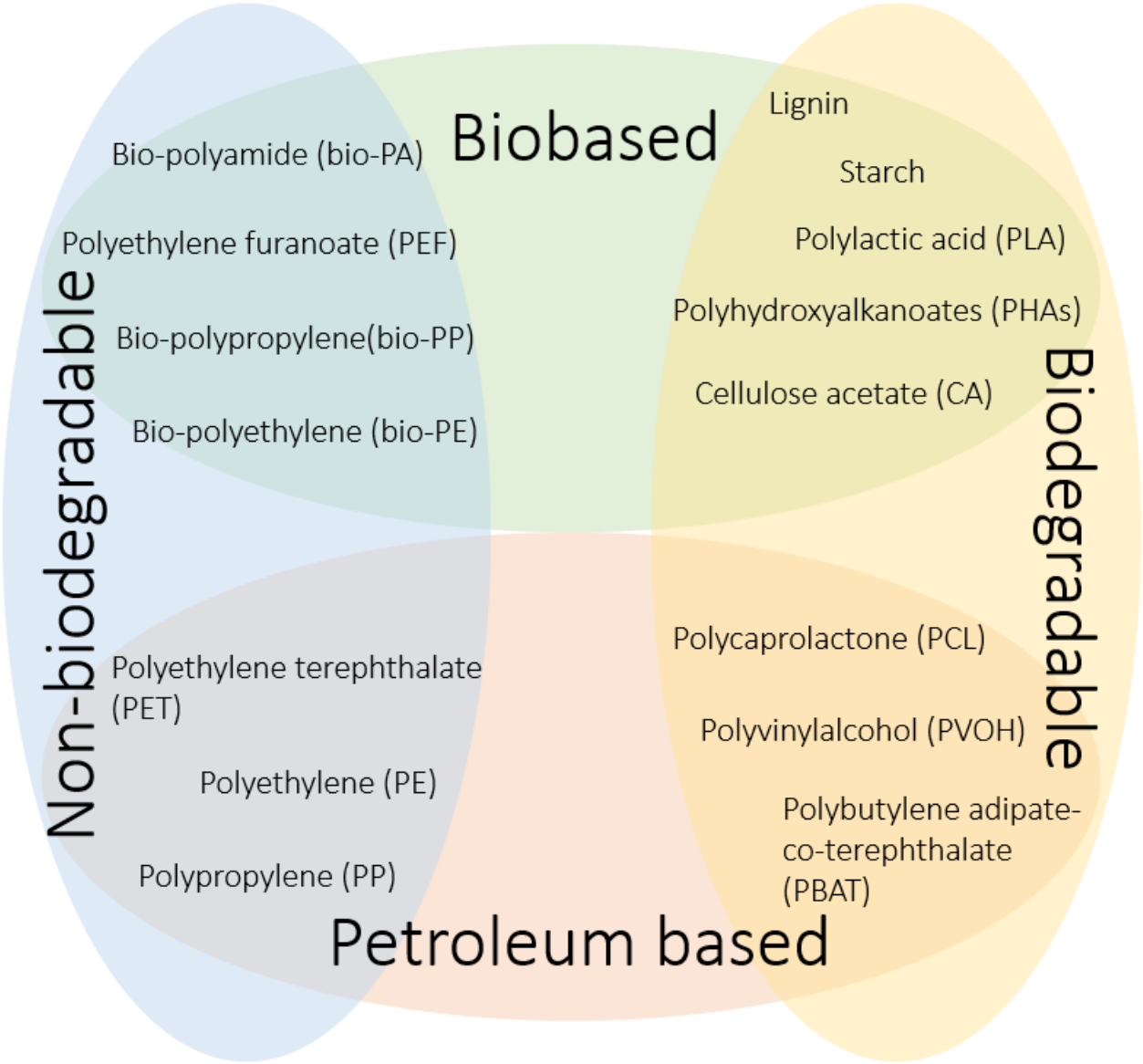


Figure 1.6. Classification of common polymers into biobased, petroleum-based, biodegradable and non-biodegradable groups.

As mentioned before, one of the most used plastic for packaging application is polyethylene terephthalate (PET)[1]. It is mainly synthesized by two methods: polyesterification of terephthalic acid with ethylene glycol or transesterification of dimethyl terephthalate with ethylene glycol[39,40].No matter the synthetic process employed the needed monomers are petroleum-based, nevertheless, it could be partly

biobased, as ethylene glycol could be obtained from natural resources. However, the other monomer, terephthalic acid, could not be obtained competitively using a green process. Therefore, it has been seen the need of finding alternative biobased monomers for the synthesis of more sustainable polymers[41,42].

Furandicarboxylic acid has emerged as a possible biobased alternative to petroleum-based terephthalic acid. This green alternative is a sugar-derived compound that together with ethylene glycol could synthesize polyethylene furanoate (PEF) polymer. Furandicarboxylic acid is obtained by the dehydration reaction of common 6-carbon sugars, such as glucose and therefore, the US Department of Energy identified it as one of the 12 priority chemicals for the sustainable production of polymers. According to the literature, the replacement of PET with PEF would reduce the energetic cost of the synthesis process together with the harmful emission of gases into the atmosphere[43].

Another biobased polymer that is attracting interest is polyhydroxybutyrate (PHB); this polymer is a naturally occurring polyester that is synthesized by microorganisms (*Cupriavidus necator*, *Methylobacterium rhodesianum* or *Bacillus megaterium*) under physiological stress as an energy storage system. Apart from being biobased and therefore sustainable, it has been seen that could be a good alternative for packaging applications as it has excellent barrier properties, giving a better performance like water, oxygen and carbon dioxide barrier than polyethylene terephthalate (PET)[19]. In addition, like most aliphatic polyesters, PHB is biodegradable in soil and water, which makes it interesting especially for single-use applications, for instance, packaging[44]. However, the main inconvenience of PHB is that is expensive, more than conventional petroleum-based polymers so it has been seen as too high cost for single-use applications. One alternative to make this polymer profitable for single-use applications is to reuse it. However, in the case of PHB, the mechanical recycling is not feasible as it

shows little difference between the melting temperature (T_m) (170-180 °C) and the degradation temperature (200-220 °C)[45–48], and therefore it degrades considerably during mechanical recycling. Due to the temperature limitations, chemical recycling seems to be the most effective process for the end-of-life assessment of PHB. Different chemical recycling mechanisms could be found for polyesters, such as hydrolysis and alcoholysis. Indeed, hydroxy acid monomers are interesting monomers that have a broad range of applications in various fields including cosmetics, pharmaceutical, and food industries. In cosmetics, hydroxy acids are used for the treatment of various skin diseases such as photoaging, acne, pigmentation disorders, and psoriasis. A wide range of pharmaceutically important chiral synthons is also being synthesized using hydroxy acids as precursors, for instance, mandelic acid that is used in the synthesis of antitumor agents, antiobesity agents, semi-synthetic penicillin, and cephalosporin[17].

1.3. From high energy demanding polymerizations to reactions at room temperature

As mentioned before, conventional industrial polyesters synthesis in bulk required high reaction temperatures to polymerize (Figure 1.7). Except for the industrial process for the preparation of PHB, which is made by baceteria at room temperature, all industrial processes for polyesters are performed at elevated temperatures. This limits the application of this type of materials, such as coatings or adhesives, which in many cases require low-temperature curing. Most produced polyesters are synthesized by a polycondensation reaction and request elevated temperatures and vacuum to obtain high molecular weights, for instance, PET needs up to 240-280 °C for its synthesis[49].

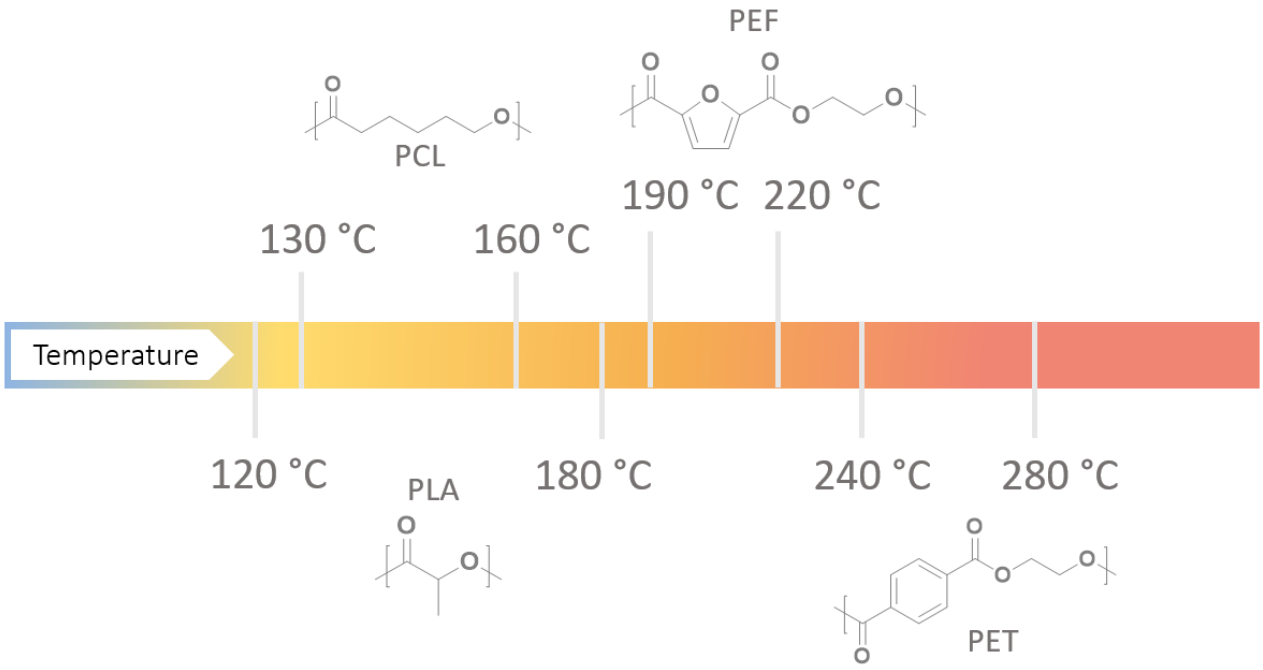


Figure 1.7. Polymerization temperatures for most known polyesters.

Hirabayashi et al. reported the synthesis of polyesters by polycondensation reaction of dicarboxylic acid and diols at room temperature by the use of scandium-based catalysts[50]. These catalysts can promote polycondensation reactions due to their low hydrolysis constant and insensitivity to protic compounds. However, as they are based on rare-earth metals, their large use is not a possibility, being difficult to implement this method for high scale polyesters synthesis. Morevoer, only low molecular weights could be obtained.

It is assumed that room temperature polyester synthesis via polycondensation reaction is an extreme challenge considering the use of sustainable catalysts, as the presence of water or some other small molecules that are released in each linkage creation will deactivate them. Therefore, some authors have tried to investigate the synthesis of polymers at room temperature by the use of ROP method.

Lu et al. described a method for the synthesis of polythioesters at room temperature by the ring-opening copolymerization of succinic thioanhydride and propylene sulfide[51]. To initiate and catalyze the ROP reaction an organic base, DBU, was used at first, however, low conversions were obtained after one hour of reaction. To enhance the polymerization, DBU was substituted by an ammonium salt, bis(triphenylphosphine)iminium) chloride salt, which gives full conversion in an hour. Even though the synthesis of the polymer is successfully promoted, the depolymerization of this polythioester into the initial monomers is not easy as the highly strained 3-membered propylene sulfide is not easy to close.

Lu et al. propose an interesting pathway to solve the depolymerization problem of highly strained cyclic monomers[52]. They synthesized polythioesters by the ROP of four-membered cyclic thioesters; however, to tune the thermodynamics to improve the depolymerization process, they introduce a germinal dimethyl group on the ring. The addition of this substituent makes the thermodynamics of depolymerization together with the polymerization ones to be near equilibrium, enabling better control of these two processes by reducing the activity. Therefore, the depolymerization reaction could be carried out at 60 °C and the ROP at room temperature, obtaining high molecular weight (≈ 70 kDa) in a controlled way.

In the case of polyesters, Coulembier et al. reported one of the few works where the ROP of cyclic esters at room temperature is carried out[53]. They observe that the use of a halogenated catalyst could enable the synthesis of PLA under mild conditions by halogen-bonding ROP activation catalyzed by ICl_3. However, they observe that at room temperature the reaction kinetics are low and the increase in temperature must be needed for the improvement of polymerization speed.

Zhu et al. were able to synthesize PCL at mild conditions (25-40 °C) by the use of a titanium-based compound as initiator and catalyst[54]. Even though the polyester is efficiently synthesized the use of a metallic compound could cause some inconveniences for future applications.

In most of the cases reported in the literature, the key of polyester synthesis at room temperature is focused on the search for an efficient catalyst. However, we think that new routes for the synthesis of polyesters at room temperature are required, such as the search for monomers with higher reactivity that can polymerize under milder conditions.

1.4. Objectives of the thesis

Having underlined in the present chapter three of the challenges that polyester synthesis has to achieve for more sustainable materials and processes, this work will focus on these three topics: natural catalysts, biobased polymers, and less energy demanding polymerizations.

Herein, this thesis could be divided into three parts, the first one (Chapter 2) will focus on the research of a sustainable natural catalyst, the second one (Chapters 3 and 4) is related to biobased polymers and their recycling and upcycling processes and the last one (Chapter 5), with a new synthesis method for polyester synthesis at room temperature.

In order to design a sustainable and efficient polyesters synthesis process at high temperature, Chapter 2, will test five different naturally occurring catalysts that are resistant to harsh thermal conditions intending to employ them in the ROP of cyclic esters in bulk conditions. The five catalysts are characterized and tested in the ROP of L-lactide to evaluate their efficiency as catalysts. The most efficient naturally occurring

catalyst, taurine, is furtherly characterized to understand the catalytic mechanism and the toxicity of the synthesized materials. The scope of the synthesis approach is expanded to the synthesis of other polymers by ROP.

In Chapter 3 a biobased alternative to PET, the most synthesized polyester for packaging application, is proposed by the implementation of PEF. Different thermal, barrier and mechanical property tests have been carried out for the comparison of both polyesters and a recycling process have been depicted for the biobased one. The organocatalyzed glycolytic depolymerization procedure that has been described enables the chemical closed-loop recycling of the polyester by the polycondensation reaction of two steps of the depolymerization product.

Continuing with biobased polymers in Chapter 4, PHB, a naturally occurring polyester synthesized by the microorganism, is investigated as a source of high-value β-hydroxy acid monomer. By the wise choice of the catalyst and the hydrolytic depolymerization conditions, the depolymerization process was tuned to the maximum yield of the hydroxy acid monomer. The upcycling approach was extended to PHBV and PHBH copolyesters, together with synthetic PHB and post-consumed trays.

Going upon to the third part of the thesis, in Chapter 5 a new highly reactive five-membered dilactone monomer has been synthesized for the polymerization of polyesters at room temperature. The ring-opening polyaddition reaction has been studied by the use of a diol as the nucleophile and different catalysts to promote rapid polymerization. Finally, diamine and dithiol nucleophiles have been used for the ring-opening of the dilactone for the synthesis of polyamides and polythioesters by the same polymerization method.

In Chapter 6, the results and the most relevant conclusions in regard to the challenges considered in this thesis will be summarized and commented on.

1.5. References

1 Plasctics Europe, *Plastics-the Facts 2021 An analysis of European plastics production, demand and waste data*, 2021.

2 M. University, Sustainable Polymers 101 | NSF Center for Sustainable Polymers, https://csp.umn.edu/sustainable-polymers-101/, (accessed February 23, 2022).

3 European Environment Commission, Waste and recycling, https://ec.europa.eu/environment/topics/waste-and-recycling_es, (accessed March 11, 2022).

4 J. M. Garcia and M. L. Robertson, *Science*, 2017, **358**, 870–872.

5 L. D. Ellis, N. A. Rorrer, K. P. Sullivan, M. Otto, J. E. McGeehan, Y. Román-Leshkov, N. Wierckx and G. T. Beckham, *Nat. Catal.*, 2021, **4**, 539–556.

6 J. Payne and M. D. Jones, *ChemSusChem*, 2021, **14**, 4041–4070.

7 C. Jehanno, J. W. Alty, M. Roosen, S. De Meester, A. P. Dove, E. Y.-X. Chen, F. A. Leibfarth and H. Sardon, *Nature*, 2022, **603**, 803–814.

8 M. Zhang, S. M. June and T. E. Long, in *Polymer Science: A Comprehensive Reference, 10 Volume Set*, Elsevier, Amsterdam, 2012, vol. 5, pp. 7–47.

9 A. Bossion, K. V. Heifferon, L. Meabe, N. Zivic, D. Taton, J. L. Hedrick, T. E. Long and H. Sardon, *Prog. Polym. Sci.*, 2019, **90**, 164–210.

10 P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, New York, 1995.

11 G. Odian, *Principles of polymerization*, John Willey & Sons, New Jersey, 4th edition, 2004.

12 M. E. Rogers, T. Long and S. Turner, *Introduction to synthetic methods in step-growth polymers*, John Willey & Sons, New Jersey, 2003.

13 B. Raeskinet, S. Moins, L. Harvey, J. De Winter, C. Henoumont, S. Laurent and O. Coulembier, *Macromolecules*, 2019, **52**, 6382–6392.

14 R. Löfgren, A. Albertsson, A.C. Dubois and P. Jerome, *J. Macromol. Sci.*, 1995, **C35**, 379–418.

15 I. K. Albertson and A.C. Varma, *Aliphatic polyesters: Synthesis, properties and applications in Degradable aliphatic polyesters*, Springer-Verlag, Berlin, 2001.

16 C. Lecomte and P. Jérôme, *Adv. Polym. Sci.*, 2012, **245**, 173–218.

17 E. Gabirondo, A. Sangroniz, A. Etxeberria, S. Torres-Giner and H. Sardon, *Polym. Chem.*, 2020, **11**, 5548.

18 C. Jehanno, I. Flores, A. P. Dove, A. J. Müller, F. Ruipérez and H. Sardon, *Green Chem.*, 2018, **20**, 1205–1212.

19 A. Sangroniz, J. B. Zhu, X. Tang, A. Etxeberria, E. Y. X. Chen and H. Sardon, *Nat. Commun.*, 2019, **10**, 1–7.

20 F. D. B. de Sousa, *Clean. Responsible Consum.*, 2021, **3**, 100020.

21 United Nations, Sustainable Development Goals, https://sdgs.un.org/goals, (accessed May 15, 2022).

22 L. T. Lim, R. Auras and M. Rubino, *Prog. Polym. Sci.*, 2008, **33**, 820–852.

23 G. Gunn, *Critical Metals Handbook*, John Wiley & Sons, Ltd, West Sussex, UK, 2014.

24 M. Jaishankar, T. Tseten, N. Anbalagan, B. B. Mathew and K. N. Beeregowda,

Interdiscip. Toxicol., 2014, **7**, 60–72.

25 F. Nederberg, E. F. Connor, M. Möller, T. Glauser and J. L. Hedrick, *Angew. Chemie - Int. Ed.*, 2001, **40**, 2712–2715.

26 M. K. Kiesewetter, E. J. Shin, J. L. Hedrick and R. M. Waymouth, *Macromolecules*, 2010, **43**, 2093–2107.

27 I. Flores, J. Demarteau, A. J. Müller, A. Etxeberria, L. Irusta, F. Bergman, C. Koning and H. Sardon, *Eur. Polym. J.*, 2018, **104**, 170–176.

28 A. Basterretxea, C. Jehanno, D. Mecerreyes and H. Sardon, *ACS Macro Lett.*, 2019, **8**, 1055–1062.

29 A. Basterretxea, E. Gabirondo, C. Jehanno, H. Zhu, O. Coulembier, D. Mecerreyes and H. Sardon, *Macromolecules*, 2021, **54**, 6214–6225.

30 I. Flores, A. Etxeberria, L. Irusta, I. Calafel, J. F. Vega, J. Martínez-Salazar, H. Sardon and A. J. Müller, *ACS Sustain. Chem. Eng.*, 2019, **7**, 8647–8659.

31 V. Hevilla, A. Sonseca, C. Echeverría, A. Muñoz-Bonilla and M. Fernández-García, *Macromol. Biosci.*, 2021, **21**, 2100156.

32 H. Taira, H. Taira, K. I. Sugimura and Y. Sakurai, *Agric. Biol. Chem.*, 1965, **29**, 1074–1079.

33 I. M. Weiss, C. Muth, R. Drumm and H. O. K. Kirchner, *BMC Biophys.*, 2018, **11**, 2.

34 A. Sanchez-Sanchez, I. Rivilla, M. Agirre, A. Basterretxea, A. Etxeberria, A. Veloso, H. Sardon, D. Mecerreyes and F. P. Cossío, *J. Am. Chem. Soc.*, 2017, **139**, 4805–4814.

35 M. He, Y. Cheng, Y. Liang, M. Xia, X. Leng, Y. Wang, Z. Wei, W. Zhang and Y. Li, *Polym. J.*, 2020, **52**, 567–574.

36 P. McKeown and M. D. Jones, *Sustain. Chem.*, 2020, **1**, 1–22.

37 M. Abhilash and D. Thomas, in *Biopolymer Composites in Electronics*, Elsevier, Amsterdam, 2017, pp. 405–435.

38 K. Helanto, L. Matikainen, R. Talja and O. J. Rojas, *BioResources*, 2019, **14**, 4902–4951.

39 B. Xiao, L. Wang, R. Mei and G. Wang, *J. Polym. Res.*, 2011, **18**, 2221–2227.

40 P. Švec, P. Hubená, Z. Růžičková, J. Holubová, M. Pouzar, J. Merna and A. Růžička, *Appl. Organomet. Chem.*, 2016, **30**, 20–25.

41 M. Shiramizu and F. D. Toste, *Chem. Eur. J.*, 2011, **17**, 12452–12457.

42 T. P. Vispute, H. Zhang, A. Sanna, R. Xiao and G. W. Huber, *Science*, 2010, **330**, 1222–1227.

43 A. J. J. E. Eerhart, A. P. C. Faaij and M. K. Patel, *Energy Environ. Sci.*, 2012, **5**, 6407–6422.

44 N. Altaee, G. A. El-Hiti, A. Fahdil, K. Sudesh and E. Yousif, *Springerplus*, 2016, **5**, 762.

45 W. M. Pachekoski, C. Dalmolin and J. A. M. Agnelli, *Mater. Res.*, 2013, **16**, 237–332.

46 P. Anbukarasu, D. Sauvageau and A. Elias, *Sci. Rep.*, 2016, **5**, 17884.

47 W. Maurício Pachekoski, C. Dalmolin and J. Augusto Marcondes Agnelli, *Mater. Res.*, 2013, **16**, 237–332.

48 P. Anbukarasu, D. Sauvageau and A. Elias, *Sci. Rep.*, 2016, **5**, 17884.

49 A. Basterretxea, C. Jehanno, D. Mecerreyes and H. Sardon, *ACS Macro Lett.*, 2019,

8, 1055–1062.

50 A. Takasu, Y. Lio, Y. Oishi, Y. Narukawa and T. Hirabayashi, *Macromolecules*, 2005, **38**, 1048–1050.

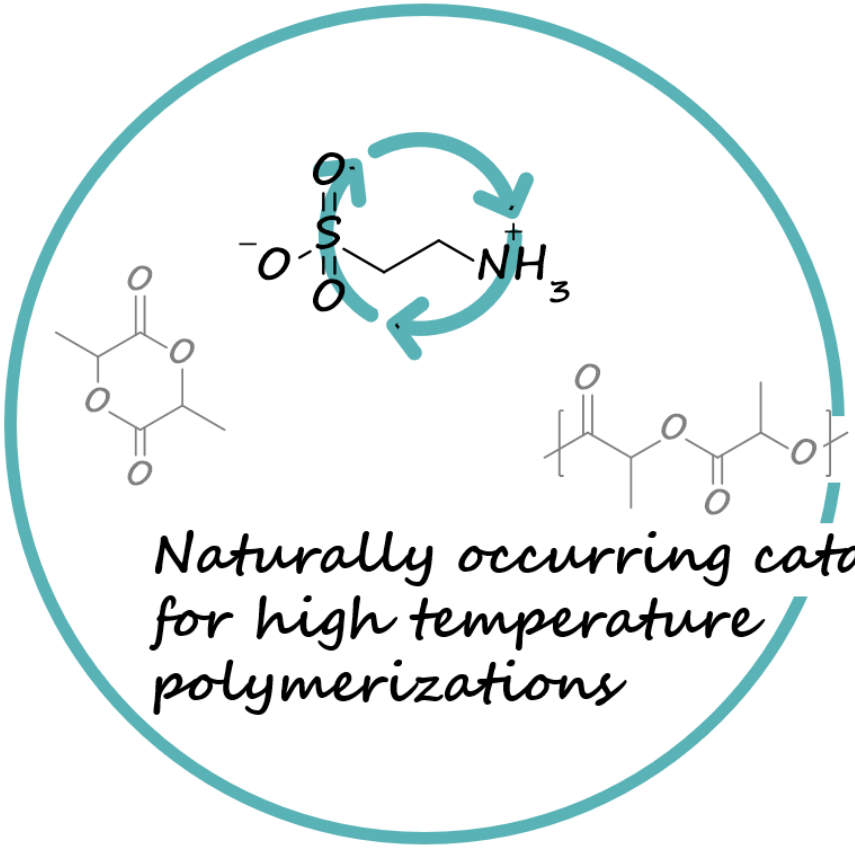
51 T. Yue, M. Zhang, G. Gu, L. Wang, W. Ren and X. Lu, *Angew. Chemie*, 2019, **58**, 618–623.

52 W. Xiong, W. Chang, D. Shi, L. Yang, Z. Tian, H. Wang, Z. Zhang, X. Zhou, E. Q. Chen and H. Lu, *Chem*, 2020, **6**, 1831–1843.

53 O. Coulembier, F. Meyer and P. Dubois, *Polym. Chem.*, 2010, **1**, 434–437.

54 J. B. Fan, F. Long, M. P. Aldred, Y. J. Li, Z. W. Liang and M. Q. Zhu, *Macromol. Chem. Phys.*, 2012, **213**, 1499–1508.

Chapter 2


Naturally occurring catalyst
for high temperature
polymerizations

Naturally occurring catalyst for high temperature polymerizations

2.1. Introduction

Polymers are part of our daily life since they show a wide range of properties; they are cheap and easy to process. Thus, they are employed in several diverse applications ranging from large-scale low-value applications such as food packaging or construction to low-volume high added value applications including biomedicine or aerospace applications[1]. Among several polymer families, polyesters have garnered great attention since they can be obtained from biomass, they show great mechanical performance, considerable barrier character and could be potentially recycled. In addition, certain polyesters have shown to be degraded under appropriate conditions[2,3]. Polyesters were discovered almost 100 years ago and represent one of the main classes of polymers. They are defined by the R-COO-R' ester linkage in their backbone, where R and R' represent an aliphatic or aromatic moiety. Different routes have been explored for the preparation of polyester, the step-growth polymerization of diols and diacids or dianhydrides, and the Ring-Opening Polymerization (ROP) of cyclic esters, the ones exploited industrially.

Among these polymerization methods, ring-opening offers some advantages: well-controlled microstructure, high molecular weights and narrow dispersities[4–6]. While the industrial polymerization requires relatively high temperatures (150-200 °C) does not require the use of high energy-intensive processes such as high vacuum (for the removal of low molecular weight molecules (i.e. water)) to push the conversion and to obtain high molecular weights. Furthermore, in some cases the cyclic monomers can

be recovered by depolymerization from the polymer in a truly circular economy approach, recovering the economic value of the material.

While temperature is usually needed to favor the polymerization kinetics, the use of catalysts is a key factor in producing polymers with decent molecular weights and good mechanical properties. Industrially metal catalysts are mostly used, such as tin (II) octoate and titanium (IV) tetrabutoxide. They have great performance, however, their availability is limited and they have a high cost. In addition, some of them are toxic and as it is not possible to remove them by purification step from the material, due to their coordination abilities, they remain stacked in the polymer causing problems, especially for biomedicine and electronic applications.

In the last decade, extensive attempts have been performed to reduce the toxicity of organometallic catalysts using catalysts using more benign catalysts. In this regard, the employ of fully organic compounds to promote the ring-opening polymerization of cyclic esters is gaining a lot of interest. A key reason for transitioning to organocatalysts in polymerization reactions is their ability to be effectively removed from resultant polymers[7–12]. Moreover, it has been coined that some organocatalysts show much lower toxicity than conventional transition-metal-based catalysts.

Several organocatalysts have shown to be effective to catalyze ring-opening polymerization reactions such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). One of the main limitations of the utilization of organocatalysts is their poor thermal stability at temperatures that would be practical for polymerization and as such, full or partial thermal degradation of the catalyst may occur during the polymerization[13]. Recently, ionic compounds have emerged as an interesting alternative for carrying out polymerizations at high temperatures. For instance, Peruch et al. prepared some DMAP-based protic ionic compounds to mediate

the ROP of L-LA at elevated temperatures[14]. Similarly, Fradet et al. and Sardon et al. utilized some Brønsted acid ionic liquid to promote polyesterification and ring-opening polymerizations respectively[15,16]. 4-dimethylaminopyridine (DMAP):methanesulfonic acid (MSA) mixture has been determined to be an efficient organocatalysis for the stereoregular ring-opening polymerization of L-lactide in bulk[17]. Similarly, we recently demonstrated the ability of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD):methanesulfonic acid (MSA) protic ionic compound for PET depolymerization[18]. However, as these catalysts are relatively toxic, such as MSA that could not be used in food industry[19], there is a need to implement a purification process, which implies an extra step in the production system, increasing considerably the cost of the process. Due to that, non-toxic organocatalyst could be the most promising alternative, in order not to have the requirement to remove them from the media after the reaction, as it would not cause any harmful effect.

Nature offers a broad range of compounds that could work as catalyst, as they catalyze living processes in plants and animals. Some amino acids and their derivatives have been used to promote polymerization reactions. Coulembier et al. employed ammonium betaines for the ring-opening polymerizations at room temperature of L-lactide and cyclic carbonates in solution, obtaining rapid polymerizations[20]. L-proline and its derivatives have been used by Nozaki et al. for aldol polymerizations of acetaldehyde at room temperature in the presence of acetic acid[21]. Creatine has been used as an initiator in the ring-opening polymerization of polylactide (PLA) and polycaprolactone (PCL) in bulk at 150 °C[22]. While several naturally occurring catalysts have been investigated, as far as we are aware none of them have shown to be competitive in terms of performance with other non-natural organocatalysts.

In this chapter, five naturally occurring compounds have been chosen for the deep study of high temperature polymerization of cyclic esters. Taking inspiration from current reports from our group showing the excellent performance of acid-base mixtures based on organic acids and bases, all the candidates are amino acids, vitamins or their derivatives and have acid and base groups. Due to that, it is though that they could work as dual activators, activating the initiator together with the carbonyl group of the cyclic ester and therefore, enable the polymerization reaction. Moreover, it is envisioned that the acid-base nature will provide them with unique thermal stability. We have explored their potential for the ring-opening polymerization of L-lactide at 180 °C in bulk, industrially relevant conditions, and the results were analyzed. The best catalyst has been furtherly studied by X-ray diffraction and FTIR to provide some insight into their activation mechanism. Moreover, some cytotoxicity tests have been carried to evaluate their lack of toxicity. Finally, it has been shown that the selected catalyst not only catalyzes the ring-opening polymerization of L-lactide but also some other polyesters and polyamides.

2.2. Results and discussion

2.2.1. Characterization of naturally occurring catalysts

As mentioned before, some authors have reported the use of amino acid derivatives as catalysts for polymerization reactions. In this chapter, five possible natural catalyst candidates have been chosen: taurine, betaine, L-proline, nicotinic acid and creatine. The catalysts will be compared with DMAP:MSA base-acid mixture as it is a very efficient organocatalyst for the ring-opening polymerization of L-lactide in bulk. The candidates have both, acid and base groups, and it is thought that they could work similarly to the base-acid mixture (Figure 2.1).

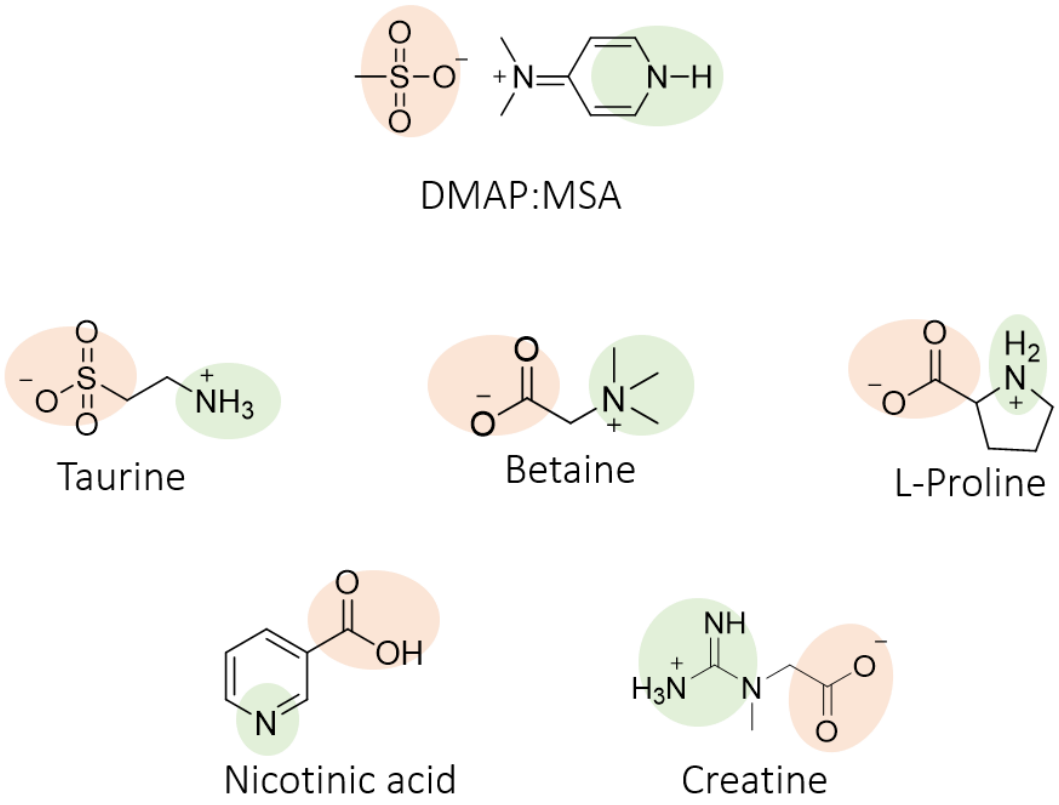


Figure 2.1. Naturally occurring catalysts compared with DMAP:MSA acid-base mixture.

It has been reported the use of MSA:pyridine derivatives, such as MSA:TBD and MSA: DMAP, for the ring-opening polymerization of polyesters. These acid-base mixtures work as dual catalysts as at high temperatures they dissociate and the sulfonic group of the MSA activates the nucleophile and the amine group of the pyridine the carbonyl group of the cyclic monomer, increasing the polymerization speed. Therefore, we think that taurine could be an interesting catalyst as it has a sulfonic group and an amine group in the structure. As 1,8-diazabicyclo[5.4.0]undec-7-ene:benzoic acid (DBU:BA) also has shown great performance for catalyzing ROP, we have also investigated naturally occurring catalysts with carboxylic acids, such as nicotinic acid, betaine, L-proline, and creatine.

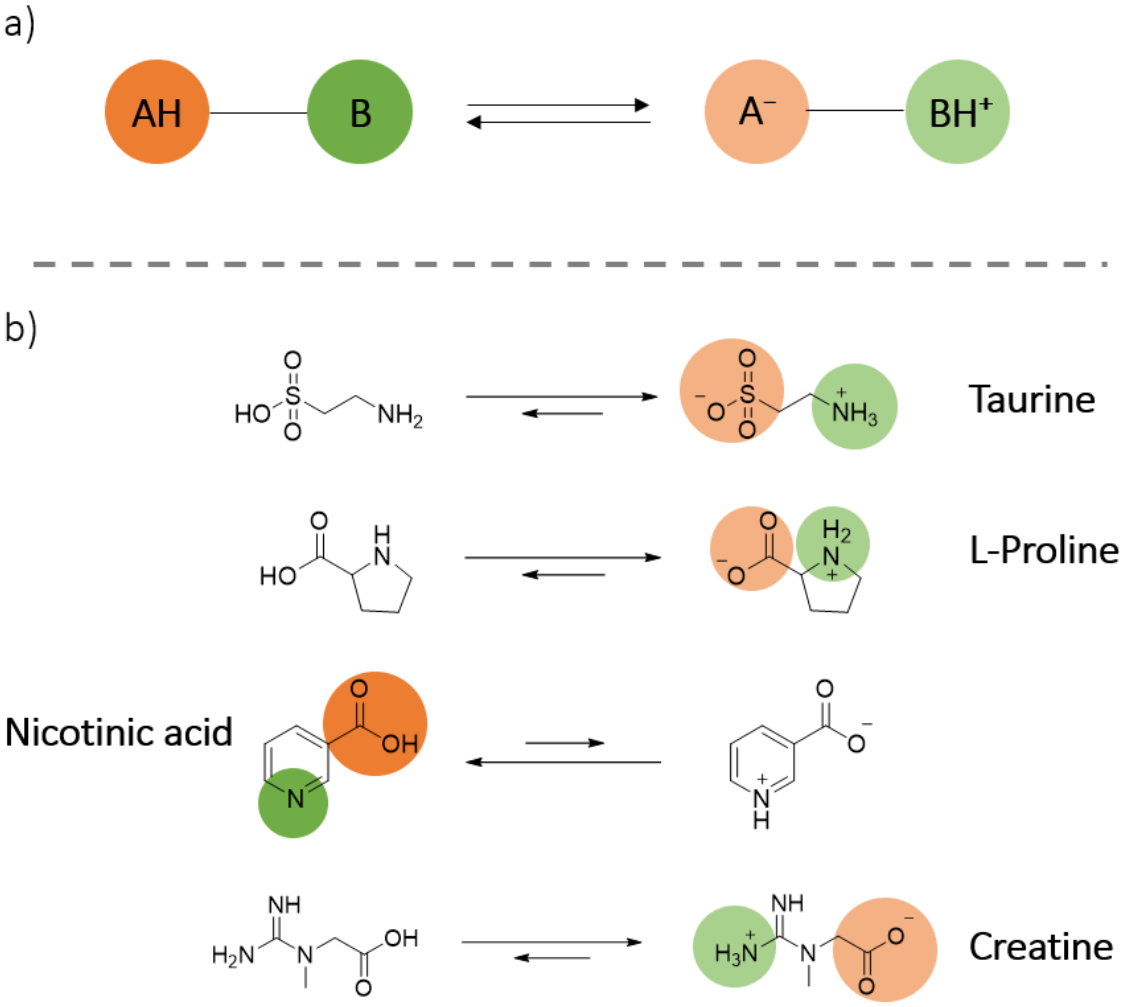


Figure 2.2. a) The structures that the naturally occurring catalysts could have, the non-charged one and the charged one, and b) the major structure for each catalyst.

In order to get some insight into the structure of the naturally occurring catalysts ^{1}H NMR spectra have been carried out in DMSO. Each catalyst could have two possible structures due to their acid and base groups, the non-charged structure and the charged one (Figure 2.2). In the case of betaine catalyst, the only structure possible for it is the charged one, as it has three methylenes attached to the amine group. The ^{1}H NMR of taurine reveals that taurine is mainly present in the charged form, meaning that the proton of the sulfonic acid migrated to the amine group, showing a signal at 7.6 ppm that corresponds to the charged amine group. In the case of L-Proline, the major

structure is also the charged one, having a broad peak at 8.4-9.0 ppm in the ^{1}H NMR spectrum. The nicotinic acid instead, does not show any signal of being charged, it shows a peak at 13.4 ppm that corresponds to the acid group, and therefore it is known that the preferential structure is the non-charged one. This could be due to the tertiary amine that it has in the aromatic ring and therefore, the basicity of the amine is reduced because the electron density is distributed through the ring. Creatine is also in the charged form, giving a signal at 6.9 ppm that it certifies the protonation of the amine group (Appendix 2.1-2.5).

The thermal stabilities of the compounds have been measured by TGA analysis carried out under nitrogen flow (Figure 2.3). They must be stable at high temperatures, as they need to be active for industrially relevant polyester synthesis. Nicotinic acid is the compound with the lowest thermal stability; it degrades at around 100 °C. This could be due to its non-ionic form and therefore it does not create nets between other nicotinic acid molecules. L-Proline is stable up to 170 °C, less than the rest of the compounds, which could be due to the 5-member ring that it has, that it might decrease the stability of the naturally occurring catalyst. Creatine and betaine are similar to DMAP:MSA mixture, with stabilities of around 200 °C. Taurine is the compound with the highest thermal stability, is stable until 250-300 °C, which could be due to the sulfonic group that it presents, stronger than the carboxylic group.

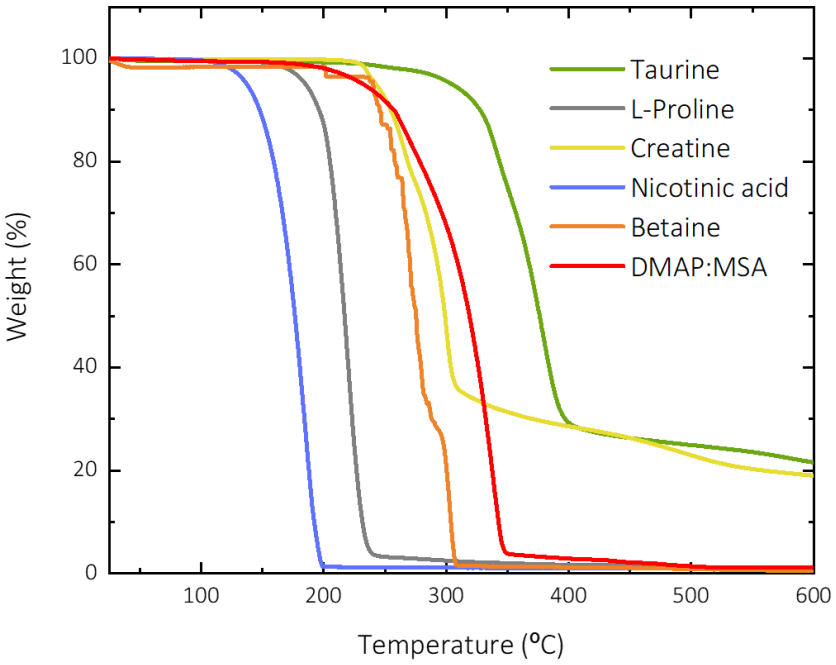


Figure 2.3. TGA analysis of DMAP:MSA and naturally occurring catalysts.

2.2.2. Catalyst evaluation in the ring-opening polymerization of L-lactide in bulk

In order to validate the efficiency of the catalyst, we explore its utility for the polymerization of the largest produced biobased polyester, PLA. The catalytic activities of the five catalyst candidates were first assessed for the ROP of L-lactide at 180 °C in bulk, which are commonly employed industrial conditions (Figure 2.4).

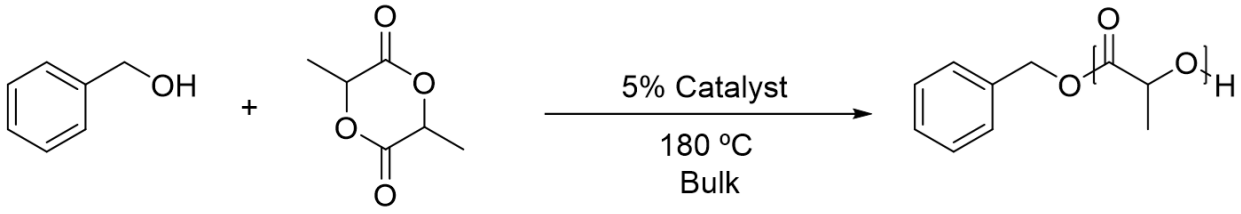


Figure 2.4. General scheme of the ROP of L-lactide catalyzed using different catalysts.

Polymerizations were initiated by benzyl alcohol targeting a degree of polymerization of 100. DMAP:MSA mixture was also tested in the same reaction as reference as it has shown excellent performance for the ROP of L-lactide at elevated temperatures. To

determine the performance of each catalyst, conversion kinetics of the reactions were followed by ^{1}H NMR in chloroform (Figure 2.5).

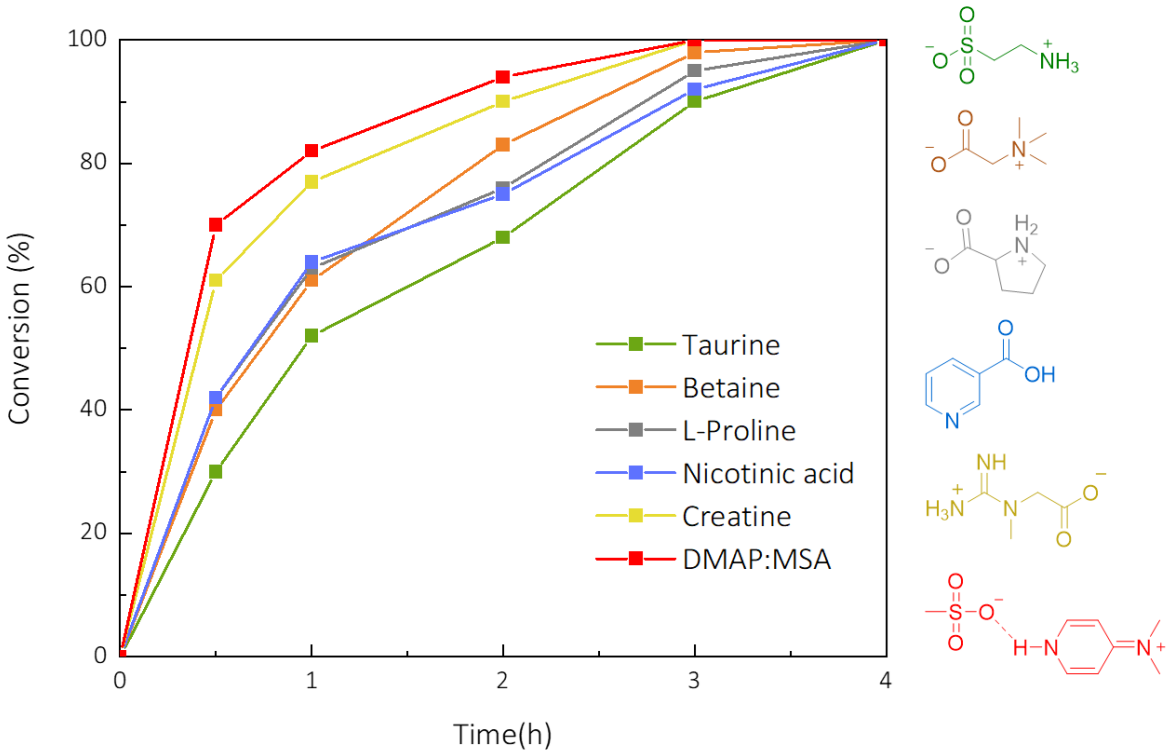


Figure 2.5. Conversion kinetics of ROP of L-lactide using different catalysts.

It was observed that the five naturally occurring catalysts were giving full conversion before 4 h, most of them slightly slower than DMAP:MSA mixture that needed 3 h (Figure 2.6, entry 6). Creatine was the catalyst that fastest give full conversion, however, the molecular weight of the obtained polymer measured by SEC indicates that is very low (Figure 2.6, entry 5). L-Proline also gives, lower molecular weights than expected as it gets half DP than the target one as reported by others due to the ability of proline to initiate the ROP[23] (Figure 2.6, entry 3). Taurine and nicotinic acid were the ones that got the highest molecular weights and the lowest dispersities, similar to the polymers that are synthesized by the use of DMAP:MSA mixture (Figure 2.6, entry 1 and 4).

a)

entry	catalyst	time (h)	conv. (%)	$M_{n,\ theo}$ (g mol^{-1})	$M_{n,\ SEC}$ (g mol^{-1})[a]	Đ
1	Taurine	4	98	14200	14100	1.1
2	Betaine	4	99	14400	10100	1.4
3	L-Proline	4	100	14500	7300	1.5
4	Nicotinic acid	4	100	14500	12500	1.2
5	Creatine	3	99	14400	2500	1.6
6	DMAP:MSA	3	100	14500	15000	1.2

[a] Determined by SEC in THF with polystyrene standards and correction factors.

b)

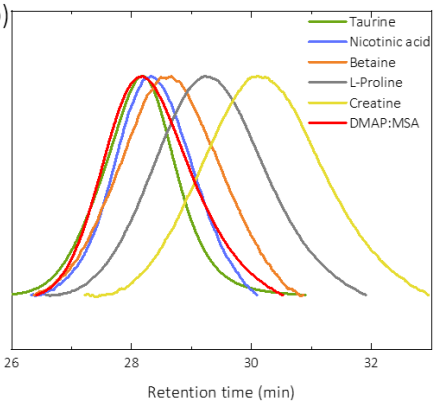


Figure 2.6. a) Results of the ring-opening polymerization of L-lactide in bulk at 180 °C, initiated with benzyl alcohol and using different catalysts with DP_{tot} = 100, and b) SEC graphs.

MALDI-TOF analysis was carried out after synthetizing polymers of low molecular weight (DP ≈ 10) using benzyl alcohol as an initiator at 180 °C in bulk. The analysis indicates the polymer synthesize using creatine as catalyst (Figure 2.7a) has a separation of 72.04 m/z between the peaks, indicating a difference of a lactyl unit between the chains. That difference conclude that PLA cycles have been synthesized during the polymerization by back-biting reaction, where the final alcohol attacks a carbonyl of the same chain. The same result was also obtained when nicotinic acid is used as catalyst (Appendix 2.6). The polymers synthesized with taurine catalyst instead (Figure 2.7b), show a separation of 144.06 m/z between the peaks, lactide monomer molecular weight, concluding that there is no back-biting reaction when this catalyst is employed. Betaine and L-proline also display a separation of 144.06 m/z (Appendix 2.7-2.8).

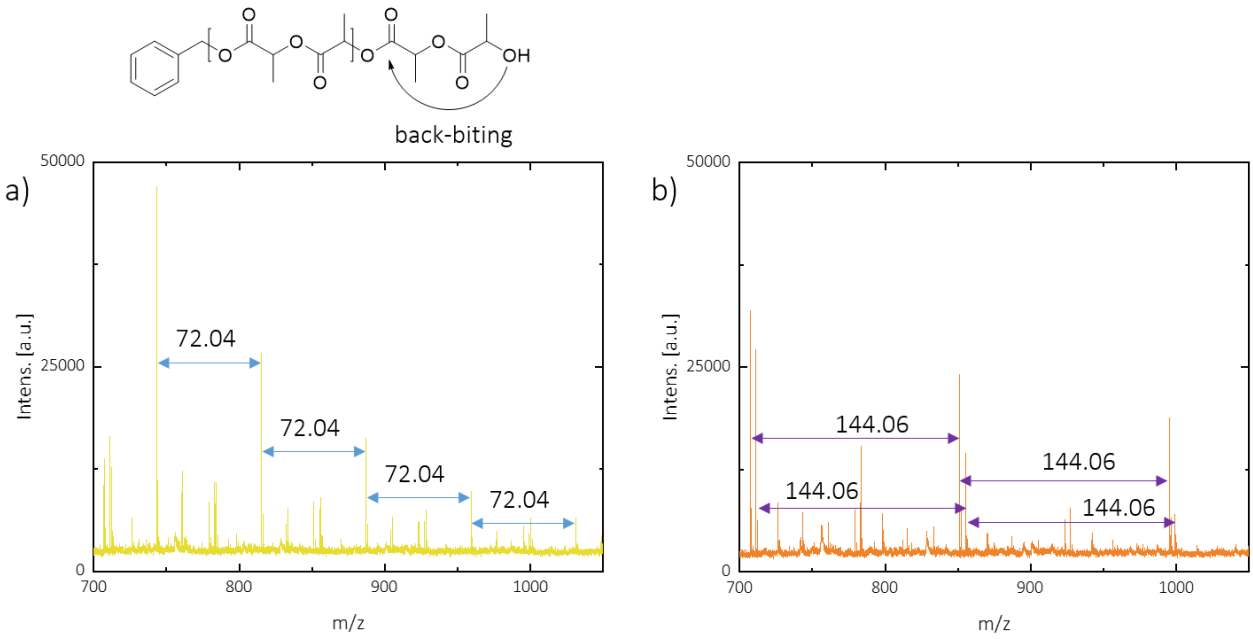


Figure 2.7. MALDI-TOF analysis of PLA using a) creatine as the catalyst and b) taurine as the catalyst.

The low molecular weights of some of the polymers (Figure 2.6) indicate that the use of different catalysts affects polymerization. In order to understand the consequence of using each of the catalysts, reactions with 1:1 equivalents of lactide monomer and catalyst were done at 180 °C in bulk and the results were characterized by ^{1}H NMR in chloroform (Figure 2.8).

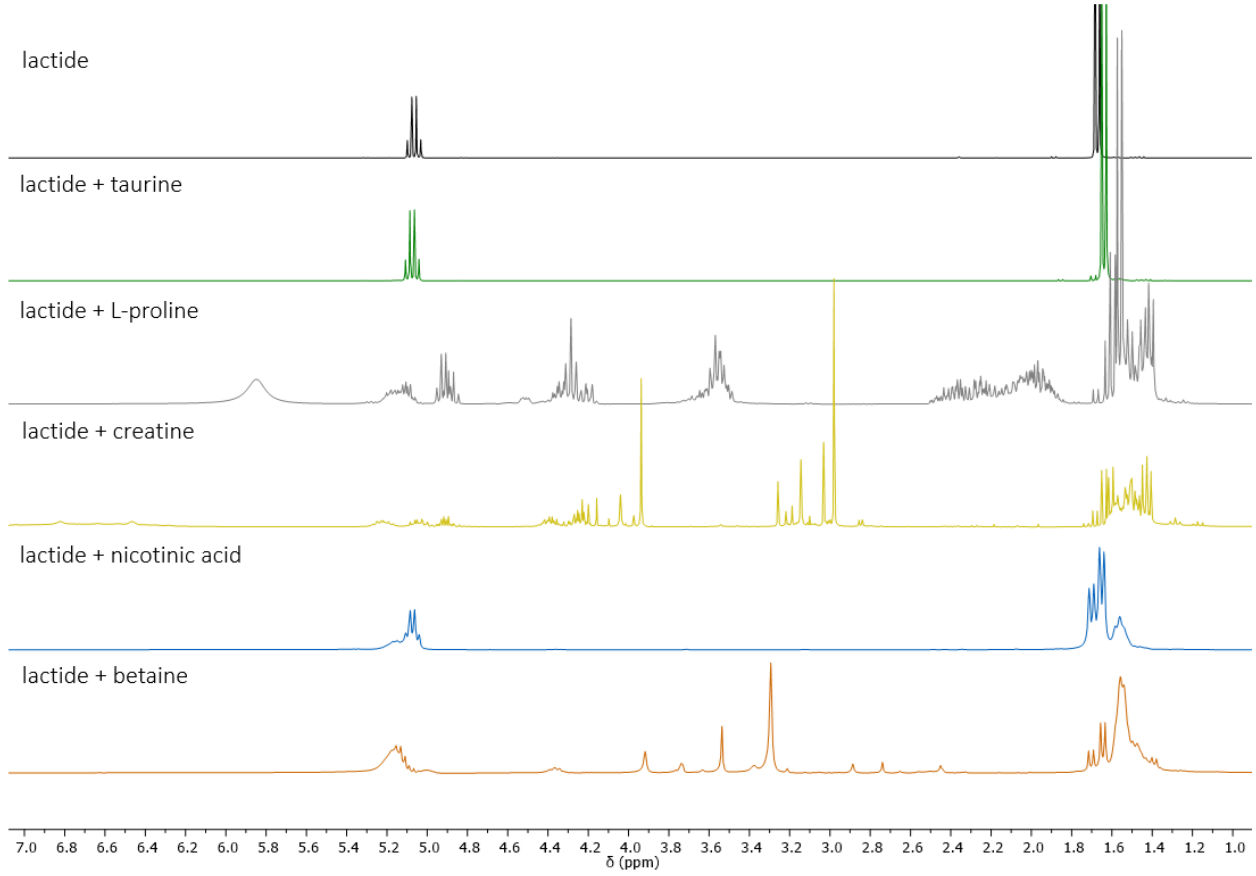


Figure 2.8. ^{1}H NMR spectra of equimolar L-lactide and catalyst in bulk at 180 °C and its comparison with lactide monomer.

It could be observed that when lactide and the catalysts are combined and heated, in most of the cases a reaction is occurring. In the case of creatine, it is observed that lactide is ring-opened as the signal of lactide monomer of 5.0-5.1 ppm disappeared and two peaks in 6.47 and 6.83 ppm appeared, signals of the amines protons when they are linked with the lactide, indicating the reaction between the catalyst and the monomer. When L-proline is used as a catalyst, the same result could be identified, with the creation of a signal in 5.12-5.25 ppm, the ring-opened L-lactide. Betaine and nicotinic acid are also able to ring-open the L-lactide, however, lactide monomer signal could be still see after the reaction at 180 °C. In the case of taurine catalyst, the ^{1}H NMR spectrum in chloroform did not show any difference from the lactide monomer spectrum, the

signals observed correspond to lactide, which could be due to the insolubility of taurine in chloroform. To confirm any reaction between taurine and lactide, the spectrum was also done in DMSO (Figure 2.9).

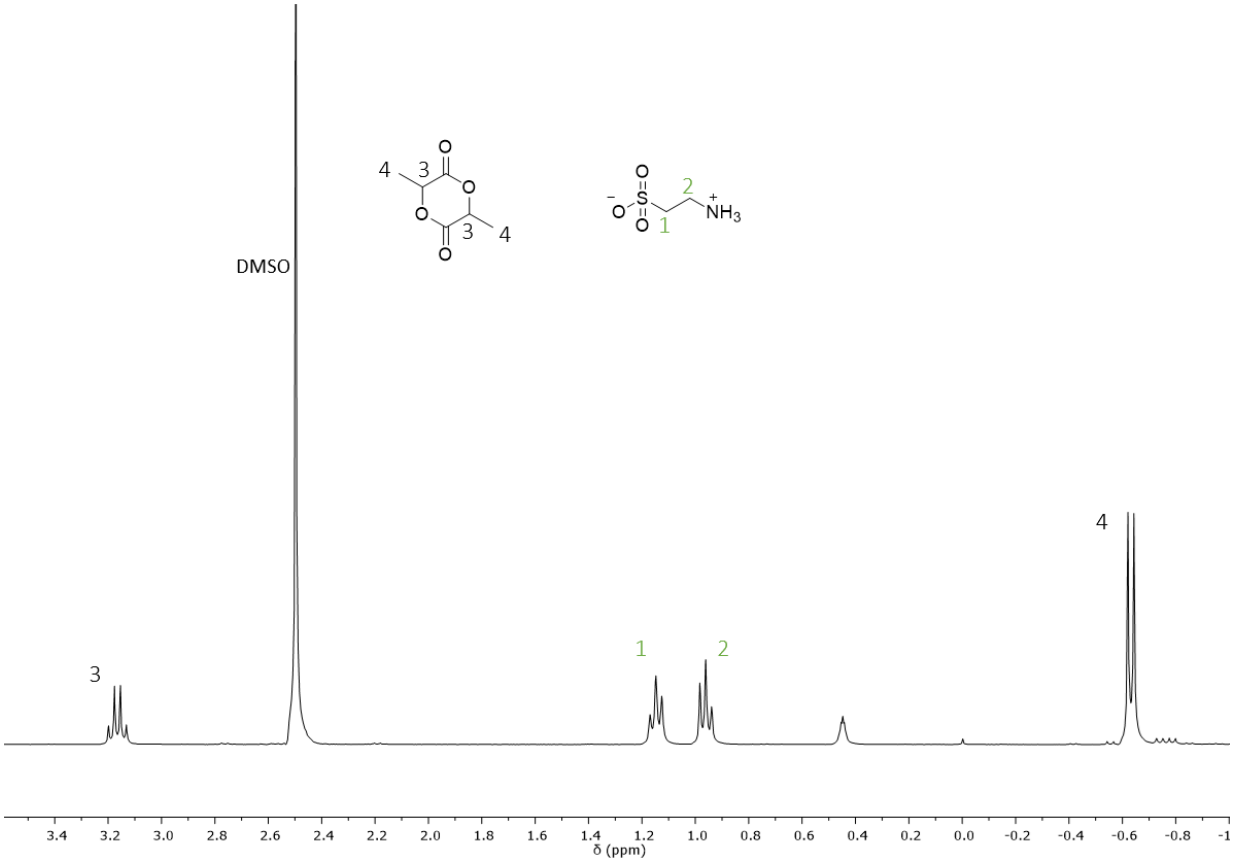


Figure 2.9. ^{1}H NMR spectrum of the reaction between equimolar lactide and taurine at 180 °C in bulk using deuterated DMSO.

The spectrum indicates that there was no reaction between taurine and L-lactide as just the signals of the monomer and taurine are appreciated together with a signal in 0.42 ppm that corresponds to the deprotonated amine of taurine.

In consequence, it could be concluded that except for taurine, the rest of the catalysts are able to ring-open the L-lactide in different proportions, therefore proclaiming taurine the most suitable catalyst as it gives the chance to control the rate of the polymerization reaction without any effect in the molecular weight.

The effect of the temperature was analyzed when using taurine as the catalyst for the synthesis of PLA in bulk (Figure 2.10). It could be seen that the reaction at lower temperatures has an evident effect on the speed of the polymerization, having just 20 % of conversion after 4 h when the reaction is carried out at 130 °C and almost 55 % at 160 °C. The kinetic data outcome in an activation energy (E_a) of 73 kJ/mol, which indicates the need for high temperatures for the polymerization.

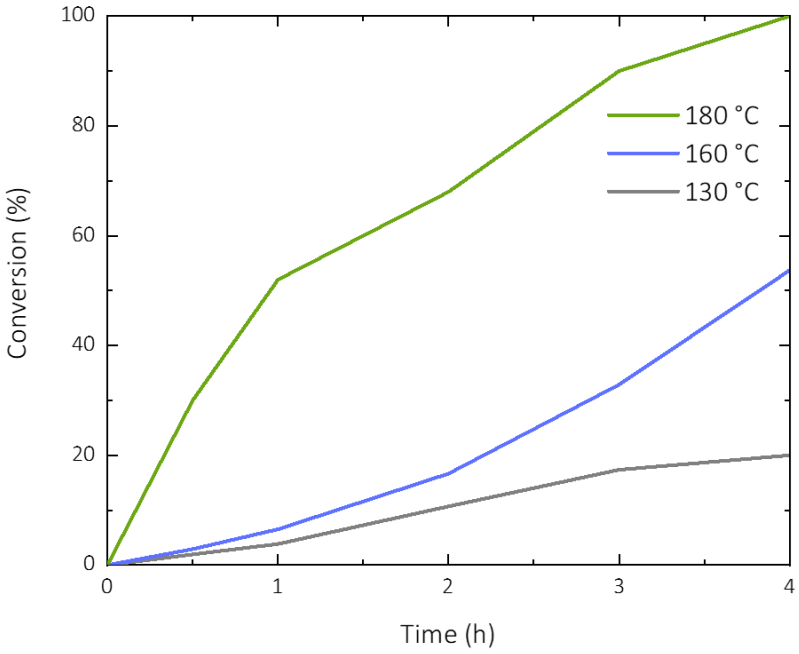


Figure 2.10. Conversion kinetics of PLA synthesis using taurine as catalyst and benzyl alcohol as an initiator at different temperatures in bulk.

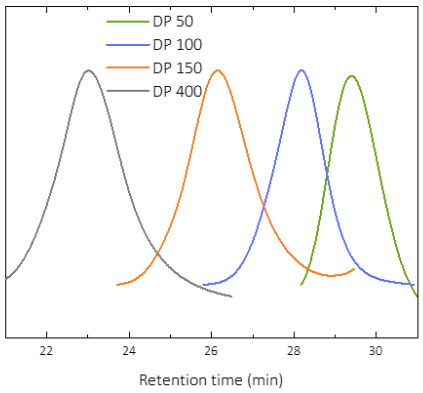
Polylactide of different DP (50, 100, 150 and 400) have been synthesized catalyzed by taurine at 180 °C and in bulk (Figure 2.11). The results indicate that the polymerizations were successfully carried out and that the target molecular weights were obtained. The dispersity (Đ) suffered a slight increase when increasing the molecular weight, however, it is still low.

a)

entry	DP	conv. (%)	$M_{n,\ theo}$ (g mol^{-1})	$M_{n,\ SEC}$ (g mol^{-1})[a]	Đ
7	100	98	14200	14100	1.1
8	50	99	7200	7000	1.1
9	150	97	21000	20500	1.2
10	400	97	56000	50400	1.2

[a] Determined by SEC in THF with polystyrene standards and correction factors.

b)



c)

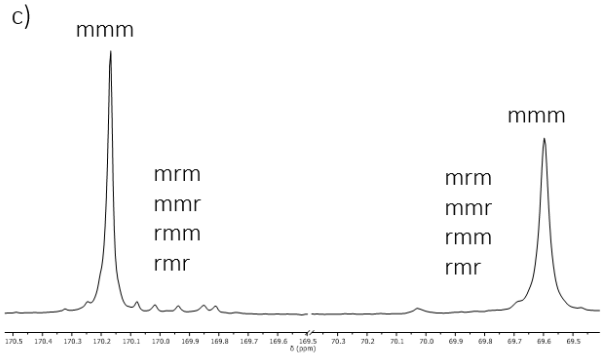


Figure 2.11. a) Results of the ring-opening polymerization of L-lactide of different DP in bulk at 180 °C initiated with benzyl alcohol and catalyzed by taurine, b) SEC graphs and c) ^{13}C NMR spectrum of DP 100 and the triads that could be observed.

Afterward, the polylactides were analyzed by ^{13}C NMR to calculate the stereoregularity (Figure 2.11c). The PLA of DP 100 presents an L- to D-isomer ratio of Pm=0.94, the same as the polymer of DP 400 (Appendix 2.9). Considering that a minor amount of epimerization has a great impact on the stereoregularity of PLA, it could be affirmed that taurine is a quite good catalyst to synthesize stereoregular PLA.

It could be concluded that taurine is an effective catalyst for the synthesis of PLA by ring-opening polymerization of L-lactide. To further understand the polymerization mechanism and its properties, several techniques have been employed. On one side, a standard X-ray diffraction analysis has been carried out at 100 K to confirm the structure of taurine. On another side, FTIR measurements at different temperatures have been

recorded to conclude the changes that the catalyst could suffer with the temperature and finally, its cytotoxicity has been measured to ensure its lack of toxicity.

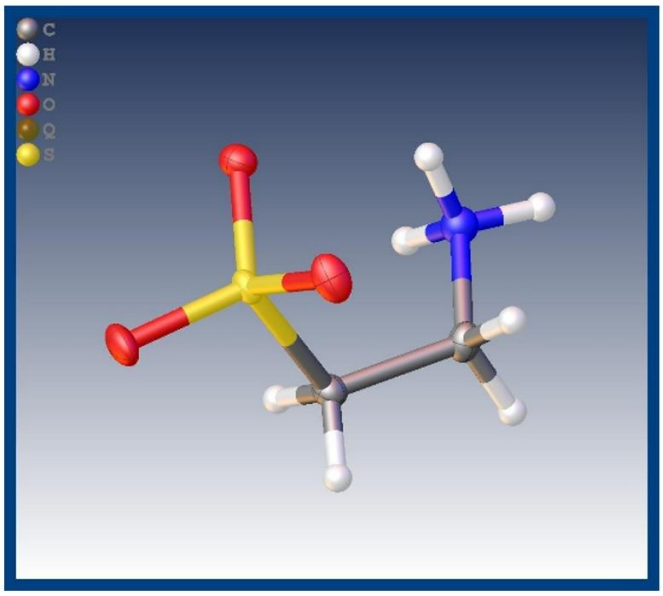


Figure 2.12. X-ray diffraction analysis of taurine at standard conditions (100 K).

X-ray diffraction analysis of taurine catalyst indicates that the compound at low temperatures is forming a salt (Figure 2.12). The sulfonic acid group shows that it lost the proton, having a negative charge, and the amine group took the proton charging positively. The result obtained by this technique is in accordance with the results obtained by ^{1}H NMR in DMSO, where the signal of the protonated amine was observed at 7.6 ppm. The charges that are formed in the compound induce the bent of the molecule, having a shape of a half-circle.

Taurine FTIR analysis at 25 °C shows a clear and well-defined double band at 1570-1650 cm^{-1}, a signal that corresponds to the protonated amine group of the catalyst (Figure 2.13). With the increase of the temperature, 150-250-270 °C, the protonated amine band starts to lose the definition of two bands and a single broad band starts to be formed. At 150 °C and 250 °C, the double band could still be observed, however, it is

not defined as well as at the spectrum at 25 °C. In the measurement carried out at 270 °C, the double band completely disappeared and a single band could just be appreciated. The spectra were compared with butylamine (Appendix 2.10), which is known to have a non-protonated amine. It could be noticed that butylamine shows a single broad band at 1570-1650 cm^{-1}, which corresponds to the amine. The signal of butylamine and taurine at 270 °C have the same shape, indicating that they belong to the same functional group. These results determine that taurine deprotonates the amine with temperature, having complete deprotonation at 270 °C.

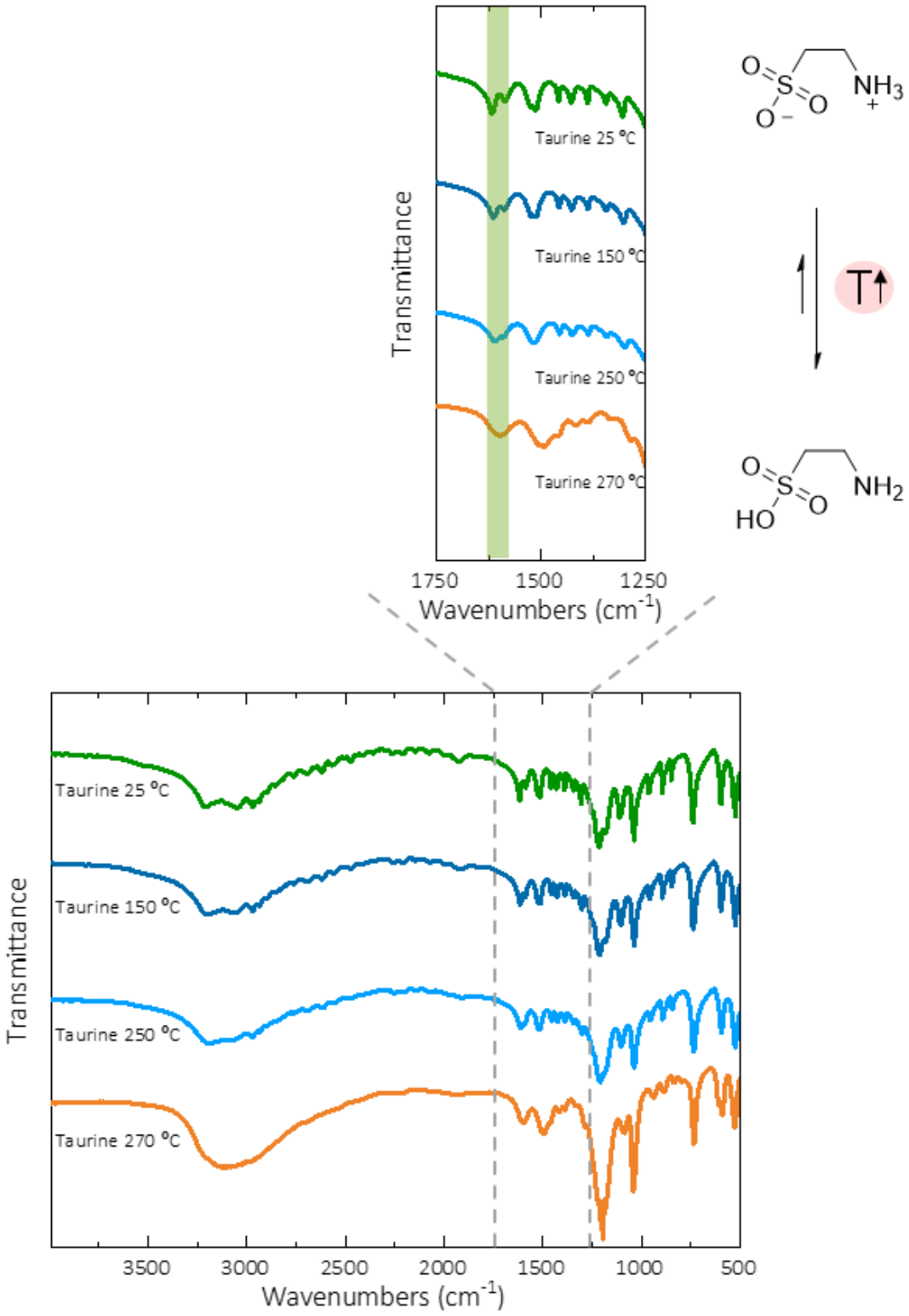


Figure 2.13. FTIR analysis of taurine at different temperatures and its comparison.

By the information that X-ray diffraction and FTIR analysis give and the results obtained by polymerization kinetics, the ring-opening polymerization mechanism of L-lactide catalyzed by taurine has been proposed (Figure 2.14). At low temperatures, the amine of the taurine is protonated and the sulfonic acid is deprotonated, making the amine side to be a bad acid and the sulfur side a bad base. It was confirmed by FTIR analysis that when increasing the temperature, the equilibrium of taurine shifts to the side of the deprotonation of the amine and therefore, the protonation of the sulfonic acid, becoming the amine a strong base and the sulfonic acid a strong acid, that can perform the ring-opening polymerization of L-lactide. Taurine acts as a dual catalyst, that from the side of the sulfonic acid activates the carbonyl group of the L-lactide and from the side of the amine group the initiator. This last compound will attack the carbonyl group of the monomer initiating the ring-opening polymerization. Once the first L-lactide is opened, the amine group of the taurine will activate the alcohol that has been formed at the end of the chain and will help the propagation of the polymerization until the polymerization reaches the end.

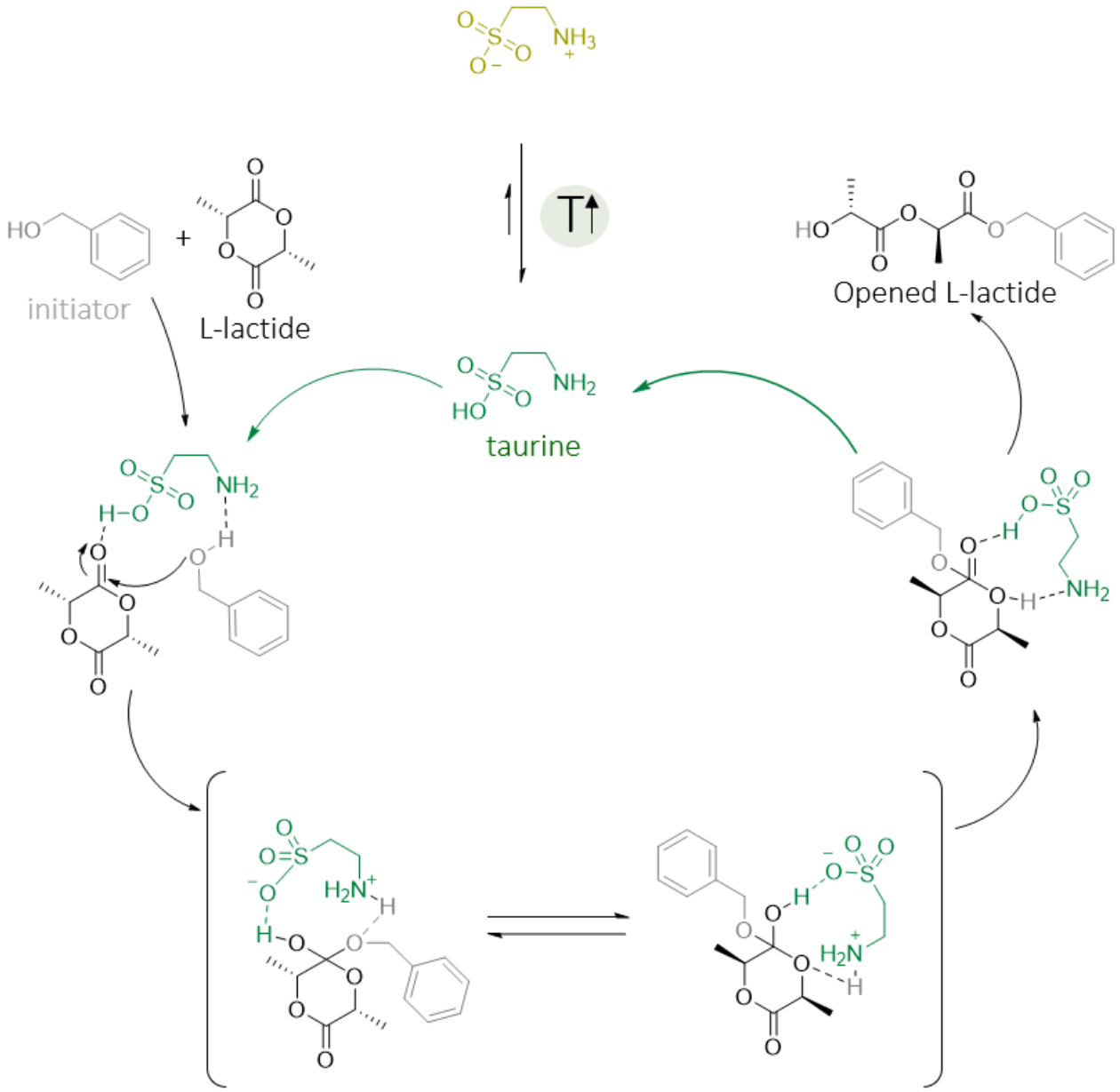
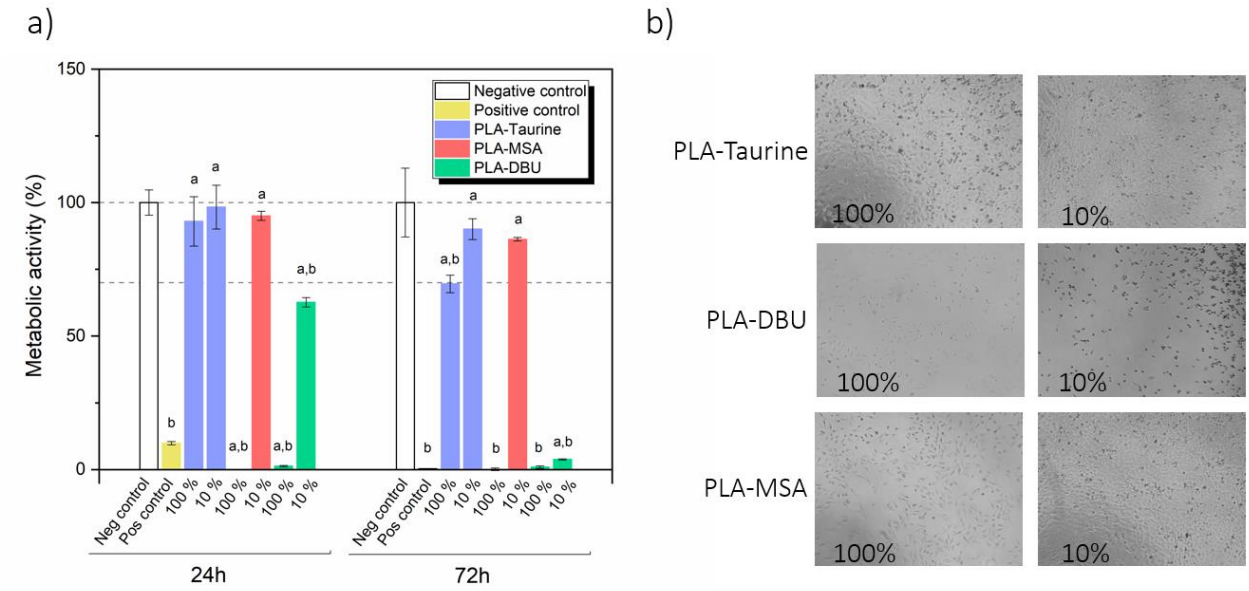


Figure 2.14. Proposed mechanism of the ring-opening polymerization of L-lactide catalyzed by taurine.

As mentioned before, taurine is a naturally occurring catalyst that could be found in many animals and therefore, it is interesting as it is considered a sustainable compound. In addition, as it is present in animal tissue it is thought to be a non-toxic substance, which will make it highly relevant industrially as will help to avoid the purification step of the polymer. To certify if taurine is toxic or not, cytotoxicity test was carried out.

In order to proceed with the test, three ring-opening polymerizations of L-lactide were carried out each of the reaction catalyzed with 5 mol % of a different catalyst, one of them by taurine, another one by 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) and the last one by methanesulfonic acid (MSA). DBU and MSA catalysts were also tested, to have a comparison for taurine. Once the polymers (PLA) were synthesized, they were analyzed without any purification (Figure 2.15).



(a) Significant difference ($p<0.05$) compared to the positive control (Complete medium + 10 % DMSO)
(b) Significant difference ($p<0.05$) compared to the negative control (Complete medium)

Figure 2.15. Cytotoxicity test of PLA synthesized by taurine and its comparison to the ones syntheseized by DBU and MSA.

For each polymer two different conditions were prepared: 100 %, that is the extract obtained from the incubation (37 °C, 24 h) of the polymer with the medium at a ratio of 200 mg of polymer/ 1 mL of medium, and 10 % that is the diluted extract obtained by the dilution (1:10) of the concentrated extract.

The medium used for the test has a pH indicator (phenol red) that changes to yellow color for pH values lower than 6.8 and becomes purple at higher values than 8. When

PLA-DBU, polylactide synthesized using DBU as the catalyst, and PLA-MSA, polylactide synthesized using MSA as catalyst, got in contact with the medium it was observed an instantaneous color change to yellow, indicating that these two polymers induce the acidification of the medium. In the case of PLA-Taurine, polylactide synthesized using taurine as the catalyst, no color change was observed in the medium.

In the case of PLA-Taurine, with both concentrations (10 % and 100 %), the cells maintain the metabolic activity above 90 %, which indicates that taurine has almost no toxicity. For the test at 72 h using a concentration of 100 %, the metabolic activity is 70 %, which is at the limit of the permitted toxicity. The polymer synthesized using DBU as catalyst decreases significantly the metabolic activity of the cells, in the case of 10 % at 24 h, which is around 60 %, but at 72 h, the activity decreases almost to zero. In the test where the concentrated extract was used, the cells reduced their activity to zero in the two tests, 24 h and 72 h. For the case of PLA-MSA at 100 % concentration, the metabolic activity is null, however, at diluted concentrations the metabolic activity is maintained above 80%, which indicates that it is not toxic.

Therefore, it could be assured, that the polylactide that is synthesized by 5 % of taurine is not toxic and could be used without the need for purification. The polymers synthesized by DBU and MSA instead, show toxicity and consequently, they need a purification step.

2.2.3. Extending the catalytic scope of taurine

It has been demonstrated that taurine is an effective catalyst for the ROP of L-lactide. In order to try to expand its catalytic scope, it has been tried as a catalyst for the polymerization of different cyclic monomers (Figure 2.16).

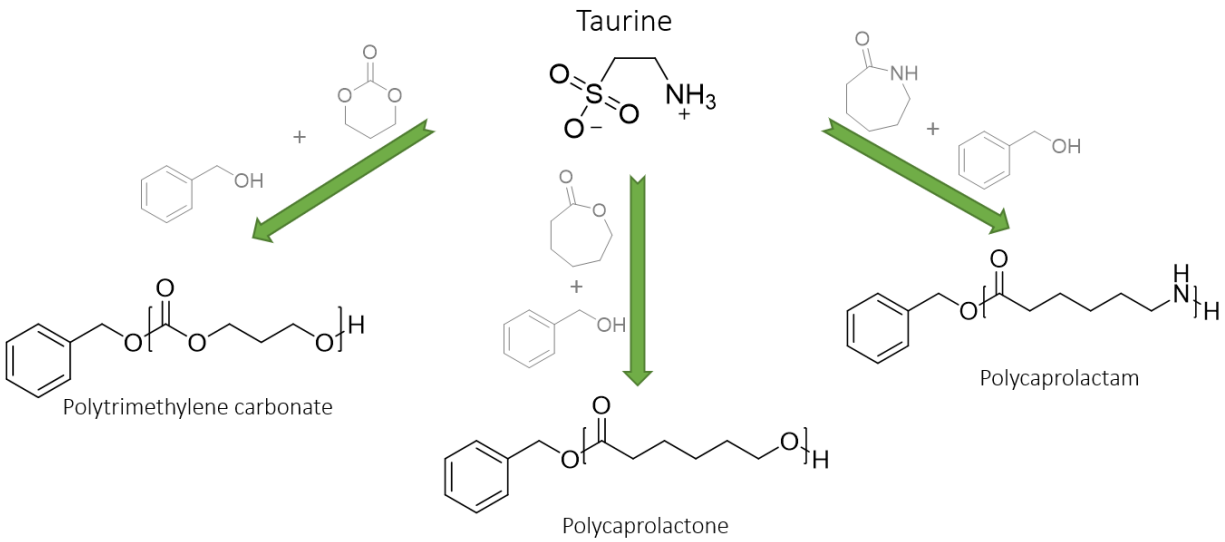


Figure 2.16. Scheme of polymerization reactions that have been catalyzed by taurine.

First, the potential of taurine catalyst for the synthesis of other cyclic esters has been investigated. To do so we explore the ROP of ε-caprolactone using the same initiator as before, benzyl alcohol, at 180 °C in bulk with 5 % of taurine. ^{1}H NMR in chloroform after 4 h confirmed that the polymerization reaction worked effectively and polycaprolactone was obtained (Appendix 2.11). Considering that the catalyst is effective for the ROP of L-lactide and of ε-caprolactone, we explore the potential of taurine to prepare polylactide-co-polycaprolatone (PLA-b-PCL) block copolymer (Figure 2.17a).

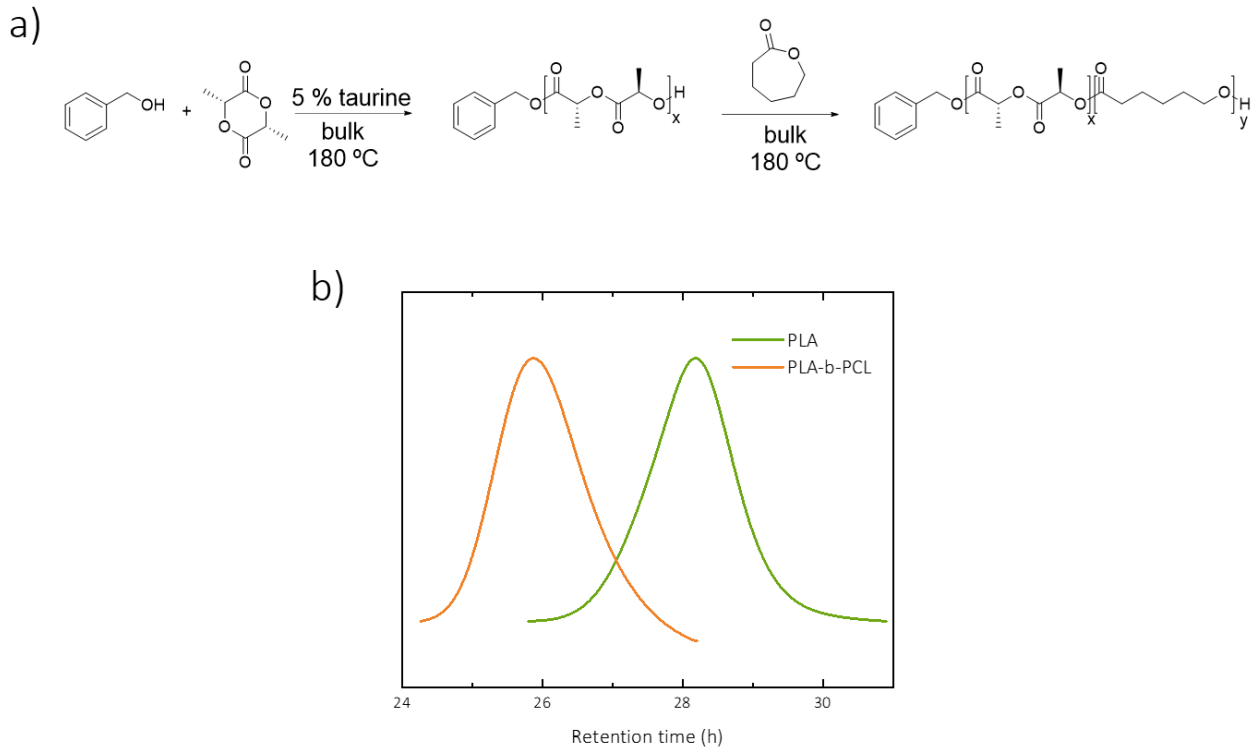


Figure 2.17. a) General scheme of the block copolymerization between L-lactide and ε-caprolactone, and b) the SEC analysis of PLA and PLA-b-PCL.

First, the polymerization of L-lactide was performed, using the same reaction conditions as described before and the resulted polymer was analyzed by SEC, having a molecular weight of 14100 g·mol^{-1} and dispersity of 1.1. After that, ε-caprolactone was added to the reaction mixture. It was confirmed by SEC that the reaction worked well, observing an increase in the molecular weight up to 24000 g·mol^{-1} maintaining the dispersity in 1.1 (Figure 2.17b). This result demonstrated the potential of taurine to act as a catalyst for the living polymerization of cyclic esters.

Finally, some other ring-opening polymerizations were investigated for the preparation of a polycarbonate and a polyamide (Figure 2.16). For that, trimethylene carbonate and ε-caprolactam were ring-opened by benzyl alcohol in bulk at 180 °C with 5 % of taurine catalyst. It could be assured that both reactions performed satisfactorily, however, the

molecular weights obtained in the polymerization of polycaprolactam were low and therefore the reactions conditions need to be adjusted (Appendix 2.12-2.13).

2.3. Conclusion

In this chapter, five naturally occurring catalysts have been studied for polyester polymerizations at high temperatures, taurine, betaine, L-proline, nicotinic acid and creatine. These catalysts have been selected due to their acid and base groups which could give the chance to act as dual catalysts. It was determined that the five of them are able to catalyze the ROP polymerization of L-lactide in bulk in a short reaction time. However, ^{1}H NMR spectra confirmed that all catalysts, except taurine, together with catalyzing the reaction also initiate the ring-opening reaction. Due to that, taurine was concluded to be the most promising catalyst among the ones of choice, as it enables the control of the reaction speed without compromising the molecular weight.

The characterization of the catalyst by X-ray diffraction, FTIR and ^{1}H NMR analysis had enlighted the salt structure of taurine and its change with temperature, giving the chance of proposing a reaction mechanism for the ROP of L-lactide. Cytotoxicity test of the synthesized polymer determines the lack of toxicity when taurine is used in catalytic scale, maintaining the metabolic activity above the limit of 70 %.

Up to our knowledge, this work approaches for the first time the use of taurine as a non-toxic catalyst enabling polyester synthesis at high polymerization temperatures. Remarkably, the catalytic scope of taurine has been expanded to other high temperature polymerizations, such as the ROP of polycarbonates and polyamides have been tried. While it has shown to be able to catalyze the polymerizations, the attained molecular weights were low and therefore, polymerization conditions must be optimized.

2.4. Experimental section

2.4.1. Materials

Taurine (99 %, Sigma-Aldrich S.A.), betaine (>98 %, Sigma-Aldrich S.A.), L-proline (>99 %, Sigma-Aldrich S.A.), nicotinic acid (>98 %, Sigma-Aldrich S.A.), creatine (99 %, Sigma-Aldrich S.A.), 4-dimethylaminopyridine (DMAP) (99 %, TCI), methanesulfonic acid (MSA) (99 %, Sigma-Aldrich S.A.) and 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) (98 %, Sigma-Aldrich S.A.) were dried under vacuum before using them. L-lactide (Corbion) was purified in toluene and dried under vacuum before using it.

2.4.2. Ring-opening polymerization of L-lactide

The synthesis of polylactide polyester was performed by ROP of a cyclic ester, L-lactide. In a 5 mL vial 0.50 g ($3.47\ 10^{-3}$ mol) of L-lactide were placed with a magnetic bar, 5 mol % of catalyst ($1.73\ 10^{-3}$ mol) and 3.6 µL ($3.47\ 10^{-5}$ mol) of benzyl alcohol (DP 100).

The vial was then submerged into a pre-heated oil bath at 180 °C for 4 hours and the conversion was followed by ^{1}H NMR in deuterated chloroform. After reaction completion, the formed polylactide was let to cool down to room temperature naturally. For the purification, the sample was dissolved in chloroform and precipitated in cold methanol. The resulted polyester was filtrated and dried under vacuum at RT for 24 h before its characterization.

2.4.3. Ring-opening polymerization of trimethylene carbonate

The synthesis of polytrimethylene carbonate was performed in the same way as the ROP of L-lactide. In a 5 mL vial 0.50 g ($4.90\ 10^{-3}$ mol) of trimethylene carbonate were placed with a magnetic bar, 5 mol % of taurine ($1.73\ 10^{-3}$ mol, 0.031 g) and 5.1 µL ($4.90\ 10^{-5}$ mol) of benzyl alcohol (DP 100).

The vial was heated up to 180 °C for 4 hours and the conversion was followed by ^{1}H NMR in deuterated chloroform. After 4 h of reaction, the polycarbonate was purified using the same procedure as for the synthesis of polylactide.

2.4.4. Ring-opening polymerization of ε-caprolactone

The ROP of ε-caprolactone was done following the same reaction conditions that were used for the other polymerizations, together with the purification conditions. Employing 0.50 g ($4.38\ 10^{-3}$ mol) of ε-caprolactone, 5 mol % of taurine ($2.19\ 10^{-4}$ mol, 0.027 g) and 4.5 µL ($4.38\ 10^{-5}$ mol) of benzyl alcohol (DP 100).

2.4.5. Ring-opening polymerization of ε-caprolactam

The ROP of ε-caprolactam was done using the same reaction conditions that were used for the other polymerizations, together with the purification conditions. Weighting 0.50 g ($4.42\ 10^{-3}$ mol) of ε-caprolactone, 5 mol % of taurine ($2.21\ 10^{-4}$ mol, 0.028 g) and 4.6 µL ($4.42\ 10^{-5}$ mol) of benzyl alcohol (DP 100).

2.5. References

1 Plastics Europe, *Plastics-the Fact 2021 An analysis of European plastics production, demand and waste data*, 2021.

2 M. Hong and E. Y. X. Chen, *Green Chem.*, 2017, **19**, 3692–3706.

3 C. Jehanno, M. M. Pérez-Madrigal, J. Demarteau, H. Sardon and A. P. Dove, *Polym. Chem.*, 2019, **10**, 172–186.

4 M. E. Rogers, T. Long, S. Turner, *Introduction to synthetic methods in step-growth polymers*, John Willey & Sons, New Jersey, 2003.

5 P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, New York,

1995.

6 G. Odian, *Principles of polymerization*, John Willey & Sons, New Jersey, 4th edition, 2004.

7 W. N. Ottou, H. Sardon, D. Mecerreyes, J. Vignolle and D. Taton, *Prog. Polym. Sci.*, 2016, **56**, 64–115.

8 H. Sardon, A. Pascual, D. Mecerreyes, D. Taton, H. Cramail and J. L. Hedrick, *Macromolecules*, 2015, **48**, 3153–3165.

9 X. Zhang, M. Fevre, G. O. Jones and R. M. Waymouth, *Chem. Rev.*, 2018, **118**, 839–885.

10 D. W. C. MacMillan, *Nature*, 2008, **455**, 304–308.

11 S. Bertelsen and K. A. Jørgensen, *Chem. Soc. Rev.*, 2009, **38**, 2178–2189.

12 P. I. Dalko and L. Moisan, *Angew. Chemie - Int. Ed.*, 2004, **43**, 5138–5175.

13 L. Mezzasalma, A. Dove and O. Coulembier, *Eur. Polym. J.*, 2017, **95**, 628–634.

14 J. Kadota, D. Pavlović, H. Hirano, A. Okada, Y. Agari, B. Bibal, A. Deffieux and F. Peruch, *RSC Adv.*, 2014, **4**, 14725–14732.

15 A. Basterretxea, E. Gabirondo, A. Sanchez-Sanchez, A. Etxeberria, O. Coulembier, D. Mecerreyes and H. Sardon, *Eur. Polym. J.*, 2017, **95**, 650–659.

16 S. Zhang, V. Lemaire, A. Féret, H. Lefebvre, M. Tessier and A. Fradet, *Polym. Chem.*, 2013, **4**, 1538–1545.

17 A. Basterretxea, E. Gabirondo, C. Jehanno, H. Zhu, O. Coulembier, D. Mecerreyes

and H. Sardon, *Macromolecules*, 2021, **54**, 6214–6225.

18 C. Jehanno, I. Flores, A. P. Dove, A. J. Müller, F. Ruipérez and H. Sardon, *Green Chem.*, 2018, **20**, 1205–1212.

19 M. D. Gernon, M. Wu, T. Buszta and P. Janney, *Green Chem.*, 1999, **1**, 127–140.

20 B. Guillerm, V. Lemaur, J. Cornil, R. Lazzaroni, P. Dubois and O. Coulembier, *Chem. Commun.*, 2014, **50**, 10098–10101.

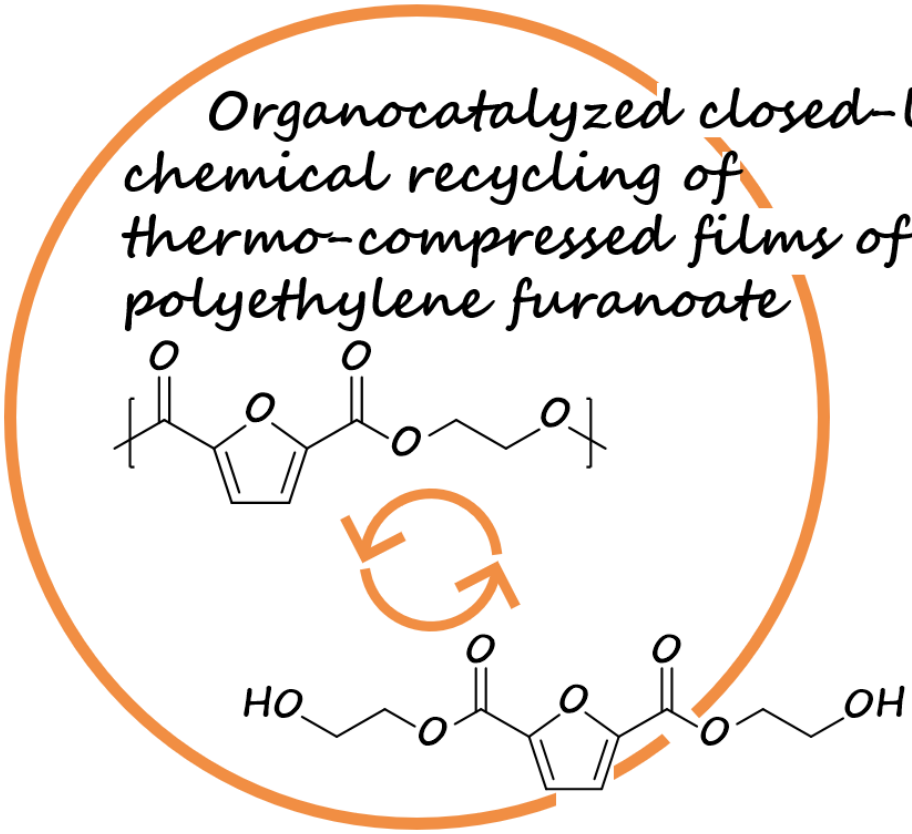
21 S. Kusumoto, S. Ito and K. Nozaki, *Asian J. Org. Chem.*, 2013, **2**, 977–982.

22 E. Oledzka, M. Sobczak, M. Kolakowski, B. Kraska, W. Kamysz and W. Kolodziejski, *Macromol. Res.*, 2013, **21**, 161–168.

23 A. Sanchez-Sanchez, I. Rivilla, M. Agirre, A. Basterretxea, A. Etxeberria, A. Veloso, H. Sardon, D. Mecerreyes and F. P. Cossío, *J. Am. Chem. Soc.*, 2017, **139**, 4805–4814.

Chapter 3

Organocatalyzed closed-loop chemical recycling of thermo-compressed films of polyethylene furanoate



Organocatalyzed closed-loop chemical recycling of thermo-compressed films of polyethylene furanoate

3.1. Introduction

There are two main strategic goals in the development of biorefineries: the displacement of petroleum in favor of renewable raw materials and the establishment of a robust biobased industry, the so-called Bioeconomy[1]. Based on this concept, chemicals from various vegetable feedstocks such as sugars, starch, lignocelluloses, vegetable oils, organic acids or glycerol have been proposed as renewable monomers for polymer production[2]. In particular, the dehydration of abundant 6-carbon sugars (e.g. fructose and galactose) to give furans is a well-known transformation for the preparation of furfurals such as 5-hydroxymethylfurfural (HMF) and 5-methoxy methyl furfural (MMF) with high selectivity (~80 %) and conversion (~90 %) rates[3]. The oxidation of HMF, MMF, and their ethers in the air over different catalysts[4,5] yields furan-2,5-dicarboxylic acid (FDCA). This furanic compound has been identified as a strategic renewable building block to replace petroleum-derived terephthalic acid (TPA) in the production of polyesters[6]. Although the current conversion of furfurals into FDCA only reaches yields of 50–60 %, this process is based on mild process conditions and requires low process energy requirements[7,8].

Petrochemical polyethylene terephthalate (PET) currently has the largest market volume in bottles for water or beverages and it is also widely used in film applications for food trays and lids with a total world production capacity of over 65 million tons of virgin polymer a year[9]. While most PET is derived from petroleum, PET can also be partly bio-sourced at ~30% by using biobased ethylene glycol (bio-EG). However, the TPA

monomer still remains petroleum-derived due to both technical and economic constraints[10,11]. Since the production of FDCA and bio-EG utilizes renewable sugars, polyethylene 2,5-furandicarboxylate, more commonly termed polyethylene furanoate (PEF), currently represents an appealing biomass-derived replacement to petrochemical PET[12]. In this regard, Eerhart et al. showed that replacing PET with PEF would reduce the non-renewable energy use by 40–50 % and the greenhouse gas (GHG) emissions by 45–55 % for the cradle-to-grave system. Therefore, large-scale production of bio-sourced PEF will significantly reduce both greenhouse gas emissions and non-renewable energy usage compared to petroleum-sourced PET[13].

Despite the fact that FDCA is one of the most stable known monocyclic furan derivatives, its thermal stability is somewhat lower than that of TPA and, hence, it has recently been shown that polymerization conditions must be optimized to obtain high molecular weights (MWs)[14,15]. Melt polycondensation using FDCA and EG yielded M_W values in the range of 10000–47000 g·mol^{-1} and dispersity (Đ) of 1.3–2.4. High-M_W PEF has also been obtained by ring-opening polymerization (ROP) using stannous octoate as a catalyst[16,17]. Using ROP, the final M_W and Đ were 50000 g·mol^{-1} and 1.4, respectively. In another study, Knoop et al.[18] produced high-M_W PEF through a two-step process consisting of melt polymerization followed by solid-state polymerization (SSP). This combination of melt polycondensation with SSP has been identified as the best procedure for obtaining high molecular weights[19–21].

While several studies have dealt with the optimization of the polymerization conditions to obtain high-M_W PEF materials, so far little attention has been paid to the end-of-life assessment of this biopolyester. As in the case of PET, due to the lack of degradation in ambient conditions, mechanical recycling may be the easiest and the cheapest method

of recycling PEF. However, as in PET, the number of reprocessing cycles is limited and after recycling, the physical properties of the material are diminished[22,23].

One solution to close the loop of PEF without downcycling the properties is through chemical recycling. This process breaks down plastic waste into raw materials for the production of new high-quality plastics[24]. For instance, it has been shown that PEF-based macrocycles can be recovered when taking advantage of the cyclodepolymerization of PEF under highly diluted conditions. These macrocycles can subsequently be repolymerized into virgin-like materials[17]. While this process can be carried out on a laboratory scale, its implementation on large scales still needs further development, as much more diluted conditions are required to obtain high yields.

Apart from cyclodepolymerization, like other polyesters, PEF can be depolymerized by solvolysis. For example, Sipos et al.[15] briefly investigated the methanolysis of PEF in the presence of sodium methoxide/methanol solution at 90 °C, but only moderate yields were obtained (∼60 %). We envision that using the solvolysis processes, the glycolysis of PEF leading to bis(2-hydroxyethyl)-furan-2,5-dicarboxylate (BHEF) has great potential to close the loop. This process has already been successfully implemented for PET (Figure 3.1 a)[25].

In this chapter, the preparation and characterization of PEF films and their subsequent chemical recycling to develop a Circular Economy model are reported (Figure 3.1 b). To this end, commercial PEF pellets were shaped into films by thermo-compression and characterized in terms of their mechanical, thermal, and barrier properties to evaluate their potential application in food and beverage packaging. Thereafter, depolymerization of the PEF film waste was carried out by glycolysis using bio-EG and a thermally stable organic catalyst system, yielding the BHEF monomer that was repolymerized into PEF by polycondensation.

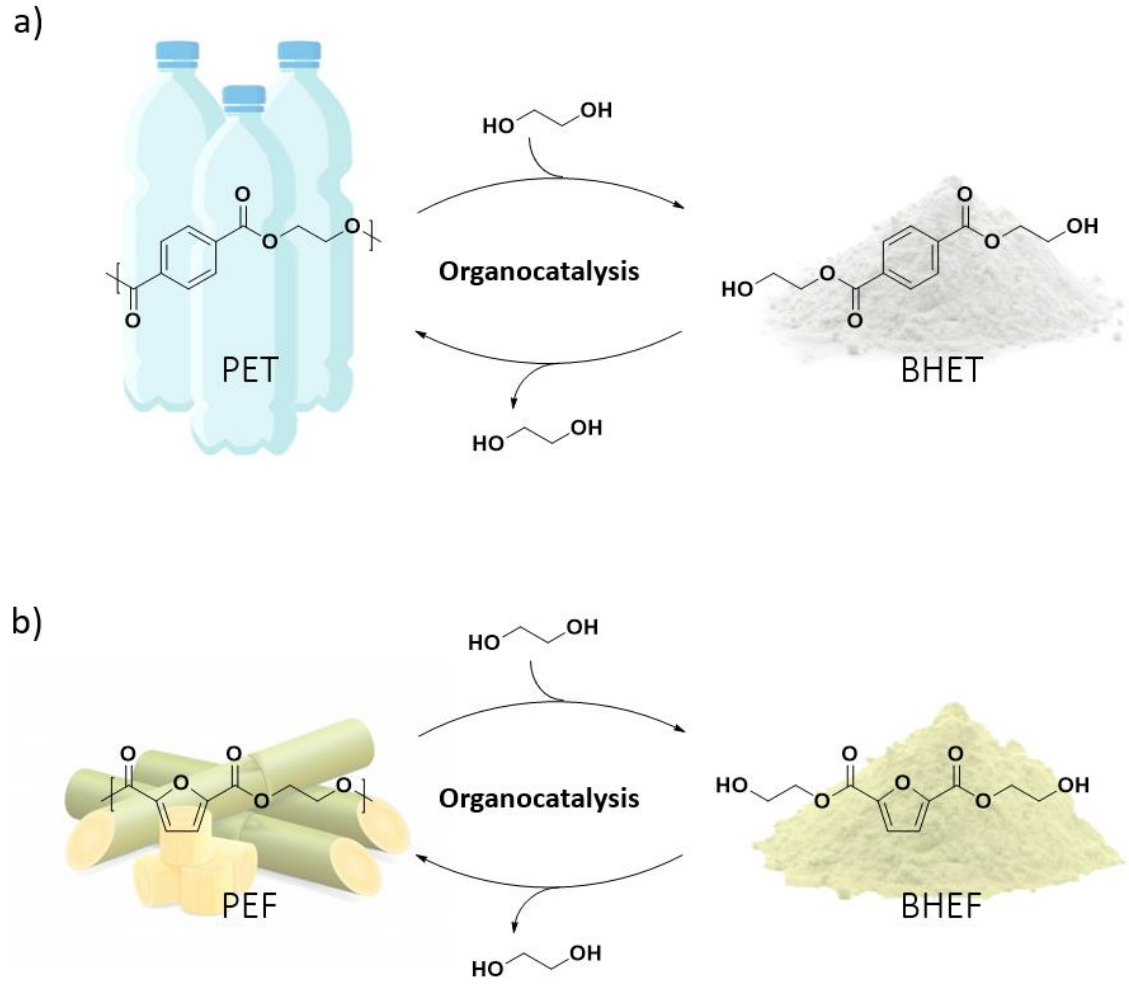


Figure 3.1. Scheme of the depolymerization by glycolysis and repolymerization using organocatalysts of a) polyethylene terephthalate (PET), and b) polyethylene furanoate (PEF) to yield bis(2-hydroxyethyl) terephthalate (BHET) and bis(2-hydroxyethyl)-furan-2,5-dicarboxylate (BHEF), respectively.

3.2. Results and discussion

3.2.1. Characterization of PEF

Prior to exploring the chemical recycling of the PEF film, further knowledge about its structure-property relationship was analyzed since it can be of prime interest in the framework of the optimization of its end-use properties in food packaging applications. To do so, the thermal, mechanical, and barrier properties of the thermo-compressed

PEF films were determined and compared with those of commercial PET films and also other biopolyesters. Thermo-compression was selected since this melt processing methodology is habitually performed with small samples but it can also be easily scaled up and the results of the films can be compared and transferred to manufacturing processes such as compression molding or injection molding used for high production volumes.

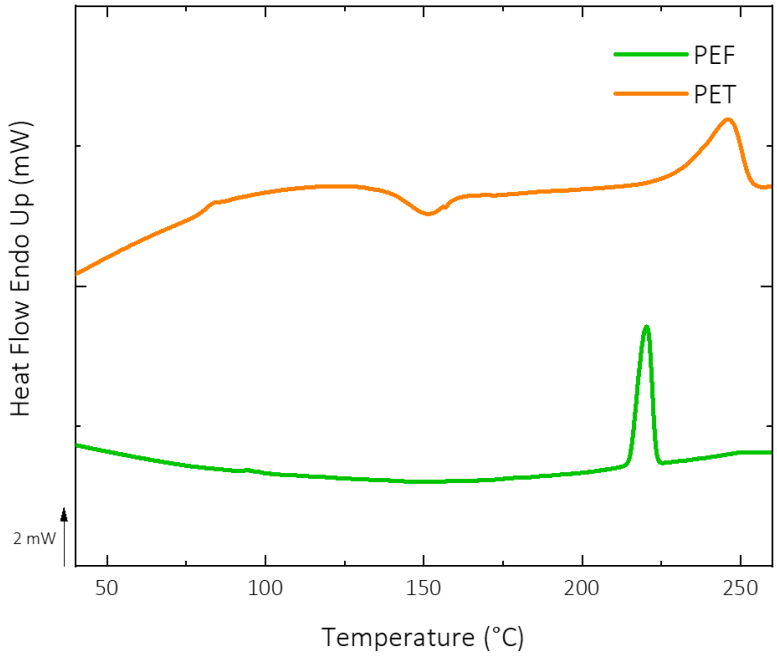


Figure 3.2. Differential scanning calorimetry (DSC) curves taken during the first heating of polyethylene terephthalate (PET) and polyethylene furanoate (PEF).

First, the thermal properties of the thermo-compressed commercial PEF film were analyzed and compared to the ones of PET (Table 3.1 and Figure 3.2). It can be observed that the amorphous region of PEF showed a T_g of 84 °C, which is similar to the ones reported by other authors[12,26] and slightly higher than that of the PET used here (59 °C) and of other studies (76–83 °C).[27] Cold crystallization was not observed at higher temperatures and a sharp endothermic peak was attained at 220.5 °C, corresponding to the melting of the PEF crystals. Therefore, the T_m value of PEF is lower than that of

PET by nearly 25 °C or even more depending on its crystallinity (~250–270 °C)[28]. Indeed, compared to PET, PEF usually shows a lower degree of crystallinity and also lower rates of crystallization arising from the difference in geometry between FDCA and TPA[29]. However, herein PEF showed higher crystallinity than PET, 32.1 % and 12.9 %, respectively, which can be related to the long crystallization time carried out during film formation by thermo-compression as well as the relatively low M_W of the biopolyester. In any case, the lower T_m can allow some energy savings in the processing step as lower temperatures will be required. It is worth noting that melting was observed in a single peak, which differs from that reported by both Knoop et al.[18] and Berkel et al.[30]. The absence of cold crystallization and the presence of a single melting peak both suggest that PEF developed a more perfect single crystal with a similar lamellae thickness during cooling after thermo-compression.

Table 3.1. Thermal properties of the thermo-compressed polyethylene furanoate (PEF) and polyethylene terephthalate (PET) films in terms of glass transition temperature (T_g), melting temperature (T_m), melting enthalpy (ΔH_m), and degree of crystallinity (X_c), onset temperature of degradation measured at a mass loss of 5% ($T_{5\%}$), degradation temperature (T_{deg}), mass loss at T_{deg}, and residual mass at 700 °C.

	DSC				TGA			
	T_g (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)	$T_{5\%}$ (°C)	T_{deg} (°C)	Mass loss (%)	Residual mass (%)
PEF	84.3 ± 0.2	220.5 ± 2.7	44.0 ± 1.2	32.1 ± 0.8	324.9 ± 2.3	396.7 ± 3.4	56.7 ± 2.2	10.6 ± 0.2
PET	69.0 ± 1.1	245.0 ± 2.3	18.0 ± 0.8	12.9 ± 1.4	405.4 ± 1.9	446.8 ± 4.0	58.3 ± 0.7	1.3 ± 0.1

Thermogravimetric tests were performed on the PEF commercial sample by heating at 10 °C/min under a nitrogen atmosphere and also compared to commercial PET film (Figure 3.3). In the evolution of mass as a function of temperature, it can be observed that PEF degradation occurred in a single step weight-loss process and that the thermal

degradation profile of PEF was also similar to that observed for bio-PET, being above 300 °C, though the thermal stability was slightly lower[31,32].

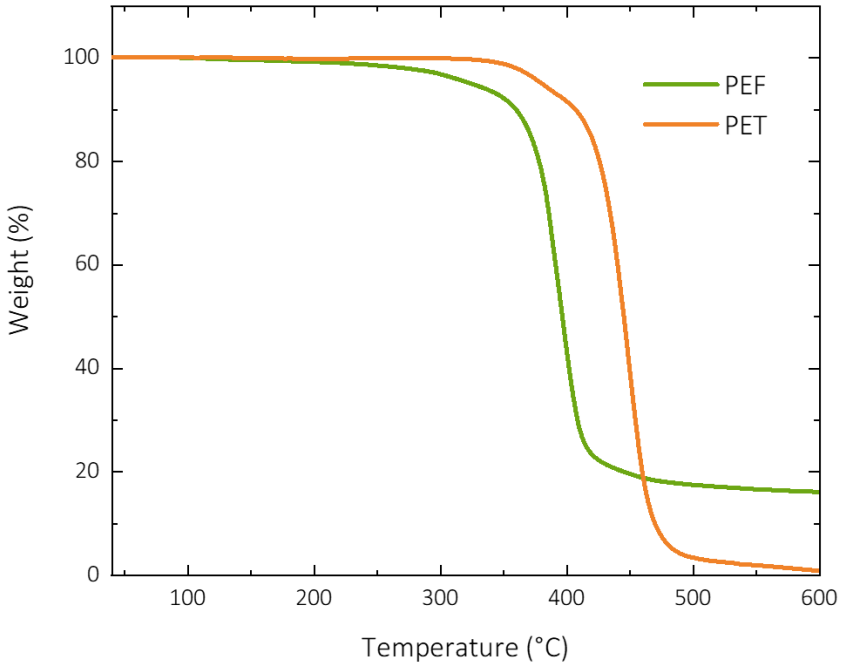


Figure 3.3. Thermogravimetric analysis (TGA) of polyethylene terephthalate (PET) and polyethylene furanoate (PEF).

The mechanical properties of the PEF and PET films and some other biopolyesters have been compared (Figure 3.4). The averaged values of Young's modulus (E) and tensile strength at yield (σ_y) were 3364.0 ± 95.0 MPa and 83.3 ± 4.5 MPa, respectively, while the elongation at yield (ε_y) and break (ε_b) were 3.8 ± 0.8 % and 4.1 ± 0.6 %, respectively. For the industrial benchmark PET films, lower values of E and maximum tensile strength (σ_{max}) have been reported, in the range of 1000-1100 MPa and 50-600 MPa, respectively[33]. However, in contrast to PEF, PET films displayed higher ε_b values of approximately 50 % and 90 % for amorphous and semi-crystalline PET, respectively[33]. Therefore, the PEF film displayed brittle behavior, which is further supported by the lack of a yield point in its tensile stress vs. strain curve (Appendix 3.1).

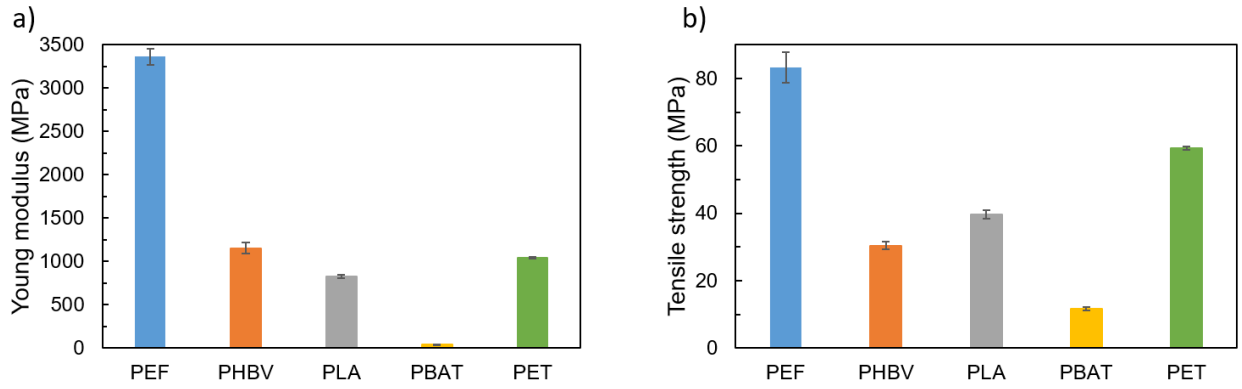


Figure 3.4. a) Young's modulus and b) tensile strength at yield of polyethylene furanoate (PEF), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polylactide (PLA), poly(butylene adipate-co-terephthalate) (PBAT), and polyethylene terephthalate (PET).

In comparison with other partially or fully biobased polyesters, such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polylactide (PLA), and poly(butylene adipate-co-terephthalate) (PBAT), the PEF films tested herein are also considerably more elastic and mechanically stronger[34]. Their ductility is in the same range as that of PLA and PHBV, though significantly lower than that of PBAT, which is mostly used in flexible film applications.

The low ductility of the PEF films used here can be related to the relatively low M_W of the currently available PEF. Most grades are still under development at the industrial scale or in a pre-market trading stage, and thus PEF biopolymers with higher viscosities and hence lower crystallinity and higher toughness should be expected in a near future. However, it is also noteworthy that the mechanical properties of the thermo-compressed PEF film showed higher mechanical properties than those of injection-molded pieces prepared by Zhou and coworkers[35]. The slightly higher mechanical properties of the thermo-compressed film concerning some of the previously developed PEF articles may be related to the PEF grade but also to improved crystallinity during their manufacturing.

In summary, whereas the low ductility of PEF can be limiting for flexible film applications, it can be still useful for rigid articles and high strength fiber applications. It can be particularly interesting for applications where a higher mechanical resistance is needed. Furthermore, the higher elasticity in combination with the higher T_g would allow for an improvement of the thermomechanical stability of the PEF films in comparison to those of PET, such as heat deflection temperature (TDT) or Vicat softening point (VST).

Besides optimal thermal and mechanical properties, the key parameter for implementing a material in food packaging applications is its response to different permeants such as vapors and gases. Permeabilities of the thermo-compressed PEF film as well as that of PET and some other biopolyesters to water and limonene vapors and oxygen gas were measured (Figure 3.5). PEF showed a water vapor permeability (WVP) value of 1.20 x 10^{-15} kg·m·m^{-2}·Pa^{-1}·s^{-1}, which is approximately 2.5 times lower than the WVP of PET (3.01 x 10^{-15} kg·m·m^{-2}·Pa^{-1}·s^{-1}). The WVP reduction for PEF in comparison to PET falls in the range that of reported by Avantium[36] and Burguess et al.[37]. The aforementioned permeability reduction can be attributed to fundamental differences in segmental mobility that originate from the rigid furan moiety in PEF compared to the mobile phenyl moiety in PET[12]. In comparison with other commercial biopolyesters, the water vapor barrier properties of PEF showed a slight improvement over PHBV (1.82 x 10^{-15} kg·m·m^{-2}·Pa^{-1}·s^{-1}) and were significantly superior to PLA (12.31 x 10^{-15} kg·m·m^{-2}·Pa^{-1}·s^{-1}) and PBAT (33.13 x 10^{-15} kg·m·m^{-2}·Pa^{-1}·s^{-1})[34]. Furthermore, its WVP is equivalent to that of low-density polyethylene (LDPE) (1.20 x 10^{-15} kg·m·m^{-2}·Pa^{-1}·s^{-1}) and close to that of polypropylene (PP) (0.73 x 10^{-15} kg·m·m^{-2}·Pa^{-1}·s^{-1}), some of the standard water barrier polymers used in food packaging applications[38].

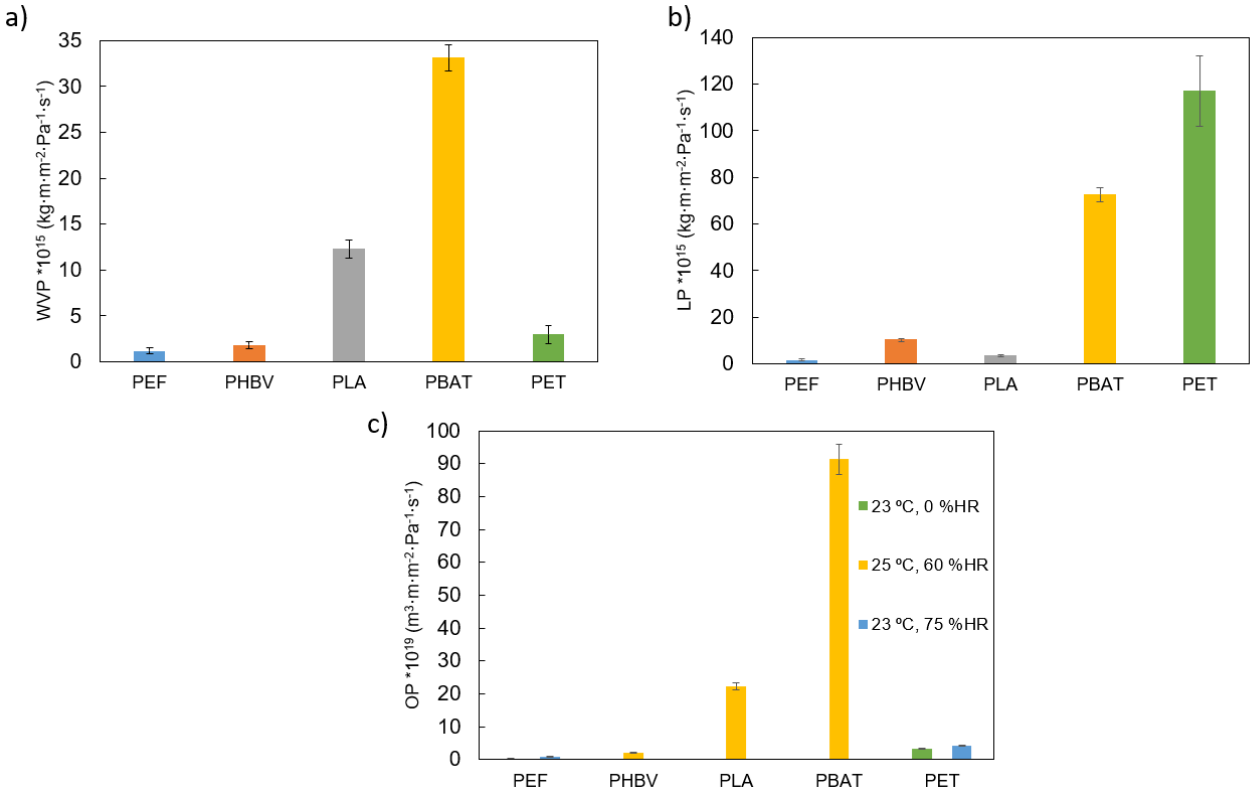


Figure 3.5. Permeability of a) water, b) limonene vapour, and c) oxygen gas at for polyethylene furanoate (PEF), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polylactide (PLA), poly(butylene adipate-co-terephthalate) (PBAT), and polyethylene terephthalate (PET).

Whereas both water vapor and oxygen barrier properties are important to avoid physical and chemical deterioration, limonene transport properties are usually used as a standard system to test aroma barriers in food packaging. It can be observed that the LP of the PEF film was 1.7 x 10^{-15} kg·m·m^{-2}·Pa^{-1}·s^{-1}, which nearly represents a 70-fold reduction in aroma permeability in comparison to PET (1.17 x 10^{-13} kg·m·m^{-2}·Pa^{-1}·s^{-1}). This result can be attributed to the fact that the PET film is known to be strongly plasticized by limonene and, thus, loses its dimensional stability[39]. The high barrier of PEF against aroma certainly opens up new uses for food preservation for this biopolymer since it outperforms the barrier properties of current commercial biopolyesters such as PLA (3.30 x 10^{-15} kg·m·m^{-2}·Pa^{-1}·s^{-1}), PHBV (10.30 x 10^{-15} kg·m·m^{-2}·Pa^{-1}·s^{-1}), and PBAT (72.58 x 10^{-15} kg·m·m^{-2}·Pa^{-1}·s^{-1})[34].

One can also observe that PEF exhibited significantly improved oxygen barrier properties as compared to PET. In particular, the oxygen permeability (OP) values of the PEF film were 3.00 x 10^{-20} $m^3 \cdot m \cdot m^{-2} \cdot Pa^{-1} \cdot s^{-1}$ at 0 % rate of humidity (RH) and 9.20 x 10^{-20} $m^3 \cdot m \cdot m^{-2} \cdot Pa^{-1} \cdot s^{-1}$ at 75 % RH. These conditions were chosen to describe more accurately the dry and humid conditions found in film packaging applications. Compared to PET, the values reported here correspond to a permeability reduction of 10.8 times at 0 % RH (3.27 x 10^{-19} $m^3 \cdot m \cdot m^{-2} \cdot Pa^{-1} \cdot s^{-1}$) and 4.6 times at 75 % RH (4.26 x 10^{-19} $m^3 \cdot m \cdot m^{-2} \cdot Pa^{-1} \cdot s^{-1}$) for oxygen in PEF. The reduction attained in OP at low humidity is similar to that of ~11 times reported by Burguess et al.,[12] who explained this improvement primarily by a difference in chain mobility, since both polyesters exhibit similar oxygen solubilities at 35 °C. Furthermore, the higher crystallinity attained in the thermo-compressed PEF films could also contribute to the high gas barrier properties. Finally, the PEF films also outperformed the oxygen barrier properties of films made of PLA, PHBV, and PBAT (2.22, 0.21, and 9.14 x 10^{-18} $m^3 \cdot m \cdot m^{-2} \cdot Pa^{-1} \cdot s^{-1}$, respectively, measured at 60 % RH)[34].

The low permeability values for water, aroma, and, more notably, oxygen further confirm the notion that PEF can potentially serve as a viable alternative to PET in the beverage market. Nevertheless, the significant oxygen barrier improvements for PEF compared to PET greatly expand the opportunities for introduction of PEF into markets beyond that of beverage applications such as barrier food packaging, particularly in low moisture conditions. Furthermore, the overall high barrier performance in terms of water and limonene vapors and oxygen gas makes PEF a great candidate for mono-material packaging. This notion is complemented by PEF exhibiting improved mechanical strength, but lower ductility and thermal properties compared to PET.

As shown above, PEF offers excellent properties for food packaging applications and the production of this biopolyester represents an effective biomass-derived replacement

for the petrochemical PET. However, sustainable end-of-life options should be sought for PEF for it to become a viable alternative to PET since both polyesters are neither biodegradable nor compostable. Considering the current low production of PEF, chemical recycling is foreseen to be the best sustainable solution.

3.2.2. Chemical recycling of PEF

In this regard, the chemical glycolysis of PEF using bio-EG in combination with different catalysts was performed at 180 °C. The catalysts that were explored consisted of DBU, TBD, BA, and the protic ionic salt DBU:BA. The expected product of the reaction is BHEF, which is similar to the bis(2-hydroxyethyl) terephthalate (BHET) monomer obtained from the depolymerization of PET (Figure 3.6)[25].

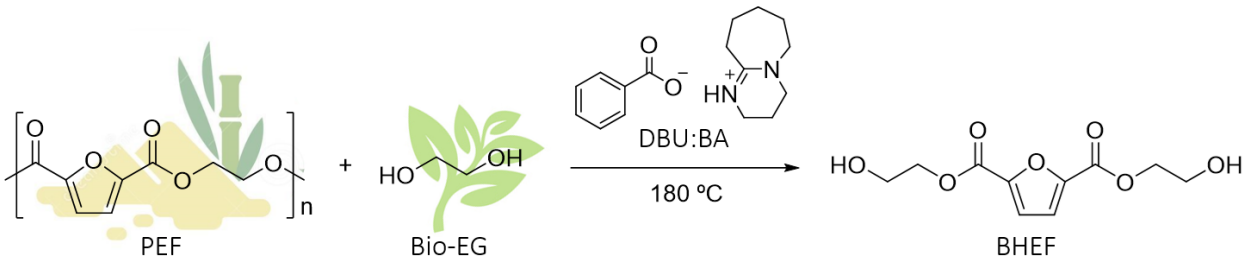


Figure 3.6. Depolymerization reaction of commercial polyethylene furanoate (PEF) with biobased ethylene glycol (bio-EG) and catalyzed by 1,8-diazabicyclo[5.4.0]undec-7-ene:benzoic acid (DBU:BA) to yield the bis(2-hydroxyethyl)-furan-2,5-dicarboxylate (BHEF) monomer.

Results showed that the acid, that is, BA, was not able to depolymerize PEF into the BHEF monomer. Both basic catalysts, DBU and TBD, gave the desired product with yields of 55 % and 72 %, respectively, whereas DBU:BA resulted in a 92 % of yield (Figure 3.7a). The catalyst DBU:BA is an acid-base mixture that combines the excellent catalytic ability of organic compounds with the thermal stability of metal-based catalysts, resisting degradation up to >250 °C, and it has shown to be efficient to depolymerize PET[40,42]. As the catalyst is soluble in water, it could be easily removed and recovered in the purification step and, thus, it could be reused. The reaction was completed in nearly 2.5

h, slightly slower than for PET,[25] when using 5 wt % of organocatalyst at 180 °C (Figure 3.7a).

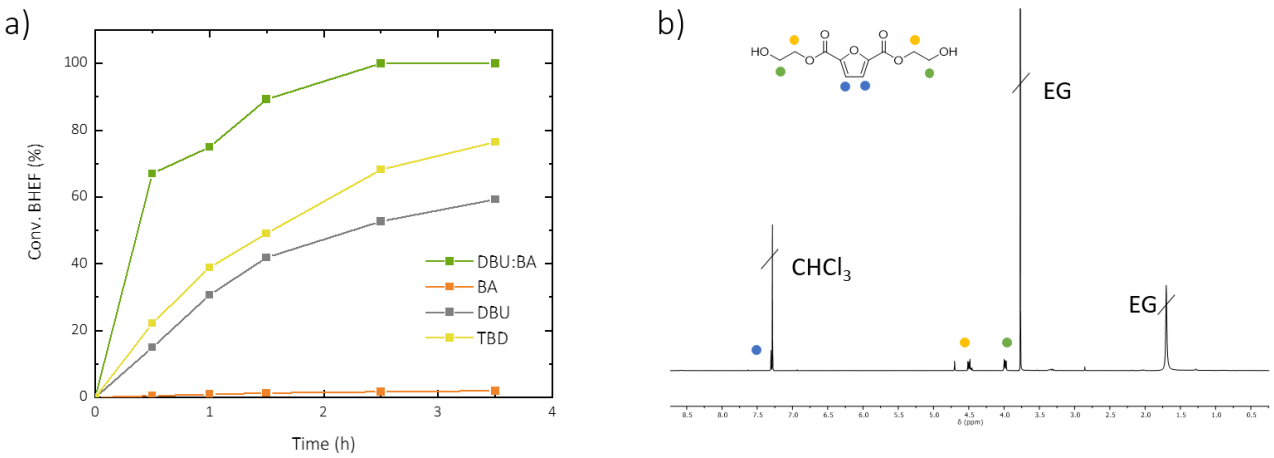


Figure 3.7. a) Depolymerization kinetics of polyethylene furanoate (PEF) into bis(2-hydroxyethyl)-furan-2,5-dicarboxylate (BHEF) using different catalysts, and b) ^{1}H NMR of the obtained BHEF product.

It was observed that at lower temperatures the reaction was considerably slower (Figure 3.8a). With higher organocatalyst contents (7.5 wt %), the reaction was completed slightly faster, but without any significant improvement, while at 2.5 wt % of organocatalyst the reaction was significantly slower (Figure 3.8b). The kinetic data resulted in an activation energy (E_a) of 163 kJ/mol, which justifies the relatively high temperatures required to successfully depolymerize PEF.

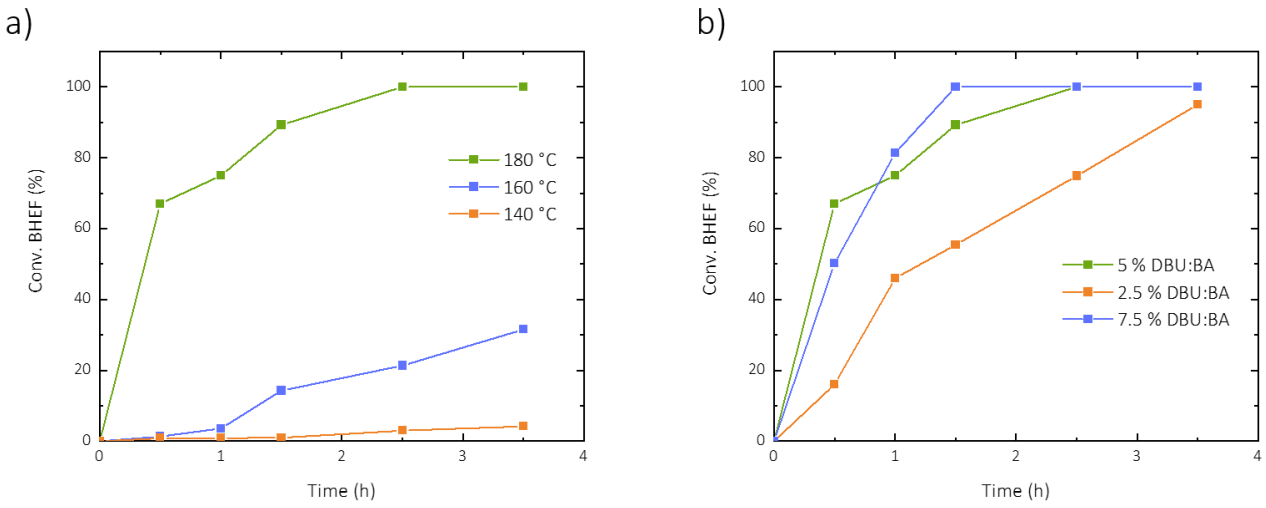


Figure 3.8. a) Influence of the temperature on the conversion speed, and b) influence of the amount of 1,8-diazabicyclo[5.4.0]undec-7-ene:benzoic acid (DBU:BA) catalyst in the conversion.

The final product resulting from depolymerization was analyzed using ^{1}H NMR and MALDI-TOF spectroscopy. Resonances in the ^{1}H NMR spectrum of the reaction product were at δ = 4.0, 4.5, and 7.3 ppm, which are assigned to the ester linkage and confirmed the formation of BHEF (Figure 3.7b). The peaks at 4.0 and 4.5 ppm belong to the EG monomer when attached to the furanoate and the signal at 7.3 ppm to the furanoate ring. The additional low-intensity resonance seen at 4.7 ppm indicates that other products than the desired BHEF were also formed, most likely corresponding to BHEF oligomers. In order to determine the presence of other species different from BHEF, the samples were further analyzed using MALDI-TOF spectroscopy. As found in the MALDI-TOF spectrum, together with the monomer, the BHEF dimer was also observed (Figure 3.9). As the final goal was focused on the repolymerization of the obtained BHEF into PEF, monomer and dimer were not separated.

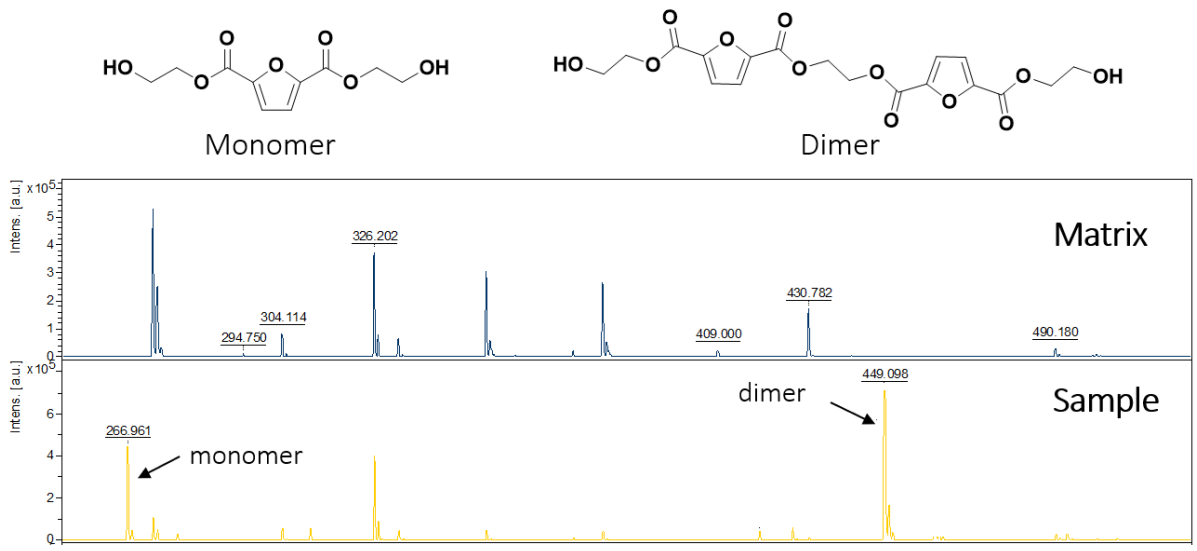


Figure 3.9. MALDI-TOF analysis of the depolymerized product.

After successfully achieving the chemical recycling of the PEF film, the obtained BHEF was investigated as a source to produce PEF by polycondensation. It was envisaged that BHEF would enable the repolymerization of PEF polymer by self-polycondensation reaction (Figure 3.10). As in the case of PET, the BHEF monomer will enable the preparation of low-M_W PEF by melt condensation. In each condensation, a molecule of EG is released and needs to be removed from the reaction media to promote the synthesis of the biopolymer, so that both vacuum and high temperatures are required. The process was performed using the same organocatalyst as for the depolymerization, that is, the DBU:BA mixture, and the temperature was gradually increased from 170 to 220 °C and vacuum from 200 to 3.4 mbar to minimize sublimation of the monomer[43].

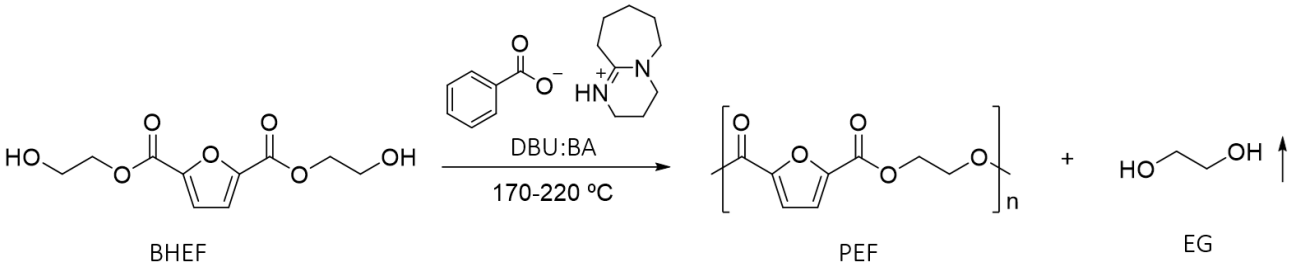


Figure 3.10. Melt polycondensation of polyethylene furanoate (PEF) starting from bis(2-hydroxyethyl)-furan-2,5-dicarboxylate (BHEF).

Melt-polycondensed product from BHEF was characterized by ^{1}H NMR, observing signals at 7.3 and 4.7 ppm that correspond to the furanoate ring and the ethylene glycol unit, respectively, when they are linked by an ester bond (Figure 3.11). After this first step, the attained M_Ws were relatively low (up to 8450 g·mol^{-1}).

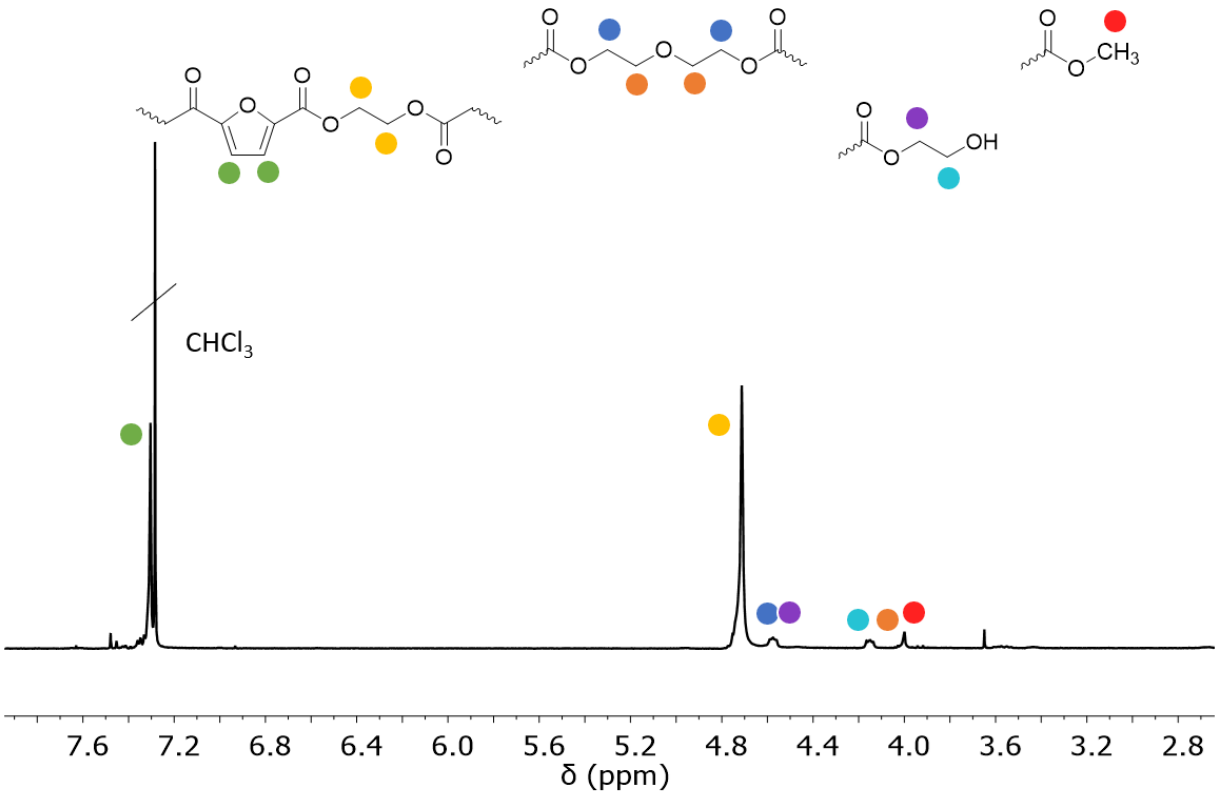


Figure 3.11. Proton nuclear magnetic resonance (^{1}H NMR) spectrum of the reaction product from the melt polycondensation of the depolymerized polyethylene furanoate (PEF).

In order to obtain higher M_Ws, SSP was performed in a second stage using the material obtained from melt polymerization. In this process, the previously synthesized oligomers were treated using four different temperatures, that is, 100, 170, 190, and 200 °C. Polymerization did not occur at 100 °C, and the M_w was the same as the one obtained by melt polymerization (Appendix 3.2).

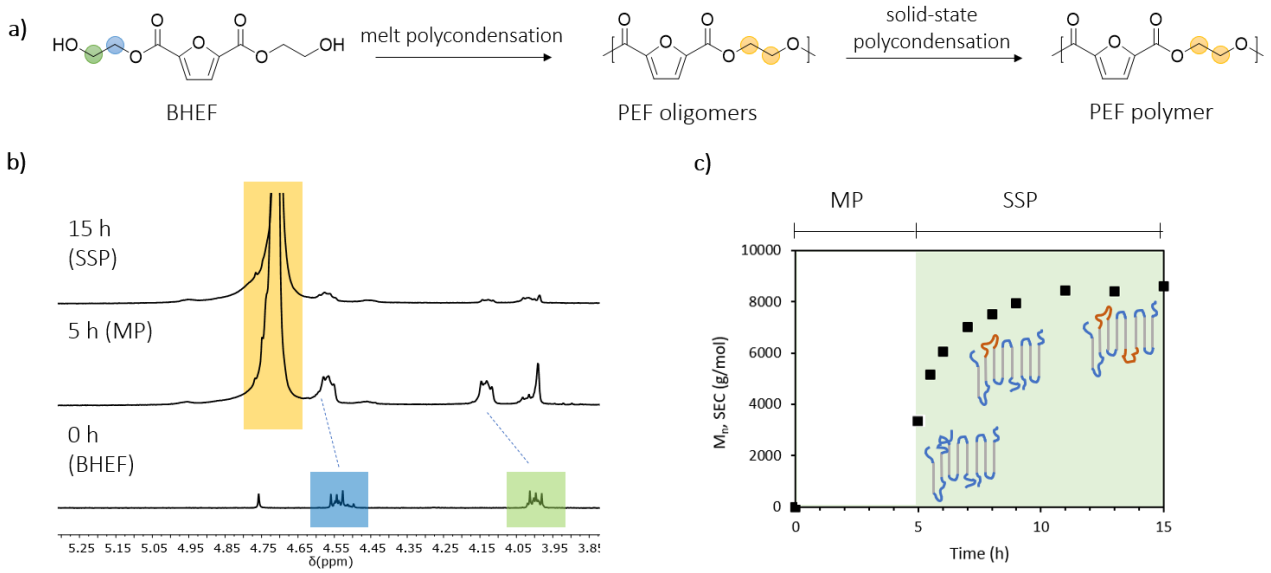


Figure 3.12. a) Synthesis process of polyethylene furanoate (PEF) from bis(2-hydroxyethyl)-furan-2,5-dicarboxylate (BHEF) in two stages: melt polycondensation (MP) and solid-state polycondensation (SSP); b) Proton nuclear magnetic resonance (^{1}H NMR) spectra of the reaction kinetics; c) number average molecular weight (M_n) evolution during the synthesis determined by size-exclusion chromatography (SEC).

The other temperatures led to an increase in M_W, however, the optimum temperature was attained at 200 °C. This temperature is above the T_g and below the T_m of PEF (Appendix 3.3), there it can promote the growth of the chain in the amorphous regions of the oligomers. This post-condensation technique is environmentally benign compared to conventional melt polycondensation, as it is a solvent-free method and no toxic waste is released during the polymerization[21]. The kinetics of the polymerization reaction was followed by ^{1}H NMR and SEC analysis (Figure 3.12). The evolution of M_n, M_w, Đ, and the dimerization of PEF was analyzed overtime during SSP (Appendix 3.4 and 3.5). It was observed that SSP at 200 °C led to higher M_Ws (M_n = 11200 g·mol^{-1}, M_w = 38000, and Đ = 3.4) than at lower temperatures. These parameters are comparable with those of commercial PEF (M_n = 12400 g·mol^{-1}, M_w = 32600 g·mol^{-1}, and Đ = 2.6). During the SSP process, the concentration of the biopolymer chains and the mobility of the

end-group were enhanced. The overall increase of M_W with long times is due to the elimination of by-products formed during SSP, which follows a diffusion-controlled mechanism[19]. One can also notice that Đ remained in the range 2.0–2.6 for the first 8 h of reaction and, thereafter, it significantly increased up to 3.6 and 3.4 after 24 and 48 h, respectively. It is also worth highlighting that the dimerization, which indicates the degree of EG that dimerized (Appendix 3.6), was kept below the 1.8–2.2 % range, being slightly lower than that attained in the commercial PEF sample (2.3 %). This observation can be related to the fact that SSP was implemented under relatively mild conditions and, therefore, fewer side reactions and thermal degradation could occur[18,20,21]. Finally, the depolymerization of the repolymerized PEF was carried out following the procedure that was used for the commercial one, obtaining the same yield, that is, 92 % of BHEF product (Figure 3.13).

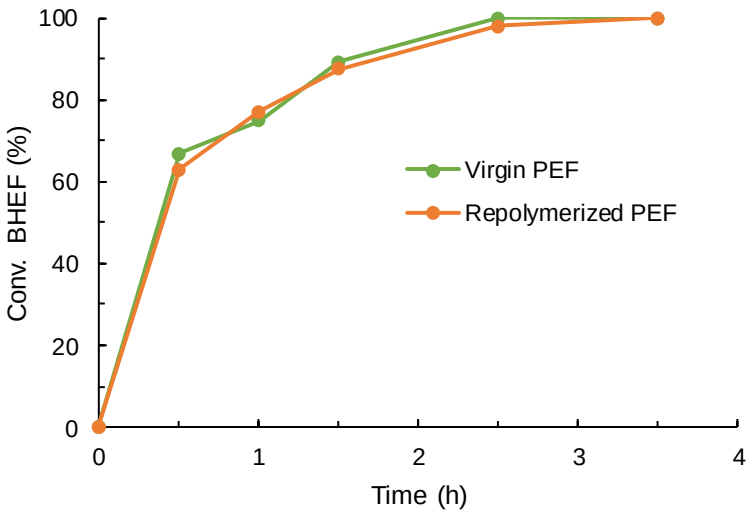


Figure 3.13. Kinetics of the depolymerization reaction of virgin and repolymerized polyethylene furanoate (PEF).

The oligomer and polymer obtained after each step were also compared with the commercial PEF by DSC (Figure 3.14). The oligomers that were synthesized after the melt polymerization (labeled as "PEF 5h") showed lower T_g (~85 °C) and T_m (~210 °C)

values than the commercial polymer due to their reduced M_w and higher monomer content. After SSP ("PEF 15 h"), the transition temperatures increased, resulting in a T_g value of nearly 87 °C and a T_m of 224 °C. These values are in the range of that of commercial PEF, which showed a T_g of 93 °C and a T_m of 213 °C, confirming the successful recycling of PEF from its depolymerization and subsequent repolymerization of BHEF.

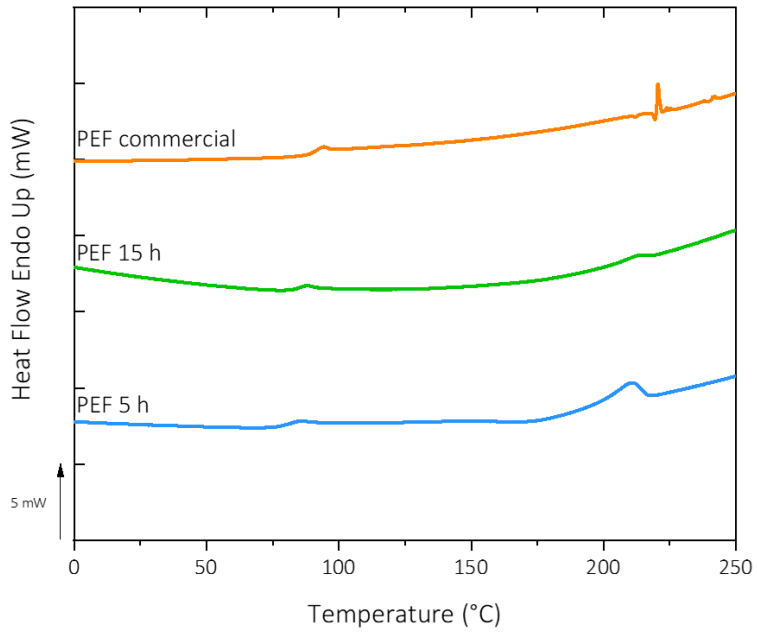


Figure 3.14. Differential scanning calorimetry (DSC) curve taken during the second heating of polyethylene furanoate (PEF) at different times compared with the commercial of polyethylene terephthalate (PET).

3.3. Conclusion

In this chapter, first, the suitability of biobased PEF for food packaging applications using an industrially relevant film-processing method was studied. It was compared with PET, the most used polyester for this application, by DSC and TGA techniques, observing that PEF shows a lower T_m value, which will help the industrial processing step. Afterward, PEF mechanical properties were analyzed together with PET and some other

biodegradable polyesters, such as PHBV and PLA. It was determined that PEF shows low ductility making it an interesting material for high-strength needed applications. When testing the barrier properties, it was seen that it shows excellent properties, better than PET ones. The water permeation is 2.5 times lower than the one of PET, the limonene permeation 70 times, and the oxygen one 10 times in 0 % RH and 4 times in 75 % RH. After determining the properties of PEF, the depolymerization step was carried out. The depolymerization process was done by glycolysis using a biobased glycol, bio-EG, and a thermally stable organocatalyst, DBU:BA. After investigating and monitoring different depolymerization conditions, the depolymerization products were analyzed using ^{1}H NMR and MALDI-TOF, confirming the synthesis of BHEF monomer and dimer. The obtained recycled monomers were finally repolymerized by melt polycondensation followed by solid-state polycondensation to get virgin-like PEF.

Through this work, we were able to move a step forward into the industrial implementation of PEF, offering a sustainable end-of-life option in the Circular Economy frame.

3.4. Experimental section

3.4.1. Materials

PEF was supplied in the form of cylindrical pellets by AVA Biochem BSL AG (Muttenz, Switzerland). According to the manufacturer, its intrinsic viscosity is 0.557 $dl \cdot g^{-1}$, and weight- and number-average-molecular weights (M_w, M_n) are 32600 $g \cdot mol^{-1}$ and 12400 $g \cdot mol^{-1}$, respectively, resulting in a Đ value of 2.6. A commercial PET film, with a thickness of approximately 80 µm, of Belectric OPV GmbH (OPVIUS-Organic Photovoltaic Solutions, Kitzingen, Germany) was used as control material. Bio-EG, purum 99.8 %, was kindly provided by India Glycols Ltd. (Uttar Pradesh, India). Benzoic

acid (BA) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) were purchased from Sigma-Aldrich S.A. (Madrid, Spain) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 98 % of purity, was obtained from TCI (Eschborn, Germany) and distilled prior to use. Methanol, hexafluoro-2-propanol (HFIP), deuterated chloroform ($CDCl_3$), trifluoroacetic acid (TFA), and D-limonene with 98 % purity were all supplied by Sigma-Aldrich S.A. (Madrid, Spain) and used without further purification.

3.4.2. Preparation of PEF films

The as-received PEF pellets were dried under vacuum at 80 °C for 12 h to remove any residual moisture and, thereafter, thermos-compressed into films using a hot-plate hydraulic press (Carver 4122, Wabash, IN, USA). To this end, the samples were first placed in the plates at 240 °C for 1 minute, without pressure, to remove any residual moisture and then hot-pressed at 4-5 bars for 2 min. The samples were removed from the press and cooled to room temperature in ambient conditions. Flat films with a thickness of ~100 µm were obtained and stored in a desiccator at 25 °C and 0 % RH for, at least, 48 h before characterization.

3.4.3. Chemical recycling of PEF films

A similar procedure to that described by Jehanno et. al.[25] for the catalytic degradation of PET was followed. Briefly, 1 g of PEF film was placed with 5 g of bio-EG in the presence of the protic ionic salt of DBU:BA (0.020 g DBU: 0.017 g BA) in a 10 mL schlenk flask. The flask was closed and heated to 180 °C for 2 h under atmospheric pressure and vigorous stirring conditions until complete disappearance of any residual PEF. When the reaction was complete, the crude product was cooled to room temperature and a large excess of distilled water was added. The resulting solution was vortexed and filtered. Thus, the resultant aqueous transparent filtrate was stored at 4 °C in a refrigerator overnight. The

precipitate was centrifuged and separated from the solution and finally dried at 40 °C for 24 h.

3.4.4. Repolymerization of PEF

Polymerization of PEF using the depolymerized product was performed in two steps. The first one consisted of a melt polycondensation step as described by Kasmi et. al.[19,20], where the monomers react with each other by transesterification reactions and EG units are formed and removed from the media. In this step, low-M_w oligomers were formed. The second step was a SSP process in which the oligomers reacted one with the other to increase the final M_w of the polymer. The first polymerization unit consisted of a 100 mL glass batch reactor with 5 necks that was equipped with a gas inlet, a rotor with a stainless-steel blade, and gas outlet with a Vigreaux column heated at 140 °C and connected to a distillation column with an open gas exit and graduated round glass flask. First, 46.7 g of the precipitate obtained from the depolymerization process and 1 g of DBU:BA salt catalyst were charged to the glass reactor. Then, the mixture was purged for 60 min with nitrogen at a flow rate of 200 mL/min at room temperature to remove the oxygen in the reactor headspace prior to the reaction. The temperature was raised to 170 °C, under nitrogen atmosphere, and the reaction media was stirred at 80 rpm for another 60 min in order to melt the reactant. Once the mixture was homogenized, the pressure was gradually reduced from 200 mbar to 3.4 mbar over 1 h by connecting a vacuum pump Vacuubrand RZ 2.5 equipped with a VACUU-SELECT vacuum controller (VAcuubrand GmbH & Co. KG, Wertheim, Germany) to the gas exit and, thereafter, the temperature of the reaction system was slowly raised to 220 °C at 1 °C/min for 1 h under a nitrogen atmosphere to avoid excessive foaming and minimize oligomer sublimation. The reaction was kept at 220 °C for 2 h and stirred at 80 rpm and, finally, cooled to room temperature at room conditions. The viscous mass was removed from the reactor and

milled in an IKA A11 basic analytical mill (IKA – Werke GmbH & Co. KG, Staufen, Germany). The resultant powder was gently washed overnight at room temperature with methanol under vigorous stirring to remove the excess of diol and dried overnight in vacuum oven (Selecta Vaciotem-T, J.P. SELECTA, Barcelona, Spain) at 80 °C.

In the next step, the SSP reaction was carried out in a SSP reactor kindly donated by Prof. Cor Koning (DSM Coating Resins Geleen, The Netherlands). To this end, 500 mg of PEF oligomer powder was introduced into the SSP reactor and it was purged with nitrogen gas heated at 200 °C at a flow rate of 10 mL·min^{-1}. Approximately 50 mg of samples were extracted at different times, from 0.5 h to 48 h, and analyzed by ^{1}H NMR and SEC.

3.5. References

1 J. Wenger and T. Stern, *Biofuels, Bioprod. Biorefining*, 2019, **13**, 1347–1364.

2 G. Lligadas, J. C. Ronda, M. Galià and V. Cádiz, *Mater. Today*, 2013, **16**, 337–343.

3 Y. Román-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, **312**, 1933–1937.

4 P. Verdeguer, N. Merat and A. Gaset, *J. Mol. Catal.*, 1993, **85**, 327–344.

5 W. Partenheimer and V. V. Grushin, *Adv. Synth. Catal.*, 2001, **343**, 102–111.

6 C. Moreau, M. N. Belgacem and A. Gandini, *Top. Catal.*, 2004, **27**, 11–30.

7 J. J. Bozell and G. R. Petersen, *Green Chem.*, 2010, **12**, 539–55.

8 H. Nakajima, P. Dijkstra and K. Loos, *Polymers*, 2017, **9**, 523.

9 S. H. Park and S. H. Kim, *Fash. Text.*, 2014, **1**, 1.

10 M. Shiramizu and F. D. Toste, *Chem. - A Eur. J.*, 2011, **17**, 12452–12457.

11 T. P. Vispute, H. Zhang, A. Sanna, R. Xiao and G. W. Huber, *Science*, 2010, **330**, 1222–1227.

12 S. K. Burgess, J. E. Leisen, B. E. Kraftschik, C. R. Mubarak, R. M. Kriegel and W. J. Koros, *Macromolecules*, 2014, **47**, 1383–1391.

13 A. J. J. E. Eerhart, A. P. C. Faaij and M. K. Patel, *Energy Environ. Sci.*, 2012, **5**, 6407–6422.

14 J. Ma, X. Yu, J. Xu and Y. Pang, *Polymer*, 2012, **53**, 4145–4151.

15 E. De Jong, M. A. Dam, L. Sipos and G. J. M. Gruter, in *ACS Symposium Series*, American Chemical Society, 2012, **1105**, 1–13.

16 J. Carlos Morales-Huerta, A. Martínez De Ilarduya and S. Muñoz-Guerra, *Polymer*, 2016, **87**, 148–158.

17 J. G. Rosenboom, D. K. Hohl, P. Fleckenstein, G. Storti and M. Morbidelli, *Nat. Commun.*, 2018, **9**, 1–7.

18 R. J. I. Knoop, W. Vogelzang, J. van Haveren and D. S. van Es, *J. Polym. Sci. Part A Polym. Chem.*, 2013, **51**, 4191–4199.

19 N. Kasmi, G. Z. Papageorgiou, D. S. Achilias and D. N. Bikiaris, *Polymers*, 2018, **10**, 471.

20 N. Kasmi, M. Majdoub, G. Z. Papageorgiou, D. S. Achilias and D. N. Bikiaris, *Polymers*, 2017, **9**, 607.

21 Y. Chebbi, N. Kasmi, M. Majdoub, G. Papageorgiou, D. Achilias and D. Bikiaris, *Polymers*, 2019, **11**, 438.

22 A. Pawlak, M. Pluta, J. Morawiec, A. Galeski and M. Pracella, *Eur. Polym. J.*, 2000, **36**, 1875–1884.

23 V. Dulio, R. Po, R. Borrelli, A. Guarini and C. Santini, *Angew. Makromol. Chemie*, 1995, **225**, 109–122.

24 E. Gabirondo, A. Sangroniz, A. Etxeberria, S. Torres-Giner and H. Sardon, *Polym. Chem.*, 2020, **11**, 4861-4874.

25 C. Jehanno, I. Flores, A. P. Dove, A. J. Müller, F. Ruipérez and H. Sardon, *Green Chem.*, 2018, **20**, 1205–1212.

26 G. Stoclet, G. Gobius Du Sart, B. Yeniad, S. De Vos and J. M. Lefebvre, *Polymer*, 2015, **72**, 165–176.

27 S. Montava-Jorda, D. Lascano, L. Quiles-Carrillo, N. Montanes, T. Boronat, A. V. Martinez-Sanz, S. Ferrandiz-Bou and S. Torres-Giner, *Polymers*, 2020, **12**, 174.

28 S. Torres-Giner, Y. Echegoyen, R. Teruel-Juanes, J. D. Badia, A. Ribes-Greus and J. M. Lagaron, *Nanomaterials*, 2018, **8(10)**, 745.

29 J. A. Moore and W. W. Bunting, in *Advances in Polymer Synthesis*, Springer US, Boston, 1985, pp. 51–91.

30 J. G. van Berkel, N. Guigo, J. J. Kolstad, L. Sipos, B. Wang, M. A. Dam and N. Sbirrazzuoli, *Macromol. Mater. Eng.*, 2015, **300**, 466–474.

31 G. Z. Papageorgiou, V. Tsanaktsis and D. N. Bikiaris, *Phys. Chem. Chem. Phys.*, 2014, **16**, 7946–7958.

32 P. Ji, D. Lu, S. Zhang, W. Zhang, C. Wang and H. Wang, *Polymers*, 2019, **11**, 2105.

33 S. Thomas and Visakh P. M., *Handbook of engineering and specialty thermoplastics. Volume 3, Polyethers and polyesters*, Scrivener, 2011.

34 L. Quiles-Carrillo, N. Montanes, J. M. Lagaron, R. Balart and S. Torres-Giner, *J.*

Polym. Environ., 2019, **27**, 84–96.

35 M. Jiang, Q. Liu, Q. Zhang, C. Ye and G. Zhou, *J. Polym. Sci. Part A Polym. Chem.*, 2012, **50**, 1026–1036.

36 Avantium enters into the commercialisation phase for PEF, Bioenergy International, https://bioenergyinternational.com/biochemicals-materials/avantium-enters-into-the-commercialisation-phase-for-pef, (accessed May 5, 2022).

37 S. K. Burgess, O. Karvan, J. R. Johnson, R. M. Kriegel and W. J. Koros, *Polymer*, 2014, **55**, 4748–4756.

38 B. Raj and R. S. Matche, in *Multifunctional and Nanoreinforced Polymers for Food Packaging*, Elsevier, Amsterdam, 2011, pp. 669–691.

39 D. Cava, E. Giménez, R. Gavara and J. M. Lagaron, *J. Plast. Film Sheeting*, 2006, **22**, 265–274.

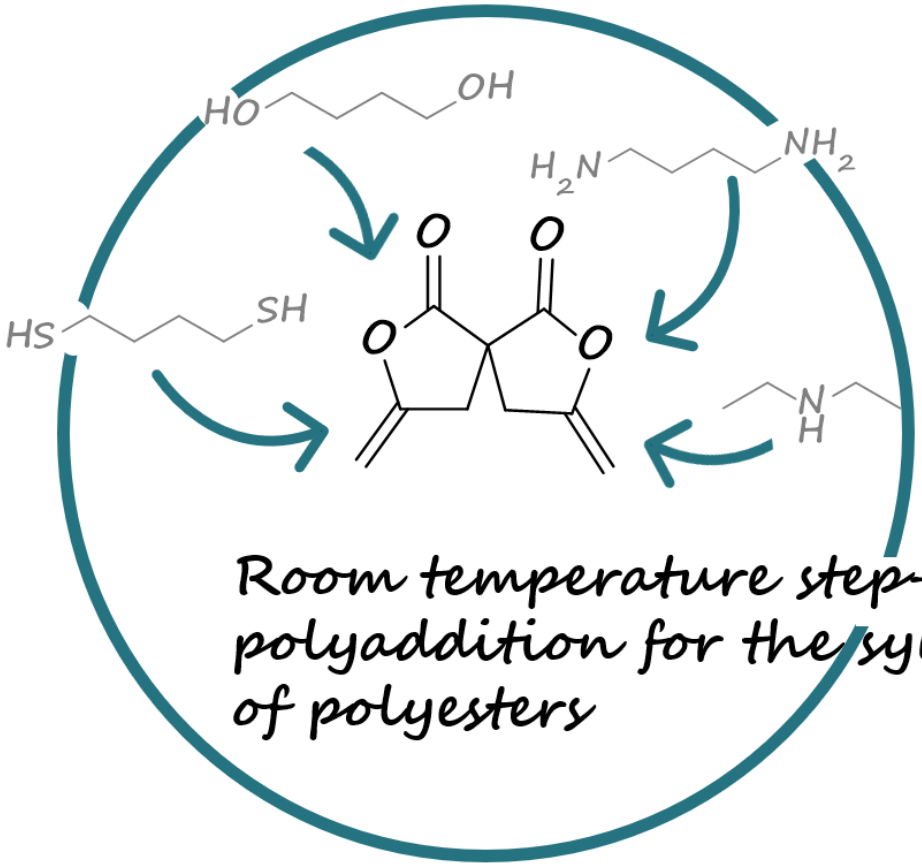
40 I. Flores, J. Demarteau, A. J. Müller, A. Etxeberria, L. Irusta, F. Bergman, C. Koning and H. Sardon, *Eur. Polym. J.*, 2018, **104**, 170–176.

41 D. J. Coady, K. Fukushima, H. W. Horn, J. E. Rice and J. L. Hedrick, *Chem. Commun.*, 2011, **47**, 3105–3107.

Chapter 4

Capítulo sujeto a confidencialidad por la autora

Chapter 5



Room temperature step-growth polyaddition for the synthesis of polyesters

Room temperature step-growth polyaddition for the synthesis of polyesters

5.1. Introduction

Polyesters are highly produced materials due to their interesting properties that make them the polymer of choice for different applications. The consumption of this material is increasing year by year being just 4.14 Mt the production of polyethylene terephthalate (PET) in 2020[1]. However, industrial polyester synthesis requires high-energy consumption, as the polymerization reaction is performed at elevated temperatures.

In the frame of the "Sustainable Development Goals" impulse by the United Nations[2], many different approaches have been done to find sustainable synthesis methods. As it has been discussed in the introduction of this thesis, one of the goals is to try to find monomers from biomass, eliminating the use of petroleum in the polyesters production process[3]. This fossil fuel eradication will on one side, decrease the number of harmful gases released into the atmosphere, but on the other side, the energy consumption would be reduced considerably as harsh conditions would be needed for the monomer obtaining.

Nevertheless, industrially produced polyesters, such as polyethylene terephthalate (PET), polycaprolactone (PCL), and polybutylene terephthalate (PBS), demand high temperatures to carry out polymerization reactions[4–7]. In addition, the necessity to reduce the polymerization temperature is not only a matter of economy and sustainability but also a requirement for some applications, such as coatings or 3D printing.

One of the methods to reduce the polymerization temperature, as explained in the general introduction, is to find powerful catalysts that can catalyze reactions at low temperatures. However, normally these catalysts are composed of rare-earth metals, such as lanthanides, being high-priced, and due to their reduced available amounts, difficult to implant them in a high scale industrial production process[8–10]. Therefore, a different approach must be proposed to come up with a solution to mild condition polyester synthesis.

Some authors proposed the use of organocatalysis to produce polyesters at low temperatures, such as the ROP of L-lactide in just 2 hours of polymerization time using a combination of thiourea and sparteine as catalyst[11]. Continuing with the use of organocatalysis, Bourissou et al. proposed the use of *O*-carboxyanhidrides as monomers for the synthesis of narrow dispersity polyesters using DMAP and some protic initiators to conduct polymerizations at room temperature[12]. *O*-carboxyanhidrides are thermodynamically much more favorable than lactones due to the liberation of CO_2, which works as a driving force for polymerization.

As described before there are some examples of polyester synthesis at room temperature, however, in all the cases the synthesis method employed is the ring-opening polymerization. Up to our knowledge, up to now, there is no method reported for the synthesis of polyester at room temperature by the step-growth polymerization method. The main reason behind this is that industrially available polyesters are produced by polycondensation reaction, which demands high temperatures since the condensate formed, such as water or methanol, must be removed from the reaction mixture in order to increase the molecular weight of the polymer. In consequence, it is difficult to use this method for the synthesis of polyesters at room temperature[13].

While this is true for polyesters, other authors have found that it is possible to obtain step-growth polymers at low temperatures by condensation reactions. For instance, Odelius et al. exploited the ring-opening aminolysis-condensation method to create biobased polyamides at moderate temperatures, 100 °C. They showed that using a diamine and ethylene brassylate together with TBD catalalyst they were able to synthesize by aminolysis-condensation reaction polyamides. Due to the cyclic nature of ethylene brassylate, the ester groups are more reactive than the analog aliphatic diesters and therefore, higher conversions are obtained, reaching up to molecular weights of 6000 $g \cdot mol^{-1}$ without the use of any solvent[14]. For instance, Detrembleur et al. proposed an interesting method for the synthesis of polycarbonates and polyurethanes at room temperature[15]. First, they managed to prepare exovinylene dicyclic carbonates by the use of CO_2 as a reactant. Taking advantage of the higher reactivity of α-alkylidene carbonates due to the presence of an exocyclic olefinic group, they were able to make step-growth polymerization reactions at room temperature, even without a catalyst. Changing the nucleophile they were able to synthesize different polymer families, by the use of a diol, polycarbonates were synthesized and when a diamine was employed, polyurethanes. This method enables the step-growth polymerization of different polymers at room temperature, as polymers are synthesized by polyaddition reaction, meaning that there is no sub-product produced during the polymerization that needs to be removed from the reaction media. In addition, this polymerization method enables the atom economy, as it maximizes the efficiency of the reactants and therefore, minimizes waste production, which is an important fact in the green chemistry goal. We hypothesize that if we can prepare exovinylene dicyclic esters we will manage to prepare polyesters by step-growth in milder conditions than the current ones. The possibility of polymerizing polyesters by step-growth polymerization

would help valorize a large number of available diols, including those that could be obtained from renewable sources, creating more biobased polymers.

In this chapter, following the work described above, polyesters by step-growth polyaddition had been polymerized. First, a model carboxylic monolactone was synthesized to evaluate its reactivity against different nucleophiles. Employing the model monomer, the ring-opening reaction was studied by observing the formation of the ester group at room temperature by the use of DBU as the catalyst. Afterward, in order to prepare polymers, a five-membered spiro-dilactone was synthesized by a three synthetic step pathway. The spiro-dilactone monomer enables the synthesis of interesting polyesters at room temperature, using a diol as a nucleophile. In addition, the synthesis of polyamines and polythioesters was also investigated, modifying the nucleophiles and selecting diamines and dithiols. This work was carried out in collaboration with the group "Ligands Bifunctionnels et Polymères Biodègradables" led by Dr. Bourisssou in the Université III - Paul Sabatier of Toulouse, France.

5.2. Results and discussion

5.2.1. Synthesis of the model monomer

It is known that five-member cyclic compounds have low strain energy, therefore are difficult to ring-open and include in a polymer chain. However, in this chapter, it is thought that having an exocyclic double bond would increase the strain energy of the five-membered cycle, becoming more reactive and therefore enlarging the possibilities of polymerizing it at mild reaction conditions.

First, the synthesis of the model carboxylate-monolactone (C-ML) monomer, methyl-3-methyl-5-methylene-2-oxotetrahydrofuran-3-carboxylate was carried out in three steps (Figure 5.1). The first step of the C-ML preparation was done adapting a reported

procedure[16], where dimethyl propargylmalonate was used as the starting compound. Sodium hydride was used as a Brønsted base to enable the C-alkylation between the starting material and methyl iodide, obtaining dimethyl methyl propargylmalonate (**1**) compound in 85 % yield. In a second step, the hydrolysis of one of the two ester groups was done using NaOH[17] to acquire the acid (**2**) in a 90 % yield. Finally, the cyclization reaction was accomplished by the use of 0.5 mol % of a palladium complex catalyst[18] in dichloromethane to synthesize in 99 % yield the five-member carboxylate monolactone monomer. The catalyst employed is a palladium complex bearing a non-innocent pincer ligand acting according to a metal-ligand cooperative mode of action that enables the cycloisomerization of alkynoic acids. The final monomer was characterized by ^{1}H NMR in chloroform (Appendix 5.1).

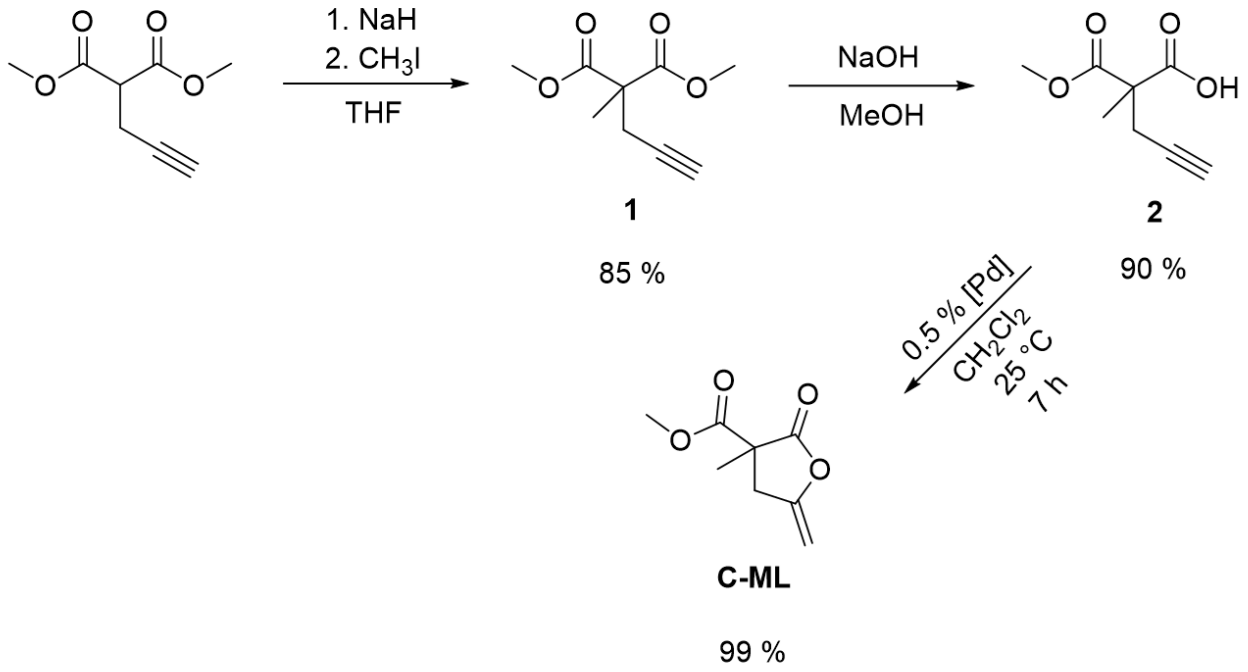


Figure 5.1. Synthesis of carboxylate-monolactone (C-ML) monomer.

5.2.2. Ring-opening study of C-ML model monomer for the synthesis of esters

Once the C-ML model monomer was synthesized ring-opening reaction of the lactone was carried out in order to study the reaction. The ring-opening was done using 1-butanol as the nucleophile, at room temperature using chloroform as solvent (Figure 5.2).

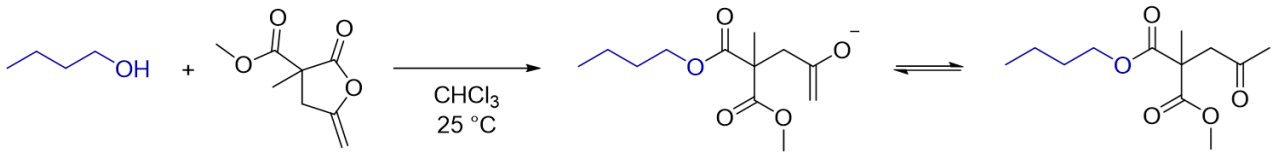


Figure 5.2. Scheme of the ring-opening reaction of C-ML monomer by 1-butanol.

It was observed that after 6 hours of reaction there was no conversion in ^{1}H NMR, so it could be concluded that alcohol nucleophile is not able to ring-open the C-ML model monomer in the reaction conditions that have been tested.

In order to improve the nucleophilicity of the alcohol and make it possible for the ring-opening of the lactone a catalyst was added to the reaction mixture. Five different catalysts were investigated, DBU, TBD, DMAP, DABCO (1,4-diazabicyclo[2.2.2]octane), and MSA in 1.25 mol % concerning the lactone (Figure 5.3).

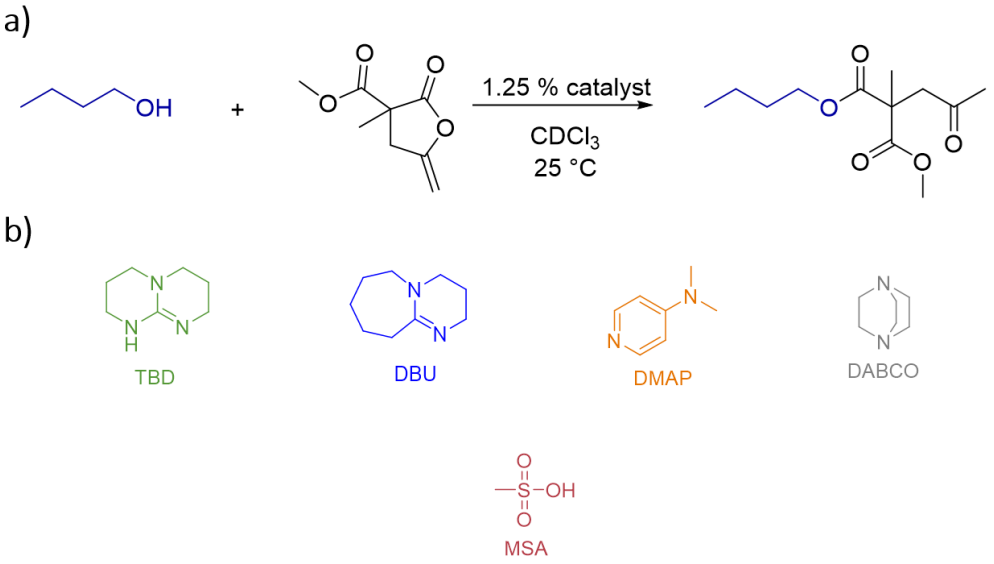


Figure 5.3. a) Ring-opening reaction of the model monolactone by the use of 1-butanol as the nucleophile and b) the different catalysts employed for the reaction.

The ring-opening reaction of the monolactone was carried out in the same conditions described before and the reaction kinetics were followed by ^{1}H NMR (Figure 5.4b). It was observed that when MSA acid is used there is no ring-opening reaction; this could be due to the fact that the work of the acid is to activate the lactone and therefore the nucleophilicity of the alcohol is not increased, making no able to attack the lactone. In the case of the use of a weak base, DMAP and DABCO, the ring-opening reaction does not occur either; this could be due to the weakness of the catalyst that is not strong enough to deprotonate the alcohol and therefore make it more nucleophilic.

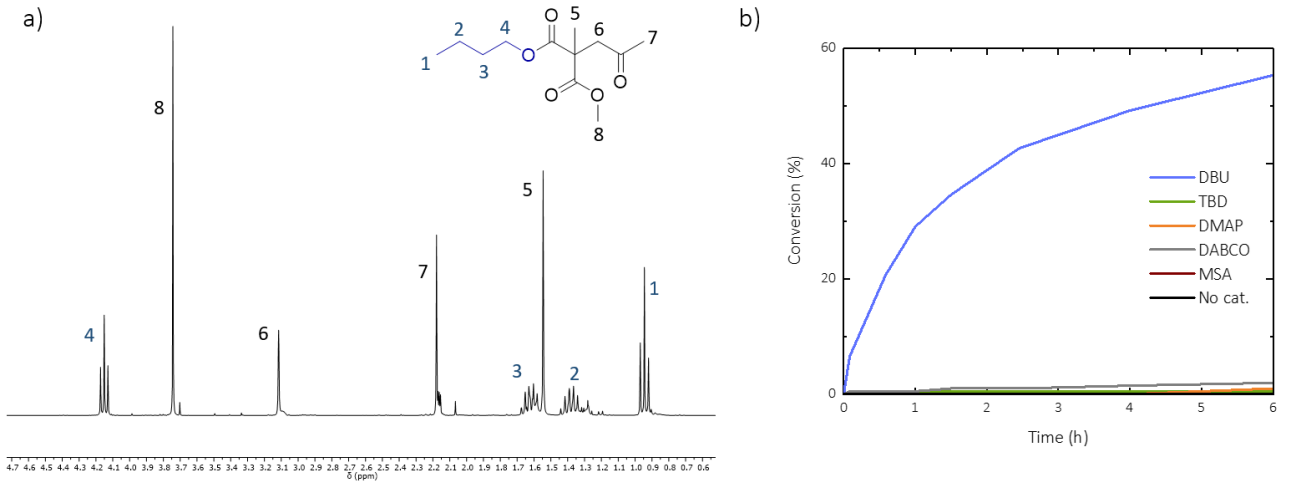


Figure 5.4. a) ^{1}H NMR of the ring-opening product of C-ML initiated by 1-butanol and b) ring-opening reaction kinetics catalyzed by different catalysts.

DBU and TBD catalysts instead are strong bases and they are able to remove the proton of the alcohol and make it a better nucleophile that might be able to ring-open the C-ML monomer. It was determined that when DBU was used in 1.25 mol % the model monomer was opened in around 55 % in 6 hours(Figure 5.4b blue line), giving an ester (Figure 5.4a). TBD is a dual base catalyst and in principle, it should work better, however, it was observed by ^{1}H NMR that there was no conversion over time (Figure 5.4b green line). The reason for the lack of ring-opening reaction could be that TBD acts as a nucleophile for the opening of the lactone and therefore it gets deactivated (Figure 5.5 b).

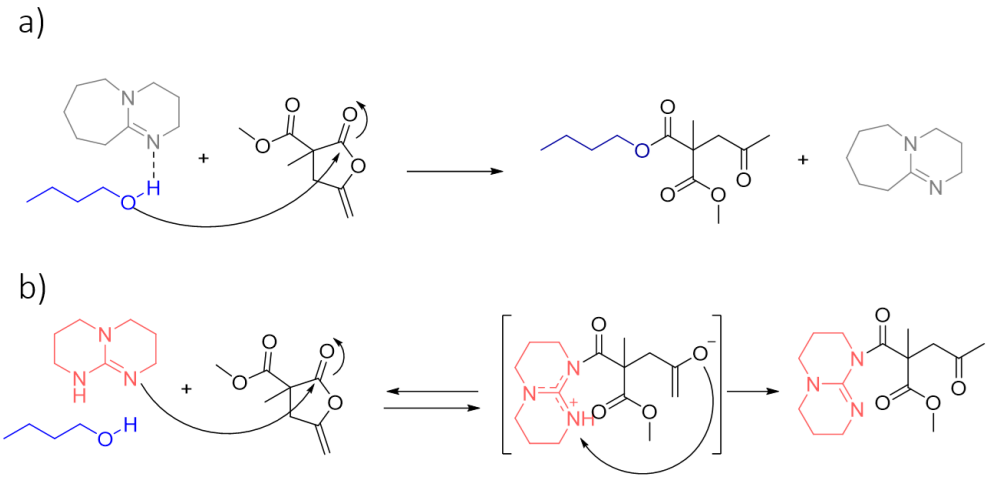


Figure 5.5. Ring-opening reaction of C-ML initiated by 1-butanol and catalyzed by a) DBU and b) TBD.

It has been concluded by ^{1}H NMR kinetics (Figure 5.4b), that DBU acts as a catalyst, deprotonating the alcohol group and therefore making it a better nucleophile for the ring-opening reaction of the lactone (Figure 5.5a). In the case of TBD, it was observed in the reaction kinetics, that there was no conversion after 6 hours (Figure 5.4b). That might be due to the structure of the catalyst, which has a sp^2 amine that could work as a nucleophile. Amines are better nucleophiles than alcohols, so in the presence of 1-butanol, TBD could compete with the reaction and open the lactone. Therefore, the TBD is attached to the lactone and is deactivated, not catalyzing the reaction between the alcohol and the lactone (Figure 5.5b). In that case, the ring-opening reaction of C-ML will never be catalyzed by TBD catalyst, being DBU the best catalyst to carry out the ring-opening reaction.

5.2.3. Synthesis of the spiro-dilactone

The synthesis of the spiro-dilactone (S-DL) monomer, 3,8-dimethylene-2,7-dioxaspiro[4.4]nonane-1,6-dione was followed in a similar way as the synthesis of C-ML (Figure 5.6). In the first step instead of adding methyl iodide, propargyl bromide was added to the reaction mixture, synthesizing dimethyl dipropargylmalonate (**3**)

compound in 80 % yield. Afterward, the hydrolysis of one malote was carried out using KOH and the acid groups were created (**4**), to enable the cyclization reaction of the lactone. The S-DL monomer was synthesized in 99 % yield by the use of 5 % of palladium complex in dichloromethane and confirmed its formation by ^{1}H NMR (Appendix 5.2).

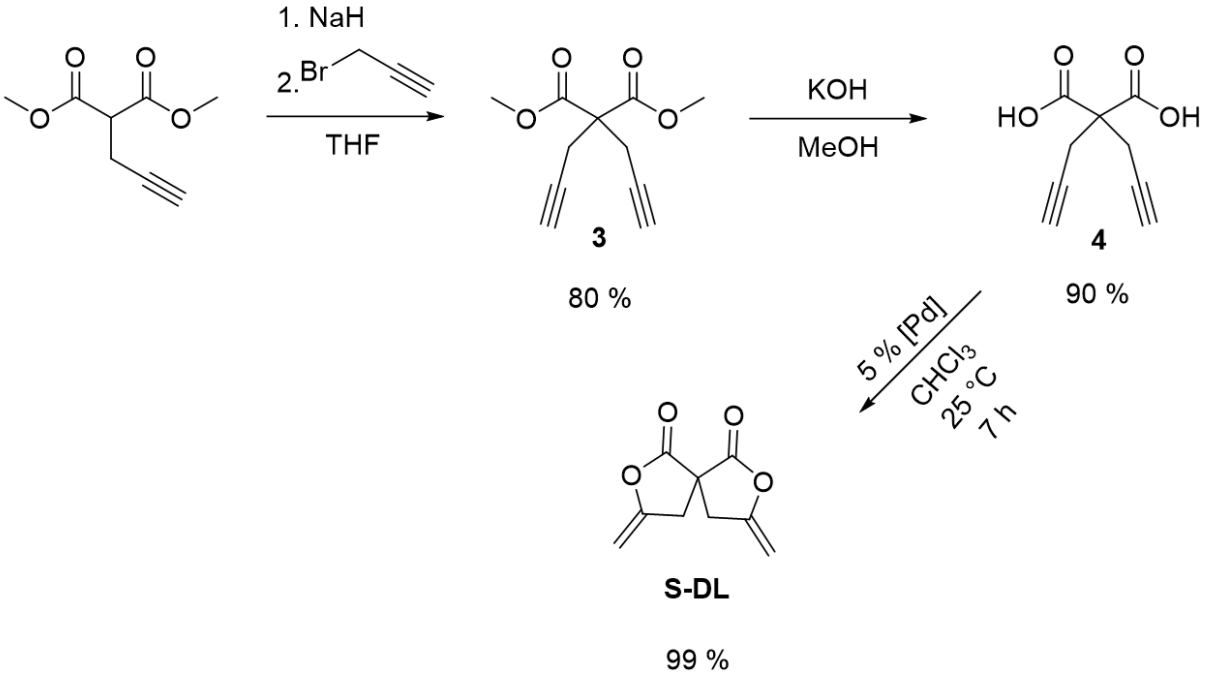


Figure 5.6. Synthesis of spiro-dilactone monomer.

5.2.4. Step-growth ring-opening polymerization of spiro-dilactone monomer for the synthesis of polyesters

After analyzing the ring-opening reaction of the model monolactone monomer, the ring-opening polymerization of spiro-dilactone was carried out. As it was concluded in the model reaction, 1.25 mol % of DBU is required to perform the reaction, so the same reaction conditions have been used for the ring-opening polymerization reaction.

The S-DL monomer was mixed with stoichiometric equivalents of 1,4-butanediol in the presence of the catalyst and using chloroform as solvent (Figure 5.7).

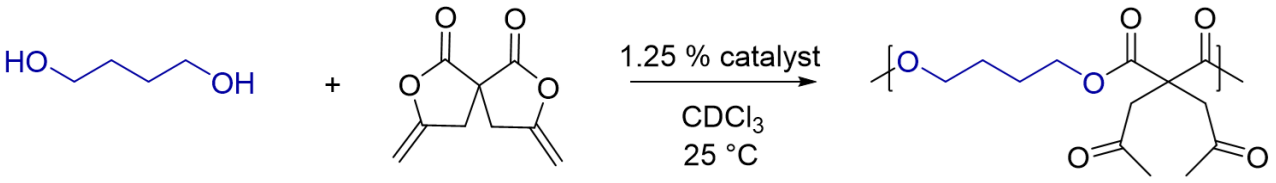


Figure 5.7. Scheme of the ring-opening polymerization of S-DL monomer and 1,4-butanediol.

The polymerization reaction was carried out for 10 hours at room temperature and the result was characterized by ^{1}H NMR and SEC (Figure 5.8).

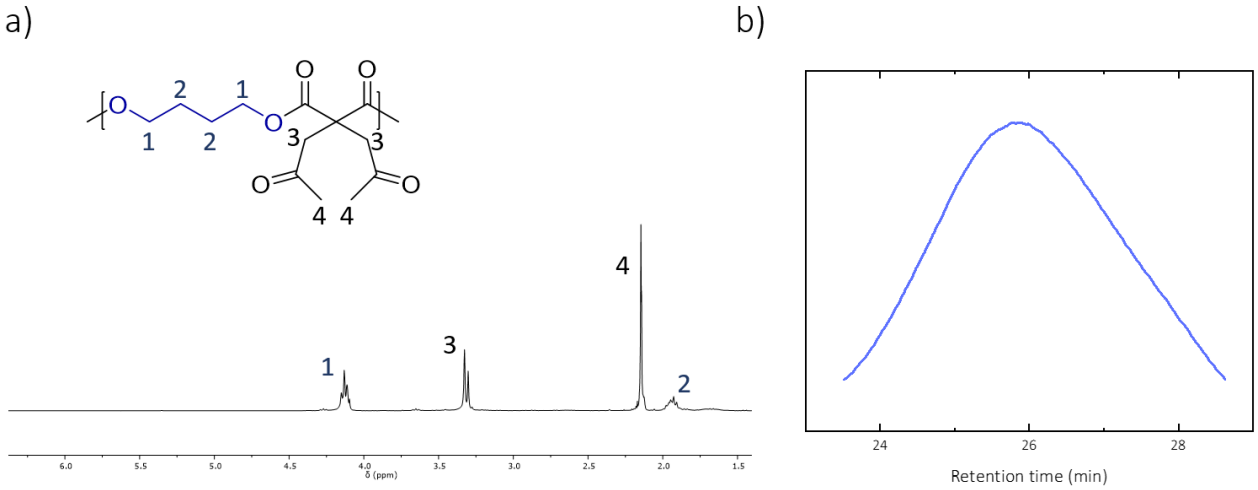


Figure 5.8. Ring-opening polymerization reaction product analyzed by a) ^{1}H NMR and b) SEC.

^{1}H NMR shows that after 10 hours of reaction full conversion was achieved, as no signals of S-DL monomer could be observed, and the signals of the polyester formation between the dilactone and the diol could be identified (Figure 5.8a). In order to measure the molecular weight of the synthesized polymer SEC analysis was carried out in chloroform and the analyses revealed that the polyester has a M_n of 13400 g·mol^{-1} and dispersity of 1.6 (Figure 5.8b). After analyzing the results obtained from the polymerization reaction, it could be said that this step-growth ring-opening polymerization process is a successful method for the preparation of polyesters at room temperature.

5.2.5. Extending the polymerization scope to other polymers

As the principal monomer used, S-DL, is a cyclic monomer that allows the preparation of new polymers changing the nucleophile employed and creating new polymers with a different backbone. As it has been described before by the use of a diol, polyesters could be obtained, however, if a diamine is used polyamides should be synthesized and polythioesters when dithiols are applied.

5.2.5.1. Ring-opening study of C-ML model monomer for the synthesis of amides and thioesters

In order to study if the synthesis of the described polymers is feasible C-ML model monomer was used to understand the ring-opening reaction by other nucleophiles. For that purpose, three different nucleophiles were chosen, a primary amine, 1-butylamine, a thiol, 1-butanethiol, and a secondary amine, diethylamine, and the reactions were carried out at room temperature in chloroform (Figure 5.9).

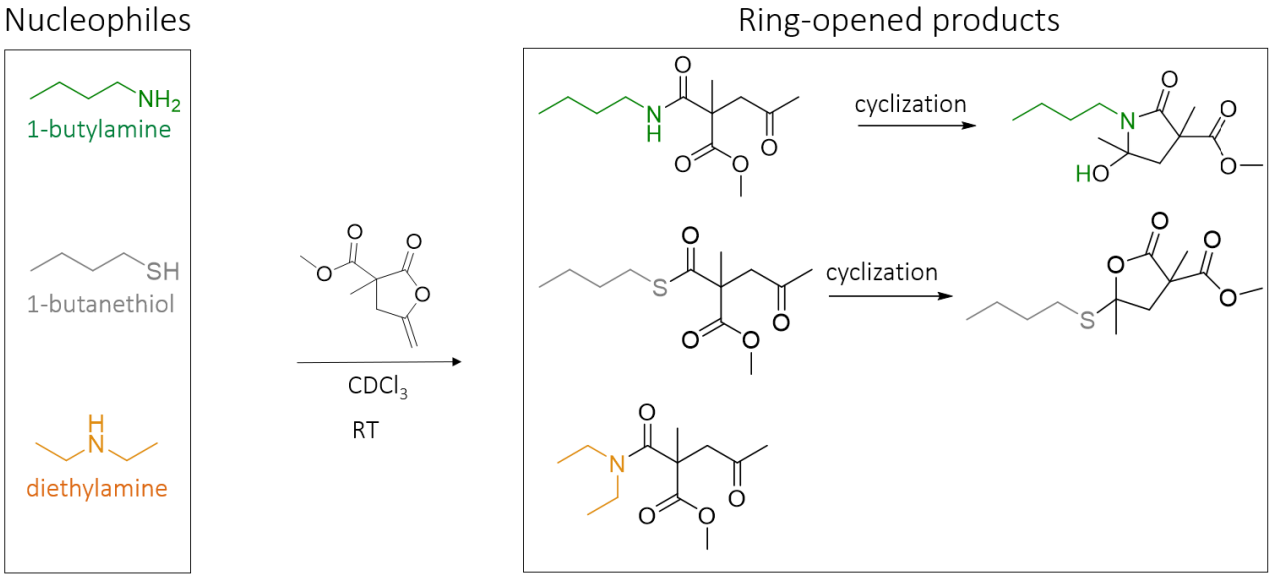


Figure 5.9. Scheme of ring-opening reactions of C-ML monomer with different nucleophiles and the ring-opened products obtained.

Amines and thiols are better nucleophiles than alcohols so at first the ring-opening reaction of C-ML without the use of the catalyst was tried (Figure 5.10a). The ring-opening reaction was followed by ^{1}H NMR and it was determined that 1-butylamine is able to carry out the reaction by itself, at 6 hours of reaction time 60 % of conversion was achieved (Figure 5.10a, green line). The rest of the nucleophiles are almost not capable to ring open the model monolactone, the secondary amine shows 7 % of conversion (Figure 5.10a, orange line) and the thiol 2 % (Figure 5.10a, grey line). Therefore, it was checked if the use of 1.25 mol % DBU catalyst would increase the reaction speed of these three nucleophiles (Figure 5.10b).

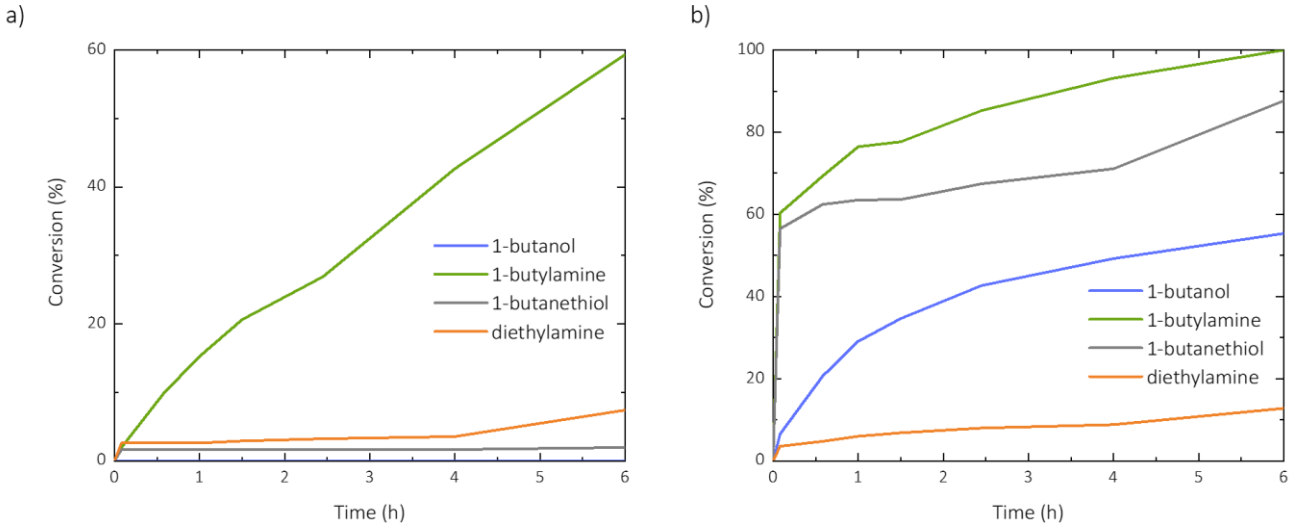


Figure 5.10. Ring-opening reaction kinetics a) without the use of the catalyst and b) using 1.25 mol % of DBU.

In the presence of DBU, the reactions with 1-butylamine and 1-butanethiol were sped up considerably. Even the primary amine, 1-butylamine, was working without the need of a catalyst, in the presence of it, it was showing full conversion at 6 h, with a rapid start, 60 % conversion at 5 minutes reaction time (Figure 5.10b, green line). The 1-butanethiol nucleophile also displays a considerable increase in the reactivity, going from no conversion in a non-catalyzed media to almost 90 % of conversion in 6 h (Figure

5.10b, grey line). The primary amine and the thiol show a change in slope in the conversion kinetics, it is though that could be caused by the deactivation of the catalyst. Diethylamine did not suffer a representative change in the presence of the catalyst, hardly 12 % of conversion could be appreciated (Figure 5.10b, orange line). That effect could be caused by the steric hindrance that the secondary amine has to attack the carbonyl group.

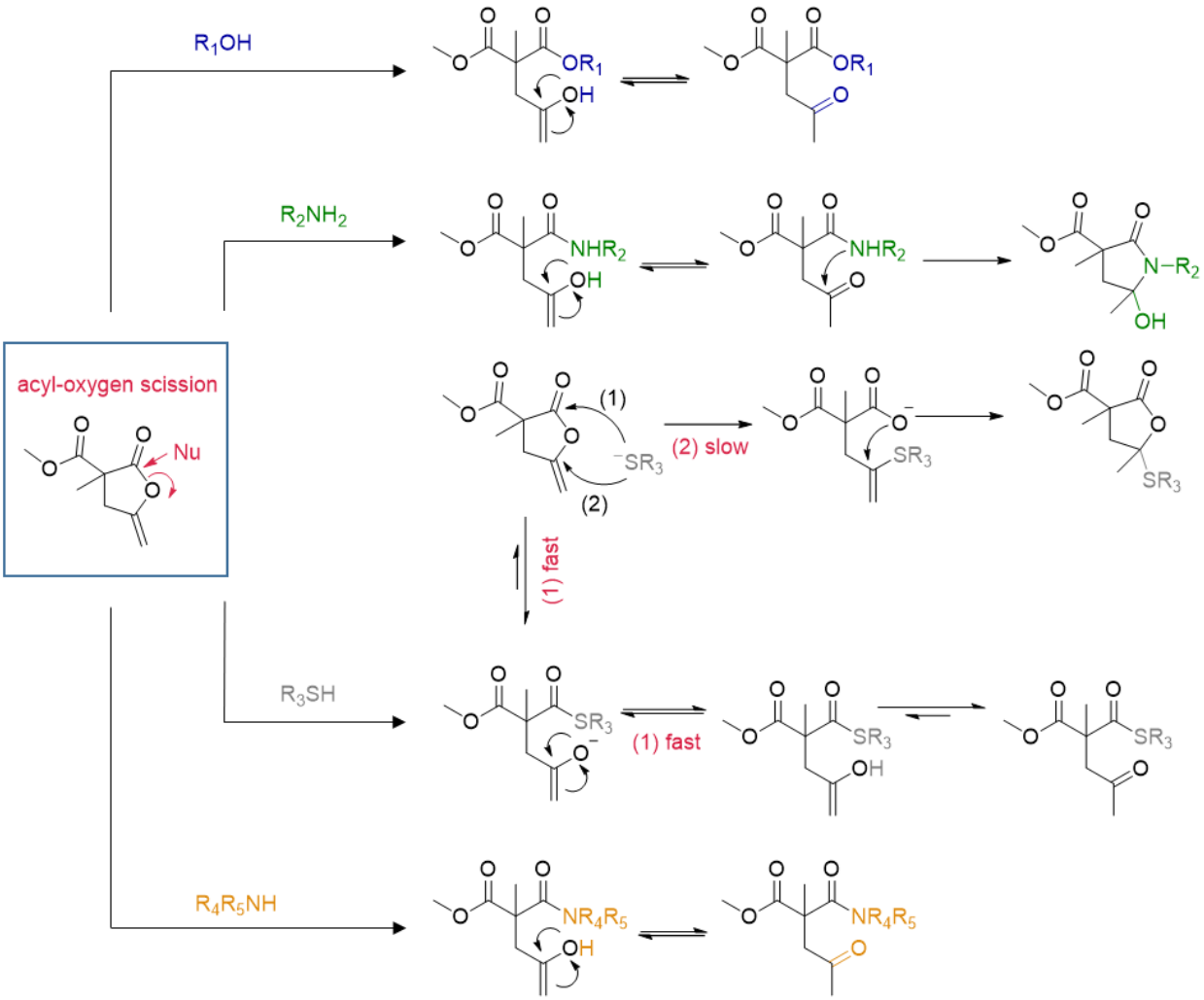


Figure 5.11. Ring-opening reaction mechanism for the different nucleophiles and the products obtained.

Analyzing the ring-opened products by ^{1}H NMR, the reaction mechanisms have been proposed (Figure 5.11). As mentioned before, the ring-opening reaction for the

synthesis of polyesters only gives one reaction product, the ring-opened ester compound, which suffered the tautomerization rearrangement. In the ring-opening reaction of the C-ML monomer by the primary amine, two different products could be observed by ^{1}H NMR (Appendix 5.3). First, the expected ring-opened amide is formed, however, with time this compound evolves into a hemiaminal cyclic product, by the attack of the new secondary amine into the ketone. The formation of the second product starts before the full conversion of the ring-opening reaction, revealed by ^{1}H NMR kinetics (Figure 5.12). When the catalyst is used to speed up the ring-opening reaction, at 6 hours full conversion is obtained being 80 % of the product the cyclized hemiaminal. In the case of the 1-butanethiol nucleophile, it also suffers a cyclization reaction, where the lactone is closed-back (Appendix 5.4). At first, the thioester is synthesized, after opening the ring and rearranged by tautomerization, however, as this reaction is an equilibrium, could migrate back and suffer the alkyl oxygen scission by the thiol. Although this scission reaction is much slower than the first reaction, once is given it would not go back, and the cyclic compound would be formed. Finally, the secondary amine nucleophile just gives one product, the ring-opened polyamide (Appendix 5.5). Once the ring-opening reaction took place, the amine does not have any proton available, therefore it does not migrate into the cyclic compound.

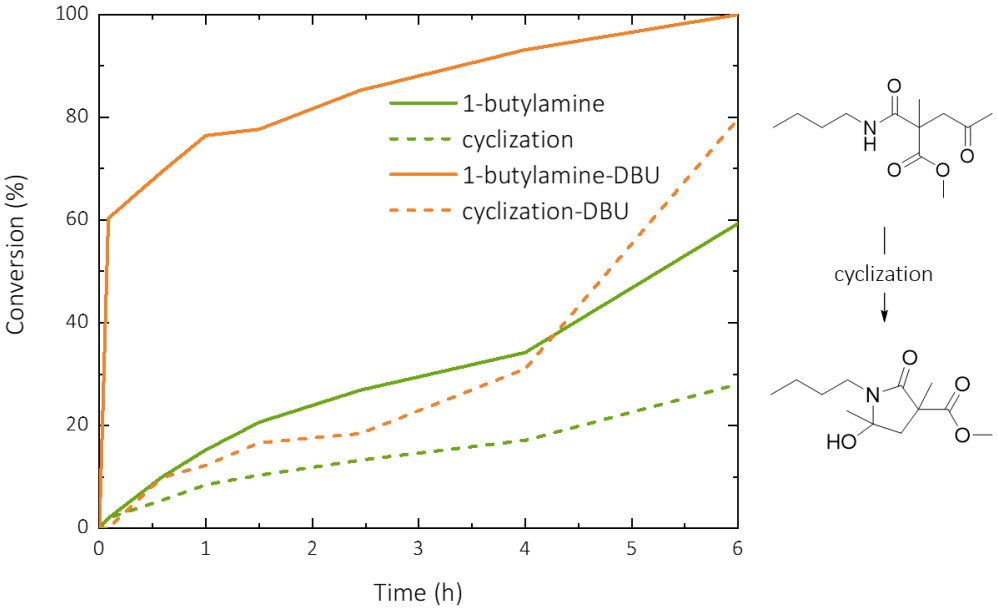


Figure 5.12. Hemiaminal compound formation kinetics for the case where non-catalyst is used and for the case where DBU is used as the catalyst.

5.2.5.2. Step-growth ring-opening polymerization of spiro-dilactone monomer for the synthesis of polyamides and polythioesters

After observing that in order to get polymers at good reaction speed at room temperature the use of DBU catalyst is necessary and that two different products are obtained in the case where a primary amine and a thiol are used the ring-opening polymerization reactions were carried out. For that, the spiro-dilactone and three nucleophiles were used: 1,4-butanediamine, 1,4-butanedithiol, and N,N-dimethylethylenediamine (Figure 5.13).

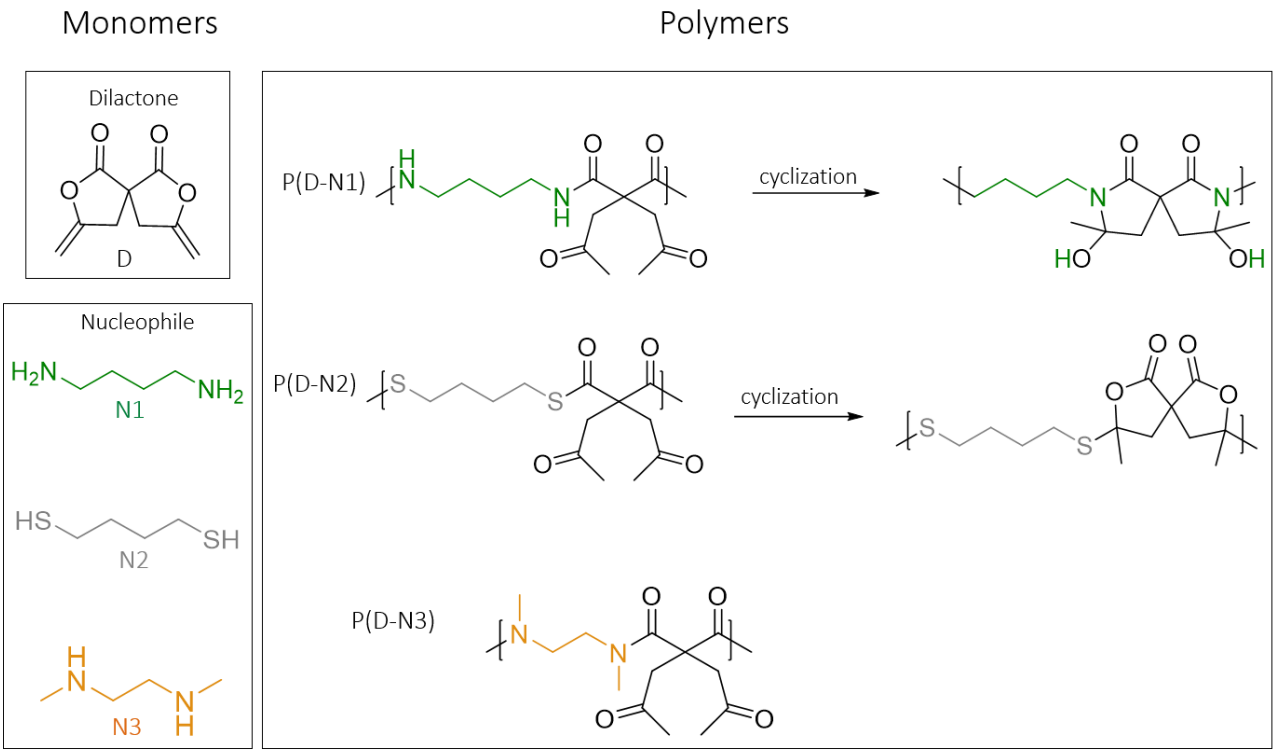


Figure 5.13. Scheme of ring-opening polymerizations of spiro-dilactone monomer with different nucleophiles and the polymers obtained.

The reactions were prepared using stoichiometric amounts of the dilactone and the nucleophile selected. As the step-growth polymerization reaction is A-B type is extremely important to add stoichiometric amounts in order to get high molecular weights. The polymerizations were carried out for 10 hours and after that time they were precipitated and analyzed by ^{1}H NMR and SEC.

^{1}H NMR analysis shows that in the case of the polymerization between the dilactone and 1,4-butanediamine (N1) after 10 hours of reaction and 1.25 mol % of DBU catalyst, full conversion was reached and two different products are obtained (Appendix 5.6), as it was observed in the ring-opening model reactions. It was determined by ^{1}H NMR that 83 % of the product is a hemiaminal cyclic and the rest the ring-opened compund. The SEC indicates that the synthesized polyamide has a molecular weight of 12800 g·mol^{-1} and dispersity of 1.8 (Figure 5.14).

It was determined in the model reaction that the primary amine does not need a catalyst to promote the ring-opening of the lactone and that is why a polymerization reaction without DBU was tried. The result indicates that after 10 hours of reaction time the conversion was 78 % and 76 % of it was in hemiaminal and the rest in the opened way. Due to the lack of full conversion, the molecular weight of the polymer was also lower than the one catalyzed by DBU, 8800 g·mol^{-1} and dispersity of 1.6 (Figure 5.14).

a)

entry	polymer	catalyst	$M_{n,\ SEC}$ (g mol^{-1})[a]	Đ
1	P(D-N1)	DBU	12800	1.8
2	P(D-N1)	-	8800	1.6
3	P(D-N2)	DBU	11000	1.7
4	P(D-N3)	DBU	7800	1.6
5	P(D-N3)	-	5900	1.7

[a] Determined by SEC in THF with polystyrene standards and correction factors.

b)

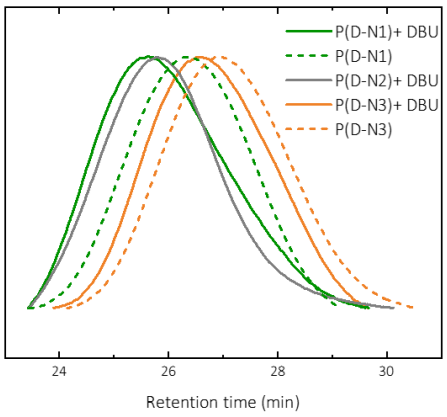


Figure 5.14. a) Results of the Polymerization of spiro-dilactone and different nucleophiles in chloroform at room temperature and b) SEC graphs.

For the synthesis of polythioesters, 1,4-butanedithiol (N2) nucleophile was used together with 1.25 mol % of DBU catalyst. ^{1}H NMR results show that 100 % conversion was reached within 10 hours of reaction time and as was confirmed in the model reactions, two different products are obtained, the ring-opened product and the relactonated product. The amount of the recyclized product is 25 % confirmed by ^{1}H NMR in chloroform (Appendix 5.7) and the molecular weight is 11000 g·mol^{-1} and dispersity 1.7 (Figure 5.14).

In the case of the secondary amine, the model reaction indicate that it is not a very efficient nucleophile for the ring-opening reaction of the C-ML monomer (Figure 5.10), however, it was thought that it could be due to the steric hindrance that the amine has.

Therefore, it was decided to try a less sterically hindered secondary amine, N,N-dimethylethylenediamine (N3), for the polymerization reaction.

Results confirmed the successful polymerization between the dilactone and the secondary amine in 10 hours of reaction using 1.25 mol % of DBU (Appendix 5.8). The SEC analysis shows that the polyamide obtained has a molecular weight of 7800 g·mol^{-1} and dispersity of 1.6 (Figure 5.14). As in the case of the primary diamine, the polymerization reaction without any catalyst was tried in order to see if the secondary amine is able to ring open the lactone. It was concluded by SEC analysis that the polyamide created has a M_n of 5900 g·mol^{-1} and Đ of 1.7 (Figure 5.14). Therefore, it could be concluded that the secondary diamine is also able to ring open the dilactone without the need for a catalyst and synthesize a polyamide.

5.3. Conclusion

In this chapter, the synthesis of a new dilactone has been reported for the synthesis of polyesters under mild conditions. The prepared spiro-dilactone is a reactive monomer that at room temperature in the presence of a diol is able to create a polyester by polyaddition reaction. It was confirmed by model reactions that without the use of a catalyst there was no reaction and therefore five catalysts have been tried to promote the polyester synthesis. Among the catalyst tested, DBU was the best one to carry out the polymerization of the lactone at room temperature. After concluding the need for the catalyst the polyester polymerization was done using 1,4-butanediol as the nucleophile and the resulting product was analyzed by ^{1}H NMR and SEC. The results conclude that this polymerization method is a promising process for the synthesis of polyesters at room temperature.

Extending the scope of the synthesis of polyamides and polythioester was also tried by changing the nucleophile employed. It was observed that the mentioned polymerizations work well, however, the use of a primary diamine and dithiol give two different products, a ring-opened product first and a consequent cyclized product that was determined by ^{1}H NMR.

Up to our knowledge, this work approaches for the first time the synthesis of polyesters at room temperature using a facile polymerization method. In addition, due to the versatility of the method, the synthesis process could be extended for the polymerization of different polymers.

5.4. Experimental section

5.4.1. Materials

Dimethyl propargylmalonate (97 %) was purchased from Fluorochem, the rest of the reactants for the monomer synthesis, sodium hydride (NaH), propargyl bromide, potassium hydroxide (KOH), methyl iodide, and sodium hydroxide (NaOH) were obtained from Sigma-Aldrich S.A. and used as received. The nucleophiles, 1-butanol, 1-butylamine, 1-butanethiol, and diethylamine were also got from Sigma-Aldrich S.A. and they were dried under vacuum before use, as well as, the monomers 1,4-butanediol, 1,4-butanediamine, 1,4-butanedithiol, and N,N-dimethylethylenediamine. The catalyst 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (98 %) was acquired from TCI and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (98 %), 4-dimethylaminopyridine (DMAP) (>99 %), 1,4-diazabicyclo[2.2.2]octane (DABCO) (>99 %) and methanesulfonic acid (>99 %) were from Sigma-Aldrich S.A. and used without further purification. The solvents tetrahydrofuran, methanol, chloroform, and dichloromethane were used as received.

5.4.2. Model monomer ring-opening reaction

The model ring-opening reactions were carried out using the previously synthesized methyl-3-methyl-5-methylene-2-oxotetrahydrofuran-3-carboxylate monomer and a nucleophile. The model reactions were done in a NMR tube and for that, 0.12 10^{-3} mol (20.41 mg) of monomer and 0.12 10^{-3} mol of nucleophile (8.89 mg 1-butanol, 8.77 mg 1-butylamine, 10.81 mg 1-butanethiol, and 8.77 mg diethylamine) were mixed in a vial together with 0.5 mL of deuterated chloroform. Afterward, 1.25 mol % of catalyst (0.91 mg, 0.90 µL of DBU) was added to the vial. Finally, the reaction was transferred to the NMR tube and the room temperature reaction kinetics were followed by ^{1}H NMR.

5.4.3. Step-growth polymerization of spiro-dilactone

The polymerization of 3,8-dimethylene-2,7-dioxaspiro[4.4]nonane-1,6-dione, spiro-dilactone was carried out by ring-opening step-growth polymerization, by the use of a nucleophile as a comonomer. In a vial, 1 10^{-3} mol (180.04 mg) spiro-dilactone and 1 10^{-3} mol nucleophilic comonomer (90.07 mg 1,4-butanediol, 88.10 mg 1,4-butanediamine, 122.02 mg 1,4-butanedithiol and 88.1 mg N,N-dimethylethylenediamine) were placed. After that, 5 mL of chloroform were added to dissolve the monomers and 1.25 mol % (7.61 mg, 7.46 µL) of DBU to catalyze the reaction. The reactions were left stirring for 10 hours at room temperature before they were purified. The purification was done by precipitating the chloroform solution into cold methanol and filtering the polymers obtained. Finally, they were let to dry under vacuum for 24 hours before analyzing them by ^{1}H NMR and SEC.

5.5. References

1 Plastics Europe, *Plastics-the Facts 2021 An analysis of European plastics*

production, demand and waste data, 2021.

2 United Nations, Sustainable Development Goals, https://sdgs.un.org/, (accessed May 14, 2022).

3 S. A. Miller, *Polym. Chem.*, 2014, **5**, 3117–3118.

4 A. Basterretxea, C. Jehanno, D. Mecerreyes and H. Sardon, *ACS Macro Lett.*, 2019, **8**, 1055–1062.

5 X. Zhang, M. Fevre, G. O. Jones and R. M. Waymouth, *Chem. Rev.*, 2018, **118**, 839–885.

6 I. Flores, J. Demarteau, A. J. Müller, A. Etxeberria, L. Irusta, F. Bergman, C. Koning and H. Sardon, *Eur. Polym. J.*, 2018, **104**, 170–176.

7 L. T. Lim, R. Auras and M. Rubino, *Prog. Polym. Sci.*, 2008, **33**, 820–852.

8 A. Takasu, Y. Iio, Y. Oishi, Y. Narukawa and T. Hirabayashi, *Macromolecules*, 2005, **38**, 1048–1050.

9 I. Cota, *Phys. Sci. Rev.*, 2019, **2**, 20160129.

10 A. Takasu, T. Makino and S. Yamada, *Macromolecules*, 2010, **43**, 144–149.

11 K. Fukushima and K. Nozaki, *Macromolecules*, 2020, **53**, 5018–5022.

12 O. Thillaye Du Boullay, E. Marchal, B. Martin-Vaca, F. P. Cossío and D. Bourissou, *J. Am. Chem. Soc.*, 2006, **128**, 16442–16443.

13 A. Bossion, K. V. Heifferon, L. Meabe, N. Zivic, D. Taton, J. L. Hedrick, T. E. Long and H. Sardon, *Prog. Polym. Sci.*, 2019, **90**, 164–210.

14 G. Hua and K. Odelius, *Biomacromolecules*, 2018, **19**, 1573–1581.

15 S. Gennen, B. Grignard, T. Tassaing, C. Jérôme and C. Detrembleur, *Angew. Chemie*

Int. Ed., 2017, **56**, 10394–10398.

16 J. Alemán, V. Del Solar and C. Navarro-Ranninger, *Chem. Commun.*, 2010, **46**, 454–456.

17 B. D. Ravetz, K. E. Ruhl and T. Rovis, *ACS Catal.*, 2018, **8**, 5323–5327.

18 N. A. Espinosa-Jalapa, D. Ke, N. Nebra, L. Le Goanvic, S. Mallet-Ladeira, J. Monot, B. Martin-Vaca and D. Bourissou, *ACS Catal.*, 2016, **6**, 1565–1566.

Chapter 6

Conclusions and perspective

Polyesters are promising materials to fulfill target number 12, “ensure sustainable consumption and production patterns”, within the “Sustainable Development Goals” promoted by the United Nations. These materials could be obtained from biomass and as they have an ester group, they are potentially recyclable. In addition, some of these materials are biodegradable under appropriate conditions. However, as furtherly discuss in the introduction chapter, most of the polyesters employed are petroleum-based and the reaction conditions that industries need to employ require metal catalysts and high energy consumption.

Therefore, it has been seen that there is a need to find new materials and methods to improve the sustainability of polyester synthesis. On one side, to find polyesters that could be obtained from biomass and consequently reduce dependence on petroleum, and on the other side to find greener synthesis methods, without the use of metals and lower reaction temperatures.

In this thesis, first, the replacement of the metal catalyst with a naturally occurring catalyst was carried out. To do so, five thermally stable catalysts were tried for the ring-opening polymerization of L-lactide, concluding that taurine was the best catalyst among the tested ones. It was determined that it is an excellent catalyst as it is able to synthesize polylactide in a relatively short reaction time. The polymers synthesized show narrow dispersities, indicating that taurine can control the polymerization reaction, reducing the side reactions. In addition, the cytotoxicity test reveals that the polylactide produced by the employment of the natural catalyst is not toxic, giving the chance of implementing its use in a broad range of applications. Furthermore, taurine

was tested for the ring-opening polymerization of other types of polymers, concluding that it is also able to synthesize polycarbonates and polyamides.

Focusing on the reduction of fossil fuel use for the synthesis of monomers and polymers, the implementation of two different methods to enhance the use of biobased materials have been proposed. On one side, the closed-loop recycling of PEF polymer has been designed to find a sustainable end-of-life assessment of the polymer and therefore be a promising alternative to current PET polyester. It has been seen that PEF has excellent barrier properties, better than PET, however, like PET, it is not biodegradable and therefore, a recycling method is needed to find out. A solvent-free glycolysis depolymerization process has been proposed by the use of a thermally stable DBU:BA organocatalyst leading to very high yields of BHEF monomer, up to 92 %. Afterward, the repolymerization reaction was carried out by the use of the same organocatalyst to carry out the polycondensation reaction. The polymerization was done in a two-step process, starting with a melt polycondensation and finishing with a solid-state polycondensation, obtaining a virgin-like PEF polymer. This process enlights the possibility of implementing this material for industrial processes, especially for packaging applications.

On the other side, the synthesis of 3-hydroxybutyric acid monomer has been done by a sustainable process. The chemical synthesis of this kind of hydroxy acids is a tedious process; however, in this work a facile depolymerization process of PHB polymer catalyzed by taurine has been carried out, giving an upcycling end-of-life assessment to the polymer. Nevertheless, the hydrolytic depolymerization process gives two products, the desired 3-hydroxybutyric acid and the crotonic acid, created by an elimination reaction of the hydroxy acid. In this work, it has been minimized the formation of the crotonic acid, obtaining high yields of hydroxy acid monomer, 98 %. It has been

concluded that this depolymerization process is an interesting method to obtain hydroxy acids in very high yield, by the use of green and facile synthesis procedure.

To finish, a novel method for the polymerization of polyesters at room temperature has been designed. In this part of the thesis, first, the chemical synthesis of a new five-membered spiro-dilactone was performed in order to synthesize a reactive monomer that could enable the synthesis of polyesters at mild reaction conditions. In a second step, the ring-opening polymerization between the newly synthesized dilactone and a 1,4-butanediol was carried out. Results showed that the polymerization catalyzed by DBU succeeded and that polyesters of up to 13400 $g \cdot mol^{-1}$ and 1.6 dispersities could be obtained. In addition, it has been seen that this step-growth ring-opening polymerization method is a very promising method for the synthesis of different polymers, such as polyamides and polythioesters.

In the light of these results, it has been seen that polyesters are interesting materials to overcome the sustainability issue that needs to be solved, as they could be synthesized from biomass and have recycling potential. In this thesis, we have done a step forward to create greener monomer and polymers and polymerization methods, working with naturally occurring compounds and using environmentally friendly conditions. The approaches of this work could be industrially implemented as cheap and facile synthetic methods have been designed.

Even though promising results have been obtained during this thesis, considerable improvements still need to be done. On one side, the employed catalysts loads are high compared to the metal catalysts, and the reactivity rates are low, obtaining lower molecular weight polymers. On another side, the spiro-dilactone synthesis needs to be optimized for high scale production, finding alternatives to decrease the high cost of the process.

Finally, it should be emphasized that this thesis has only studied some of the aspects to be improved in order to obtain more sustainable polyesters, but there is still a long way to go and many advances to be made. Therefore, it is of vital importance to continue research on polyesters, since they are materials with great potential to enhance the sustainability of our society.

Methods

Nuclear Magnetic Resonance (NMR) spectroscopy

^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy.was recorded in a Bruker Avance DPX 300 at 300.16 MHz and at 75.5 MHz of resonance frequency respectively, using deuterated chloroform ($CDCl_3$), deuterated dimethyl sulfoxide (DMSO) or deuterium oxide (D_2O) as solvent at room temperature. Experimental conditions were as follows: a) for ^{1}H 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 more than 10000 scans.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) measurements were performed using a DSC8500 from Perkin Elmer, Inc. calibrated with indium and tin standards. The DSC scans were performed with approximately 5 mg of film sample at a heating rate of 10 °C/min from -20 °C to 250 °C and subsequent cooling down to 25 °C under a nitrogen flow rate of 20 mL/min.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) were carried out using a Q500 Thermogravimetric Analyzer from TA Instruments. Samples were heated from room temperature to 600 °C at a rate of 10 °C/min under a constant N_2 flow.

Matrix Assisted Laser Desorption Ionization - Time of Flight (MALDI-TOF) analysis

MALDI-TOF measurements were performed on a Bruker Autoflex Speed system (Bruker, Germany) instrument, equipped with a 355 nm NdYAG laser using methanol or chloroform as solvent and DCTB-NaTFA and DCTB-KTFA substrates.

Size Exclusion Chromatography (SEC)

Depending on the solvent used different SEC equipment were used:

a) Chloroform

Size Exclusion Chromatography (SEC) was performed at 30 °C using a Waters chromatograph equipped with four 5 mm Waters columns (300 mm x 7.7 mm) connected in series with increasing pore sizes. Toluene was used as a marker and the calibration was done using polystyrene standards.

b) Tetrahydrofuran (THF)

SEC measurements were performed at 30 °C on an Agilent 1200 system equipped with PLgel 5 µm Guard and PLgel 5 µm MIXED-C columns and a differential refractive index (RI) detector (Optilab Rex, Wyatt). THF was used as eluent at a flow rate of 1 ml/min and calibrated using narrow polystyrene standards ranging from 595 to 3.95 · 10−6 g mol^{-1} (5^{th} order universal calibration).

c) 1,1,1,3,3,3 Hexafluoro-2-propanol (HFIP)

Size exclusion chromatography (SEC) was performed on a Waters equipment provided with refractive index (RI) and ultraviolet (UV) detectors. For this, 100 µL of 0.1 (wt/vol) sample solution in HFIP was injected and the analysis was performed at a flow rate of 0.5 mL/min. HR5E and HR2 Waters linear Styragel columns (7.8 mm x 300 mm, pore size

10^3-10^4 Å) packed with cross-linked polystyrene (PS) and protected with a pre-column were used. Molar mass averages and distributions were calculated against poly(methyl methacrylate) (PMMA) standards.

X-ray diffraction

Single crystal diffractometer (SuperNova Cu) with four-circle goniometer, Kappa geometry and microfocus Cu source was used equipped with a large Atlas model two-dimensional CCD detector. The measurements were done at standards conditions, at 100 K.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared pectrophotometer (Nicolet 6700 FT-IR, Thermo Scientific Inc., USA) was used 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 32 scans.

Cytotoxicity test

HeLa cells (ATCC) were seeded, following the protocol ISO/EN 10993. A density of 5000 cells/well on a 96-well plate was used for metabolic activity measurements. A density of 10000 cells/well on a 24-well plate was used for internalization studies.

Three polymer-to-cell ratios (10, 100, and 1000 polymer/cell) and two time points (24 and 72 h) were analyzed, and AlamarBlue was used to measure the metabolic activity of cells.

The uptake of the polymers by HeLa cells was also analyzed. Polymer at 10 polymer/cell were incubated with cells during 2, 4, and 24 h. Afterward, the cells were fixed and

stained. The cells were observed under an inverted fluorescence microscope (Nikon Eclipse Ts2).

Mechanical properties

Tensile tests were performed using dumbbell-shaped film samples sizing 115 mm x 16 mm using a Instron 4400 universal testing machine, equipped with a 1-kN load cell, from Instron (Norwood, MA, USA) according to the ASTM standard method D638. The tests were conducted using a cross-head speed of 10 mm/min. Samples were conditioned for 24 h prior to analysis and the tests were performed at room conditions, that is, at 40 % RH and 25 °C. A minimum of six specimens was tested.

Barrier properties

Permeabilities of water vapor, limonene and oxygen were measured:

a) Water vapor

The gravimetric method ASTM E96-95 was used to determine the water vapor permeability (WVP). Payne permeability cups (diameter of 3.5 cm) from Elcometer Sprl (Hermallfsous-Argenteau, Belgium) were filled with 5 mL of distilled water. The films were not in direct contact with water but exposed to 100 % RH on one side and secured with silicon rings. They were placed within a desiccator and sealed with dried silica gel at 0 % RH and 25 °C. The control samples consisted of cups with aluminum films to estimate solvent loss through the seal. The cups were weighted periodically using an analytical balance (±0.0001 g). WVP was calculated from the regression analysis of weight loss data versus time, whereas the weight loss was calculated as the total loss minus the loss through the seal. The permeability was obtained by multiplying the permeance by the film thickness.

b) Limonene

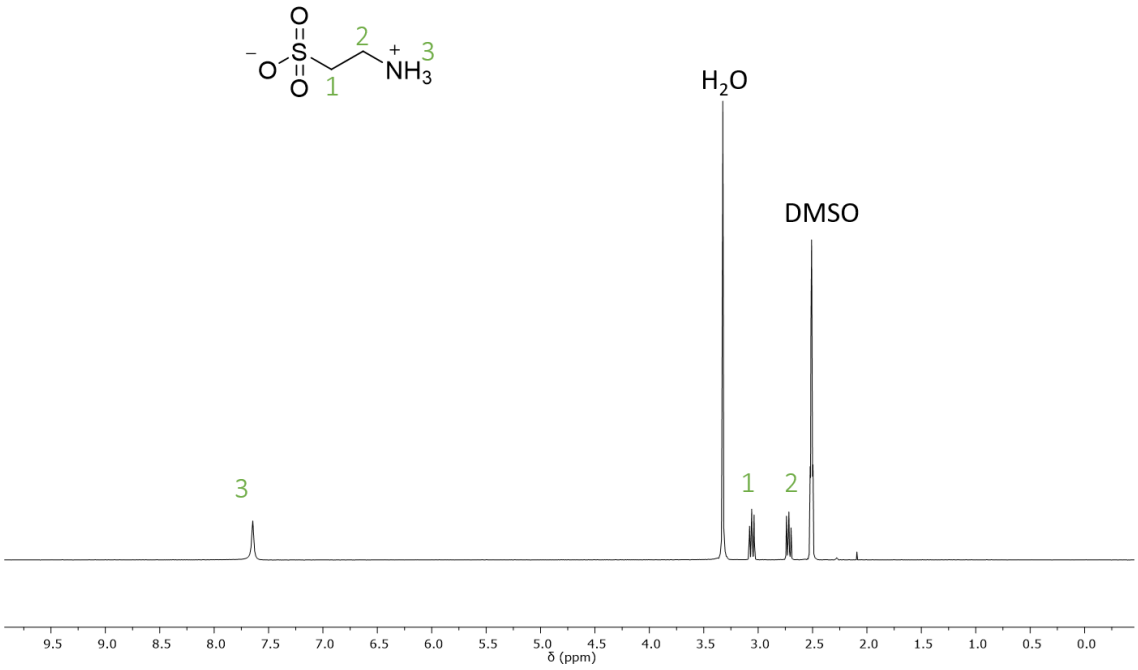
The limonene permeability (LP) was measured using a similar method as that for WVP, placing 5 mL of D-limonene inside the Payne permeability cups. The cups containing the films were placed at controlled room conditions of 40 % RH and 25 °C. The limonene vapor permeation rate (LPRT) values were estimated from the steady-state permeation slopes and the weight loss was calculated as the total cell loss minus the loss through the seal. LP was calculated taking into account the average film thickness in each case. All the WVP and LP measurements were performed in triplicate.

c) Oxygen

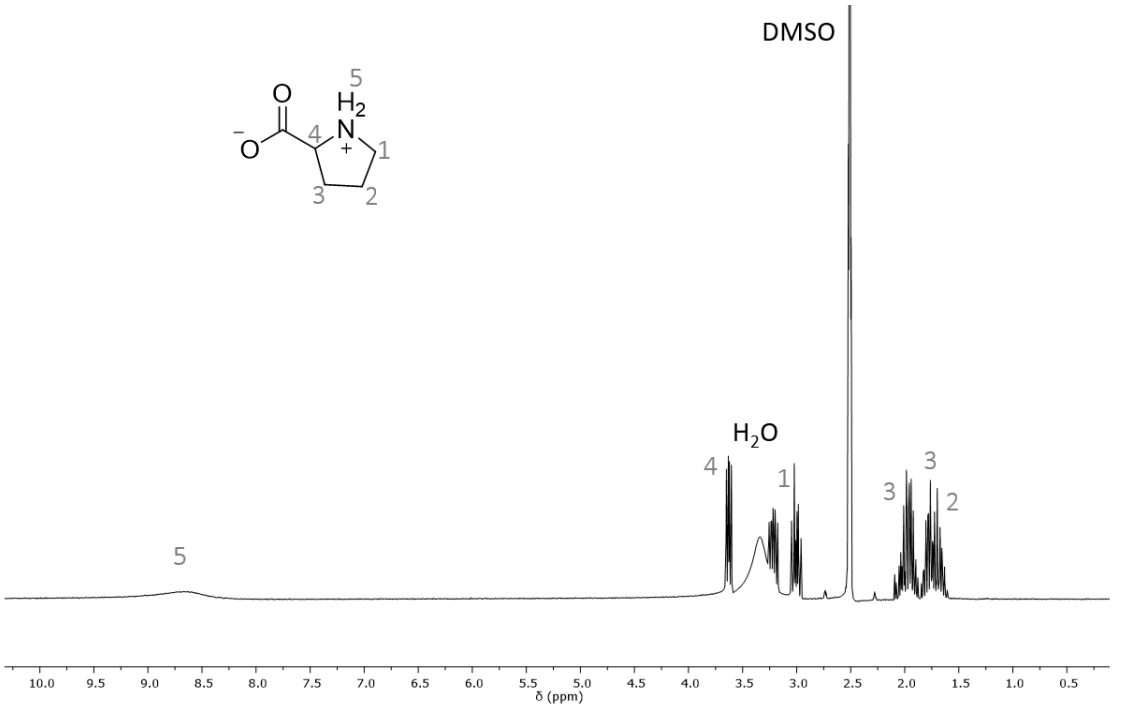
Oxygen permeability (OP) was obtained from the oxygen transmission rate (OTR) measurements, recorded in duplicate, using an Oxygen Permeation Analyzer M8001 from Systech Illinois (Thame, UK) at 23 °C and 0 % and 75 % RH to simulate both dry and humid packaging conditions. The samples were previously purged with nitrogen in the humidity-equilibrated samples and then exposed to an oxygen flow of 10 mL/min. The exposure area during the test was 5 cm^2. Sheet thickness and gas partial pressure were determined. Measurements were performed in duplicate.

Appendix

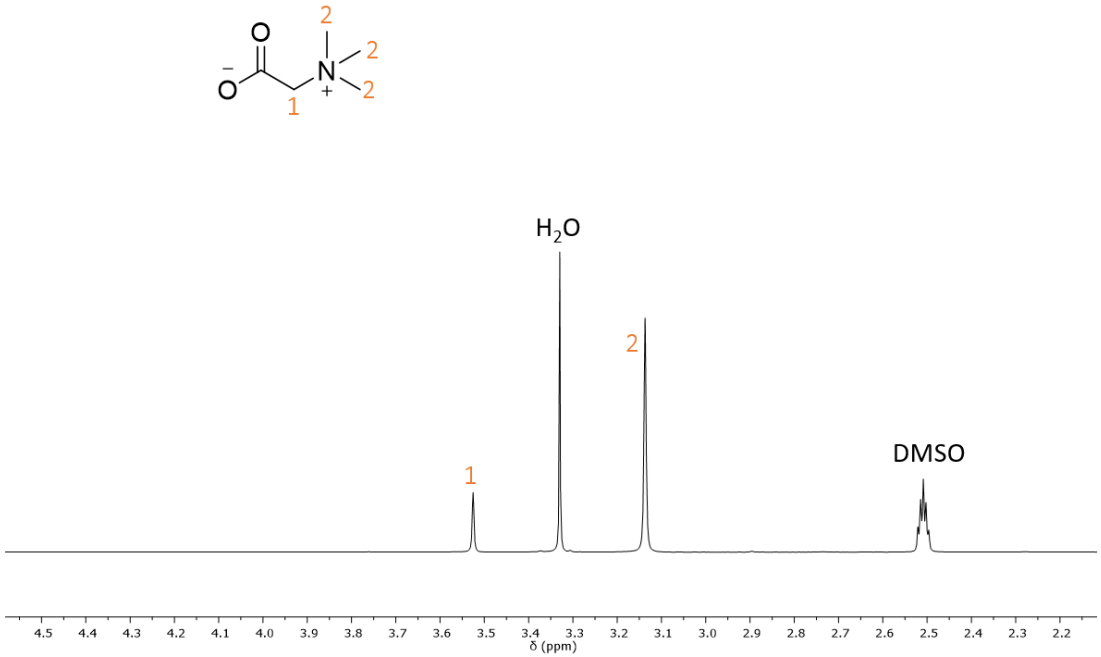
Chapter 2.



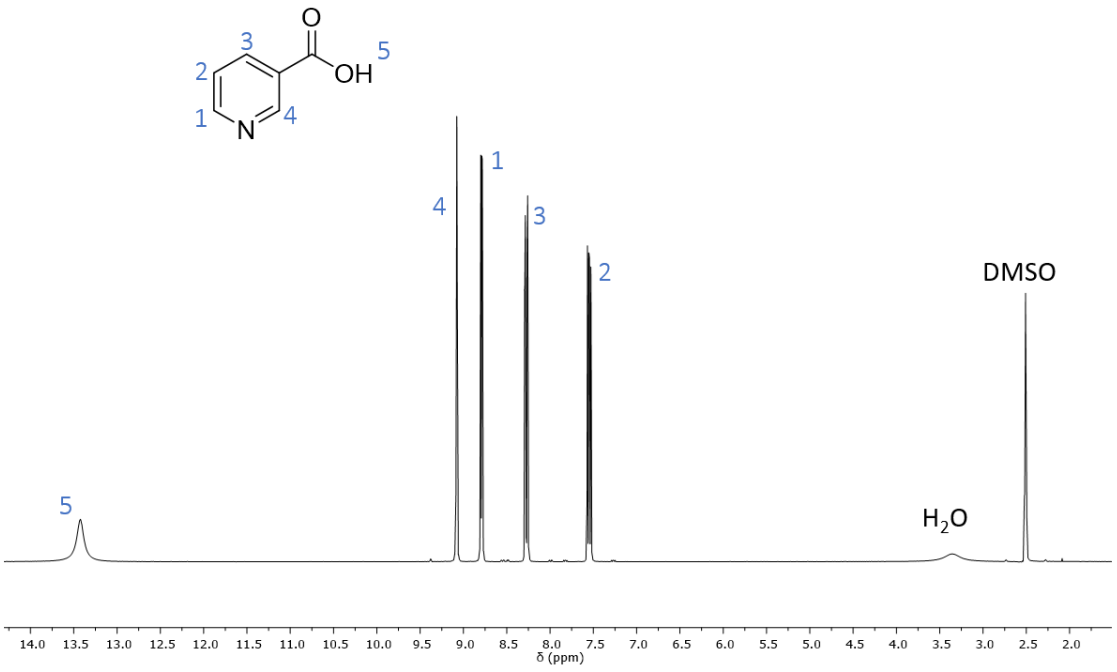
Appendix 2.1. ^{1}H NMR spectra of taurine in deuterated DMSO.



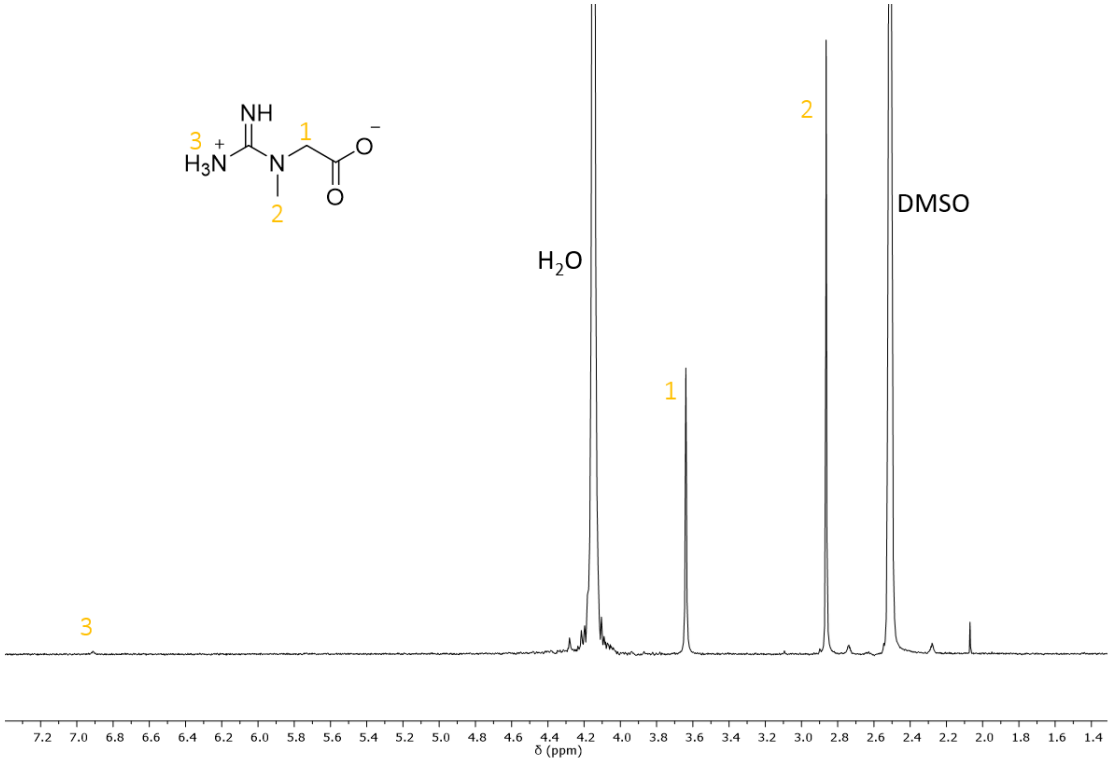
Appendix 2.2. ^{1}H NMR spectra of L-proline in deuterated DMSO.



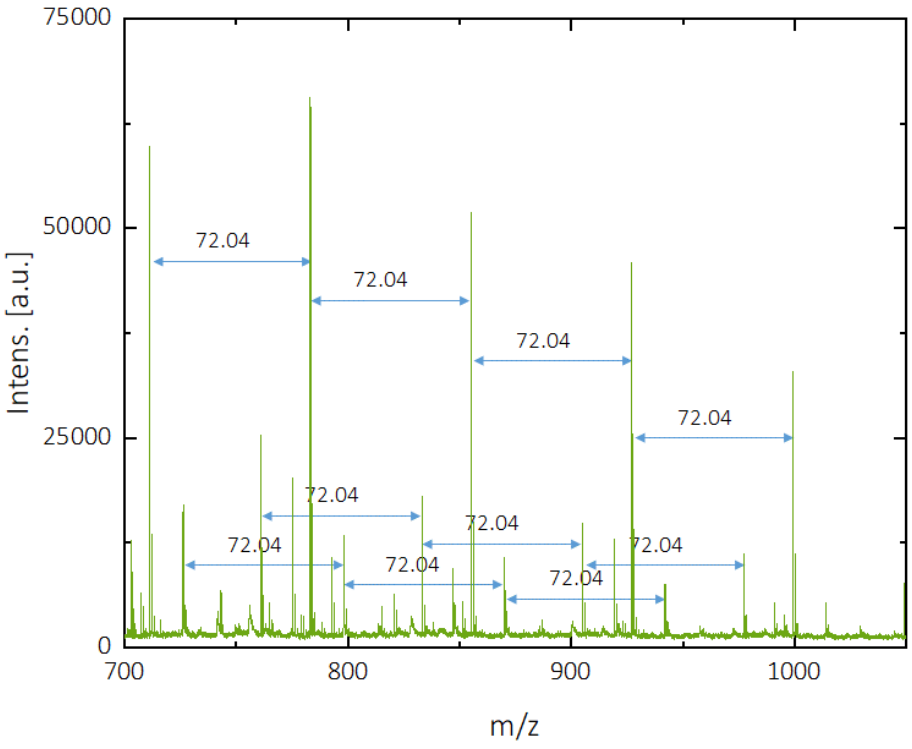
Appendix 2.3. ^{1}H NMR spectra of betaine in deuterated DMSO.



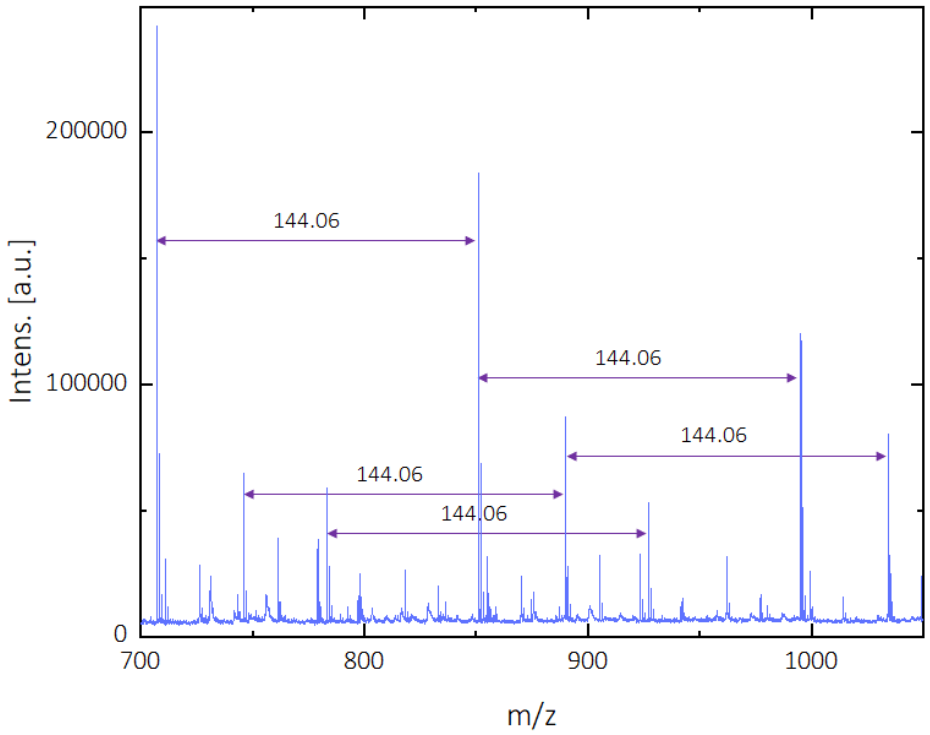
Appendix 2.4. ^{1}H NMR spectra of nicotinic acid in deuterated DMSO.



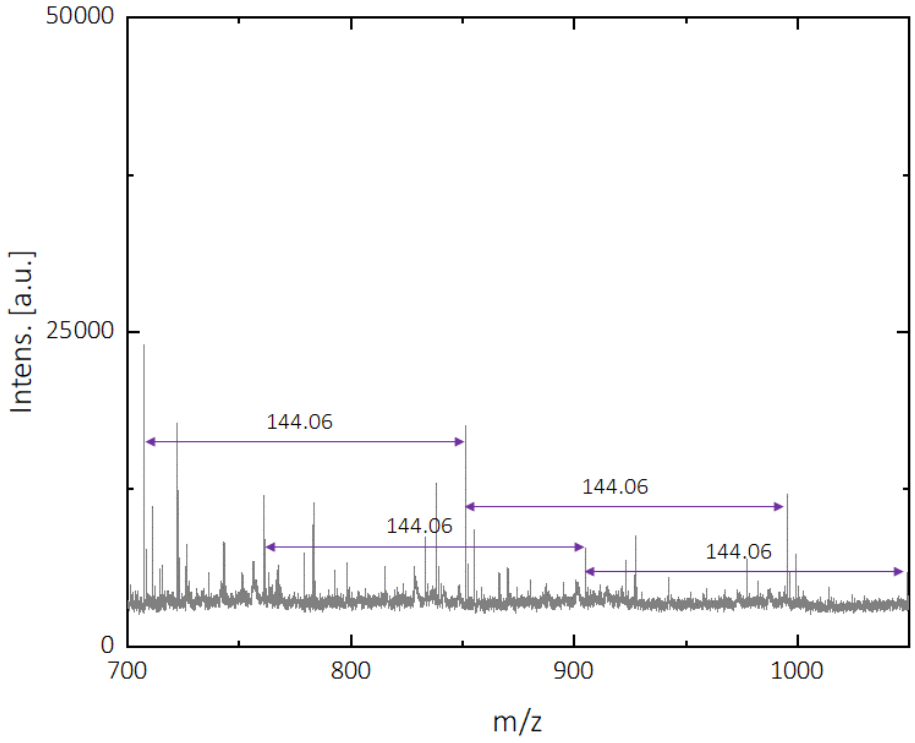
Appendix 2.5. ^{1}H NMR spectra of creatine in deuterated DMSO.



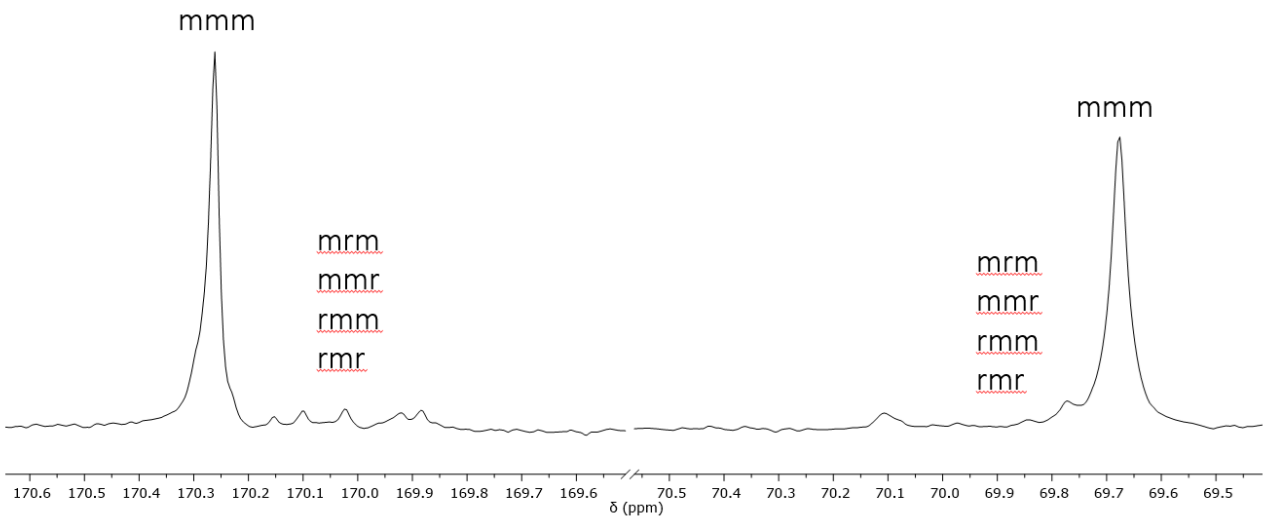
Appendix 2.6. MALDI-TOF analysis of the ROP of L-lactide at 180 °C in bulk using nicotinic acid as catalyst.



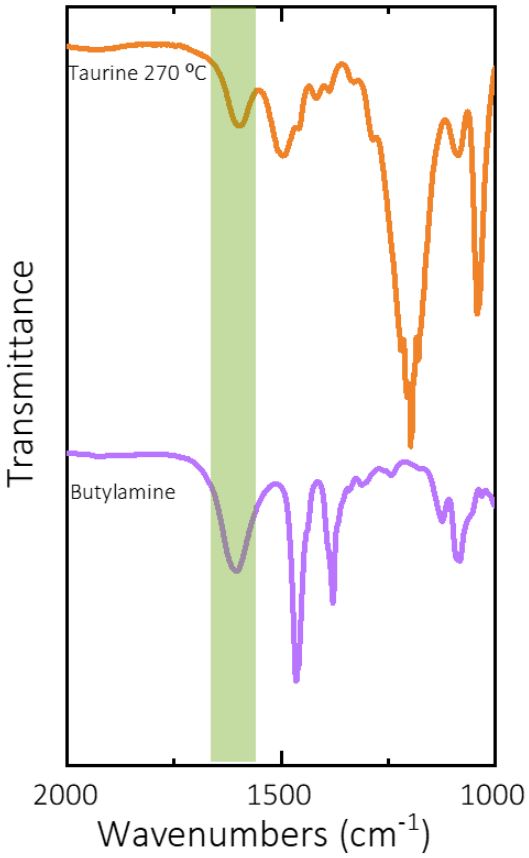
Appendix 2.7. MALDI-TOF analysis of the ROP of L-lactide at 180 °C in bulk using betaine as catalyst.



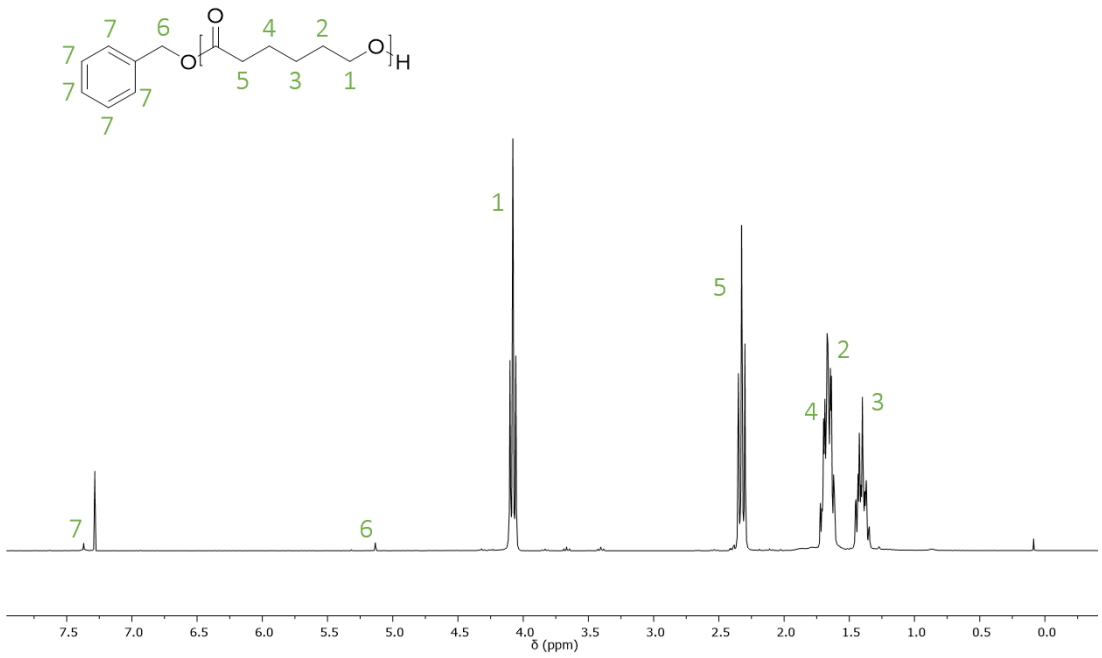
Appendix 2.8. MALDI-TOF analysis of the ROP of L-lactide at 180 °C in bulk using L-proline as catalyst.



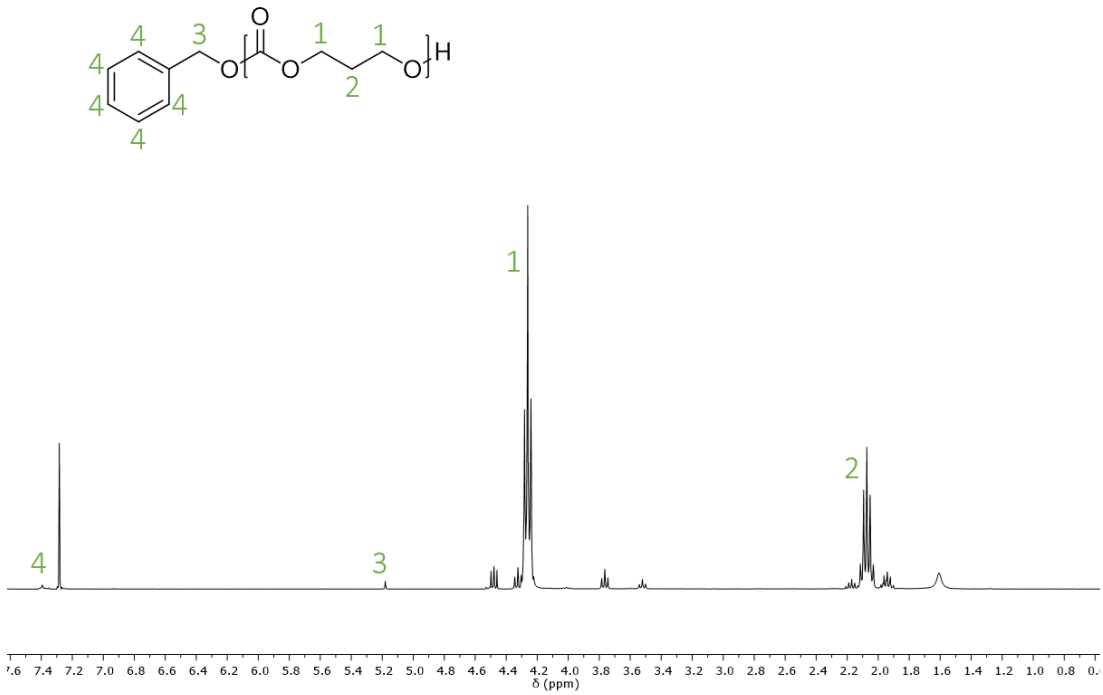
Appendix 2.9. ^{13}C NMR spectrum of DP 400 and the triads that could be observed.



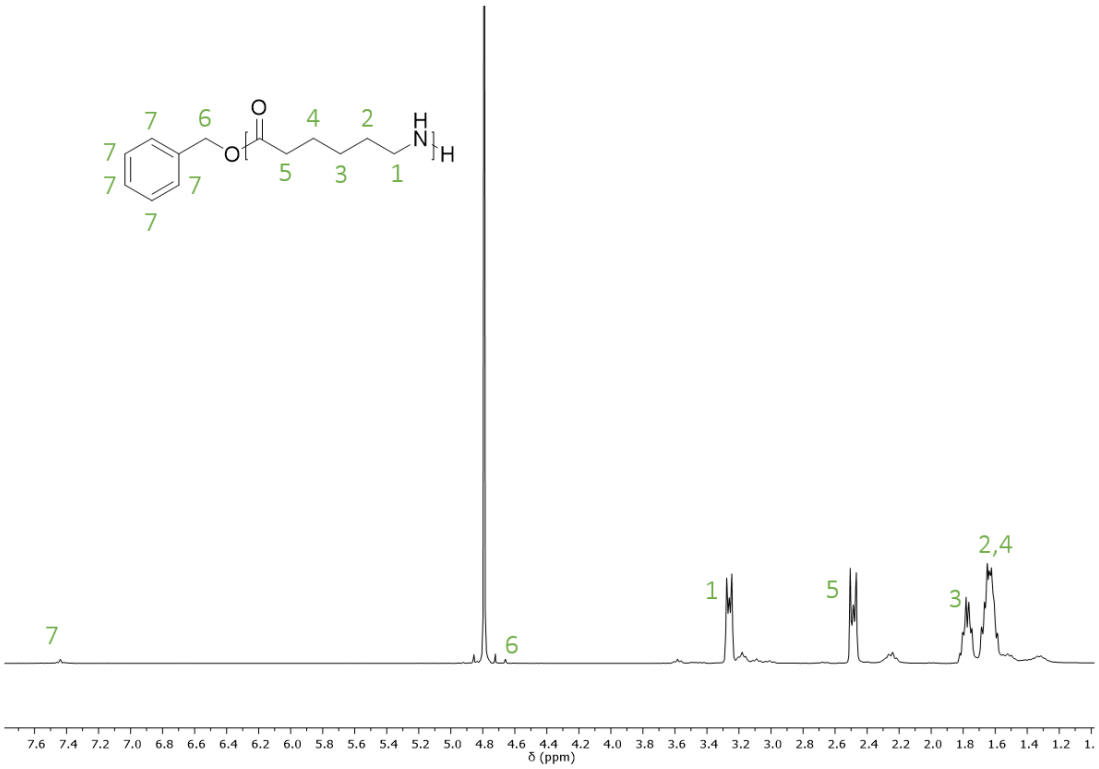
Appendix 2.10. FTIR analysis of taurine at 270 °C and its comparison to butylamine.



Appendix 2.11. ^{1}H NMR spectrum of polycaprolactone synthesized using taurine as catalyst at 180 °C in bulk.

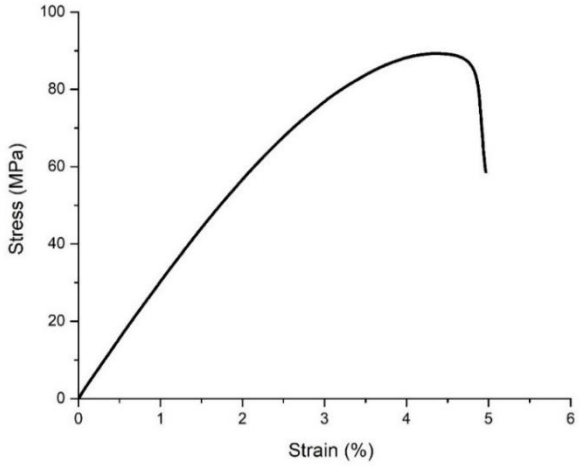


Appendix 2.12. ^{1}H NMR spectrum of polytrimethylene carbonate synthesized using taurine as catalyst at 180 °C in bulk.

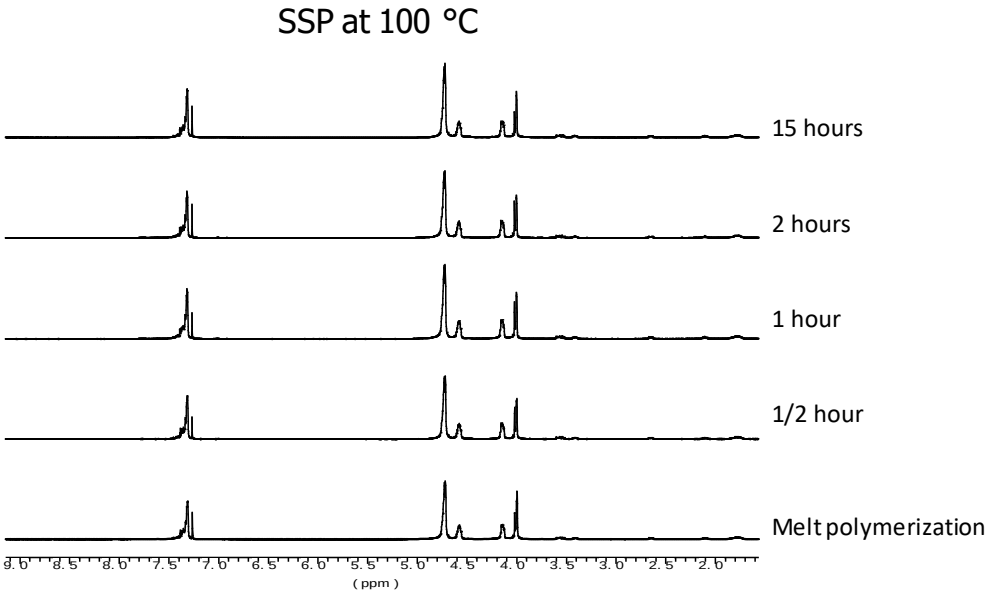


Appendix 2.13. ^{1}H NMR spectrum of polycaprolactam synthesized using taurine as catalyst at 180 °C in bulk.

Chapter 3.



Appendix 3.1. Typical stress vs. strain curve of the thermos-compressed polyethylene furanoate (PEF) film.

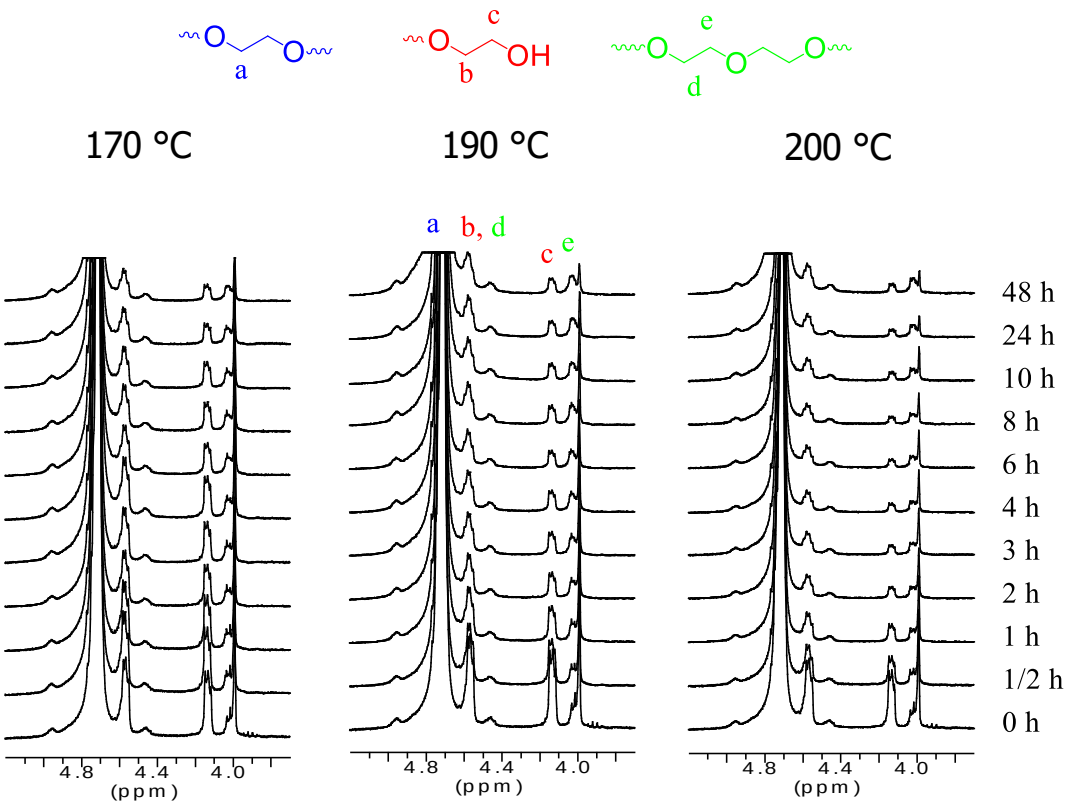


Appendix 3.2. Comparative ^{1}H NMR spectra of polyethylene furanoate (PEF) during the solid-state polycondensation (SSP) at 100 °C.

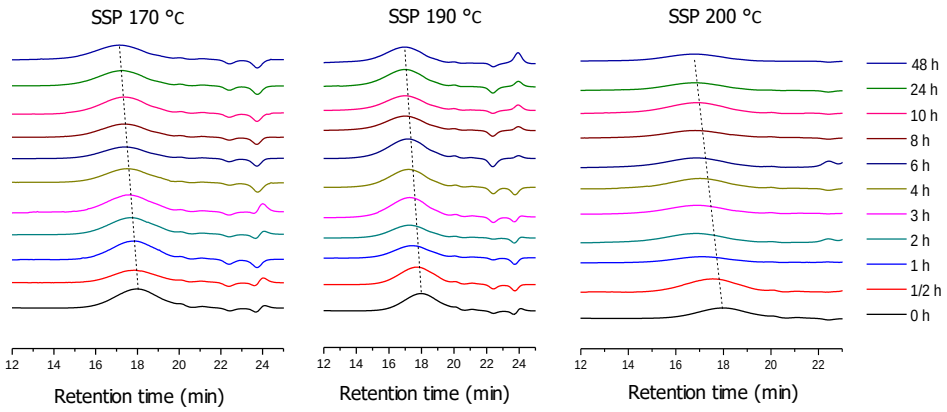
Appendix 3.3. Evolution of the number- and weight-average molecular weight (M_n, M_W) and dispersity (Đ) of polyethylene furanoate (PEF) after solid-state polycondensation (SSP) at different temperatures.

Sample	SSP Temperature									
	170 °C			190 °C			200 °C			
	M_n[a] (g/mol)	M_w[a] (g/mol)	Đ [a]	M_n[a] (g/mol)	M_w[a] (g/mol)	Đ [a]	M_n[a] (g/mol)	M_w[a] (g/mol)	Đ [a]	*Dimer (%)*
PEF Oligomer	3500	8450	2.4	3500	8450	2.4	3500	8450	2.4	1.8
30 min SSP	3850	9000	2.3	5250	10650	2.0	5650	12150	2.1	2.0
1 h SSP	4200	9700	2.4	6350	13200	2.1	7550	16700	2.2	2.0
2 h SSP	4450	10550	2.0	7050	14800	2.1	8350	20500	2.5	2.1
3 h SSP	5750	11360	2.0	7100	15750	2.2	8500	21150	2.6	2.2
4 h SSP	6100	12200	2.1	7450	16300	2.2	8900	22800	2.6	2.0
6 h SSP	6500	13400	2.1	7350	16700	2.3	8900	23450	2.6	2.2
8 h SSP	6500	13750	2.1	8150	19100	2.3	9000	23600	2.6	2.0
10 h SSP	6750	14100	2.1	8200	19500	2.4	9300	25000	2.7	1.9
24 h SSP	7300	15600	2.1	8450	19850	2.3	10600	38750	3.6	1.9
48 h SSP	7550	17500	2.3	9100	24300	2.7	11200	38000	3.4	2.1

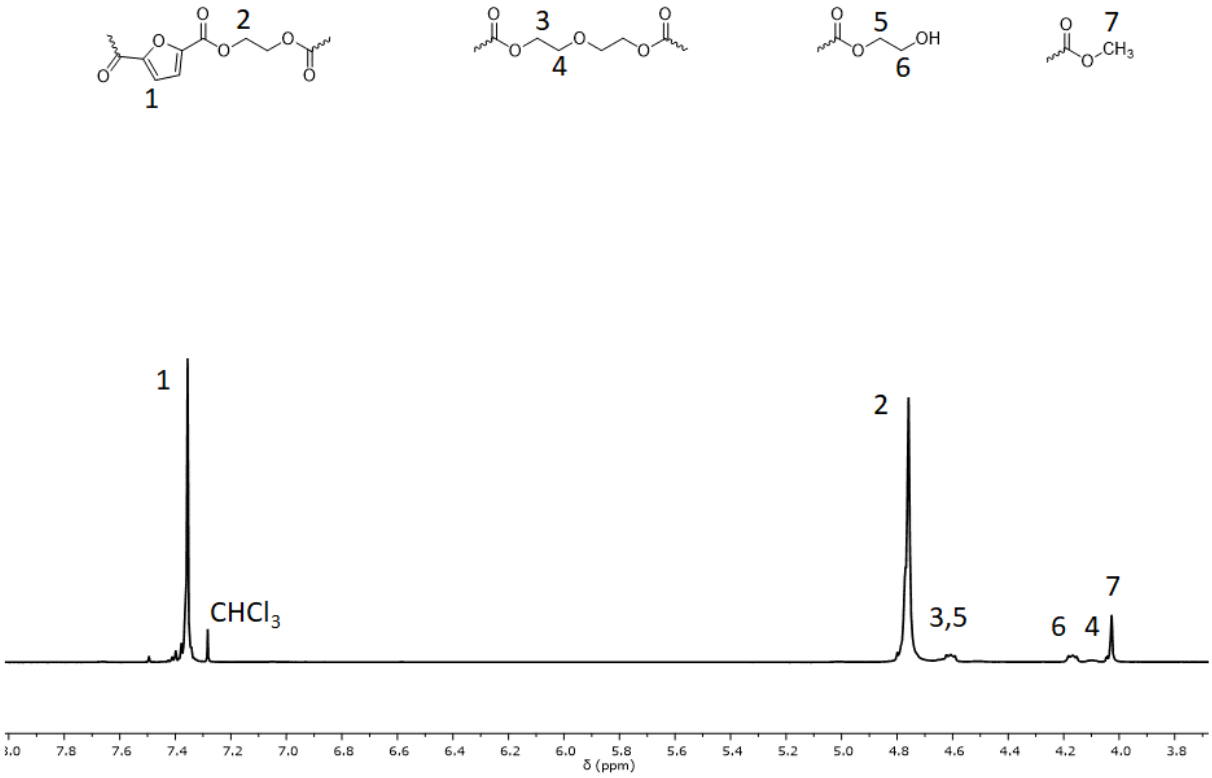
[a] Calculated by size exclusion chromatography (SEC).



Appendix 3.4. Comparative ^{1}H NMR spectra of polyethylene furanoate (PEF) during solid-state polymerization (SSP) at different temperatures.



Appendix 3.5. Comparative SEC chromatograms of polyethylene furanoate (PEF) during solid-state polymerization (SSP) at different temperatures.



Appendix 3.6. Proton nuclear magnetic resonance (^{1}H NMR) spectrum of the synthesis of polyethylene furanoate (PEF).

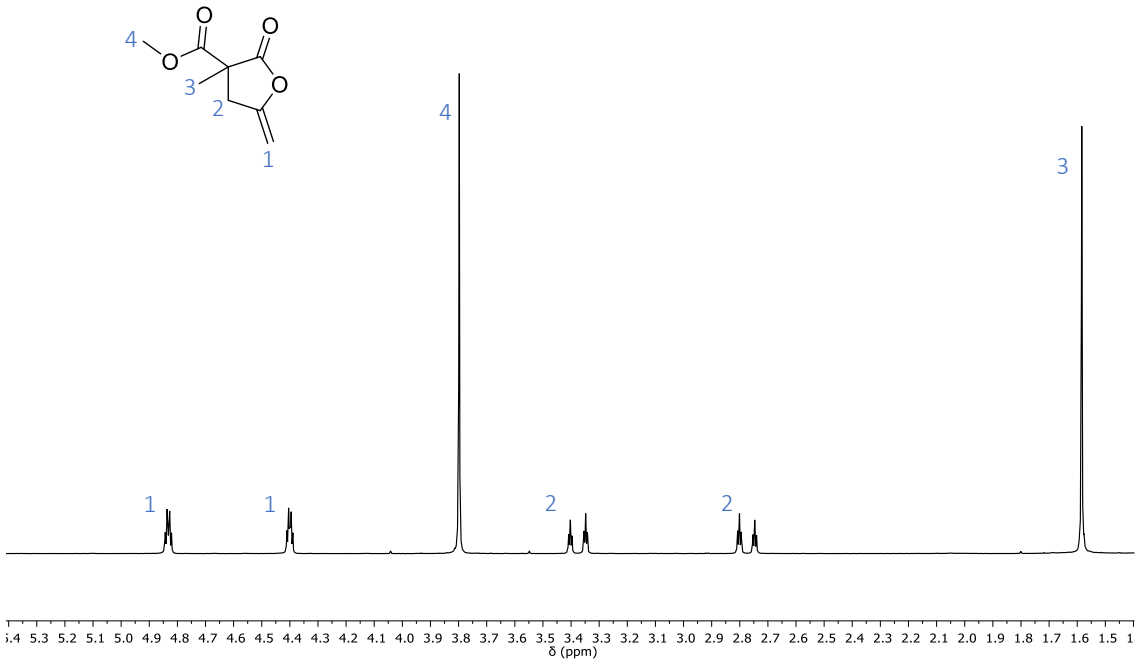
To calculate the dimerization the integral of the signal number 3 was compared with the integral of the signal number 2. In order to calculate the integral of signal number 3 it was integrated the signal that corresponds to 3 and 5 and substracted the value of the integration of signal number 6, that should be the same as the signal 5.

$$H_3 = (H_3 + H_5) - H_6$$

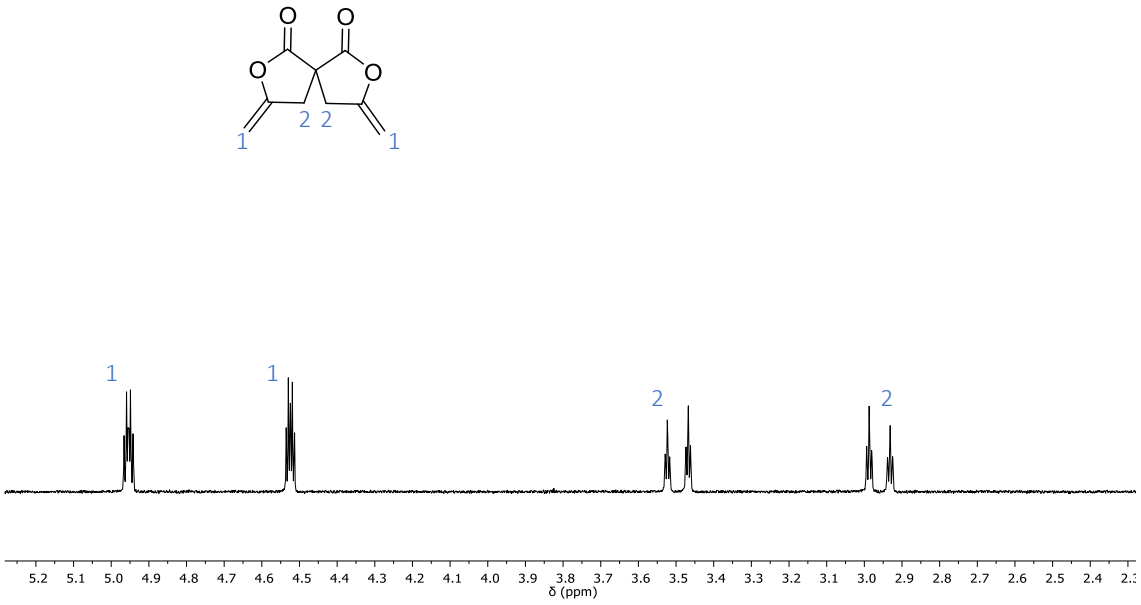
Then, it was compared the integral of signal number 3 with the integral of signal number 2 in order to obtain the dimerization degree (mol-%).

$$dimerization\ \% = {}^{H_3}/_{H_2} * 100$$

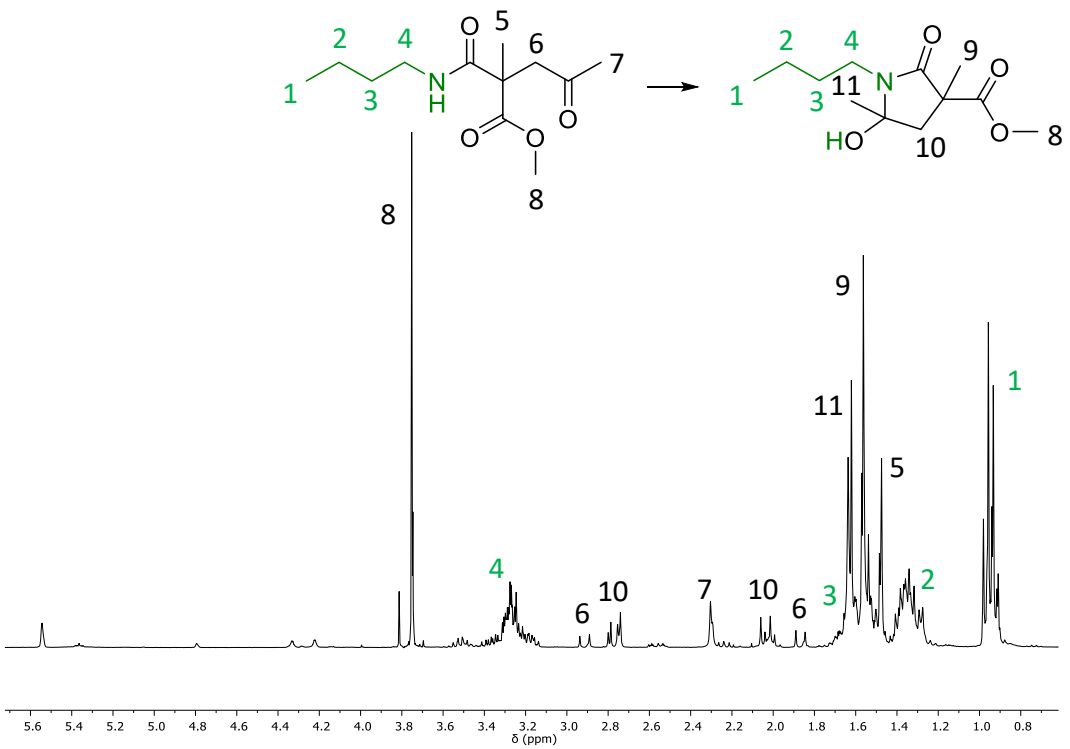
Chapter 5.



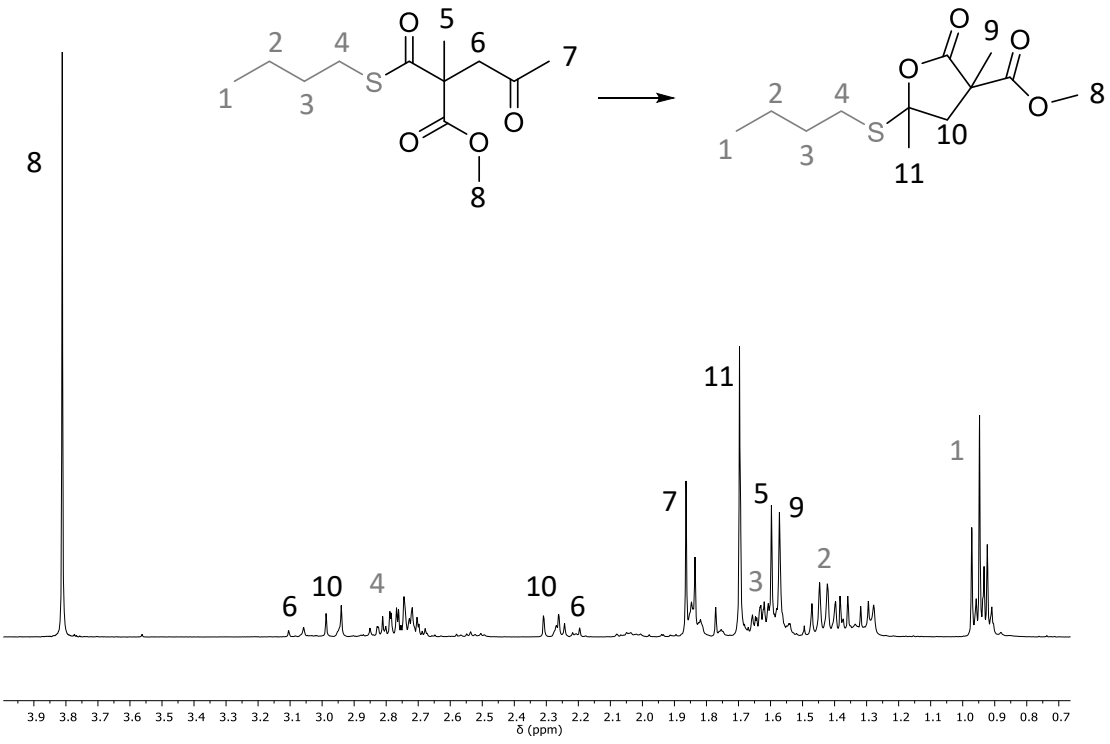
Appendix 5.1. ^{1}H NMR of the synthesized C-ML monomer.



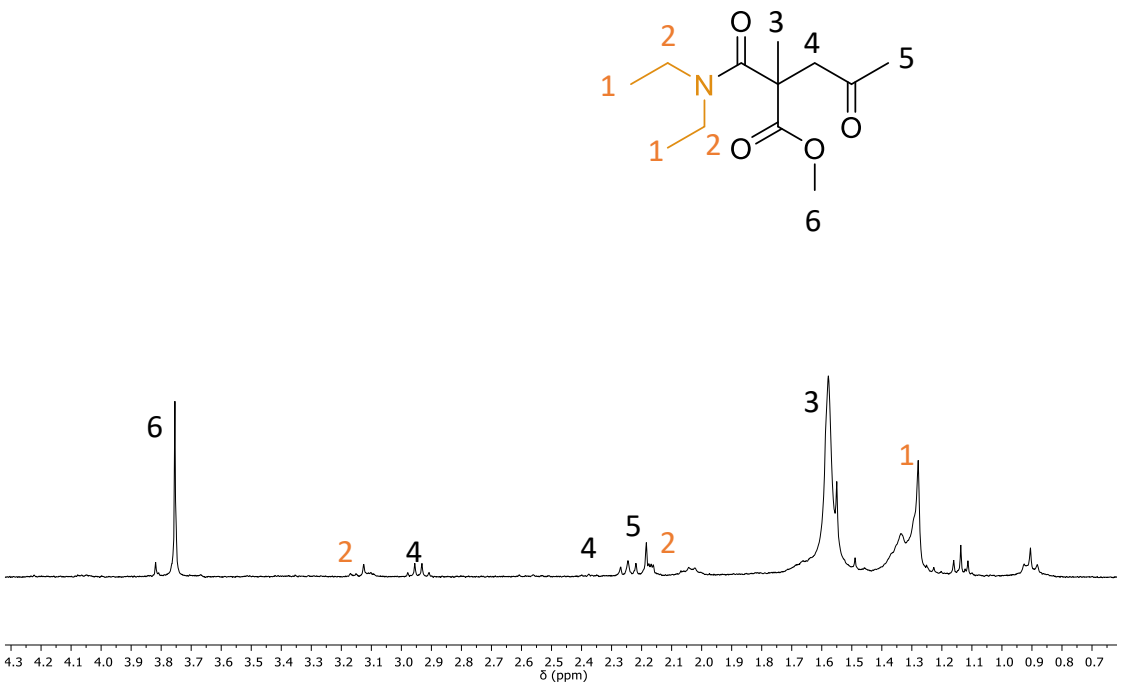
Appendix 5.2. ^{1}H NMR of the synthesized S-DL monomer.



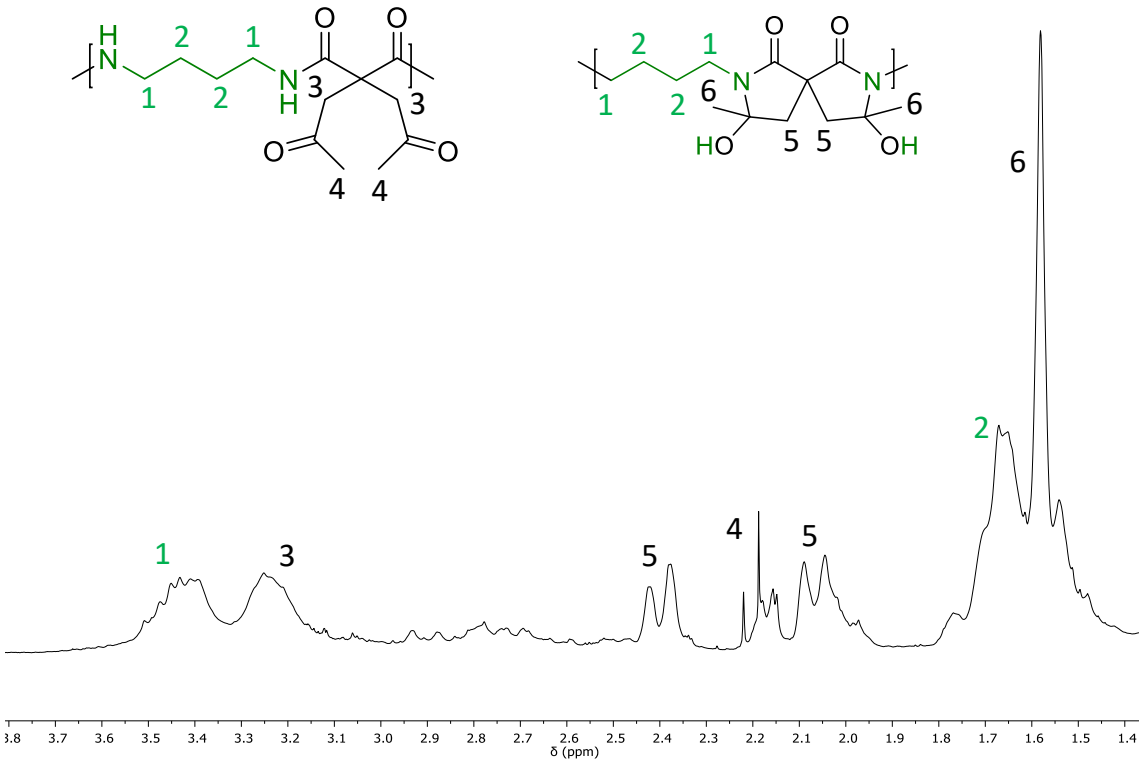
Appendix 5.3. ^{1}H NMR of the ring opened product of C-ML using 1-butylamine as nucleophile.



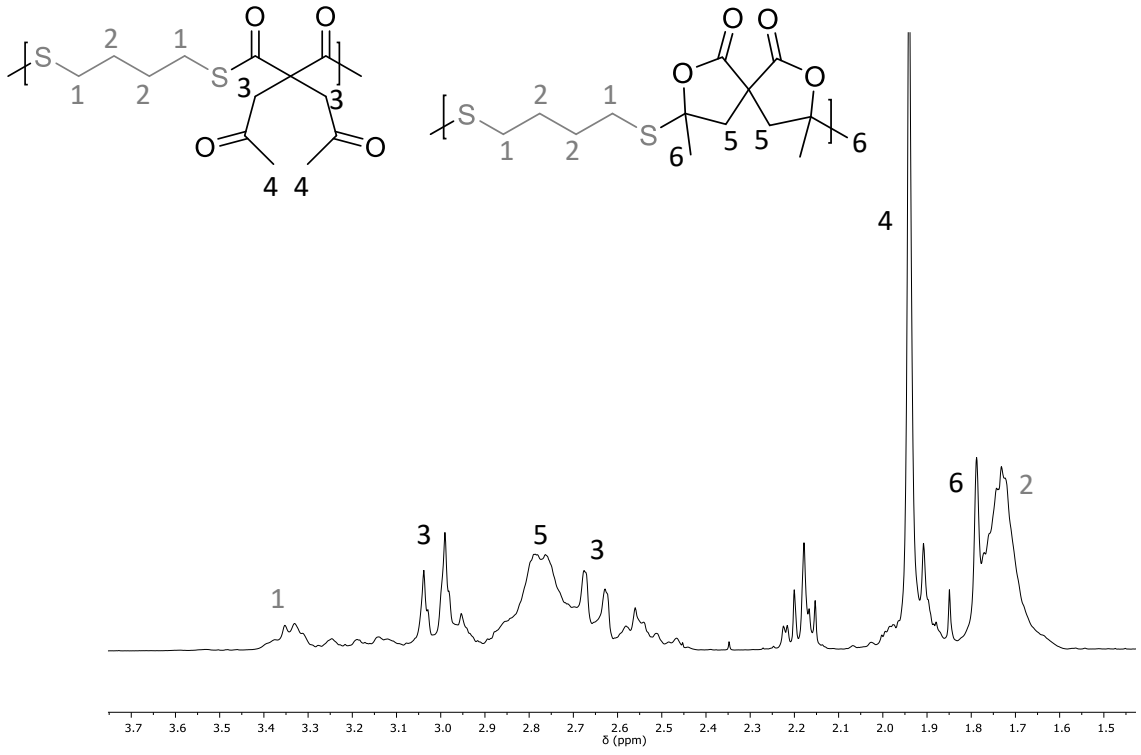
Appendix 5.4. ^{1}H NMR of the ring opened product of C-ML using 1-butanethiol as nucleophile.



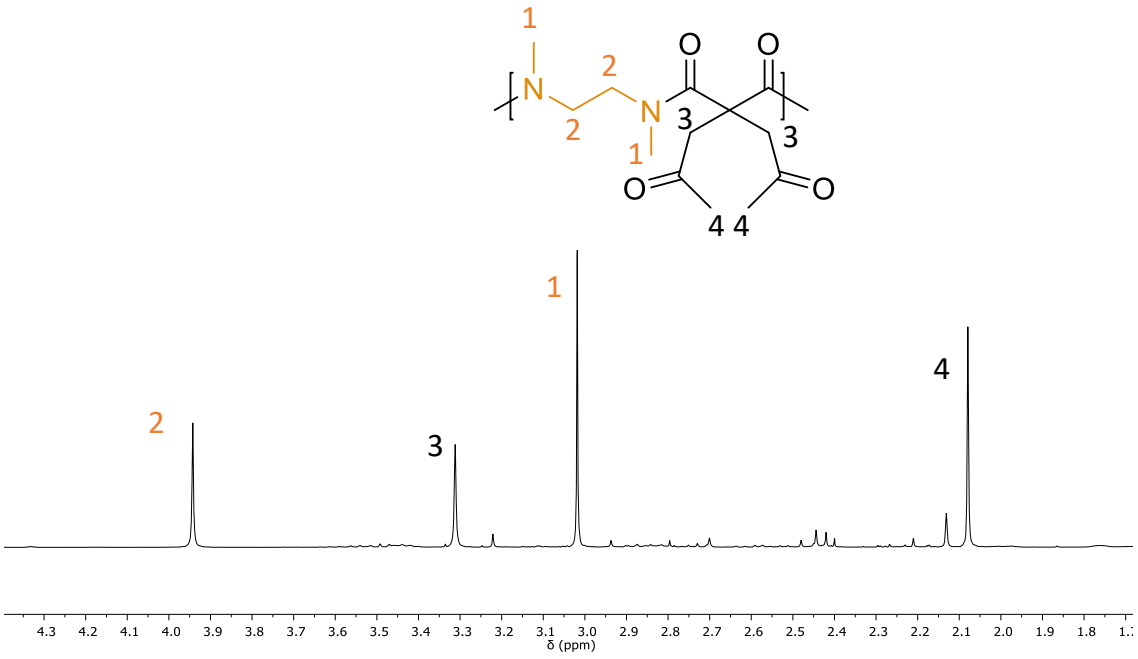
Appendix 5.5. ^{1}H NMR of the ring opened product of C-ML using diethylamine as nucleophile.



Appendix 5.6. ^{1}H NMR of the step-growth polymerization between S-DL and 1,4-butanediamine.



Appendix 5.7. ^{1}H NMR of the step-growth polymerization between S-DL and 1,4-butanedithiol.



Appendix 5.8. ^{1}H NMR of the step-growth polymerization between S-DL and N,N-dimethylethylenediamine.

Poliesterren sintesirako joera berriak: katalizatzaileen diseinutik birziklapen kimikora

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Oharra

Euskaraz idatzirik dagoen zati honetan, ingelesezko zatian azaltzen diren kapitulu batzuk baino ez dira biltzen, 1., 2., 4. eta 6. kapituluak, hain zuzen ere. Bi zatien arteko erlazioa mantendu nahian, kapituluen zenbakiak bere horretan mantentzea erabaki da.

Laburpena

Poliesterrak material interesgarriak dira Nazio Batuek "Garapen Jasangarriko Helburuen" esparruan proposatzen duten jasangarritasun misiorako. Horretarako poliesterrak aukeratzearen oinarrizko arrazoietako bat baldintza egokietan biodegradatzeko ahalmena izateaz gain, birziklatzeko ahalmena eta biomasatik prestatzeko ahalmena ere bada. Polimero hau biomasatik lor daitekeen arren, eta birziklagarritasuna areagotzeko hainbat ahalegin egin diren arren, industrialki ekoitzitako poliester gehienak petrolioan oinarrituta daude, eta erabilitako metodo sintetikoak ez dira behar bezain ekologikoak, Garapen Iraunkorreko Helburuak kontuan hartuta, sintesian trantsizio-metalak eta energia-prozesu intentsiboak erabiltzen baitira.

Polimeroen familia honek eskaintzen dituen aukerak aprobetxatuz, poliester materialen jasangarritasuna eta sintesi-prozesu berdeagoak lortzeko oraindik beharrezkoak diren erronka batzuei heltzen die lan honek.

Gaia testuinguruan kokatzeko, 1. kapituluak poliesterren sintesian egin diren aurrerapenak aurkezten ditu, literaturan aurkitutako azken emaitzak azalduz eta poliester jasangarriak lortzeko aurre egin beharreko erronkak nabarmenduz. Lehenik eta behin, poliesterrak eta haien sintesirako ibilbideak deskribatu dira, eta, ondoren, tesi honetan jorratzen diren hiru erronkak azaldu dira. Alde batetik, katalizatzaile naturalen erabilera; bestetik, petroliotik eratorritako monomeroetatik jatorri biologikoko monomeroetara igarotzea eta, azkenik, poliesterrak baldintza leunetan prestatzea.

2. kapituluak jatorri naturaleko katalizatzaile interesgarri bat proposatzen du industrialki erabiltzen diren baldintzetan L-laktida eraztun irekiera bidez

polimerizatzeko. Erreakzio-tenperatura altuetan polilaktidaren sintesirako katalizatzaile natural desberdinak ikertu dira, eta ondorioztatu da taurina oso eraginkorra den katalizatzaile bat dela, normalean erabiltzen diren katalizatzaileekin konpara litekeena. Emaitza onak lortu zirenez, are gehiago ezaugarritu zen katalizatzaile naturala bere mekanismo katalitikoa ulertzeko, sintetizatutako materialen toxikotasunarekin batera. Gainera, taurina beste monomero batzuen eraztun irekiera polimerizaziorako erabili zen, hala nola, amida ziklikoak eta karbonato ziklikoak polimerizatzeko.

3. eta 4. kapituluetan oinarri biologikoko monomeroak eta polimeroak aplikatzeko bidean aurrera egin da. 3. kapituluan, polietilen furanoatoa (PEF) petrolioan oinarritutako polietilen tereftalatoaren (PET) alternatiba biologiko gisa aurkezten da, zenbait aplikaziotarako PETarekin lehiakorra izan daitezkeen propietate onak baititu. Industria-aplikaziorako egokia izan dadin, ziklo itxiko birziklatze-prozesu bat bizitzaren amaierako ebaluazio jasangarri gisa aztertu zen, termikoki egonkorra den organokatalizatzaile bat erabiliz. 4. kapituluan, polihidroxibutiratoarentzat, mikroorganismoek modu naturalean sintetizatzen duten polimeroarentzat, bizi amaierako aukera bat deskribatu da. Polimeroaren despolimerizazio hidrolitikoa erabiliz β-hidroxiazido monomero interesgarriak lortu dira metodo sinple baten bidez. Despolimerizazio prozesua taurina katalizatzaile moduan erabiliz egin da eta erreakzioaren optimiziazioaren ondoren albo produktuen sorrera % 2ra arte murriztu da.

Tesi honetan proposatutako azken erronkari dagokionez, 5. kapituluan poliesterren giro-tenperaturako sintesirako etapa polimerizatzeko metodo bat aurkezten da. Horretarako, espiro-dilaktona erreaktibo berri baten sintesia egin da, hiru urratseko ibilbide sintetiko baten bidez. Ondoren, diol batekin batera sintetizatutako dilaktonaren polimerizazioa egin da, poliester interesgarriak lortuz giro-tenperaturan poliadizio

erreakzio bidez, DBU organokatalizatzailea erabiliz. Giro-tenperaturan egiten den etorkizun handiko etapa polimerizazio metodo berri honen sintesi aukerak handitzeko, beste nukleofilo batzuk probatu ziren, diaminak eta ditiolak, poliamiden eta poliesterren sintesia gauzatzeko.

Amaitzeko, 6. kapituluak tesi honetan lortutako ondorioak biltzen ditu, poliester polímero eta metodo sintetiko jasangarriak lortzeko hiru erronkari aurre eginez. Horrez gain, prozesu industrialetarako metodo hauek ezartzeko perspektiba bat eskaintzen da, agerian utziz prozedura jasangarrietan ikertzen jarraitzeko beharra dagoela, ekologikoki eta ekonomikoki errentagarriagoa den gizarte bat sortzeko.

Laburduren zerrenda

AcOH	azido azetikoa
BA	azido benzoikoa
BHEF	bis(2-hidroxietil)-furan-2,5-dikarboxilatoa
BHET	bis(2-hidroxietil) tereftalatoa
BINAP-Ru	rutenio 2,2′-bis(difenilfosfino)-1,1′-binaftiloa
bio-EG	oinarri biologikoko etilen glikola
bio-PET	oinarri biologikoko polietilen tereftalatoa
CA	azido krotonikoa
$CDCl_3$	kloroformo deuteratua
C-ML	metil-3-metil-5-metileno-2-oxotetrahidrofuran-3-karboxilatoa
DABCO	1,4-diazabiziklo[2.2.2]oktanoa
DBU	diazabiziklo[5.4.0]undek-7-enoa
DMAP	4-dimetilaminopiridina
DMT	dimetil tereftalatoa
DP	polimerizazio maila
DSC	ekorketako kalorimetria diferentziala
D_2O	ur deuteratua
E	Young-en modulua
E_a	aktibazio energia
EG	etilen glikola
E1	eliminazio unimolekularra
E1cB	base konjukatuko eliminazio unimolekularra
FDCA	azido furan-2,5-dikarboxilikoa
FTIR	fourierren transformatuko espektroskopia infragorria
GHG	berotegi efektua sortzen duen gasa
HBA	azido 3-hidroxibutirikoa
HCl	azido klorhidrikoa

HHA	azido hidroxihexanoikoa
HMF	5-hidroximetilfurfurala
HVA	azido hidroxibalerikoa
H_2SO_4	azido sulfurikoa
LDPE	dentsitate baxuko polietilenoa
LP	limoneno permeabilitatea
MALDI-TOF	matrizaz lagunduriko desortzio ionizazio laserra- hegaldi denbora
MMF	5-metoxi metil furfurala
M_n	zenbakizko batez besteko pisu molekularra
MP	polikondentsazio urtuan
MSA	azido metanosulfunikoa
MT	milioi tona
M_w	masazko batez besteko pisu molekularra
NADH	nikotinamida adenina dinukleotido erreduzitua
NaOH	sodio hidroxidoa
NMR	erresonantzia magnetiko nuklearra
OP	oxigeno permeabilitatea
PBAT	poli(butilen adipato-ko-tereftalato)a
PBS	polibutilen tereftalatoa
PCL	polikaprolaktona
PE	polietilenoa
PEF	polietilen furanoatoa
PET	polietilen tereftalatoa
PHB	polihidroxibutiratoa
PHBH	poli(hidroxibutirato-ko-hidroxihexanoato)a
PHBV	poli(hidroxibutirato-ko-hidroxibalerato)a

PLA	polilaktida
PLA-b-PCL	polilaktida-ko-polikaprolaktona blokezko kopolimeroa
PM	pisu molekularra
PP	polipropilenoa
pTSA	azido p-toluensulfonikoa
PT6HP-co-PγBL	poli(*trans*-hexahidroftalida)-ko-(γ-butirolaktona)
RH	hezetasun erlatiboa
ROP	eraztun irekiera polimerizazioa
RT	giro-tenperatura
S-DL	3,8-dimetileno-2,7-dioxaespiro[4.4]nonane-1,6-diona
SEC	tamaina esklusio kromatografia
SSP	solido egoerako polikondentsazioa
TBD	1,5,7-triazabiziklo[4.4.0]dek-5-enoa
T_{deg}	degradazio tenperatura
TDT	beroa desbideratzeko tenperatura
T_g	beira trantsizio tenperatura
TGA	analisi termograbimetrikoa
T_m	urtze tenperatura
TPA	azido tereftalikoa
$T_{5\%}$	degradazioaren hasierako tenperatura % 5eko masa-galeran neurtua
VST	Vicat leuntze puntua
WVP	ur-lurrunaren permeabilitatea
ΔH_m	urtze entalpia
σ_y	trakzio erresistentzia etekinean
σ_{max}	trakzio erresistentzia maximoa
Đ	sakabanatzea

ε_b	hausturan luzapena
ε_y	etekinean luzapena
X_c	kristalinitate maila

Aurkibidea

1. kapitulua

Sarrera

Plastikoak munduko kontsumo produktu sintetiko ugariena dira, 2018an 359 milioi tona metrikora iritsi zen urteko ekoizpena[1]. Material hauek hainbat aplikaziotarako erabiltzen dira, hala nola ontzi arinetan, eraikuntzan, elektronikan, gailu biomedikoetan eta energiaren biltegiratzean, pisu arina, kostu txikia, prozesagarritasun erraza eta beste hainbat propietate dituztelako. Maila molekularrean, plastikoak monomero kate luzeak dira, eta kate horien mugimenduak eta antolamenduak zehazten dituzte materialen propietateak. Izan ere, propietateak ez dira soilik monomeroen egituretara mugatzen, pisu molekularraren banaketa eta kristaltasuna ere funtsezko faktoreak dira. Abantaila horiek gorabehera, bizitza baliagarriaren amaieran hondakin plastikoen kudeaketak ez du aurrera egin ekoizpenaren erritmo berean; ondorioz, degradatzen ez diren hondakin plastikoen pilaketak eragin negatiboa sortu du ingurumenean, ez bakarrik plastikoen bolumen handiagatik, baita ingurumenean aurkitu daitezkeen mikroplastikoengatik ere.

Plastikoen erabilera jasangaitzaren inguruko kezka geroz eta handiagoa da eta gizartea ahalegin handia egiten ari den arren plastikoaren kontsumoa murrizteko, 10 milioi tona murriztu dira 2017tik hona[1]; plastikoaren ekoizpena handia izaten jarraitzea espero da datozen urteetan. Beraz, plastikoentzat bizitza baliagarria amaitu ondorenerako irtenbideak bilatu behar dira, eta polimero jasangarriak diseinatu eta ekoitzi. Polimero jasangarriak material plastikoak dira non ingurumenean, kontsumitzaileen osasunean eta ekonomian eragin kaltegarririk ez duten sortzen[2]. Polimero jasangarriek honako baldintzak bete behar dituzte a) lehengai berriztagarrien erabilera, b) disolbatzaile organikoen erabilera murriztea, berotegi-efektuko gasen isurketa eta horiek ekoiztean

sortzen diren hondakinak gutxitzeko, c) ekoitzitako plastikoen bizi-amaiera bideragarria.

Europar Batasuneko Ingurumen Batzordea buru-belarri ari da lanean plastiko komertzialen jasangarritasuna areagotzeko politika eta programa espezifikoak aplikatzen, eta ahalegin berezia egiten ari da produktu polimerikoen zirkularitatea hobetzeko eta egungo hondakin-tasak murrizteko. Izan ere, Europar Batasuna plastikoaren egungo ekoizpen linealetik ekoizpen zirkularrerako trantsizioa gidatzen ari da, plastiko berriak fabrikatzeko kalitate handiko iturri gisa plastikozko hondakinak erabiliz[3].

Hala ere, bidea hasi besterik ez da egin; bildutako hondakinen % 23,4ak zabortegian bukatu zuen 2020an, % 42a energia berreskuratzeko erabili zen eta gainerakoa birziklatu egin zen, % 34,6. Joera horrek etorkizun handikoa dirudi, birziklapena % 117 igo baita eta zabortegietan utzitako hondakinak % 46 murriztu baitira 2006tik hona[1]. Zoritxarrez, gaur egun birziklatzen diren plastikoak ia beti mekanikoki birmoldatzen dira erabilera berria emango zaien materialak lortzeko Izan ere, plastikoak sailkatzeko tekniken mugak direla eta, gehigarriak, kutsatzaileak, gaizki sailkatutako polimeroak edo geruza anitzeko produktuak elkartzen dira, hondakin plastikoen birziklatze prozesuetan eta propietateetan kalteak sortzen dituztelarik, hots, lortutako plastiko birziklatuak balio erantsi txikiko aplikazioetan bakarrik erabil daitezkeelarik.

Beraz, birziklatze mekanikoak plastikoak berrerabiltzea ahalbidetzen duen arren, birziklatze prozesua mugatua da, denborarekin materialek hasierako propietateak galtzen baituzte eta ondorioz, ezin dira jatorrizko aplikaziorako erabili. Bestalde, birziklatze mekanikoaren ordez birziklatze kimikoa aplikatu daiteke, polimeroari birziklatze-ziklo amaigabea ematez. Birziklatze metodo honek plastikoa despolimerizatzen du eta ondoren jatorrizko materialaren antzeko propietateak dituen

plastiko berria polimerizatzeko (birziklapena) edo balio erantsiko beste produktu batzuk lortzeko (upcycling) aukera ematen du[4].

Birziklapen kimikoko estrategiei dagokienez, polimero sintetikoak honela sailka daitezke: C-C loturak dituzten polimeroak eta C-N eta C-O loturak dituzten polimeroak[5]. C-O eta C-N loturen bidez lotutako eskeleto heteroatomikoak dituzten polimeroen despolimerizazio erreakzioak (adibidez, PET, poliamidak eta poliuretanoak) nahiko errazak izaten dira, energia askea berezkotik gertu izaten dutelako poliolefinekin alderatuz gero, C-O edo C-N loturak normalean C-C edo C-H loturak baino ahulagoak izaten baitira[5]. Ekoizpen handieneko polimero batzuk, hala nola, polietilenoa (PE) edo polipropilenoa (PP), jatorrizko materialak lortzeko despolimerizatzea oso zaila izaten da, C-C eta C-H lorturak dituztelako eta ondorioz, plastiko horiek energia berreskuratzeko material gisa erabiltzen dira, pirolisi-prozesuan energia kantitate handia sortzen baitute.

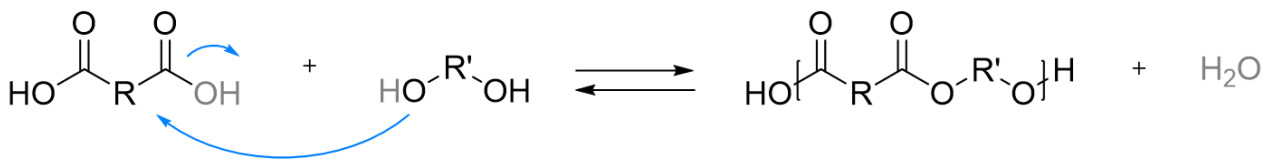
Eskeletoan heteroatomoak dituzten polimeroen C-O eta C-N lotura ahulengatik, C-C eta C-H loturekin alderaturetan baino errazago ematen dira despolimerizazio erreakzioak[5]. Normalean, despolimerizazio erreakzioa talde nukleofilo baten bidez gauzatzen da; nukleofilo horrek karbonilo taldearekin erreakzionatzen du eta horrek katea zatitzea eragiten du. Polimero heteroatomikoak bi despolimerizazio metodo bidez despolimerizatu daitezke, solbolisi bidez, zehazki hidrolisi, alkoholisi edo aminolisi bidez eta despolimerizazio termiko bidez.

Solbolisian disolbatzaileak nukleofilo gisa jarduten du ordezkatze- edo eliminazio-erreakzioak gauzatzeko[6]. Metodo hori erabiltzeak polimeroa despolimerizatzea ahalbidetzen du polimero beraren birsintesia ahalbidetzen duten monomeroetan, baina baita balio erantsi handiko monomeroetan ere[7]. Despolimerizazio termikoa, aldiz, polimero bat monomeroetan despolimerizatzean datza, tenperatura erabiliz[6]. Prozesu

horrek ez du erreaktiborik erabiltzen; hala ere, kasu batzuetan katalizatzaile bat gehitzen da despolimerizazio prozesua hobetzeko.

Heteroatomoak dituzten polimeroen artean poliesterrak dira gehien aztertu direnak eta horien artean polietilen tereftalatoa (PET).

Poliesterrak 1926an aurkitu zituen Wallace Carothersek Ameriketako Estatu Batuetako DuPont enpresako laborategietan. Poliesterrarekin batera, poliamidak ere sintetizatu zituen lehen aldiz Carothersek, polikondentsazio-erreakzioen oinarria ezarriz. Poliesterren kasuan, diazido karboxilikoen eta diolen arteko konbinazioak zuntz sintetikoak ematen zituela erakutsi zuen, inoiz ikusi gabeko propietateekin. Polimero horien izaera itzulgarria ere aztertu zuen, izan ere polimerotik berriro ere monomeroak lortzeko gaitasuna dute poliesterrek, pisu molekular handiko kateak lortzeko arazoak sortzen dituelarik (1.1 irudia)[8].



1.1. irudia. Carothersek aurkitutako poliesterren sintesiaren eskema.

Carothersen lan aitzindariaren ondoren, ikertzaile askok aztertu dituzte poliesterrak, hala nola, polietilen tereftalatoa, 1941ean John Whinfield eta James Dickson zientzialari britainiarrek lehen aldiz sintetizatua. Hainbat propietatetako poliesterrak sortu izan dira, eta beraz, hainbat aplikaziotan erabiltzeko aukera eman dute, hala nola biomedikuntzan, ontzi arinen industrian, eraikuntzan, elektronikan, ehungintzan eta automobilgintzan (1.2 irudia)[8].

1.2. irudia. Poliesterren aplikazio nagusiak.

Polietilen tereftalatoa (PET) gehien ekoizten den poliesterretako bat da, urtero 4,14 milloi tona merkaturatuz Europan. Polimero hau dimetil tereftalatoaren (DMT) eta etilen glikolaren (EG) arteko erreakzioaren bidez sintetizatu ohi da industrialki.

Poliesterrak etapa polimerizazio eta kate polimerizazio bidez presta daitezke, eta bien arteko alde nagusia pisu molekularrean dago. Etapa polimerizazioa monomerotik abiatuta dimeroen sintesiarekin hasten da eta sortutako katearen tamaina handituz doa pisu molekular handiko polimeroak lortu arte. Pisu molekular handiak luzera

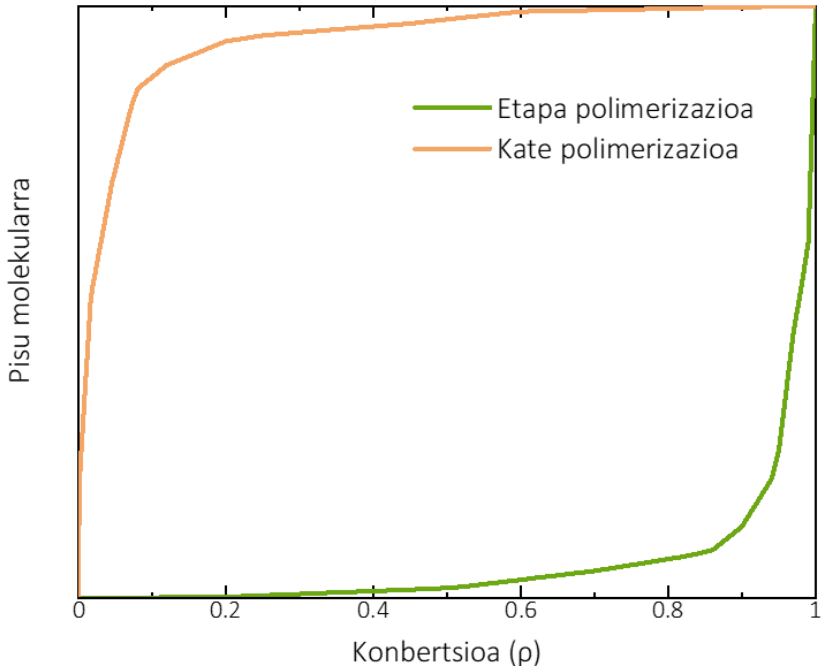
desberdinetako oligomeroen konbinazioaren bidez lortzen dira eta horregatik konbertsio-maila altuak behar dira (1.3 irudia, lerro berdea)[9]. Aipatu bezala, Carothersek polikondentsazio-erreakzioaren printzipioak adierazi zituen, eta konbertsioak polimerizazio-mailarekiko duen mendekotasuna ezarri zuen (1. ekuazioa).

$$X_{n,\ step-growth} = \frac{2}{2-\rho f_{avg}} \qquad (1)$$

Non X_n polimerizazio-maila den, ρ konbertsioa, eta f_{avg} sistemaren batez besteko funtzionaltasuna.

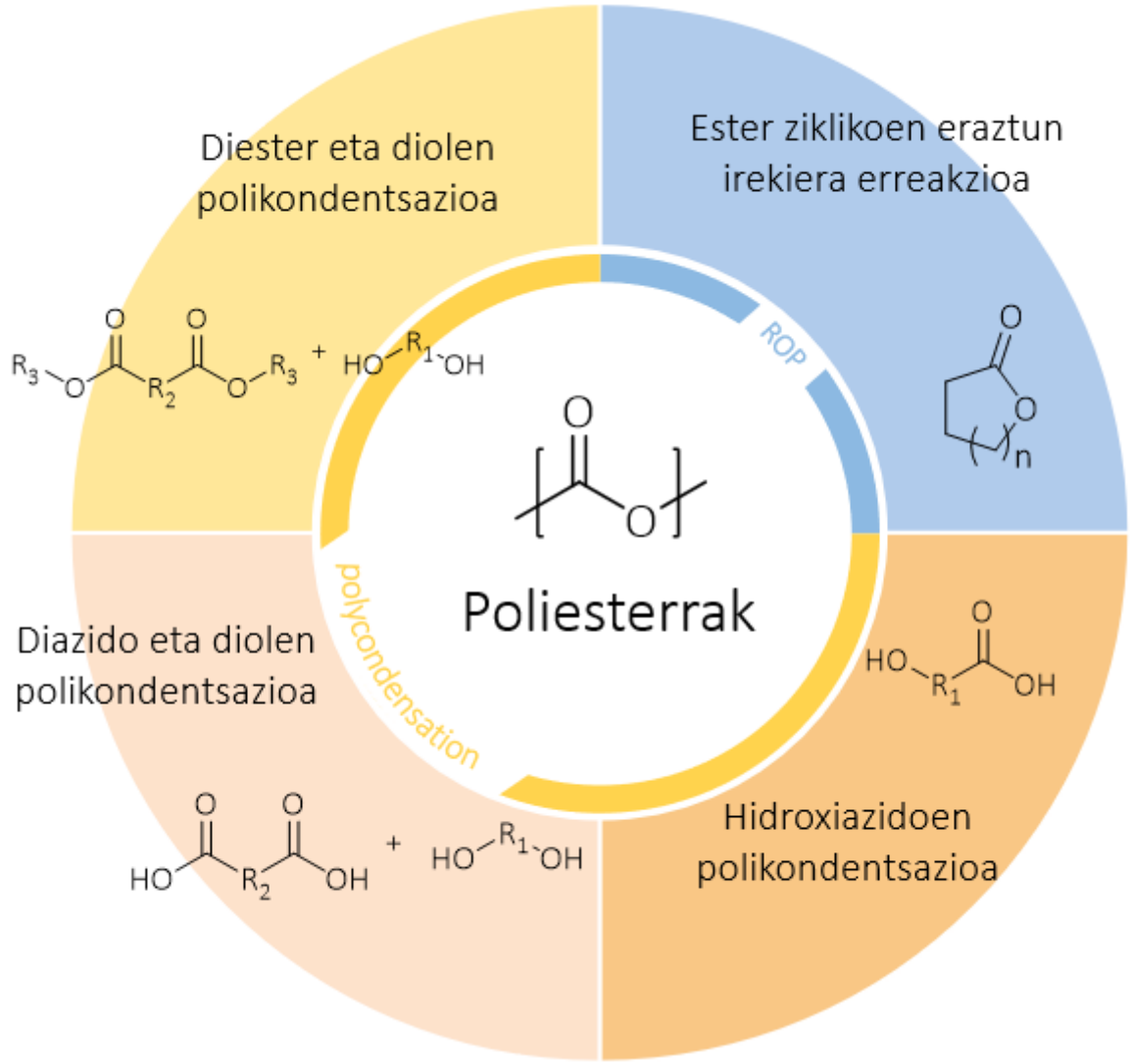
Hala ere, polimerizazio-metodo honen bidez pisu molekular altuak lortzeko polimeroen sintesian baldintza batzuk bete behar dira: a) 2ko monomeroen funtzionaltasuna, 1eko talde funtzionalen arteko estekiometria, albo-erreakzioen murrizketa, erreakzio-konbertsio altuak (% 99,9) eta kondentsatuen deuseztatze eraginkorra, hala nola ura eta metanola[9].

Kate polimerizazioaren kasuan, polimerizazioari hasiera emango dion erreakzioak gertatu behar du, normalean haztarazle baten laguntzaz, non bitarteko erreaktiboa eratzen den. Gero, hedatzea deritzona gertatzen da, bertan bitarteko erreaktiboak monomeroari eraso egingo dio eta espezie aktibo berria sortuko du, horrela monomeroa etengabe gehituz. Pisu molekularra kateari monomeroa gehituz handitzen da, eta ez hainbat kateren konbinazioaren bidez; horrek pisu molekularraren sakabanaketa baxua izatea eragiten du. Kasu horretan, pisu molekularra erreakzioaren hasieratik handitzen da (1.3 irudia, lerro laranja)[9].



1.3. irudia. Pisu molekularra konbertsioaren aurrean polimerizazio-metodo desberdinentzat: etapa polimerizazioa eta kate polimerizazioa.

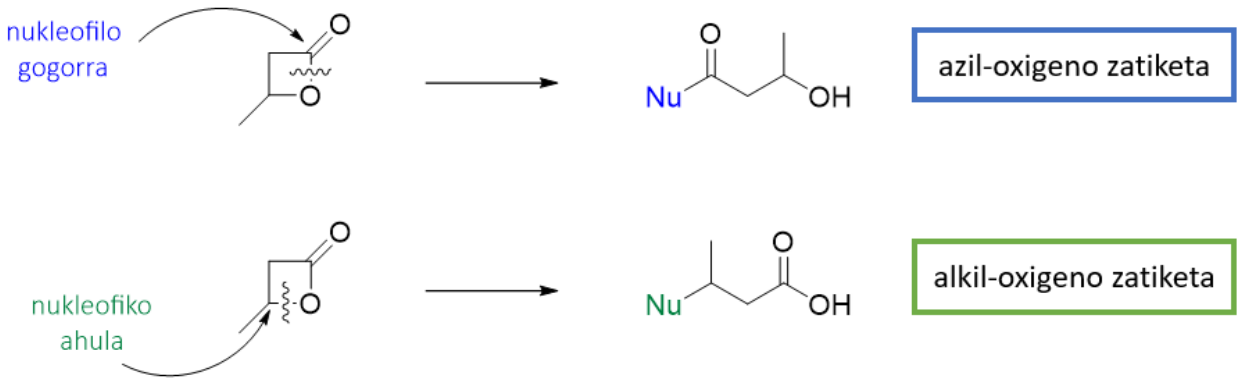
Poliesterraren sintesirako kate polimerizazioa erabiltzen denean, ester ziklikoen eraztun irekiera polimerizazioa (ingelesez ring-opening polymerization (ROP)) da erabilitako bidea (1.4 irudia)[10-12].



1.4. irudia. Poliesterren sintesi-metodo nagusien irudikapen grafikoa.

Eraztun irekiera bidezko monomero ziklikoen polimerizazioak arreta handia erakarri du, pisu molekular (PM) handiko poliesterrak lortzeko metodo erraza baita. ROPan monomeroa kate aktiboaren muturrera gehituz doa eta polimerizazioa bi modutan eman daiteke: azil-oxigeno edo alkil-oxigeno apurketa bidez (1.5 irudia)[13]. Hainbat poliester sintetizatzen dira ROP bidez, hala nola, polilaktida (PLA) eta polikaprolaktona (PCL). Polimerizazio metodo honen abantaila nagusia polimero ongi definituak, sakabanatze baxuekin eta PM altuekin lortzeko aukera dagoela da. Hala ere, polimerizazioa aurrera emateko monomero ziklikoak behar direnez, ROP bidez

polimerizagarriak diren monomeroetara mugatzen da prozesua[10-12,14-16]. Gainera, kasu askotan, monomero ziklikoa prestatzea ez da erraza eta hainbat urratsetako sintesi konplexua behar da egitura ziklikoak lortzeko.



1.5. irudia. Kate polimerizazioa azil-oxigeno edo alkil-oxigeno zatiketa erabiliz.

Kate polimerizazioaz gain, poliesterrak etapa polimerizazio bidez ere presta daitezke. Etapa polimerizazioan hiru metodo nagusi erabil daitezke: diazidoen eta diolen arteko polikondentsazioa, diesterren eta diolen arteko polikondentsazioa eta hidroxiazidoen polikondentsazioa (1.4 irudia). Diolen eta diazido edo diesterren arteko polikondentsazioa da poliesterrak ekoizteko industrian gehien ikertu den ibilbidea. Metodo horren abantaila nagusia monomero horien aukera zabala dagoela da, ziklazio-etapa gehigarririk behar izan gabe, eta, horren ondorioz, prozesua ekonomikoki eskuragarriagoa eta azkarragoa da. Hala ere, desabantaila batzuk ere baditu. Adibidez, prozesu honek polimerizazio-baldintza gogorrak eskatzen ditu, hala nola tenperatura altuak, kondentsatua ezabatzeko hutsunea egitea eta PM altuak lortzeko estekiometriaren kontrol bikaina[9-12].

Aipatutako bi polikondentsazio moduez gain, poliesterrak hidroxiazidoen polikondentsazioaren bidez ere lor daitezke. Metodo honen abantaila nagusia diazidoen eta diolen edo diesterren eta diolen arteko polikondentsazioarekin

alderatuta estekiometria ez dela kontrolatu behar da. Beraz, polimerizazio baldintza egokiak aukeratuta, hau da, tenperatura ondo kontrolatua, errendimendu handiko katalizatzaile batekin eta hutsunepean, PM altuak lor daitezke[17].

Lehen azaldu bezala, poliesterrak polimero idealak dira despolimerizaziorako, nukleofiloek ester lotura erraz aktiba dezaketelako. Poliesterraren arabera, hainbat bide erabil daitezke: solbolisi bidezko despolimerizazioa edo ester zikliko monomeroa lortzeko despolimerizazioa. Jehanno et al.-ek PET polimeroa glikolisi bidez despolimerizatu zuten, non etilen glikol monomeroak polimeroaren esterrari erasotzen dion, loturaren haustura sortuz[18]. Ondorioz, bis(2-hidroxietil) tereftalato monomeroa eratzen da (BHET), ziklo itxiko birziklatze-prozesu batean PET polimeroa birpolimerizatzea ahalbidetuko duena edo balio erantsiko monomeroen sorrera (*upcycling)*. Sangroniz et al.-ek beste estrategia bat erabili zuten poli(trans-hexahidroftalida)-ko-(γ-butirolaktona) (PT6HP-co-BL) kimikoki despolimerizatzeko[19]. Kasu horretan, kopolimeroaren sintesirako erabili ziren monomeroak ester ziklikoak ziren eta, beraz, ester ziklikoak lortzeko despolimerizazio kimikoa egin ahal izan zen. Horretarako, $ZnCl_2$ katalizatzailea erabili zen % 2ko kantitatean, toluenotan, 120 °C-an eta 60 orduko erreakzio-denbora utziz, amaieran jatorrizko ester ziklikoak, trans-hexahidroftalida eta γ-butirolaktona lortu ziren.

Ikerketa-proiektu askok poliester berrien garapenean jarri dute funtsa eta ondorioz, poliester jasangarrien ekoizpena asko hobetu da, ingurumena gehiago errespetatuz[20]. Nazio Batuek bultzatutako "Garapen Jasangarriko Helburuak" misioak dituen 17 helburuen artean, plastikoekin lotura handia duen helburu bat du, 12. helburua "Kontsumo eta ekoizpen eredu jasangarriak bermatzea"[21]. Helburu horrek gizartean iturri naturalen kudeaketa iraunkorra eta erabilera eraginkorra sustatuko ditu, baita hondakinen gutxitzea ere, besteak beste, prebentzioaren, murrizketaren,

birziklatzearen eta berrerabiltzearen bidez. Gaur egun, gehien ekoizten diren poliesterrak ez dira jasangarriak.

1.1. Naturan inspiratutako katalizatzaileak

Poliesterren sintesirako erabilitako sintesi-bidea edozein dela ere, tenperatura altuak behar dira polimerizazioa gerta dadin, 150 eta 300 °C artekoak, eta horrek egonkortasun termiko handiko katalizatzailea eskatzen du[22]. Industrian katalizatzaile metalikoak erabiltzen dira, hala nola, eztainu (II) oktoatoa, titanio (IV) tetrabutoxidoa eta aluminiozko eta zinkezko konplexuak. Katalizatzaile metalikeok selektibitate handia erakusten dute, oso eraginkorrak dira eta kantitate baxuak eskatzen dituzte. Hala ere, katalizatzaile hauen arazoa ingurumen- eta ekonomia-kostu handia dakartela da; iragarpen batzuen arabera, metal batzuk desagertzeko arriskuan egon litezke datozen hamarkadetan, kobaltoa eta magnesioa, adibidez[23]. Gainera, horietako batzuk toxikoak dira eta koordinazio-gaitasuna dutenez materiala garbitzeko etapa baten bidez ezabatzea ezinezkoa da, hori dela eta, aplikazio biomediko eta baita elektronikoetan ere arazoak eragiten dituzte, birziklatze-prozesuan zailtasunak sortzearekin batera[24].

Organokatalisia poliesterren sintesirako sistema katalitiko eraginkor gisa sortu da; izan ere, aldakortasuna eta selektibitate handia erakusten du eta gainera, erreakzio-ingurunetik kentzeko aukera ematen du, garbiketa-etapa baten bidez[9,25,26]. Hala ere, azido eta base organiko ohikoenek, hala nola, azido metanosulfonikoak (MSA), triazabiziklodezenoak (TBD), diazabiziklo[5.4.0]undek-7-enoak (DBU) eta 4-dimetilaminopiridinak (DMAP), egonkortasun termiko txikia erakusten dute (50-110 °C), hori dela eta, ez dira egokiak polimerizaziorako[18,27]. Egonkortasun termiko baxuaren arazoa gainditzeko asmoz, azido-base nahasketa estekiometrikoak eta ez-estekiometrikoak aztertu dira, azidoaren eta basearen arteko protoi-transferentziak konposatuen egonkortasuna nabarmen handitzen duela ikusi baitzen. Adibidez,

TBD:MSA, DBU:BA eta DMAP:MSA gatzak beren osagaiak baino askoz egonkorragoak dira eta 300 °C-ko egonkortasun termikoa lortzen dute zenbait kasutan[27-29]. Katalizatzaile horiek oso egokiak dira poliesterren polimerizazio-erreakzioetarako, ROP bidez, L-laktidaren polimerizaziorako eta polikondentsazio bidez, PETaren sintesirako, dimetil tereftalatoa (DMT) eta etilen glikola (EG) erabiliz monomero gisa[30]. Lehen aipatu moduan, organokatalizatzaileen abantailetako bat erreakzio-ingurunetik kentzeko aukera da, ingurumenean eta bizidunetan eragin kaltegarririk ez izateko. Hala ere, arazketa-prozedura baten beharrak urrats gehigarri bat eskatzen du ekoizpen-sisteman, prozesuaren kostua nabarmen handituz, azidoaren eta baseen prezio altuekin batera. Horregatik, toxikoak ez diren organokatalizatzaileak izan litezke aukerarik oparoena, erreakzioaren ondoren ingurunetik kendu beharrik ez izateko, ez bailukete inolako ondorio kaltegarririk eragingo.

Entzimek polimerizazio-erreakzioak eta funtzionalizazio-erreakzioak modu eraginkorrean kataliza ditzaketela ikusi izan da eta sintesi kimikoaren aurrean abantaila nagusia katalizatzailearen iraunkortasuna da, haren espezifikotasunarekin eta polimerizazio-prozesurako baldintza gogorren deusezatzearekin batera[31]. Hala ere, polimerizazio-erreakzioak muturreko baldintzak eskatzen dituenean, hala nola pH-aren baldintza gogorrak edo 40-50 °C-tik gorako tenperaturak, entzimen jardueraren murriztea edo desnaturalizazio prozesua emango lirateke. Aminoazidoen kasuan, aldiz, frogatu da oso erresistenteak direla tenperaturaren aurrean eta aztertutako kasu gehienetan 200 °C-tik gorako degradazio-tenperaturak erakusten dituzte[32,33].

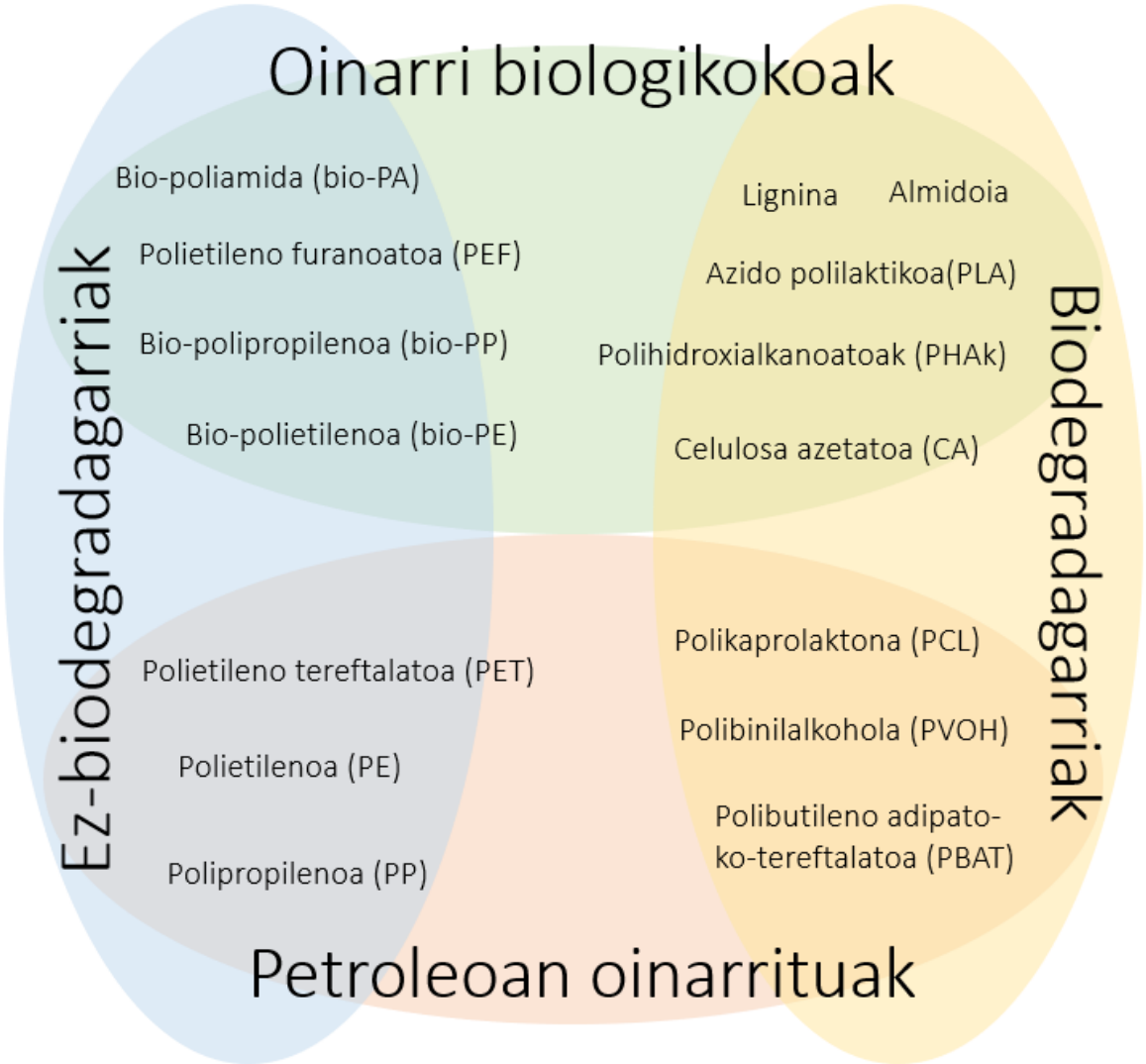
Aminoazidoak erreakzio polimerikoak katalizatzeko asko erabili ez diren arren, ikertzaile batzuek beren katalizatzaileen aitzindari gisa erabili dituzte. Sanchez-Sanchez et al.-ek dentsitate altuko taldeen bidez ordezkatu zuten L-prolina eta DBUrekin konbinatuz estereokontrol handiko rac-laktidaren polimerizazioa gauzatu zuten[34]. He et al.-ek ere

PLA sintetizatu zuten, eztainuzko aminoazido konplexuak erabiliz eta pisu molekular handiko eta ondo kontrolatutako polimeroak lortuz[35]. Konplexu horiek errendimendu handia erakutsi badute ere, haien kostu handiak ez ditu erabilgarriak egiten polimeroen ekoizpen-prozesuetarako eta ondorioz, aminoazidoen erabilera zuzena industrialki askoz interesgarriagoa izan daitekeela uste da. Aminoazioen egituran talde azidoak eta basikoak daudenez eta termikoki oso egonkorrak direnez, poliesterren polimerizaziorako eraginkorrak izango direla espero da, azido-base gatzen antzera funtziona dezaketela pentsa baitaiteke. Gainera, giza gorputzean aurki daitezkeenez, ez direla toxikoak izango edo toxikotasun txikia izango dutela uste da, sintetizatutako materialak garbitzeko beharra saihestuz.

1.2. Petroliotik eratorritako monomeroetatik biomasatik egindako monomeroetara

Garrantzi industriala duten polimero gehienak petrolioan oinarrituta daude; monomeroak petroliotik findu eta polimerizazioetarako erabiltzen dira. Fintzeko prozesuan baldintza gogorrak erabiltzen dira, hala nola tenperatura eta presio altuak eta, gainera, atmosferara gas kaltegarriak askatzen dira, metanoa eta karbono dioxidoa, besteak beste, klima-aldaketaren erantzule direnak. Joera hori aldatzen saiatzeko, oinarri biologikoa duten polimeroak sortu dira eta horien interes industriala handitzen hasi da, batez ere erabilera bakarreko aplikazioetarako. Oinarri biologikoko polimeroak bi modutakoak izan daitezke, batetik modu naturalean sortutakoak, normalean mikroorganismoen bidez, eta bestetik, polimeroak prestatzeko erabiltzen diren monomeroak naturan aurki daitezke, adibidez azido polilaktikoa (PLA), poliester oso ezaguna sintetizatzeko azido laktiko monomeroa landareetan eta esne garratzean aurki daiteke. Gainera, PLA material biodegradagarrien multzoan ere sailka daiteke, horrek balio gehigarria ematenik polimeroari[36].

Polimero biodegradagarriak erabat hondatzen eta degradatzen dira mikroorganismoen eraginpean jartzen direnean eta azpiproduktu naturalak sortzen dira, hala nola gasak (CO_2 eta N_2), ura eta biomasa. Prozesu hau oso interesgarria da iraunkortasunaren ikuspegitik, polimeroa lurrera itzuliko baita bizitza baliagarriaren aldia amaitutakoan eta ondorioz, tratatu beharreko hondakin kopurua murriztuko da. Polimero biodegradagarrien jatorria askotarikoa izan daiteke, oinarri biologikoa duten polimeroak edo petrolioan oinarrituak izan daitezke (1.6 irudia)[38].



1.6. irudia. Ohiko polimeroen sailkapena, oinarri biologikokoak, petrolioan oinarrituak, biodegradagarriak eta ez-biodegradagarriak taldeetan.

Aipatu bezala, ontziratze industrian gehien erabiltzen den plastikoetako bat polietilen tereftalatoa (PET) da[1] eta batez ere bi metodoren bidez sintetizatzen da: etilen glikolaren eta azido tereftalatoaren arteko poliesterifikazio bidez edo etilen glikolaren eta dimetiltereftalatoaren arteko transesterifikazioaz[39,40]. Erabilitako sintesi-prozesua edozein dela ere, beharrezko monomeroak petrolio-jatorrikoak dira, baina, neurri batean, PET bio-oinarritua lortu daiteke, etilen glikola baliabide naturaletatik lor baitaiteke. Hala ere, beste monomeroa, azido tereftalikoa, ezin da prozesu ekologiko baten bidez lortu. Beraz, oinarri biologikoa duten monomero alternatiboak aurkitzeko beharra ikusi da polimero jasangarrien sintesirako[41,42].

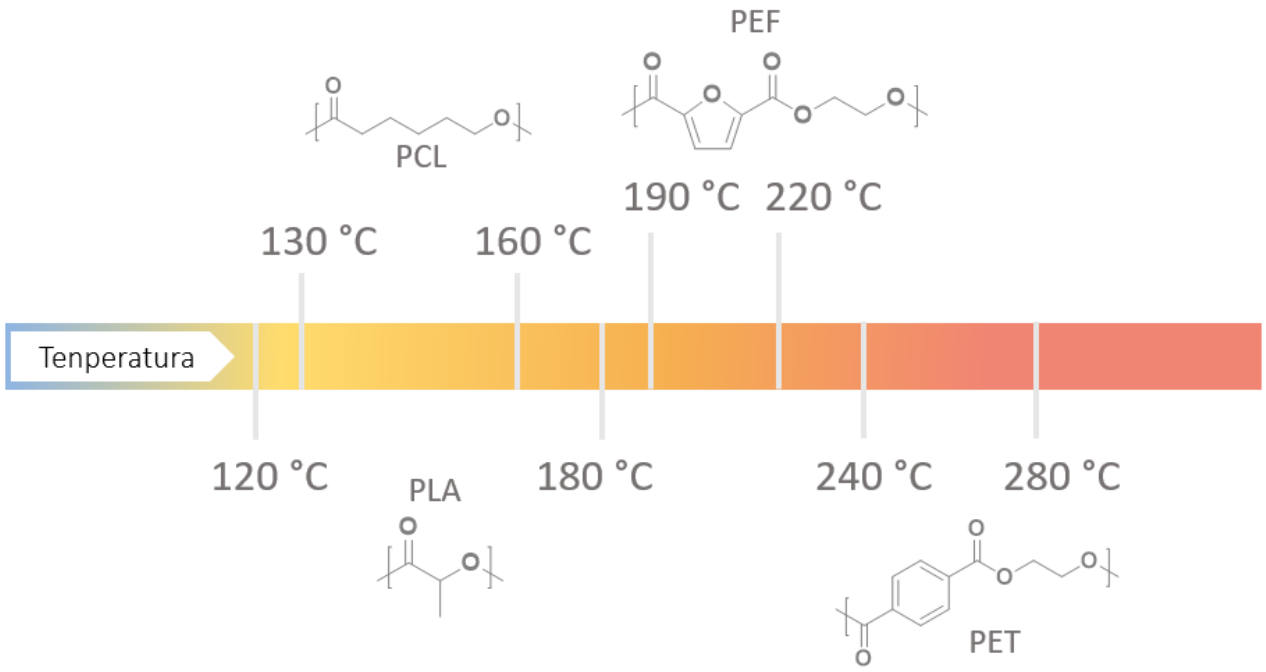
Azido furandikarboxilikoa petroliotik eratorritako azido tereftalikoaren oinarri biologikoko ordezko monomeroa izan daitekeela uste da. Konposatu jasangarri hau azukretik eratorritako konposatu bat da, etilen glikolarekin batera polietilen furanoato (PEF) polimeroa sintetizatu dezakeena. Literaturaren arabera, PETaren ordez PEF polimeroa erabiltzeak sintesi-prozesuaren kostu energetikoa murriztuko luke, atmosferara gas kaltegarrien isurtzea gutxitzearekin batera[43].

Interesa erakartzen ari den beste oinarri biologikoko polimero bat polihidroxibutiratoa da (PHB). Polimero honek garraio propietate bikainak erakusten ditu eta gainera, poliester alifatiko gehienak bezala, biodegradagarria da lurrean eta uretan, eta horrek interesgarri egiten du, batez ere erabilera bakarreko aplikazioetarako, adibidez, ontzi arinetarako[44]. Hala ere, PHBren eragozpen nagusia garestia dela da, petrolioan oinarritutako polimero konbentzionalak baino garestiagoa eta ondorioz, erabilera bakarreko aplikazioetarako polimero hau errentagarri bihurtzeko aukera bat berrerabiltzea da. Hala ere, PHBren kasuan, birziklatze mekanikoa ez da posible, alde txikia baitago urtze-tenperaturaren (Tm) (170-180 °C) eta degradazio-tenperaturaren (200-220 °C) artean[45-48]; beraz, birziklatze mekanikoak nabarmen degradatzen du

polimeroa. Tenperatura-mugak direla eta, badirudi birziklapen kimikoa dela prozesurik eraginkorrena PHBren bizitza baliagarriaren amaiera ebaluatzeko. Orokorrean poliesterrentzako erabil daitezkeen birziklapen kimikoko hainbat mekanismo aplika daitezke, hala nola hidrolisia eta alkoholisia. Hidrolisi bidez hidroxiazido monomero interesgarriak lortuko lirateke, hainbat alorretan aplikazio ugari dituztenak, kosmetika, farmazia eta elikadura industrian besteak beste. Kosmetikan, hidroxiazidoak azaleko hainbat gaixotasun tratatzeko erabiltzen dira, horien artean, fotozahartzea, aknea, pigmentazioaren nahasmenduak eta psoriasia. Era berean, garrantzi farmazeutikoa duten konposatu kiral ugari sintetizatzeko lehen gaia dira, adibidez, azido mandelikoa, zein agente antitumoralen, obetsitatearen aurkako agenteen, penizilina erdisintetikoaren eta zefalosporinaren sintesian erabiltzen den[17].

1.3. Energia kostu handiko polimerizazioetatik giro-tenperatura erreakzioetara

Lehen adierazi moduan, masan egiten diren poliester industrial konbentzionalen sintesiak erreakzio tenperatura altuak eskatzen ditu (1.7 irudia). Horrek mugatu egiten du material horien aplikazioa, izan ere, askotan tenperatura baxuak behar izaten dira, hala nola, estaldura eta itsasgarriak sortzeko. Gehien ekoizten diren poliesterrak polikondentsazio-erreakzio bidez sintetizatzen dira eta tenperatura altuak eta hutsunea behar dituzte pisu molekular handiak lortzeko; adibidez, PETak 240-280 °C behar ditu polimerizazioa emateko[49].



1.7. irudia. Poliester ezagunenen polimerizazio-tenperaturak.

Hirabayashi et al.-ek giro-tenperaturan sintetizatutako poliesterren berri eman zuten azido dikarboxilikoaren eta diolen polikondentsazio-erreakzioaren bidez, eskandioan oinarritutako katalizatzaileak erabiliz[50]. Katalizatzaile horiek polikondentsazio-erreakzioak sustatzeko gai dira, hidrolisi-konstante txikia dutelako eta konposatu protikoekiko sentiberatasunik ez dutelako. Hala ere, lurrean arraroak diren metaletan oinarrituta daudenez, ezin dira eskala handian erabili, eta ondorioz, zaila da metodo hori ezartzea eskala handiko poliesterren sintesirako.

Giro-tenperaturan poliesterren polikondentsazio bidezko sintesia organokatalizatzaileak erabiliz egitea erronka handia dela onartu da, izan ere, lotura-sorkuntza bakoitzean askatzen diren uraren edo beste molekula txiki batzuen presentziak desaktibatu egingo ditu. Horregatik, ikertzaile batzuk giro-tenperaturan polimeroen sintesia ikertzen saiatu dira eraztun irekiera polimerizazio metodoa erabiliz.

Lu et al.-ek giro-tenperaturan poliesterren sintesia gauzatzeko metodo bat deskribatu zuten, tioanhidrido sukzinikoaren eta propileno sulfuroaren eraztun irekiera kopolimerizazioaren bidez[51]. Polimerizazio erreakzioa hasteko eta katalizatzeko, base organiko bat, DBU, erabili zen; hala ere, ordubeteko erreakzioaren ondoren, konbertsio txikiak lortzen zirela ikusi zen. Polimerizazioa hobetzeko, amonio-gatz batekin ordezkatu zen DBU, bis(trifenilfosfina) iminioarekin, ordubetean % 100eko konbertsioa emanez. Polimeroaren sintesia arrakastaz sustatzen bada ere, poliester hori hasierako monomeroetan despolimerizatzea ez da erraza, tentsio oso handian dauden 3 kideko propileno-sulfuroa ez baita erraz ixten.

Lu et al.-ek tentsio handia duten monomeroen despolimerizazio arazoa konpontzeko bide interesgarri bat proposatu zuten[52]. Lau kideko tioester ziklikoei dimetilo germinal bat sartu zioten eraztunean eraztun irekiera polimerizazio bidez politioesterrak sintetizatu ondoren, despolimerizazio prozesua errazteko helburuarekin. Ordezkatzaile hori gehituta, despolimerizazioaren termodinamika eta polimerizazioarena orekara hurbiltzen dira, eta ondorioz bi prozesu horiek hobeto kontrolatzen dira jarduera murriztean. Horrela, despolimerizazio erreakzioak 60 °C-an egin litezke, eta polimerizazioa, giro-tenperaturan, pisu molekular altuak lortuz (≈ 70 kDa) modu kontrolatuan.

Poliesterren kasuan, Coulembier et al.-ek giro-tenperaturan ester ziklikoen eraztun irekiera polimerizazioa egin den lan bakanetako baten berri eman zuten[53]. Katalizatzaile halogenatu baten, ICl_3 erabilerak PLAren sintesia baldintza leunetan egitea ahalbidetu dezakeela ikusi zuten, hala ere, giro-tenperaturan erreakzio-zinetika baxua dela adierazi zuten eta tenperatura igo beharko litzatekeela polimerizazio-abiadura hobetzeko.

Zhu et al.-ek PCL baldintza leunetan (25-40 °C) sintetizatzea lortu zuten, titaniozko konposatu bat hastarazle eta katalizatzaile gisa erabiliz[54]. Poliesterra modu

eraginkorrean sintetizatzen bada ere, konposatu metaliko bat erabiltzeak etorkizunean aplikatzeko eragozpen batzuk eragin ditzake.

Literaturan jasotako kasu gehienetan, poliesterrak giro-tenperaturan sintetizatzeko gakoa katalizatzaile eraginkorra bilatzean dago. Hala ere, giro-tenperaturan poliesterren sintesia ahalbidetzeko bide berriak aurkitu behar direla uste dugu, hala nola, polimerizazio-metodo berriak edota baldintza leunagoetan polimerizatzeko gai diren monomero erreaktiboagoak.

1.4. Tesiaren helburuak

Kapitulu honetan poliester jasangarriagoak lortzeko dauden erronka guztien artean hiru azpimarratu ondoren, gai horietan oinarrituko da lan hau: katalizatzaile naturaletan, oinarri biologikoko polimeroetan eta energia gutxiago eskatzen duten polimerizazioetan.

Ildo horretan, tesi hau hiru zatitan bana daiteke: lehena (2. kapitulua) katalizatzaile natural jasangarri baten ikerketan zentratzen da; bigarrena (3. eta 4. kapituluak) oinarri biologikoko polimeroetan eta horien birziklatze eta *upcycling* prozesuetan; eta azkena (5. kapitulua), poliesterrak giro-tenperaturan sintetizatzeko metodo berri batean.

Tenperatura altuan poliesterren sintesi-prozesu jasangarria diseinatzeko, 2. kapitulua jatorri naturaleko bost katalizatzaile ezberdin ikertu dira, baldintza termiko gogorren aurrean erresistenteak direnak, masan ester ziklikoen eraztun irekiera polimerizazioa katalizatzeko helburuarekin. Bost katalizatzaileak L-laktidaren eraztun irekiera polimerizazioan probatu dira, katalizatzaile gisa duten eraginkortasuna ebaluatzeko. Katalizatzaile natural eraginkorrena, taurina, sakonago aztertu da bere katalisi mekanismoa eta sintetizatutako polimeroen toxikotasuna ezagutzeko.

Katalizatzailearen sintesi gaitasuna beste polimero batzuen eraztun irekiera polimerizaziora tzabaldu da.

3. kapituluan, PETarentza, hau da, ontzi arinen industrian gehien erabiltzen den poliesterrarentzat, oinarri biologikoko alternatiba bat proposatu da. Hesi propietate eta propietate termiko eta mekanikoen hainbat proba egin dira bi poliesterrak alderatzeko eta ondoren oinarri biologikoko materialarentzat birziklatze-prozesu bat deskribatu da. Organokatalisi bidez katalizatutako glikolisi despolimerizazio prozedurak PEFaren birziklapen kimiko zirkularra ahalbidetu du, polimeroa berriro ere polimerizatuz bi etapetako polikondentsazio prozedura baten bidez.

Oinarri biologikoko polimeroekin jarraituz, 4. kapitulua**n**, PHB ikertzen da, mikroorganismoek sintetizatutako jatorri naturaleko poliesterra, balio handiko β-hidroxiazidoaren monomero-iturri gisa. Katalizatzailea eta despolimerizazio hidrolitikoaren baldintzak ondo aukeratuta, despolimerizazio prozesua hidroxiazido monomeroaren errendimendu altuak lortzeko egokitu zen. *Upcycling* ikuspegia poli (hidroxibutirato-ko-hidroxibalerato) (PHBV) eta poli (hidroxibutirato-ko-hexanoato) (PHBH) kopoliesterretara zabaldu zen, PHB sintetikoarekin eta kontsumo ondorengo PHBarekin batera.

Tesiaren hirugarren zatian, 5. kapitulua**n**, bost kideko erreaktibitate handiko dilaktona monomero berri bat sintetizatu da, poliesterrak giro-tenperaturan polimerizatzeko helburuarekin. Diol bat nukleofilo gisa erabiliz eta katalizatzaile ezberdinak probatu ondoren, eraztun irekiera poliadizio-erreakzioa proposatu da. Azkenik, diamina eta ditiolezko nukleofiloak erabili dira dilaktonaren eraztuna irekitzeko eta ondorioz, poliamidak eta poliesterrak polimerizazio-metodo beraren bidez sintetizatzeko.

Ondorio gisa, tesi honetan aintzat hartutako erronkei buruzko emaitza eta ondorio garrantzitsuenak laburbildu eta komentatu dira 6.kapitulua**n**.

1.5. Erreferentziak

1 Plasctics Europe, *Plastics-the Facts 2021 An analysis of European plastics production, demand and waste data*, 2021.

2 M. University, Sustainable Polymers 101 | NSF Center for Sustainable Polymers, https://csp.umn.edu/sustainable-polymers-101/, (2022ko otsailaren 23an kontsultatua).

3 European Environment Commission, Waste and recycling, https://ec.europa.eu/environment/topics/waste-and-recycling_es, (2022ko martxoaren 11an kontsultatua).

4 J. M. Garcia and M. L. Robertson, *Science*, 2017, **358**, 870–872.

5 L. D. Ellis, N. A. Rorrer, K. P. Sullivan, M. Otto, J. E. McGeehan, Y. Román-Leshkov, N. Wierckx and G. T. Beckham, *Nat. Catal.*, 2021, **4**, 539–556.

6 J. Payne and M. D. Jones, *ChemSusChem*, 2021, **14**, 4041–4070.

7 C. Jehanno, J. W. Alty, M. Roosen, S. De Meester, A. P. Dove, E. Y.-X. Chen, F. A. Leibfarth and H. Sardon, *Nature*, 2022, **603**, 803–814.

8 M. Zhang, S. M. June and T. E. Long, in *Polymer Science: A Comprehensive Reference, 10 Volume Set*, Elsevier, Amsterdam, 2012, vol. 5, pp. 7–47.

9 A. Bossion, K. V. Heifferon, L. Meabe, N. Zivic, D. Taton, J. L. Hedrick, T. E. Long and H. Sardon, *Prog. Polym. Sci.*, 2019, **90**, 164–210.

10 P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, New York,

1995.

11 G. Odian, *Principles of polymerization*, John Willey & Sons, New Jersey, 4th edition, 2004.

12 M. E. Rogers, T. Long and S. Turner, *Introduction to synthetic methods in step-growth polymers*, John Willey & Sons, New Jersey, 2003.

13 B. Raeskinet, S. Moins, L. Harvey, J. De Winter, C. Henoumont, S. Laurent and O. Coulembier, *Macromolecules*, 2019, **52**, 6382–6392.

14 R. Löfgren, A. Albertsson, A.C. Dubois and P. Jerome, *J. Macromol. Sci.*, 1995, **C35**, 379–418.

15 I. K. Albertson and A.C. Varma, *Aliphatic polyesters: Synthesis, properties and applications in Degradable aliphatic polyesters*, Springer-Verlag, Berlin, 2001.

16 C. Lecomte and P. Jérôme, *Adv. Polym. Sci.*, 2012, **245**, 173–218.

17 E. Gabirondo, A. Sangroniz, A. Etxeberria, S. Torres-Giner and H. Sardon, *Polym. Chem.*, 2020, **11**, 5548.

18 C. Jehanno, I. Flores, A. P. Dove, A. J. Müller, F. Ruipérez and H. Sardon, *Green Chem.*, 2018, **20**, 1205–1212.

19 A. Sangroniz, J. B. Zhu, X. Tang, A. Etxeberria, E. Y. X. Chen and H. Sardon, *Nat. Commun.*, 2019, **10**, 1–7.

20 F. D. B. de Sousa, *Clean. Responsible Consum.*, 2021, **3**, 100020.

21 United Nations, Sustainable Development Goals, https://sdgs.un.org/goals, (2022ko maiatzak 15ean kontsultatua).

22 L. T. Lim, R. Auras and M. Rubino, *Prog. Polym. Sci.*, 2008, **33**, 820–852.

23 G. Gunn, *Critical Metals Handbook*, John Wiley & Sons, Ltd, West Sussex, UK, 2014.

24 M. Jaishankar, T. Tseten, N. Anbalagan, B. B. Mathew and K. N. Beeregowda, *Interdiscip. Toxicol.*, 2014, **7**, 60–72.

25 F. Nederberg, E. F. Connor, M. Möller, T. Glauser and J. L. Hedrick, *Angew. Chemie - Int. Ed.*, 2001, **40**, 2712–2715.

26 M. K. Kiesewetter, E. J. Shin, J. L. Hedrick and R. M. Waymouth, *Macromolecules*, 2010, **43**, 2093–2107.

27 I. Flores, J. Demarteau, A. J. Müller, A. Etxeberria, L. Irusta, F. Bergman, C. Koning and H. Sardon, *Eur. Polym. J.*, 2018, **104**, 170–176.

28 A. Basterretxea, C. Jehanno, D. Mecerreyes and H. Sardon, *ACS Macro Lett.*, 2019, **8**, 1055–1062.

29 A. Basterretxea, E. Gabirondo, C. Jehanno, H. Zhu, O. Coulembier, D. Mecerreyes and H. Sardon, *Macromolecules*, 2021, **54**, 6214–6225.

30 I. Flores, A. Etxeberria, L. Irusta, I. Calafel, J. F. Vega, J. Martínez-Salazar, H. Sardon and A. J. Müller, *ACS Sustain. Chem. Eng.*, 2019, **7**, 8647–8659.

31 V. Hevilla, A. Sonseca, C. Echeverría, A. Muñoz-Bonilla and M. Fernández-García, *Macromol. Biosci.*, 2021, **21**, 2100156.

32 H. Taira, H. Taira, K. I. Sugimura and Y. Sakurai, *Agric. Biol. Chem.*, 1965, **29**, 1074–1079.

33 I. M. Weiss, C. Muth, R. Drumm and H. O. K. Kirchner, *BMC Biophys.*, 2018, **11**, 2.

34 A. Sanchez-Sanchez, I. Rivilla, M. Agirre, A. Basterretxea, A. Etxeberria, A. Veloso, H. Sardon, D. Mecerreyes and F. P. Cossío, *J. Am. Chem. Soc.*, 2017, **139**, 4805–

4814.

35 M. He, Y. Cheng, Y. Liang, M. Xia, X. Leng, Y. Wang, Z. Wei, W. Zhang and Y. Li, *Polym. J.*, 2020, **52**, 567–574.

36 P. McKeown and M. D. Jones, *Sustain. Chem.*, 2020, **1**, 1–22.

37 M. Abhilash and D. Thomas, in *Biopolymer Composites in Electronics*, Elsevier, Amsterdam, 2017, pp. 405–435.

38 K. Helanto, L. Matikainen, R. Talja and O. J. Rojas, *BioResources*, 2019, **14**, 4902–4951.

39 B. Xiao, L. Wang, R. Mei and G. Wang, *J. Polym. Res.*, 2011, **18**, 2221–2227.

40 P. Švec, P. Hubená, Z. Růžičková, J. Holubová, M. Pouzar, J. Merna and A. Růžička, *Appl. Organomet. Chem.*, 2016, **30**, 20–25.

41 M. Shiramizu and F. D. Toste, *Chem. Eur. J.*, 2011, **17**, 12452–12457.

42 T. P. Vispute, H. Zhang, A. Sanna, R. Xiao and G. W. Huber, *Science*, 2010, **330**, 1222–1227.

43 A. J. J. E. Eerhart, A. P. C. Faaij and M. K. Patel, *Energy Environ. Sci.*, 2012, **5**, 6407–6422.

44 N. Altaee, G. A. El-Hiti, A. Fahdil, K. Sudesh and E. Yousif, *Springerplus*, 2016, **5**, 762.

45 W. M. Pachekoski, C. Dalmolin and J. A. M. Agnelli, *Mater. Res.*, 2013, **16**, 237–332.

46 P. Anbukarasu, D. Sauvageau and A. Elias, *Sci. Rep.*, 2016, **5**, 17884.

47 W. Maurício Pachekoski, C. Dalmolin and J. Augusto Marcondes Agnelli, *Mater.*

Res., 2013, **16**, 237–332.

48 P. Anbukarasu, D. Sauvageau and A. Elias, *Sci. Rep.*, 2016, **5**, 17884.

49 A. Basterretxea, C. Jehanno, D. Mecerreyes and H. Sardon, *ACS Macro Lett.*, 2019, **8**, 1055–1062.

50 A. Takasu, Y. Lio, Y. Oishi, Y. Narukawa and T. Hirabayashi, *Macromolecules*, 2005, **38**, 1048–1050.

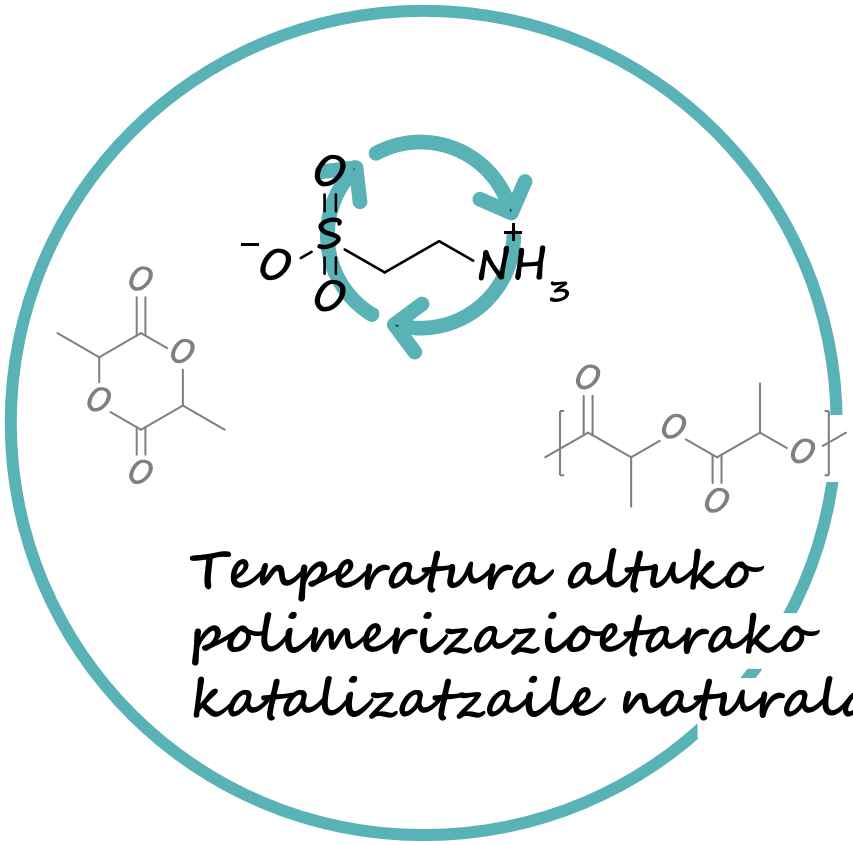
51 T. Yue, M. Zhang, G. Gu, L. Wang, W. Ren and X. Lu, *Angew. Chemie*, 2019, **58**, 618–623.

52 W. Xiong, W. Chang, D. Shi, L. Yang, Z. Tian, H. Wang, Z. Zhang, X. Zhou, E. Q. Chen and H. Lu, *Chem*, 2020, **6**, 1831–1843.

53 O. Coulembier, F. Meyer and P. Dubois, *Polym. Chem.*, 2010, **1**, 434–437.

54 J. B. Fan, F. Long, M. P. Aldred, Y. J. Li, Z. W. Liang and M. Q. Zhu, *Macromol. Chem. Phys.*, 2012, **213**, 1499–1508.

2. kapitulua



Tenperatura altuko polimerizazioetarako katalizatzaile natürala

Tenperatura altuko polimerizazioetarako katalizatzaile naturala

2.1. Sarrera

Polimeroak gure eguneroko bizitzaren parte dira propietate interesgarriak dituztelako, merkeak direlako eta prozesatzeko errazak. Hori dela eta, hainbat aplikaziotan erabiltzen dira, hala nola, eskala handian balio baxuko aplikazioetan (elikagaien ontziratzean edo eraikuntzan) eta baita bolumen txikiko baina balio erantsi handiko aplikazioetan ere (biomedikuntzan edo aplikazio aeroespazialetan)[1]. Polimeroen familien artean, poliesterrek arreta handia piztu dute, biomasatik lor daitezkeelako, errendimendu mekaniko handia dutelako, hesi izaera nabarmena dutelako eta ester taldeei esker birziklatu egin daitezkeelako. Gainera, poliester batzuk baldintza egokietan degradatu egiten direla frogatu da[2,3]. Poliesterrak duela ia 100 urte aurkitu ziren eta gaur egun polimero mota nagusietako bat dira. Kate nagusiko ester (R-COO-R') loturak definitzen ditu, non R eta R'-k frakzio alifatiko edo aromatiko bat adierazten duten. Poliesterrak sintetizatzeko hainbat ibilbide erabil daitezke, etapa polimerizazioa, non diolen eta diazidoen, edo diol eta diesterren artean egin daitekeen eta baita hidroxiaxidoen artean ere, eta eraztun irekiera polimerizazioa (ingelesez ring-opening polymerization (ROP)), ester ziklikoak polimerizatuz egiten dena.

Polimerizazio-metodo horien artean, eraztun-irekiera bidezko polimerizazioak abantaila batzuk eskaintzen ditu: mikroegituraren kontrola, pisu molekular altuak lortzea eta sakabanatze baxuak[4-6]. Nahiz eta polimerizazio industrialak tenperatura altuak eskatzen dituen (150-200 °C), ez du ekipamendu berezirik behar, hala nola, hutsune handia (pisu molekular txikiko molekulak (hau da, ura) ezabatzeko),

konbertsioa handitzeko eta pisu molekular altuak lortzeko. Gainera, kasu batzuetan, monomero ziklikoak berreskuratu daitezke polimeroa despolimerizatuz, ekonomia zirkularraren ikuspegitik, materialaren balio ekonomikoa berreskuratuz.

Tenperatura polimerizazio-zinetika errazteko beharrezkoa izaten den arren, katalizatzaileen erabilera funtsezko faktorea da pisu molekular egokiak eta propietate mekaniko onak dituzten polimeroak sortzeko. Industrian batez ere katalizatzaile metalikoak erabiltzen dira, hala nola, eztainu (II) oktoatoa eta titanio (IV) tetrabutoxidoa. Katalizatzaile hauek selektibitate handia erakusten dute, oso eraginkorrak dira eta gainera, kantitate baxuetan erabiltzearekin nahikoa da. Hala ere, katalizatzaile metalikoen arazoa ingurumen- eta ekonomia-kostu handia dakartela da; iragarpen batzuen arabera, baliteke datozen hamarkadetan metal batzuk desagertzeko arriskuan egotea. Gainera, horietako batzuk toxikoak dira eta duten koordinatzeko gaitasunagatik materialetatik kentzea ezinezkoa da polimeroan harrapatuta geratzen baitira. Hori dela eta, zenbait aplikaziotarako ez dira egokiak izaten, batez ere, aplikazio biomedikoetarako eta elektronikoetarako.

Azken hamarkadan, katalizatzaile organometalikoen toxikotasuna murrizteko ahalegin handiak egin dira, katalizatzaile onberagoak erabiliz. Zentzu horretan, ester ziklikoen eraztun irekiera polimerizazioetarako katalizatzaile guztiz organikoen erabilerak geroz eta interes handiagoa sortu du. Polimerizazio-erreakzioetan organokatalizatzaileak erabiltzeko funtsezko arrazoia azken produktutik eraginkortasunez ezabatzeko ematen duten aukera da[7-12].

Hainbat organokatalizatzailek erakutsi dute eraginkorrak direla eraztun irekiera polimerizazio-erreakzioak katalizatzeko, hala nola, 1,8-diazabiziklo[5.4.0]undek-7-enoak (DBU) edo 1,5,7-triazabiziklo[4.4.0]dek-5-enoak (TBD). Organokatalizatzaileak erabiltzeko eragozpen nagusietako bat polimerizaziorako egokiak izango liratekeen

tenperaturetan egonkortasun termiko eskasa dutela da, hori dela eta, katalizatzaileen degradazio termiko osoa edo partziala gerta daiteke polimerizazioan zehar[13]. Azken hamarkadetan, konposatu ionikoak aurkitu dira tenperatura altuak eskatzen dituzten polimerizazoak katalizatzeko. Adibidez, Peruch et al.-ek konposatu ioniko batzuk prestatu zituzten DMAPn (4-dimetilaminopiridina) oinarrituta, L-laktidaren ROP tenperatura altuetan egiteko[14]. Era berean, Fradet et al.-ek eta Sardon et al.-ek Brønsted azidodun likido ioniko batzuk erabili zituzten poliesterren etapa polimerizazioa eta eraztun irekiera polimerizazioa sustatzeko, hurrenez hurren[15,16]. 4-dimetilaminopiridina (DMAP):azido metanosulfonikoa (MSA) base-azido nahastea organokatalizatzaile eraginkorra da L-laktidaren eraztun irekiera estereoerregularraren polimerizazioa bultzatzeko[17]. Era berean, oraintsu frogatu da 1,5,7-triazabiziklo[4.4.0]dek-5-eno (TBD):azido metanosulfonikoa (MSA) nahastea konposatu protiko ioniko eraginkor bat dela PETaren despolimerizazio erreakziorako[18]. Hala ere, katalizatzaile horiek nahiko toxikoak direnez, garbiketa-prozesu bat eskatzen dute, eta horrek produkzio-prozesuan urrats gehigarri bat gehitzea eragiten du, prozesuaren kostua nabarmen handituz[19]. Horregatik, toxikoak ez diren organokatalizatzaileak erabiltzea izan liteke aukerarik onena, polimerizazioaren ondoren erreakzio ingurunetik kendu beharrik ez izateko, ez bailukete inolako ondorio kaltegarririk eragingo.

Naturak katalizatzaile gisa funtziona dezaketen konposatu sorta zabala eskaintzen du,izan ere landare eta animalietan prozesu biziak katalizatzeko hainbat konposatu baitaude. Aminoazido eta horien deribatu batzuk polimerizazio-erreakzioak katalizatzeko erabili izan dira. Coulembier et al.-ek amonio betainak erabili zituzten soluzioan L-laktida eta karbonato ziklikoak polimerizatzeko eraztun irekiera polimerizazio bidez giro-tenperaturan, polimerizazio azkarrak lortuz[20]. Nozaki et al.-ek L-prolina eta horren deribatuak erabili zituzten giro-tenperaturan azetaldehidoaren

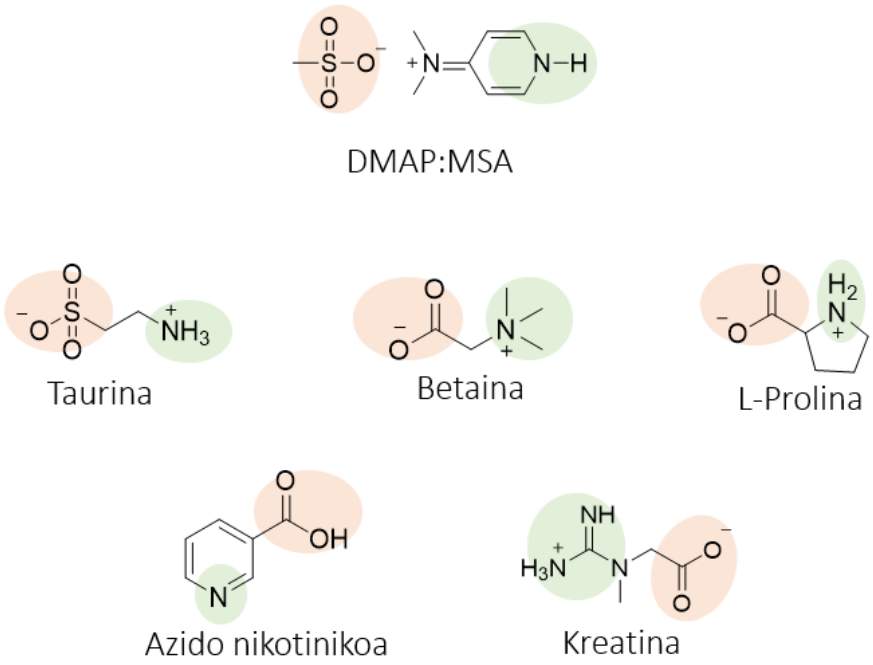
aldol polimerizazioak bultzatzeko azido azetikoaren presentzian[21]. Kreatina L-laktidaren eta ε-kaprolaktonaren eraztun irekiera polimerizazioetarako katalizatzaile moduan erabili da 150 °C-an[22]. Nahiz eta zenbait katalizatzaile natural erabili diren, dakigunez ez dute erakutsi katalizatzaile ez-naturalen adinako eraginkortasuna.

Kapitulu honetan bost konposatu natural aukeratu dira tenperatura altuko polimerizazioak katalizatzeko. Hautagai guztiak aminoazidoak, bitaminak edo horien deribatuak dira, eta talde azidoak eta basikoak dituzte euren egituran. Horregatik, azido-base nahaste gisa funtziona dezaketela uste da, hastarazlea eta ester ziklikoaren karbonilo taldea aktiba ditzaketelako eta, ondorioz, polimerizazio-erreakzioak ahalbidetu. Katalizatzaileen egonkortasun termikoak egiaztatu ondoren, L-laktidaren eraztun irekiera polimerizazioa katalizatzeko erabili ziren 180 °C-an eta emaitzak aztertu ziren. Behin katalizatzaile onena aukeratuta, X izpien difrakzioaren, FTIRen eta zitotoxikotasun-proben bidez sakonago aztertu zen. Azkenik, hautatutako katalizatzailea beste poliester eta poliamida batzuk katalizatzeko ere erabili da.

2.2. Emaitzak eta eztabaida

2.2.1. Katalizatzaile naturalen karakterizazioa

Sarreran aipatu bezala, ikertzaile batzuek jakinarazi dute aminoazidoen deribatuak erabili direla polimerizazio-erreakzioak katalizatzeko. Kapitulu honetan katalizatzaile naturaletarako bost hautagai posible aukeratu dira: taurina, betaina, L-prolina, azido nikotinikoa eta kreatina. Katalizatzaileak DMAP:MSA base-azido nahastearekin alderatuko dira, nahastea oso organokatalizatzaile eraginkorra da L-laktidaren eraztun irekitera polimerizaziorako. Hautagaiek bi taldeak dituzte, basea eta azidoa, eta uste da base-azido nahasketaren antzera funtziona dezaketela (2.1 irudia).

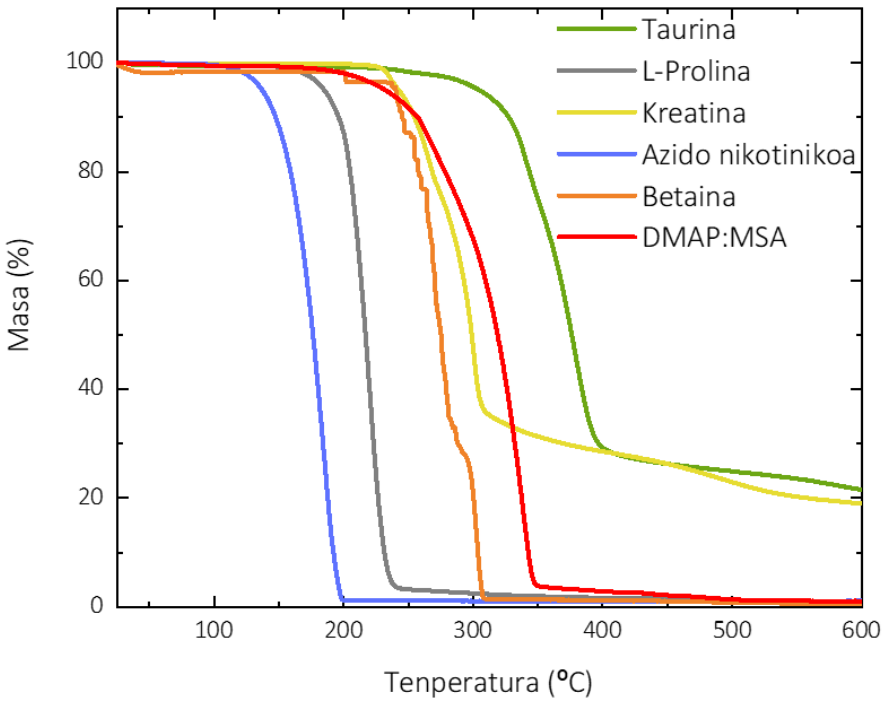


2.1 irudia. Katalizatzaile naturalak, DMAP: MSA nahasketarekin alderatuta.

MSA:piridina deribatuen erabileraren berri eman da, hala nola, MSA:TBD eta MSA:DMAP, poliesterren eraztun irekiera polimerizazioetarako. Azido-base nahasketa horiek katalizatzaile dual gisa funtzionatzen dute, tenperatura altuetan disoziatu egiten baitira, MSAren talde sulfonikoak nukleofiloa aktibatuz eta piridinaren amino taldeak, berriz, monomero ziklikoaren karbonilo taldea. Hori dela eta, uste dugu taurina katalizatzaile interesgarria izan daitekeela, talde sulfonikoa eta amino taldea baititu egituran. DBU:BA base:azido nahasteak ere errendimendu handia erakutsi du ROP katalizatzeko, kasu honetan talde sulfoniko baten ordez talde karboxiliko batek aktibatzen du nukleofiloa. Proposatutako gainerako hautagaiak base-azido nahasketa horren antzekoagoak dira, talde karboxilikoak baitituzte, azido taldeak.

DMSOtan egindako ^{1}H NMR espektroek aukeratutako katalizatzaile gehienen forma ionikoa berretsi dute baldintza estandarretan. Taurinak kargadun aminaren protoien seinalea 7,6 ppm-an erakusten du, betainaren egitura kargatuta dago bere egituraren

ondorioz, L-prolinak 8,4-9,0 ppm-an seinalea erakusten du, hau ere aminari dagokiona, eta azkenik, kreatinak 6,9 ppm-an. Azido nikotinikoak ez zuen erakutsi aminari egotz dakiokeen seinalerik; hala ere, 13,4 ppm-an seinalea ematen du, talde azidoari dagokiona, eta ondorioz, espezie ionikorik eza erakusten du (2.1-2.5 eranskina).

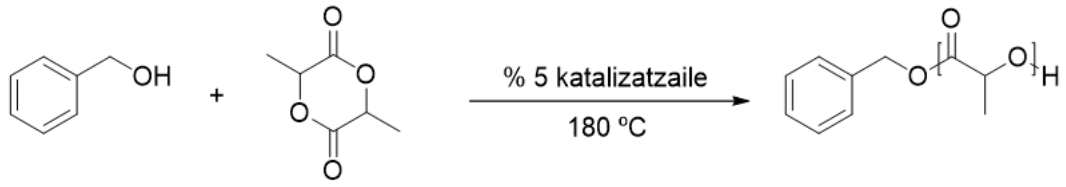


2.2 irudia. DMAP:MSA eta katalizatzaile naturalen TGA analisia.

Konposatuen egonkortasun termikoa nitrogeno-fluxuan egindako TGA analisi baten bidez neurtu da (2.2 irudia). Garrantzitsua da industria baldintzetan egonkorrak izatea, hau da, tenperatura altuetan, poliesterren sintesirako aktibo izan daitezen. Emaitzek erakutsi dute azido nikotinikoa egonkortasun termiko txikieneko konposatua dela, 100 °C-an degradatzen baita. Hori forma ez-ionikoaren ondorio izan daiteke, azido nikotinikoak beste molekula batzuen artean sarerik sortzeko aukerarik ez izatearena. L-Prolina azido nikotinikoa baino egonkorragoa da, 170 °C-ra arteko egonkortasuna erakutsiz. Kreatina eta betainak berriz, DMAP:MSA nahasketaren antzeko egonkortasuna erakusten dute, 250 °C inguruko. Azkenik, taurina dela egonkortasun

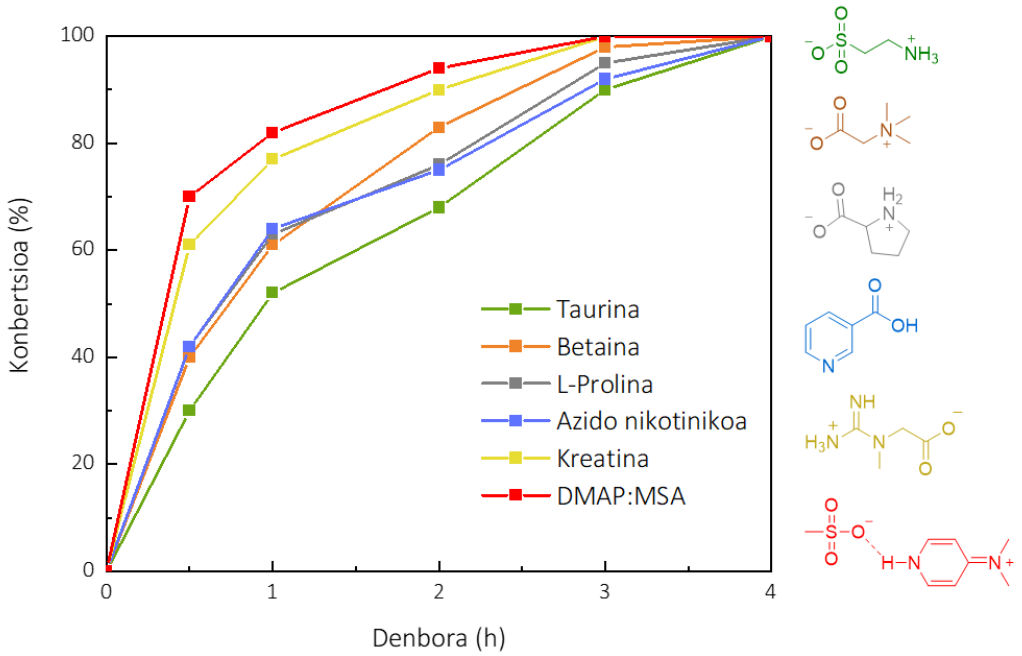
termiko handieneko konposatua ondorioztatu da, egonkorra da 250-300 °C-raino, horren arrazoia talde sulfonikoa izan daiteke, talde karboxilikoa baino sendoa.

2.2.2. Katalizatzaileen ebaluazioa L-laktidaren eraztun irekiera polimerizazioan



2.3 irudia. L-laktidaren eraztun irekiera polimerizazioaren eskema orokorra.

Lehenik eta behin, bost katalizatzaile hautagaien jarduera katalitikoak ebaluatu ziren, 180 °C-an L-laktidaren ROPrako masan (2.3 irudia). Polimerizazioak 100eko polimerizazio maila (ingelesez degree of polymerization (DP)) lortzeko helburuarekin egin ziren alkohol bentzilikoa erabiliz hastarazle modura. DMAP:MSA nahasketa ere probatu zen erreakzio berean, gainerako katalizatzaileentzako eraginkortasun-erreferentzia gisa. Katalizatzaile bakoitzaren errendimendua zehazteko, zinetikak ^{1}H NMR bidez jarraitu ziren kloroformotan (2.4 irudia).



2.4. irudia. L-laktidaren ROP zinetikak kataliatzaile ezberdinak erabiliz.

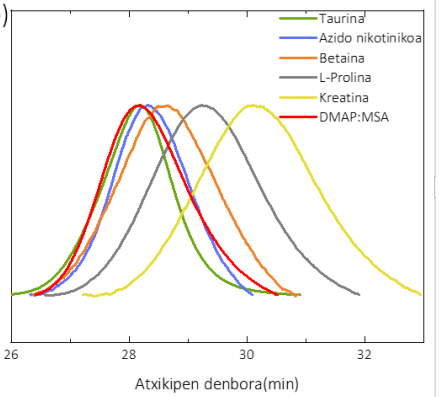
Bost katalizatzaile naturalek 4 ordutan L-laktidaren konbertsioa osoa ematen zutela ikusi zen, gehienak DMAP:MSA nahasketa baino apur bat motelagoak, nahasteak 3 ordutan ematen baizuen % 100eko konbertsioa (2.5.a irudia, 6. sarrera). Kreatina izan zen konbertsio osoa azkarren eman zuen katalizatzailea, baina SEC bidez neurtutako polimeroaren pisu molekularrak oxo baxuak ziren (2.5.a irudia, 5. sarrera). L-Prolinak ere espero baino pisu molekular baxuagoak eman zituen, pisu molekular teorikoaren erdia (2.5.a irudia, 3. sarrera). Taurina eta azido nikotinikoa izan ziren pisu molekular altuenak eta sakabanatze baxuenak lortu zituztenak, DMAP:MSA nahasketaren bidez sintetizatzen diren polimeroen antzekoak (2.5.a irudia, 1. eta 4. sarrera).

a)

sarrera	katalizatzailea	denbora (h)	konb. (%)	$M_{n,\ teo}$ (g mol^{-1})	$M_{n,\ SEC}$ (g mol^{-1})[a]	Đ
1	Taurina	4	98	14200	14100	1.1
2	Betaina	4	99	14400	10100	1.4
3	L-Prolina	4	100	14500	7300	1.5
4	Azido nikotinikoa	4	100	14500	12500	1.2
5	Kreatina	3	99	14400	2500	1.6
6	DMAP:MSA	3	100	14500	15000	1.2

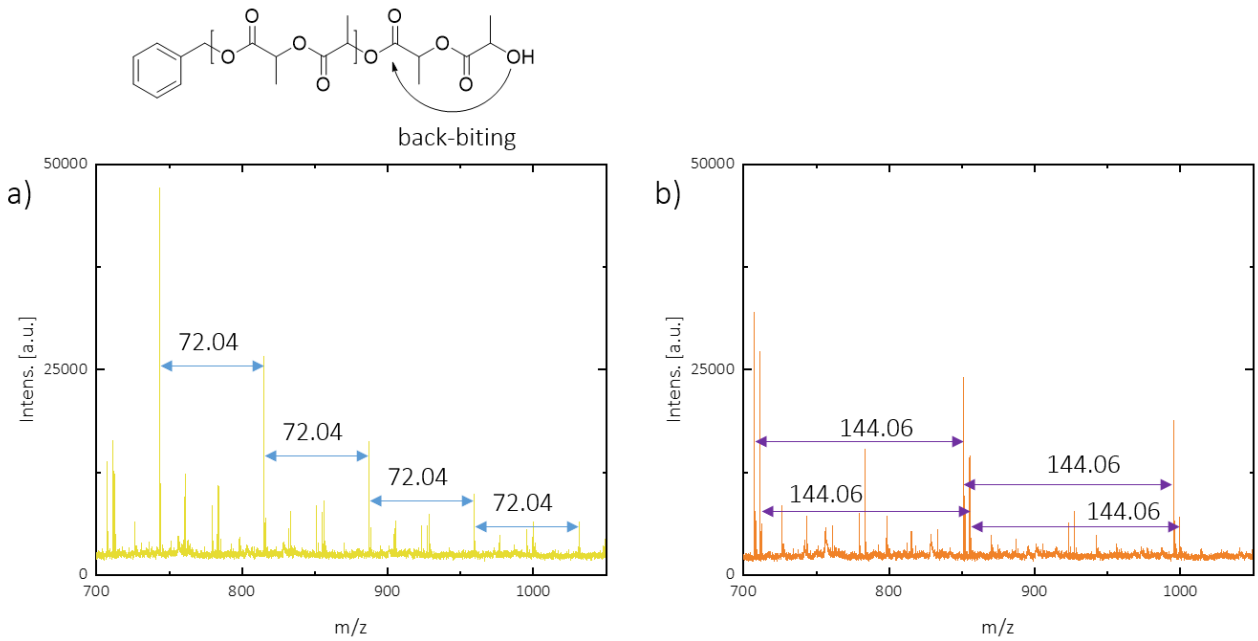
[a] SEC bidez neurtua poliestireno estandarrak erabiliz eta zuzenketa-faktoareak aplikatuz.

b)



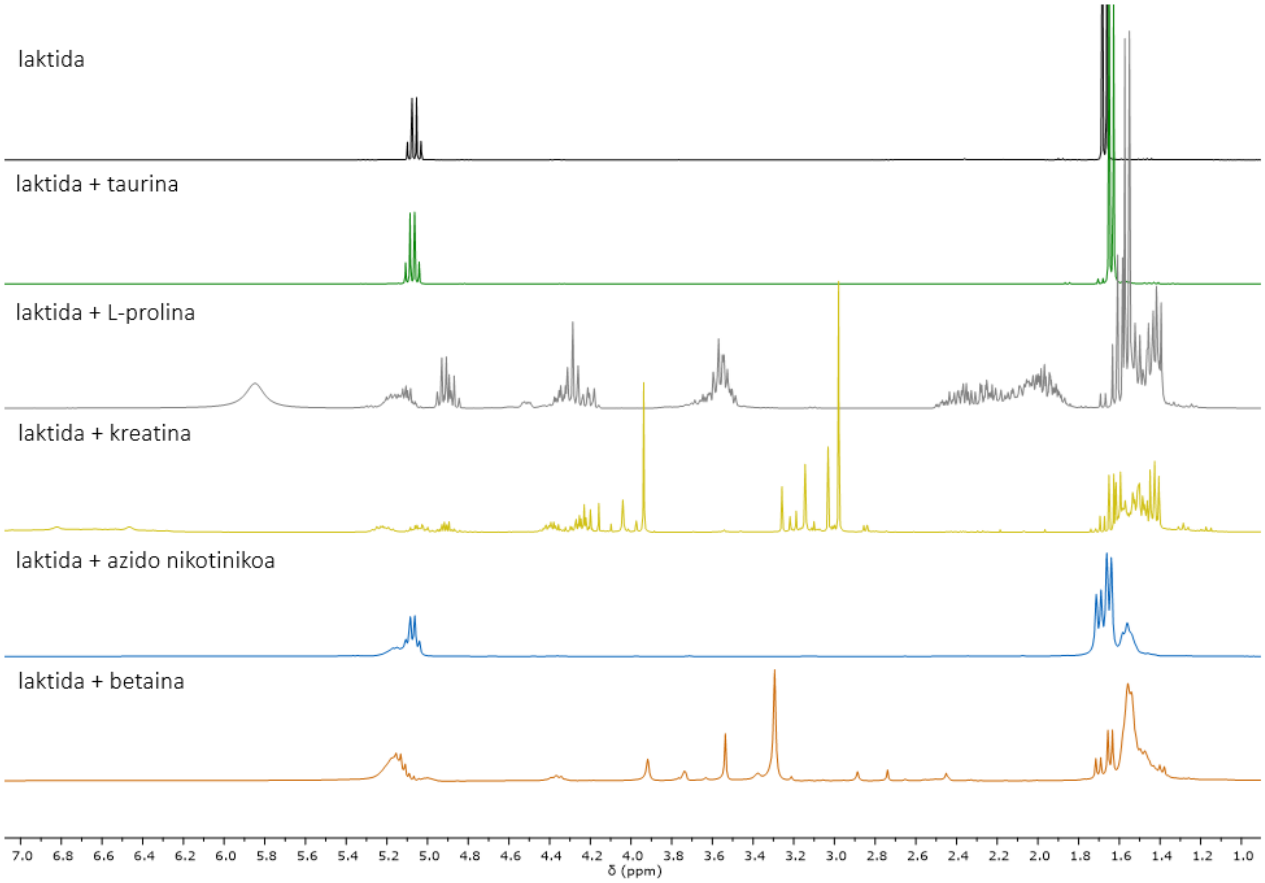
2.5. irudia. a) katalizatzaile ezberdinak erabiliz ROP bidezko L-laktidaren polimerizazioaren emaitzak 180 °C-tan, masan, alkohol bentzilikoa hastarazle gisa erabiliz eta DP totala 100 izateko helburuarekin eta b) SEC grafikoak.

MALDI-TOF analisia pisu molekular txikiko polimeroak (DP=10) sintetizatu ondoren egin zen alkohol bentzilikoa erabiliz hastarazle modura, 180 °C-an eta masan. Analisiak adierazten du kreatina katalizatzaile gisa erabiliz sintetizatutako polimeroak (2.6a irudia) 72,04 m/z-ko tartea duela seinaleen artean, ondorioz laktil unitate bateko tartea dagoela kateen artean. Laktil unitatearen diferentzia horrek PLAren kate ziklikoak sortu direla erakusten du back-biting erreakzioaren bidez, non amaierako alkoholak kate bereko karbonilo bati erasotzen dion. Emaitza bera lortu zen azido nikotinikoa katalizatzaile gisa erabili zenean ere (2.6 eranskina). Taurina katalizatzailearekin sintetizatutako polimeroak aldiz, 144,06 m/z-ko tartea erakusten du tontorren artean (2.6b irudia), laktidaren monomeroaren pisu molekularra, eta ondorioz back-biting erreakziorik ez dagoela ondoriozta daiteke. Betainak eta L-prolinak ere 144,06 m/z-ko tartea erakusten dute (2.7-2.8 eranskina).



2.6 irudia. PLA-ren MALDI-TOF analisia, a) kreatina katalizatzaile gisa eta b) taurina katalizatzaile gisa erabiliz.

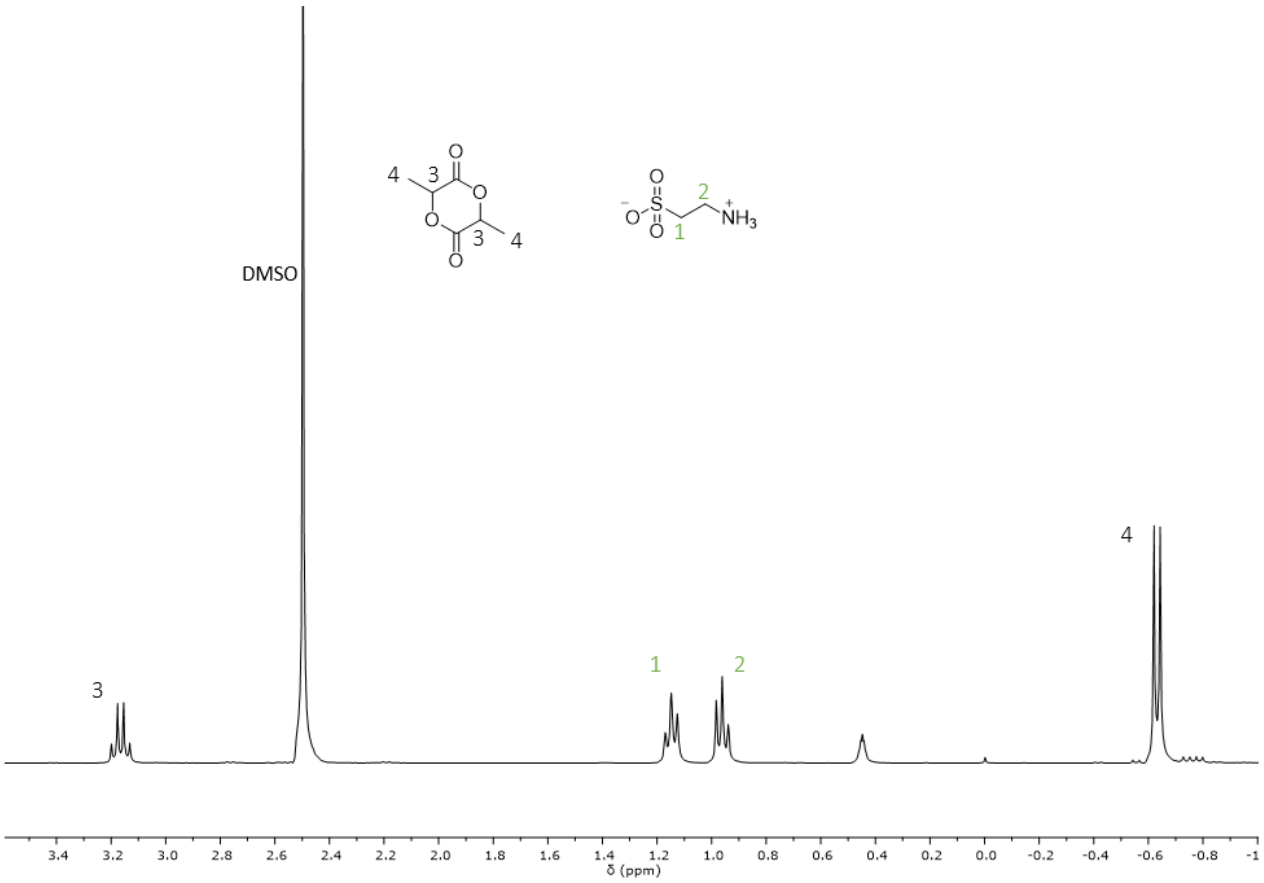
Polimero batzuen pisu molekular baxuek (2.5 irudia) adierazten dute katalizatzaile desberdinak erabiltzeak polimerizazioan eragin nabarmena duela. Katalizatzaile bakoitzaren erabileraren ondorioak ulertzeko, erreakzioak egin ziren laktida monomero eta katalizatzaileen 1:1 baliokideekin, erreakzio baldintza berdinak erabiliz, 180 °C eta masan, eta emaitzak ^{1}H NMR bidez karakterizatu ziren kloroformotan (2.7 irudia).



2.7. irudia. ^{1}H NMR espektroak L-laktida monomero:katalizatzaile (1:1 baliokide) erabiliz, 180 °C-an eta masan, eta L-laktida monomeroarekin konparaketa.

^{1}H NMR espektroek erakusten dute ia kasu guztietan laktida monomeroa eta katalizatzailea 180 °C-an kontaktuan jartzean aldaketaren bat gertatzen dela. Kreatinaren kasuan, L-laktidaren eraztun irekiera gertatzen dela ikusten da, 5,0-5,1 ppm-ko seinalea desagertzen baita eta 6,47 eta 6,83 ppm-an bi seinale agertzen baitira, aminen protoien seinaleak, laktidari lotzen zaizkionean, katalizatzailearen eta monomeroaren arteko erreakzioa adieraziz. L-prolina katalizatzaile gisa erabiltzen denean, emaitza bera identifika daiteke, 5,12-5,25 ppm-ko tartean seinale bat sortuz, laktidaren irekitzearena. Betaina eta azido nikotinikoa ere gai dira laktidaren eraztunean irekiera hasteko, hala ere, laktida-monomeroaren seinalea 180 °C-ko erreakzioaren ondoren ere ikus daiteke. Taurina katalizatzailearen kasuan,

kloroformotan egindako ^{1}H NMR espektroak ez du inolako alderik erakutsi laktida-monomeroaren espektroarekin, hala ere, kloroformotan taurina disolbagaitza delako izan daiteke. Taurinaren eta L-laktidaren arteko erreakziorik egon den konfirmatzeko espektroa DMSOan ere egin da (2.8 irudia).

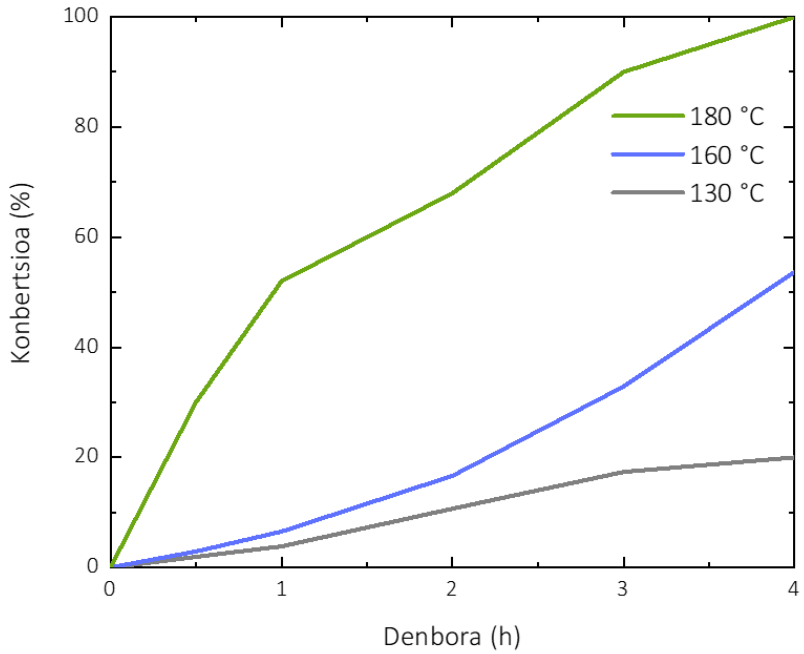


2.8. irudia. 180 °C-an egindako L-laktidaren eta taurinaren arteko erreakzio ekimolarraren ^{1}H NMR espektroa DMSOan.

DMSOan egindako espektroak adierazten du ez dela erreakziorik egon taurinaren eta laktidaren artean; izan ere, espektroan monomeroaren eta taurinaren seinaleak eta 0,42 ppm-ko seinalea baino ez dira ikusten, taurinaren amina desprotonatuari dagokiona.

Ondorioz, esan daiteke, taurina izan ezik, gainerako katalizatzaileak gai direla L-laktidaren eraztun irekiera hasteko proportzio desberdinetan, eta beraz, taurina dela katalizatzailerik onena, polimerizazio-erreakzioaren abiadura kontrolatzeko aukera ematen baitu, pisu molekularrean inolako eraginik izan gabe.

Behin taurina katalizatzailerik egokiena zela ondorioztatuta, tenperaturaren eragina aztertu zen PLAren sintesian (2.9 irudia). Tenperatura baxuagoetan egindako erreakzioek tenperaturak polimerizazioaren abiaduran ageriko eragina duela erakutsi zuten, soilik % 20ko konbertsioa lortu baitzen 4 orduren ondoren erreakzioa 130 °C-an egin zenean eta ia % 55koa 160 °C-an gauzatu zenean. Datu zinetikoen ondorioz, polimerizazioak 73 kJ/mol-eko aktibazio-energia (Ea) duela ikusi zen, polimerizaziorako tenperatura altuen beharra adieraziz.



2.9 irudia. Tenperatura desberdinetan PLAren sintesi konbertsio zinetika, taurina katalizatzaile gisa eta alkohol bentzilikoa hastarazle gisa erabilita.

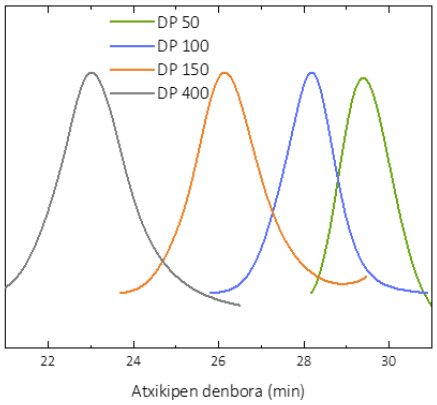
Taurina bidez katalizatutako hainbat DPko (50, 100, 150 eta 400) polilaktida polimeroak sintetizatu ziren 180 °C-an eta masan (2.10 irudia). Emaitzek adierazten dute polimerizazioak arrakastaz egin zirela eta lortu nahi ziren pisu molekularrak lortu zirela, sakabanatzeak baxuak izanik, nahiz eta DP altuagoetan pixka bat handitu.

a)

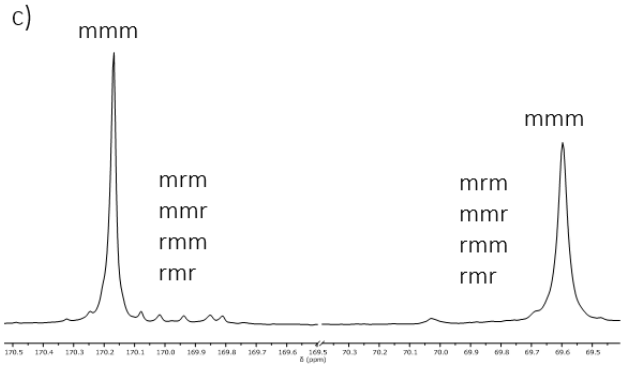
sarrera	DP	konb. (%)	$M_{n,\ teo}$ (g mol^{-1})	$M_{n,\ SEC}$ (g mol^{-1})[a]	Đ
7	100	98	14200	14100	1.1
8	50	99	7200	7000	1.1
9	150	97	21000	20500	1.2
10	400	97	56000	50400	1.2

[a] SEC bidez neurtua poliestireno estandarrak erabiliz eta zuzenketa-faktoareak aplikatuz.

b)



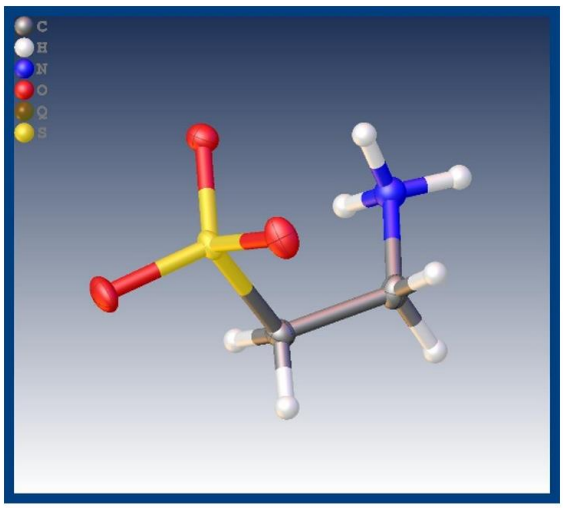
c)



2.10. irudia. a) 180 °C-an eta masan egindako DP desberdinetako L-laktidaren eraztuna irekiera polimerizazioen emaitzak, hastarazle modura alkohol bentzilikoa erabiliz eta katalizatzaile modura taurina, b) SEC grafikoak eta c) DP 100eko polimeroaren ^{13}C NMR espektroa eta bertan ikusten diren triadak.

Ondoren, polimeroak ^{13}C NMR bidez aztertu ziren estereoerregularitatea kalkulatzeko (2.10c irudia). DP 100eko PLAk Pm = 0,94 L eta D isomeroen arteko erlazioa erakusten du, DP 400ko polimeroak bezala (2.9 eranskina). Kontuan hartuta epimerizazio-kantitate txikiak eragin handia duela PLAren estereoerregularitatean, esan daiteke taurina katalizatzaile nahiko ona dela PLA estereoerregularra sintetizatzeko.

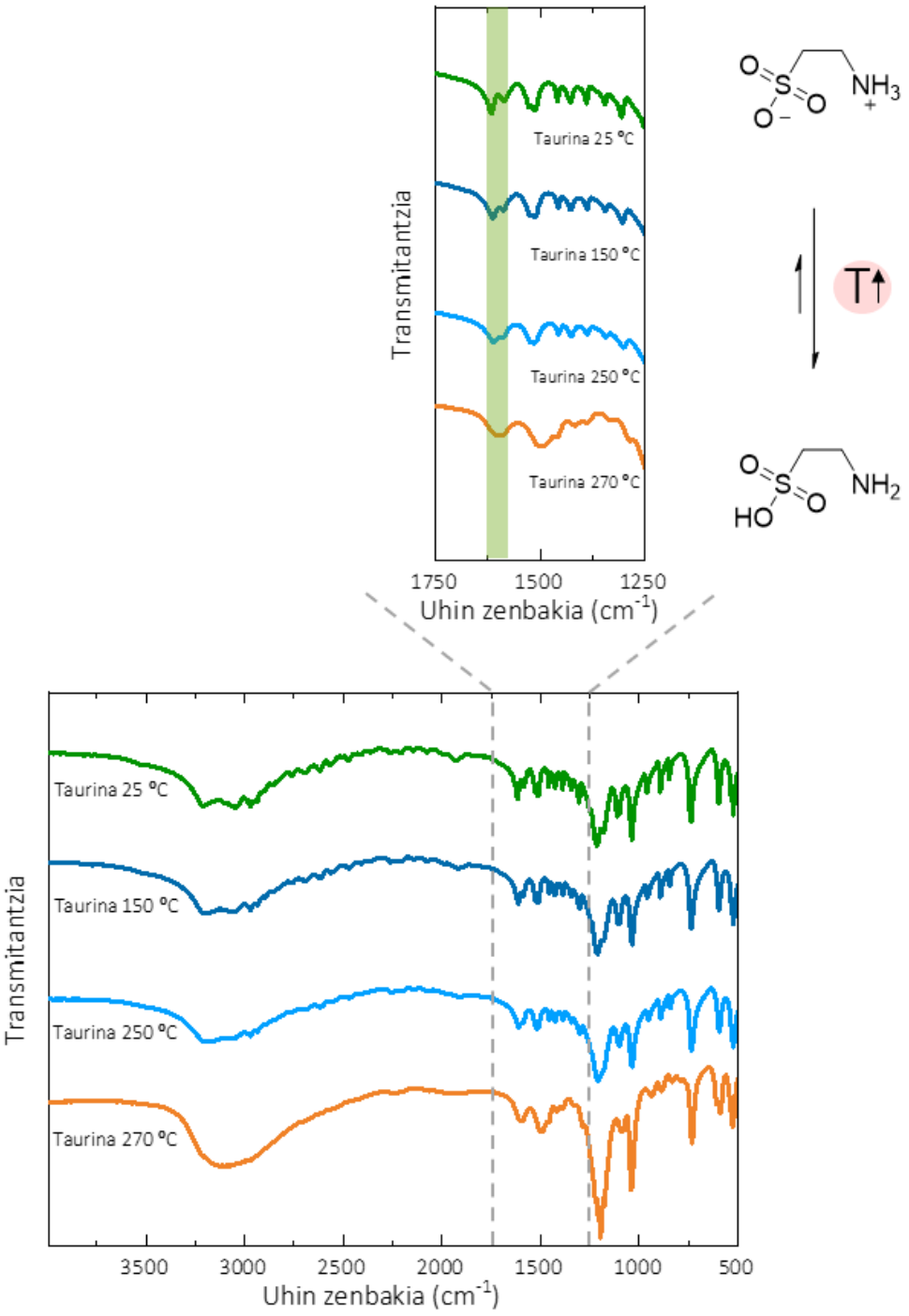
Emaitzak ikusirik ondoriozta daiteke taurina katalizatzaile eraginkorra dela laktidaren eraztun irekiera polimerizazioa gauzatzeko. Polimerizazio-mekanismoa eta lortutako polimeroaren propietateak hobeto ulertzeko, hainbat teknika erabili dira. Alde batetik, 100 K-an X izpien difrakzio analisi estandar bat egin da, 1H NMR espektroak erakutsitako taurinaren egitura berresteko. Bestalde, tenperatura desberdinetako FTIR neurketak erregistratu dira, katalizatzaileak tenperaturarekin izan ditzakeen aldaketak aztertzeko, eta azkenik, taurinaren bidez sintetizatutako polimeroaren zitotoxikotasuna neurtu da.



2.11. irudia. Taurinaren X izpien difrakzio-analisia baldintza estandarretan (100 K).

Taurina katalizatzailearen X izpien difrakzioaren analisiak adierzi zuen tenperatura baxuetan konposatua gatz egoeran zegoela (2.11 irudia). Azido sulfonikoaren taldeak protoia galtzen zuela ikusi zen, negatiboki kargaturik geratuz, eta amina taldeak protoia hartu zuela, positiboki kargatuz. Teknika honen bidez lortutako emaitza bat dator DMSOan egindako ^{1}H NMR-ean lortutako emaitzekin; izan ere, NMR espektroan amina protonatuaren seinalea ikusi zitekeen 7,6 ppm-an. Konposatuan sortzen diren kargek molekularen kurbadura eragiten dute, zirkulu erdi forma hartuz.

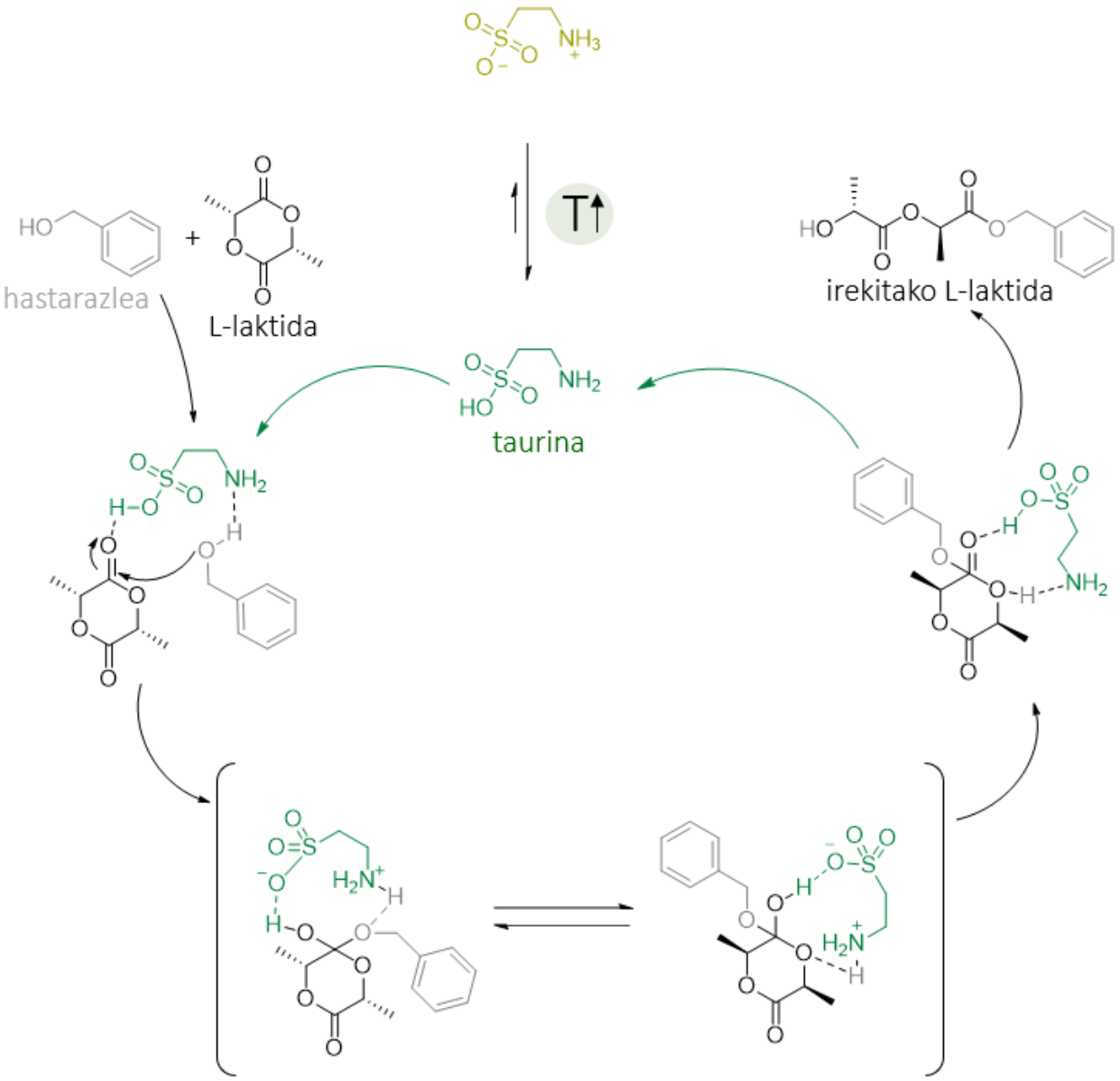
Ondoren FTIR analisia egin zen eta 25 °C-an egindako taurinaren analisiak banda bikoitz argia eta ondo definitua erakutsi zuen 1570-1650 cm^{-1}-ean, katalizatzailearen amina protonatu taldeari dagokiona (2.12 irudia). Tenperatura igotakoan, 150-250-270 °C, amina protonatuaren bi bandak definizioa galtzen hasi ziren eta banda zabal bakarra sortzen zuten. 150 °C eta 250 °C-an banda bikoitza ikus zitekeen, baina ez 25 °C-an egindako espektroan bezain ondo definituta, 270 °C-an egindako neurketan aldiz, banda bikoitza erabat desagertu zen eta banda bakarra ikusi zitekeen. Espektroak butilaminaren espektroarekin alderatu ziren (2.10 eranskina), protonatu gabeko amina bat duela baitakigu. Ikusi zen butilaminak banda zabal bakarra erakusten zuela 1570-1650 cm^{-1}-ean, aminari dagokiona. Butilaminaren eta 270 °C-an egindako taurinaren seinaleak forma bera dute, eta horrek esan nahi du talde funtzional berekoak direla. Emaitza horien arabera, adierazi daiteke taurinaren amina taldea tenperaturarekin desprotonatu egiten dela, 270 °C-tarako desprotonazio osoa erakutsiz.



2.12. irudia. Taurinaren FTIR analisia tenperatura desberdinetan.

X izpien difrakzio eta FTIR analisiek eta polimerizazio-zinetikaren bidez lortutako emaitzek ematen duten informaziotik abiatuta, taurinak katalizatutako L-laktidaren eraztun irekiera polimerizazio-mekanismoa proposatu da (2.13 irudia). Tenperatura

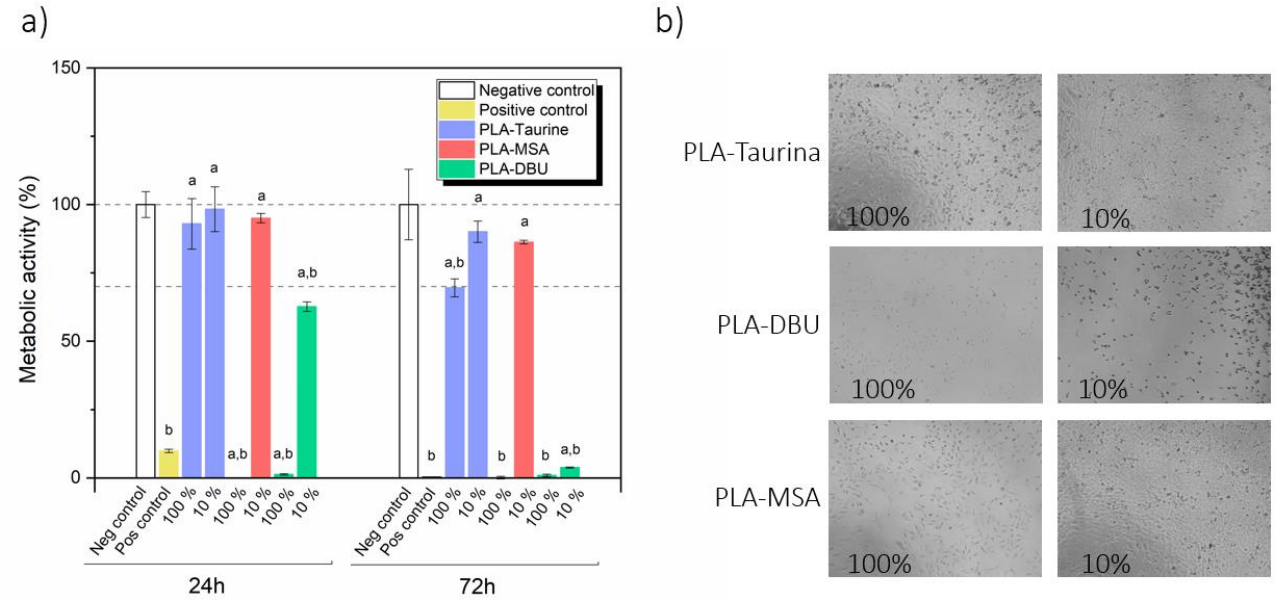
baxuetan, taurinaren amina protonatuta dago eta azido sulfonikoa protoirik gabe, horren ondorioz, aminaren aldea azido ahula da, eta sufrearen aldea, berriz, base ahula. FTIR analisiaren bidez baieztatu zen tenperatura igotakoan, taurinaren oreka aminaren desprotonazio aldera desplazatzen dela, eta beraz, azido sulfonikoaren protonazioaren aldera. Horrela, amina base indartsu bihurtzen da, eta azido sulfonikoa azido indartsu, L-laktidaren eraztun irekiera polimerizazioa katalizatzeko gai bihurtuz. Taurinak katalizatzaile bikoitz gisa jokatzen du, azido sulfonikoaren aldetik L-laktidaren karbonilo taldea aktibatzen du eta amina taldearen aldetik hastarazlea. Azken konposatu horrek monomeroaren karbonilo taldeari erasoko dio, eta horrela eraztun irekiera polimerizazioari hasiera emango dio. L-laktida ireki ondoren, taurinaren amino taldeak katearen amaieran sortu den alkohola aktibatuko du eta polimerizazioa hedatzen lagunduko du, katearen amaierara iritsi arte.



2.13. irudia. Taurinak katalizatutako L-laktidaren ROP-arentzat proposatutako mekanismoa.

Lehen aipatu moduan, taurina jatorri naturaleko katalizatzailea da, animalia askorengan aurki daitekeena, eta ondorioz interesgarria da konposatu jasangarritzat jotzen delako. Gainera, animalia-ehunetan agertzen denez, substantzia ez-toxikoa dela pentsatzen da, eta horrek oso garrantzitsu egingo du industria ikuspegitik, polimeroaren garbiketa-urratsa saihesten lagunduko baitu. Taurinaren toxikotasuna aztertzeko helburuarekin zitotoxikotasun-probak egin ziren.

Zitotoxikotasuna neurtzeko L-laktidaren hiru eraztun irekiera polimerizazio egin ziren, bakoitza katalizatzaile desberdin baten % 5 molekin: bat taurina erabiliz, beste bat 1,8-diazabiziklo (5.4.0)undek-7-enoa (DBU) erabiliz, eta azkena, azido metanosulfonikoaren bidez (MSA). DBU eta MSA katalizatzaileak taurinaren emaitzekin alderatzeko sintetizatu ziren. Behin polimeroak sintetizatu ondoren eta inolako purifikaziorik egin gabe zitotoxikotasuna neurtzeko erabili ziren (2.14 irudia).



(a) Diferentzia esanguratsua ($p<0,05$) kontrol positiboarekin alderatuta (medio osoa + % 10 DMSO)
(b) Diferentzia esanguratsua ($p<0,05$) kontrol negatiboarekin alderatuta (medio osoa)

2.14. irudia. Taurinaren bidez sortutako PLAren zitotoxikotasun proba eta DBUrekin eta MSArekin lortutakoekin alderatzea.

Polimero bakoitzerako bi baldintza desberdin prestatu ziren: % 100 deritzona, polimeroaren inkubaziotik (37 °C, 24 h) lortutako ingurunearen estraktua, 200 mg polimero/1 mL medio eta % 10 deritzona, estraktu kontzentratuaren diluziotik (1:10) lortutako estraktu diluitua.

Saiakuntza egiteko erabili zen medioak pH adierazle bat zuen (fenol-gorria), eta horrek kolore aldaketa ematen du, 6,8tik beherako pH balioetarako kolore horia hartuz, eta

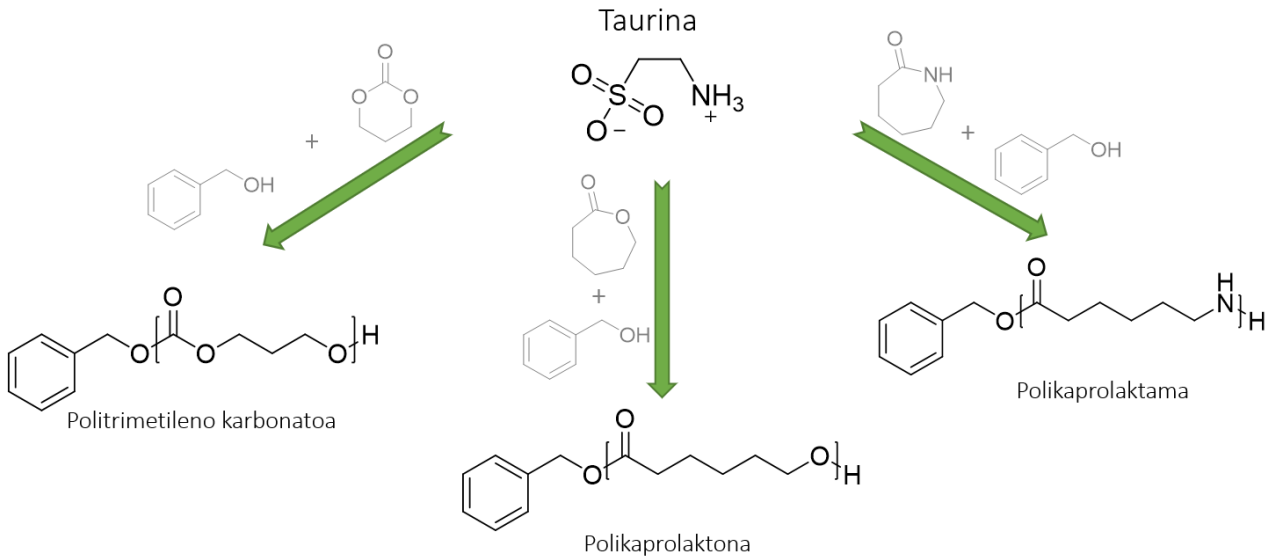
purpura kolorekoa bihurtuz 8tik gorako balioetan. PLA-DBU polilaktida sintetizatua, DBU katalizatzaile gisa erabiliz lortutakoa, eta PLA-MSA polilaktida sintetizatua, MSA katalizatzaile gisa erabiliz sintetizatutakoa, ingurunearekin kontaktuan jartzean hori kolorera aldatu zuten. Taurina katalizatzaile gisa erabiliz sintetizatutako polilaktidan, ez zen ingurunean kolore aldaketarik antzeman.

Taurinaren kasuan,24 ordutan bi kontzentrazioekin (% 10 eta % 100), zelulek jarduera metabolikoa % 90etik gora mantendu zuten, taurinak ia inolako toxikotasunik ez duela adieraziz. 72 ordutan, % 100eko kontzentrazioan, jarduera metabolikoa % 70era jaitsi zen, baimendutako toxikotasunaren mugan zegoelarik. DBU katalizatzaile gisa erabiliz sintetizatutako polimeroak zelulen jarduera metabolikoa nabarmen murrizten zuen, % 10eko kontzentrazioak 24 ordutan % 60 inguruko jarduera metabolikoa azalduz, baina 72 ordutan, jarduera ia zerora jaitsi zen. Estraktu kontzentratua erabili zen proban, zelulek zerora murriztu zuten beren jarduera bi probetan, 24 ordutan eta 72 ordutan. PLA-MSAren kasuan, jarduera metabolikoa nulua da % 100eko kontzentrazioan; hala ere, kontzentrazio diluituetan, jarduera metabolikoa % 80tik gorakoa da, eta horrek adierazten du modu horretan ez dela toxikoa.

Beraz, % 5eko taurinarekin sintetizatutako polilaktida ez dela toxikoa eta ondorioz garbitu gabe erabil daitekeela ziurta daiteke. DBUk eta MSAk sintetizatutako polimeroek aldiz, toxikotasuna erakusten dute eta, ondorioz, purifikazio-etapa beharko lukete.

2.2.3. Taurinaren katalizatzeko gaitasunaren zabaltzea

Lan honen bidez taurina L-laktidaren eraztun irekiera polimerizazioa aurrera eramateko katalizatzile eraginkorra dela frogatu da. Taurinak beste polimero batzuentzat katalizatzaile moduan balioko ote lukeen aztertu da (2.15 irudia).



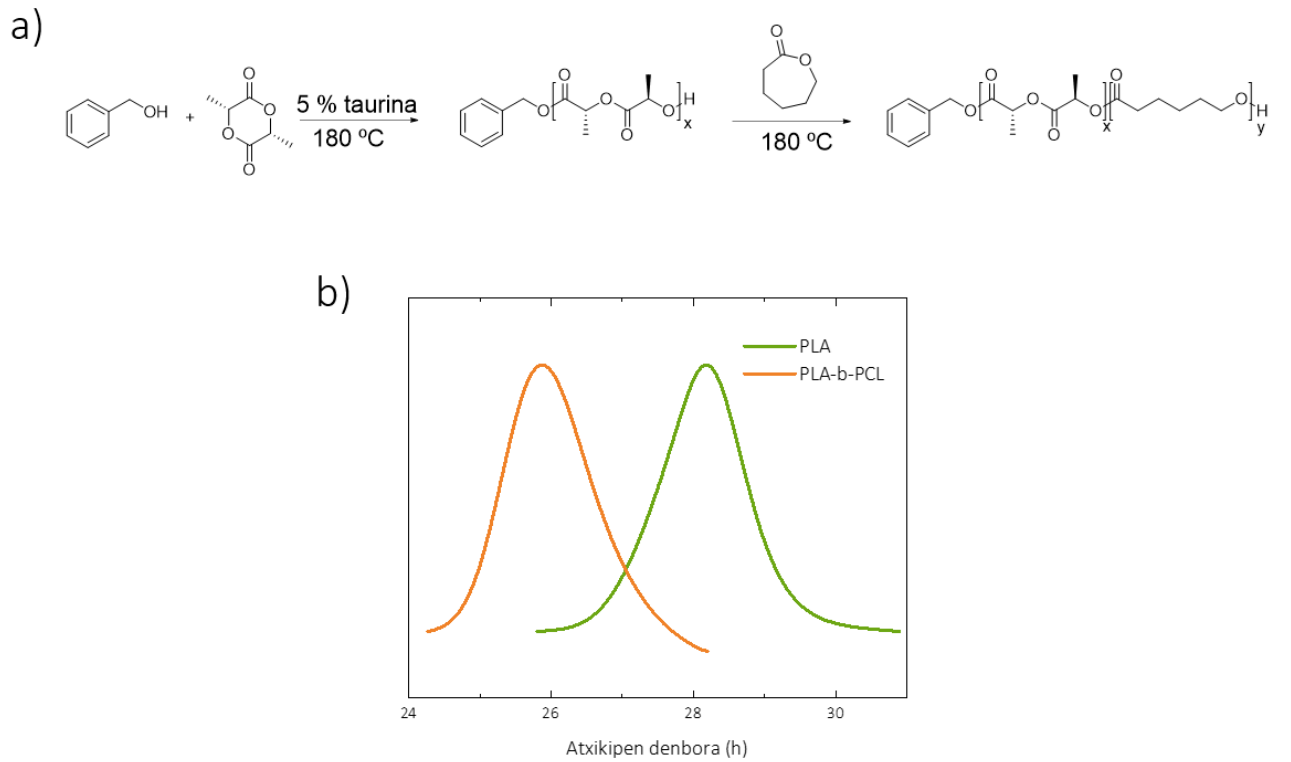
2.15. irudia. Taurinak katalizatutako polimerizazio-erreakzioen eskema.

Polilaktida eraztun irekiera polimerizazioaren bidez sintetizatu ondoren, ε-kaprolaktona polimerizatzeko saiakuntza egin zen, aurreko baldintza berdinak erabiliz: hastarazle modura alkohol bentzilikoa, 180 °C-an, masan, taurinaren % 5 molekin. 4 orduko erreakzio deboraren ondoren, kloroformotan ^{1}H NMR espektroa egin zen eta polimerizazio-erreakzioak eraginkortasunez funtzionatzen zuela baieztatu zen, polikaprolaktona poliesterra lortuz(2.11 eranskina).

Ondoren, eraztun irekiera erabiliz beste polimerizazio batzuk polimerizatu ziren, polikarbonato bat eta poliamida bat, hain zuzen ere. Horretarako, trimetileno karbonatoa eta ε-kaprolaktama polimerizatu ziren, aurreko baldintza berdinak erabiliz. Bi erreakzioak behar bezala burutu zirela ziurtatu zen, baina polikaprolaktamaren polimerizazioan lortutako pisu molekularrak baxuak izan ziren eta, beraz, erreakzio-baldintzak doitzeko beharra ikusi da (2.12-2.13 eranskina).

Taurina hainbat polimeroren sintesi-erreakzioak katalizatzeko gai dela ikusi da, hala ere, material bakoitzaren sintesian erabili ahal izateko, polimerizazio bakoitzerako erreakzio-baldintza onenak baieztatu behar dira.

Azkenik, taurina katalizatzaileak blokezko polilaktida-ko-polikaprolatona (PLA-b-PCL) kopolimeroa sintetizatzeko duen ahalmena frogatu zen (2.16a irudia).



2.16. irudia. a) L-laktidaren eta ε-kaprolaktonaren arteko bloke-kopolimerizazioaren eskema orokorra, eta b) PLAaren eta PLA-b-PCLren SEC analisia.

Lehenik eta behin, L-laktidaren polimerizazioa egin zen, aurretik deskribatutako erreakzio-baldintza berberak erabiliz, lortutako polimeroa SEC bidez aztertu zen, 14100 $g \cdot mol^{-1}$-eko pisu molekularra eta 1,1eko sakabanatzea erakutsiz. Jarraian, erreakzio-nahasketari ε-kaprolaktona gehitu zitzaion eta erreakzionatzen utzi zen. Amaieran, SEC analisiak baieztatu zuen erreakzioak ondo funtzionatzen zuela eta 24000 $g \cdot mol^{-1}$-era igo zela pisu molekularra, sakabanatzea 1,1ean mantenduz (2.16b irudia).

2.3. Ondorioak

Kapitulu honetan bost katalizatzaile natural aztertu dira tenperatura altuan poliesterrak polimerizatzeko: taurina, betaina, L-prolina, azido nikotinikoa eta kreatina.

Katalizatzaile horiek egituran dituzten azido eta base taldeengatik aukeratu dira, katalizatzaile dual gisa jarduteko aukera eman baitezakete. Frogatu zen bost katalizatzaieak gai zirela L-laktidaren ROP katalizatzeko denbora laburreko erreakzio batean, 3-4 ordutan. Hala ere, ^{1}H NMR espektroek baieztatu zuten katalizatzaile guztiek, taurinak izan ezik, erreakzioa katalizatzeaz gain, eraztun irekiera erreakzioa ere ematen zutela, hau da, hastarazle gisa ere jokatzen zutela. Horregatik, taurina aukeratutakoen artean katalizatzaile onena zela ondorioztatu zen, erreakzio-abiadura kontrolatzea ahalbidetzen baitu, pisu molekular handien lorpena arriskuan jarri gabe.

X izpien difrakzio, FTIR eta ^{1}H NMR analisien bidez taurinaren gatz-egitura baieztatu da, baita tenperaturarekin jasaten dituen aldaketak ere, erreakzio mekanismo bat proposatuz. Polimero sintetizatuaren zitotoxikotasun probek zehaztu zuten taurina ez dela toxikoa eskala katalitikoan erabiltzen denean, jarduera metabolikoa % 70eko mugatik gora mantentzen baitu.

Dakigunez, lan honek lehen aldiz jorratzen du taurinaren erabilera katalizatzaile ez-toxiko moduan polimerizazio-tenperatura altuetan poliesterren sintesia egiteko. Azkenik, taurinaren irismen katalitikoa tenperatura altuko beste polimerizazio batzuetara ere zabaldu da. Hala ere, karakterizazio sakonagoa behar da azken polimerizazio-erreakzio horietarako, erreakzio-baldintza egokienak aurkitu ahal izateko.

2.4. Atal esperimentala

2.4.1. Materialak

Taurina (% 99, Sigma-Aldrich S.A.), betaina (>% 98, Sigma-Aldrich S.A.), L-prolina (>% 99, Sigma-Aldrich S.A.), azido nikotinikoa (>% 98, Sigma-Aldrich S.A.), kreatina (% 99, Sigma-Aldrich S.A.), 4-dimetilaminopirina (DMAP) (% 99, TCI), azido metanosulfonikoa

(MSA) (% 99, Sigma-Aldrich S.A. eta 1,8-diazabiziklo(5.4.0)undek-7-eno (DBU) (% 98, Sigma-Aldrich S.A.) hutsunepean lehortu ziren erabili aurretik. L-laktida (Corbion) toluenoz garbitu zen eta hutsunepean lehortu zen erabili baino lehen.

2.4.2. L-laktidaren eraztun irekiera polimerizazioa

Polilaktida poliesterraren sintesia ROP bidez egin zen, L-laktida ester ziklikoa erabiliz. 5 mL-ko bial batean 0,50 g (3,47 10^{-3} mol) L-laktida jarri ziren barra magnetiko batekin, % 5 mol katalizatzaile (1,73 10^{-3} mol) eta 3,6 µL (3,47 10^{-5} mol) alkohol bentzilikorekin (DP 100) batera.

Ondoren, biala 180 °C-ko olio-bainu aurreberotuan murgildu zen 4 orduz eta konbertsioa ^{1}H NMR bidez jarraitu zen kloroformotan. Erreakzioa amaitu ondoren, sortutako polilaktida giro-tenperaturara modu naturalean hozten utzi zen. Garbiketarako, lagina kloroformoan disolbatu eta metanol hotzean prezipitatu zen, ondoren iragazi eta hutsunepean lehortzen utziz 24 orduz karakterizatu aurretik.

2.4.3. Trimetileno karbonatoaren eraztun irekiera polimerizazioa

Politrimetilenkarbonatoaren sintesia L-laktidaren ROParen modu berean egin zen. 5 mL-ko bial batean 0,50 g (4,90 10^{-3} mol) trimetilen karbonato jarri ziren barra magnetiko batekin, % 5 mol taurina (1,73 10^{-3} mol, 0,031 g) eta 5,1 µL (4,90 10^{-5} mol) alkohol bentziliko (DP 100).

Biala 180 °C-an berotu zen 4 orduz eta kloroformo ^{1}H NMR bidez jarraitu zen konbertsioa. Erreakzioaren ondoren, polikarbonatoa araztu egin zen polilaktidaren sintesirako erabilitako prozedura bera erabiliz.

2.4.4. ε-kaprolaktonaren eraztun irekiera polimerizazioa

ε-kaprolaktonaren ROPa beste polimerizazioetarako erabili ziren erreakzio-baldintza berberei jarraiki egin zen. 0,50 g (4,38 10^{-3} mol) ε-kaprolaktona erabili ziren, % 5 mol taurina (2,19 10^{-4} mol, 0,027 g) eta 4,5 µL (4,38 10^{-5} mol) alkohol bentziliko (DP 100).

2.4.5. ε-kaprolaktamaren eraztun irekiera polimerizazioa

ε-kaprolaktamaren ROPa beste polimerizazioetarako erabili ziren erreakzio-baldintza berberak erabiliz egin zen. 0,50 g (4,42 10^{-3} mol) ε-kaprolaktama, % 5 mol taurinarekin (2,21 10^{-4} mol, 0,028 g) eta 4,6 µL (4,42 10^{-5} mol) alkohol bentzilikorekin (DP 100).

2.5. Erreferentziak

1 Plastics Europe, *Plastics-the Fact 2021 An analysis of European plastics production, demand and waste data*, 2021.

2 M. Hong and E. Y. X. Chen, *Green Chem.*, 2017, **19**, 3692–3706.

3 C. Jehanno, M. M. Pérez-Madrigal, J. Demarteau, H. Sardon and A. P. Dove, *Polym. Chem.*, 2019, **10**, 172–186.

4 M. E. Rogers, T. Long, S. Turner, *Introduction to synthetic methods in step-growth polymers*, John Willey & Sons, New Jersey, 2003.

5 P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, New York, 1995.

6 G. Odian, *Principles of polymerization*, John Willey & Sons, New Jersey, 4th edition, 2004.

7 W. N. Ottou, H. Sardon, D. Mecerreyes, J. Vignolle and D. Taton, *Prog. Polym. Sci.*, 2016, **56**, 64–115.

8 H. Sardon, A. Pascual, D. Mecerreyes, D. Taton, H. Cramail and J. L. Hedrick, *Macromolecules*, 2015, **48**, 3153–3165.

9 X. Zhang, M. Fevre, G. O. Jones and R. M. Waymouth, *Chem. Rev.*, 2018, **118**, 839–885.

10 D. W. C. MacMillan, *Nature*, 2008, **455**, 304–308.

11 S. Bertelsen and K. A. Jørgensen, *Chem. Soc. Rev.*, 2009, **38**, 2178–2189.

12 P. I. Dalko and L. Moisan, *Angew. Chemie - Int. Ed.*, 2004, **43**, 5138–5175.

13 L. Mezzasalma, A. Dove and O. Coulembier, *Eur. Polym. J.*, 2017, **95**, 628–634.

14 J. Kadota, D. Pavlović, H. Hirano, A. Okada, Y. Agari, B. Bibal, A. Deffieux and F. Peruch, *RSC Adv.*, 2014, **4**, 14725–14732.

15 A. Basterretxea, E. Gabirondo, A. Sanchez-Sanchez, A. Etxeberria, O. Coulembier, D. Mecerreyes and H. Sardon, *Eur. Polym. J.*, 2017, **95**, 650–659.

16 S. Zhang, V. Lemaire, A. Féret, H. Lefebvre, M. Tessier and A. Fradet, *Polym. Chem.*, 2013, **4**, 1538–1545.

17 A. Basterretxea, E. Gabirondo, C. Jehanno, H. Zhu, O. Coulembier, D. Mecerreyes and H. Sardon, *Macromolecules*, 2021, **54**, 6214–6225.

18 C. Jehanno, I. Flores, A. P. Dove, A. J. Müller, F. Ruipérez and H. Sardon, *Green Chem.*, 2018, **20**, 1205–1212.

19 M. D. Gernon, M. Wu, T. Buszta and P. Janney, *Green Chem.*, 1999, **1**, 127–140.

20 B. Guillerm, V. Lemaur, J. Cornil, R. Lazzaroni, P. Dubois and O. Coulembier, *Chem. Commun.*, 2014, **50**, 10098–10101.

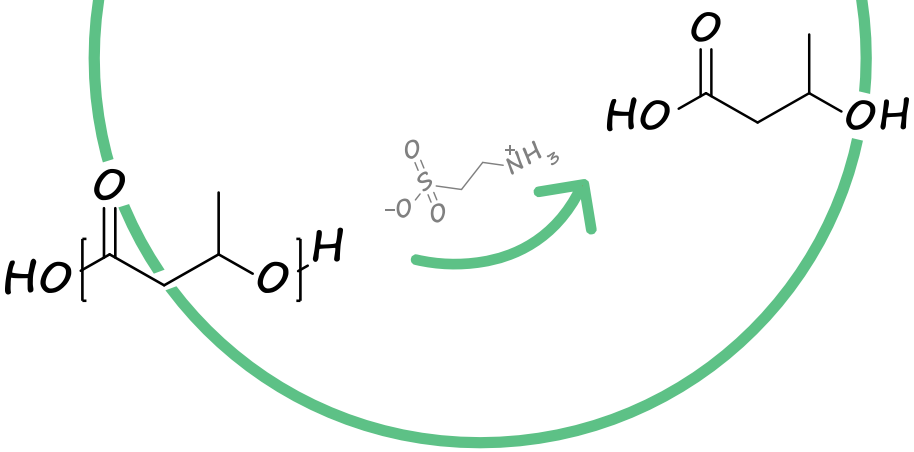
21 S. Kusumoto, S. Ito and K. Nozaki, *Asian J. Org. Chem.*, 2013, **2**, 977–982.

22 E. Oledzka, M. Sobczak, M. Kolakowski, B. Kraska, W. Kamysz and W. Kolodziejski, *Macromol. Res.*, 2013, **21**, 161–168.

23 A. Sanchez-Sanchez, I. Rivilla, M. Agirre, A. Basterretxea, A. Etxeberria, A. Veloso, H. Sardon, D. Mecerreyes and F. P. Cossío, *J. Am. Chem. Soc.*, 2017, **139**, 4805–4814.

4. kapitulua

Polihidroxibutiratoaren birziklapen kimikoa balio erantsi handiko hidroxiazidoetan organokatalizatzaile berezi bat erabiliz



Polihidroxibutiratoaren birziklapen kimikoa balio erantsi handiko hidroxiazidoetan organokatalizatzaile berezi bat erabiliz

4.1. Sarrera

β-Hidroxiazido kiralak monomero oso garrantzitsuak dira, batez ere industria farmazeutikoan, izan ere, produktu kimiko espezifikoen sintesirako lehengai gisa erabiltzen dira, hala nola antibiotikoak, bitaminak, zaporeak, lurrinak eta feromonak sortzeko[1]. Azido 3-hidroxibutirikoa bereziki lesio traumatikoak tratatzeko erabiltzen da, larruazaleko erredurak, miokarditisa, garuneko hipoxia, iskemia eta anoxia besteak beste[2,3]. Gainera, eragin positiboa du osteoblastoen *in vitro* hazkundean eta osteoporosiaren *in vivo* murrizketan[4]. Hala ere, azido 3-hidroxibutirikoa ekoizteko arazo nagusia kantitate handiak lortzeko prozesu eraginkorrik ez dagoela da[5].

Hainbat metodo ikertu dira β-hidroxiazidoen prestaketarako, sintesi kimiko nahiz sintesi biokatalitikoak. Hidroxiazidoen sintesi kimikoa lan neketsua da, metal astunen, katalizatzaileen eta erreaktibo toxikoen erabilera dela eta. Gainera, prozesuak urrats sintetiko ugari eskatzen ditu, azpiprodukturen kopuru esanguratsuak sortuz, talde hidroxiloaren muturreko erreaktibotasuna dela eta. Horrez gain, oro har, sintesirako erabilitako erreakzioen enantioselektibitatea ez da behar bezain altua; hala ere, badira jarraitu daitezkeen bide sintetiko batzuk, hala nola, Reformatsky erreakzio asimetriko katalitikoa eta Noyori hidrogenazio asimetrikoa. Lehenengo kasua, konposatu α-halokarbonilikoetatik eta aldehidoetatik edo zetonetatik abiatuta, zinkezko katalizatzailearen bidez β-hidroxialkanoatoen sintesia da[6]. Noyori hidrogenazio asimetrikoak, aldiz, zetonen hidrogenazio asimetriko katalitikoa ahalbidetzen du,

BINAP-Ru (2,2′-bis(difenilfosfino)-1,1′-binaftilo rutenioa) haluroetan eta karboxilatoetan oinarritutako katalizatzaileen bidez[7]. Sintesi biokatalitikoak abantaila handiak eskaintzen ditu metodo tradizionalen aldean, adibidez, enantiopurutasun handiko produktuen sintesia, erreakzio baldintza leunak erabiliz. Hala ere, desabantaila handi bat du, prozesua kantitate handiagoetan eskalatzeko zailtasuna, alegia[8]. Bide biokatalitikoa erabiliz β-hidroxiazido kiralen sintesia ahalbidetzen duen bide bat β-zetoesterren auto erredukzioa da, NADH-k (nikotinamida adenina dinukleotido erreduzitua) koinmobilizatutako alkohol deshidrogenasa termofilo sendo batek katalizatzen duena[9]. Prozesu horrek hidroxiester kiral bat ematen du, hidroxiazidoa lortzeko hidrolizatu egin beharko litzatekeena.

Seguruenik, azido 3-hidroxibutirikoaren sintesirako metodorik interesgarriena PHBren despolimerizazio kimikoa da. Polihidroxibutiratoa (PHB) mikroorganismoek (*Cupriavidus necator, Methylobacterium rhodesianum edo Bacillus megaterium*) estres fisiologikoan sintetizatzen duten jatorri naturaleko poliesterra da, energia biltegiratzeko sistema gisa. Jatorri biologikokoa eta, beraz, jasangarria izateaz gain, ontziratze-aplikazioetarako alternatiba ona izan daitekeela ikusi da, hesi-propietate bikainak baititu, polietilen tereftalatoak (PET) baino hobeak urari, oxigenoari eta karbono dioxidoari dagokienez[10]. Gainera, poliester alifatiko gehienak bezala, PHB biodegradagarria da lurrean eta uretan, eta horrek interesgarri egiten du, batez ere erabilera bakarreko aplikazioetarako, adibidez, ontziratzerako[11]. Hala ere, PHBren eragozpen nagusia ekoizpen-prozesua garestia dela da, petrolioan oinarritutako polimero konbentzionalena baino garestiagoa; horregatik, birziklatze-prozesu bat ezartzeko beharra ikusi da, materiala degradazioz ez galtzeko eta beste erabilera bat emateko. Beraz, PHB β-hidroxiazido bihurtzeak materialaren balioa gorde lezake, prozesuaren iraunkortasuna areagotuz.

Nahiz eta poliesterren kasuan birziklapen kimikoan hainbat mekanismo erabili daitezkeen, hala nola metanolisia, hidrolisia, glukolisia eta alkoholisia, β-hidroxiazidoak lortzeko hidrolisia hobesten da, izan ere, β-hidroxiazidoak pauso bakar batean lortzea ahalbidetzen luke. Hainbat ikertzailek PHBren transformazio kimikoa ikertu dute; besteak beste, azidoak, baseak eta entzimak erabiliz.

Prieto et al.-ek metodo interesgarri bat diseinatu dute hidroxiazidoak zuzenean sintetizatzeko, *Pseudomonas putida* bakterioaren egoera metabolikoa kontrolatuz. Biokatalizatzaile horrek polihidroxialkanoatoak sintetizatzen ditu zelulan; hala ere, *phaZ* genea ezabatzean eta *phaZ* adierazpen diferentziala sortzean, polimeroa hidrolizatzeko gai da hidroxiazidoak zuzenean lortzeko[12].

Katalisi entzimatikoaz gain, hainbat azido eta base ikertu dira PHB β-hidroxiazidoan despolimerizatzeko. Azido sulfuriko kontzentratua probatu zenean, 12 ordutan polimeroaren % 72 despolimerizatu zen, azido krotonikoaren % 29 eta azido 3-hidroxibutirikoaren % 43 lortuz[5]. Ingurune azidoan, azido krotonikoaren sorrera azido 3-hidroxibutirikoa E1 eliminazio-mekanismo bidez ezabatzean ematen da, bi urratseko prozesu batean gertatzen dena. Erreakzio horretan alkohola protonatu egiten da eta, beraz, ur-molekula bat askatzen da, lotura bikoitza sortuz.

Yu et al.-ek polimeroaren hidrolisi bidezko despolimerizazioa aztertu zuten 70 °C-an ingurune basikoan, kontzentrazio alkalinoa aldatuz haren eragina ikusteko[13]. Ikusi zen kontzentrazio alkalino baxuetan PHBren despolimerizazioaren konbertsioa baxua zela; NaOHren 4 M-eko soluzioa behar zen, 4 ordutan % 75 inguruko despolimerizazioa behatzeko. Hidrolisiaren produktuen karakterizazioak egiaztatu zuen azido 3-hidroxibutirikoaren monomeroaren presentzia % 47 ingurukoa zela eta azido krotonikoarena % 27 inguru. Ingurune basikoan, E1cB mekanismoaren bidez (oinarri konjugatuko ezabatze unimolekularra) ematen da β-hidroxiazidoaren eliminazioa.

Mekanismo horrek karbanio bitarteko bat sortzen du, eta ondoren, azido krotonikoa sortzen da.

Gainera, bi produktuen bereizketa, azido 3-hidroxibutirikoa (HBA) eta azido krotonikoa (CA), ez da prozesu erraza, hidroxiazidoak erraz jasaten baitu tenperatura altuan eliminazio erreakzioa.

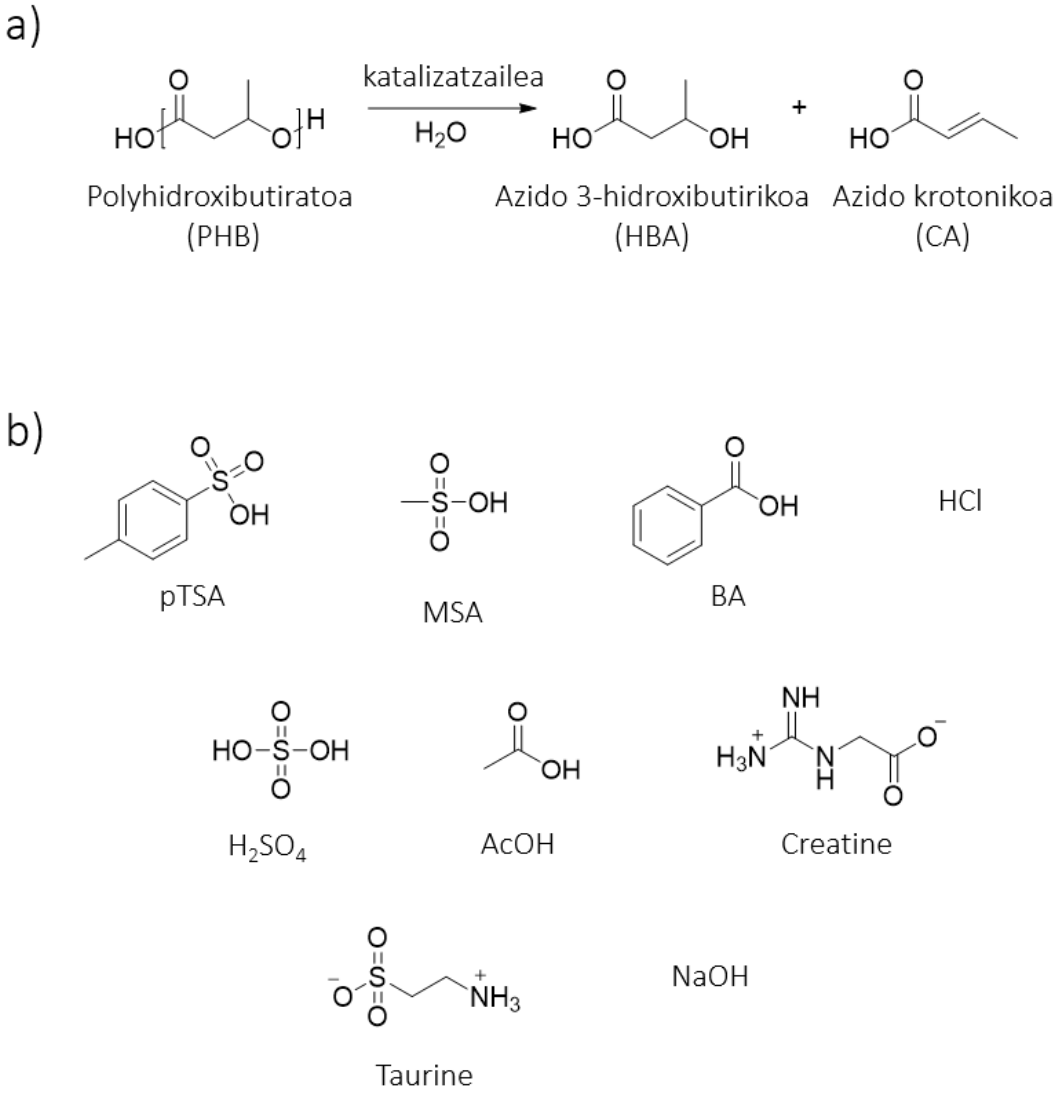
Lan honen helburua despolimerizazio baldintza desberdinak ikertzea da, PHBren despolimerizazioan β-hidroxiazidoaren edukia maximizatzeko. Hainbat katalizatzaile, tenperatura, pH eta ur/PHB proportzio aztertu dira, eta aurkitu da azido 3-hidroxibutirikoaren edukia oso mendekoa dela katalizatzailearekiko eta tenperaturarekiko. Izan ere, baldintza optimizatuetan, hidroxiazidoaren lorpena % 98koa izatera iritsi da. Gainera, bi proudktuak banatzeko azido krotonikoaren erauzketa-metodo bat diseinatu da. Despolimerizazio metodoaren egokitasuna PHB kopolimero batzuetara zabaldu da, hala nola, poli(hidroxibutirato-ko-hidroxibalerato) (PHBV) eta poli(hidroxibutirato-ko-hexanoato) (PHBH), baita sintetikoki prestatutako PHB eta kontsumitu-ondorengo PHB laginetara ere.

4.2. Emaitzak eta eztabaida

4.2.1. PHBren despolimerizazio kimikoa

Sarreran aipatu bezala, PHBren despolimerizazio kimikoa helburu interesgarria da, PHBa baliatuz balio erantsi handiko monomeroak sintetizatu baitaitezke, poliesterra ingurumenera degradatu beharrean. Ildo horretan, PHBren despolimerizazio hidrolitikoa (4.1 a irudia) egin zen, horretarako katalizatzaile desberdinak probatuz, % 10 mol kantitatean polimeroaren unitate errepikakorrarekiko, 180 °C-tan eta 15 ur baliokide erabiliz. Hainbat katalizatzaile ikertu ziren, hala nola azido organiko eta ez-organikoak, azido p-toluenosulfonikoa (pTSA), azido metanosulfonikoa (MSA), azido

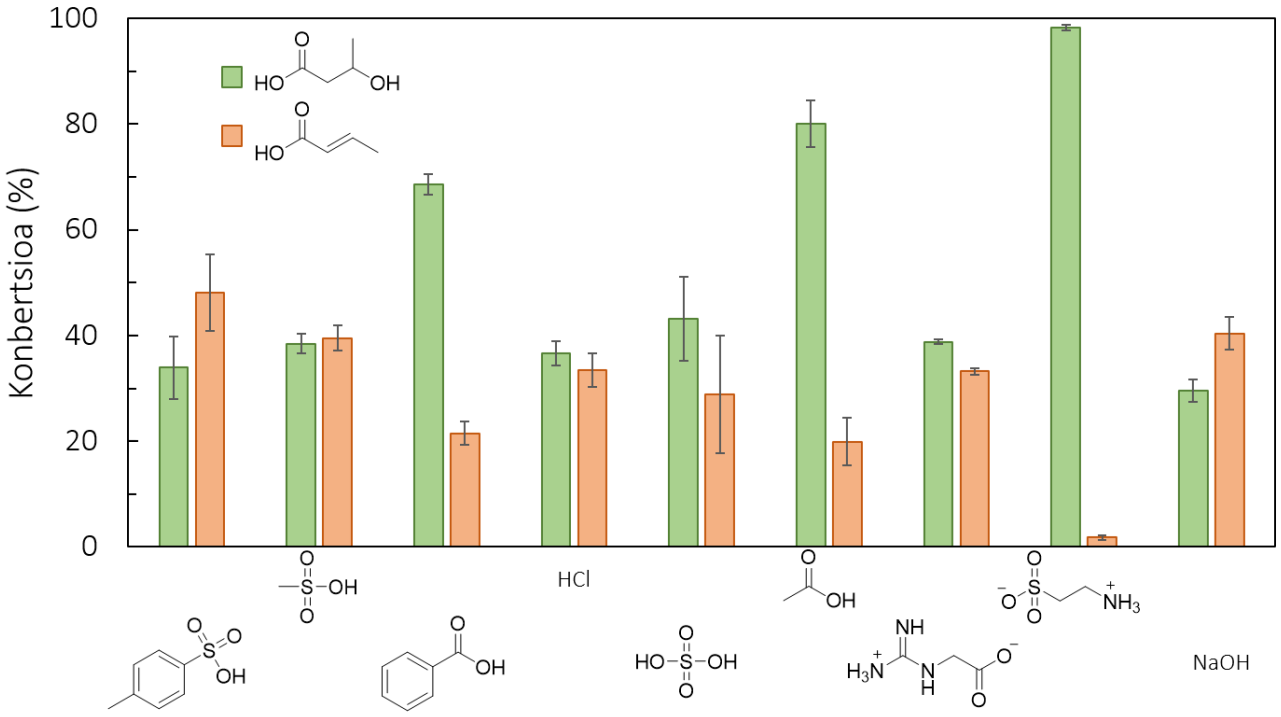
benzoikoa (BA), azido klorhidrikoa (HCl), azido sulfurikoa (H_2SO_4) eta azido azetikoa (AcOH). Base ez-organikoa, sodio hidroxidoa (NaOH), eta jatorri naturaleko katalizatzaile pare bat, kreatina eta taurina, talde azido nahiz basikoak dituztenak euren egituran (4.1 b irudia).



4.1. irudia. a) PHB polimeroaren despolimerizazioa hidrolisi bidez eta b) despolimerizazio prozesuan erabilitako katalizatzaileak.

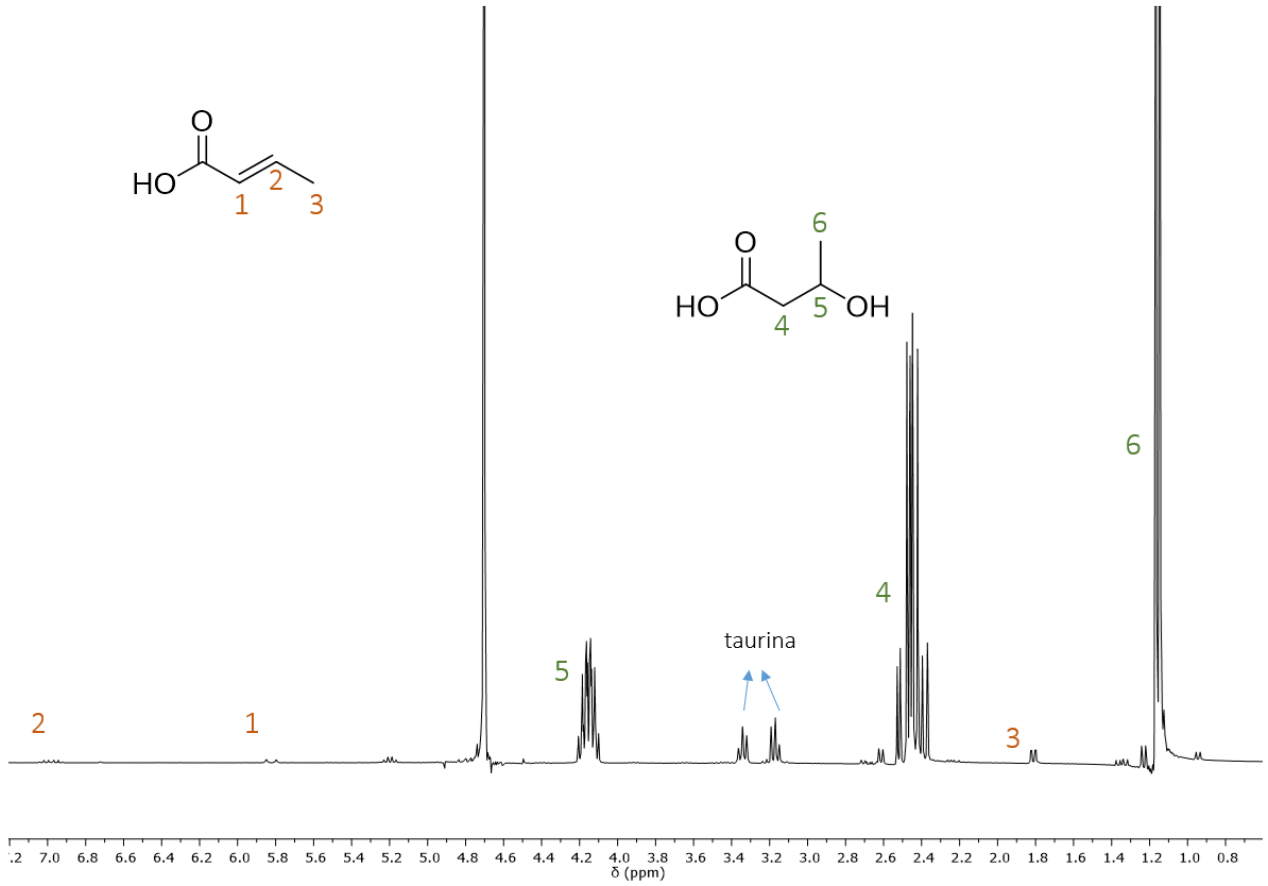
Despolimerizazio prozesua PHB hautsaren desagerpenaren bidez jarraitu zen, hau da, nahaste homogeneo baten lorpenaren bidez. Irudian ikus daitekeenez, katalizatzaileek

eragin nabarmena dute despolimerizazio erreakzioan (4.2 irudia). Despolimerizazio konberstioa ebaluatuz esan daiteke azido azetikoa eta taurina gai izan zirela PHB polimeroa 12 ordutan guztiz despolimerizatzeko; gainerako katalizatzaileekin, berriz, despolimerizazio erreakzioa ez zen amaitu erreakzio denbora horretan, % 70-90 arteko despolimerizazio konbertsioak lortuz.



4.2. irudia. Katalizatzaile desberdinak erabiliz lortutako HBA eta CA-ren konbertsioak.

Despolimerizazio konbertsioaz gain, prozesuaren selektibitatea ere ebaluatu zen. Lehen aipatu den moduan, PHBren despolimerizaziotik bi produktu nagusi lor daitezke: zinetikoki lerratutako β-hidroxiazidoa edo azido krotonikoa, termodinamikoki egonkorragoa dena. Despolimerizazio prozesuak erreakzio ingurunean solidoaren desagerpena ikusiz jarraitu ziren, eta amaierako produktuak ^{1}H NMR-ren bidez aztertu ziren, ur deuteratua erabiliz (4.3 irudia).



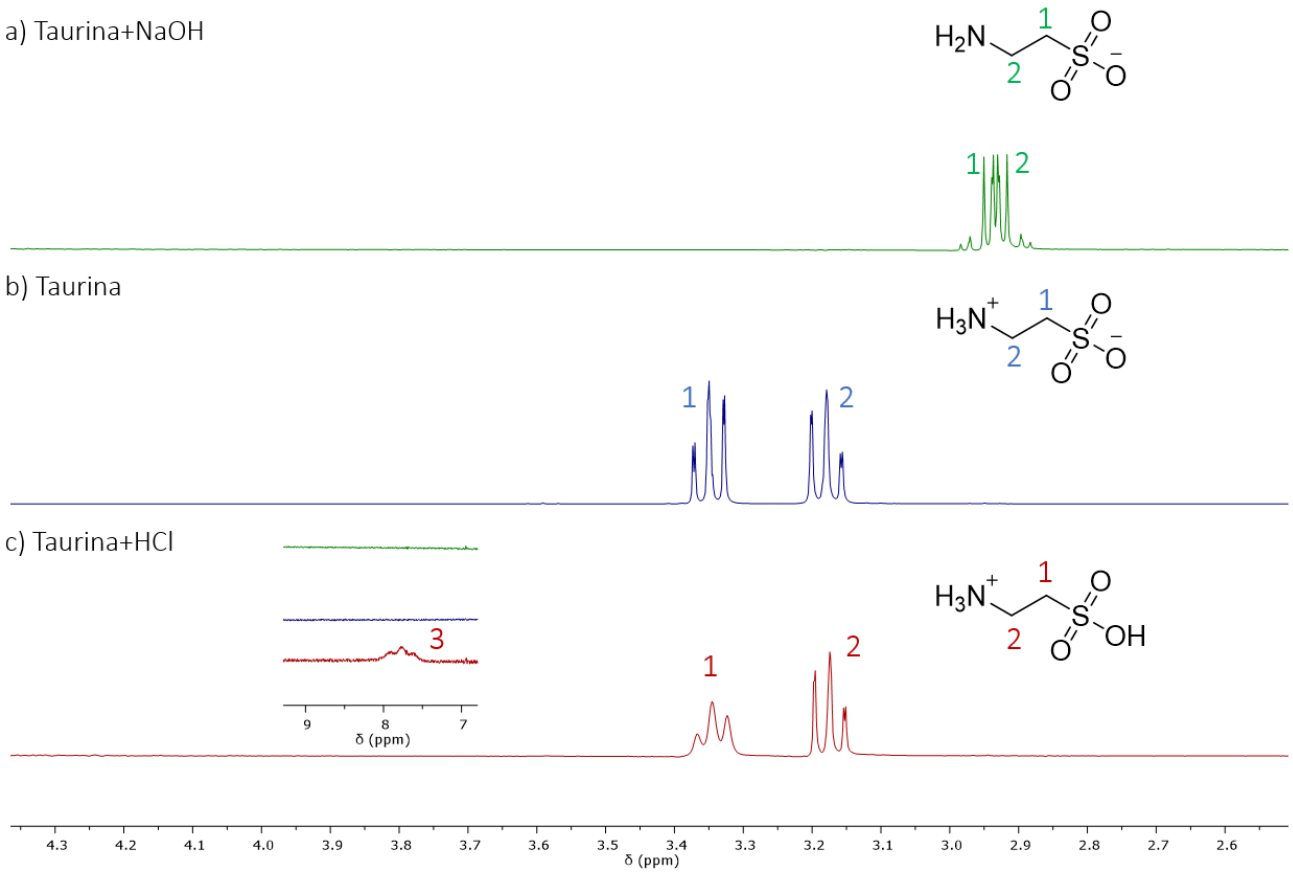
4.3. irudia. PHB polimeroaren despolimerizazioan lortutako produktuen ^{1}H NMR.

HBA-ren presentzia 4,1, 2,4 eta 1,1 ppm-ko seinaleen bitartez ziurtatu zen, eta azido krotonikoarena 6,9, 3,8 eta 1,8 ppm-ko seinaleen bidez. Oso azidoak eta oso basikoak diren katalizatzaileek, hala nola, sodio hidroxidoak (NaOH), azido p-toluenosulfonikoak (p-TSA) eta azido metanosulfonikoak (MSA), azido krotoniko gehiago sortu zuten despolimerizazio erreakzio denbora berean. Enolatoen eraketa nagusiki baldintza azido eta basiko indartsuetan gertatzen denez, ondorioztatu da katalizatzaile horien presentziak eliminazio erreakzioa bultzatzen dutela. HCl eta kreatinaren kasuan, zertxobait handiagoa da β-hidroxiazidoen edukia, azido eta base indartsuekin alderatuta. Azido karboxilikoak, azido benzoikoak eta azido azetikoak adibidez, hobekuntza handia izan zuten beste katalizatzaile batzuekin alderatuta, izan ere, azido benzoikoaren kasuan, % 90eko despolimerizazio konbertsioa lortu baitzen. Taurina,

azido sulfonikoa duen aminoazido naturala, izan zen katalizatzaile guztien artean errendimendu onena erakutsi zuena, azido 3-hidroxibutirikoa % 98an ekoitzi baitzen.

4.2.2. Taurinaren portaera berezia despolimerizazio mekanismoan

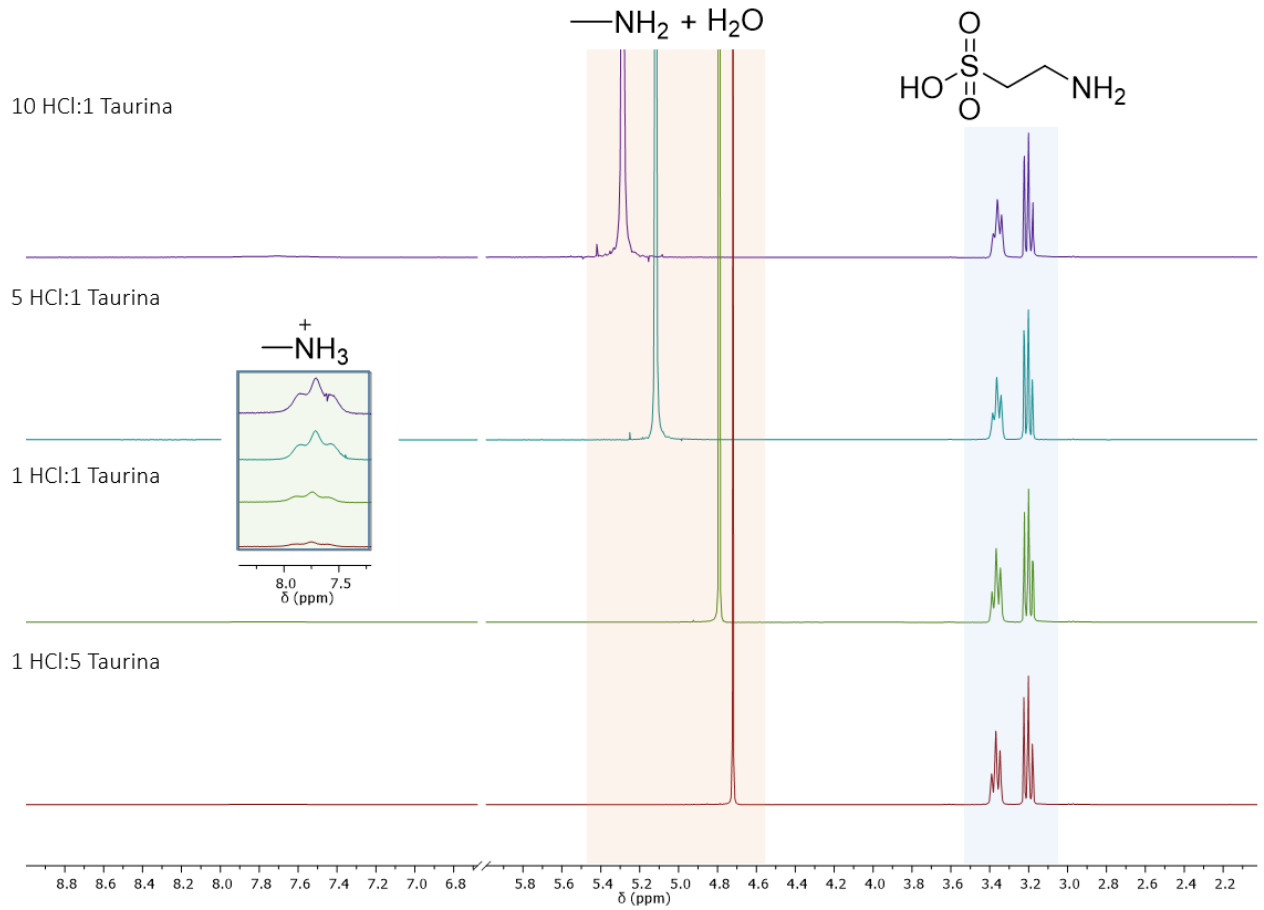
Lehen frogatu moduan, PHB ur ingurunean despolimerizatzeko katalizatzaile onena, lan honetan erabilitakoen artean, taurina izan zen. Taurinaren egitura aztertzeko, eta kontuan hartuta azido eta base talde bana dituela bere egituran, ur-ingurunean duen egitura kimikoa ezagutu nahi izan zen. Horretarako, ^{1}H NMR azterketa bat egin zitzaion hainbat pHtan, ingurune basikoa, neutroa eta azidoa erabiliz (4.4 irudia).



4.4. irudia. Taurinaren ^{1}H NMR a) ingurune basikoan, b) ingurune neutroan eta c) ingurune azidoan.

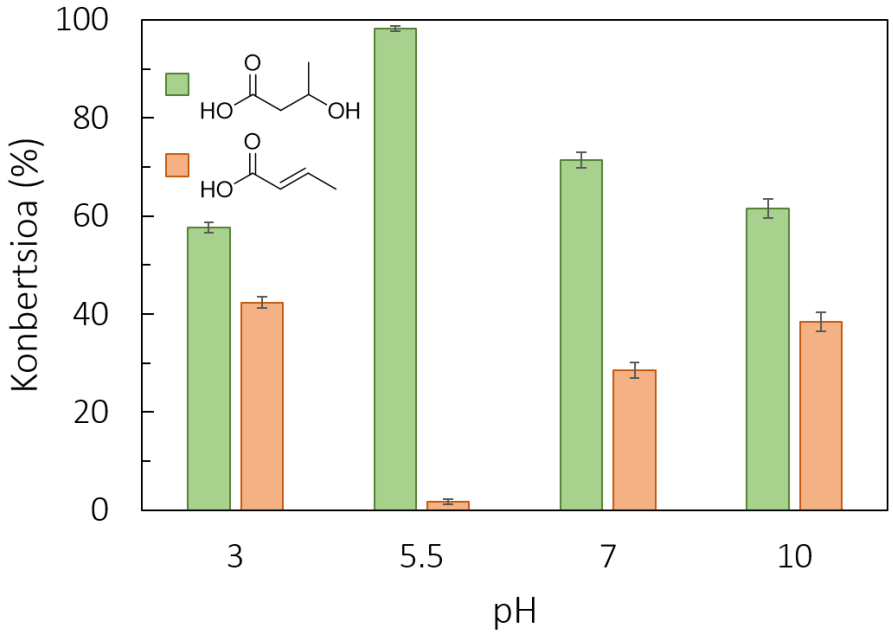
Lortutako NMR espektroak aztertuz ingurune neutroetan oreka gatzaren egitura aldera lerratuta dagoela ikusi zen, non amina protonatua dagoen eta azido sulfonikoa

desprotonatuta (4.4 b irudia). Ingurune basikoan (4.4 a irudia), produktu nagusia protonatu gabeko taurina da, non bai amina bai azido sulfonikoa protonatu gabe dauden eta ingurune azidoan berriz (4.4 c irudia), taurina protonatuta dagoen. Azken kasu horretan, 7,7 ppm inguruan seinale egonkor bat ikus daiteke, amina protonatuari dagokiona. Ingurunearen azidotasunak orekan ere eragina du, ingurunea zenbat eta azidoagoa izan, orduan eta protonatuagoa egongo da taurina (4.5 irudia). Zehaztu ahal izan denez, taurinarekiko HCl baliokide gehiago erabiltzen direnean, 7,7 ppm-ko seinalea egonkorrago bihurtzen da, eta, beraz, taurinaren oreka amina-protonazioaren aldera desplazatuago dagoela ziurta daiteke.



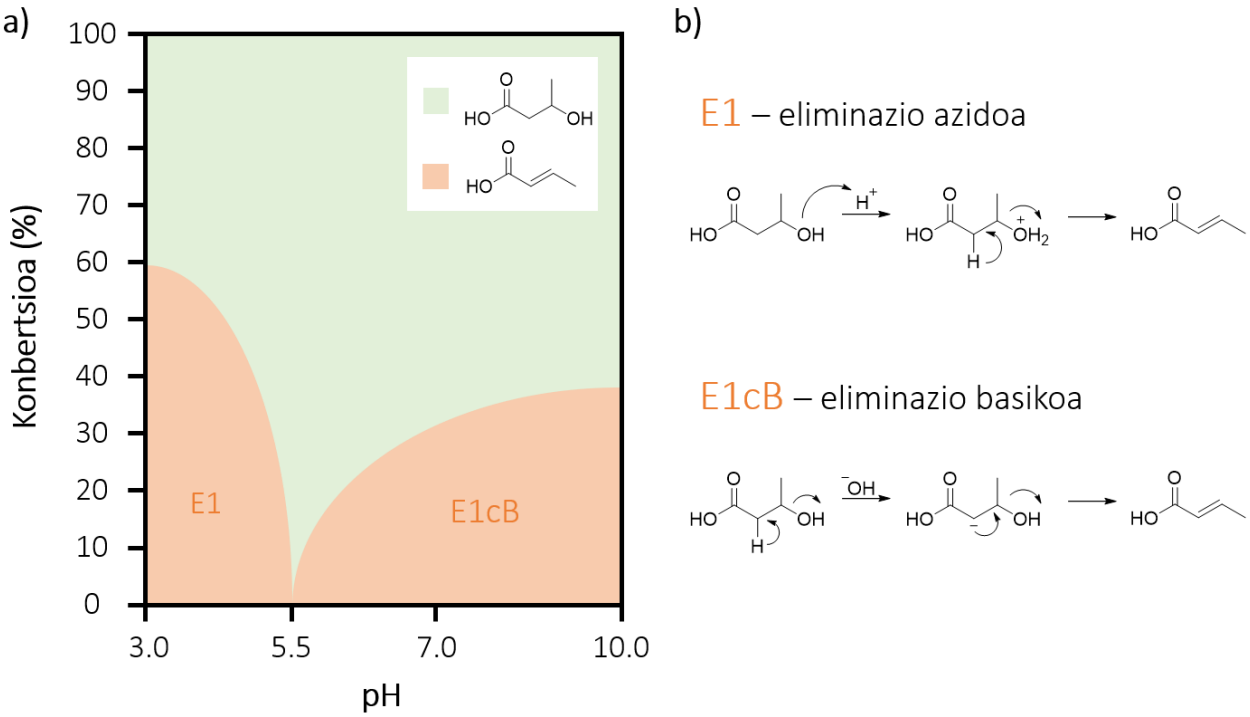
4.5. irudia. HCl baliokide desberdinak dituen taurinaren ^{1}H NMR azterketa.

Taurinaren egituran pH-ak duen garrantzia ulertu ondoren, pH-ak taurinak katalizatutako despolimerizazio prozesuan duen eragina ikertu da.



4.6. irudia. pH-ak PHB-ren despolimerizazioan eta HBAren eta CAren sorreran duen eragina.

3, 7 eta 10 pH-ko hiru tanpoi prestatu eta probatu ziren, eta lehenago frogatutako 5,5 pH-ko laginarekin alderatu ziren (4.6. irudia). Kasu guztietan, despolimerizazioaren konbertsioa % 100ekoa izan zen, polimeroaren desagerpen totala ikusiz. Hala ere, badirudi pH-ak eragin handia duela hidroxiazidoaren eta azido krotonikoaren arteko erlazioan (4.7 irudia). Aztertutako pH balio guztien artean, onena 5,5ekoa da, HBAren % 98 lortzen baita, eta ondorioz, ia ez dagoela eliminazio erreakziorik esan daiteke. pH balio azidoetan, hidroxiazidoak E1 eliminazio erreakzioa jasaten du azido krotonikoa emanez, non alkoholak inguruneko protoi bati erasotzen dion eta ura askatzen den. Ingurune basikoan ere azido krotonikoaren eraketa ikusten da, baina kasu honetan E1cB mekanismoaren bidez, non tarteko karbanio bat sortzen den.



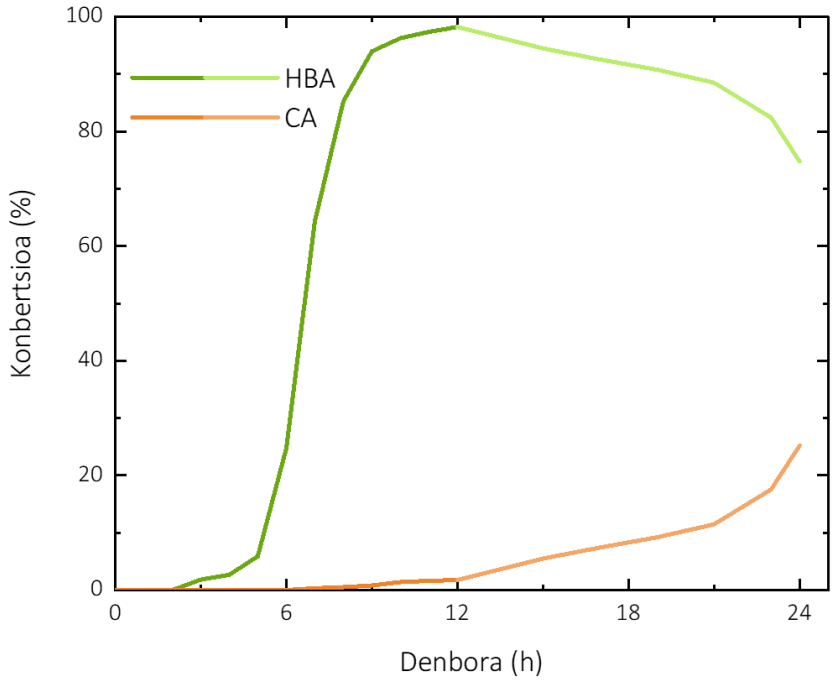
4.7. irudia. a) pH-aren eragina hidroxiazidoaren eta azido krotonikoaren arteko erlazioan eta b) eliminazio mekanismoa ingurune azido edo basikoan.

4.2.3. Despolimerizazio baldintzen optimizazioa

Taurina prozesu honetarako katalizatzailerik onena zela ikusi zenez, despolimerizazio prozesua sakontasun handiagoarekin ebaluatu zen. Ikusi zenez, PHBren hidrolisiaren produktuak azido 3-hidroxibutirikoa eta azido krotonikoa dira; hala ere, bi produktuak despolimerizazioaren hasierako etapan sortzen diren edo azido krotonikoa sortzea saihestu daitekeen ebaluatu nahi izan zen. Horretarako, despolimerizazio zinetika ^{1}H NMR bidez jarraitu zen, HBA eta CAren sorrera denboran zehar aztertuz, % 10 mol taurina erabiliz, 15 ur baliokiderekin eta 180 °C-an(4.8 irudia).

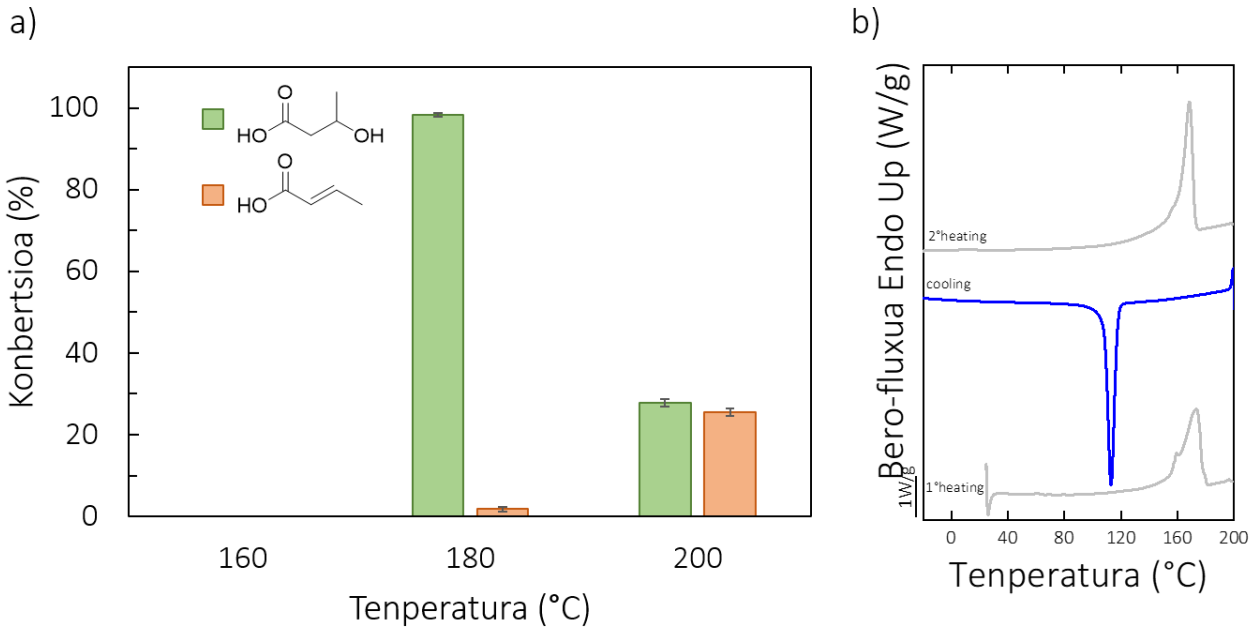
Despolimerizazio zinetikak despolimerizazio erreakzioaren 6. ordura arte HBA zela sortzen zen produktu bakarra erakutsi zuen, ondoren, azido krotonikoaren sorrera

hasiz. Izan ere, badirudi azido krotonikoaren ekoizpena zinetikoki handitzen dela, ziurrenik, ingurunearen azidotasuna handitzen delako.



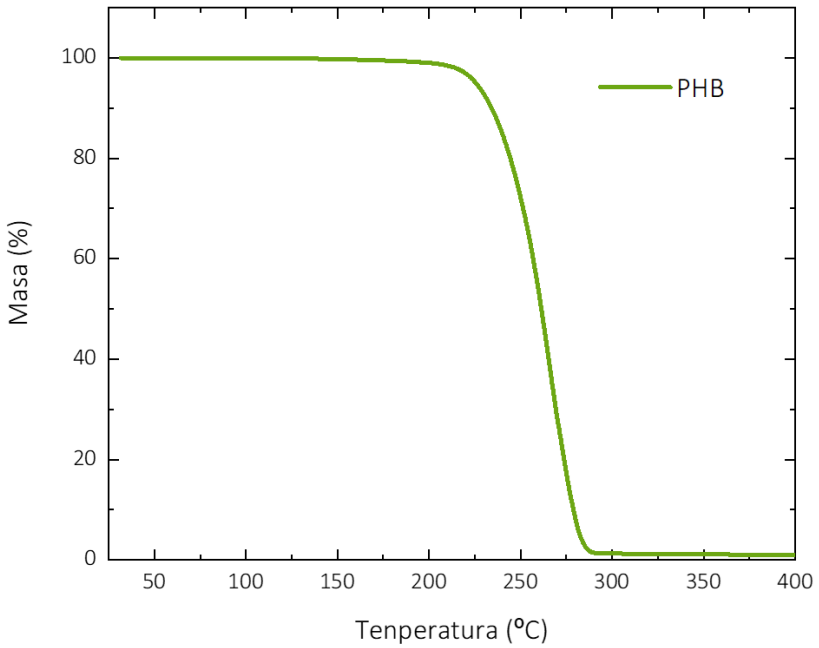
4.8. irudia. PHBren despolimerizazio erreakziotik datozen HBA eta CAren sorreraren zinetika.

PHBaren despolimerizazioa arrakastaz lortu ondoren, beste erreakzio baldintza batzuk aztertu ziren, ahalik eta kantitate handienean lortzen saiatzeko β-hidroxiazidoa. Horretarako, despolimerizazio denborak eta tenperaturak murriztuz, termodinamikoki bultzatutako azido krotonikoaren sortzea saihesteko. Hasieran, erreakzioan tenperaturak duen eragina aztertu zen, 160 °C-tan eginez erreakzioa, gainerako baldintzak mantenduz (4.9 a irudia). ^{1}H NMR bidez ez da despolimerizaziorik ikusten, hori PHBren Tm balioa 168,5 °C-koa delako izan daiteke. Izan ere, PHBren kristalinitate maila altua kontuan hartuta (86 J/g-ko urtze entalpia balioa, ΔHm), katalizatzailea ez da gai izan polimeroarekin elkarreragiteko (4.9 b irudia).



4.9. irudia. a) tenperaturak PHBren despolimerizazioan duen eragina eta b) PHBren DSC emaitzak.

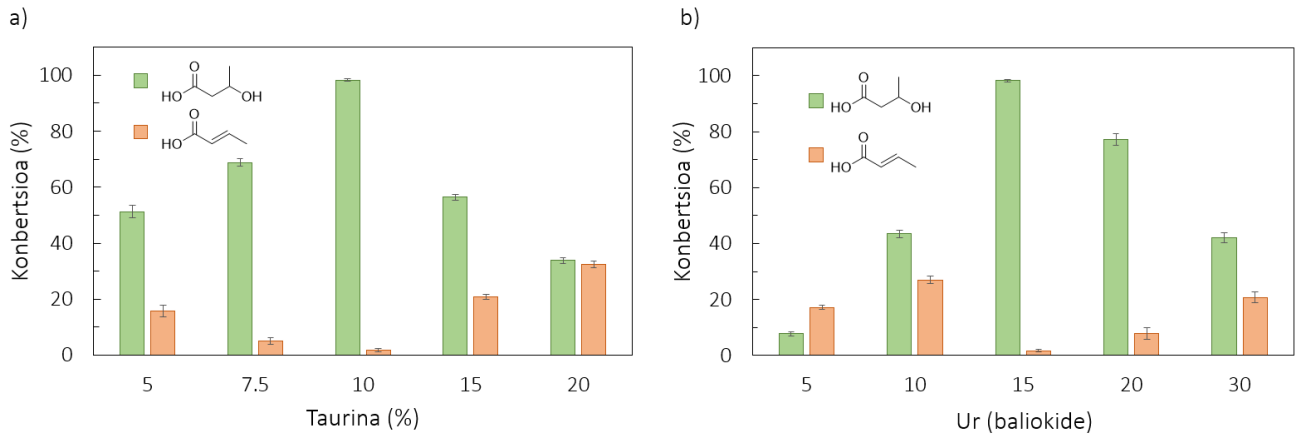
Tenperatura 180 °C-tik 200 °C-ra igotzean, despolimerizazio konbertsioak gora egin zuen, baina, aldi berean, azido krotonikoaren kantitatea nabarmen handitu zen (4.9 a irudia). Gainera, albo erreakzio bidez sortutako espezie ez disolbagarri batzuk hauteman ziren. Nabarmentzekoa da PHBren analisi termograbimetrikoak degradazioa erakusten duela pisu-galerako salto bakar batean 200 °C-an, eta, beraz, baliteke polimeroa deskonposizio kimikoren bat jasaten ari izatea despolimerizazio hidrolitikoarekin batera (4.10 irudia).



4.10. irudia. PHBren analisi termograbimetrikoa nitrogeno-fluxuan.

Era berean taurinaren kantitate ezberdinak probatu ziren despolimerizazioa katalizatzeko, % 5, % 7,5, % 10, % 15 eta % 20 mol polimeroaren unitate errepikakorrarekiko (4.11 a irudia). Emaitzek adierazten dute katalizatzailearen edukiak eragin handia duela azido 3-hidroxibutirikoaren edukian, kantitate optimoa % 10 mol taurina izanik. Izan ere, katalizatzaile kantitate handiagoek despolimerizazio zinetika handitzen dute, baina askoz azido krotoniko gehiago sortzen da.

Katalizatzailearen kantitateak eta tenperaturak duten eragina ikertzeaz gain, kontzentrazioak despolimerizazio prozesuan duen eragina ere aztertu da. Despolimerizazio erreakzioetarako ur-kantitate egokiena zehazteko, 5, 10, 15, 20 eta 30 ur baliokide ikertu ziren polimeroaren unitate errepikakorrarekiko (4.11 b irudia). Despolimerizazio osoa lortzeko gutxieneko ur-kantitatea behar dela dirudien arren, kantitate handienek azido 3-hidroxibutirikoaren kantitatea nabarmen murrizten dute % 98tik % 40ra, ur-edukia 15 baliokidetik 30era igotzean.



4.11. irudia. a) taurina kopuruaren eta b) ur-baliokideen eragina PHBren despolimerizazioan.

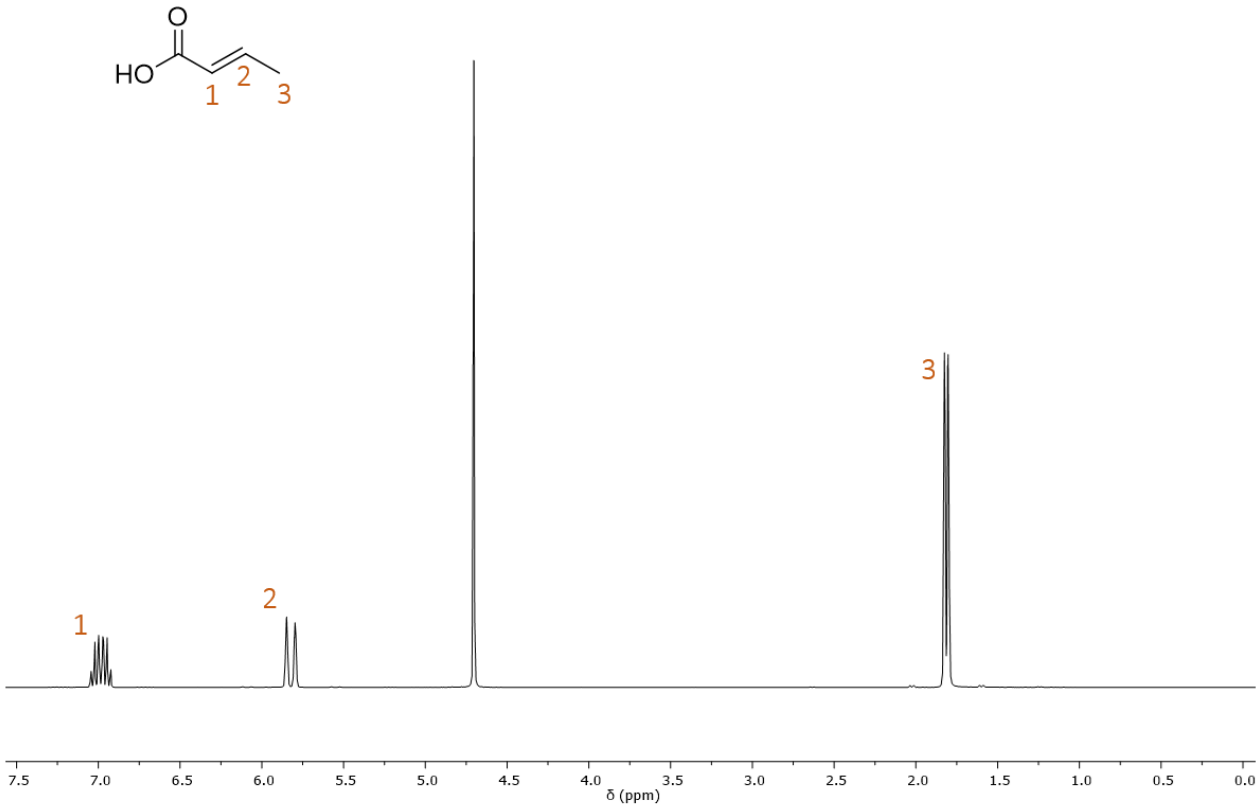
4.2.4. Azido 3-hidroxibutirikoaren purifikazioa

HBA monomeroa garbitzea ez da prozesu erraza, CAk eta HBAk antzeko egiturak baitituzte. Lehenik eta behin, ur ingurunetik taurina kendu zen, horretarako hainbat disolbatzaile probatu zirelarik, hala nola, etanola, metanola, dimetilsulfosidoa eta kloroformoa. Nahasteari etanola gehitzen zitzaionean taurina prezipitatzen zela ikusi zen, eta filtrazio bidez bereizi ahal izan zen.

Katalizatzailea ezabatu ondoren, HBA eta CA bereizteko hainbat prozesu ezberdin probatu ziren. Literaturaren arabera, kristalizazio-prozesu batek funtziona lezake; izan ere, HBAren urtze-tenperatura 45 °C-koa da, eta CA-rena 72 °C-koa. Hala ere, ez zen kristalen eraketarik ikusi, bi konposatuek gel baten antzeko nahastea sortu baitzuten, eta beraz, ezinezkoa izan zen HBA garbitzea.

Beste saiakera batean, konposatuak destilazio bidez banatzeko saiakuntza egin zen, jakinda HBAren irakite-puntua 269 °C-koa dela eta CArena 185 °C-koa. Hasieran, prozedura eraginkorra dela zirudien, kondentsadorean konposatu zuri baten eraketa ikusi baitzen, CA zirudiena. Hala ere, destilazio denbora baten ondoren ondorioztatu zen HBA osoa CA bihurtu zela banantze metodoarentzat beharrezkoa zen beroaren

ondorioz, erabat purua zen CA monomero bat lortuz, ^{1}H NMR bidez berretsia (4.12 irudia).

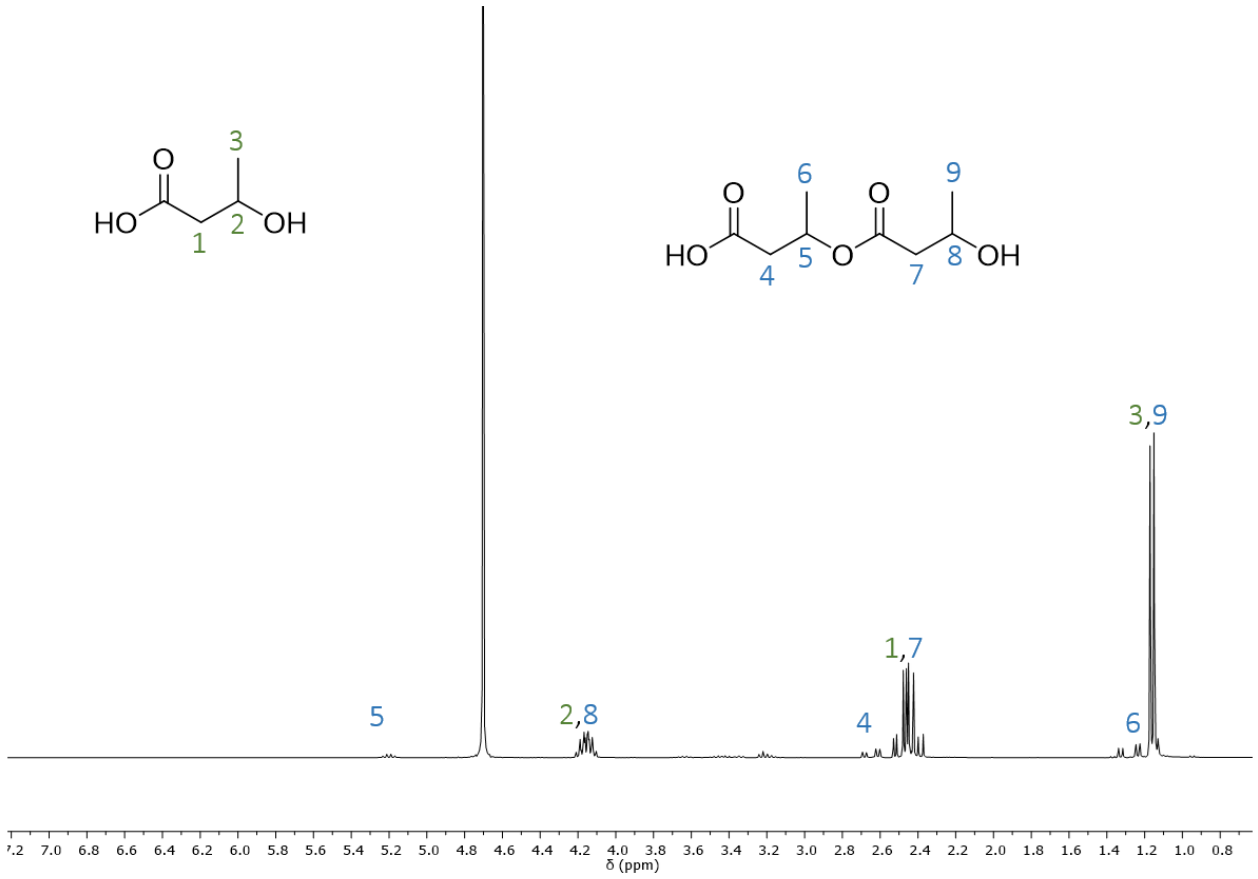


4.12. irudia. CAren ^{1}H NMR espektroa, despolimerizazio produktuaren destilazio-prozesuaren ondoren.

Ondoren, osagaietako baten hauspeatzea selektiboa ikertu zen, hainbat disolbatzaile erabiliz, hala nola kloroformoa, azetona, etil azetatoa, toluenoa, dimetilsulfoxidoa, eter dietilikoa eta diklorometanoa. Disolbatzaile horietako batzuetan prezipitatu bat sortu zen; hala ere, prezipitatua ^{1}H NMR bidez aztertu ondoren, HBA eta CAren banaketarik ez zegoela ikusi zen.

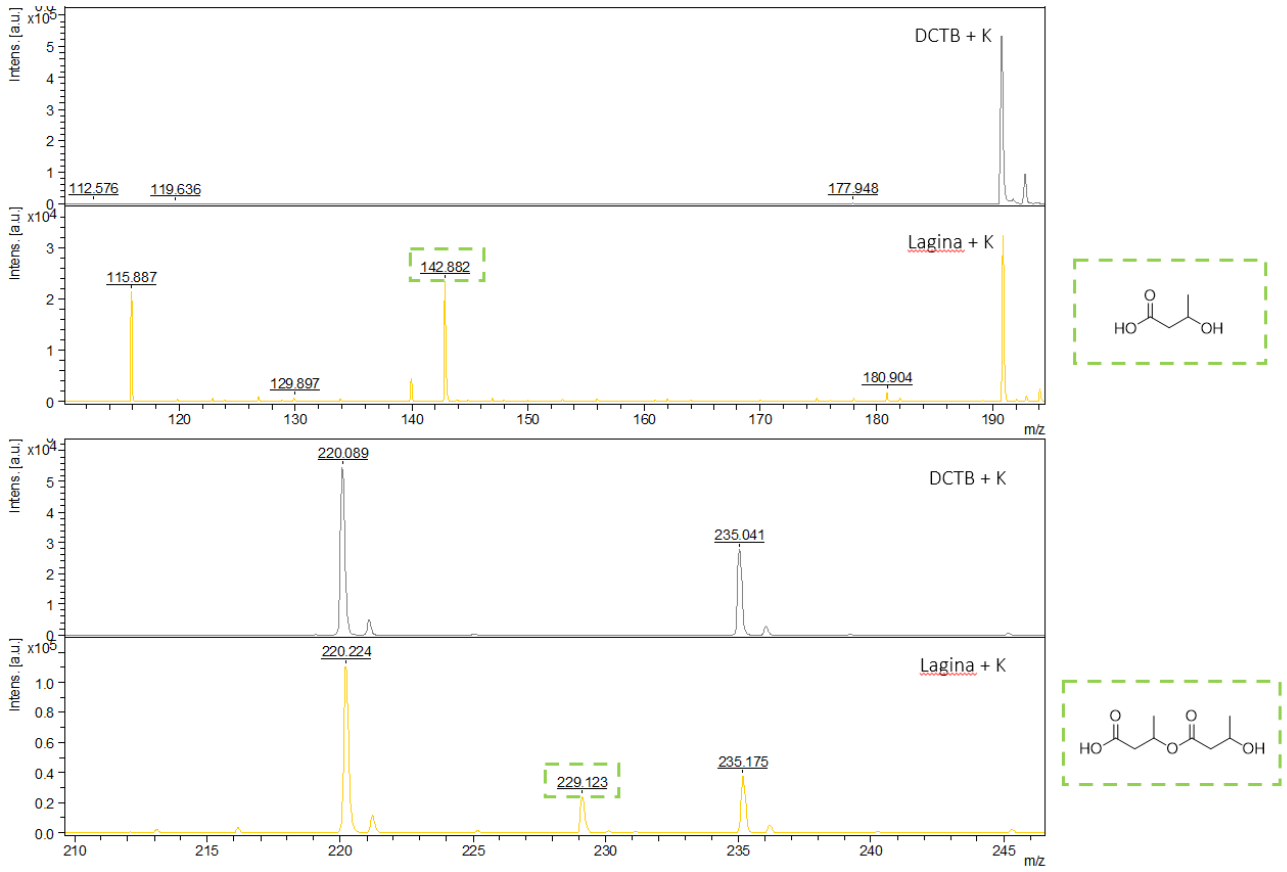
Azkenik, uretan dagoen erreakzio-nahasketaren eta hainbat disolbatzaile organikoren arteko likido-likido erauzketa aztertu zen, horien artean diklorometanoa eta eter dietilikoa. Uraren eta eter dietilikoaren konbinazioa erabiliz, HBAren eta CAren

banaketa arrakastatsua lortu zen. HBA ur-fasean geratzen zen eta CAk fase organikora migratzen zuen, eter dietilikora. Ondoren, ur-fasearen lurrunketa egin zen, ur guztia kentzeko eta HBA purua lortzeko. Produktua honela karakterizatu zen: ^{1}H NMR bidez uretan (4.13 irudia) eta MALDI-TOF espektroskopia bidez (4.14 irudia).



4.13. irudia. Purifikatu ondorengo HBA monomeroa eta dimeroaren arrastoak ^{1}H NMR espektroan.

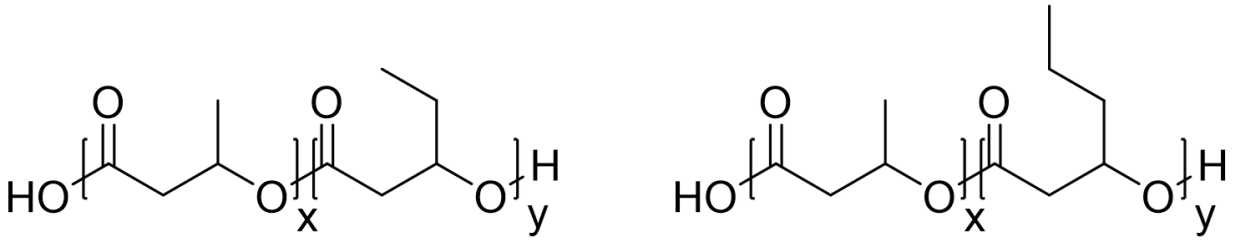
^{1}H NMR espektroak monomeroaren presentzia erakutsi zuen, baita dimeroaren arrasto txikiak ere (% 4); horrek iradokitzen du polimero kantitate txiki bat zegoela, erabat despolimerizatu ez zena (4.13 irudia). MALDI-TOF espektroskopiak ere emaitza bera berretsi zuen, HBA monomeroaren presentzia 104,1 g·mol^{-1}eko masa zehatzarekin eta dimeroaren presentzia 190,1 g·mol^{-1}eko masa zehatzarekin (4.14 irudia).



4.14. irudia. HBA monomeroaren eta dimeroaren MALDI-TOF espektroak.

4.2.5. Despolimerizazio prozesuaren zabaltzea

PHB polimeroa oso polimero interesgarria da, bere jatorri biologikoagatik, biobateragarritasunagatik, biodegradagarritasunagatik eta hesi propietateengatik; hala ere, lehen aipatu den bezala, bere kristalinitate handiagatik propietate mekanikoak eskasak dira. Alderdi hori hobetzeko, hainbat kopolimero sintetizatu izan dira komonomeroen proportzio aldakorrekin, PHBV eta PHBH dira kopolimero ezagunenetako bi.

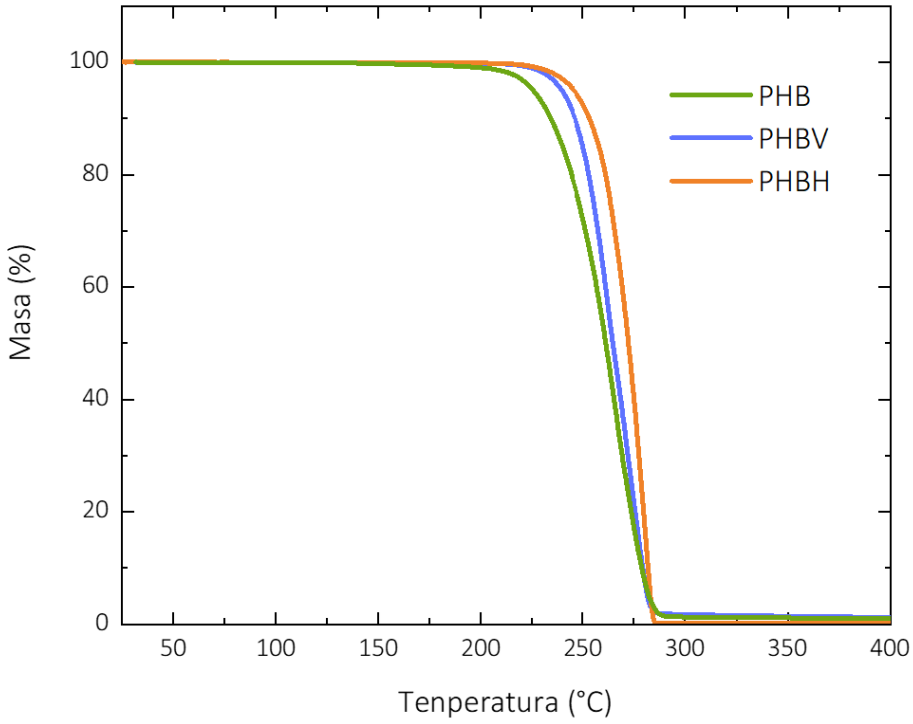


Poli(hidroxibutirato-ko-hidroxibalerato) (PHBV)

Poli(hidroxibutirato-ko-hidroxihexanoato) (PHBH)

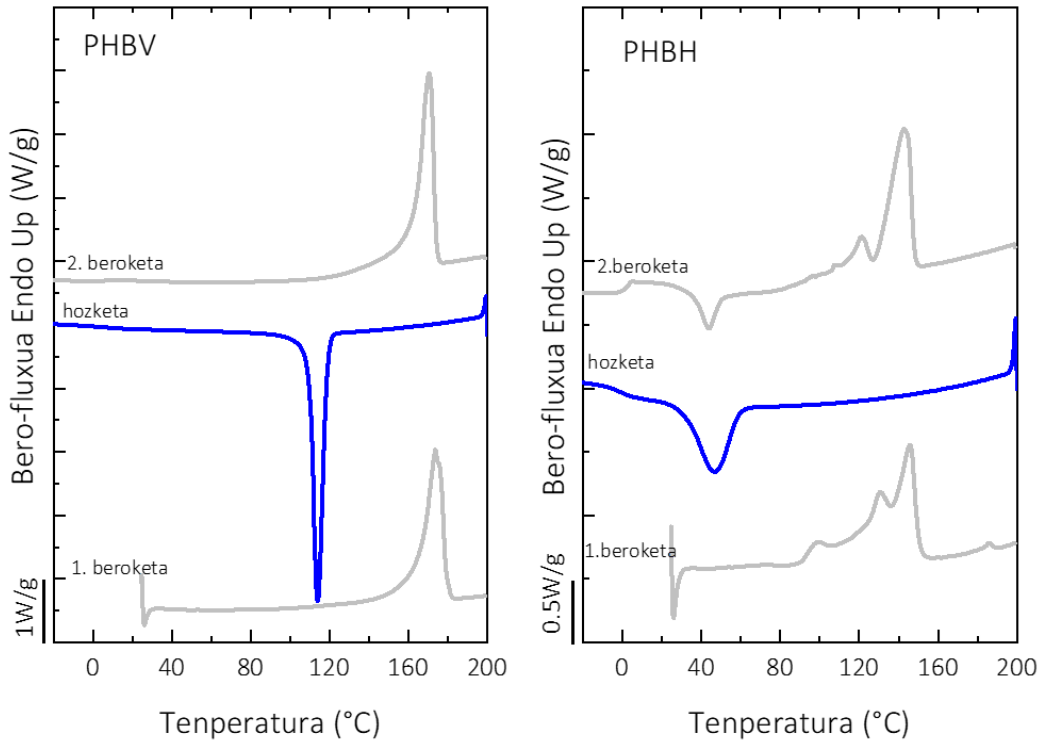
4.15. irudia. PHBV eta PHBH kopolimeroen egitura.

PHBV kopolimeroak bigarren komonomeroa (azido hidroxibalerikoa) soilik % 2 mol proportzioan du eta PHBHk hidroxihexanoatoa % 10 molean. Kopolimeroen propietate termikoek erakusten dute degradazio-tenperatura altuagoa dela bi kopolimeroetan PHBren homopolimeroan baino, 225 °C-ko degradazio-tenperatura dutelarik (4.16 irudia).



4.16. irudia. PHBV eta PHBH kopolimeroen analisi termograbimetrikoa eta PHBrekin konparaketa.

DSC analisiari dagokionez (4.17 irudia), ikusi zen PHBVk ez zuela alde handirik PHBrekiko Tm balioan eta kristalinitate mailan, eta beraz, ondorioztatu zen azido hidroxibaleriko komonomeroaren % a2k ez duela eraginik polimeroaren propietate termikoetan. PHBH kopolimeroaren kasuan, aldiz, balioak nabarmen aldatu ziren: bi Tm balio, 121 °C-an, hidroxihexanoato unitateei dagokiena, eta 143 °C-an, hidroxibutirato unitateei dagokiena, 4 J/g eta 34 J/g-ko urtze-entalpiaren balioekin, hurrenez hurren. Azido hidroxihexanoikoa gehituz, kristalinotasun maila nabarmen jaisten da, % 23ko balioa erakutsiz, eta, beraz, lortutako polimeroa malguagoa da eta ez hain hauskorra. Tm balioa gutxitzean polimeroen propietate mekanikoak hobetzen dira, baina hesi propietateek galera jasaten dute.

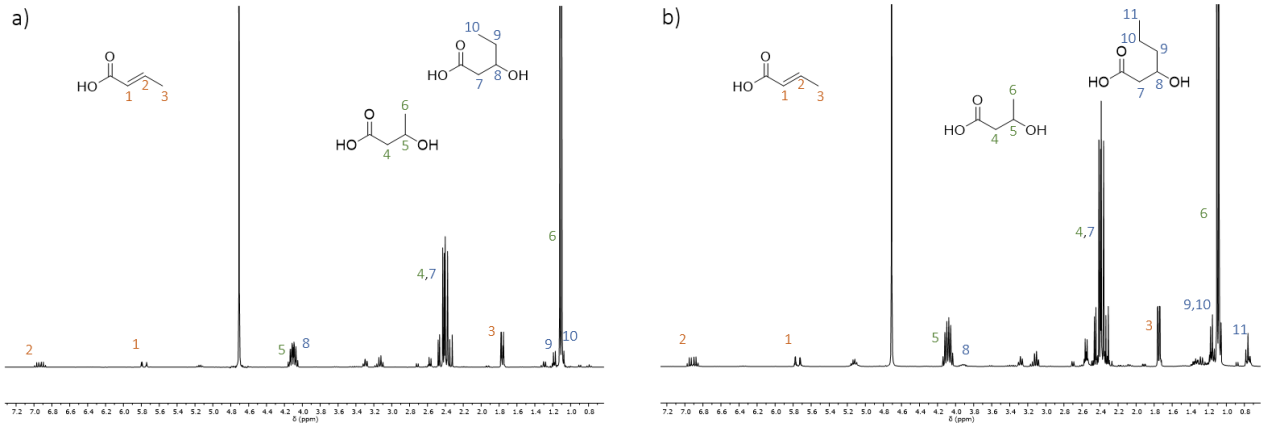


4.17. irudia. PHBV eta PHBH kopolimeroen DSC analisia.

PHB polimerorako proposatu zen despolimerizazio prozesua PHBV eta PHBH kopolimeroetarako ere probatu zen, prozesuaren bertsatilitatea zehazteko. Bi

kopolimeroei erreakzio-baldintza berberak aplikatu zitzaizkien: % 10 mol taurina, 5,5eko pH-a, 15 ur-baliokide, 180 °C eta 12 h-ko erreakzio-denbora.

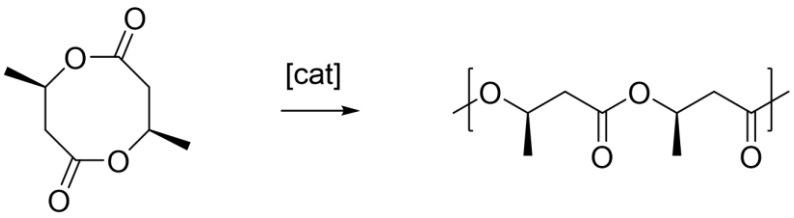
^{1}H NMR analisiko emaitzek zehazten dute lehen deskribatutako despolimerizazio prozesuak ere arrakasta izan zuela PHBV eta PHBH kopolimeroetarako. PHBVren kasuan (4.18 a irudia), produktu nagusiak HBA (% 88) eta CA (% 10) direla ikusi zen, eta kantitate txikiagoan azido hidroxibalerikoa (HVA), polimeroan soilik % 2an baitago. PHBH kopolimeroaren kasuan (4.18 b irudia), bigarren komonomeroaren kopurua handiagoa da, % 10ekoa, eta, beraz, azido hidroxihexanoikoaren (HHA) seinaleak agerikoagoak dira, HBArekin (% 78) eta CArekin (% 12) batera.



4.18. irudia. a) PHBV kopolimeroaren despolimerizazioaren ^{1}H NMR espektroa eta b) PHBH kopolimeroaren despolimerizazioaren ^{1}H NMR espektroa

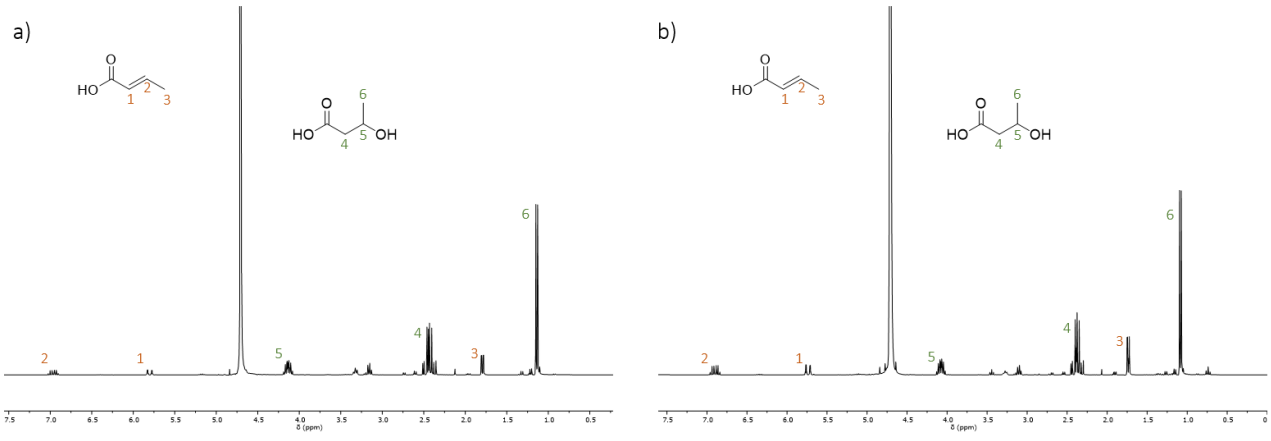
Despolimerizazio erreakzioaren baldintzak kopolimero bakoitzerako doitu behar dira, bereziki PHBHrako. Azken kopolimero horrek PHBak baino Tm balio baxuagoa du, eta, ondorioz, pentsa liteke erreakzio tenperatura baxuagoak despolimerizaziorako mesedegarriagoak izan beharko luketela, eratutako CA kantitatea murrizteko.

PHB sintetikoak, Chen et al.-ek sintetizatuak izan dira, zortzi kideko diolida ziklikoaren eraztun irekiera bidez (4.19 irudia)[14] eta lehen deskribatutako baldintza onenak erabiliz despolimerizatu da.



4.19. irudia. PHB sintetikoaren eraztu irekiera polimerizazio erreakzioaren eskema.

12 orduko despolimerizazio erreakzioaren ondoren, polimero osoa erabat despolimerizatu zen eta ^{1}H NMR espektroak HBAren % 90eko eraketa adierazi zuen, gainerakoa CA (% 10) izanik (4.20 a irudia). Ikusten den eliminazio-tasa handia polimero sintetikoaren pisu molekularrarekin lotuta egon daiteke. Oinarri biologikoko PHBak pisu molekular handiagoa du sintetikoak baino, eta, beraz, izan liteke azken polimero honek denbora gutxiago behar izatea despolimerizazioa osatzeko eta, ondorioz, denbora motzagoek CAren sorreraren murrizketa eragitea.



4.20. irudia. a) PHB sintetikoa eta b) kontsumo osteko PHB polimeroen despolimerizazio erreakzioen ^{1}H NMR espektroak.

Kontsumitu osteko PHBak gehigarriak ditu elikagaiak ontziratzeko material gisa erabiltzeko propietateak hobetzeko. Gehigarri horiek HBA monomeroa lortzeko eraginik duten ondorioztatzeko, despolimerizazio erreakzioa egin zen. Ikusi zen hauts beltzaren kantitate txiki bat (% 6) lortu zela erreakzioaren amaieran, eta hori erretiluan erabili ziren gehigarriei dagokiela uste da. Gainera, ^{1}H NMR espektroak iradoki zuen HBA/CA erlazioa txikiagoa zela PHB puruaren despolimerizazio erreakzioan lortzen dena baino, % 72 HBA eta % 22 CA lortu baitzen (4.20 b irudia).

4.3. Ondorioak

Kapitulu honetan azido 3-hidroxibutiriko monomeroa lortzeko etorkizun handiko metodo bat aztertzen da. Proposatutako prozesuan balio erantsia duen hidroxiazido monomeroak lortzen dira PHB polimeroaren despolimerizazio prozesuaren bidez. Hala ere, HBA monomeroa lortzeko oinarri biologikoa duen polimeroa despolimerizatzeko prozesua ez da urrats erraza, azido krotonikoaren eraketa termodinamikoki bultzatua baitago. Hainbat katalizatzaileren azterketa egin da, despolimerizazio erreakzioan duten eraginkortasuna zehazteko, ematen duten HBA/CA erlazioarekin batera. Taurina katalizatzaile egokiena dela ondorioztatu zen, PHB erabat despolimerizatzen baitu hidroxiazido monomeroa % 98ko kantitatean emanez.

Hainbat erreakzio baldintza aztertu ziren, HBA monomeroa ahalik eta kantitate handienean lortzeko eta CAren eraketa murrizteko. Ikusi zen pH-a funtsezko faktorea dela despolimerizazioan, 5,5eko pH-a izanik idealena, ia ez baita eliminazio erreakziorik gertatzen. pH baxuago eta altuagoetan E1 edo E1cB eliminazio erreakzioak sustatzen dira, hurrenez hurren. Gainera, Tm-tik gora lan egiteko beharra ondorioztatu zen, tenperatura horretatik behera ez baitago erreakziorik.

Azkenik, PHBren despolimerizazio prozesua PHBV eta PHBH kopolimero, PHB sintetiko eta kontsumo ondoko PHB batzuetara zabaldu zen, eta kasu guztietan emaitza oparoak lortu ziren, erreakzio baldintzak kasu bakoitzerako egokitu beharko liratekeen arren. Dakigunez, hau da PHB polimeroa HBA monomeroa konbertsio handitan despolimerizatzea ahalbidetzen duen lehen lana, eta ia erabat murrizten duena CAren eraketa. Gainera, urrats bakarreko prozesu erraza izanik, metodo egokia da azido 3-hidroxibutirikoaren kantitate handian ekoizteko.

4.4. Atal esperimentala

4.4.1. Materialak

Polihidroxibutiratoa (PHB) Sigma Aldrich S.A. konpainiatik lortu zen. Erabilitako katalizatzaile guztiak Sigma Aldrich S.A.-koak dira: azido p-toluenosulfonikoa (p-TSA) (% 95), azido metanosulfonikoa (MSA) (% 99), azido benzoikoa (BA) (% 99,5), azido klorhidrikoa (HCl) (% 37), azido sulfurikoa (H_2SO_4) (% 95), azido azetikoa (AcOH) (% >99), kreatina (% 99), taurina (% >99) eta sodio hidroxidoa (NaOH) (>98 %). PHBV polimeroa Biomer Biopolyesters (Schwalbach/Alemania) enpresari erosi zitzaion eta PHBH Kaneka Corporation (Osaka, Japonia) enpresari, eta jaso bezala erabili ziren. Eter dietilikoa Fischer Scientific-engandik eskuratu zen eta purifikaziorik gabe erabili zen.

4.4.2. PHB despolimerizatzeko prozedura

PHB despolimerizazioa hidrolisi bidez egin zen, hidroxiazido monomeroak lortzeko. Horretarako, presio handiko schlenk batean 1 g (0,012 mol) PHB polimero gehitu ziren, 15 baliokide (0,174 mol, 3,14 mL) ur eta % 10 mol (polimeroaren unitate errepikakorrarekiko) katalizatzaile (taurinaren kasuan 0,001 mol, 0,145 g). Ontzia 180 °C-ko olio-bainu batean murgildu zen, polimeroa desagertu zen arte. Despolimerizazio erreakzioa amaitu ondoren, bainutik ontzia atera eta hozten utzi zen giro-

tenperaturaraino. Erreakzioak ^{1}H NMR bidez jarraitu ziren, HBA monomeroaren eta CA produktu sekundarioaren sorrera ikusteko.

4.4.3. HBAren purifikazioa

Despolimerizazio prozesuaren ondoren, erreakzioan despolimerizatu gabeko polimero hondar edo beste edozein partikula solido iragazi ziren. Ondoren, etanola gehitu eta katalizatzailea, taurina, hauspeatu zen. Behin bi produktuak edukirik (HBA eta CA), eter dietilikoarekin likido-likidoa erauzketa egin zen. CA fase organikora igarotzen da eta HBA monomeroa ur fasean geratzen da. Amaitzeko uretan disolbatutako HBA lehortu eta ^{1}H NMR eta MALDI-TOF bidez karakterizatu zen.

4.5. Erreferentziak

1 D. Seebach, M. Albert, P. I. Arvidsson, M. Rueping and J. V. Schreiber, *Chimia*, 2001, **55**, 345.

2 L. Massieu, M. L. Haces, T. Montiel and K. Hernández-Fonseca, *Neuroscience*, 2003, **120**, 365–378.

3 K. Tieu, C. Perier, C. Caspersen, P. Teismann, D. C. Wu, S. D. Yan, A. Naini, M. Vila, V. Jackson-Lewis, R. Ramasamy and S. Przedborski, *J. Clin. Invest.*, 2003, **112**, 892–901.

4 Y. Zhao, B. Zou, Z. Shi, Q. Wu and G. Q. Chen, *Biomaterials*, 2007, **28**, 3063–3073.

5 Q. Ren, K. Ruth, L. Thöny-Meyer and M. Zinn, *Appl. Microbiol. Biotechnol.*, 2010, **87**, 41–52.

6 P. G. Cozzi, *Angew. Chemie Int. Ed.*, 2006, **45**, 2951–2954.

7 R. Noyori, T. Ohkuma, M. Kitamura, H. Takaya, N. Sayo, H. Kumobayashi and S.

Akutagawa, *J. Am. Chem. Soc.*, 1987, **109**, 5856–5858.

8 A. Schmid, J. S. Dordick, B. Hauer, A. Kiener, M. Wubbolts and B. Witholt, *Nature*, 2001, **409**, 258–268.

9 A. H. Orrego, D. Andrés-Sanz, S. Velasco-Lozano, M. Sanchez-Costa, J. Berenguer, J. M. Guisan, J. Rocha-Martin and F. López-Gallego, *Catal. Sci. Technol.*, 2021, **11**, 3217–3230.

10 A. Sangroniz, J. B. Zhu, X. Tang, A. Etxeberria, E. Y. X. Chen and H. Sardon, *Nat. Commun.*, 2019, **10**, 1–7.

11 N. Altaee, G. A. El-Hiti, A. Fahdil, K. Sudesh and E. Yousif, *Springerplus*, 2016, **5**, 762.

12 M. T. Manoli, J. Nogales and A. Prieto, *MBio*, 2022, **13**, e01794-21.

13 J. Yu, D. Plackett and L. X. L. Chen, *Polym. Degrad. Stab.*, 2005, **89**, 289–299.

14 X. Tang, A. H. Westlie, E. M. Watson and E. Y. X. Chen, *Science*, 2019, **366**, 754–758.

6. kapitulua

Ondorioak eta perspektiba

Poliesterrak etorkizun handiko materialak dira Nazio Batuek sustatutako "Garapen Jasangarriko Helburuak" misioaren barruan 12. helburua betetzeko, “Kontsumo eta ekoizpen eredu iraunkorrak bermatzea”. Poliesterrak biomasatik lor daitezke eta, ester talde bat dutenez, birziklagarriak izan daitezke. Gainera, material horietako batzuk biodegradagarriak dira baldintza egokietan, material jasangarri bihurtuz. Hala ere, sarrerako kapituluan aipatu den bezala, erabilitako poliester gehienak petroliotik datoz, eta industriek erabiltzen dituzten erreakzio-baldintzek katalizatzaile metalikoak eta energia-kontsumo handiak eskatzen dituzte.

Beraz, poliesterren sintesiaren jasangarritasuna hobetzeko material eta metodo berriak aurkitzeko beharra ikusi da. Alde batetik, biomasatik lor daitezkeen poliesterrak aurkitzea eta, ondorioz, petrolioarekiko mendekotasuna murriztea, eta, bestetik, sintesi-metodo ekologikoagoak aurkitzea, metalen erabilera ezabatuz eta erreakzio-tenperatura baxuagoak erabiliz.

Tesi honetan, lehenik katalizatzaile metalikoak ordezkatzeko katalizatzaile natural baten ikerketa egin zen. Horretarako, termikoki egonkorrak ziren bost katalizatzaile probatu ziren L-laktida eraztun irekiera polimerizazio bidez sintetizatzeko, eta frogatutakoen artean taurina katalizatzailerik onena zela ondorioztatu zen. Katalizatzaile bikaina dela ikusi zen, erreakzio denbora nahiko laburrean polilaktida sintetizatzeko gai delako, dispertsio baxuak lortuz. Ondorioz, taurinak polimerizazio-erreakzioa kontrolatzeko gaitasuna duela adierazi daiteke, bigarren mailako erreakzioak eragotziz. Gainera, zitotoxikotasun probak agerian uzten du katalizatzaile naturala erabiliz sortutako polilaktida ez dela toxikoa, horrek aukera ematen du taurina aplikazio-sorta zabal batean ezartzeko. Azkenik, beste polimero batzuen eraztun irekiera polimerizaziorako

probatu zen katalizatzailea, polikarbonatoak eta poliamidak sintetizatzeko gai ere badela ondorioztatuz.

Monomeroen eta polimeroen sintesirako erregai fosilen erabilera murrizteari dagokionez, oinarri biologikoko materialen erabilera bultzatzeko bi metodo aplikatu dira. Alde batetik, PEF polimeroaren birziklapen zirkularra diseinatu da polimeroaren bizitza baliagarriaren amaierako ebaluazio jasangarri gisa eta, ondorioz, egungo PET poliesterraren etorkizun handiko alternatiba izan daiteke. PEF polimeroak hesi-propietate bikainak dituela egiaztatu zen, PET-enak baino hobeak, baina azken hau bezala, ez da biodegradagarria, eta beraz, birziklatzeko metodo bat aurkitzeko beharra ikusi zen. Disolbatzailerik gabeko glikolisi bidezko despolimerizazio prozesu bat proposatu zen, DBU termikoki egonkorra den organokatalisia erabiliz, errendimendu oso altuak lortuz, % 92. Ondoren, PEF polimeroaren birpolimerizazio erreakzioa gauzatu zen organokatalizatzaile bera erabiliz bi etapetan, lehenik polikondentsazioa fase urtuan eta ondoren solidon, hasierako PEFaren antzeko PEF birziklatua lortuz. Prozesu honek material hau industrialki ezartzeko aukera ematen du, bereziki ontziratze aplikazioetarako.

Bestalde, azido 3-hidroxibutiriko monomeroaren sintesia egin zen prozesu jasangarri baten bidez. Hidroxiazido mota horren sintesi kimikoa prozesu zaila den arren, lan honetan PHB polimeroa despolimerizatuz lortu da prozesu erraz baten bidez, taurina katalizatzaile modura erabiliz eta polimeroari bizi-amaierako ebaluazio jasangarri bat emanez. Despolimerizazio hidrolitikoaren prozesuak bi produktu ematen ditu: interesgarria den azido 3-hidroxibutirikoa eta hidroxiazidoaren eliminazio erreakzioak sortutako azido krotonikoa. Lan honetan azido krotonikoaren eraketa minimizatu zen, hidroxiazido monomeroaren errendimendu altuak lortuz, % 98-koa, alegia. Atal honetan proposatutako despolimerizazio prozesua metodo interesgarri bat dela ikusi da

hidroxiazidoak lortzeko, izan ere oso errendimendu altuak lortzen dira, sintesi ekologiko eta errazeko prozesu baten bidez.

Amaitzeko, poliesterrak giro-tenperaturan polimerizatzeko metodo berritzaile bat diseinatu zen. Tesiaren zati honetan, lehenik, bost kideko espiro-dilaktona berri baten sintesi kimikoa egin zen, erreakzio baldintza leunetan poliesterren sintesia ahalbidetuko zuen monomero erreaktibo bat lortzeko. Bigarren urrats batean, eraztun irekiera polimerizazioa egin zen dilaktona sintetizatu berriaren eta 1,4-butanodiolaren artean. Emaitzek erakutsi zuten DBUk katalizatutako polimerizazioak arrakasta izan zuela eta 13400 $g \cdot mol^{-1}$ pisu molekularreko eta 1,6 dispertsitateko poliesterrak lortu ziren. Gainera, ikusi da eraztun irekiera etapa polimerizazio metodoa etorkizun handiko metodoa dela hainbat polimeroren sintesirako, hala nola poliamidak eta politioesterrak.

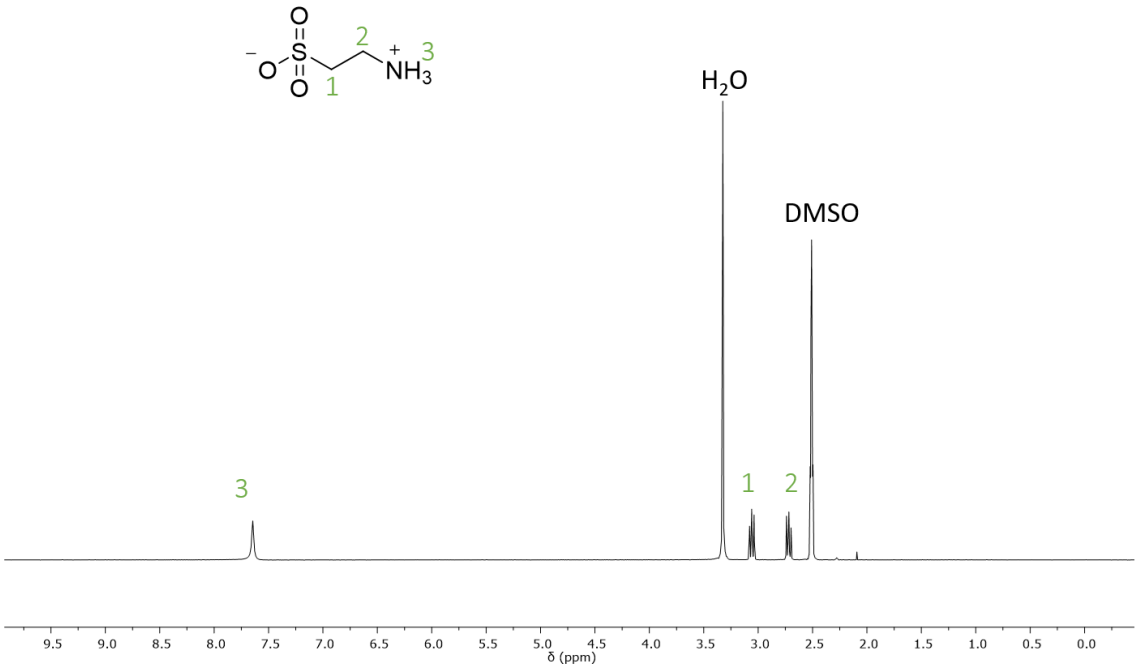
Emaitza horiek ikusita, ondorioztatu da poliesterrak material interesgarriak direla iraunkortasunaren arazoa konpontzeko, biomasatik abiatuta sintetizatu daitezkeelako eta birziklatzeko ahalmen handia dutelako. Tesi honetan, aurrerapausoa eman da monomero eta polimero ekologikoagoak eta polimerizazio metodo jasangarriagoak sortuz, jatorri naturaleko konposatuekin lan eginez eta ingurumena errespetatzen duten baldintzak erabiliz. Bestalde, lan honetako metodoak industrialki aplika litezkeela uste da, metodo sintetiko merke eta errazak diseinatu baitira.

Tesi honetan emaitza oparoak lortu badira ere, oraindik hobekuntza nabarmenak egin behar dira. Alde batetik, organokatalizatzaile kantitate handiak erabiltzen dira katalizatzaile metalikoekin alderatuta, eta erreaktibitateak baxuak dira, pisu molekular txikiko polimeroak lortuz. Gainera, espiro-dilaktonaren sintesia optimizatu behar da eskala handian ekoitzi ahal izateko eta prozesuaren kostu handia murrizteko alternatibak aurkitu behar dira.

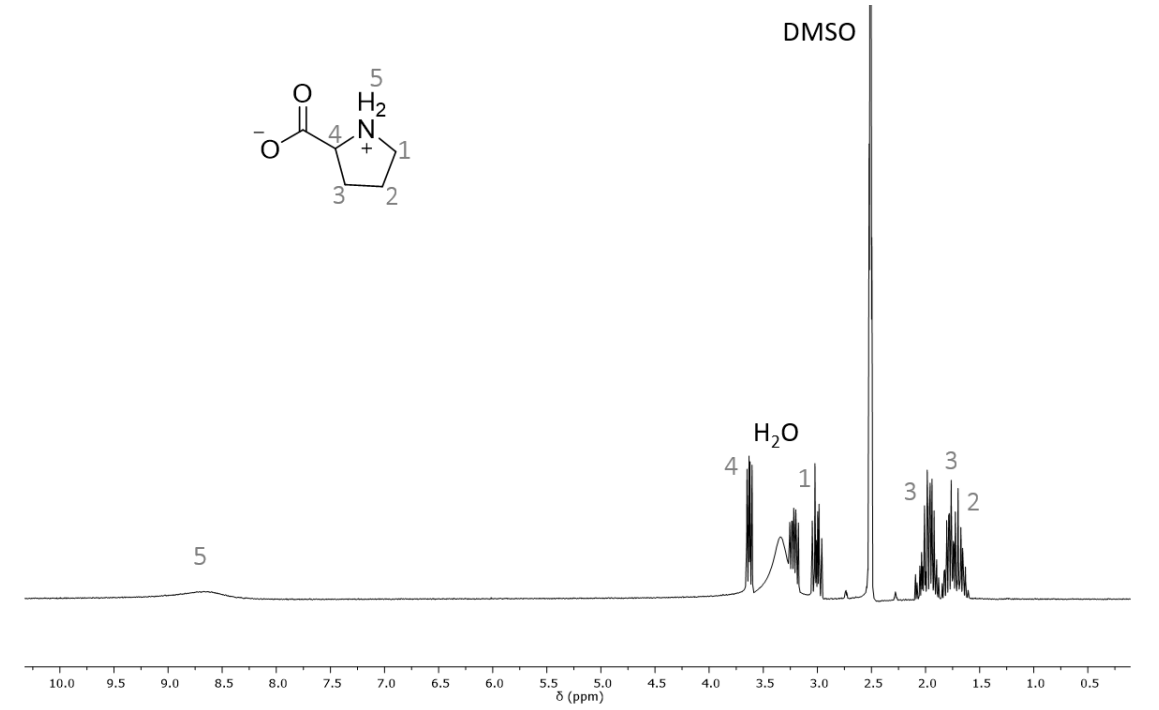
Azkenik, azpimarratzekoa da tesi honetan poliester ekologikoagoak lortzeko hobetu beharreko alderdi batzuk baino ez direla aztertu, oraindik aurrerapen asko egonik egiteko. Horregatik, oso garrantzitsua da poliesterrei buruz ikertzen jarraitzea, gizarte jasangarriagoa lortzeko potentzial handiko materialak baitira.

Eranskinak

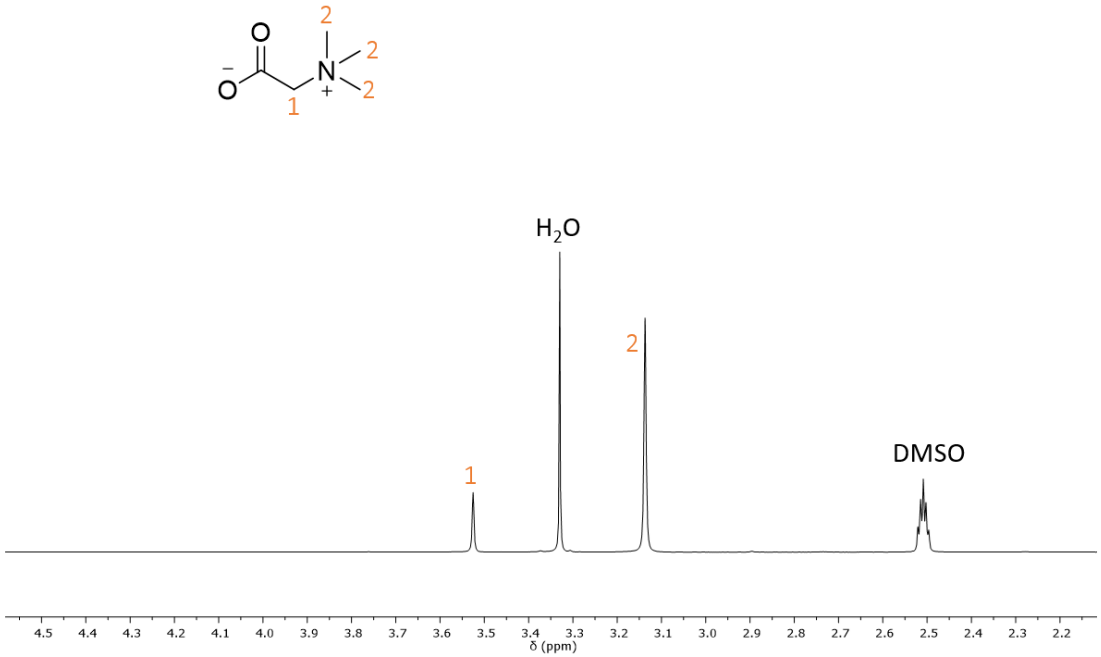
2. kapitulua



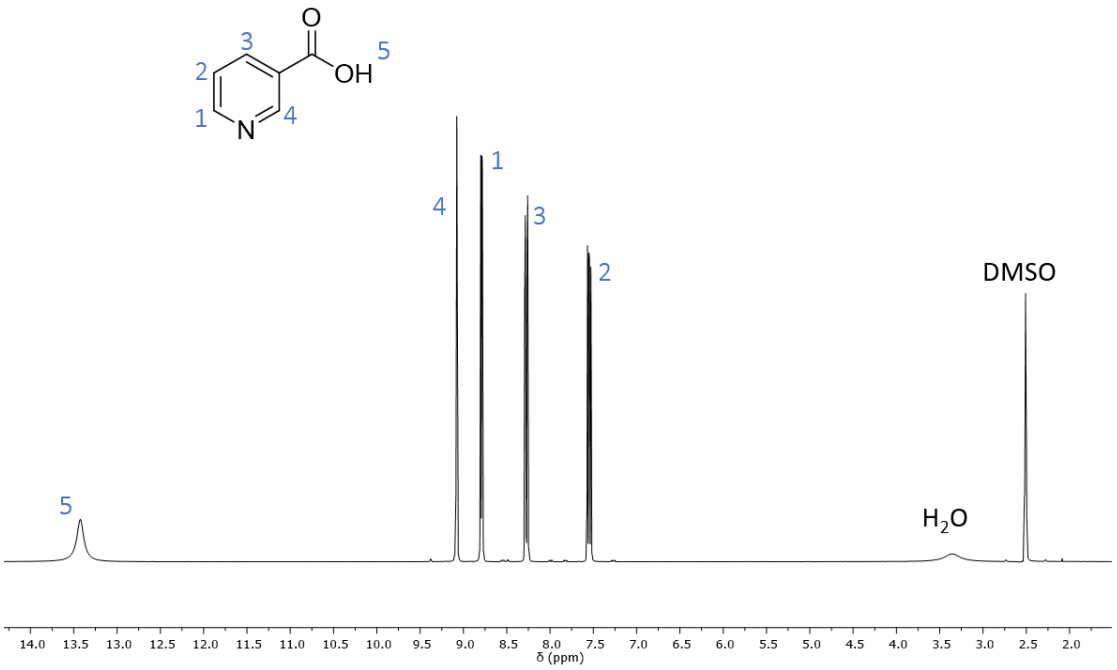
2.1. eranskina. Taurinaren ^{1}H NMR espektroa DMSO-tan.



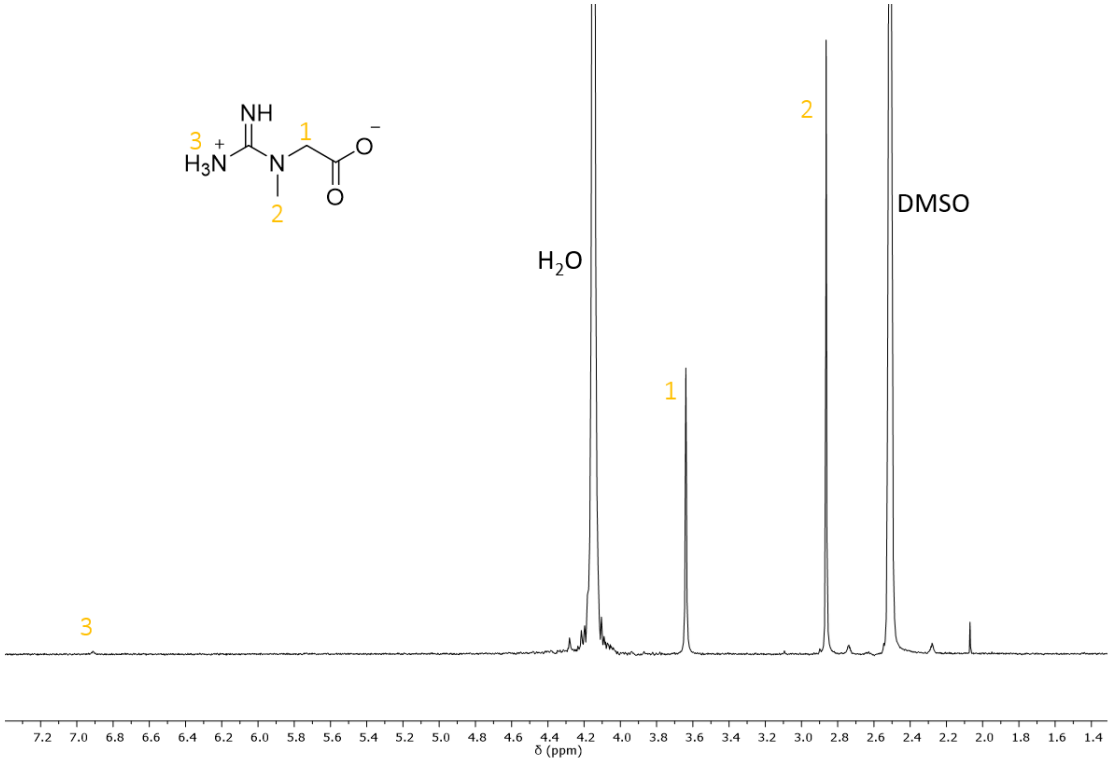
2.2. eranskina. L-prolinaren ^{1}H NMR espektroa DMSO-tan.



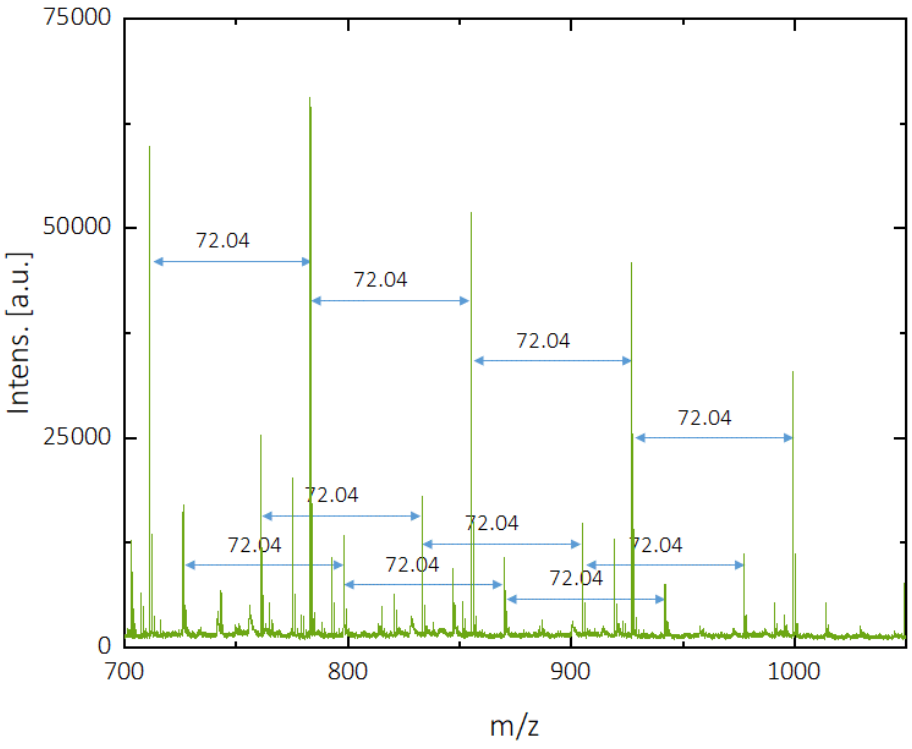
2.3. eranskina. Betainaren ^{1}H NMR espektroa DMSO-tan.



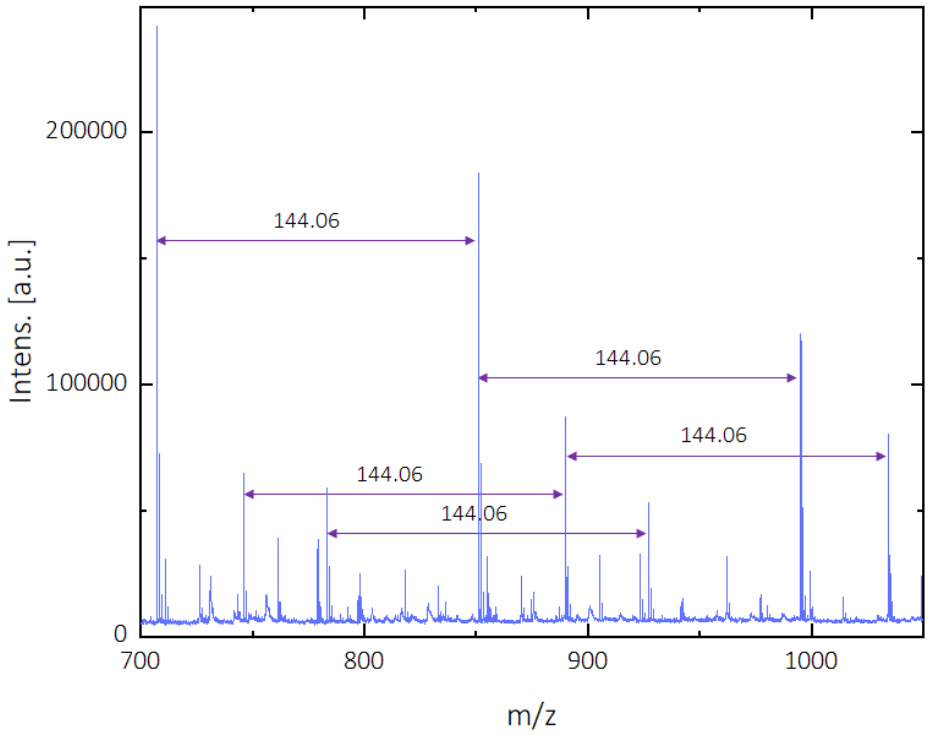
2.4. eranskina. Azido nikotinikoaren ^{1}H NMR espektroa DMSO-tan.



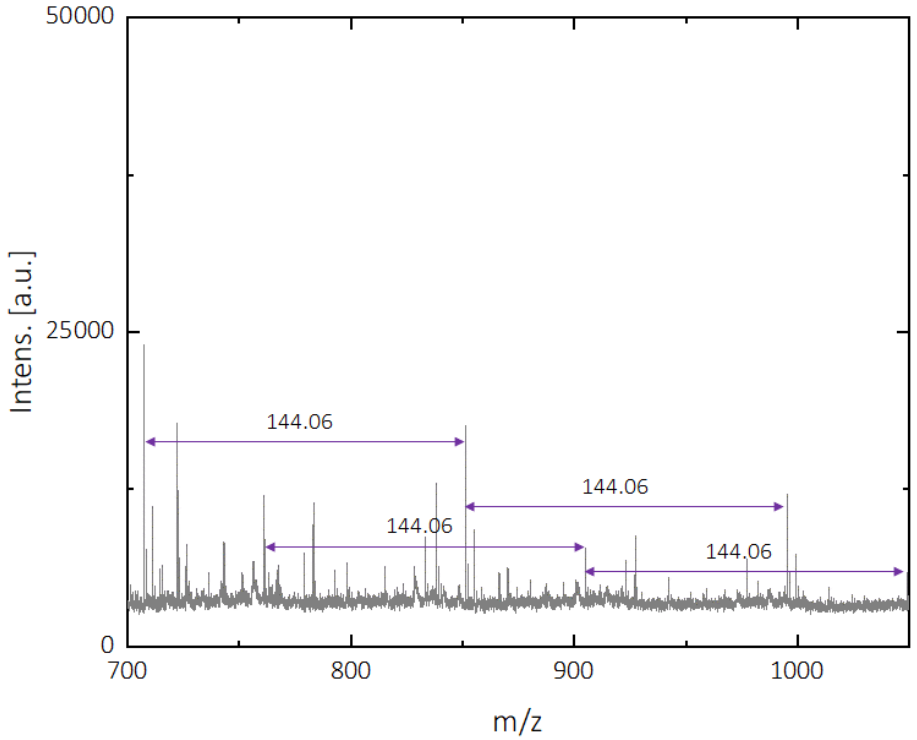
2.5. eranskina. Kreatinaren ^{1}H NMR espektroa DMSO-tan.



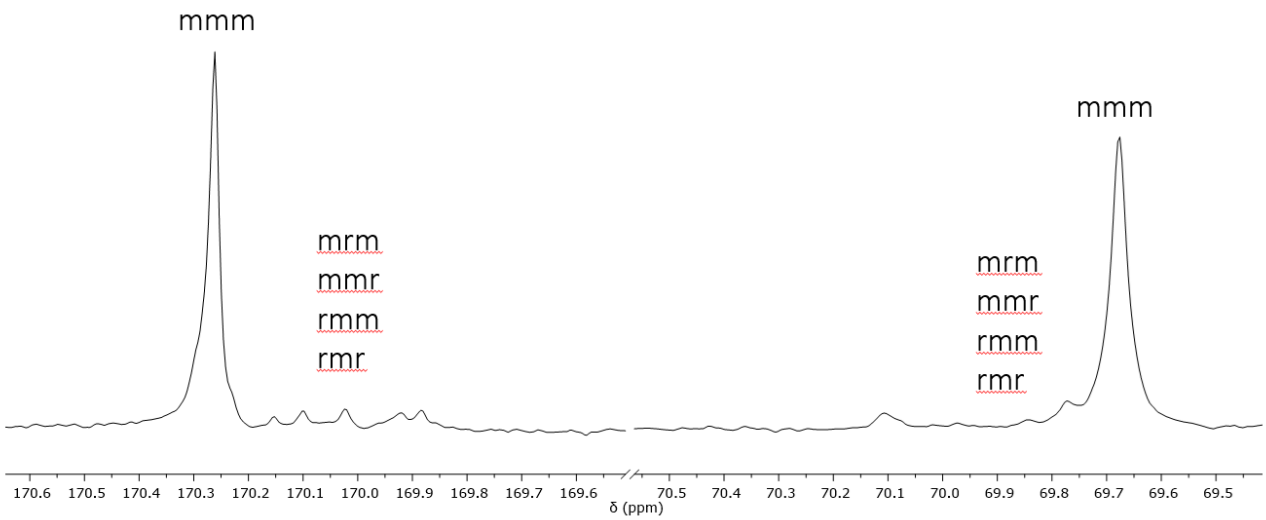
2.6. eranskina. Azido nikotinikoa katalizatzaile bezala erabiliz lortutako L-laktidaren ROParen MALDI-TOF analisia.



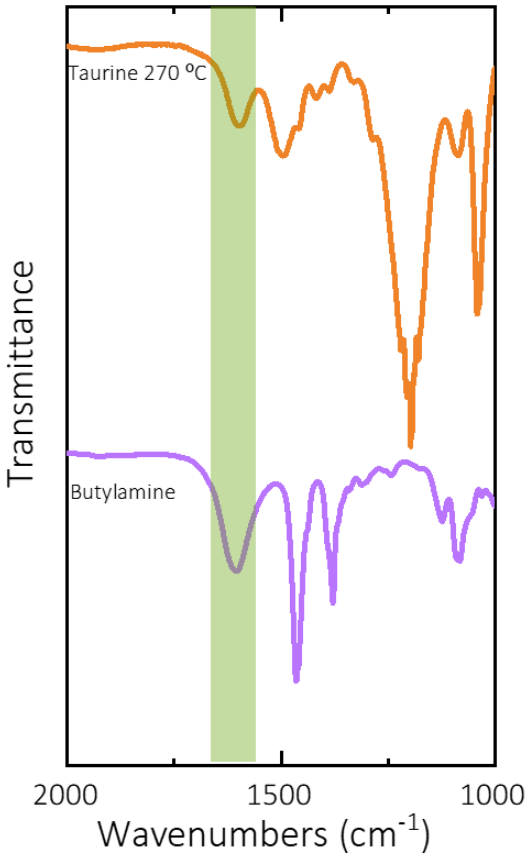
2.7. eranskina. Betaina katalizatzailea erabiliz lortutako L-laktidaren ROParen MALDI-TOF analisia.



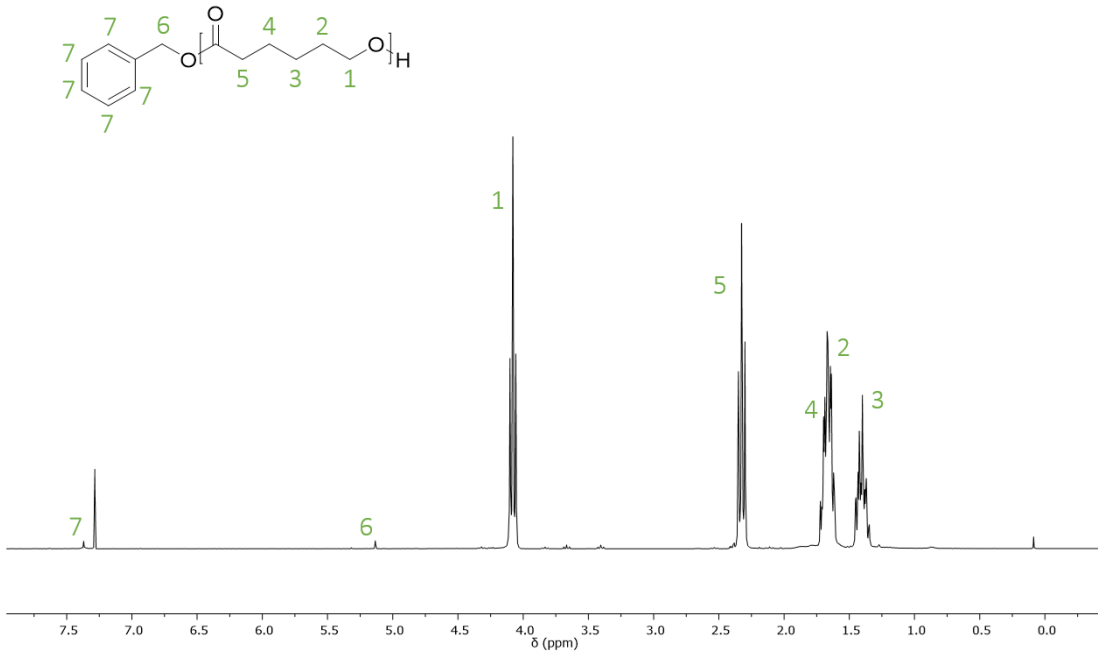
2.8. eranskina. L-prolina katalizatzailea erabiliz lortutako L-laktidaren ROParen MALDI-TOF analisia.



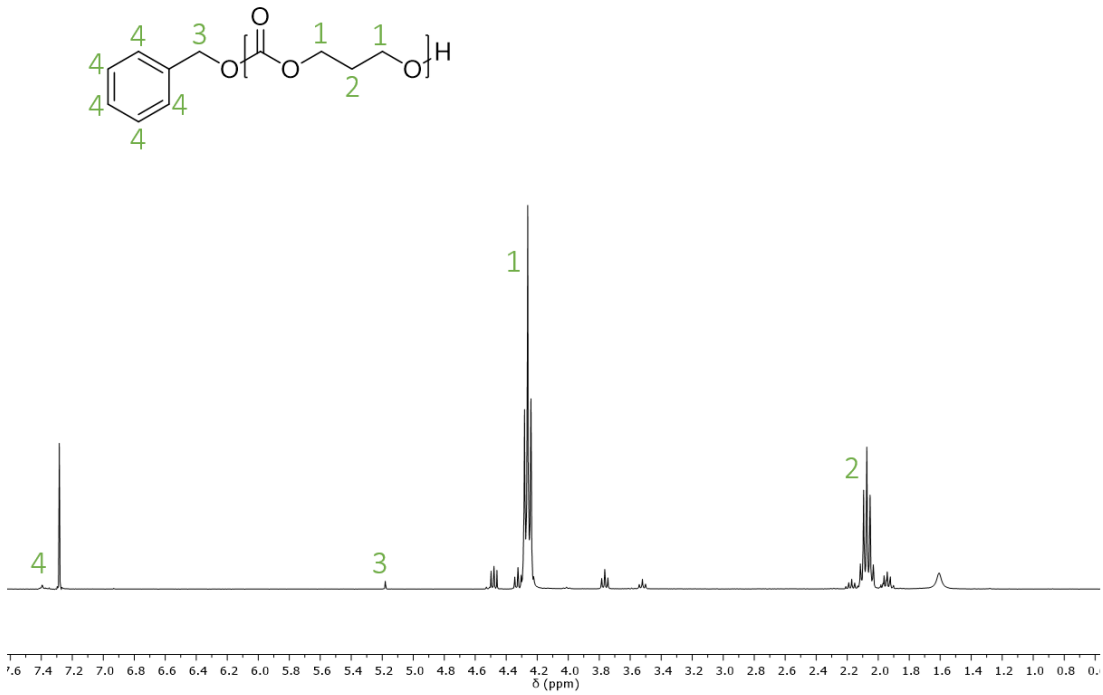
2.9. eranskina. DP 400eko polilakidaren ^{13}C NMR eta ikusten diren triadak.



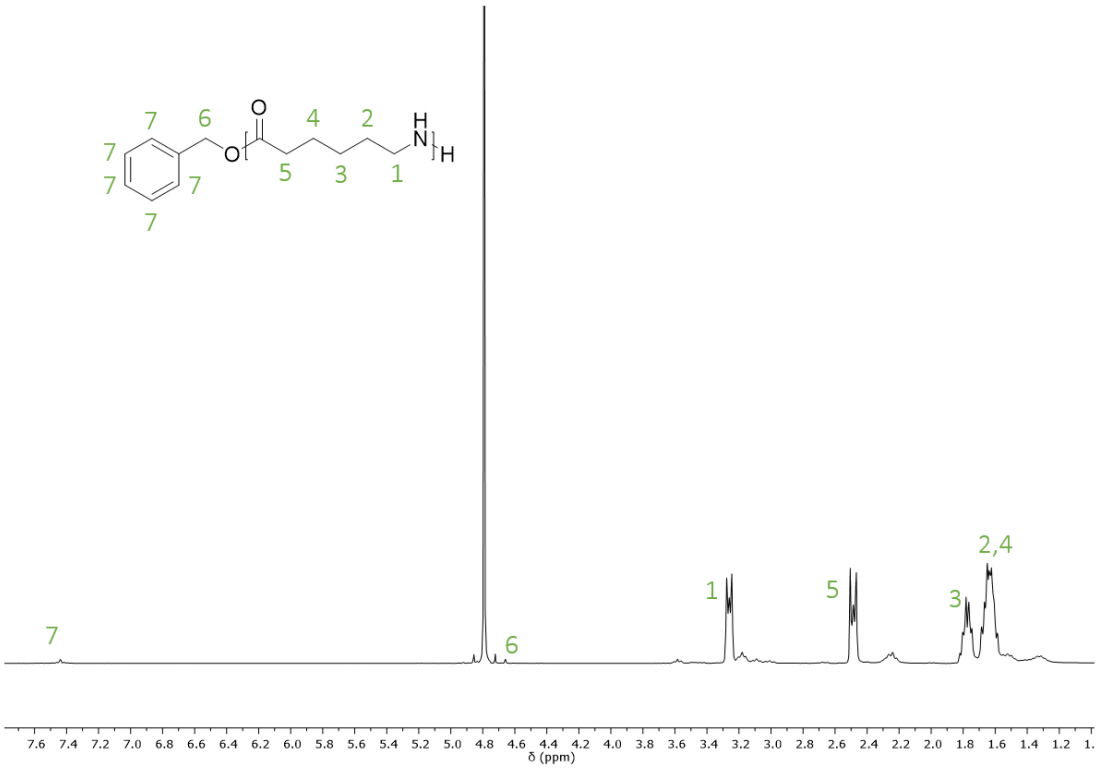
2.10. eranskina. 270 °C-ko taurinaren FTIR analisia eta butilaminarekin konparaketa.



2.11. eranskina. Polikaprolaktonaren sintesiaren ^{1}H NMR espektroa taurina katalizataile bezala erabiliz 180 °C-tan masan.



2.12. eranskina. Politrimetileno karbonatoren sintesiaren ^{1}H NMR espektroa taurina katalizataile bezala erabiliz 180 °C-tan masan.



2.13. eranskina. Polikaprolaktamaren sintesiaren ^{1}H NMR espektroa taurina katalizataile bezala erabiliz 180 °C-tan masan.