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GRADU AMAIERAKO LANA

Synthesis and characterisation of innovative  
polyesteramides using organocatalysis

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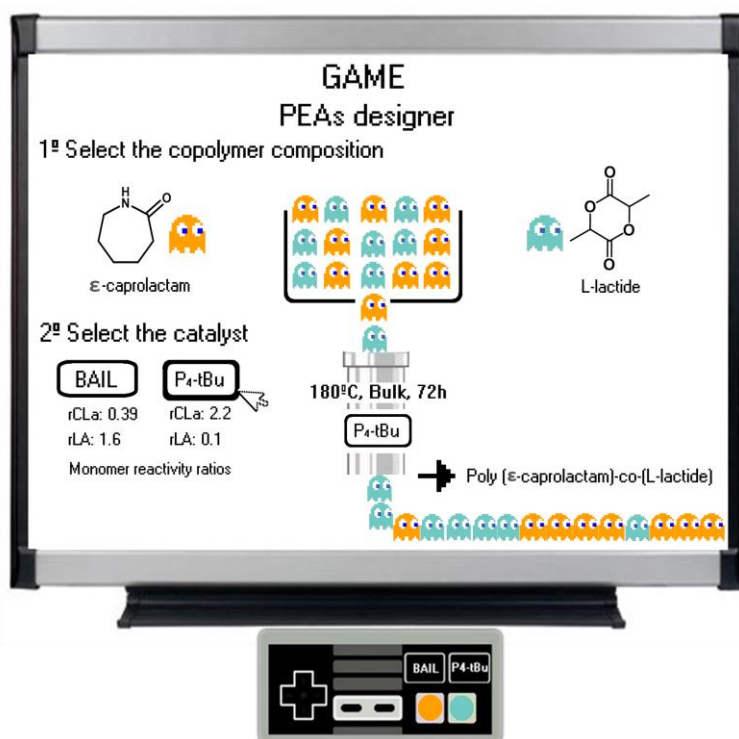
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## ABSTRACT

Poly( $\epsilon$ -caprolactam) and poly(L-lactide) are well known polymers that belong to polyamide and polyester families respectively. The aim of this project was to synthesise new poly(esteramide)s, poly( $\epsilon$ -caprolactam-co-lactide) copolymers, using two different organocatalysts for the purpose of combining the good properties of each specie. Afterwards, the obtained copolymers were characterised by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, ATR-FTIR, SEC, DSC and TGA. It was determined that in presence of the Brønsted acidic ionic liquids (BAILs) catalyst the L-lactide polymerisation was favoured, however the opposite was observed when the used catalyst was the strong Brønsted/Lewis base. The microstructures of the obtained copolymers had the dependence of the monomer composition and also of the selected catalyst. Thus, when the BAIL catalyst is used with high amounts of L-lactide, the character of the copolymer tends to be blocky, the same occurs when the catalyst is P4-t-Bu and the high composition corresponds to  $\epsilon$ -caprolactam. In the other cases, the microstructure of the copolymers could be considered as random.



## LABURPENA

Poli( $\epsilon$ -kaprolaktama) eta poli(L-laktida), poliamida lehenengoa eta poliesterra bigarrena, aski ezagunak diren polimeroak dira. Lan honen helburua bi polimero hauen propietateak biltzen dituen kopolimeroa sortzea da, poli(esteramida)k, poli( $\epsilon$ -kaprolaktama-L-laktida) kopolimeroak, horretarako bi organokatalizatzaile desberdin erabiliz. Behin kopolimeroak sintetizatu direnean beraien karakterizazioa egin da teknika ezberdinak erabiliz:  $^1\text{H}$  eta  $^{13}\text{C}$  EMN, ATR-FTIR, SEC, DSC and TGA. Aztertu da Brønsted azido likido ioniko (BAIL) katalizatzailea erabiliz L-laktidaren polimerizazioa  $\epsilon$ -kaprolaktamarena baino eraginkorragoa dela. Brønsted/Lewis base sendoa erabiltzean berriz,  $\epsilon$ -kaprolaktamaren polimerizazioa gailentzen da. Sintetizatutako kopolimeroen mikroegiturek, kopolimeroaren konposizio eta katalizatzailearekiko menpekotasuna erakusten dute. Horrela, BAIL katalizatzailea erabiltzen denean L-laktidaren konposizio altuetan, lortutako kopolimeroak blokeko itxura izango du, berdina gertatuz  $\text{P}_4$ -t-Bu katalizatzailea eta  $\epsilon$ -kaprolaktamaren kantitate handietan. Gainerako konposizioetan aldiz, kopolimeroek zorizko mikroegiturak izateko joera azaltzen dute.

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## 1. OBJECTIVES

The aim of this project is to synthesise a new class of polymers named poly(esteramide) and to analyse the properties that these polymers have. Poly(esteramide)s are an emerging group of copolymers due to their desirable properties. From one hand they have truly promising thermal and mechanical properties due to the amide groups and from the other hand they have desirable biodegradable properties that are provided by the hydrolysable ester groups.

These compounds are becoming known due to the combination of two monomers with interesting and very different properties. Among the different routes to prepare these copolymers we selected the simultaneous ring-opening polymerisation (ROP) method starting from cyclic lactams and lactones. We prepared poly( $\epsilon$ -caprolactam-co-lactide) copolymers with different compositions starting from cyclic L-Lactide and cyclic  $\epsilon$ -caprolactam monomers. Due to the different nature of the monomers the catalyst selection to promote the ring-opening process was not trivial. Therefore, two different catalyses, an acidic one and a basic, were used in order to study the behaviour of the reaction: a Brønsted/Lewis acid, 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ( $[(\text{CH}_2)_4\text{SO}_3\text{HMIm}] [\text{H}_2\text{SO}_4]$ ), and a strong Brønsted/Lewis base, Phosphazene base  $\text{P}_4$ -t-Bu solution.

The catalysts selection was based on previous reports from the literature where they found that were able to catalyse the ROP of both monomers in different polymerisation. After the synthesis, to confirm that the copolymerisation reaction occurred successfully, the polymers were characterised by  $^1\text{H}$  and  $^{13}\text{C}$ -NMR, ATR-FTIR, SEC, DSC and TGA.

The synthesis and characterisation of these materials is one of the main objectives, but also to learn different

experimental techniques and to put in practise all the skills that were obtained during the Chemistry degree.

## 2. INTRODUCTION

### 2.1. Biodegradable polymers

The production and processing of different materials had brought many benefits to the modern society, providing plastics of different kind of properties that are able to be potentially used in several applications. However, the problem of a considerable amount of those plastics is that they do not disappear easily, creating a big amount of residues. As an example, in the last year 8 million tons of plastics were poured into the oceans and according to the studies for 2050 there will be more plastic than fish in the sea (1).

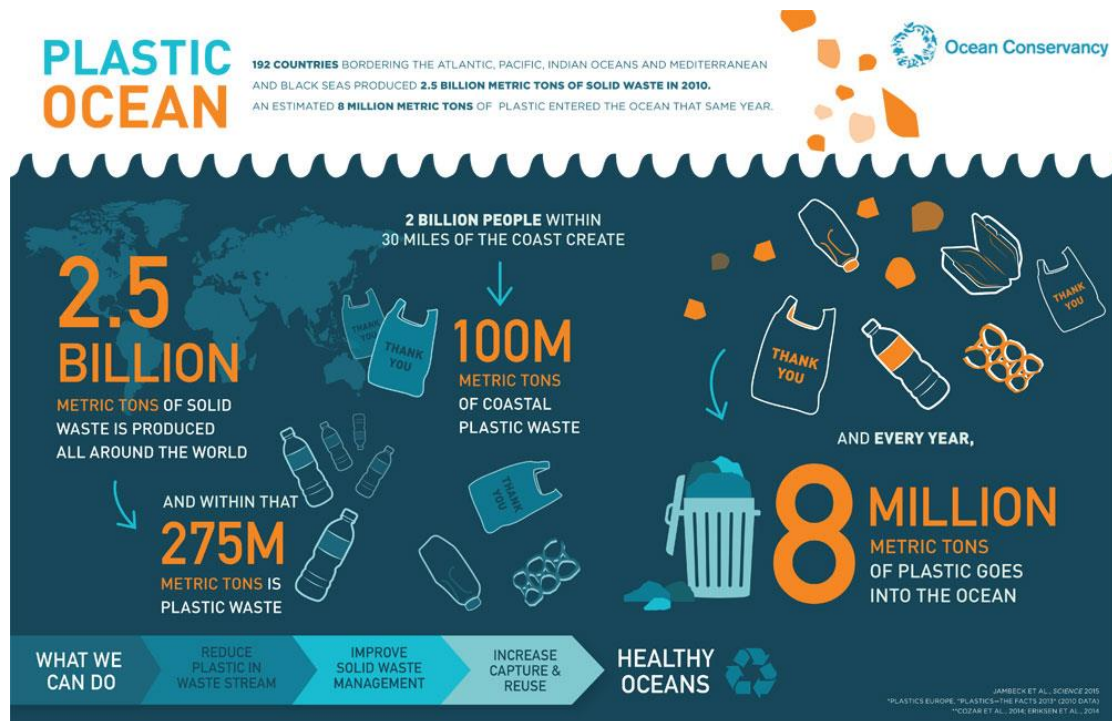


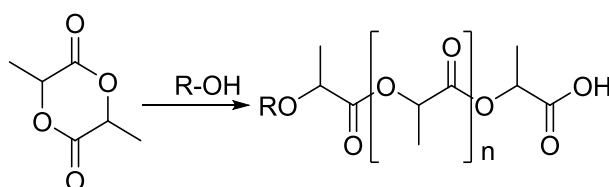
Figure 1. Illustration about the increasing levels of plastics in the oceans.

In order to solve this problem in the last years biodegradable polymers have being investigated. Those materials would be able to get disappear once they finish their use life. A polymer is considered biodegradable when it gets disintegrated under bacteria, fungi or other biological conditions to result

in natural byproducts, such as CO<sub>2</sub>, N<sub>2</sub>, water, biomass and inorganic salts (2).

## 2.2. Poly(L-lactide)

One of the polymer that has been commercialised and has the potential to be degraded under biological conditions is the Poly(L-lactide). The Poly(L-lactide) or PLLA has a hydrolysable ester group which provides high biodegradability to the materials. In addition PLLA is mainly obtained by L-Lactide (LA) cyclic ester which is obtained from renewable sources, such as, starch, sugarcane or tapioca roots (3). According to the surveys in 2010 it was the second more consumed bioplastic of the world (4).



**Reaction 1. Simple scheme of PLLA synthesis.**

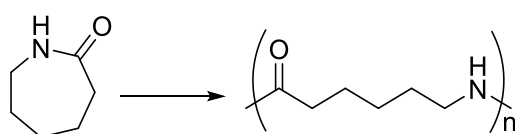
PLLA could be synthesised by using different reactions; however, the most common one is the ring-opening polymerisation of L-lactide. The reaction is usually carried out in bulk in the absence of any organic solvent and high temperatures (160-200 °C) (5).

Poly(L-lactide) is a semicrystalline homopolymer and this fact induces some excellent mechanical properties to the material. In addition it can be degraded by different enzymes such as pronase and proteinase K (6). In spite of its excellent biodegradability and biocompatibility with certain tissues, some of its mechanical properties are not the desired ones (7). PLLA is usually really brittle material and for certain applications its mechanical properties must be improved. One possibility could be to copolymerize the lactide with another monomer that would enhance the mechanical properties of PLLA.



### 2.3. Poly( $\epsilon$ -caprolactam) or Nylon 6

Nylon 6 or polycaprolactam is a semicrystalline polyamide. This polymer is one of the few polyamides that are synthesised by ring-opening polymerisation and it can be easily prepared by the ROP of  $\epsilon$ -caprolactam (CLa). In order to form polycaprolactam chain, caprolactam must be heated at about 180 °C, at that temperature the amide bond within the molecule is broken and undergoes polymerisation (8).

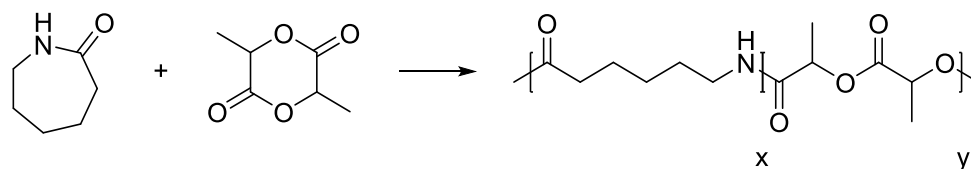


**Reaction 2. Simple scheme of Nylon6 synthesis.**

Even though Nylon 6 can be degraded due to the presence of peptidic bonds, its stability is much higher in comparison to the PLLA, thus, Nylon 6 is considered a non biodegradable polymer. Nevertheless, it has outstanding mechanical properties probably belonging to the strong hydrogen bonds between amide groups (C=O and NH) in the polymer backbone. Therefore, Nylon 6 is a widely produced material due to the broad range of its applications. It is used in electronic industry, aircraft and automotive industry, clothing industry and medicine among others (9). All the largest chemical companies produce it, for example the production of BASF is 400.000 metric tons per year (10).

The goal of this work is to copolymerize the L-lactide and the  $\epsilon$ -caprolactam monomers simultaneously to obtain poly( $\epsilon$ -caprolactam-co-lactide) copolymers with different composition. It was envisioned that these poly(esteramide)s could have the properties of both monomers, the biodegradability that L-lactide provides and the good thermal and mechanical properties of the  $\epsilon$ -caprolactam (11-13).

As we mentioned previously these copolymers could be mainly synthesised via ring-opening polymerisation of cyclic monomers. The ring-opening polymerisation (ROP) was firstly stated at the beginning of 1990s to synthesise chain-growth polymers. In these compounds, the terminal end of a chain acts as a reactive center where the cyclic monomer could get attached by opening its own ring. That way long polymer chains could be obtained (8,14,15).



**Reaction 3. Simple scheme of ring-opening polymerisation.**

This reaction is the most versatile method to synthesize major groups of biopolymers. Traditionally, the catalysts that were used to carry out the ring-opening polymerisation were based on metals. However, these type of catalysts present undesirable effects in electronic or medical applications due to the residual metal that they contain. For that reason, organocatalytic catalysts are being studied to replace the metallic ones (16,17).

## 2.4. Catalysts

As it is mentioned above metal catalysts are an effective way to synthesize PLLA and Nylon 6. However, for some applications the metal traces could give undesirable results. Therefore organic compounds were used to synthesize these materials (8).

The main goal of this project was to copolymerize L-lactide and  $\epsilon$ -caprolactam simultaneously, so an appropriate catalyst must be found to open the rings of both monomers taking into

account their differences reactivity and ring-opening mechanism. In addition, the reaction must be carried out in bulk polymerisation conditions without solvents and this requires high polymerisation temperatures such as 180-200 °C. Most of the organocatalysts cannot be used at high temperatures because they have low boiling points and low thermal stability. In this case we selected a Brønsted/Lewis acid and strong Brønsted/Lewis base because they had given good results in the polymerisation of lactams and esters at high temperatures (14).

The Brønsted acidic ionic liquids (BAILs) apart of being environmental friendly catalysts, they have lower cost than the traditional acid catalysts. It can be employed at high temperatures due to their low volatility and thermal and chemical stabilities. In the ring-opening polymerisation of poly(esteramide)s they have also displayed effectiveness (14).

The other catalyst that was tried in this project, P<sub>4</sub>t-Bu, belongs to a new family of non-ionic bases. Compared to other nitrogen non-ionic bases, such as DBU, phosphazene bases are more basic, water stable and less nucleophilic. In the same way as the BAIL is also considered to be effective for the polymerisation of polyesters and polyamides (17).

In this work, it is explored for the first time the ring-opening preparation of ( $\epsilon$ -caprolactam-co-lactide) copolymers. Two different catalysts have been investigated, i.e. a Brønsted/Lewis acids 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ( $[(\text{CH}_2)_4\text{SO}_3\text{HIm}][\text{H}_2\text{SO}_4]$ ) and a strong Brønsted/Lewis base, such as, phosphazene base P<sub>4</sub>-t-Bu solution to prepare P(CLa-co-LA) copolymers of different compositions. As it is mentioned before, the Brønsted acidic ionic liquids (BAILs) was selected due to their effectiveness in poly(esteramide)s preparation and its distinctive physicochemical properties, such as, low volatility and thermal and chemical stability (14). Similarly, P<sub>4</sub>-t-Bu

catalyst has shown to be effective to promote the ROP of lactams and therefore was selected (17).

### 3. EXPERIMENTAL PART

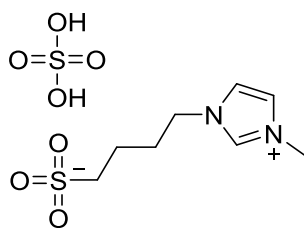
#### 3.1. Starting materials

##### Monomers

$\epsilon$ -caprolactam was acquired from SPOLANA A.S., L-lactide was purchased from Futerro (Belgium) and before using it was recrystallized and dried. The catalysts that were used in the synthesis, 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ( $[(\text{CH}_2)_4\text{SO}_3\text{HMIm}][\text{HSO}_4]$ ) obtained from Solvionic and Phosphazene base  $\text{P}_4$ -t-Bu solution from Sigma-Aldrich, were used without previous treatment. The solvent THF used for the purification of the samples was purchased from Sigma-Aldrich.

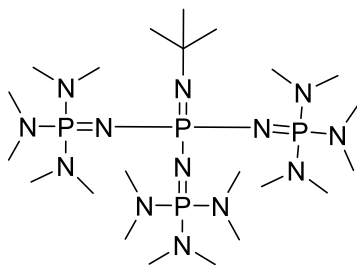
##### Catalyst

Two different catalysts were chosen to analyse the effect that they have in the behaviour of the reaction. From one side a Brønsted/Lewis acid, 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ( $[(\text{CH}_2)_4\text{SO}_3\text{HMIm}][\text{H}_2\text{SO}_4]$ ), was used and from the other, a strong Brønsted/Lewis base, Phosphazene base  $\text{P}_4$ -t-Bu solution.



**Figure 2. 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate.**

The Brønsted/Lewis acid, 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ( $[(\text{CH}_2)_4\text{SO}_3\text{HMIm}][\text{H}_2\text{SO}_4]$ ), is an organic catalyst that as it is reported in the literature, works effectively in the ring-opening polymerisation of ester and amide groups.



**Figure 3. P<sub>4</sub>-t-Bu solution.**

The strong Brønsted/Lewis base, Phosphazene base P<sub>4</sub>-t-Bu solution, was also reported in the literature for been a good catalyst for ring-opening polymerisation of lactams.

Both catalysts work in different ways, the acidic one is more effective for ring-opening polymerisation of ester groups and the basic one for amide groups. As in this project the copolymerisation of both, ester and amide, groups will be performed, the behaviour of the catalysts has to be also analysed in different copolymerisation ratios in order to conclude their effectiveness in these conditions.

### 3.2. Characterization methods

Once the copolymerisation was completed, the samples were characterised using different methods.

<sup>1</sup>H and <sup>13</sup>C Nuclear Magnetic Resonance (NMR) spectra were performed at room temperature on Bruker Avance DPX 300 at 300.16 MHz and 75.5 MHz of resonance frequency respectively, using deuterated trifluoroacetic acid or trifluoroacetic acid as solvent. The experimental conditions for the <sup>1</sup>H NMR were 10 mg of sample, 3 s acquisition time, 1 s delay time, 8.5 μs pulse, spectral width 5000 Hz and 32 scans. For the <sup>13</sup>C NMR 40 mg, inverse gated decoupled sequence, 3 s acquisition time, 4 s delay time, 5.5 μs pulse, spectral width 18,800 Hz and more than 10,000 scans. The <sup>1</sup>H NMR spectra give the conversion of each monomer during the reaction and once the samples are purified the real composition of the synthesise copolymers.

The  $^{13}\text{C}$  NMR spectra instead, due to its usual more resolution of microstructure sequences, enable the calculation of the randomness character value.

The result of different copolymers ratios was seen by Fourier transform infrared-attenuated total reflection (ATR-FTIR) spectroscopy in a Nicolet Magna 6700 spectrometer at a resolution of  $2\text{ cm}^{-1}$  and a total of 64 interferograms were signal averaged. In this technique the functional group of the copolymers were seen, the amide and the ester group. It was possible to qualitatively determine the presence of these groups in the samples.

In order to measure the molecular weight of the homo and copolymers SEC system (Agilent PL-GPC 50) was used. The analyse was done using 1,1,1,3,3,3-Hexafluoro-2-propanol (HFP) containing 10 mM of Sodium Trifluoroacetate ( $\text{C}_2\text{F}_3\text{NaO}_2$ ) as eluent at  $50\text{ }^\circ\text{C}$  and a flow rate of  $1\text{ mL min}^{-1}$  and a polystyrene standard calibration curve was used to analyse the results.

Differential scanning calorimetry (DSC) analysis of all the samples was done in order to determine the thermal properties of the materials: glass transition temperature, melting temperature and crystallization degree. The used equipment was a DSC Q2000 from TA Instruments. The measurements were carried out in sealed aluminium pans, using a heating ramp from  $-50$  to  $+250\text{ }^\circ\text{C}$  with a heating rate of  $10\text{ }^\circ\text{C/min}$  under nitrogen atmosphere.

Finally thermogravimetric analyses (TGA) were performed to measure the degradation temperatures of the copolymers. For that purpose a Q500 Thermogravimetric Analyzer from TA Instruments was used. The analysis was done heating the samples from room temperature to  $600\text{ }^\circ\text{C}$  at a rate of  $10\text{ }^\circ\text{C/min}$  under a constant  $\text{N}_2$  flow.

### 3.3. Synthesis

#### Bulk synthesis of poly ( $\epsilon$ -caprolactam) in the presence of both catalysts

In order to synthesise poly( $\epsilon$ -caprolactam) homopolymer, 3 g of  $\epsilon$ -caprolactam ( $2.65 \cdot 10^{-2}$  mol) were weighted and mixed with 1 mol % of the catalyst, 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate (0.08 g,  $2.65 \cdot 10^{-4}$  mol), in a vial with a magnetic stirrer. The same was done in the second reaction but the catalyst was replaced by Phosphazene base  $P_4$ -t-Bu solution (0.16 g,  $2.65 \cdot 10^{-4}$  mol). The reactions were prepared under nitrogen atmosphere inside a glove box to avoid undesirable reactions, because the ring-opening polymerisation is very sensible to water. The reactions were carried out in a previously heated oil bath at 180 °C. Once the reaction was finished they were stopped by rapid cooling with liquid nitrogen. The samples were purified differently depending on the composition, the poly ( $\epsilon$ -caprolactam) was purified in THF during 48 h. Then it was put in the vacuum oven at 40 °C for 24 h.

#### Bulk synthesis of poly(L-lactide) in the presence of both catalysts

The same procedure was followed to prepare the poly(L-lactide), 3 g of L-lactide ( $2.08 \cdot 10^{-2}$  mol) and 1 mol% of catalyst, 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate (0.06 g,  $2.08 \cdot 10^{-4}$  mol) and Phosphazene base  $P_4$ -t-Bu (0.13 g,  $2.08 \cdot 10^{-4}$  mol), were added to a vial separately with a magnetic stirrer. The reaction vessels were prepared in the glove box and heated in a previously heated oil bath at 180 °C and once the reaction was completed they were stopped by rapid cooling with liquid nitrogen. The poly(L-lactide) was dissolved in THF and precipitated in  $H_2O$ . Once they were purified they were dried under vacuum at 40 °C for 24 h.



## Copolymerisation of $\epsilon$ -caprolactam and L-lactide

Different ratios of copolymers were synthesised in bulk in an oil bath at 180 °C. The mixture of monomers  $\epsilon$ -caprolactam/L-lactide: 95/5 (2.7 g, 0.024 mol/0.18 g,  $1.3 \cdot 10^{-3}$  mol), 90/10 (2.6 g, 0.023 mol/0.37 g,  $2.6 \cdot 10^{-3}$  mol), 80/20 (2.35 g, 0.02 mol/0.74 g,  $5.2 \cdot 10^{-3}$  mol), 50/50 (1.47 g, 0.013 mol/1.8 g, 0.013 mol), 20/80 (0.58 g,  $5.2 \cdot 10^{-3}$  mol/2.8 g, 0.02 mol), 10/90 (0.29 g,  $2.6 \cdot 10^{-3}$  mol/3.31 g, 0.023 mol), and 5/95 (0.14 g,  $1.3 \cdot 10^{-3}$  mol/3.6 g, 0.025 mol) with 1 mol % of catalyst were prepared inside the glove box. After that the reactions were placed in the oil bath. First of all, the reactions were carried out with the Brønsted acidic ionic liquid, 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate, and then they were repeated with the Strong Brønsted/Lewis base, Phosphazene base  $P_4$ -t-Bu solution. Once the reactions were completed they were stopped by rapid cooling with liquid nitrogen. The reactions that were mainly composed by  $\epsilon$ -caprolactam were cleaned with THF during 48 h and the ones that had higher composition of L-lactide were dissolved in THF and precipitated in  $H_2O$ . Once they were purified they were dried under vacuum at 40 °C for 24 h.

### 3.4. Monomer reactivity ratios

In order to determine the effect that each catalyst has in the behaviour of the monomers in the copolymerisation reactions, the monomer reactivity ratios were calculated by Kelen-Tudos method (18).

The experimental process that needs to be followed up for this purpose is to let the copolymerisation running up to 15 % conversion. For that reason first of all a reaction was settle and kinetics were taken. Analysing the kinetics the time were 15 % of conversion was obtained was determined. The reactions must be stopped at low conversion, because that is the moment when the first monomer-monomer bonds are forming and they give

the opportunity to see the reactivity that the catalyst have towards the monomers. Relating the monomer and polymer peak integrals for each compound the monomer reactivity ratios could be calculated.

Three different parameters have to be defined to solve the following equation:

$$\frac{x(y-1)}{ay+x^2} = \frac{\left(r_{CLa} + \frac{r_{La}}{a}\right)x^2}{ay+x^2} - \frac{r_{La}}{a} \quad (1)$$

The  $x$  is the ratio of molar fractions of  $\epsilon$ -caprolactam monomer and L-lactide monomer in the monomer feed.

$$x = \frac{M_{CLa}}{M_{La}} \left( \frac{\text{mol}}{\text{mol}} \right) \quad (2)$$

The  $y$  parameter refers to the molar ratio of molar fractions of  $\epsilon$ -caprolactam and L-lactide in the copolymer at each time.

$$y = \frac{dM_{CLa}}{dM_{La}} \left( \frac{\text{mol}}{\text{mol}} \right) \quad (3)$$

The  $a$  is a constant that is calculated with this expression:

$$a = \sqrt{\frac{x_{min} x_{max}}{y_{min} y_{max}}} \quad (4)$$

The  $x_{min}$  and  $x_{max}$  are the minimal and maximal molar fractions in the molecular feed and the  $y_{min}$  and  $y_{max}$  are the minimal and maximal molar fractions in the copolymer.

To represent the results in a graph the equation 1 was changed to equation 7:

$$\tau = \frac{x(y-1)}{ay+x^2} \quad (5)$$

$$\xi = \frac{x^2}{ay+x^2} \quad (6)$$

$$\tau = \left( r_{CLa} + \frac{r_{La}}{a} \right) \xi - \frac{r_{La}}{a} \quad (7)$$

$\tau$  versus  $\xi$  was represented and the values were adjusted to a straight line. The extrapolation of the line to  $\xi = 1$  would give the  $r_{CLa}$  value:

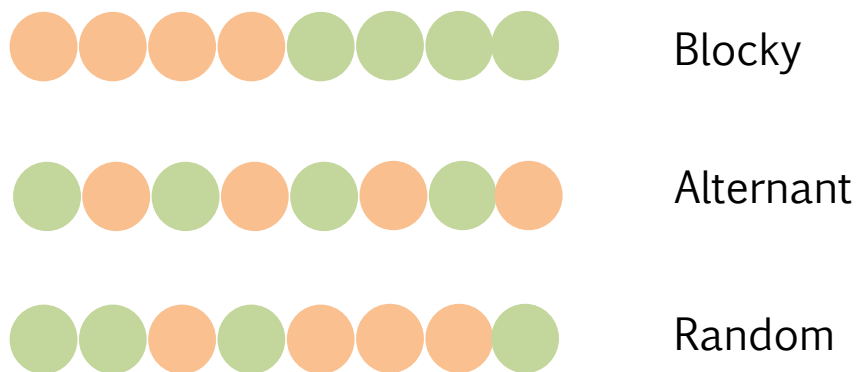
$$\tau = r_{CLa}$$

Whereas the extrapolation of the line to  $\xi = 0$  would show the  $r_{La}$  value:

$$\tau = -\frac{r_{La}}{a}$$

### 3.5. Randomness character value

Copolymers could have different characters, such as, blocky, random or alternant microstructures and that fact changes considerably the properties that they present. The microstructures of the samples are defined by the sequences of monomers that the copolymers contain.



**Figure 4. Blocky, alternant and random microstructures scheme.**

These sequences could be detected and quantified by nuclear magnetic resonance. Sometimes the  $^1\text{H}$  NMR could be able to give that information, however, due to that the chemical surrounding in different sequences are not too large,  $^{13}\text{C}$  NMR has usually more resolution than  $^1\text{H}$  one in order to study the microstructure of polymeric materials.

In order to calculate the microstructure of the samples the randomness character value ( $R$ ) is defined:

$$R = \frac{(LA - CLa)}{2(LA)(CLa)} \quad (8)$$

Where  $(LA-CLa)$  is the molar fraction of the LA-CLa dyad and  $(LA)$  and  $(CLa)$  refer to the molar fraction of these species.

When the obtained value tends to 0 the copolymer is considered that has a blocky microstructure, when the  $R$  tends to 1 the copolymer would have a random character and when the randomness character tends to 2 would be alternant (19).

In the  $^{13}\text{C}$  NMR dyads, triads or even further sequences could be seen. However, in the spectra performed in this work only dyads could be well identified, which were enough to calculate the randomness character value. But it has to be said that if the identification and quantification of longer sequences were enable, the characterization of microstructure would be more reliable and complete.

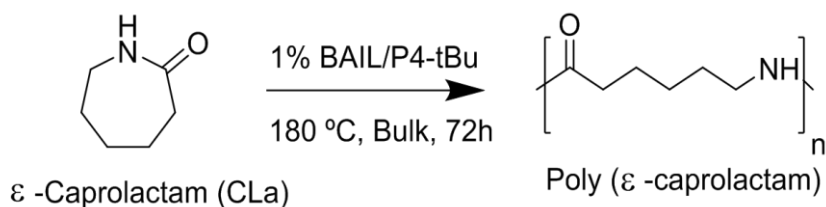
## 4. RESULTS AND DISCUSSION

### 4.1. Bulk polymerisation of poly ( $\epsilon$ -caprolactam) and poly (L-lactide)

First of all, the homopolymerization reactions were performed in bulk, using both catalysts, BAIL and P<sub>4</sub>-t-Bu, separately. In this way will be possible to determine how the catalysts work with each monomer and the main differences between them.

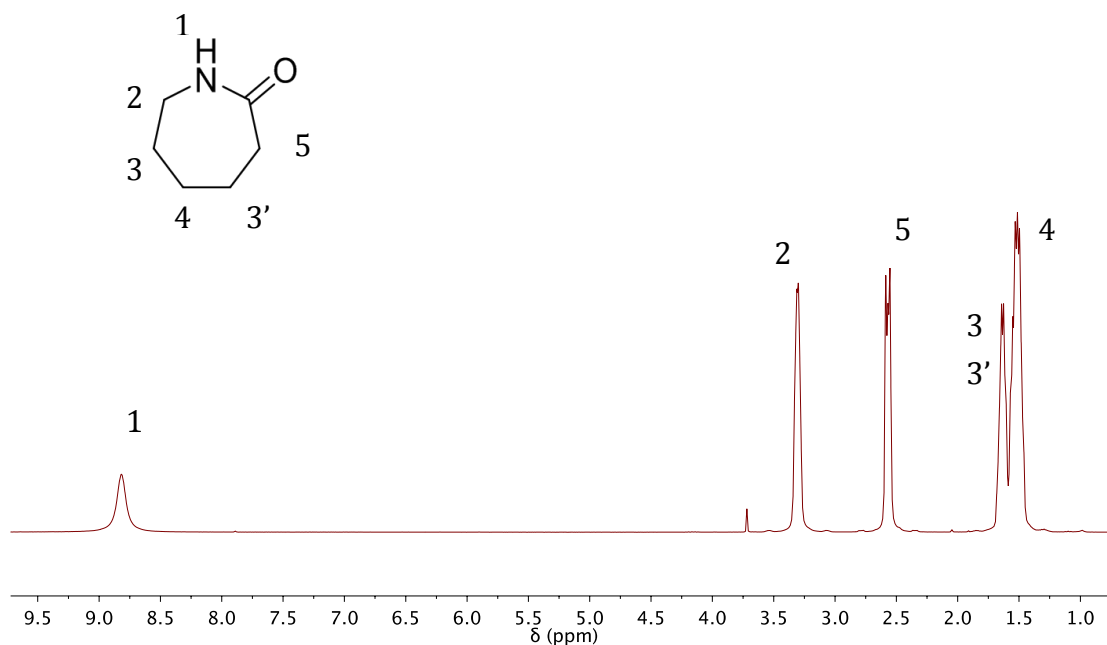
The ring-opening polymerisation reaction conditions were established based on previous reports and essaying different percentages of catalysts in preliminary reactions. The aim was to use the minimum amount of catalysts and finally the chosen conditions were 180 °C, 72 h, 1 mol % of catalyst and under vacuum (8,20).

The following scheme shows the reaction process that was carried out in order to synthesize poly ( $\epsilon$ -caprolactam).



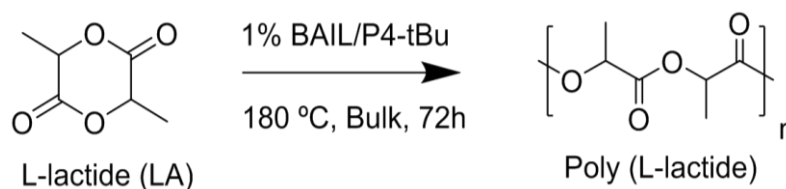
#### Reaction 4. Ring -opening polymerization of $\epsilon$ -caprolactam.

Afterwards, the <sup>1</sup>H NMR of the  $\epsilon$ -caprolactam monomer is showed in the following spectrum.



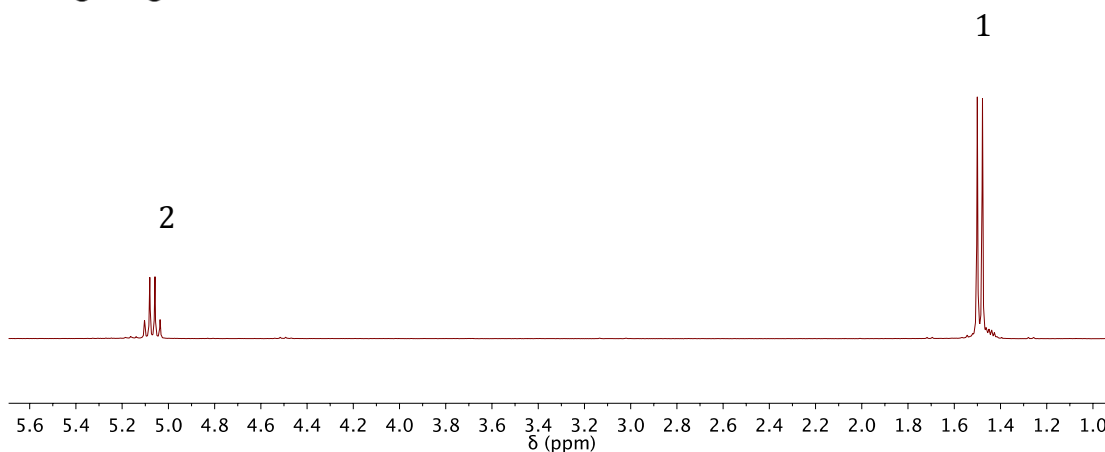
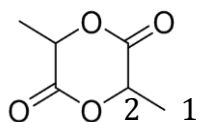
**Spectrum 1.** <sup>1</sup>H NMR of ε-caprolactam monomer.

The reaction process carried out for the polymerization of L-lactide is showed in the Reaction 5.



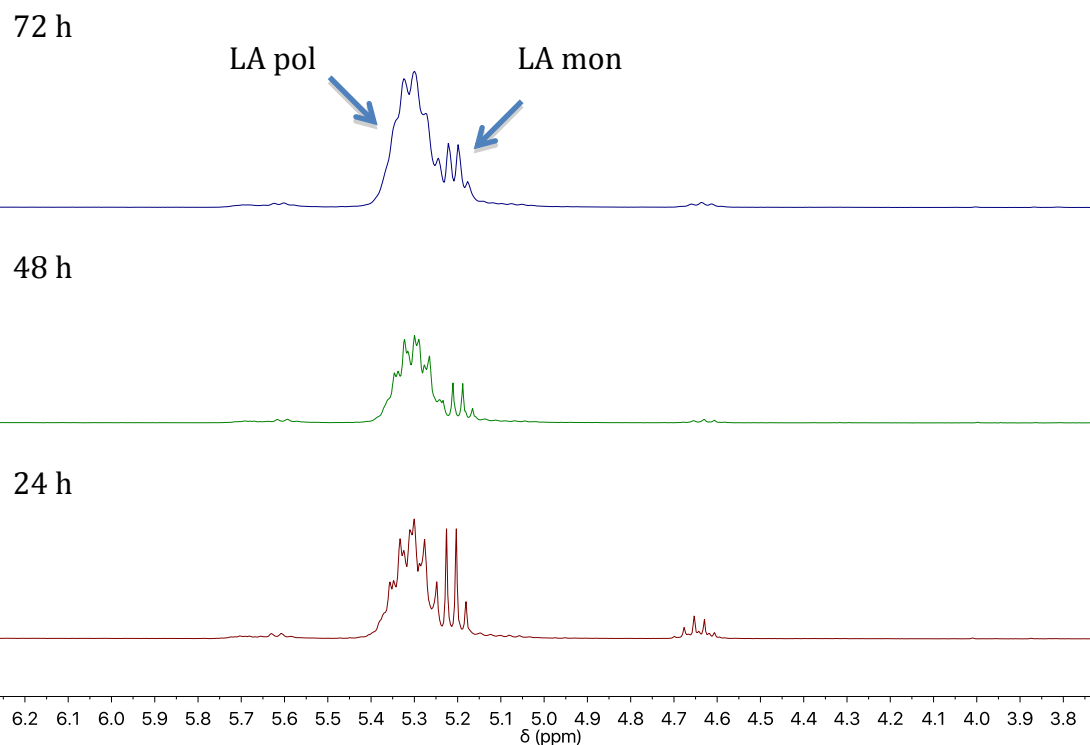
**Reaction 5.** Ring-opening polymerization of L-lactide.

And the spectrum of the L-lactide monomer is represented in the Spectrum 2.



**Spectrum 2.  $^1\text{H}$  NMR of L-lactide monomer.**

The reaction kinetic was followed by  $^1\text{H}$  NMR comparing the signals corresponding to both monomer and polymerised units. They could give a view of the reaction effectiveness, determining if the reaction has had a full conversion and how much time needed to reach that point and also how has been the behaviour of the reaction in order to get the final situation.



**Spectrum 3.  $^1\text{H}$  NMR of L-lactide homopolymer conversion.**

As it is appreciated in this set of spectra, the polymer peak area is increasing with the time, while the monomer one is decreasing, because the monomer is polymerizing. So it could be easy to identify the monomer and polymer peaks due to its behaviour. In this first stage, each monomer has been studied independently, the monomer of one compound with the polymer of it. The outcome will be interesting to know which monomer would react first when the copolymerisation will be carried out.

Relating the monomer and the polymer signal areas conversion could be calculated. For example, to calculate the L-lactide conversion, the area of the peak of L-lactide polymer is divided by the sum of L-lactide polymer and monomer peaks areas. Mathematically:

$$X_{PLA} \% = \frac{A_{LA_{pol}}}{A_{LA_{mon}} + A_{LA_{pol}}} * 100 \quad (9)$$

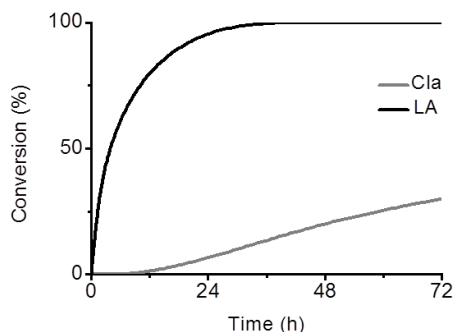
$$X_{PCLa} \% = \frac{A_{CLa_{pol}}}{A_{CLa_{mon}} + A_{CLa_{pol}}} * 100 \quad (10)$$

With these expressions the polymerized material quantity could be also determined. The same is done to calculate the  $\epsilon$ -caprolactam conversion.

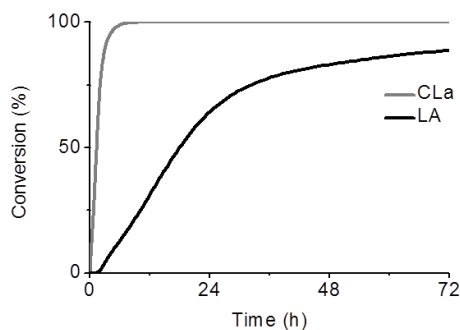
It is seen that depending on the catalyst used the conversion of the homopolymers change considerably.



(a) BAIL



(b) P4-t-Bu



**Figure 5. Monomer conversions plot vs time of  $\epsilon$ -caprolactam (CLA) and L-lactide (LA) monomers catalysed by (a) BAIL and (b) P<sub>4</sub>-t-Bu.**

The graphics that are above show the conversion of the homopolymers during the time. It is determined that using BAIL as catalyst the conversion of LA is 100 % before 48 h, however the conversion of the CLA is very low, at 72 h is not converted even the 50 % of the monomer. Whereas using the P<sub>4</sub>-t-Bu catalyst, the conversion of CLA is 100 % at around 4 h and the LA presents almost full conversion at 72 h. Analysing the conversion results it is observed that both catalysts carried out the polymerisation of the homopolymers. However, the strong Brønsted/Lewis base is seen to be the best catalyst to promote the polymerisation of both monomers at least at 1 % of catalyst quantity.

As it was proved that both catalyst promote the homopolymerization of the  $\epsilon$ -caprolactam and L-lactide monomers, it can be assumed that the copolymerisation of  $\epsilon$ -caprolactam and L-lactide with both catalysts will be successful.

## 4.2. Copolymerisation of $\epsilon$ -caprolactam and L-lactide

The copolymers were synthesised using the same reaction conditions as used for the homopolymerization of the poly( $\epsilon$ -



is confirmed that the catalyst is effective to promote both monomers polymerisation at the same time.

NMR allows us to quantify the monomer conversion. However, characterization of molecular weight of the copolymer is a primordial task in this type of studies, thus SEC analysis was performed.

### 4.3. Size exclusion chromatography

The size exclusion chromatography (SEC) analysis determines the molecular weights and the dispersity values of the copolymers and homopolymers, with the obtained values it is possible to know if the polymerisation has occurred or not. If the molecular weights are very small it is going to be that instead polymers oligomers have been synthesised. This technique however does not give any information about the structure of the obtained polymers.

It is seen that using BAIL as catalyst poly(L-lactide) of high molecular weight is obtained comparing to the one obtained by P<sub>4</sub>-t-Bu. The opposite occurred when basic catalyst was used, in that case the poly( $\epsilon$ -caprolactam) was the one that gives a high molecular weight. The ( $\epsilon$ -caprolactam-co-lactide) copolymers instead, have low molecular weights in all the ratios and with both catalysts, showing molecular weights of between 2 and 4 kDa and also low dispersity values ( $\mathfrak{D}$ ) between 1.2 and 1.6.

The dispersity is a parameter that indicates the heterogeneity of polymer chain weights in the sample and it is defined in the following way:

$$\mathfrak{D} = \frac{M_w}{M_n} \quad (11)$$

Where  $M_w$  is the weight-average molar mass and  $M_n$  is the number-average molar mass.

**Table 1. Molecular weights and dispersity values using BAIL.**

Feed CLa/LA	BAIL	
	Mn (kg/mol)	Đ
100/0	3.5	1.4
95/5	2.1	1.2
90/10	1.8	1.4
80/20	1.8	1.7
50/50	2.0	1.2
20/80	2.5	1.3
10/90	2.5	1.5
5/95	9.9	1.6
0/100	17.8	1.3

*The values were determined using a polystyrene standard calibration curve.*

**Table 2. Molecular weights and dispersity values using P<sub>4</sub>-t-Bu.**

Feed CLa/LA	P <sub>4</sub> -t-Bu	
	Mn (kg/mol)	Đ
100/0	60.1	1.5
95/5	1.8	1.5
90/10	3.0	1.4
80/20	2.3	1.6
50/50	3.8	1.4
20/80	2.8	1.3
10/90	3.6	1.4
5/95	2.4	1.3
0/100	3.9	1.2

*The values were determined using a polystyrene standard calibration curve.*

Once the polymer synthesis was confirmed by SEC analysis the ATR-FTIR analysis was carried out to have a qualitative view of the effectiveness of the copolymerisation reaction.

#### 4.4. Fourier transform infrared spectroscopy

This technique gives qualitative information of the functional groups that appear in the sample. In this sense, the presence of peaks corresponding to functional groups of both repeating units in the spectra would confirm the successfulness of the polymerisation synthesis. It has to be mentioned that the polymer spectrum in this case would not differ much from the monomers one. The monomers and the polymers have the same functional groups. The FTIR analysis was carried out after purifying the samples, so the remaining monomer had been eliminated before it. The spectra were obtained using ATR-FTIR method due to the difficulty to dissolve the copolymers and then to evaporate the dissolvent. An example is given in the Figure 6.

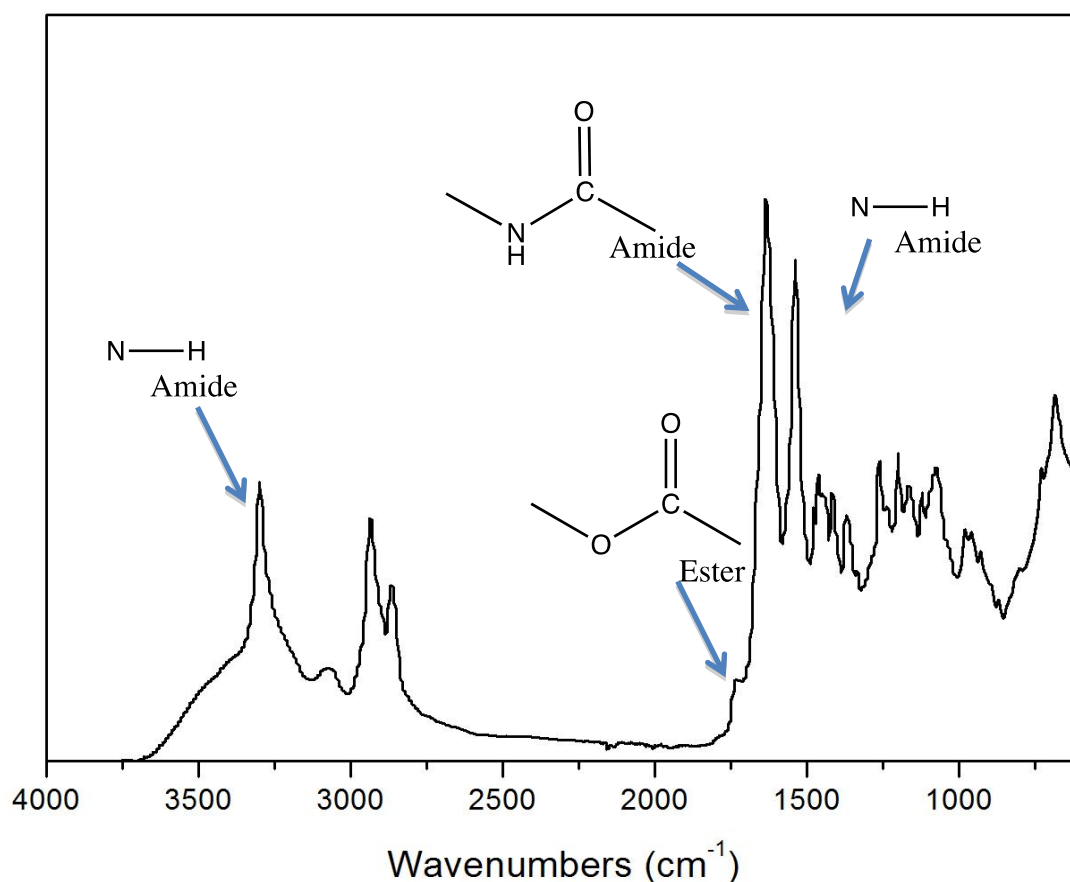
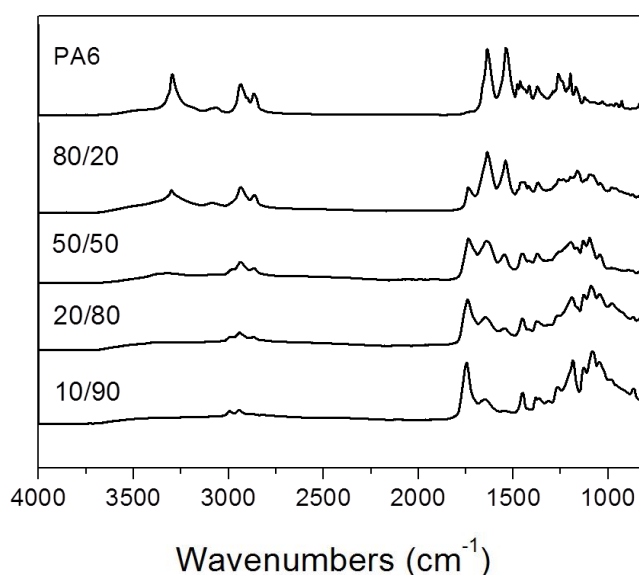


Figure 6. ATR-FTIR spectrum of 90CLa/10LA using P<sub>4</sub>-t-Bu.

In the spectrum above amide and ester groups are seen. The amide group signal could be observed in different wavenumbers, one peak is shown at  $3300\text{ cm}^{-1}$ , which corresponds to the stretching vibration of N-H group, and two other peaks at around  $1600\text{ cm}^{-1}$ . One of them, located at  $1690\text{ cm}^{-1}$ , is the carbonyl vibration of the amide group and the one that appears at  $1550\text{ cm}^{-1}$  corresponds to the bending in plane of the N-H group. The most remarkable peak of the other repeating unit is the carbonyl vibration of the ester group at  $1735\text{ cm}^{-1}$ . In this case the peak of the ester group is very small, due to the low composition of L-lactide; the analysed spectrum corresponds to 90CLa/10LA ratio. Of course, depending on the composition ratios, the peaks corresponding to one repeating unit will be more visible than the other one.

In this set of spectra, the poly( $\epsilon$ -caprolactam) homopolymer has been compared with different composition ratios of poly( $\epsilon$ -caprolactam-co-lactide) copolymers.



**Figure 7. FTIR spectra of different composition ratios of copolymers.**

The poly( $\epsilon$ -caprolactam) spectrum just shows the peaks of amide group. The others samples instead have both groups, the ester

and the amide. However the ones that have high ratios of L-lactide monomer, show bigger peak of ester group than the peaks of amide group. The opposite occurs when the high composition ratio corresponds to the  $\epsilon$ -caprolactam monomer.

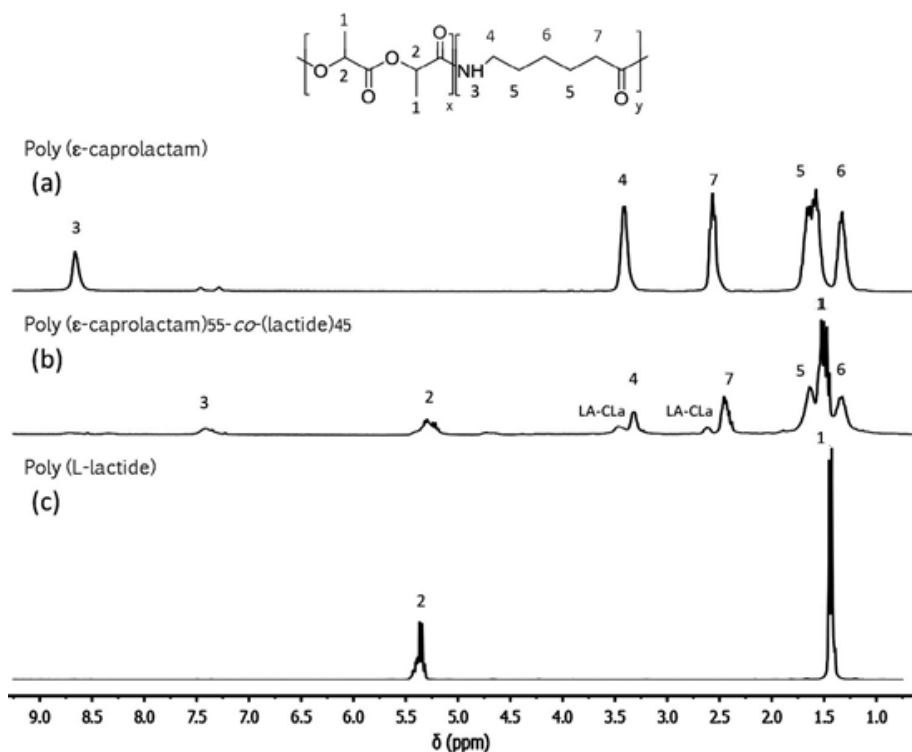
In conclusion, the copolymers ATR-FTIR spectra corroborated us that the two monomers have polymerized and that they are in the analysed sample. Nevertheless, FTIR has more difficulty to show signals that would be only appear in the copolymers and not in their physical blend spectra. In our case, any additional peak has not been observed, thus, FTIR does not confirm that the monomers have copolymerized, because it could be possible that our samples would be constituted by both homopolyester and homopolyamide chains.

So after confirming by  $^1\text{H}$  NMR, SEC and ATR-FTIR analysis that the polymerisation reaction has successfully progressed, the next point will be to prove that the copolymerisation took place. For that  $^1\text{H}$  and  $^{13}\text{C}$  NMR is going to be used, due to the possibility to observe in the spectra the signal corresponding to new linkages formed in the copolymer microstructure as well as to determine the copolymer composition.

#### 4.5. Copolymer composition by $^1\text{H}$ NMR

This technique enables the determination of the compound that has been synthesised during the reaction. With the use of this analysis it is going to be possible to know if the copolymerisation had occurred or not, by analysing the signals and the shifts of the spectra.

First of all, one copolymer spectrum has been compared with the homopolymers ones in order to see how the signals change and to identify the new peaks that appear.



**Figure 8.**  $^1\text{H}$  NMR spectra of the homopolymers and one of the copolymers.

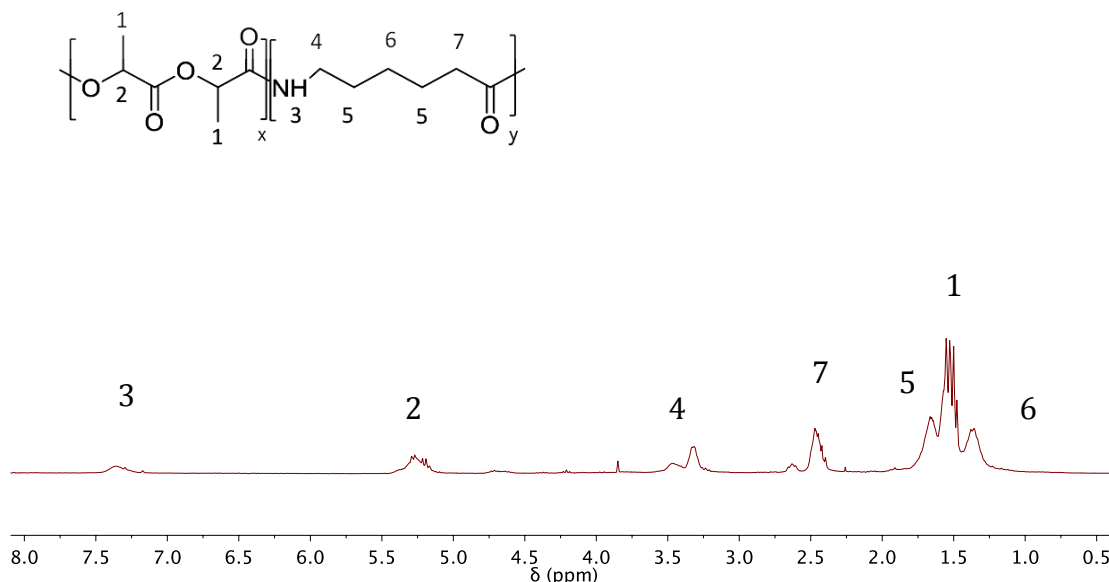
As it is seen in the figure above, the copolymer spectrum show the peaks of both homopolymers, the poly ( $\epsilon$ -caprolactam) and poly (L-lactide), however new peaks also appear. The presence of additional peaks could assured the copolymers formation (21). If there were not new peaks in the copolymer spectrum it was not going to be possible to determine that the copolymerisation reaction occurred and, as pointed above in the FTIR part, spectra would also correspond to a homopolymers mixture.

Once the presence of the copolymer is confirmed, the first magnitude, which allows us to characterise them, is their real composition. It has be pointed out that the composition obtained at the end of the reaction could not match the composition feed values, this effect could happen when there is no full conversion of the monomers.



Moreover, the real composition should give us an idea of how the reaction works. For this purpose, the assignment of proton and carbon peaks as well as sequences must be carried out.

The calculation of the real composition could be conducted analysing both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. However, it is usually performed using  $^1\text{H}$  spectra.



**Spectrum 5.  $^1\text{H}$  NMR spectrum of 50/50 CLa/LA copolymer synthesised with BAIL.**

The spectrum that is shown above corresponds to the 50/50 CLa/LA copolymer that was synthesised using BAIL as catalyst. The peak that appears at around 3.3 ppm refers to the poly( $\epsilon$ -caprolactam) methylene that is next to the nitrogen of the amide group and the one that is shown in around 5.3 ppm is the L-lactide methylene. Those two peaks were the ones that were used to calculate the real composition.

Relating the area of the peak that corresponds to the  $\epsilon$ -caprolactam with the one of L-lactide it is possible to calculate the molar percentage of each component in the copolymer:

$$\%LA = \frac{A_{LA_{pol}}}{A_{CLA_{pol}} + A_{LA_{pol}}} * 100 \quad (12)$$

$$\%CLA = \frac{A_{CLA_{pol}}}{A_{CLA_{pol}} + A_{LA_{pol}}} * 100 \quad (13)$$

In this case the  $\epsilon$ -caprolactam/L-lactide real ratio is 55/45, where the feed ratio was 50/50. So that means that the yield was not 100 %, because if it was it is not possible to have 55 %, more than what it was added at the beginning. Anyway, the real composition is not very different to the feed value. With the corresponding  $^1\text{H}$  NMR spectrum and the expressions showed before the real composition values were calculated to all the samples.

**Table 3. Real compositions of copolymers synthesised with BAIL.**

Feed CLa/LA (%)	BAIL
	Comp. (%)
100/0	100/0
95/5	97/3
90/10	91/9
80/20	80/20
50/50	55/45
20/80	23/77
10/90	8/92
5/95	7/93
0/100	0/100

As it is seen in the table, the real compositions do not differ much from the feed values.

Table 4. Real compositions of copolymers synthesised with P<sub>4</sub>-t-Bu.

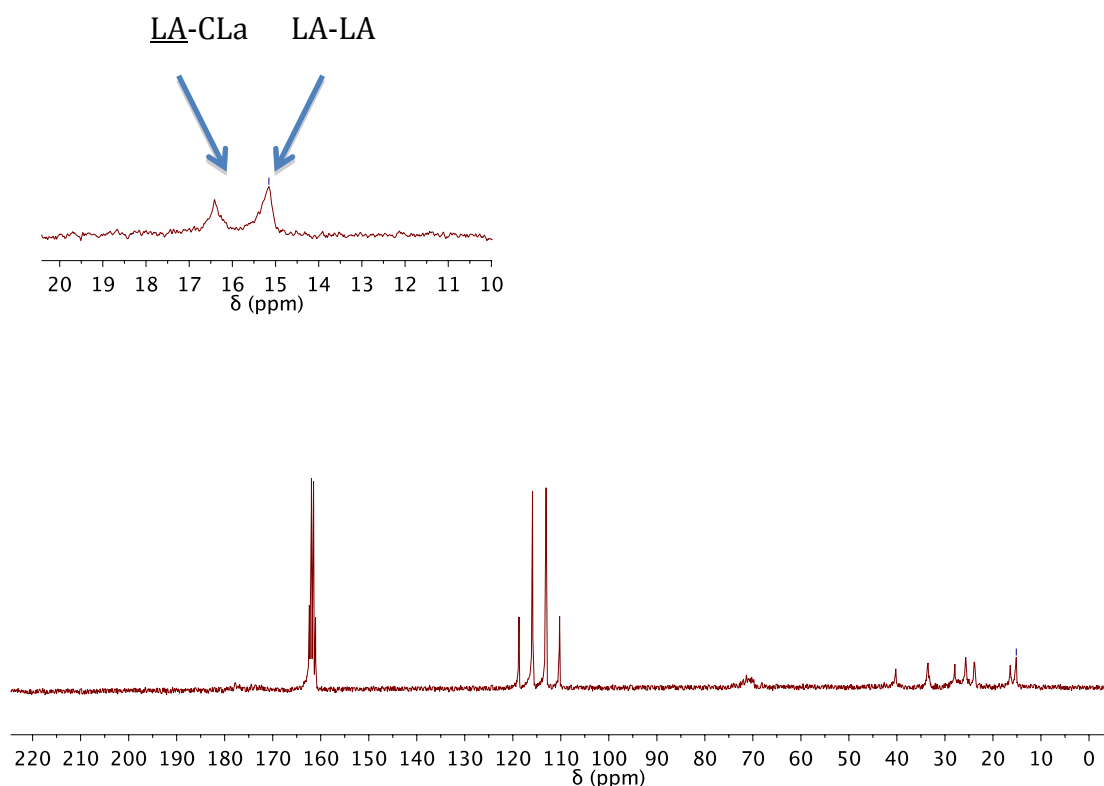
	P <sub>4</sub> -t-Bu
Feed CLa/LA (%)	Comp. (%)
100/0	100/0
95/5	96/4
90/10	95/5
80/20	84/16
50/50	63/37
20/80	30/70
10/90	18/82
5/95	11/89
0/100	0/100

The feed composition values and the real ones are a little bit different in the case of using the P<sub>4</sub>-t-Bu as catalyst.

In order to understand the microstructure of the copolymers <sup>13</sup>C NMR spectra were performed, with this technique the randomness character value was determined.

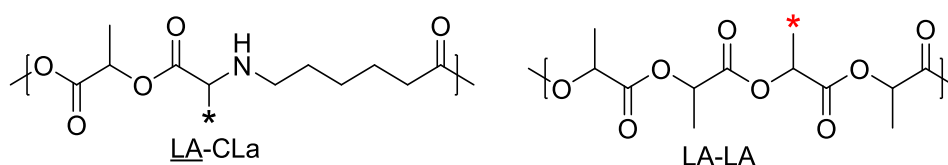
#### 4.6. Randomness character value

The randomness character value (*R*) determines the microstructure of the synthesised copolymers, in other words, it says if the compound has blocky, random or alternant character. This value is usually calculated by <sup>13</sup>C NMR spectra, it could be possible to do it by <sup>1</sup>H NMR (21); however, in many cases it is not easy to assign that kind of sequences in the <sup>1</sup>H NMR spectra.



**Spectrum 6.  $^{13}\text{C}$  NMR 50/50 synthesised with BAIL.**

Three different sequences could be formed during the copolymerisation reaction, LA-LA, CLa-LA and CLa-CLa. Although the signal of the last one was not possible to be assigned, with the first two it was enough to calculate the randomness character value.



**Figure 9. Structures of LA-CLa and LA-LA sequences.**

These are the structures of the identified sequences. In our copolymers, these sequences have been assigned in the methyl group of the L-lactide in  $\alpha$  position to the ester group. Once assigned the signal of the interchange dyad LA-CLa, its relative area is available and therefore the characterization of the copolymer microstructure.

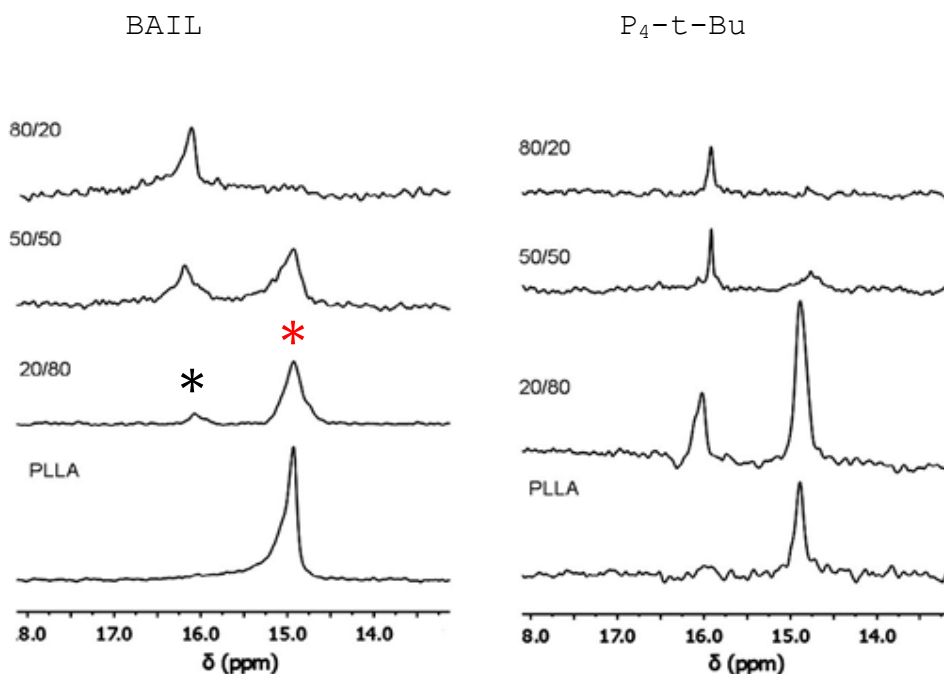


Figure 10. The  $^{13}\text{C}$  NMR spectra of different compositions in order to calculate the randomness character values.

In the  $^{13}\text{C}$  NMR spectrum of PLLA the signal of the methyl of the L-lactide is observed. However when the L-lactide is copolymerized with  $\epsilon$ -caprolactam a new peak is shown apart to the previously mentioned one. These two peaks could belong to the presence of different dyads. Thereby, the adjacent repeating units cause the chemical shift that suffers the methyl group of the L-lactide. The LA-LA dyad signal appears at 15 ppm and the LA-CLa at 16.2 ppm (22). Other C atoms also could give the information of the copolymer sequences in their signal splitting, however their split was more complicated, as well as, some different C signals were overlapped. Also, some splitting is observed in the  $^1\text{H}$  NMR spectra, which would be also ascribed to copolymer sequences, but the analysis based on dyads, showed some inconsistencies in the integral values. Thus, we decided not to consider them for this calculation.

As pointed above, randomness character value ( $R$ ) was calculated using the relative molar area of the LA-CLa sequence and the relative molar fractions of L-lactide (LA)

and  $\epsilon$ -caprolactam (CLa), calculated by the relative integrated area of the  $^{13}\text{C}$  NMR spectra and applying the equation that follows:

$$R = \frac{(LA - CLa)}{2(LA)(CLa)} \quad (8)$$

Remember that the value of  $R$  allows a simple characterization of the microstructure of the copolymers. When the  $R$  tends to 0 the character of the sample is considered to be blocky, when it tends to 1 random, and would be alternant when the  $R$  tends to 2 (19).

In the following table the randomness character values of all the composition ratios of poly( $\epsilon$ -caprolactam-co-lactide) copolymers synthesised using both catalysts are shown.

**Table 5. Randomness character values.**

Feed CLa/LA	R (BAIL)	R ( $P_4$ -t-Bu)
95/5	0.83	0.48
90/10	0.90	0.43
80/20	0.95	0.56
50/50	0.73	0.83
20/80	0.45	0.76
10/90	0.36	0.65
5/95	0.41	0.79

It is observed that the character of the samples is different depending on the catalyst and the composition ratios used.

As L-lactide is very reactive with BAIL, when the quantity of LA in the feed is high the copolymers obtained have a blocky character. However when the ratios of L-lactide decrease the copolymers tend to be random. Although the reactivity of LA is higher, the high amount of  $\epsilon$ -caprolactam makes the microstructure to be more random, because there is more chance

to link a  $\epsilon$ -caprolactam monomer to the chain than a L-lactide one.

The opposite phenomenon occurred when using  $P_4$ -t-Bu as catalyst. In high ratios of  $\epsilon$ -caprolactam in the feed, the character of the copolymer tend to 0 being blocky and when the L-lactide quantity is larger than the  $\epsilon$ -caprolactam one, random copolymers are obtained.

Finally, there is a fact that must be pointed out. Since our copolymers have been obtained at high conversions, the values obtained for  $R$  are an average of the different microstructures that can be formed throughout the reaction.

In order to understand the effect that was seen in the microstructure, monomer reactivity ratios were calculated by Kelen-Tudos method.

#### 4.7. Reactivity ratios

The reactivity ratio is a parameter that determines how reactive is a monomer in presence of other monomer under specific reaction conditions, in this case the catalyst. These values would explain the character of the copolymers, such as, if they are blocky, random or alternant.

The graphs that are shown below are the ones obtained after following the Kelen-Tudos method. The first graph corresponds to the homopolymers that were synthesised by the use of BAIL and the second one to the  $P_4$ -t-Bu catalyst.

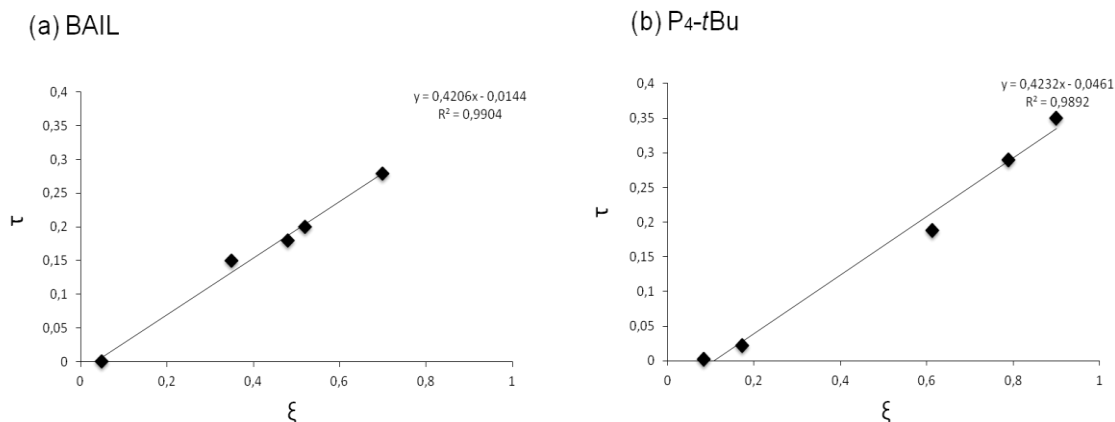


Figure 11. Graphs obtained by Kelen-Tudos method.

Drawing a trendline in the calculated points, an equation is obtained and extrapolating that line the reactivity ratio values of  $\epsilon$ -caprolactam and L-lactide are obtained. When  $\xi=0$  the value of  $r_{LA}$  is calculated and when doing  $\xi=1$  the  $r_{CLa}$  reactivity ratio.

In this case the reactivity ratio values obtained for the monomers are the following ones:  $r_{CLa} = 0.39$  and  $r_{LA} = 1.6$  and  $r_{CLa} = 2.2$  and  $r_{LA} = 0.1$ . The first two values correspond to the reactions that were carried out using BAIL and the next ones to P<sub>4</sub>-t-Bu. This values show that the L-lactide has a high reactivity ratio when the catalyst used is the Brønsted/Lewis acid, 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfatate ( $[(CH_2)_4SO_3HMI] [H_2SO_4]$ ). However the  $\epsilon$ -caprolactam has a low reactivity towards this catalyst. When the catalyst is P<sub>4</sub>-t-Bu the  $\epsilon$ -caprolactam shows a high reactivity ratio, while the L-lactide low.

These values explain the randomness character values that were obtained before. The  $\epsilon$ -caprolactam is very reactive in P<sub>4</sub>-t-Bu catalyst presence and that is why blocky copolymers are formed, especially in the samples were the composition of CLa is high, the opposite occurred with LA. However the  $\epsilon$ -caprolactam have higher reactivity ratio towards the basic catalyst than the L-lactide to the acidic, so blockier

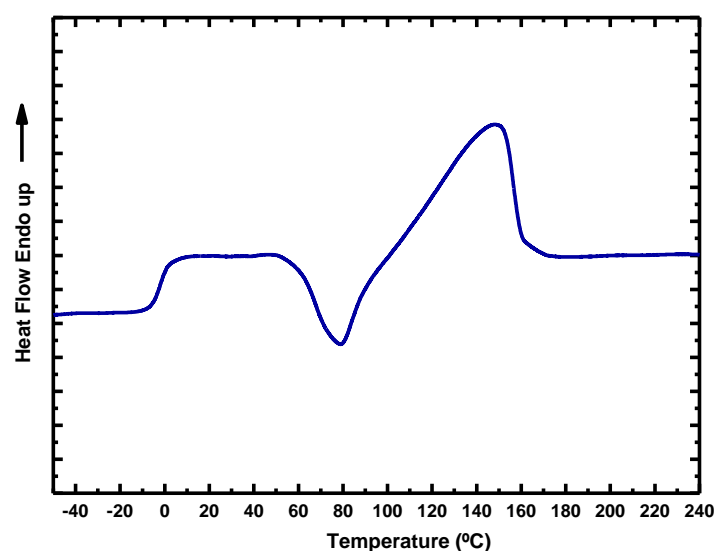


microstructure would present the samples that were synthesised with P<sub>4</sub>-t-Bu.

Once probed the formation of the copolymers by NMR and SEC and the characterization of their microstructure by NMR, the determination of thermal properties of the polymeric materials has a primordial interest. Moreover, both glass transition and crystallinity could be strongly influenced by the microstructure.

#### 4.8. Thermal properties

The differential scanning calorimetry analysis gives the possibility to determine the thermal properties of the copolymers, making possible to know if the compound is semicrystalline or completely amorphous.



**Figure 12. DSC thermogram of the 97/3 composition synthesised by BAIL.**

This DSC thermogram above corresponds to the 97/3 poly( $\epsilon$ -caprolactam-co-lactide) copolymer synthesised by BAIL. Three facts are seen: the first one corresponds to the glass transition, the second one to a cold crystallization and the last one to the fusion of crystals. The T<sub>g</sub> is the glass transition of a polymer, at that point the chains of the amorphous part of the polymer start moving. The cold

crystallization occurs when the cooling after the first heating has been too fast that the crystalline part of the copolymer did not have enough time to crystallize. When the sample is heated for the second time the crystals start formatting giving an exothermic peak in the thermogram. Finally, the crystals melting of the crystalline part of the polymer gives an endothermic peak, the maximum of that peak corresponds to the melting temperature,  $T_m$ .

In this case the  $T_g$  and the  $T_m$  values are quite low taking into account that 97 % of the sample is CLA. However this effect could be justified by the low molecular weights values that were obtained. If the polymer has short chains the  $T_g$  and  $T_m$  could decrease considerably. Although the  $T_m$  of the thermogram corresponds to the CLA it could be though that it is the melting temperature of the LA, but as occurs with the crystallization of CLA, in our samples the melting of LA crystals is quite low (115 °C) in comparison to the usual PLA melting temperature (around 180 °C). Moreover, in this sample only a 3 % of LA is present and it can be supposed that its crystallization is practically impossible.

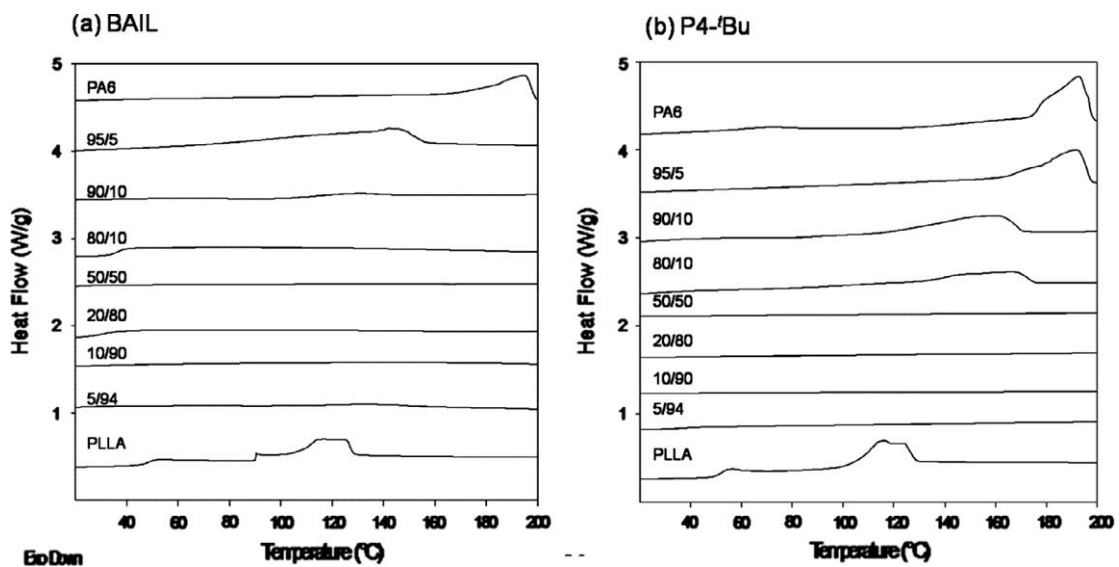


Figure 13. DSC heating curves of the different copolymers synthesised with (a) BAIL and (b)  $P_4$ -t-Bu.

In this set of DSC thermograms the  $T_m$  of the poly( $\epsilon$ -caprolactam) and poly(L-lactide) homopolymers and the poly( $\epsilon$ -caprolactam-co-lactide) copolymers is represented. In the following tables the values obtained are shown, where the values of the enthalpy of 100 % crystalline species are:

$$\Delta H_{m(\text{CLa})} = 399 \text{ J/g (23)}$$

$$\Delta H_{m(\text{LA})} = 93 \text{ J/g (23)}$$

**Table 6. Thermic characterisation of copolymers obtained by BAIL.**

Feed CLa/LA	BAIL			
	$T_g$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )	$\Delta H_m$ (J/g)	Crystal. %
100/0	46.17	193	93	23
97/3	-1.87	160	79	20/21*
91/9	-10.97	-	-	-
80/20	8.15	-	-	-
55/45	11.10	-	-	-
23/77	14.54	-	-	-
8/92	26.55	-	-	-
7/93	31.35	-	-	-
0/100	52.31	115	52	56

\* Is the percentage of crystallinity taking into account the composition of the CLa.

It is observed that both homopolymers are semicrystalline not mattering the catalyst used. The  $T_g$  and the  $T_m$  values of the synthesised poly(L-lactide) homopolymer are lower than the values of the pure homopolymer. This may be derived by the low molecular weights that the poly(L-lactide) has, see Tables 1 and 2. The reported  $T_g$  value of the pure homopolymer is  $60^{\circ}\text{C}$  and the  $T_m$   $180^{\circ}\text{C}$  (24). It has to be also mentioned that the crystallinity value of the poly(L-lactide) is too high, so it could be thought that the measurement is not reliable. In the case of homopoly( $\epsilon$ -caprolactam) obtained using  $P_4$ -t-Bu catalyst, the values of both  $T_g$  and  $T_m$  are similar to the reported ones for PCLa (23) while the one prepared with BAIL

gives also lower values of both  $T_g$  and  $T_m$ . It should be remembered that the PCLa with  $P_4$ -t-Bu catalyst is the unique synthesized material that has sufficiently high molecular weight value.

**Table 7. Thermic characterisation of copolymers obtained by  $P_4$ -t-Bu.**

Feed CLa/LA	$P_4$ -t-Bu			
	$T_g$ ( $^{\circ}$ C)	$T_m$ ( $^{\circ}$ C)	$\Delta H_m$ (J/g)	Crystal. %
100/0	61.21	222	98	25
96/4	40.38	188	92	23/24*
95/5	18.54	162	86	22/23*
84/16	15.99	-	-	-
63/37	-1.54	-	-	-
30/70	-4.47	-	-	-
18/82	11.35	-	-	-
11/89	20.92	-	-	-
0/100	50.83	115	53	57

\* Is the percentage of crystallinity taking into account the composition of CLa.

However, when L-lactide units were introduced, the melting point and enthalpy decrease considerably from 193  $^{\circ}$ C to 160  $^{\circ}$ C in the copolymers prepared with BAIL, and from 222  $^{\circ}$  to 188 and 162  $^{\circ}$ C when using  $P_4$ -t-Bu catalyst. This could be explained with the microstructures of the copolymers. L-lactide makes crystallization difficult and even when are possible, crystals are more imperfect. The ones synthesised with  $P_4$ -t-Bu show semicrystallinity in high  $\epsilon$ -caprolactam compositions, up to 10% of L-lactide composition, this fact could be related with the microstructure. At high  $\epsilon$ -caprolactam ratios the microstructure is blocky and that helps the semicrystallinity. In the other compositions the copolymers are random what hinders the creation of semicrystals.

When using BAIL catalyst, there is not observed the endothermic melting for the copolymers with low L-lactide compositions, thus these copolymers are not semicrystalline possibly due to their random microstructure. However, spite of being the character of the copolymers blocky at high L-lactide ratios the melting point is not observed either. Thus, a little amount of  $\epsilon$ -caprolactam is enough to lose the ability to create crystals. This could be related with the breakdown of L-lactide in lactyl units, which would happen due to the harsh polymerisation conditions employed.

It is observed that although the homopolymers are semicrystallines few copolymers show crystallinity. Also, it has been mentioned that this fact could be related with the microstructure. For this purpose, the use of number-average sequence lengths ( $l$ ) could be more appropriate than random character magnitude. The number-average sequence lengths magnitude defines how many repeating units of a specie are attached one to the other before an unit of the other specie enters in the chain (25,26).  $l$  can be calculated with the following expressions:

$$l_{CLa} = \frac{2(CL_a)}{(LA - CL_a)} \quad (14)$$

$$l_{LA} = \frac{2(LA)}{(LA - CL_a)} \quad (15)$$

All the magnitudes that appear in these equations have been already defined and calculated in order to determine the random character values. In the tables below the obtained copolymer number-average sequence lengths are shown:

**Table 8. Copolymer number-average sequence lengths of the ones synthesise with BAIL.**

Feed CLa/LA	BAIL	
	$l_{CLa}$	$l_{LA}$
97/3	32.66	1.01
91/9	10.41	1.03
80/20	4.64	1.16
55/45	2.95	2.41
23/77	2.88	9.64
8/92	2.92*	33.58*
7/93	0.49*	6.56*

\* This values are not reliable .

**Table 9. Copolymer number-average sequence lengths of the ones synthesise with P<sub>4</sub>-t-Bu.**

Feed CLa/LA	P <sub>4</sub> -t-Bu	
	$l_{CLa}$	$l_{LA}$
96/4	25.44	1.06
95/5	21.47	1.13
84/16	5.93	1.13
63/37	4.04	2.37
30/70	1.53	3.56
18/82	13.70*	62.40*
11/89	4.68*	37.86*

\* This values are not reliable.

The 97/3 composition copolymer of BAIL and the 96/4 and 95/5 of P<sub>4</sub>-t-Bu show semicrystallinity while their  $l_{CLa}$  values are superior to 20. However, the copolymer 91/9 of BAIL does not show crystallinity and  $l_{CLa}$  is slightly superior to 10. Other copolymers have lower values of  $l_{CLa}$  and are totally amorphous. From this, it can be concluded that blocks of CLa with at least more than 10 repeating units are required to create crystals in the conditions used in the DSC measurements. Further studies of DSC would corroborate that our copolymers are able to crystallize in other conditions or not, but this

type of measurements are totally outside the objectives of this work.

The monomer number-average sequence lengths of the last two compositions of both catalyst are not reliable due to the integration of such small signals is subject to a very considerable error.

Finally the thermogravimetric analysis was performed in order to determine the degradation behaviour of the materials: when they start degrading and when they finish.

#### 4.9. Thermogravimetric analysis

The thermogravimetric analysis (TGA) measures the amount of weight change of a sample as a function of increasing the temperature, in that way the degradation temperature of the polymer could be determine and therefore the stability of it.

Even though this technique has not been studied in detail, some samples were analysed, the ( $\epsilon$ -caprolactam) and (L-lactide) homopolymers and the ( $\epsilon$ -caprolactam-co-lactide) copolymers of 95/5 and 80/20 CLa/LA ratios.

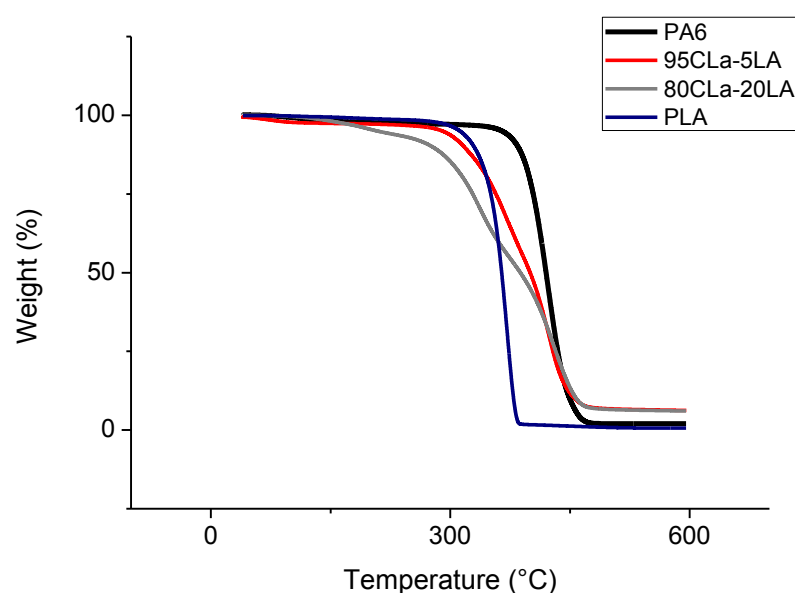


Figure 14. The TGA analysis.

As can be observed in the figure 14 the poly( $\epsilon$ -caprolactam) is the most stable sample of the analysed ones. It starts degrading at around 380 °C and needs around 100 °C more to degrade completely. However, the poly(L-lactide) homopolymer degrades in lower temperatures. Its beginning of degradation is at 310 °C approximately and the ending at 375 °C. So it could be said that the poly(L-lactide) homopolymer is not as stable as the poly( $\epsilon$ -caprolactam), as expected.

The degrading way of the 80CLa/20LA copolymer it is seen to be different from the others, because two jumps are observed. The first jump corresponds to the degradation of L-lactide and the second one to the  $\epsilon$ -caprolactam one. The L-lactide has a lower degradation value than the  $\epsilon$ -caprolactam and many times before the degradation occurs the L-lactide polymer becomes in monomer due to effect of the temperature.

Although the copolymers start degrading before the homopolymers the degradation ending is at the same temperature as the one of ( $\epsilon$ -caprolactam) homopolymer. This could happen because when synthesising copolymers the structure changes and the stability of the copolymers decreases. It is also observed that when higher the ( $\epsilon$ -caprolactam) concentration is higher the degradation temperature, this could be because the ( $\epsilon$ -caprolactam) gives more stability to the copolymer than the L-lactide.



This final degree project has given to the following publication:

Basterretxea A, Gabirondo E, Sanchez-Sanchez A, Etxeberria A, Coulembier O, Mecerreyes D, et al. Synthesis and characterization of poly( $\epsilon$ -caprolactam-co-lactide) polyesteramides using Brønsted acid or Brønsted base organocatalyst.

Eur Polym J. Available from:

<http://www.sciencedirect.com/science/article/pii/S0014305717305451>

DOI: 10.1016/j.eurpolymj.2017.05.023

## 5. CONCLUSIONS

In this project, two different catalysts were studied, a Brønsted/Lewis acid, 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ( $[(\text{CH}_2)_4\text{SO}_3\text{HMIm}] [\text{H}_2\text{SO}_4]$ ), and a strong Brønsted/Lewis base, Phosphazene base  $\text{P}_4\text{-t-Bu}$  solution, to copolymerize for the first time different ratios of  $\epsilon$ -caprolactam and L-lactide.

In order to confirm that the copolymerisation occurred and to characterise the samples obtained, the following techniques were used:  $^1\text{H}$  and  $^{13}\text{C}$  NMR, ATR-FTIR, DSC, SEC and TGA.

It is concluded that the acidic catalyst promotes the polymerisation of L-lactide rather than  $\epsilon$ -caprolactam one. The opposite happens when the basic catalyst is used; in that case the promoting monomer is the  $\epsilon$ -caprolactam. This could be confirmed by the reactivity ratios calculated by Kelen-Tudos method.

Therefore, when using the acidic catalyst the copolymers with high rates of L-lactide monomer tend to have a blockier character than the ones of low L-lactide percentage, which show random character. When the basic catalyst is used instead, the copolymers with high concentration of  $\epsilon$ -caprolactam monomer have a blockier microstructure.

Regarding the crystallinity, both homopolymers are semicrystalline using either of the catalyst. In the case of copolymers the ones that were synthesised using the basic catalyst are semicrystalline, at least in the compositions where the  $\epsilon$ -caprolactam is the dominant monomer, due to the blockier microstructure that they present. In terms of number-average sequence lengths, values of  $l_{\text{CLa}}$  superior to 10 are required in order to achieve crystallization. Due to larger random character of the other copolymers, they behave as amorphous materials.

Analysing the results, it is seen that the reactivity ratios, which are related to the catalyst, make possible to select the most optimum reaction conditions to obtain the desired microstructures in the copolymers.

## 5. ONDORIOAK

Proiektu honetan, bi katalizatzaile ezberdin aztertu dira, batetik Brønsted/Lewis azido bat, 1-(4-sulfobutil)-3-metilimidazolio hidrogeno sulfatoa ( $[(\text{CH}_2)_4\text{SO}_3\text{HMIm}] [\text{H}_2\text{SO}_4]$ ), eta bestetik Brønsted/Lewis base sendo bat, Fosfazeno base  $\text{P}_4$ -t-Bu soluzioa, lehenengo aldiz  $\epsilon$ -kaprolaktama eta L-laktidaren arteko konposizio ezberdinetako kopolimeroak sintetizatzeke.

Lehenik eta behin, kopolimeroen sintesia eman dela ziurtatzeko eta ondoren, konposatuaren karakterizazioa egiteko jarraian izendatzen diren teknikak erabili dira:  $^1\text{H}$  eta  $^{13}\text{C}$  EMN, ATR-FTIR, DSC, SEC and TGA.

Ondorioztatu da katalizatzaile azidoak L-laktidaren polimerizazioa bultzatzen duela  $\epsilon$ -kaprolaktamarenaren aurretik, non alderantzizkoa gertatzen den katalizatzaile basikoa erabiltzen denean. Efektu hau ziurtatzeko monomeroen erreaktibitate erlazioak kalkulatu dira Kelen-Tudos metodoa erabiliz.

Horregatik, BAIL katalizatzailea erabiltzean, L-laktidaren konposizio altua duten kopolimeroek bloke itxura hartzen dute, gainerako konposizioek berriz, zorizkoa.  $\text{P}_4$ -t-Bu katalizatzailea erabiltzean aldiz,  $\epsilon$ -kaprolaktamaren kontzentrazio altuko kopolimeroek dute blokezko mikroegitura eta gainontzekoek zorizkoa.

Kristaltasunari erreparatuz, zehaztu da homopolimeroak erdikristalinoak direla bietako edozein katalizatzaileekin sintetizatuta izanda ere. Kopolimeroen kasuan aldiz, katalizatzaile basikoa erabili deneko kopolimeroak erdikristalinoak dira  $\epsilon$ -kaprolaktamaren konposizio altuetan, blokezko mikroegituraren eraginez. Zenbakizko batzuetan beste sekuentzia luzera aztertuz ikusi da  $l_{\text{CLa}}$  balioak 10 baino handiagoa izan behar duela kristalizazioa eman dadin. Beste

kopolimeroek erakusten duten zorizko izaera nabarmenagatik konposatu amorfotzat jokatzen dute.

Kopolimeroen erreaktibitate erlazioak kalkulatu ondoren, nahi den mikroegiturako eta ondorioz kristaltasuneko kopolimeroak sortzeko gaitasuna dagoela ondorioztatu da erreakzio baldintza egokiak aukeratuz.

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