Acidic Catalyzed Ring-Opening (co)Polymerization of γ-lactones

M. Monteiro [a,b,c], F. Peruch[b,c], S. Carlotti[b,c], M.Rosário. Ribeiro[a]

[a] Universidade de Lisboa, Instituto Superior Técnico, Avenida Rovisco Pais, 1, 1049-001, Lisboa, Portugal
[b] Univ. Bordeaux, LCPO, UMR 5692, F-33600 Pessac, France
[c] CNRS, LCPO, UMR 5629, F-33600 Pessac, France

ABSTRACT

The aim of this work was the study of several polymerization systems using lactones as monomers, such as, Ɛ-caprolactone and ɣ-butyrolactone, by a ring opening mechanism. The experiments were performed with acidic catalysts such as, methanesulfonic acid and triflic acid. As indicated in the literature, the ring opening polymerizations with these types of catalysts and ɣ-lactones were not possible under the operating conditions due to the thermodynamic stability of this type of monomer. Thus, to obtain an efficient system, the copolymerization of the two monomers, Ɛ-caprolactone and ɣ-butyrolactone, was performed at different temperatures (-40 °C to 30 °C) and with the two catalysts mentioned above. Novel copolymers, γ-butyrolactone-co-Ɛ-caprolactone were obtained at all tested temperatures showing the incorporation of ɣ-butyrolactone as desired.

KEYWORDS: Ɛ-caprolactone, ɣ-butyrolactone, Ring-opening Polymerization, lactones, copolymers

1. INTRODUCTION

Nowadays, plastics are used in an enormous and expanding range of products and markets, such as packaging, building and construction, electrical and electronic products. There is a large range of variety of plastics for different needs (PP, PE-LD, PE-LLD, PVC, etc.). In 2014, the world production of plastics was 314 million tons of which 59 million of tones was from Europe. The most worrying problem of the plastics is the ending up of this after being consumed. In 2014, 25.8 million tonnes of post-consumer plastics waste ended up in the waste upstream. 69.2% was recovered through recycling and energy recovery processes while 30.8% still went to landfill. Many of these plastics have a long time of degradation so there are a lot of environmental problems associated. [1]

To solve this problem, some investigators and researchers started to study the synthesis of biodegradable polymers. One of the most studied and the most important groups of biodegradable polymers are polyesters, thanks to their physical and chemical properties the range of applications can be varied. [2] Biodegradable polyesters due to the characteristics of the main-chain structure and a certain extent of hydrophilicity can degrade easily in the environment. These attributes make them a leading candidate in biomedical and pharmaceutical industries. [3-13]

Two different approaches can be applied in the synthesis of these polyesters: Ring-Opening Polymerization (ROP) of cyclic esters and polycondensation. [14] [15]

In recent decades, Ring-Opening Polymerization (ROP) of cyclic esters has been investigated to study new reaction pathways and new catalytic processes to create novel and high performing materials. Biodegradable and biocompatible polymers have become readily accessible by chemical synthesis via ROP from cyclic esters or lactones, with a big variety of applications or even be incorporated in another polymer in the form of blends or copolymers. [16] [17]

This work will focus on the synthesis of new biodegradable polyesters obtained by catalyzed ROP of ɣ- butyrolactone, this lactone is said to be non-polymerizable because of unfavourable thermodynamics which prevents the opening of the cycle. [18] [19]

Several studies described in the literature succeeded to (co)polymerize γ-lactones. As an example, Tadokoro *et al.* [20] investigated the polymerization of spirocyclic γ-butyrolactone. This polymerization proceeded with success at room temperature, in tetrahydrofuran (THF) as the solvent and tert-butoxide (t-BuOK) or methyllithium (MeLi) as the initiator. Hong and Chen [21] investigated the polymerization of γ-butyrolactone, with phosphazene as the catalyst and an alcohol as the initiator. They developed the first organopolymerization of γ-BL, that operates in THF and at low temperature (-40ºC). Hong and Chen [22] have also described the first ring-opening copolymerization based on the coordination-insertion mechanism of α-methylene-γ-butyrolactone (MBL) and ε-CL. The catalyst used for these copolymerization is $La[N(SiMe_3)_2]_3$ and

this reaction exclusively produce an unsaturated PMBL-co-PCL copolyester, with an incorporation up to 40% of MBL and without any formation of homoPMBL. Gagliardi et al. [23] reported the copolymerization of Ɛ-CL and ɣ-VL, by ROP using methoxy polyethyleneglycol (mPEG) as the initiator. It was shown that the reaction can occur in a controlled way in the temperature range from 120 °C to 180 °C. Lee *et al.* [24] investigated the copolymerization of ɣ-VL with β-butyrolactone in bulk conditions with $BF_3.OEt_2$ as the catalyst, at room temperature. Very recently, Undin *et al.* [25] have demonstrated that by using an organic catalyst, diphenyl phosphate (DPP), a conversion close to 100% is obtained for α-bromo-γ-butyrolactone (α-Br-γBL) whatever the co-monomer (TMC, AOMEC (2-allyloxymethyl-2- ethyl-trimethylene carbonate), ε-CL).

2. EXPERIMENTAL SECTION

2.1. Materials

Toluene (XiLab, 99%) and dichloromethane (Sigma Aldrich, 99%) were dried and cryodistilled just before use. ε-caprolactone (ε-CL, Alfa Aesar, 99%), γ-Butyrolactone (γ-BL, Alfa Aesar, 99%) and γ-Valerolactone (γ-VL, Alfa Aesar, 98%) were stirred with CaH_2 for 2 days, cryodistilled and stored under nitrogen. Biphenyl-4-methanol (BPM, Alfa Aesar, 98%) was recrystallized from dichloromethane. Methanesulfonic Acid (MSA, Aldrich, 99,5%) and Trifluoromethanesulfonic Acid (TfOH, Aldrich, 99%) were bubbled for some hours with nitrogen, prior to use, then stored in a flask under this gas. N,N-diisopropylethylamine (DIPEA, Aldrich, 99%) was used as received.

2.2. General polymerization procedure

The typical polymerization procedure is as follows: ε-CL (2.5 mL, 20 mmol) and dried toluene (43 mL) were taken from burettes and introduced into a 100mL round-bottom flask with a stirrer, under nitrogen. This flask was immersed in a thermostated bath. After the homogenization of the mixture, BPM (50 mg, 0.258 mmol) was added. A catalyst solution of MSA (17 µL, 0.258 mmol, 1 equivalent / initiator) was finally added with a micro syringe. Small aliquots (2 mL) were taken from the reaction and quenched with DIPEA (Hünig's base) to quench the MSA and stop the polymerization. The analysis of the sample was made to check the conversion of the monomer by ^{1}H NMR spectroscopy. The sample is precipitated in cold methanol, dried under vacuum and washed several times with cold methanol. After this procedure, the sample was analyzed by SEC analysis.

The procedure was further repeated for the copolymers with $[\varepsilon\text{-CL}]_0/[\gamma\text{-BL}]_0$ ratios at 1:2, 1:4 and 4:1. The copolymerization was performed with $[\varepsilon\text{-CL}]_0+[\gamma\text{-BL}]_0$=10M and using biphenyl-4-methanol as initiator. Monomer conversions were again surveyed by ^{1}H NMR spectroscopy in deuterated solvent containing DIPEA. The product was recovered as described above, and characterized by ^{1}H NMR and SEC. [26]

2.3. Measurements & characterization

2.3.1 Nuclear Magnetic Ressonance Spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy (NMR) was used to analyze the extent of the reaction, the composition of the polymer formed and the average-number molar mass. ^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.62 MHz) spectra were recorded with a Bruker Avance 400 spectrometer at 298 K. For the measurements, either 10 mg (^{1}H NMR) or 100 mg (^{13}C NMR) of the polymer was dissolved in 0.8 mL of $CDCl_3$ in a sample tube that has 5 mm in diameter. The spectra were calibrated using the residual proton of the solvent signal (i.e., 7.26 ppm (^{1}H NMR) and 77.0 ppm (^{13}C NMR) for $CDCl_3$).

For the homopolymerization of caprolactone, the monomer conversion was calculated by the ^{1}H NMR of the unpurified sample Figure 2, using the peak areas of the monomer (CH_2, δ=2.48 ppm, number 1), with the peak area for the signal of the polymer (CH_2, δ=2.30 ppm, number 1'). Equation 1 is used to calculate the conversion of Ɛ-CL, with the signals acquired from the ^{1}H NMR spectrum.

$$x_{\varepsilon-CL}(\%) = \frac{(I_{peak_{1'}})/2}{\frac{I_{peak_{1'}}}{2} + \frac{I_{peak_1}}{2}} \times 100 \qquad \text{(Eq. 1)}$$

The molar masses can be calculated through Equation 5, using the average of DP of the three peaks of the polymeric chain in the ^{1}H NMR of polycaprolactone purified: at 3.6 ppm, the signal corresponds to the final CH_2OH (Equation 2); at 5.2 ppm the signal corresponds to the Ph-$PhCH_2O$ (Equation 3); In the range 7.1-7.5 ppm the signal corresponds to the aromatic protons of the initiator (Equation 4).

$$DP\ (3.6ppm) = \frac{I_{peak_{1'}}/2}{I_{peak_{7'}}/2} \qquad \text{(Eq. 2)}$$

$$DP\ (5.2ppm) = \frac{I_{peak_{1'}}/2}{I_{peak_{6'}}/2} \qquad \text{(Eq. 3)}$$

$$DP\ (7.3ppm) = \frac{I_{peak_{1'}}/2}{I_{peak_{aromatics}}/9} \qquad \text{(Eq. 4)}$$

$$Mn_{Poly(\varepsilon-CL)}(g/mol) = \overline{DP} \times M_{\varepsilon-CL} + M_{BPM} \qquad \text{(Eq. 5)}$$

$$\overline{Mn}\ th = \frac{[\varepsilon - CL]_0}{[BPM]_0} \times M_{\varepsilon-CL} \times x_{\varepsilon-CL} + M_{BPM} \qquad \text{(Eq. 6)}$$

For the copolymerization of Ɛ-CL and ɣ-BL, the conversion of ɣ-butyrolactone is calculated using the spectrum of the unpurified sample (Figure 3) and making

the integration of the peak (8) of the monomer, at 4.35 ppm, and the polymer peak at 1.95 ppm, peak (7'), as it is shown in Equation 7. On the other hand, the conversion of Ɛ-caprolactone can be calculated through the integration of the monomer peak (5) at 4.20 ppm (in Figure 8 this peak is not visible because the conversion of e-caprolactone is 100%) and the polymer peak (3') at 1.35 ppm, as shown Equation 8.

$$x_{\gamma-BL}(\%) = \frac{(I_{peak_{7'}})/2}{\frac{I_{peak_{7'}}}{2} + \frac{I_{peak_8}}{2}} \times 100 \quad \text{(Eq. 7)}$$

$$x_{\varepsilon-CL}(\%) = \frac{(I_{peak_{3'}})/2}{\frac{I_{peak_{3'}}}{2} + \frac{I_{peak_5}}{2}} \times 100 \quad \text{(Eq. 8)}$$

From the ^{1}H NMR spectrum of the purified copolymers, Figure 3, it is also possible to calculate its molar composition in ɣ-butyrolactone and Ɛ-caprolactone, through Equations 9 and 10 respectively. The peaks corresponding to two protons of poly-caprolactone and polybutyrolactone, at 1.35 ppm (3') and 1.9 ppm (7') respectively, were used.

$$Proportion_{\gamma-BL}(\%) = \frac{(I_{peak_{7'}})/2}{\frac{I_{peak_{7'}}}{2} + \frac{I_{peak_{3'}}}{2}} \times 100 \quad \text{(Eq. 9)}$$

$$Proportion_{\varepsilon-CL}(\%) = \frac{(I_{peak_{3'}})/2}{\frac{I_{peak_{7'}}}{2} + \frac{I_{peak_{3'}}}{2}} \times 100 \quad \text{(Eq. 10)}$$

Then, the molar masses of the copolymers can be calculated by the three peaks of the polymer chain, like it was referred in the case of polycaprolactone, through Equation 6. In an analogous way, to what was referred for polycaprolactone the DP and the molar masses of the copolymers can be calculated by the following equations:

$$DP_{\gamma-BL}\ (3.6ppm) = \frac{I_{peak_{7'}}/2}{I_{peak_{10'}}/2} \quad \text{(Eq. 11)}$$

$$DP_{\gamma-BL}\ (5.2ppm) = \frac{I_{peak_{7'}}/2}{I_{peak_{9'}}/2} \quad \text{(Eq. 12)}$$

$$DP_{\gamma-BL}\ (7.3ppm) = \frac{I_{peak_{7'}}/2}{I_{peak_{aromatics}}/9} \quad \text{(Eq. 13)}$$

2.3.2. Size Exclusion Chromatography (SEC)

Size exclusion chromatography (SEC) was used to evaluate the molar mass. The number-average molar mass (Mn) and dispersity (*Đ*) of the polymers during and after polymerization were determined using a Polymer Laboratories PL-GPC 50 Plus chromatograph equipped with RI and UV detectors, with one Tosoh HXL-L guard column and three Tosoh G4000HXL, G3000HXL and G2000XL columns, calibrated with polystyrene standards. Tetrahydrofuran (THF) was used as the eluent with a flow rate of 1.0 mL.min^{-1}, with trichlorobenzene as flow marker. For the measurements, 5 mg of polymer was dissolved in 1 mL of THF in a flask with a stirrer, and left for 24 hours in a magnetic agitator. After the complete homogenization of the solution, 1mL was taken from the flask, filtered at 0.45 µm and analyzed in SEC.

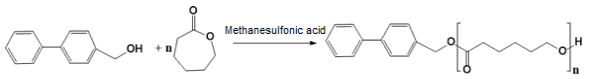
3. RESULTS AND DISCUSSION

3.1. Synthesis of homopolyesters

Before performing copolymerization reactions Ɛ-CL, ɣ-BL and ɣ-VL were first homopolymerized to evaluate the best experimental reaction conditionsThe influence of several reaction parameters are discussed in this section.

The study was made in the presence of biphenyl-4-methanol (BPM) as the initiator and an organic acid, methanesulfonic acid (MSA) or trifluoromethanesulfonic acid (TfOH) as the catalyst. Toluene was used as the solvent.

The cationic homopolymerization of Ɛ-CL is shown in Scheme 1.



Scheme 1 – General experimental procedure of ROP for Ɛ-CL with MSA as a catalyst.

In Table 1 are gathered the experimental conditions used in a first set of homopolymerizations and the corresponding information on monomer conversion, degree of polymerization and theoretical and experimental molar masses.

The ^{1}H NMR spectrum of the monomer, together with a typical spectrum of a crude and of a purified polymerization sample is shown in Figure 1. Data shows that the white solid obtained after precipitation is indeed polycaprolactone

From Table 1 it can be noticed that below -10ºC no polymerization occurred. It is important to note that the concentration had to be less than 5M at negative temperatures, because caprolactone in larger concentrations is not fully soluble.

It is also seen that the conversion increases with the temperature for MSA catalyst, reaching 100% at 30ºC and 5 hours reaction. Full conversion is also obtained for the TfOH catalyst under the tested experimental conditions (run 6).

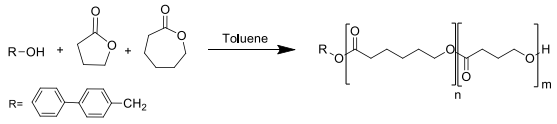
An important aspect to notice is that the degree of polymerizations, calculated for both chain ends and

based on the integration of different peaks, are quite similar (run 5). This is indicative of a good polymerization control with no side initiation. This behavior is also corroborated by the good agreement between the theoretical molar masses and the experimental ones, especially those based on NMR data. Calibration issues can account for a higher difference when dealing with SEC data.

Despite the similarity on monomer conversion and on the molar masses of PCL obtained from MSA and TfOH catalysts a higher dispersity is observed in the latter case. This may be related to a more efficient polymerization control when using MSA under the experimental conditions of run 5.

3.2. Synthesis of copolymers: Ɛ-Caprolactone with ɣ-Butyrolactone

Several copolymerizations were performed at different temperatures in the presence of the same initiator and catalysts as before. A molar ratio of 1:1 between the catalyst and the alcohol initiator was used and the molar proportion of the monomers was varied: 50/50, 25/75 and 75/25. In Scheme 2, it is shown the expected structure for the copolymer obtained.



***Scheme 2** – Copolymerization of Ɛ-CL with ɣ-BL in the presence of BPM, with MSA or TfOH as a catalyst.*

The first copolymers were synthesized at room temperature with an initial molar ratio of 50/50, varying the reaction time. The results are shown in Table 2.

With an initial molar proportion of 50/50 between the monomers, the increase of the reaction time doesn't affect the conversion of caprolactone since this monomer, has already attained full conversion after 10 hours. The increase of reaction time, increases the conversion of ɣ-BL. After 24 hours, the conversion of ɣ-BL attains 24%. Although the homopolymerization of butyrolactone at the same temperature and catalyst did not work in copolymerization conditions, ɣ-BL is successfully incorporated in the copolymer.

Due to the difference in the reactivity of the two monomers, the final composition of the copolymer is different from the theoretical one, 50% ɣ-butyrolactone and 50% Ɛ-caprolactone. Under the tested conditions an incorporation of 16% in butyrolactone is attained after 10 hours.

The molar masses calculated by NMR and SEC are in good agreement with the theoretical ones, indicating a controlled polymerization. Moreover, the dispersity is quite good, corroborating the control of the polymerization.

Another set of polymerizations were performed under different molar proportions of Ɛ-Caprolactone and ɣ-Butyrolactone of 25/75 and 75/25. The results are shown in Table 2.

Despite the increase of the proportion of *ɣ-BL* in the polymerization media from 50/50 to 25/75 there's only an increase of the *ɣ*-BL content in the copolymer from around 14% up to 25%. This is a consequence of the low reactivity of lactone and of the rather low values obtained for the butyrolactone conversion even at 144 h polymerization time. In table 2 the results also show a good agreement in the molar masses obtained from NMR and SEC analysis, along with a low value of 1.27 for dispersity.

For the copolymerizations of Ɛ-CL with ɣ-BL with a molar proportion of 75/25 it can be observed the conversion of butyrolactone is 37% and the final content of butyrolactone in the copolymer is only 8%. The molar masses calculated are in a good agreement, like the previous experiment, with a polydispersity in the same range of values (1.28-1.32).

The SEC chromatograms for copolymerization of Ɛ-CL with ɣ-BL at molar proportion of 50/50, 25/75 and 75/25 (Run 2, 3.1, 5 and 6, from Table 2) are shown in Figure 3.

In the Figure 3, it is possible to verify the existence of two populations in the blue line, which corresponds to the copolymerization of ε-CL and γ-BL with a molar proportion of 75/25. The observation of these two peaks, represents the occurrence of side reactions in this polymerization, generating additional chains with higher molar mass.

Based on the previous results, for the successful homopolymerization of Ɛ-caprolactone at 0 ºC, the copolymerization at this temperature of Ɛ-CL with ɣ-BL was also attempted. Table 3 shows the experiments made in different conditions and the corresponding results. TfOH was used as catalyst and the tested molar proportion Ɛ-CL/ɣ-BL was 50/50.

The conversion of butyrolactone does not exceed 12%, which is a lower conversion than the one obtained for the experiments at room temperature. Since the NMR has superimposition of the peaks, it is very difficult to provide a good evaluation of the proportion obtained in the copolymer. The theoretical mass is in a good agreement with the molar mass calculated by NMR and SEC, indicating that this system has a good control.

Another set of experiments were made in bulk at 50 ºC with a 50/50 molar proportion and using TfOH and MSA as catalysts (Table 4).

In Table 4, it is possible to notice that after 1 h the conversion for Ɛ-caprolactone is almost complete while the conversion of ɣ-butyrolactone is about 31% after 48h. On the other hand, the proportion of ɣ-BL reaches 15% after 2 days of polymerization. A beneficial effect from the point of view of the conversion and the incorporation of ɣ-butyrolactone on the copolymer can be observed when comparing these values with those attained at 0ºC.

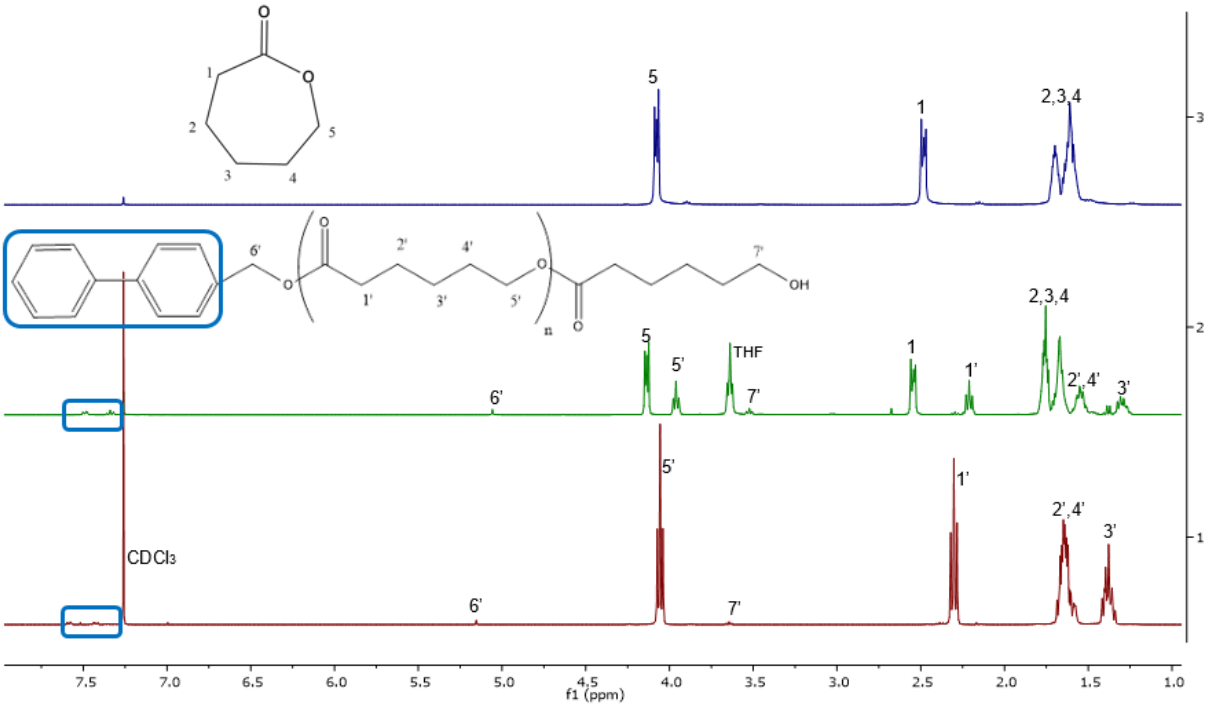


Figure 1 - ^{1}H NMR spectrum in $CDCl_3$ zoomed between 1.00 ppm and 8.00 ppm. The blue spectrum refers to the monomer Ɛ-CL, the green spectrum to unpurified polycaprolactone sample of Run 3 and the red spectrum to purified polycaprolactone of Run 5, of Table 1.

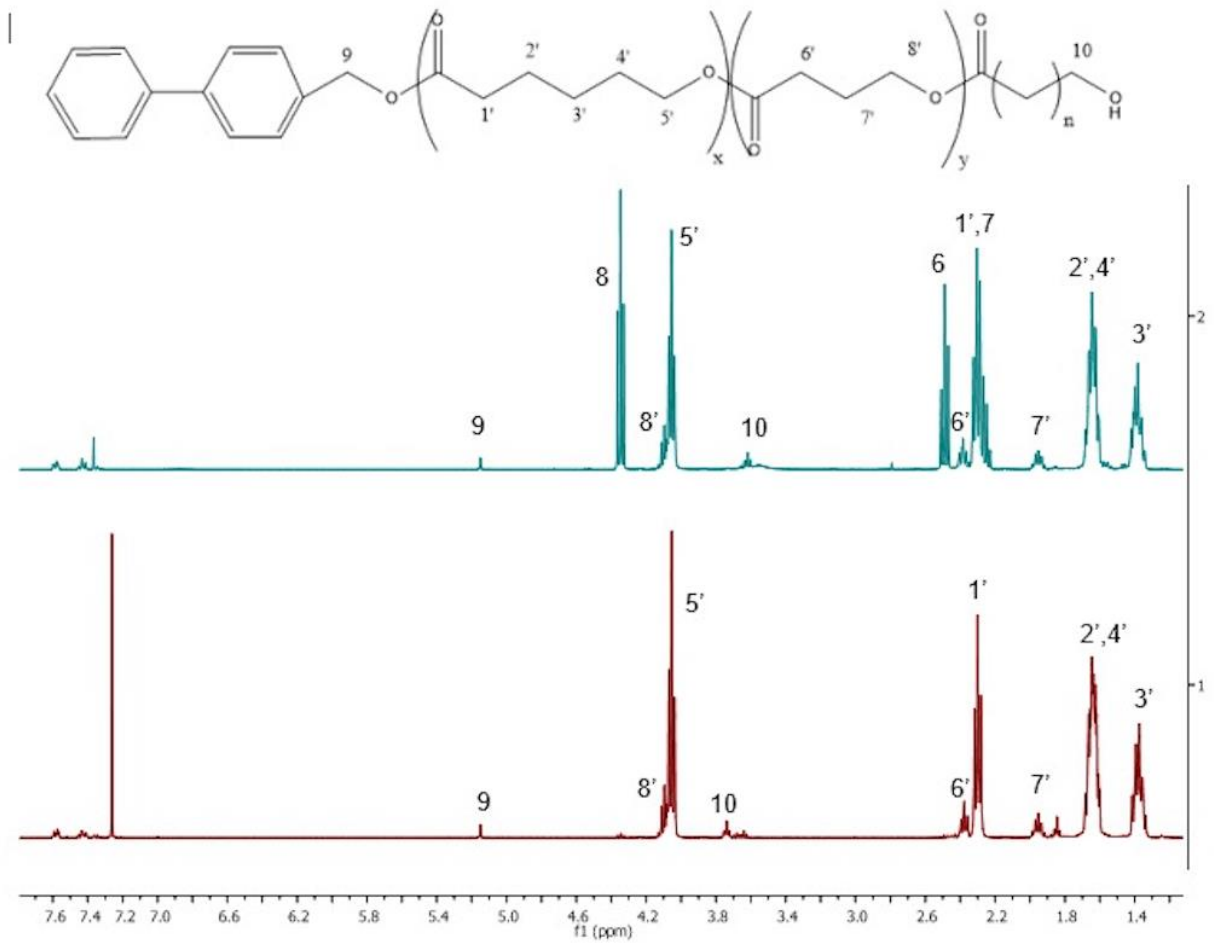


Figure 2 - *^{1}H NMR spectrum in $CDCl_3$ zoomed between 1.00 ppm and 8.00 ppm. The blue spectrum refers to the unpurified polymer Ɛ-CL+γ-BL and the red spectrum refers to purified polymer Ɛ-CL+γ-BL, sample of Run 2, table 2.*

Table 1 – *Polymerization of Ɛ-CL in toluene with MSA as the catalyst in Runs 1-5 and TfOH in Run 6.*

Run	$[\varepsilon\text{-CL}]_0$ (mol/L)	t (h)	T (°C)	$x_{\varepsilon-CL}$ a) (%)	$\overline{Mn}$ th b) (g/mol)	DP c) (g/mol)			$\overline{Mn}$ d) (g/mol)	$\overline{Mn}$ SEC d) (g/mol)	$\frac{M_w}{M_n}$ e)
						3.6-3.7 ppm	5.1-5.2 ppm	7.1-7.5 ppm			
1	1	5	-40	0	-	-	-	-	-	-	-
2	5	4	-20	0	-	-	-	-	-	-	-
3	5	8	-10	32	3 400	-	-	-	-	-	-
4	5	7	0	48	5 050	-	-	-	-	-	-
5	0.5	5	30	100	10 230	88	87	85	10 070	8 250	1.16
6(*)	9	1	50	100	10 230	-	89	90	10 400	15 620	1.44

[ε-CL]/[BPM]=88/1 ; [BPM]/[MSA]=1/1.

a) Conversions calculated by ^{1}H NMR spectroscopy of the crude sample.
b) Theoretical number-average molar mass $\overline{Mn}$ th calculated by Equation 6.
c) DP calculated by ^{1}H NMR spectroscopy of the precipitate sample, calculated by Equations 2, 3 and 4.
d) Number average molar mass calculated by Equation 5.
e) Number-average molar mass measured by SEC in THF versus PS calibration.
f) Molar mass dispersities estimated from SEC data.
(*) The reaction 6 was performed in bulk (no toluene was used).

Table 2 – *Copolymerization of Ɛ-CL with γ-BL at 25ºC, with a molar ratio of 50/50 (Runs 1-2), 25/75 (Runs 3-4.1) and 75/25 (Runs 5-6) in the presence of MSA as a catalyst.*

Run	Time (h)	$x_{\varepsilon-CL}$ a) (%)	$x_{\gamma-BL}$ a) (%)	$\overline{Mn}$ th b) (g/mol)	Proportion c) (Ɣ-BL)/(Ɛ-CL)	$\overline{Mn}$ d) (g/mol)	$\overline{Mn}$ SEC e) (g/mol)	$\frac{M_w}{M_n}$ f)
1	10	100	13	6400	16/84	6 200	-	-
2	24	100	24	6900	14/86	6 730	8240	1.17
3	24	99	12	4040	-	-	-	-
3.1	144	99	13	4140	25/75	4420(*)	5500	1.27
4	24	98	10	3860	-	-	-	-
4.1	168	99	16	4360	-	-	-	-
5	5	-	-	-	8/92	10180	8500	1.28
6	24	99	37	8810	7/93	10790	9500	1.32

[ε-CL-γ-BL]/[BPM]=100/1 (50/50) [ε-CL-γ-BL]/[BPM]=107/1 (25/75) [ε-CL-γ-BL]/[BPM]=93/1 (75/25) ; [BPM]/[MSA]=1/1

a) Conversions calculated by ^{1}H NMR spectroscopy of the brute sample, by Equations 7 and 8.
b) Theoretical number-average molar mass $\overline{Mn}$ th calculated by Equation 14.
c) Composition of the recovered polymer (molar fraction), as determined by ^{1}H NMR with Equations 9 and 10.
d) Number average molar mass calculated by Equation 15.
e) Number-average molar mass measured by SEC in THF versus PS calibration.
f) Molar mass dispersities estimated from SEC data.
(*) Number average molar mass calculated by Equation 15, with the DP only corresponding to 3.6 ppm peak.

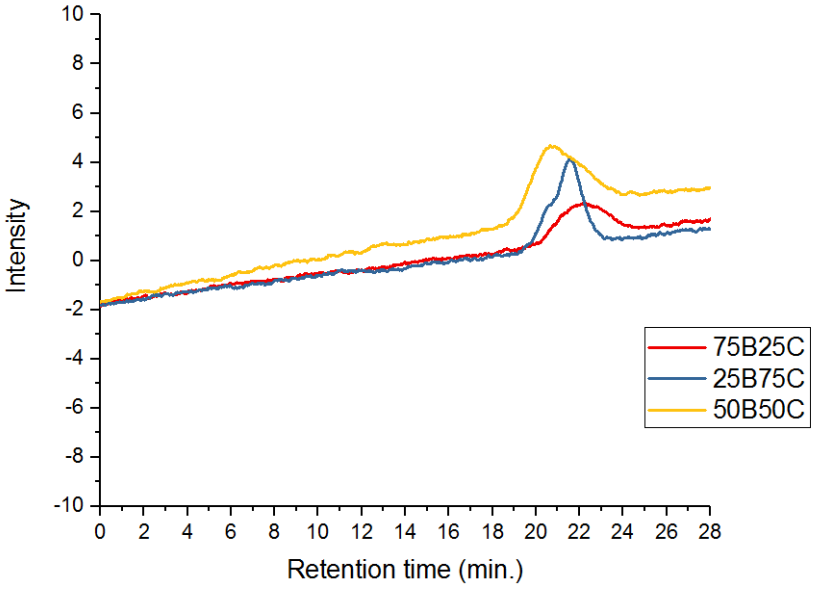


Figure 3 - *SEC chromatograms of the poly (ɣ-butyrolactone-co-ε-caprolactone) copolymers obtained at 25ºC in different molar ratios (THF with polystyrene calibration at 40 ° C).*

Table 3 - *Copolymerization of Ɛ-CL with ɣ-BL at 0ºC and with a molar ratio of 50/50. The catalyst used in these experiments is TfOH and the solvent is DCM.*

Run	*Time (h)*	$x_{\varepsilon-CL}$ [a] (%)	$x_{\gamma-BL}$ [a] (%)	$\overline{Mn}$ th [b] (g/mol)	*Proportion* [c] *(Ɣ-BL)/(Ɛ-CL)*	$\overline{Mn}$ [d] *(g/mol)*	$\overline{Mn}$ *SEC* [e] *(g/mol)*	$\frac{M_w}{M_n}$ [f]
1	7	100	10	6300	-	-	-	-
1.1	24	100	12	6400	16/84	7460	7170	1.32

Table 4 - *Copolymerization of Ɛ-CL with ɣ-BL at 50ºC in bulk with a molar ratio 50/50 and TfOH (Runs 1-2) and MSA (Runs 3-5) as the catalyst.*

Run	*Time (h)*	$x_{\gamma-BL}$ [a] *(%)*	$x_{\varepsilon-CL}$ [a] *(%)*	$\overline{Mn}$ th [c] *(g/mol)*	*Proportion* [b] *(Ɣ-BL) / (Ɛ-CL)*	$\overline{Mn}$ [d] *(g/mol)*	$\overline{Mn}$ *SEC* [e] *(g/mol)*	$\frac{M_w}{M_n}$ [f]
1	1	15%	97%	6350	14/86	10 560	-	-
2	48	31%	100%	7200	15/85	14 625(*)	5 940	1.54
3	1	99	16	6500	10/90	8030(*)	6150	1.20
4	48	99	25	6920	18/82	6000	9220	1.50
5	72	100	23	6860	15/85	5850	11885	1.48

[ε-CL-ɣ-BL]/[BPM]=100/1 ; [BPM]/[TfOH/MSA/TfOH]=1/1.

a) Conversions calculated by ^{1}H NMR spectroscopy of the brute sample, by Equations 7 and 8.
b) Theoretical number-average molar mass $\overline{Mn}$ th calculated by Equation 14.
c) Composition of the recovered polymer (molar fraction), as determined by ^{1}H NMR with Equations 9 and 10.
d) Number average molar mass calculated by Equation 15.
e) Number-average molar mass measured by SEC in THF versus PS calibration.
f) Molar mass dispersities estimated from SEC data.
(*) Number average molar mass calculated by Equation 15, with the DP only corresponding to 3.6 ppm peak.

However, the molar mass obtained by NMR is much higher than the theoretical molar masses and the dispersity given by SEC analysis is quite high, 1.54. This indicates a loss of polymerization control under the tested experimental conditions.

In these experiments, a change of color appeared from rose to violet, as it is shown in Figure 4, but the reason for that was not completely identified. One possibility is the occurrence of side reactions such as cyclization.

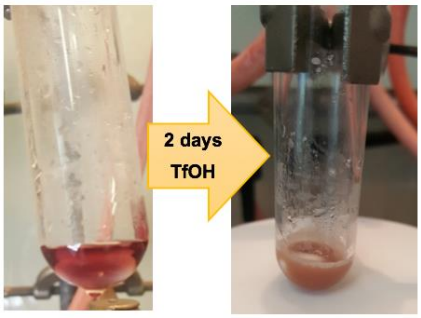


Figure 4 - *Sample from run 2 in Table 4, after 1h (crude sample) and 2 days (brute sample), with triflic acid.*

From Table 4, it is possible to notice that the conversion of butyrolactone is around 24% after two days, which is slightly higher than the one obtained for TfOH catalyst. The molar proportion of ɣ-BL/Ɛ-CL in the copolymer after three days is 15/85. In what concerns molar masses, the theoretical values are not very far from those determined by NMR. However, the corresponding values determined by SEC analysis, are much higher and the dispersites present also relatively high values, particularly for the long polymerization times. Therefore, a loss of polymerization control together with the presence of side reactions seems to occur in these conditions.

4. CONCLUSIONS

The aim of this work was to develop an effective system for the (co)polymerization of 5-membered lactones (γ-butyrolactone) with caprolactone by ROP with an acidic catalyst.

The homopolymerization of caprolactone can be done and is more effective at room temperature than with other temperatures. The polymerization of the γ-lactones (γ-butyrolactone and γ-valerolactone) wasn't successful under the same conditions.

The synthesis of novel ɣ-butyrolactone/Ɛ-caprolactone copolymers has proved to be an effective alternative to incorporate ɣ-butyrolactone units at room temperature. NMR and SEC analysis shows a good control of (co) polymerization with the formation of random copolyesters, at room temperature.

In bulk at 50 degrees, the copolymers obtained have high molar masses and polydispersity, which suggesting the presence of some side reactions.

The catalytic system used here was successfully applied to the ROP copolymerization of γ-butyrolactones not derived from renewable resources. In a future work, it would be advantageous subsequently, to use this system to polymerize bio-sourced γ-butyrolactone.

5. REFERENCES

[1] "Plastics," *Plastics Europe,* pp. 1-30, 2015.

[2] H.-T. Liao and C.-S. Wu, "Preparation and characterization of ternary blends composed of polylactide, poly(e-caprolactone) and starch," *Materials Science Engineering,* vol. A 515, pp. 207-214, 2009.

[3] K. Stridsberg, M. Ryner and A.-C. Albertsson, "Controlled Ring-Opening Polymerization: Polymers with designed Macromolecular Architecture," *Polymer Science,* vol. 157, pp. 41-65, 2002.

[4] N. Ljundegberg and B. Wesslén, *J. Appl. Polym. Sci.,* vol. 86, pp. 1227-1234, 2002.

[5] N. Ljungberg, T. Andersson and B. Wesslén, *J. Appl. Polym. Sci. ,* vol. 88, pp. 3239-3247, 2003.

[6] O. Martin and L. Avérous, *Polymer,* vol. 42, pp. 6209-6219, 2001.

[7] T. Ke and X. Sun, *J. Appl. Polym. Sci.,* vol. 88, pp. 2947-2955, 2003.

[8] T. Takayama and M. Todo, *J. Mater. Sci,* vol. 41, pp. 4989-4992, 2006.

[9] A. Hoffman, *Adv. Drug Deliv. Rev.,* vol. 54, pp. 3-12, 2002.

[10] M. Woodruff and D. Hutmacher, "The return of a forgotten polymer- Polycaprolactone in the 21st century," *Progress in Polymer Science,* vol. 35, pp. 1217-1256, 2010.

[11] E. Wissler, *Ring-opening polymerization of lactones and lactides: An organic chemistry lab synthesis,* College of Saint Benedict/Saint John's University, 2014.

[12] I. Engelberg and J. Kohn, "Physico-mechanical properties of degradable polymers used in medical applications: a comparative study," *Biomaterials,* vol. 12, pp. 292-304, 1991.

[13] E. Frazza and E. Schmitt, "A new absorbable suture," *J. Biomed. Mat. Res. Symp.,* vol. 1, pp. 43-58, 1971.

[14] A.-C. Albertsson and I. Varma, "Recent Developments in Ring Opening Polymerization of

Lactones for Biomedical Applications," *Biomacromolecules,* vol. 4, pp. 1466-1486, 2003.

[15] P. Ólsen, K. Odelius and A.-C. Albertsson, "Thermodynamic Presynthetic Considerations for Ring-Opening Polymerization," *Biomacromolecules,* vol. 17, no. 3, pp. 699-709, 2016.

[16] H. Leuchs, "Glycine-carbonic acid," *Ber. Dtsch. Chem.,* vol. 39, 1906.

[17] J. E. McGrath, Ed., Ring-Opening Polymerization, vol. 286, American Chemical Society, 1985.

[18] D. Johns, R. Lenz and A. Luick, "Ring-Opening Polymerization," *Elsevier Applied Science Publishers,* vol. 1, p. 461, 1984.

[19] R. Jerome and P. Teyssie, "Comprehensive Polymer Science," *Pergamon Press,* vol. 3, p. 501, 1989.

[20] A. Tadokoro, T. Takata and T. Endo, *Macromolecules,* vol. 26, pp. 2388-2389, 1993.

[21] M. Hong and E. Chen, *Angew. Chemie - Int Ed.,* vol. 55, pp. 4188-4193, 2016.

[22] M. Hong and . E. Y. X. Chen, *Macromolecules,* vol. 11, p. 3614–3624, 2014.

[23] M. Gagliardi, F. Di Michele, B. Mazzolai and A. Bifone, "Chemical synthesis of a biodegradable PEGylated copolymer from e-caprolactone and gamma-valerolactone: evaluation of reaction and functional properties," *J. Polym. Res.,* vol. 22, no. 17, 2015.

[24] C. Lee, R. Urakawa and Y. Kimura, "Copolymerization of gamma-valerolactone and beta-butyrolactone," *Eur. Polym. J.,* vol. 34, pp. 117-122, 1998.

[25] J. Undin, P. Ólsen, J. Godfrey, K. Odelius and A.-C. Albertsson, "Controlled Copolymerization of the functional 5-membered lactone monomer, alfa-bromo-gamma-butyrolactone, via selective organocatalysis," *Polymer,* no. 87, pp. 17-25, 2016.

[26] J. Campos, M. Ribeiro, M. Ribeiro, A. Deffieux and F. Peruch, "Copoolimerisation of e-caprolactone and trimethylene carbonate catalysed by methanesulfonic acid," *European Polymer Journal,* vol. 49, pp. 4025-4034, 2013.