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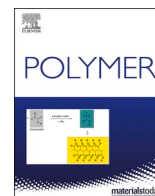
From polymer blends to a block copolymer: Ring-opening polymerization of L-lactide/ε-caprolactone eutectic system

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ABSTRACT

In this work, we provide new insights into the ring-opening polymerization (ROP) of eutectic mixtures of L-lactide and ε-caprolactone that lead to the synthesis of polymer blends and a block copolymer. The influence of a set of parameters is studied to produce polyesters with tunable average-molecular weight, crystallinity, and polymer architectures with controlled degradation profiles. The outcome depends on the selection of organocatalysts, including 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN), a new catalyst for the L-lactide/ε-caprolactone eutectic mixture ROP that enabled increasing the polymerization temperature. The mild polymerization temperatures and solventless conditions stand as green features of the ROP here described to prepare resorbable biomaterials with programmable degradation profiles.

1. Introduction

Poly(L-lactide) (PLLA) and poly(ε-caprolactone) (PCL) represent two of the most important (bio)degradable and biocompatible commercial polyesters, being critical components in materials applied in areas such as packaging, biomedicine, and 3D printing [1]. These polyesters are obtained by the catalytic ring-opening polymerization (ROP) of their respective monomers, L-lactide (LLA) and ε-caprolactone (CL) [2].

PLLA and PCL synthesis via ROP mechanism is preferred over other mechanisms such as polycondensation due to better control on the molecular weight and polydispersity of the resulting polymers [3]. Although these two polymers represent (bio)degradable alternatives to other synthetic polymers, their production typically requires high temperatures, in bulk or in solution, and avoiding undesired side reactions in these conditions is challenging. Industrial synthesis of these polyesters are typically carried out by melting (150-200 °C) due to lower environmental impact and cost [4–6]. It also includes the use of metal-based catalysts which are reported to be the most efficient in their production [7,8], e.g., tin-based catalysts allow obtaining polyesters with high molecular weights [5], and is approved by the FDA [8].

However, it demands an additional purification step, which may generate environmental issues and compromises some applications [9]. In addition, some upcoming regulations will be limiting their use [4,5, 8]. Thus, the search for catalytic alternatives to produce PLLA and PCL, excluding the use of toxic solvents, is a current challenge.

Greener routes for PLLA and PCL synthesis also mean new possibilities to apply them in diverse areas in simple manners, for instance, without demanding purification steps post-synthesis while expanding their properties. The use of organocatalysts has been proposed as a greener alternative to produce PLLA and PCL. Compared to metal catalysts, some advantages of organocatalysts include their environmentally friendly character, less toxicity, and ease of removal with greener solvents (e.g., ethanol) [2,5,10,11]. In this line, the amidine organocatalysts such as [1,8-diazabicyclo 5.4.0] undec-7-ene (DBU), which is a strong base, has been used in the ROP of LLA due to its high selectivity [12]. As for the ROP of CL, acid organocatalysts such as methanosulfonic acid (MSA) are commonly used to provide faster reactions and excellent control in the ROP [11]. The type of organocatalyst and their structure determines the mechanism by which the ROP operates, for instance, by a nucleophilic attack [12] or monomer activated chain pathway [11], in

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the case of DBU and MSA, respectively. The ROP of LLA and CL using organocatalysts can be performed in bulk and in solution. The use of organocatalysts presents some drawbacks, such as high costs and low operational temperatures resulting in low molecular weights [2,3,6,12]. However, low molecular weight polymers can lead to programmable degradation profiles in resorbable biomaterials.

Substantial efforts have been made to reduce the use of volatile organic solvents in polymer production, especially those regarded as toxic. In this context, the deep eutectic solvents (DESs) have emerged as a new family of designer solvents, many of them with notable green features. DESs comprised combinations of two or more components capable of self-associating through hydrogen bond interactions, with a resulting melting point lower than that of their individual components [13,14]. DESs implementation in polymer science goes beyond its functioning as inert solvents; they can also play the role of monomers that can polymerize in bulk for instance. These types of DESs are known as DES monomers (DESm), which exhibit greener features, meaning polymerizations are possible in solventless conditions and with a 100% atom economy [15].

Coulembier et al. first reported the ROP at 23 °C of a non-ionic DESm composed of an equimolar mixture of LLA and trimethylene carbonate using DBU organocatalyst and benzyl alcohol (BnOH) as initiator. The sequential polymerization of the eutectic mixture yielded a copolymer with a gradient composition [16]. Later, our group demonstrated the ROP at 37 °C of a eutectic mixture composed of LLA and CL in a 3:7 M ratio, respectively, using DBU and MSA organocatalysts, and BnOH as initiator. A blend of homopolymers with high crystallinity and high conversion in solventless conditions was obtained. It should be noted that a sequential polymerization took place, the homopolymerization of LLA catalyzed by DBU using BnOH as initiator first, followed by the addition of MSA for the ROP of CL [17]. Taking advantage of this approach, it was possible to produce hierarchical macroporous polyesters composed of PLLA and PCL applied for hydrocarbon separation processes. The synthesis was carried out by using high internal phase emulsions (HIPEs) as templates, where polymerization of the continuous phase composed of LLA/CL (3:7 M ratio respectively) affords macroporous polymers [17]. In the same line, it was possible to functionalize the internal walls of macroporous polyesters with non-functionalized nanohydroxyapatite, by polymerization of the continuous phase of a HIPE, to obtain polyester-hydroxyapatite composites with prospect applications in tissue engineering [18].

Polyesters are limited in some applications due to their mechanical properties, for instance, PLLA and PCL exhibit poor elasticity and toughness, respectively [2]. These properties can be improved by increasing their molecular weight and modifying their crystallinity. Strategies such as blending, synthesis of copolymers, stereocomplexation, or incorporation of nanofillers, are some alternatives [19, 20].

Herein, we present advances in obtaining a series of blends and copolymers of PLLA and PCL through a sustainable synthetic protocol in solventless conditions and without metal-based catalysts. This approach is based on the eutectic composition of LLA and CL monomer mixtures, which upon ROP at various temperatures and with the aid of strong bases (e.g., amidines) and an acid organocatalyst, resulted in a series of polyesters with tunable molecular weight, crystallinity, and molecular architecture. For this purpose, we took advantage of using a DESm, thus excluding organic solvents in the ROP and substituting metal-based catalysts with organocatalysts such as DBU and MSA at similar concentrations as reported on literature [8,12,21,22]. Additionally, we propose using 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) as a suitable organocatalyst towards the ROP of LLA in the DESm for the first time. DBN is a strong base [12] employed in the synthesis of carbolines or acylation of pyrroles and indoles [23]. Altogether, these green features open the possibility of exploring new applications for PLLA and PCL blends and copolymers in areas such as biomaterials with programmable biodegradability.

2. Experimental section

2.1. Materials

ε-Caprolactone (CL, 97%), L-lactide (LLA, 98%), 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU, 98%), 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN, 99%), methanesulfonic acid (MSA, 99.5%), and benzyl alcohol (BnOH, 99%) were obtained from Sigma-Aldrich.

The DES monomer was obtained by mixing LLA and CL with a 3:7 M ratio at 90 °C until a clear homogeneous liquid was observed; the mixture remained liquid upon cooling to room temperature. Next, the sequential ROP of the DESm (LLA/CL, 3:7 M ratio, respectively) was carried out by adding a mixture of DBU or DBN, 2.92 wt%, (organocatalyst) and BnOH, 2.08 wt%, as the initiator (1:1 M ratio, organocatalyst: initiator), together accounting 5 wt% with respect to the eutectic mixture, at different temperatures (37, 60, 80 and 92 °C). Subsequently, a second organocatalyst, MSA, was added to the reaction mixture (3 wt% to the eutectic mixture). The synthesized polyesters were named according to the first organocatalyst used (BU for DBU and BN for DBN), followed by the polymerization temperature.

It was reported that the ROP of DES LLA/CL at 37 °C, with DBU and MSA as organocatalysts, and BnOH as initiator were carried out in 6 h [17]. Thus, after 12 h it was ensured that the polymerization reached high conversions. Then, the samples were washed with ethanol to remove the organocatalysts and all residual monomers and oligomers, considering that in future applications in tissue engineering, the release of acidic oligomers may trigger the accelerated hydrolysis of the polyesters and cause toxic effects. Experimental conversions were determined by gravimetry, i.e., the ratio between the final polymer's mass and the initial mass of monomers. The experimental conversions in all the samples were *ca.* 88%.

2.2. Characterizations

^{1}H (400 MHz), NMR spectra were obtained at room temperature with a 400 MHz Bruker Avance III HD 400 N spectrometer (with a 5 mm multinuclear BBI-decoupling probe with Z grad). Chemical shifts (ppm) are relative to the remaining non-deuterated chloroform signal (from CDCl$_3$) and used as an internal reference for ^{1}H NMR spectroscopy.

Differential scanning calorimetry (DSC) measurements were carried out using a Mettler Toledo calorimeter model DSC3+ previously calibrated with indium. Scans were carried out at 10 °C min^{-1} under nitrogen flow. First, the samples were cooling from room temperature to −20 °C, then the temperature was maintained at −20 °C for 10 min, after the temperature were raised to 140 °C, and finally decreased from 140 °C to room temperature.

The X-ray diffraction patterns were obtained using a diffractometer Rigaku (Ultima IV model, Texas-USA), with a detector D/tex ultra (35 kV and 15 mA) and using a CuKα radiation wavelength (λ = 0.15406 nm).

DOSY (Diffusion Order Spectroscopy) data were acquired using the pulse program ledbpgp2s installed in the topspin 3.6.2 software from Bruker with 95 gradient levels with a linear increase from 2% to 95% using a gradient of strengths up to 54 G/cm and 8 transients. The diffusion delay (Δ) was 150 ms, and the length of the square diffusion encoding gradient pulse (δ) was 0.6 ms. Laplace transformations for generating the diffusion dimensions were obtained with the Bruker Biospin Dynamics Center using a least-squares fitting routine with Monte Carlo error estimation analysis.

Size exclusion chromatography (SEC). The molecular weight characteristics of polymers were determined by SEC using a Hewlett-Packard instrument (HPLC series 1100) equipped with UV light and refractive index detectors. A PLGel mixed column was used (1-PL Gel 10 6 A-400,000–40,000,000; 2-PL Gel mixed C 200–3,000,000), with refractive index at 40 °C. Calibration was carried out with polystyrene standards and THF (HPLC grade) was used as eluent at a flow rate of 1 mL/min.

The PLLA/PCL blends and copolymers were also analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI/TOF-MS). MALDI/TOF-MS measurements were performed on a BRUKER ULTRAFLEX III (MALDI-TOF/TOF) mass spectrometer equipped with a pulsed NdYAG laser ($\lambda = 355$ nm) and a delayed extraction ion source. Mass spectra were obtained over the m/z range of 500–10,000 Da in the reflector positive ion mode. External mass calibration was applied. *Trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) at 8 mg mL^{-1} in dichloromethane (DCM) was used as the matrix. Samples were dissolved at a concentration of 2 mg mL^{-1} in DCM, being 5 mL mixed with the matrix at a ratio of 1:4 (v/v) and 0.5 μL of sodium iodide (2 mg mL^{-1}). Then, 0.5 μL of this solution was spotted onto a flat stainless-steel sample plate and dried in air.

The optical transmittance measurements were carried out with a UV–Vis Hitachi U-1800 spectrophotometer using a 1 cm path length quartz cell, in a wavelength range from 300 to 800 nm at 20 °C.
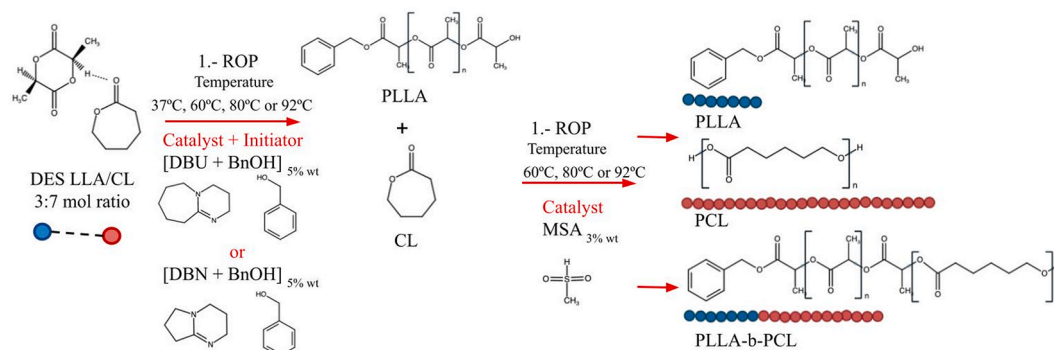
3. Results and discussion

3.1. Synthesis of homopolymers and copolymer

The sequential ROP of the LLA/CL DESm is schematically shown in Scheme 1. First, the nucleophilic organocatalysts (DBU or DBN) allow the selective ROP of LLA using the BnOH as initiator at temperatures ranging from 37 to 90 °C, depending upon the use of DBU or DBN. At this point, the composition of the medium comprises PLLA chains dispersed in the liquid CL, which was released from the liquid eutectic composition as LLA was consumed. Under these temperature conditions, pure LLA is solid (melting point of LLA is ca 98.3 °C) and thus not available to polymerize. Subsequently, MSA (second organocatalyst) was added to the reaction mixture promoting the ROP of CL. In this second ROP, the hydroxyl groups from either lactidyl previously formed or the residual water played the role of initiator [17], depending on the temperature and organocatalyst. As a result, PLLA/PCL blends or a P(LLA-b-CL) copolymer were obtained.

It is worthy of mentioning two critical aspects of the new nucleophilic organocatalyst proposed for the LLA/CL DESm ROP: 1) the DBN was able to selectively polymerize the LLA present in the eutectic mixture, similarly to DBU, and 2) it was possible to carry out the ROP at higher temperatures (e.g., 80 and 92 °C), temperatures at which DBU readily degrades [8], thus expanding the polymerization conditions for this type of polymerization. The general procedure is described in detail in the supplementary section.

3.2. Characterization of PLLA, PCL and p(LLA-b-CL)

The ROP of LLA and CL was confirmed by ^{1}H NMR spectroscopy,

where typical peaks for PLLA were found at 1.60 ppm and 5.19 ppm assigned to (-CH$_3$) and (-CH-) groups, respectively in all samples. The appearance of the terminal peak at 4.39 ppm was related to the methine end group (-CH$_3$**CH**OH). The ROP of CL was confirmed by the presence of the peak at 3.68 ppm assigned to the terminal methylene group -**CH$_2$**OH: note the very low intensity of the peak in the copolymer at 4.39 ppm (BN37) in Fig. 1, inset b), which will be further discussed below. The average molecular weight (M$_n$) was calculated by ^{1}H NMR spectroscopy. The M$_n$ of PLLA was obtained by the integration ratio of peaks that correspond to the repeating methine groups ($\delta = 5.19$ ppm) and the terminal aromatic group from BnOH ($\delta = 7.34$ ppm) [16]. The aromatic terminal group from BnOH initiation could be presented in both the PLLA homopolymer and the PLLA block in the copolymer, so it is possible to calculate the PLLA M$_n$ in both cases. The same process was applied to determine the M$_n$ of PCL. In this case, the signals were attributed to the repeating ε-methylene groups at $\delta = 4.08$ ppm and the terminal methylene group at $\delta = 3.67$ ppm [17]. The absence of peaks at 3.0 and 3.2 ppm which corresponded to the methylene and methyl groups for MSA and DBU, respectively, ensured that they were removed during the purification process.

The M$_n$ of PLLA ranged from 1736 g mol^{-1} at 80 °C to 2182 g mol^{-1} at 60 °C (Table 1). As mentioned before, LLA polymerized in a first step in the eutectic mixture of LLA/CL [17] (having a constant molar ratio of CL of 0.7). Thus, the polymerization temperatures and type of organocatalyst (DBU or DBN) did not strongly affect its molecular weight. It is important to mention that DBU and DBN belong to the amidine family. However, while DBU has been widely reported in the synthesis of PLLA [12], there is no information about DBN use as an organocatalyst for similar ROP of LLA as in this work. We propose using DBN in the ROP of the eutectic mixture LLA/CL to expand the polymerization temperatures for the first time. The DBN organocatalyst possesses selectivity for the LLA in the eutectic mixtures similarly to DBU but exhibits a higher operating temperature range. Thus, the ROP was possible above 79 °C (DBU degrades at 79 °C [8]). On the other hand, by increasing the temperature above 60 °C in the sequential ROP, i.e., just above the melting point of PCL, PCL formation takes place in unreacted CL and the molten polymer containing PLLA. Here, the viscosity of the medium decreased as compared with ROP at 37 °C, promoting the diffusion of CL available for the ROP, similarly to the ROP of trimethylene carbonate-based DESm [16]. Therefore, the M$_n$ of PCL in the resulting polyesters increased from 4013 at 37 °C to *ca.* 6988 g mol^{-1} at 92 °C, see Table 1.

The thermal properties of the synthesized polyesters were analyzed by DSC. Fig. 2 shows the corresponding thermograms, where two endothermic peaks were observed. The first one corresponds to the melting point of PCL identified from 58 to 60 °C (peak a), and the second small one corresponds to the melting point of PLLA identified from 94.2 to 116.7 °C (peak b) [17]. The samples' crystallinity was determined
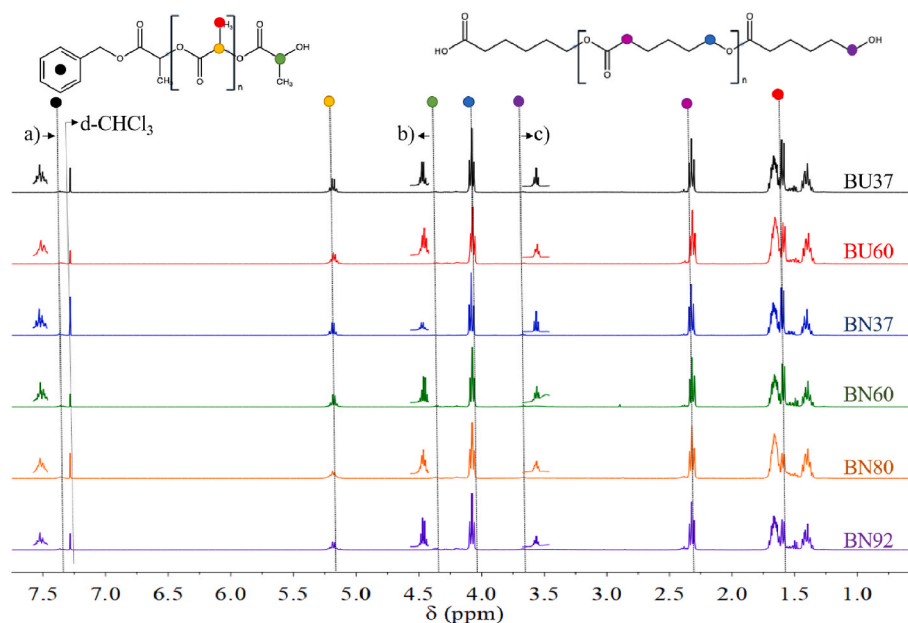

Scheme 1. Sequential Ring-Opening Polymerization of the DESm composed of LLA/CL (3:7 M ratio) at different temperatures. DBU and DBN organocatalyst were used for the selective ROP of LLA in the first step, and they were added together with the initiator BnOH (1:1, M ratio). MSA was used as a second organocatalyst to start the ROP of CL in the presence of the already formed PLLA.

Fig. 1. ^{1}H NMR spectra of synthesized polyesters: **BU37** (black), **BU60** (red), **BN37** (blue), **BN60** (green), **BN80** (orange), and **BN92** (purple). (Insets, zoom of the signals for a) $\delta = 7.34$ ppm and b) 4.39 ppm of PLLA, and c) $\delta = 3.68$ ppm of PCL). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Summary of the ROP of LLA/CL DESm. ROP temperature, experimental conversion, experimental PLLA/PCL M ratio, number-average molecular weight (M_n), melting point (T_m), crystallinity (X_c), and architecture of polyesters resulted from the ROP of DESm composed of LLA/CL (3:7 M ratio) at the indicated conditions.

Sample[a]	ROP Temp (°C)	Conv (%)[b]	PLLA/ PCL[c]	$M_{n,NMR\ PLLA}$[d] (g mol^{-1})	$M_{n,NMR\ PCL}$[d] (g mol^{-1})	$T_{m,PLLA}$[e] (°C)	$X_{c,PLLA}$[e] (%)	$T_{m,PCL}$[e] (°C)	$X_{c,PCL}$[e] (%)	Polymer architecture[f]
BU37	37	89	38 : 62	1964	4013	116.5	30	60	69	Blend
BU60	60	88	39 : 61	2182	5444	116.6	30	58	62	Blend
BN37	37	88	38 : 62	1835	4490	105.3	37	60	73	Copolymer
BN60	60	88	40 : 60	1867	5746	116.7	30	58	60	Blend
BN80	80	88	35 : 65	1736	5918	105.3	20	60	63	ND [g]
BN92	92	86	33 : 67	1962	6988	94.2	13	50	44	ND [g]

[a] Organocatalysts:initiator, DBU:BnOH:MSA or DBN:BnOH:MSA, used for the ROP of LLA. The molar ratio of catalyst (DBU or DBN): initiator (BnOH) was [1:1], respectively, and they represented 5 wt% with respect to the eutectic mixture. The weight of MSA was 3 wt% with respect to the eutectic mixture. The polymerization temperature was added to the second column.

[b] Experimental conversions obtained by gravimetry.

[c] Molar ratio.

[d] Number-average molecular weight obtained by ^{1}H NMR.

[e] Thermal properties calculated by DSC.

[f] Obtained by ^{1}H NMR diffusion-ordered spectroscopy.

[g] ND not determined.

considering the ratio of the melting enthalpy of each compound obtained by DSC (PLLA or PCL), with respect to the compound reference with 100% crystallinity (106 J g^{-1} for PLLA, and 135 J g^{-1} for PCL, more details in scheme S1) [24,25]. A closer analysis of the DSC traces reveals that, as the temperature of polymerization increases from 60 to 92 °C, using DBN as organocatalyst for LLA ROP, the T_m of PLLA decreased, as shown in Table 1. A possible scenario is that PLLA T_m decrease results from PLLA domains being in a glassy state when the ROP of CL started (the PLLA glass transition temperature is around 50 °C) [26]. At these temperatures, PLLA reorganization in a molten media could be restrained, as reported by Lv et al. during the annealing of PLLA/PCL blends, causing the reduction of their T_m and crystallinity [27].

On the other hand, it was reported that the rate of polymerization of racemic lactide in the absence of an initiator in CH$_2$Cl$_2$ or THF/CH$_2$Cl$_2$ at room temperature is lower with DBN than DBU [28]. Thus, it is possible that the lower polymerization rates (e.g., at 37 °C) enable PLLA chains to organize, improving their crystallinity, mainly in the solventless polymerization conditions like in this work. This effect was observed in

sample BN37 which showed a higher crystallinity (37%) than sample BU37 (30%) obtained under the same conditions. Han et al. reported that when the ratio of PLLA exceeded 0.57 in a P(LLA-b-CL) copolymer, the PLLA exhibited a melting point depression and an enhanced crystallinity [29]. These PLLA characteristics were observed in sample BN37, suggesting a copolymer formation. Conversely, the PCL exhibited a high crystallinity compared with PLLA in all cases regardless of the polymerization temperature. However, PCL in BU37 and BN37 samples presented the highest crystallinity with 69% and 73%, respectively. The high crystallinity of PCL at 37 °C resulted from the ROP carried out below its melting point, as discussed by Pérez-García et al. [17] The semicrystalline character of all polyesters was further demonstrated by X-ray diffraction showing the PCL and PLLA characteristic peaks (XRD; Fig. S1).

The PLLA/PCL ratio was determined by ^{1}H NMR spectroscopy by dividing the integral of the signal assigned to the repeating groups in the synthesized polyesters. In the case of PLLA, the methine group at $\delta = 5.19$ ppm was used, while for PCL, the ε-methylene group at $\delta = 3.67$
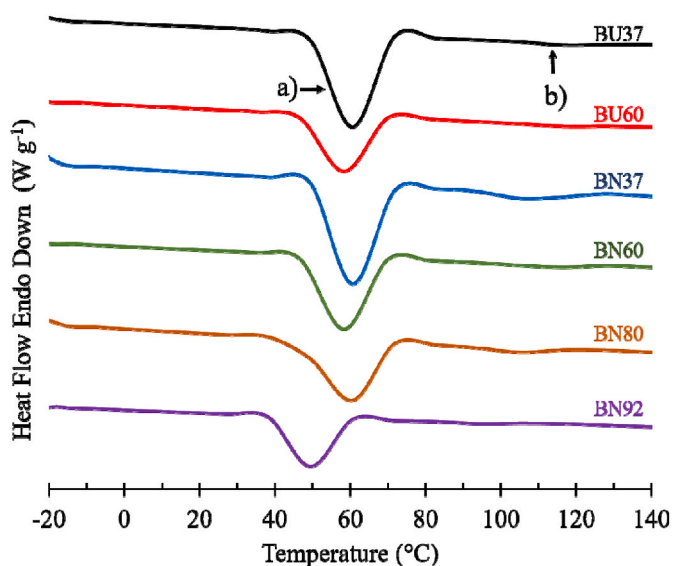
Fig. 2. DSC scans of **BU37** (black), **BU60** (red), **BN37** (blue), **BN60** (green), **BN80** (orange), and **BN92** (purple). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

ppm. The differences in the composition between the original ratio (3:7 LLA/CL) and the final PLLA/PCL ratios (Table 1) were associated with the loss of PCL oligomers during the washing process with ethanol, which also reflects the polydispersity of PCL likely due to CL diffusion constrained at high conversion in the second step of ROP, as the whole reaction mixture solidifies into polymers in the case of low temperatures, and the high viscosity of the medium even at higher temperatures. The purification of sample BU37 was followed by ^{1}H NMR, including the analysis of the washing ethanol solution (Fig. S2 in the ESI). Peaks found at 3.1–3.6 and 2.0–2.3 ppm in the sample before the purification step and in the ethanol solution, are associated to the organocatalyst and residual unreacted monomers. The additional peaks in the ethanol solution at 4.1, 3.7, 2.3 and 1.4–1.7 ppm were associated to the PCL oligomers, see Figs. S2–C.

To get deeper insights into the architecture of the final polyesters, selected samples were analyzed by ^{1}H NMR diffusion-ordered

spectroscopy (DOSY). Polyesters BU37 and BN37 were selected owing to their high crystallinity and thermal properties. Samples BU60 and BN60 were also included for comparison. DOSY spectrum of polyester BU37 (Fig. 3-A) shows two different diffusion coefficients (D_M), D_M BU37 = 9.17×10^{-9} m^2/s and $D_{M'}$ BU37 = 9.12×10^{-9} m^2/s, consistent with the M_n of PCL and PLLA, respectively, calculated in Table 1. The signals of each species were compared with the upper axis representing the corresponding ^{1}H NMR spectra. It is confirmed that the sample contains a blend of homopolymers, the higher diffusion coefficient corresponding to heavier species, which was associated with PCL. In contrast, the low diffusion coefficient corresponds to PLLA. These results corroborated that M_n of PCL was higher than PLLA as determined by ^{1}H NMR and in accord with previous MALDI-TOF results reported by our group [17].

In the case of sample BN37 (Fig. 3-B), only one diffusion coefficient was observed, D_M BN37 = 8.83×10^{-9} m^2/s, consistent with the presence of P(LLA-b-CL) copolymer, resulting from the sequential ROP of the DESm. The DOSY spectrum presented both signals in the upper axis associated with PLLA and PCL. These results revealed the successful formation of a block copolymer P(LLA-*b*-CL) from the ROP of LLA/CL DESm. As mentioned before, the polymerization rate of LLA using DBN is lower than DBU in solution [28]. In this scenario, it is possible that PLLA formed in the LLA/CL DESm presents available hydroxyl groups at the end chain, which then played the role of macroinitiator in the subsequent ROP of CL.

To determine the difference in the thermal stability of the polyesters after the purification step (all oligomers and organocatalyst, which are readily soluble in ethanol, were removed in this process, see Fig. S2 in the ESI), their thermal decomposition was measured by TGA. PLLA has been reported to have low thermal stability compared to PCL [30]. Sample BN37 composed of P(LLA-b-CL) copolymer showed higher thermal stability, e.g., at 307.1 °C the weight loss was about 5%, while for sample BU37 that contained a blend of PLLA and PCL, the 5% weight loss occurred at 212 °C. In the case of the polymer blend, the degradation of PLLA at 320.6 °C corresponded to ca. 23.7% of weight loss, which is close to the PLLA content in the blend as observed in Figs. S3–A in the ESI. In addition, a solubility test of both samples BN37 and BU37 was performed in toluene at RT. The insolubility of PLLA in toluene was greatly improved by the PCL counterpart presented in the copolymer as can be observed in Fig. S4 in the ESI, in which turbidity was lower compared to the sample containing the blend of homopolymers (BU37). Differences in transmittance were observed when measured with a
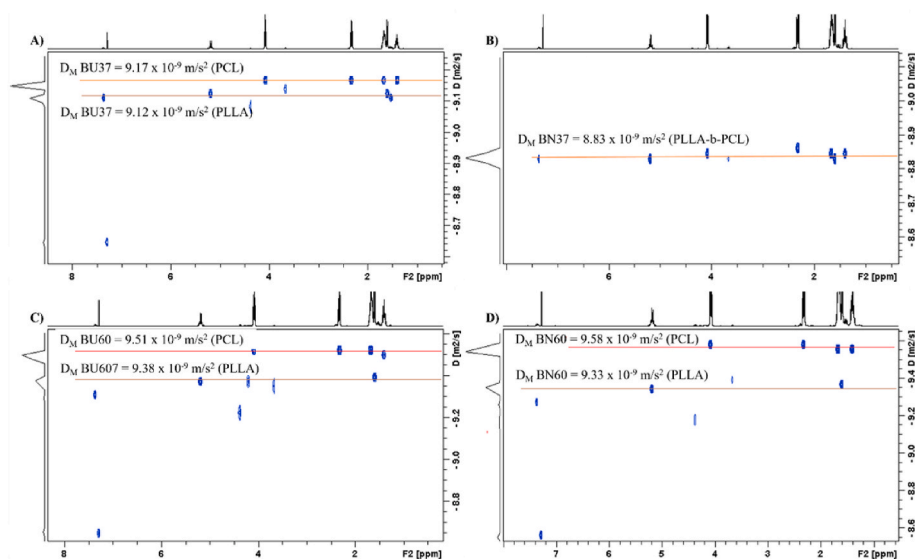

Fig. 3. DOSY spectra in deuterated chloroform of **A)** BU37 and **B)** BN37; the ROPs were carried out at 37 °C; **C)** BU60 and **D)** BN60 the ROP was carried out at 60 °C. The DOSY signals were associated with ^{1}H NMR spectra. The diffusion coefficient D_M (in m^2/s) is indicated for each component.
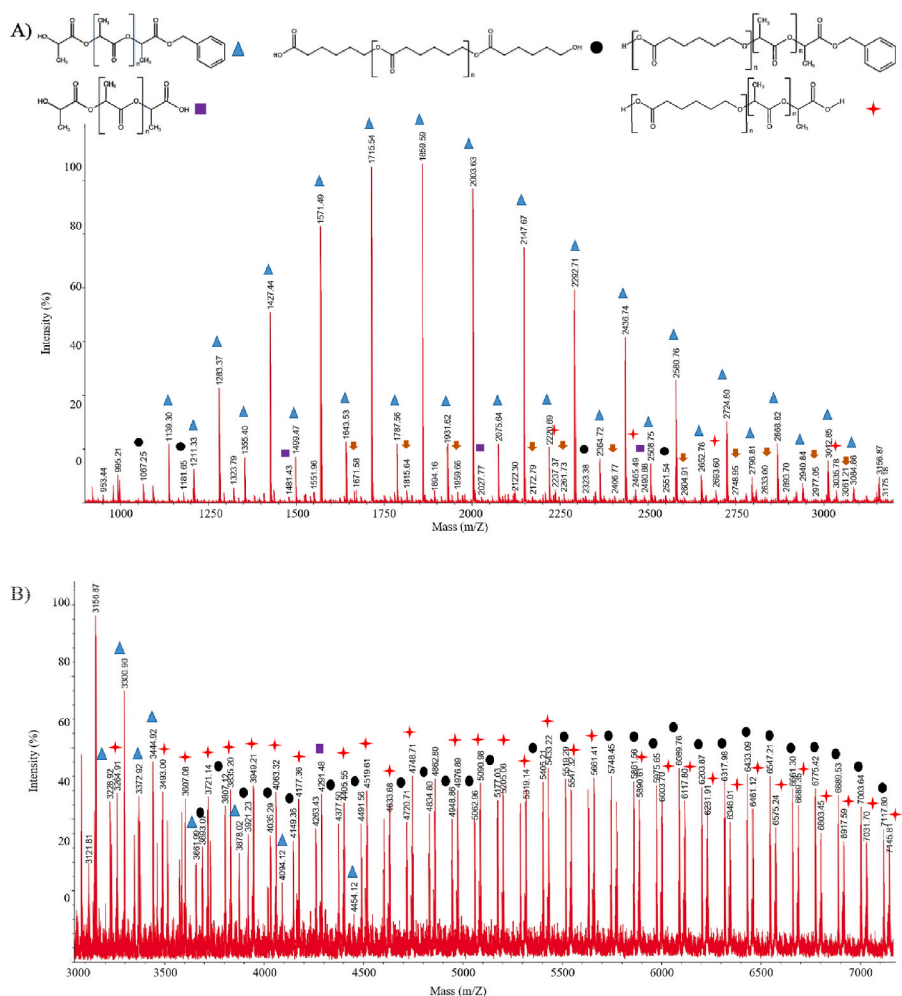
spectrometer in the range from 300 nm to 800 nm. The copolymer whose solution was less turbid showed a slight reduction in transmittance of about 20% in the whole range of the spectrum. Otherwise, turbidity was observed by the insolubility of PLLA in the blend solution, so the transmittance is reduced up to 80% in the same range. See Figs. S3–B in the ESI.

BN37 and BU37 were further analyzed by the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF MS) and two main distributions were observed in both samples between 1000 and 8000 m/z, see Figure S5-A and S5-B in the ESI, respectively. In BN37, the first population in the region between 1000 and 3000 m/z corresponded to the presence of PLLA with a separation of 72 units and initiated by BnOH. The most intense peaks were found at 1715–1900 m/z; this value matched the M_n determined by ^{1}H NMR spectroscopy. Some traces from another PLLA species were also found between 1481 and 2027 m/z, in which water played the role of initiator. In the region from 1600 to 3000 m/z the presence of a fraction of block copolymer was observed, constituted between 9 and 11 lactidyl units initiated by BnOH, followed by caproyl units between 12 and 20; the same species were also reported by Pérez-García et al. [17] (See Fig. S5 B in the supplementary section). Finally, in 2200–3000 m/z region, signals from PCL initiated by residual water, and a P(LLA-b-CL) block copolymer appeared, which will be explained in more detail below.

In the second distribution between 3000 and 8000 m/z, PCL homopolymers were found between 4000 and 6500 m/z, where the mass of 114 between adjacent peaks corresponded to CL repeating units, and residual water controlled the polymerization. See Fig. 4-B. From the second population, copolymers composed of PLLA and PCL were identified, corroborating previous results from ^{1}H NMR, DOSY, and thermal analyses. Lactidyl units initiated these copolymers, and water controlled the polymerization once the BnOH was consumed by LLA, followed by the ROP of CL monomers due to terminal hydroxyl groups in PLLA playing the role of macroinitiator. It is important to mention that the PLLA block in sample BN37 previously identified by ^{1}H NMR, M_n = 1835 g mol^{-1}, was calculated considering that BnOH initiated the ROP. From MALDI-TOF it was observed that there exist copolymers initiated by both residual water (red star in Fig. 4A) and BnOH (orange arrow in Fig. 4A). Thus, it is possible that the PLLA block determined by ^{1}H NMR corresponded to a PLLA homopolymer (ca. 1860 m/z, blue triangle in Fig. 4A).

Overall, the copolymers identified between 3500 and 6500 m/z were composed of a small fraction of LLA units followed by 18–46 CL units (Fig. 4-B). It is noteworthy that MALDI-TOF was able to identify homopolymers and copolymers in the sample, but not their ratio in the mixture. For example, in the first region that exhibited peaks associated with the presence of PLLA (Fig. S5), its relatively high intensity in the mixture was not consistent with the molar ratio of LLA which was lower than CL (3:7 M ratio LLA/CL, respectively), although it indicated that

Fig. 4. MALDI-TOF MS spectrum of BN37 A) from 1000 to 3000 m/z B) from 3000 to 7000 m/z.

PLLA ionized better than the PCL [31]. On the contrary, with the original large molar ratio of CL in the DES, it was expected that the PCL homopolymer and the P(LLA-b-CL) copolymer peaks would have relatively higher intensities, but this was not observed in the spectra, meaning that their ionization capacity was lower than for PLLA.

Thus, it is clear that the single diffusion signal observed in the DOSY (Fig. 3-B) can be ascribed mainly to the presence of copolymers in sample BN37 ultimately functioning as a compatibilizer of fractions of PCL and PLLA homopolymers, which gave rise to the enhanced thermal stability (Figs. S3–A) and also improved the toluene solvation capacity of the final products (Fig. S4). A further opportunity for future work will be to find the conditions to increase the PLLA content in the copolymer beyond the 3:7 M ratio of the eutectic composition of LLA/CL, respectively.

For the samples BU60 (Fig. 3-C) and BN60 (Fig. 3-D), no changes were observed by using either DBU or DBN organocatalysts in the ROP of the PLLA/PCL DESm at 60 °C; DOSY spectra for BU60 and BN60 resulted similarly. Their DOSY spectra were associated with the corresponding ^{1}H NMR spectra and two diffusion coefficients were observed for each sample, where both diffusion coefficients corresponded to a blend of homopolyesters (PCL/PLLA). BU60 exhibited the first diffusion coefficient D_M BU60 = 9.51×10^{-9} m^2/s and the second one $D_{M'}$ BU60 = 9.38×10^{-9} m^2/s, while BN60 showed the first diffusion coefficient D_M BN60 = 9.58×10^{-9} m^2/s and the second one $D_{M'}$ BN60 = 9.33×10^{-9} m^2/s. The higher diffusion coefficient corresponds to the PCL, whereas the lower diffusion coefficient corresponds to PLLA. These results are in line with ^{1}H NMR, as the M_n of PLLA was slightly higher in the ROP catalyzed by DBU (Table 1).

Thus, although the lower rate of LLA ROP at 37 °C in the case of DBN promoted the formation of a copolymer, increasing the temperature from 37 to 60 °C counteracted this effect possibly by increasing the polymerization rate leading to homopolymers blend at 60 °C irrespective of using DBN or BDU. Finally, size-exclusion chromatography (SEC) was performed on BU37, BU60, and BN37. SEC traces in samples BU37 and BU60 were similar due to the presence of homopolymers blend (PLLA/PCL). However, BN37 presented a different trace due to the copolymer presence P(LLA-*b*-CL) (Fig. S6).

3.3. Effect of benzyl alcohol (BnOH) as initiator on the molecular weight of PLLA

The average molecular weight of PCL in the ROP of the LLA/CL eutectic mixture was modified in the range of ca. 4000–7000 g mol^{-1} by the appropriate selection of catalysts (DBU/DBN and MSA) and the temperature of polymerization (Table 1). However, as previously noted, the ROP is a sequential reaction where LLA polymerizes first within minutes [17], and after the LLA monomer is depleted, it is not possible to increase the PLLA M_n despite raising the temperature of polymerization. Thus, lower concentrations of the initiator BnOH (2.0, 1.0, and 0.5 wt%, with respect to the monomers) were employed to increase the molecular weight of PLLA homopolymer, keeping the same conditions described before for the ROP catalyzed by DBU at 37 °C (Table 2).

The average molecular weight of PLLA increased from 1746 to 4048 mol g^{-1} as the initiator decreased from 2 wt% to 0.5 wt%, as expected, i. e., less initiator with a fixed concentration of monomer means more monomer available for the polymer chain growth. It was also observed a decrease of PLLA crystallinity from 34% to 29% as the average molecular weight increases (Table 2), pointing to unfavorable conditions to assemble larger chains into crystalline domains. Thus, the selectivity of the organocatalyst DBU for the ROP of LLA together with the different concentrations of BnOH effectively modified the molecular weight of PLLA. On the other hand, because the specific catalytic activity of MSA towards the ROP of CL and the role of water presented in the media as initiator in the second ROP, the molecular weight of PCL yielded similar values between 4477 and 4869 mol g^{-1}. The samples also were analyzed by SEC (Fig. S7). Interestingly, the trace of sample BU37-0i showed a narrower peak due to the close elution time of PLLA and PCL (Fig. S7 C), meaning similar molecular weight, which is consistent with the closer valuer of their M_n calculated from ^{1}H NMR, 4048 and 4869 mol g^{-1}, respectively. In contrast, samples BU37-1i and BU37-2i showed similar bimodal peaks (Fig. S7 A and B) as the PLLA/PCL blend in sample BU37 (Fig. S6). Based on these results, it is easy to envisage the design of block copolymers with the PLLA block of tunable length.

3.4. Effect of water

The content of residual water in the LLA/CL in the molar ratio of 3:7 is a parameter that modified the conversion, the degree of crystallinity, and the molecular weight in the polymerization. Pérez-García et al. reported that residual water in the LLA/CL DESm plays the role of initiator in the sequential ROP of CL, at 37 °C when the polymerization occurred in the presence of DBU and MSA organocatalysts and BnOH as initiator [17]. The ROP of CL is highly sensitive to water content. To study the role of water in the ROP of DESm of LLA and CL, the eutectic mixtures of LLA/CL were prepared, and 0.4 and 0.8 w% of water were added. Then, the ROP was carried out under the same conditions as mentioned before. The content of water in sample BU37, obtained by Karl Fisher titration, was 0.207 wt% in LLA/CL DES. As water content increased in the eutectic mixture, the M_n of PCL and the crystallinity of PLLA, both decreased. The rapid ROP of LLA with DBU initiated by BnOH occurred in ca. 1 min, as reported by Perez-García [17]. Residual water in the system served as initiator for remaining LLA monomer and mostly initiated the ROP of CL, aided by the second organocatalyst MSA, as MALDI TOF revealed that OH is found in some chain ends. However, the molecular weight of PCL was more significantly affected than PLLA, despite water can react acid-base with the DBU organocatalysts for the LLA ROP and promote the presence of acid species that can deactivate the polymerization and hydrolyze the polyesters [8,12]. Either of these possible scenarios was conducted to a reduction of the final conversion, mainly due to water serving as initiator of CL producing PCL with lower molecular weight oligomers that were lost during the purification process (see Table 3 and Fig. S2).

Thus, the water content in the DES plays a major role, and water above 0.2% is a critical threshold for achieving high conversions. These

Table 2

Properties of polyesters obtained by ROP of LLA/CL with different initiator (BnOH) concentration.

Sample	ROP Temp (°C)	Initiator Conc. (wt. %)	Conv (%)[b]	PLLA/PCL[c]	$M_{n,NMR\ PLLA}$[d] (g mol^{-1})	$M_{n,NMR\ PCL}$[d] (g mol^{-1})	$X_{c,PLLA}$[e] (°C)	$X_{c,PCL}$[e] (°C)
BU37-2i	37	2.0	89	41 : 59	1746	4477	34	68
BU37-1i	37	1.0	87	40 : 60	3372	4730	31	64
BU37-0i	37	0.5	88	39 : 61	4048	4869	29	66

BU37-2i, BU37-1i and BU37-0i correspond to the polyesters obtained by the ROP of LLA/CL eutectic mixture, 3:7 mol ratio, respectively. 2.92 wt% of DBU, varied concentrations of BnOH, 2.0, 1.0, and 0.5 wt%, and 3 wt% of MSA, all with respect to the eutectic mixture were used.

[b] Experimental conversions were obtained by gravimetry.

[c] Molar ratio.

[d] Number-average molecular weight were obtained by ^{1}H NMR.

[e] Thermal properties were calculated by DSC.

Table 3

Properties of polyesters obtained by ROP of LLA/CL and water.

Sample	ROP Temp (°C)	H₂O Conc. (%)	Conv (%)[b]	PLLA/PCL[c]	$M_{n,NMR\ PLLA}$[d] (g mol⁻¹)	$M_{n,NMR\ PCL}$[d] (g mol⁻¹)	$X_{c,PLLA}$[e] (°C)	$X_{c,PCL}$[e] (°C)
BU 37	37	0	89	38 : 62	1964	4013	30	69
BU37−4	37	0.4	85	36 : 64	1651	3433	19	62
BU37−8	37	0.8	81	33 : 67	1765	3171	14	67

BU37, BU37-4 and BU37-8 correspond to polyesters obtained by ROP of LLA/CL with 0, 0.4 and 0.8 wt% additional water, respectively.

[b] Experimental conversions obtained by gravimetry.

[c] Molar ratio.

[d] Number-average molecular weight obtained by ¹H NMR.

[e] Thermal properties calculated by DSC.

results provide new insights into the ROP of L-lactide/ε-caprolactone eutectic mixture that are relevant for synthetic conditions translatable to polymerization of HIPEs and preparation of hierarchical 3D scaffolds with programmable degradability [17,18]. These includes unsophisticated atmospheres and the presence of remained water from environmental conditions.

3.5. Effect of stereochemistry of lactide

Another parameter studied was the stereochemistry of lactide. In solution, secondary reactions typically occur during the ROP of LLA and cause loss of stereoregularity or tacticity in PLLA chains [6]. A powerful method to identify these changes is ¹H NMR, where the typical signal for methine repeating groups in the PLLA is found from 5.17 ppm to 5.20 ppm as a well-defined quadruplet [17]. The appearance of asymmetrically substituted methyl groups in the polymer chains modifies the quadruple signal into a multiplet [6]. Fig. S8 in the ESI shows the ¹H NMR spectra of samples in the region from 5.17 to 5.20 ppm, where the quadruplet signal is well defined in all samples (e.g., black arrow in BU37). To study the effect of the stereochemistry of the lactide in the DESm, D isomer of lactide (DLA) was incorporated into the LLA/CL eutectic mixture as a racemic mixture. The new eutectic mixtures contained both isomers of lactide. As a result, the signal of the methine repeating group in polylactide was a multiplet instead of a well-defined quadruplet, identified in Fig. S8, with red arrows. The final polyesters PLA/PCL, which contain polylactides (PLA) with disrupted stereoregularity, were atactic, completely amorphous, fragile, and presented a high rate of degradation. For instance, the samples crumble in less than 24 h, at 37 °C in phosphate-buffered saline PBS, pH = 7.4. Thus, the presence of D-lactide in a blend of PLLA/PCL prepared by the ROP of the eutectic mixture causes a reduction of the overall properties as reported to occur for traditional PLA synthesized in solution [3].

3.6. Degradability test

Overall, the remarkable green features implemented in the present work, excluding organic solvents and metallic catalysts in the synthesis of PLLA and PCL polyesters open the possibility to apply these biodegradable polymers in tissue engineering and biodegradable materials fields. From this perspective, polymers were subjected to degradation profile assays. The samples were incubated at 37 °C in phosphate-buffered saline (PBS, pH = 7.4) with orbital mixing (at 140 rpm for 14 days), then removed from the medium and rinsed with ethanol to remove any residue. Finally, samples were dried at room temperature. The final pH of the medium was measured, and the relative mass loss was calculated gravimetrically. It has been reported that the mass loss in polyesters is caused by the hydrolytic scission and surface erosion, which accelerates the hydrolysis by the autocatalytic effect of their acidic byproducts [32,33].

Fig. 5-A shows the mass loss profile degradation for the synthesized polyesters. The samples obtained above 60 °C, showed larger degradations, with mass losses between 7.5 and 11.1 wt% after 14 days. Conversely, when the ROP was carried out at 37 °C the mass loss was ca. 4 wt%. Furthermore, as degradation increased, the pH value of medium acidified with a pH value dropped to 5, as expected. The lower degradation profile caused the pH of the medium remaining close to neutral (ca. 6.4) (see Fig. 5-B). Samples BU37 and BN37 exhibited the highest crystallinity and, consequently, lower mass loss compared with the rest of the samples (Table 1, and Fig. 5-A). These results indicate that the high crystallinity restricted the diffusion of the medium inside the matrix of the samples endowing the samples with a lower hydrolysis rate [32,33]. For the samples, the surface degradation or erosion was assessed by the reduction of the diameter after the degradation test, as observed in sample BU37 (Fig. S9).

4. Conclusions

In summary, we demonstrated the successful synthesis of a series of PLLA and PCL polyesters in the form of blends (PLLA/PCL) and copolymer P(LLA-*b*-CL) through a sustainable and alternative route, excluding the use of volatile organic solvents by taking advantage of using a non-ionic DES monomer, and substituting metallic catalysts by organocatalysts such as DBU and MSA that are readily extracted from the final polymers. Furthermore, it was demonstrated for the first time the use of DBN as a suitable organocatalyst for the ROP of LLA/CL DESm, whose reaction rate enabled the formation of a block copolymer. These green features, e.g., solventless conditions and mild temperatures of polymerization, open the possibility of applying the LLA/CL DESm ROP for the synthesis of biomaterials with tunable mechanical properties, programmable biodegradability, and enhanced biocompatibility for tissue engineering and drug delivery purposes.
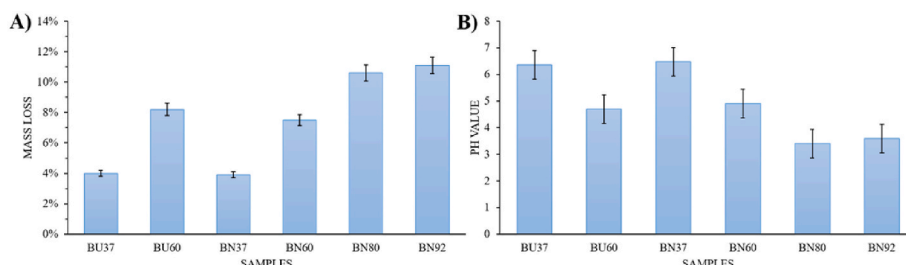
Fig. 5. A) Mass loss (wt.%) profile degradation of the samples after 14 days at 37 °C. B) pH values of final PBS solution (initial pH = 7.4).

CRediT authorship contribution statement

Martín Castillo-Santillan: Writing – original draft, Methodology, Investigation. **José Román Torres-Lubian:** Formal analysis, Validation. **Antonio Martínez-Richa:** Formal analysis, Validation. **Silvia T. Huerta-Marcial:** Formal analysis, Investigation, Writing – original draft. **María C. Gutierrez:** Formal analysis, Validation. **Katja Loos:** Validation, Resources. **María Guadalupe Peréz-García:** Conceptualization, Methodology, Validation, Formal analysis, Writing – review & editing. **Josué D. Mota-Morales:** Conceptualization, Resources, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2022.125432.

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