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Synthesis and characterization of poly (ε-caprolactam-co-lactide) polyesteramides using Brønsted acid or Brønsted base organocatalyst

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ABSTRACT

Polyesteramides (PEAs) are considered intriguing materials due to the combination of the favorable degradable capacity of aliphatic polyesters given by the hydrolizable ester groups and the desirable thermal and mechanical behavior of polyamides given by the amide groups. Between polyamides and polyester families, poly(ε-caprolactam) and poly(L-lactide) stand out due to their commercial value and outstanding properties. Nevertheless, to date these two monomers have not been co-polymerized due to their different reactivities. In this work, we report for the first time, up to our knowledge, the synthesis of poly(ε-caprolactam-*co*-L-lactide) copolymers with different compositions. Two different catalysts: (a) Brønsted acid ionic liquid 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate (BAIL) and (b) Brønsted base P_4-*t*-Bu have been explored. In the presence of Brønsted acid the L-lactide reactivity is higher than the ε-caprolactam while in the presence of Brønsted base the opposite behavior is observed. Using Kelen-Tudos method the monomer reactivity ratios are calculated and obtained as $r_{CLa} = 0.39$ and $r_{LA} = 1.6$ and $r_{CLa} = 2.2$ and $r_{LA} = 0.1$ using BAIL and P_4-*t*-Bu, respectively. These differences in the monomer reactivity ratios give us the possibility to create copolymers with different chain microstructure depending on the employed catalyst between 2 and 9 kDa. Thus, using P_4-*t*-Bu random copolymers can be obtained at high L-lactide concentration and blocky character copolymers at high ε-caprolactam concentration. Meanwhile, using BAIL catalyst random like copolymers are obtained at high ε-caprolactam contents and blocky character at high L-lactide contents.

1. Introduction

Polyesteramides (PEAs) are considered intriguing materials due to the combination of the favorable degradable capacity of aliphatic polyesters given by the hydrolizable ester groups (-COO-), and the stiffness and excellent thermal and mechanical behavior of polyamides given by the amide groups (-CONH-). This amide group is capable of forming strong molecular hydrogen bonding interactions providing excellent mechanical properties to the materials [1–3]. For this reason, over the past decades, great efforts

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have been made to design and synthesize enhanced PEAs that combine different polymer compositions, desirable and tunable properties, easily processing methods and low price.

Among polyamides, poly(ε-caprolactam) (PA6) is one of the most used polymers considering polyamides due to high strength, good fatigue resistance, moderate water absorption and good resistance to most common solvents and weak acids [4]. Its global production in 2015 was over 7 million tones, and can be found in diverse applications such as textiles, fibers, and construction materials industries [5]. Concerning polyesters, poly(L-lactide) (PLLA) attracts great attention because it can be derived from renewable natural sources such as cornstarch, and it presents high biodegradability and biocompatibility [6,7]. Furthermore, PLLA is superior to other aliphatic polyesters such as polycaprolactone (PCL) in terms of thermal and mechanical properties and transparency of the processed materials [7,8]. The limitations of PLLA are brittleness, low thermal stability and insufficient impact [9].

Some reports about organocatalytic synthesis of PEAs have been reported in the literature. The easiest and most studied method to produce polyesteramides (PEAs), is using melt polycondensation [2,10]. Dijkstra et al. reported the synthesis of PEAs from dimethyl adipate, butanediol, and diamidediols prepared from the reaction of butanediamine with caprolactone [11–13]. They found that the incorporation of well-defined amide segments in the polyester backbone resulted in improved thermal and mechanical properties. The main drawback of this polymerization strategy is that a small molecule is released during the polymerization and therefore this polymerization is not appropriate to carry out in-situ together with the polymer processing. This can be a problem because polyamides are usually difficult to process due to its poor solubility and to its high softening and melting temperatures caused by its high crystallinity [14–16]. Recently the ring opening polymerization (ROP) of ε-caprolactam and ε-caprolactone has been reported using organocatalysis and move us to study other polyesteramides [14].

ROP of ε-caprolactam and L-LA constituted the most employed method to obtain PA6 and PLLA respectively [17–19]. Both monomers are usually polymerized in bulk above monomer's melting temperature but below polymer's degradation temperature. Many metal catalysts have shown to be effective to prepare even PLLA or PA6, but organic catalysts necessarily have become an alternative [20–22]. For certain applications, such as biomedicine, food packaging and recycling, the presences of metal traces from the catalyst are highly undesirable and therefore organic compounds are preferred. The main challenge on the copolymerization of monomers with different functional groups is to find a suitable catalyst able to promote the ring opening polymerization of both monomers due to their different reaction mechanisms and molecular structure [15,17]. Strong Brønsted/Lewis bases such as phosphazenes or N-heterocylic carbenes (NHCs) and some Brønsted/Lewis acids such as methane sulfonic acid or 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ([$(CH_2)_4SO_3$HMIm] [HSO_4]) acid have shown to efficiently catalyze both the polymerization of lactams and cyclic esters [15].

In this work, we explore for the first time the ring opening preparation of poly(ε-caprolactam) (PA6) and poly(L-lactide) (PLLA) copolymers. Two different catalysts have been investigated, i.e. a Brønsted/Lewis acids 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ([$(CH_2)_4SO_3$HMIm] [HSO_4]) and a Strong Brønsted/Lewis base such as phosphazene base P_4-*t*-Bu solution to prepare P(CLa-*co*-LA) copolymers of different compositions. The Brønsted acidic ionic liquids (BAILs) was selected due to their effectiveness in polyesteramides preparation and its distinctive physicochemical properties such as low volatility and thermal and chemical stability [14]. Similarly, P_4-*t*-Bu catalyst has shown to be effective to promote the ROP of lactams and therefore was selected [20].

The prepared copolymers were analyzed by ^{1}H and ^{13}C nuclear magnetic resonance (NMR), transform infrared-attenuated total reflection (FTIR-ATR), size exclusion chromatography (SEC) and differential scanning calorimetry (DSC) analyses confirming the successful polymerization in the presence of both catalysts.

2. Experimental part

2.1. Materials and methods

ε-caprolactam (CLa) was purchased from SPOLANA A.S and dried using azeotropic distillation of toluene. L-lactide (LA) was obtained from Futerro (Belgium), and it was recrystallized twice from dried toluene prior to use. The Brønsted acid ionic liquid catalyst: 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ([$(CH_2)_4SO_3$HMIm] [HSO_4]) was purchased from Solvionic and used as received, while phosphazene base P_4-*t*-Bu solution (P_4-*t*-Bu) was purchased from Sigma-Aldrich. All other chemicals and solvents were also purchased from Aldrich and used as received.

^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded in a Bruker Avance DPX 300 at 300.16 MHz and at 75.5 MHz of resonance frequency respectively, using deuterated trifluoroacetic acid (CF3COOD) as solvent at room temperature. Experimental conditions were as follows: (a) for ^{1}H NMR spectroscopy: 10 mg of sample; 3 s acquisition time; 1 s delay time; 8.5 μs pulse; spectral width 5000 Hz and 32 scans; (b) for ^{13}C NMR spectroscopy: 40 mg; 3 s acquisition time; 4 s delay time; 5.5 μs pulse; spectral width 18,800 Hz and more than 10,000 scans. Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy was performed on Nicolet Magna 6700 spectrometer at a resolution of 2 cm^{-1}, and a total of 64 interferograms were signal averaged.

The molecular weights of the poly (ε-caprolactam) and poly (L-lactide) homopolymers as well as the poly (ε-caprolactam-*co*-lactide) copolymers were determined by a SEC analysis (Agilent PL-GPC 50) using Shodex GPC HFIP-803 (300 × 8.0 mm). 1,1,1,3,3,3-Hexafluoro-2-propanol (HFP) containing 10 mM of Sodium Trifluoroacetate ($C_2F_3NaO_2$) was used as the eluent, at 50 °C and a flow rate of 1 mL min^{-1} with polystyrene standards.

Differential scanning calorimetry (DSC) analyses of all polymers were carried out on a DSC Q2000 from TA Instruments, with a heating rate of 10 °C/min. Measurements were performed by placing the samples in sealed aluminum pans, using a heating ramp

from −50 to +250 °C under nitrogen atmosphere. Thermogravimetric analyses (TGA) were carried out using a Q500 Thermogravimetric Analyzer from TA Instruments. Samples were heated from room temperature to 600 °C at a rate of 10 °C/min under a constant N_2 flow.

2.2. Bulk homopolymerization ε-caprolactam and L-lactide

For the synthesis of poly (ε-caprolactam), 3 g of ε-caprolactam were mixed with 1 mol% of the catalyst a) Brønsted acid ionic liquid: 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ([$(CH_2)_4SO_3$HMIm] [HSO_4]) (0.08 g, 2.65 10^{-4} mol) and with 1 mol % of b) phosphazene base P_4-*t*-Bu solution (P_4-*t*-Bu) (0.16 g. $2.65 \cdot 10^{-4}$ mol) into a different vial with a magnetic stirrer. Both mixtures were prepared inside a glove box. Following the same procedure, 3 g of L-lactide were mixed with 1 mol% of Brønsted acid ionic liquid catalyst: 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ([$(CH_2)_4SO_3$HMIm] [HSO_4]) (BAIL) (0.06 g, $2.08 \cdot 10^{-4}$ mol) and 1 mol% of phosphazene base P_4-*t*-Bu solution (P_4-*t*-Bu) (0.13 g, 2.08 10^{-4} mol) into a different vial with a magnetic stirrer.

The sealed reaction vessels were placed into a pre-heated oil bath at 180 °C. The reactions were stopped by rapid cooling with liquid nitrogen. Poly (ε-caprolactam) was purified in THF during 48 h; poly (L-lactide) was dissolved in THF and precipitated in H_2O. All samples were dried under vacuum at 40 °C for 24 h.

2.3. Bulk copolymerization of ε-caprolactam and L-lactide

Copolymerization of ε-caprolactam (CLa) with L-lactide (LA) was carried out in bulk at 180 °C. A mixture of monomers containing different ε-caprolactam/L-lactide ratios: 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), were added respectively inside the glovebox. Then, the sealed reaction vessel was then removed from the glove box and submerged into a pre-heated oil bath at 180 °C. For all reactions, 1 mol% of the Brønsted acid ionic liquid and 1 mol% of phosphazene base P_4-*t*-Bu solution was used respectively (Fig. S1). The reaction was stopped by rapid cooling with liquid nitrogen. Then, the copolymers with high ratio in ε-caprolactam were purified by washing in THF, and the ones with high ratio in L-lactide were dissolved in THF and precipitated in H_2O. All copolymers were dried under vacuum before their characterization.

2.4. Monomer reactivity ratios determined by Kelen-Tudos method

In order to compare the effect of both catalysts on the behavior of the monomers in copolymerization, the monomer reactivity ratios were determined. For that the copolymerization experiments were terminated at less than 15% conversion [24]. The conversions were controlled and calculated by determining the ratio of the integrals of the proton signals of the (CH_2—C═O) repeating units in the polymer chain to the corresponding CLa monomer signal (3.00 and 3.15 ppm, respectively). For LA the conversions were calculated by the integrals of the proton signal of the (CH) repeating units in the polymer chain to the corresponding LA monomer signal (5.4 and 5.5 ppm, Fig. 1).

The monomer reactivity ratios for copolymerization of CLa and LA were determined from the monomer feed ratios and the copolymer composition. The apparent reactivity ratios of Cla and LA were calculated by Kelen-Tudos method using the Eq. (1).

$$\frac{x(y-1)}{ay+x^2} = \frac{(r_{\mathrm{CLa}} + \frac{r_{\mathrm{LA}}}{a})x^2}{ay+x^2} - \frac{r_{\mathrm{LA}}}{a}$$
$$x = \frac{M_{\mathrm{CLa}}}{M_{\mathrm{LA}}}\ (\mathrm{mol/mol})$$
$$y = \frac{dM_{\mathrm{CLa}}}{dM_{\mathrm{LA}}}\ (\mathrm{mol/mol}) \tag{1}$$

where x is the ratio of molar fractions, M_i, of monomers CLa LA in the monomer feed, y is the molar ratio of molar fractions, dM_i, of monomers CLa and LA in the copolymer and a is an equation parameter. This equation parameter can be computed according to Eq. (2):

$$a = \sqrt{\frac{x_{\min} x_{\max}}{y_{\min} y_{\max}}} \tag{2}$$

where $x_{\min}$ and $x_{\max}$ are the minimal and maximal molar fractions in the monomer feed, respectively, and $y_{\min}$ and $y_{\max}$ are the minimal and maximal molar fractions in the copolymer, respectively. Eq. (1) then transforms into the form:

$$\tau = \left(r_{\mathrm{CLa}} + \frac{r_{\mathrm{LA}}}{a}\right)\xi - \frac{r_{\mathrm{LA}}}{a}$$

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

The plot of τ versus ξ gives a straight line. Extrapolation of the line to $\xi = 1$ gives r_{Cla}, and to $\xi = 0$ gives r_{LA}/a (Fig. S2).

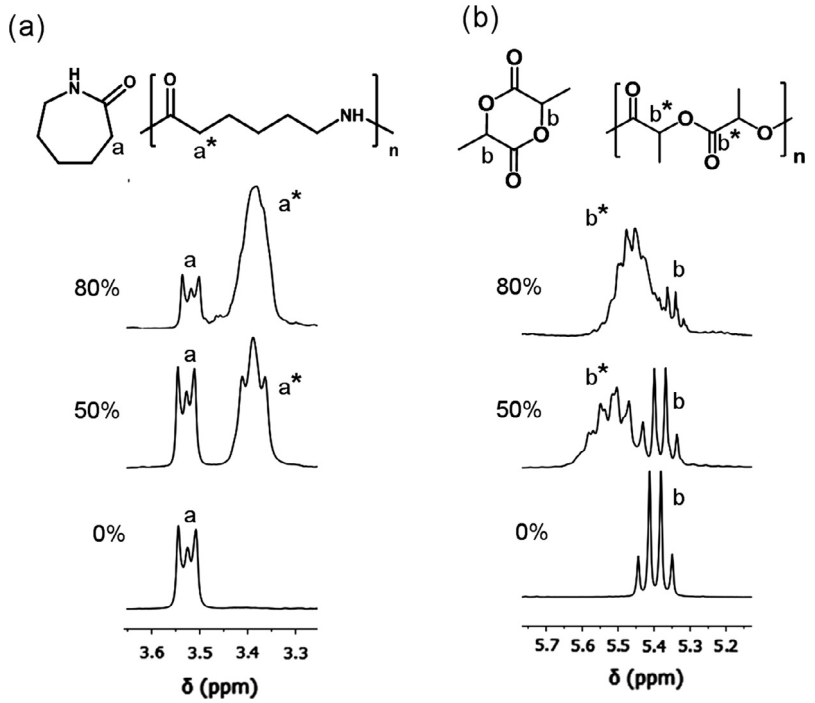


Fig. 1. ^{1}H NMR spectra region of areas integrated for the calculation of monomer conversions. (a) ε-caprolactam monomer and polymer and (b) L-lactide monomer and polymer.

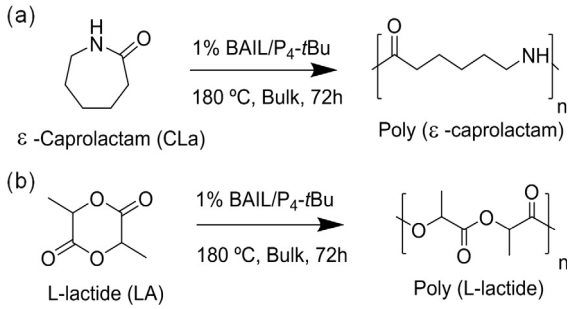
3. Results and discussion

3.1. Bulk homopolymerization of ε-caprolactam) and L-lactide in the presence of both catalysts

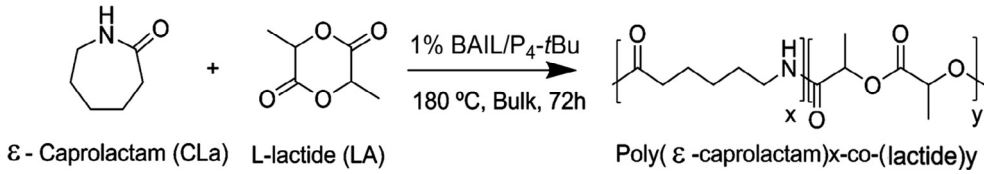
We first carried out a systematic investigation into the ROP homopolymerization of ε-caprolactam and L-lactide under bulk conditions in the presence of BAIL and P_4-*t*-Bu catalysts, to get a better understanding of which catalyst is the best suited for co-polymerization. In the second part, the preparation and characterization of copolymers of ε-caprolactam with L-lactide is discussed. Scheme 1 summarizes the polymerization conditions, 180 °C, 72 h and 1 mol% of catalyst in the hompolymerization of ε-caprolactam and L-lactide in the presence of Brønsted acid and base. We selected these polymerization conditions based on previous reports and trying to use the minimum amount of catalyst able to promote the polymerization [15,25] Scheme 2.

Polymerizations were monitored by ^{1}H NMR spectroscopy and the conversion was calculated by determining the ratio of the signals related to the monomer protons at 3.1 ppm (methylene) and 5.4 ppm (methine) from cyclic ε-caprolactam and L-lactide, and comparing them to the signal of the polymer protons at 3.4 ppm (methylene) and 5.5 ppm (methine) from poly(ε-caprolactam) and poly(L-lactide), respectively (Fig. 1).

We plotted the conversions calculated by ^{1}H NMR vs. time for both monomers in the presence of Brønsted acid (BAIL) and base (P_4-*t*-Bu) (Fig. 2a and b, respectively). We observed that both catalysts were able to promote the polymerization of both monomers. Moreover, important differences were observed in the polymerization kinetics. While the Brønsted acid was more effective to conduct the polymerization of L-lactide, in the presence of a phosphazene Brønsted base the opposite behavior was observed being the ε-caprolactam more reactive. Attending previous results obtained by Sanchez-Sanchez et al., the initiation of the polymerization of CLA



Scheme 1. Ring opening polymerization of (a) ε-Caprolactam and (b) L-lactide using BAIL or P_4-t-Bu (1 mol%) catalysts in bulk at 180 °C.



Scheme 2. Copolymerization of ε-Caprolactam and L-Lactide using BAIL and P_4-t-Bu (1 mol%) in bulk at 180 °C.

in the presence of BAIL came from the conjugate base of BAIL which is nucleophilic enough to initiate the polymerization slowly. As the ring opening of ester groups in the presence of a given nucleophile is favored respect to an amide, the polymerization of LA was much faster in the presence of BAIL because it was much easier to open LA than CLA [15]. On the other hand, P_4-*t*-Bu is a strong base which nucleophilicity is low due to its big size. Therefore, this base was stong enough to deprotonate the CLA and this could act as initiator, promoting the polymerization of CLA in a very efficient way [23]. In the case of LA, as P_4-*t*-Bu is a hindered base which nucleophilicity is low, this could not initiate the polymerization of LA by itself and therefore in the presence of P_4-*t*-Bu the polymerization of CLA is favored.

3.2. Copolymerization of ε-caprolactam and L- lactide

After studying the effectiveness of both catalysts in the polymerization of both monomers, where we found that phosphazene was more effective for ε-caprolactam while BAIL was more effective for L-Lactide, we explored which catalyst is better suited for copolymerization of CLa and LA. Thus, seven different copolymers were synthesized with varying the CLa/LA ratio using the previously described polymerization conditions (180 °C, 72 h and 1 mol% of catalysts). In order to obtain full conversion, the reactions were carried out for 72 h. Quantitative conversions were measured by ^{1}H NMR spectroscopy (Fig. 1). To further confirm the presence of polymers SEC analysis was performed. In all the cases, low molar masses between 2 and 4 kDa and rather low dispersities (*Đ*) between 1.3 and 1.5 were obtained (Table 1).

The copolymerizations were confirmed using ATR-FTIR and ^{1}H NMR spectroscopy for both catalysts. In Fig. 3 the ATR-FTIR of the samples with different ε-caprolactam/L-lactide compositions are represented as polymerized with BAIL. The presence of polylactide was confirmed by the strong band centered at 1720 cm^{-1} due to the carbonyl streching vibration of ester group. As the ratio of ε-caprolactam increased three new bands could be observed in the ATR-FTIR: two intense bands centered at 1650 and 1550 cm^{-1} assigned to the amide I and amide II bands respectively and one band centered at 3300 cm^{-1} assigned to the N-H. Similar results were obtained using P_4 -*t*-Bu catalyst (Fig. S4).

To further confirm the copolymerization ^{1}H NMR spectroscopy studies were carried out. Fig. 4 shows the ^{1}H NMR spectra of the copolymer containing 55 mol% of ε-caprolactam and 45 mol% of lactide. As expected in the copolymer we observed signals attributed to PLA at 5.4 and 1.4 ppm and signals attributed to ε-caprolactam at 3.4, 2.5, 1.5 and 1.2 ppm respectively confirming the presence of both polymers. Moreover, some extra signals were observed at 5.3 ppm, 3.5 and 2.6 ppm. In our opinion these signals could be assigned to sequences when lactide monomer unit is directly linked to ε-caprolactam monomer unit as observed in poly (lactide-co-caprolactone) copolymers [26].

To get a better understanding on the polymer microstructure and to evaluate the randomness character of the copolymers we analyzed the copolymer using ^{13}C NMR spectroscopy. In Fig. 5 the scale expanded region of the methyl group of the lactide in α position to the ester groups is shown.

In the presence of pure PLA, only one signal attributed to the methyl of the PLLA was presented. When the L-LA is copolymerized with ε-caprolactam a new signal together with previously mentioned signal of the PLA was observed. These two signals could be attributed to the presence of different dyads. Thus, the chemical shift of the methyl group would be influenced by the adjacent repeating unit. Therefore, these two signals could be assigned to LA-LA dyad (15.2 ppm) and LA-CLa (16.4 ppm) (the underlining was

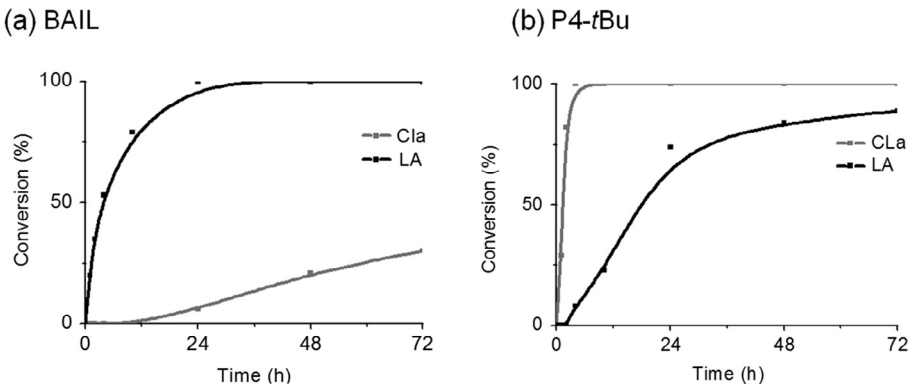


Fig. 2. Monomer conversions plot vs time of ε-caprolactam (CLa) and L-lactide (LA) monomers catalyzed by (a) BAIL and (b) P_4-t-Bu.

Table 1
Molecular and thermal characterizations of CLa/LA copolymers obtained either by BAIL or P_4-t-Bu catalysts.

Feed CLa/LA	BAIL				P_4-t-Bu			
	M_n[a] **(g/mol)	Đ[a]	T_m (°C)[b]	H_m (J/g)[b]	M_n[a] (g/mol)	Đ[a]	T_m (°C)[b]	H_m (J/g)[b]
100/0	3.5	1.4	193	93	60.1	1.5	222	98
95/5	2.1	1.2	160	79	1.8	1.5	188	92
90/10	1.8	1.4	–	–	3.0	1.4	162	86
80/20	1.8	1.7	–	–	2.3	1.6	–	–
50/50	2.0	1.2	–	–	3.8	1.4	–	–
20/80	2.5	1.3	–	–	2.8	1.3	–	–
10/90	2.5	1.5	–	–	3.6	1.4	–	–
5/95	9.9	1.6	–	–	2.4	1.3	–	–
0/100	17.8	1.3	115	52	3.9	1.2	115	53

[a] Determined by SEC analysis using a polystyrene standard calibration curve in HFP using 10 mM of $C_2F_3NaO_2$ as eluent, at 50 °C.
[b] Determined by differential scanning calorimetry (DSC).

used to denote that the analyzed nuclei belongs to that unit) [27]. Other C atoms also showed signal splitting which could be attributed to the copolymer sequences (Fig. S4).

Using the relative molar fraction of lactide (LA), and ε-caprolactam, (CLa) based on the relative integrated areas of the ^{13}C NMR spectra, randomness character value (R) of the polyesteramide copolymers was calculated using the following equation.

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

It should be mentioned that when R value tends to 0, the copolymer is considered blocky, when it trends to 1 random, and alternant when R tends to 2 [28]. In Table 1 the values of R for all copolymers synthesized using both catalysts are shown (see Table 2).

It is clear that the nature of the poly(CLa-*co*-LA) copolymers was different depending on the composition and the catalyst used. For instance, when BAIL catalyst was used, at high ratios of LA R tended to 0 meaning that the copolymers had a blocky character (in the literature, copolymers with these intermediate values are also called multiblock copolymers). Nevertheless, above 50% of CLa, R tended to 1 meaning that the copolymers had a more random structure. Thus, at high L-LA concentration, first all the L-LA was reacting forming a "pure" PLA polymer promoting the blocky nature of the copolymer. Nevertheless, at low L-LA concentration in spite of the higher reactivity of L-LA respect to CLa there were not enough LA monomer units to form blocky structure and the polymer tended to form more random microstructure. In the case of P_4-*t*-Bu catalyst the opposite behavior was observed. Thus, at high CLa contents the value of R tended to 0 meaning that the polymer was more blocky. Meanwhile at low CLa concentrations the R tended to 1 meaning that the polymer had a random microstructure. In order to confirm this fact, monomer reactivity ratios were calculated using the Kelen-Tudos method in the presence of both catalysts.

This value could give us an idea of the comonomer units along the copolymer chains, and randomness character of the copolymers as a function of the catalyst. Copolymerizations with different monomer feeds were targeted varying ε-caprolactam from 5 to 95 mol %. The molar fractions in the final copolymers were obtained by ^1H NMR spectroscopy. The copolymerizations were quenched at low overall monomer conversions (< 15%) in order to avoid the effects of compositional drift during the copolymerization [29].

When BAIL catalyst was used the reactivity ratios were calculated and obtained as $r_{CLa} = 0.39$ and $r_{LA} = 1.6$. Meanwhile, when

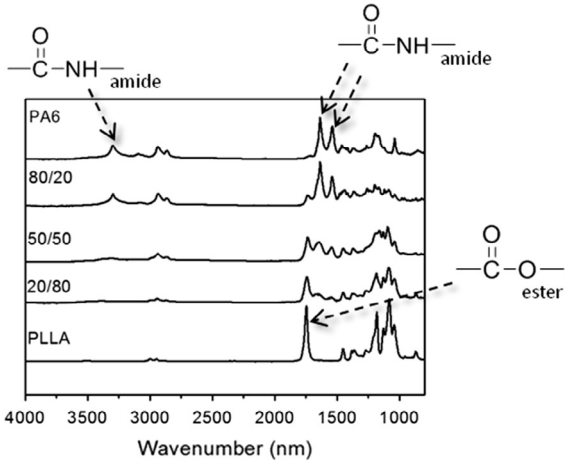


Fig. 3. FTIR spectroscopy of homopolymers and copolymers of different compositions synthesized with BAIL.

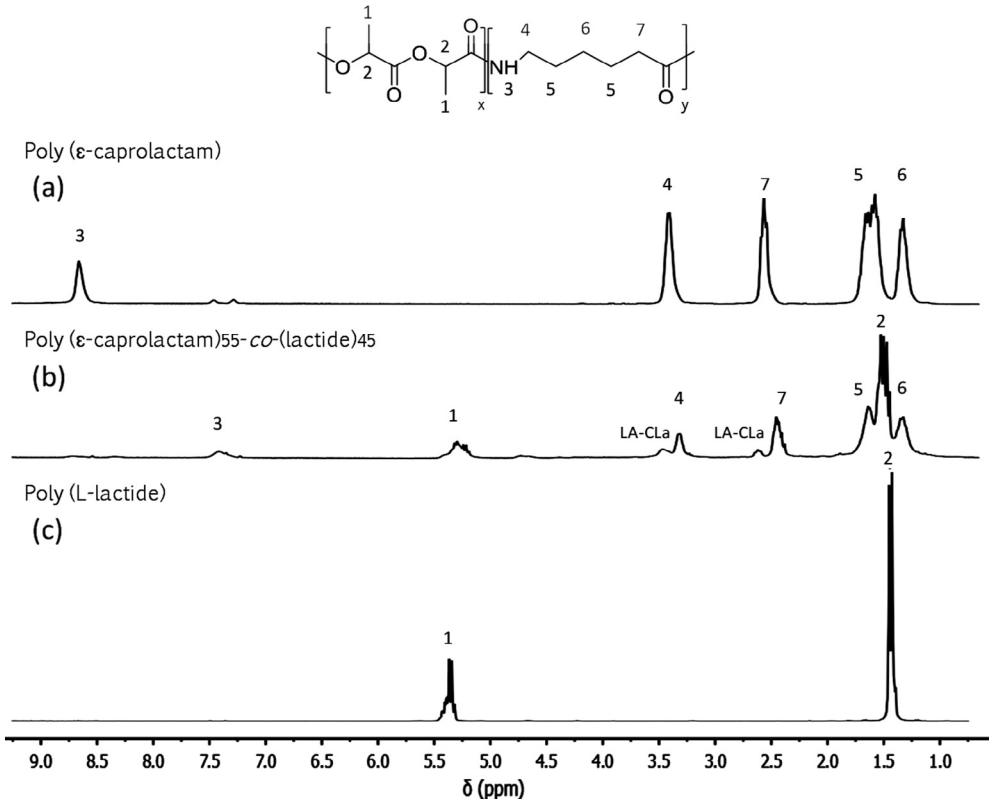


Fig. 4. ^{1}H NMR spectra of (a) poly (ε-caprolactam), (b) poly[(ε-caprolactam)$_{55}$-co-(lactide)$_{45}$] copolymer (using BAIL) and c) poly(L-lactide). The solvent used was d-TFA.

P_4-*t*-Bu was used the opposite trend was observed being much higher for ε-caprolactam than lactide r_{CLa} = 2.2 and r_{LA} = 0.1, respectively. As expected, when using BAIL catalyst the apparent reactivity for LA was three times higher than for CLa, meaning that the probability of LA entry into the chain was greater than that of CLa entry, which suggests a low randomness character especially when the L-LA co-monomer in the feed was greater than CLa. On the contrary, when P_4-*t*-Bu was used, CLa reactivity ratio is substantially higher than the one of LA, which confirmed that the polymer would have a block character especially when low LA was used confirming the values obtained by ^{13}C NMR spectroscopy.

3.3. Thermal properties of poly(ε-caprolactam-co-L-lactide) copolymers synthesized using different catalysts

Thermal properties of the poly(ε-caprolactam-*co*-LA) copolymers were determined by DSC analyses. Fig. 6 shows the DSC thermograms of different copolymers prepared from BAIL and P_4-*t*-Bu catalysts.

As can be observed in Fig. 6, when L-LA units were introduced in poly(ε-caprolactam) a significant decrease in both the melting temperature and enthalpy was observed for both catalysts being the decrease in the crystallinity more pronounced in the case of BAIL catalyst. Thus, with BAIL catalyst the melting temperature decreases from 193 to 160 °C and the enthalpy from 93 to 78 J/g with the incorporation of 5 mol% of lactide while in the case of P_4-*t*-Bu the value only decreases from 193 to 188 °C and the enthalpy from 98 to 92 J/g. The difference of the thermal properties as a function of the catalysts could be explained taking into account the different microstructures of both polymers. While in the case of P_4-*t*-Bu the co-polymer had a more blocky character and consequently the co-polymer had larger tendency to crystallize, using BAIL catalysts and low lactide concentration the co-polymers has a more random structure and found more difficulties to crystallize. Therefore, the copolymers in the presence of P_4-*t*-Bu were able to crystallize even at lactide concentration up to 10 mol%. Above this concentration the samples were not showing any melting temperature promote by the randomness of the co-polymers.

Surprisingly we did not observe any melting at low ε-caprolactam contents using BAIL catalyst in spite of the blocky character of the copolymers. This fact could be explained due to racemization of LA due to the employed harsh polymerization conditions which limited the crystallization ability of PLA segments.

4. Conclusions

In this work, the ability of two different organocatalysts a Brønsted/Lewis acid 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ([$(CH_2)_4SO_3$HMIm] [HSO_4]) (BAIL) and a Strong Brønsted/Lewis base such as phosphazene base (P_4-*t*-Bu solution) was used

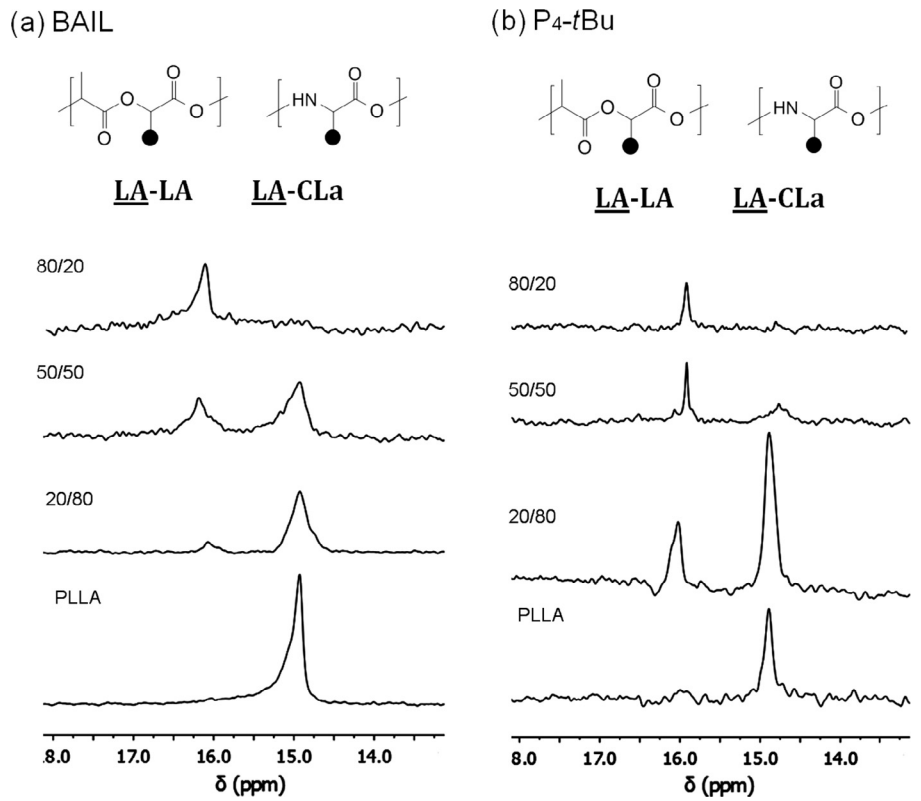


Fig. 5. Expansion of ^{13}C NMR spectra representing the copolymer dyads and the corresponding linkages between units. (a) represents results obtained for BAIL, and (b) for P_4-t-Bu.

to promote for the first time the copolymerization of L-lactide and ε-caprolactam; obtaining polyesteramides with different compositions. The co-polymerization is confirmed by NMR spectroscopy, ATR-FTIR and SEC analyses. Our findings suggest that Brønsted/Lewis acid promotes better the polymerization of L-lactide rather than ε-caprolactam. Meanwhile, the Brønsted/Lewis base is more effective catalyst to promote the polymerization kinetics of ε-caprolactam than L-lactide. This is confirmed by determining the apparent reactivity ratios as $r_{CLa} = 0.39$ and $r_{LA} = 1.6$ and $r_{CLa} = 2.2$ and $r_{LA} = 0.1$ for BAIL and P_4-*t*-Bu, respectively. The different monomer reactivity ratios as a function of the catalyst allow us to select the most convenient catalyst to synthetize copolymers with different compositions and microstructures. Thus at high ε-caprolactam contents using P_4-*t*-Bu catalyst the microstructure tends to be more blocky and permits the formation of a semi-crystalline polymer, while using BAIL catalyst as the microstructure tends to be more random the polymers are less crystalline. This difference in reactivity as a function of the organocatalyst type can be further exploited to promote the preparation of co-polymers of different natures and with different microstructures.

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Table 2
Randomness character value (R) results for the polyesteramide copolymers obtained from either BAIL and P_4-t-Bu catalysts.

Feed ratioCLa/LA	*R* (BAIL)[a]	*R* (P_4-*t*-Bu)[a]
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

[a] Determined by ^{13}C NMR spectroscopy in d-TFA.

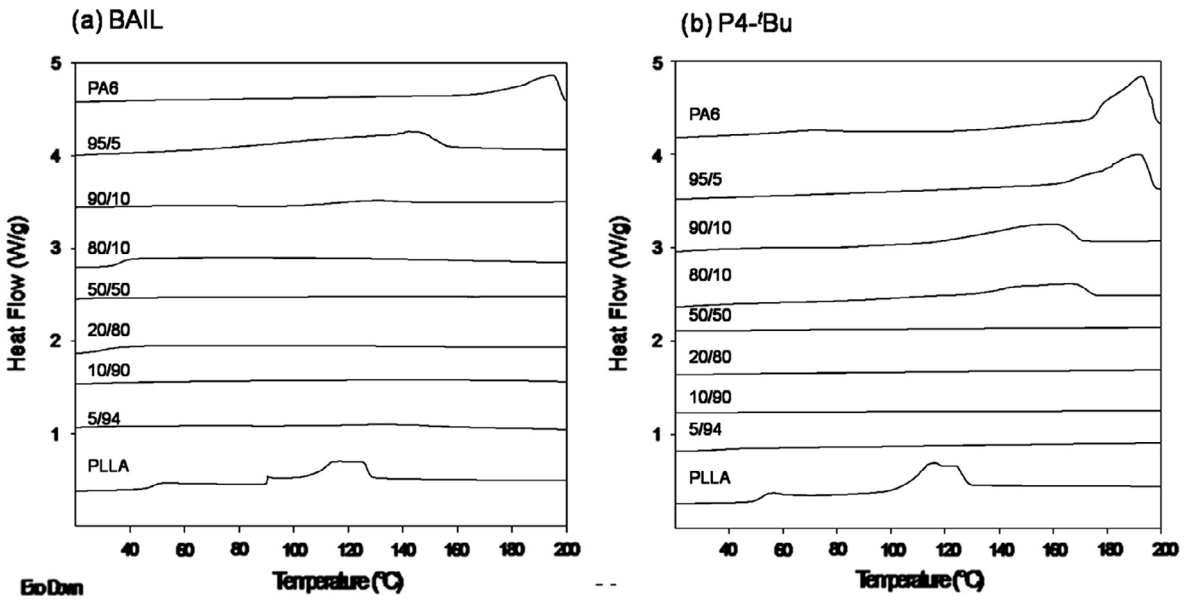

Fig. 6. DSC heating curves of the different copolymers synthetized with (a) BAIL and (b) P_4-t-Bu.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.eurpolymj.2017.05.023.

References

[1] M. Winnacker, B. Rieger, Poly(ester amide)s: recent insights into synthesis, stability and biomedical applications, Polym. Chem. 7 (2016) 7039–7046, http://dx.doi.org/10.1039/C6PY01783E.
[2] G.P. Felton (Ed.), Biodegradable Polymers: Processing, Degradation, and Applications, Nova Science Publishers, Hauppauge, N.Y, 2011.
[3] J. Rydz, W. Sikorska, M. Kyulavska, D. Christova, Polyester-based (Bio)degradable polymers as environmentally friendly materials for sustainable development, Int. J. Mol. Sci. 16 (2014) 564–596, http://dx.doi.org/10.3390/ijms16010564.
[4] R.A. Kudva, H. Keskkula, D.R. Paul, Properties of compatibilized nylon 6/ABS blends: Part I. Effect of ABS type, Polymer 41 (2000) 225–237, http://dx.doi.org/10.1016/S0032-3861(99)00105-6.
[5] H.-G. Elias, Macromolecules: Volume 2: Industrial Polymers and Syntheses. Wiley-VCH Verlag GmbH, D-69451 Weinheim, Germany, 2006. doi: http://dx.doi.org/10.1002/9783527627226.
[6] K. Masutani, Y. Kimura, Chapter 1. PLA Synthesis. From the Monomer to the Polymer, in: A. Jiménez, M. Peltzer, R. Ruseckaite (Eds.), RSC Polym. Chem. Ser., Cambridge: Royal Society of Chemistry; 2014, p. 1–36. doi: http://dx.doi.org/10.1039/9781782624806-00001.
[7] J.L. Robert, K.B. Aubrecht, Ring-opening polymerization of lactide to form a biodegradable polymer, J. Chem. Educ. 85 (2008) 258, http://dx.doi.org/10.1021/ed085p258.
[8] A. Jiménez, M. Peltzer, R. Ruseckaite (Eds.), Poly(lactic acid) Science and Technology. Royal Society of Chemistry, Cambridge, 2014, doi: http://dx.doi.org/10.1039/9781782624806.
[9] S. Pivsa-Art, N. Phansroy, W. Thodsaratpiyakul, C. Sukkaew, W. Pivsa-Art, S. Lintong, et al., Preparation of biodegradable polymer copolyesteramides from L-lactic acid oligomers and polyamide monomers, Energy Procedia 56 (2014) 648–658, http://dx.doi.org/10.1016/j.egypro.2014.07.204.
[10] A. Díaz, R. Katsarava, J. Puiggalí, Synthesis, properties and applications of biodegradable polymers derived from diols and dicarboxylic acids: from polyesters to poly(ester amide)s, Int. J. Mol. Sci. 15 (2014) 7064–7123, http://dx.doi.org/10.3390/ijms15057064.
[11] P.A.M. Lips, R. Broos, M.J.M. van Heeringen, P.J. Dijkstra, J. Feijen, Synthesis and characterization of poly(ester amide)s containing crystallizable amide segments, Polymer 46 (2005) 7823–7833, http://dx.doi.org/10.1016/j.polymer.2005.07.013.
[12] H.R. Stapert, A.-M. Bouwens, P.J. Dijkstra, J. Feijen, Environmentally degradable aliphatic poly(ester-amide)s based on short, symmetrical and uniform bisamide-diol blocks, 1. Synthesis and interchange reactions. Macromol, Chem. Phys. 200 (1999) 1921–1929, http://dx.doi.org/10.1002/(SICI)1521-3935(19990801)200:8<1921::AID-MACP1921>3.0.CO;2-R.
[13] H.R. Stapert, P.J. Dijkstra, J. Feijen, Synthesis and characterization of aliphatic poly(esteramide)s containing symmetrical bisamide blocks, Macromol. Symp. 130 (1998) 91–102, http://dx.doi.org/10.1002/masy.19981300109.
[14] K. Hashimoto, Ring-opening polymerization of lactams. Living anionic polymerization and its applications, Prog. Polym. Sci. 25 (2000) 1411–1462, http://dx.doi.org/10.1016/S0079-6700(00)00018-6.
[15] A. Sanchez-Sanchez, A. Basterretxea, D. Mantione, A. Etxeberria, C. Elizetxea, A. de la Calle, et al., Organic-acid mediated bulk polymerization of ε-caprolactam and its copolymerization with ε-caprolactone, J. Polym. Sci. Part Polym. Chem. 54 (2016) 2394–2402, http://dx.doi.org/10.1002/pola.28114.
[16] D. Tunc, C. Le Coz, M. Alexandre, P. Desbois, P. Lecomte, S. Carlotti, Reversible cross-linking of aliphatic polyamides bearing thermo- and photoresponsive cinnamoyl moieties, Macromolecules 47 (2014) 8247–8254, http://dx.doi.org/10.1021/ma502083p.
[17] D. Bourissou, B. Martin-Vaca, A. Dumitrescu, M. Graullier, F. Lacombe, Controlled cationic polymerization of lactide, Macromolecules 38 (2005) 9993–9998, http://dx.doi.org/10.1021/ma051646k.
[18] N. Susperregui, D. Delcroix, B. Martin-Vaca, D. Bourissou, L. Maron, Ring-opening polymerization of ε-caprolactone catalyzed by sulfonic acids: computational evidence for bifunctional activation, J. Org. Chem. 75 (2010) 6581–6587, http://dx.doi.org/10.1021/jo101346t.
[19] K. Udipi, R.S. Davé, R.L. Kruse, L.R. Stebbins, Polyamides from lactams via anionic ring-opening polymerization: 1. Chemistry and some recent findings, Polymer

38 (1997) 927–938, http://dx.doi.org/10.1016/S0032-3861(96)00566-6.
[20] A.P. Dove, Organic catalysis for ring-opening polymerization, ACS Macro Lett. 1 (2012) 1409–1412, http://dx.doi.org/10.1021/mz3005956.
[21] H. Yang, J. Zhao, M. Yan, S. Pispas, G. Zhang, Nylon 3 synthesized by ring opening polymerization with a metal-free catalyst, Polym. Chem. 2 (2011) 2888, http://dx.doi.org/10.1039/c1py00334h.
[22] S. Naumann, S. Epple, C. Bonten, M.R. Buchmeiser, Polymerization of ε-caprolactam by latent precatalysts based on protected N-heterocyclic carbenes, ACS Macro Lett. 2 (2013) 609–612, http://dx.doi.org/10.1021/mz400199y.
[23] W. Memeger, G.C. Campbell, F. Davidson, Poly(aminophosphazene)s and Protophosphatranes Mimic Classical Strong Anionic Base Catalysts in the Anionic Ring-Opening Polymerization of Lactams, Macromolecules 29 (1996) 6475–6480, http://dx.doi.org/10.1021/ma960659i.
[24] C. Hou, L. Ying, C. Wang, Determination of monomer apparent reactivity ratios for acrylonitrile-acrylamide copolymerization system, J. Mater. Sci. 40 (2005) 609–612, http://dx.doi.org/10.1007/s10853-005-6297-6.
[25] W.N. Ottou, H. Sardon, D. Mecerreyes, J. Vignolle, D. Taton, Update and challenges in organo-mediated polymerization reactions, Prog. Polym. Sci. 56 (2016) 64–115, http://dx.doi.org/10.1016/j.progpolymsci.2015.12.001.
[26] J. Fernández, A. Etxeberria, J.-R. Sarasua, Synthesis, structure and properties of poly(L-lactide-co–caprolactone) statistical copolymers, J. Mech. Behav. Biomed. Mater. 9 (2012) 100–112, http://dx.doi.org/10.1016/j.jmbbm.2012.01.003.
[27] D. Newman, E. Laredo, A. Bello, P. Dubois, Combined effect of humidity and composition on the molecular mobilities of poly(ε-caprolactone- *ran* -ε-caprolactam) copolymers, Macromolecules 47 (2014) 2471–2478, http://dx.doi.org/10.1021/ma500260e.
[28] J. Fernández, A. Etxeberria, J.R. Sarasua, In vitro degradation of poly(lactide/δ-valerolactone) copolymers, Polym. Degrad. Stab. 112 (2015) 104–116, http://dx.doi.org/10.1016/j.polymdegradstab.2014.12.019.
[29] G.G. Hedir, C.A. Bell, R.K. O'Reilly, A.P. Dove, Functional degradable polymers by radical ring-opening copolymerization of MDO and vinyl bromobutanoate: synthesis. Degradability and Post-Polymerization Modification, Biomacromolecules 16 (2015) 2049–2058, http://dx.doi.org/10.1021/acs.biomac.5b00476.