Organic-acid mediated bulk polymerization of ε-Caprolactam and its Copolymerization with ε-Caprolactone

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ABSTRACT

Polyamides (PA) constitute one of the most important classes of polymeric materials and have gained strong position in different areas, such as: textiles, fibers and construction materials. Whereas most polyamides are synthesized by step-growth polycondensation, polyamide 6 is synthesized by ring opening polymerization (ROP) of ε-caprolactam. The most popular ROP methods involve the use of alkaline metal catalyst difficult to handle at large scale. In this article, we propose the use of organic acids for the ROP of ε-caprolactam in bulk at 180 °C (below the polymer's melting point). Among evaluated organic acids, sulfonic acids were found to be the most effective for the polymerization of ε-caprolactam, being the Brønsted acid ionic liquid: 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate the most suitable due to its higher thermal stability. End-group analysis by ^{1}H nuclear magnetic resonance (NMR) and model reactions provided mechanistic insights and suggested that the catalytic activity of sulfonic acids was a function of not only the acid strength, but of the nucleophilic character of conjugate base as well. Finally, the ability of sulfonic acid to promote the copolymerization of ε-caprolactam and ε-caprolactone is demonstrated. As a result, poly(ε-caprolactam-*co*-ε-caprolactone) copolymers with considerably randomness are obtained. This benign route allows the synthesis of poly(ester amide)s with different thermal and mechanical properties.

KEYWORDS: polyamides; sulfonic acids; poly(ester amide)s; organocatalysis; ring-opening polymerization (ROP), biodegradable polymers

INTRODUCTION

Polyamides (PAs) represent a versatile group of plastics that have been successful for 70 years in the field of engineering, textiles, transport and fibers because of its good combination of thermal and mechanical properties.[1,2] Among different polyamides, poly(ε-caprolactam) (P(CLa)), commercially named nylon6 or PA6 has attained interest due to its high strength, good fatigue resistance, moderate water absorption (about 8-10 %), and good resistance to most common solvents and weak acids.[3-5] Besides those attractive properties, PA6 is difficult to process due to its poor solubility and to its high softening and melting temperatures caused by its high crystallinity.[6-9] The ring opening polymerization (ROP) of ε-caprolactam constituted the most employed method to obtain PA6 (P(CLa)). PA6 is mostly prepared above monomer´s melting temperature but below polymer´s melting temperature. This

reaction can be carried out in-situ together with the polymer processing. First, melted monomers are blended with the catalyst. After, the mixture is poured into a heated mold where the polymerization occurs. Indeed, the polymerization and the filling of the mold occur in a single step. This in-situ polymerization process is the base for the technology, named reaction injection molding. This is widely used industrially due to the advantages related to time processing and the possibilities for preparing (nano)composite materials.

Nowadays, the most studied and industrially relevant route for the ROP of ε-caprolactam is the anionic polymerization.[10-12] The anionic route is the fastest process and therefore has concentrated most of the scientific efforts. Strong bases such as alkali/alkaline metals, hydrides or Grignard reagents have been mostly used to initiate the ROP of ε-caprolactam.[10] Nevertheless, handling of these compounds can be difficult and in certain applications such as biomedicine, food packaging and recycling, the presence of metal traces from the catalyst are highly undesirable.[13-15] An alternative option to overcome the limitation of metal and Grignard reagents can be the use of more benign catalysts such as organic compounds. [16,17] In fact, the removal of the transition metal catalysts from the polymer is often extremely difficult.[10, 18-19]

Many studies have shown the effectiveness of organic catalysts to promote ROP of lactones such as: valerolactone, caprolactone[20,21] or more recently ethylene brassylate[22,23] and cyclic carbonates to synthesize well-defined polymers. However, there have been only a few studies utilizing organic catalysts in ring opening polymerization (ROP) of lactams.[24,25] Some years ago, the polymerization of ε-caprolactam at temperatures < 200 °C, below T_m of PA6, was reported by the use of strong organic base catalysts such as poly(aminophosphazenes) and protophosphatranes[12]. More recently, the ring opening polymerization of ε-caprolactam and laurolactam was investigated using N-heterocylic carbenes (NHCs) as organocatalysts at 180 °C by Buchmeiser and coworkers.[26] It is worth to remark that in those two examples of organocatalysis strong bases were used and the polymerization mechanism was pseudo- or anionic type.

In this work we explore for the first time the organocatalyzed ring opening polymerization of ε-caprolactam using several organic acids. Back in the 70s it was reported that inorganic acids (such as H_3PO_4 and HCl) were able to promote the cationic polymerization of ε-caprolactam using really high temperatures (> 250 °C, above T_m of PA6). We report the ring opening polymerization of ε-caprolactam using different organic acids as catalyst in bulk at 180 °C. This temperature is below the polymer's melting point (~ 215 °C) and it is the most-popular reaction temperature used for anionic ring-opening polymerization of ε-caprolactam.

Furthermore, we report for the first time the organocatalyzed copolymerization of ε-caprolactam amide monomer with its lactone analogue (ε-caprolactone), to obtain biodegradable poly(ester amide)s (PEAs) which are known for its interesting thermal and mechanical properties as well as biodegradability.

EXPERIMENTAL

Materials

ε-caprolactam (ε-CLa) was purchased from SPOLANA a.s. ε-caprolactone (ε-CLo, 97%) was obtained from Aldrich. The catalysts triflic acid, methyl triflate, trifluoroacetic acid (TFA), acetic acid, bis(trifluoromethane)sulfonimide (TFMI), methane sulfonic acid (MSA), diphenyl phosphate (DPP) and p-toluenesulfonic acid (PTSA) were purchased from Aldrich and were dried under vacuum for 24 hours. The Brønsted acid ionic liquid: 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ($[(CH_2)_4SO_3HMIm]$ $[HSO_4]$) was purchased from Solvionic and used as received. All other

chemicals and solvents were also purchased from Aldrich and used as received.

Instrumentation and Measurements

^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded at room temperature on Bruker spectrometers operating at 300, 400 MHz or 500 MHz, using deuterated trifluoroacetic acid (CF_3COOD) or trifluoroacetic acid as solvent.

The molecular weights of the poly (ε-caprolactam) samples were determined by solution viscometry with the Mark–Houwink equation:

$$[\eta]=KM_{\eta}^{\alpha} \qquad (1)$$

where constants K and α are equal to 22.6 $x10^{-3}$ cm^3/g and 0.82, respectively, in this solution system.[27] An intrinsic A Ubbelohde viscometer, with a capillary diameter of 0.53 mm, was used to measure the viscosity of the solutions at 25 °C. Samples were dissolved in 85% formic acid for the preparation of solutions with concentrations of 0.015 g/mL.

Differential scanning calorimetry (DSC) analysis of poly (ε-caprolactam), poly (ε-caprolactone) and poly (ε-caprolactam-*co*-ε-caprolactone) copolymers 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 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.

Model reactions studies

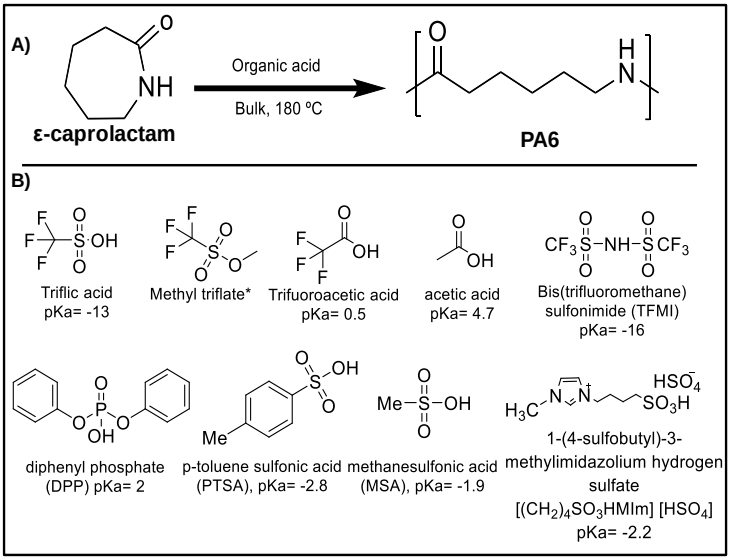
To a mixture of 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate (0.25 g, 2.20 mmol), the monomer ε-caprolactam (0.696 g, 2.20 mmol) was added. The mixture was stirred at 180 °C for 24 h. The reaction was stopped by rapid cooling with liquid nitrogen. After cooling to room temperature, the mixture was diluted with trifluoroacetic acid (CF_3COOH) and filtered for characterization of crude reaction. The resulting compound was characterized by ^{1}H NMR, ^{13}C NMR and ^{1}H diffusion-ordered spectroscopy (DOSY). In the DOSY spectra the horizontal axis (F2) encodes the chemical shift of the ^{1}H nucleus observed. The vertical dimension, encodes the diffusion constant D (F1).

Bulk polymerization of ε-caprolactam

Inside a glove box, 3 g of ε-caprolactam were mixed with the desired amount of different catalyst (63-830 mg) and put into a vial with a magnetic stirrer. The sealed reaction vessel was placed into a pre-heated oil bath at 160 °C, 180 °C or 200 °C. The reaction was stopped by rapid cooling with liquid nitrogen. The polymer was purified by Soxhlet extraction for 24 h in THF. The extracted samples were dried under vacuum at 40 °C for 24 h. ^{1}H NMR (300 MHz, CF_3COOD, 25 °C, δ, ppm): 3.8 (t, 2H; CH_2-NH), 3.1 (t, 2H; CH_2-C=O), 2.1 (m, 4H; CH_2) 1.8 (d, 2H; CH_2); ^{13}C NMR (400 MHz, CF_3COOD, 25 °C δ, ppm): 179 (1C, C=O), 42.3 (1C, -C*H_2-NH-), 33 (C1,-C*H_2-CO-), 26 (1C), 25.3 (1C), 24.8 (1C).

Bulk copolymerization of ε-caprolactam and ε-caprolactone with Brønsted acid ionic liquid

Copolymerization of ε-caprolactam (CLa) with ε-caprolactone (CLo) was carried out in bulk at 180 °C. A mixture of monomers containing different ε-caprolactam / ε-caprolactone ratios: 80/20 (2.39 g, 0.021mol / 0.60 g, 5.3 10^{-3} mol), 50/50 (1.49 g, 0.013mol / 1.51 g, 0.013 mol) and 20/80 (0.59 g, 5.3 10^{-3} mol / 2.41 g, 0.021 mol) were added respectively inside the glovebox. Then, the sealed reaction vessel was then removed from glove box and submerged into a pre-heated oil bath at 180 °C. For all reactions, 5 mol % of the Brønsted acid ionic liquid (0.42 g, 1.32 10^{-3} mol) was used. The reaction was stopped by rapid cooling with liquid nitrogen.



SCHEME 1. A) Organic Acid-Catalyzed Synthesis of poly(ε-caprolactam) and **B)** Acid Catalysts employed in the screening process.*Methyl triflate is not an organic acid, but it is hydrolyzed giving the triflic acid.

Then, the copolymers were dissolved in THF or formic acid, centrifugated and precipitated in H_2O. After washing with H_2O, the remaining substance was dried under vacuum. ^{1}H NMR (300 MHz, CF_3COOD, 25 °C, δ, ppm): 4.6 (t, 2H, CH_2-O $_{CLO}$), 3.8 (t, 2H, CH_2-NH $_{CLA}$), 3.1 (t, 2H, CH_2-C=O $_{CLA}$), 2.8 (t, 2H, CH_2-C=O $_{CLO}$), 2.1 (m, 4H; $CH_{2\ CLO}$), 2.1 (m, 4H; $CH_{2\ CLA}$), 1.8 (m, 2H, CH_2 $_{CLO}$), 1.8 (m, 2H, CH_2 $_{CLA}$) ; ^{13}C NMR (400 MHz, CF_3COOD, 25°C δ, ppm): 179 (2C, C=O), 65.9 (1C, CH_2-O_{CLO}), 42.3 (1C, CH_2-NH_{CLA}), 33 (2C, C*H_2-C=O), 26 (2C), 25.3 (2C), 24.8 (2C).

RESULTS AND DISCUSSION

In this work, first a systematic investigation into acid-catalyzed ROP of ε-caprolactam under bulk conditions at 180 °C is carried out. In the second part, the random copolymerization of ε-caprolactam with ε-caprolactone is discussed.

Thus, the ROP of ε-caprolactam under bulk conditions was investigated using different organic acids as shown in Scheme 1. Among the different organic acids we screened sulphonic acids such as: triflic acid, methyl triflate, methyl p-toluenesulfonic acid (PTSA), methanesulfonic acid (MSA), carboxylic acids such as; trifluoroacetic acid and acetic acid and other acids such as bis(trifluoromethane)sulfonimide (TFMI) (very strong acid) and diphenyl phosphate (DPP) (weak acid). We also investigated 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate, which is a Brønsted (sulfonic) acid ionic liquid (BAIL)[28-31] known for its high thermal stability. It is known that the unique combination of properties of BAILs ionic liquids, i.e. negligible vapor pressure, high thermal and chemical stabilities, non flammability and reusability, makes them very interesting candidates for polymer synthesis.[31]

Table 1 summarizes the polymerization conditions and the results we obtained using different organic acid catalyst. The polymerizations were carried out at 180 °C for 72 h with 5 mol % of catalyst and conversions were measured by ^{1}H NMR spectroscopy. The conversion was 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 ε-caprolactam monomer signal (3.1 ppm and 3.25 ppm respectively) (Supporting Information (SI), Figure S1). The molecular weights were measure by solution

TABLE 1. Polymerization Conditions for ROP of ε-caprolactam (ε-CLa) using 5 mol % of different organic catalyst at T=180° C in 72 h.

Entry	Catalysts	Conv(%).[a]	Mη(g/mol)[b]
1	no catalyst	0	-
2	$[(CH_2)_4SO_3HMIm]$ $[HSO_4]$	95	2800
3	p-toluenesulfonic acid (PTSA)	89	1700
4	Methanesulfonic acid (MSA)	98	1300
5	Diphenyl phosphate (DPP)	20	-
6	Triflic acid	27	-
7	Methyl triflate	28	-
8	Bis(trifluoromethane)sulfonimide (TFMI)	32	
9	Acetic acid	0	-
10	TFA	0	-

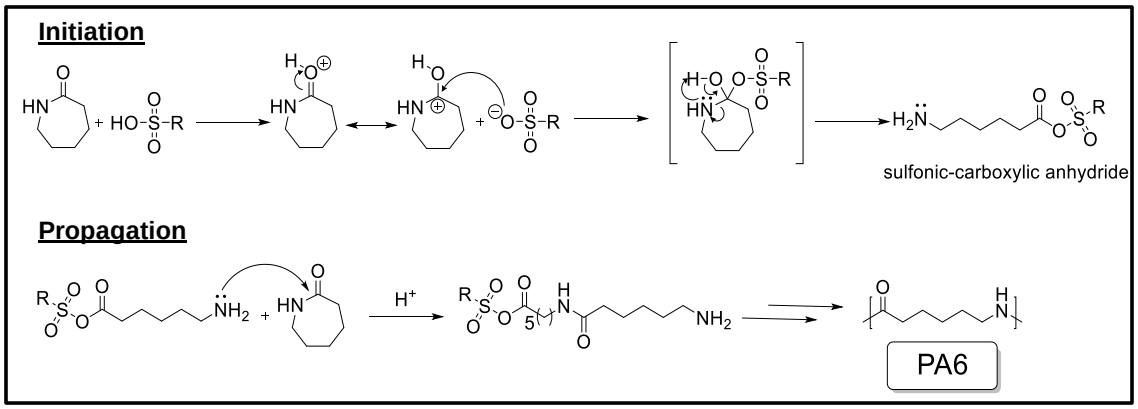
[a] As determined by ^{1}H NMR in *d*-TFA (see Figure S1 in the Supporting Information).
[b] Determined by viscosimetric measurements in formic acid.

viscosimetry when high monomer conversions were obtained.

It is obvious, that the rates of polymerization were found to be highly catalysts dependent. Depending on the organic catalyst, the resulting yields range from 98% consumption of monomer (entry 2, 3 & 4, Table 1) to complete inactivity (entry 9 & 10, Table 1). In case no polymerization occurred, the reaction mass remained liquid and was soluble in dicloromethane (DCM) or tetrahydrofuran (THF) after cooling. When polymerization took place, the reaction mixture solidified. Control reactions lacking a catalyst did not deliver any poly(ε-caprolactam) (P(CLa)) (entry 1, Table 1).

As it is shown in Table 1, the conversion of polymerization is increased by the acid organic catalyst in the following order: methane sulfonic acid (MSA) > 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate (BAIL) > p-toluenesulfonic acid (PTSA) > bis(trifluoromethane)sulfonimide (TFMI) > Triflic acid > diphenyl phosphate (DPP) > trifluoroacetic acid (TFA) = Acetic Acid. The sulfonic acids: 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate, PTSA and MSA were the most active, exhibiting almost quantitative conversions after 72 h (SI, Figure S3). Looking to these results, it seems that there is a weak correlation between pKa value of the acid (namely acidity) and catalytic activity of different organic acids. For instance, one of the strongest acid, triflic acid and one of the weakest acids diphenyl phosphate (DPP) have similar conversions after 72 h (conv. ≈ 25 mol %) and much lower compared to medium strength sulfonic acids (conv. > 89 mol %).

In order to get a better understanding about the parameters are governing the polymerization in the presence of organic acids a model reaction was carried out with equimolecular amounts of ε-caprolactam and the Brønsted acid ionic liquid: 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate, in order to get more information about the polymerization mechanism. After 24 h, the NMR spectroscopy revealed signal associated to the formation of the sulfonic-carboxylic anhydride by ^{1}H NMR, ^{13}C NMR and DOSY [32] (SI, Figure S4, S5 and S6). As can be observed in the DOSY spectra (SI, Figure S6) the 2D peaks for each component are align themselves along horizontal lines, confirming that for the



SCHEME 2. Reaction mechanism for the organic acid mediated synthesis of poly(ε-caprolactam) with the chemical structure of the sulfonic-carboxilic anhydride.

sulfonic-carboxilic anhydride compound, we have one molecule. Therefore, we propose that the acidic hydrogen atom of the sulfonic acid is transferred to the amide group of the monomer promoting the ring opening and the formation of sulfonic-carboxilic anhydride. Afterwards, the nucleophilic addition proceeds *via* primary amine of sulfonic-carboxilic anhydride, which is able to attach a new molecule of lactam and starts the polymerization to obtain poly(ε-caprolactam) (PA6) (Scheme 2). Nevertheless, it cannot be discharged that the primary amine of the sulfonic-carboxylic anhydride could react with itself making the polyamide by condensation. But taking into account the harsh polymerization conditions and the larger lactam to 1-(4-sulfonyl)-3-methylimidazolium hydrogenosulfate ratio we believe that statistically is more probable the nucleophilic attack of primary amine to the monomer than to the sulfonic-carboxylic anhydride moiety. This result suggests that not only the acid has to be strong enough to protonate the ε-caprolactam and activate the monomer but also its conjugate base must be nucleophilic enough to attack the carbonyl and initiate the polymerization. [15,23,33]

This finding is congruent with the polymerization trend observed for the different organic acids due to the negligible nucleophilicity of strong acids such as triflic acid, which limits its ability to promote the initiation of ε-caprolactam. This dual behavior of organic acid catalyst in ring opening polymerization of cyclic ester[34] and carbonates[35] and in the synthesis of poly(urethanes)[33] has been already recognized.

As a conclusion, the activity of the different organic acids used correlates with the pKa values of the corresponding acid and the nucleophicility of its conjugated base, being the medium strength acids the most suitable for the initiation of ROP of ε-caprolactam. Thus, polymerization catalyzed by sulfonic acids such as: Brønsted acid ionic liquid (1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate) (pKa= -2. 2), p-toluenesulfonic acid (PTSA, pKa= -2.8) and methane sulfonic acid (MSA, pKa=-1.9) are faster than reaction carried out using strong acids like bis(trifluoromethane)sulfonimide (TFMI, pKa= -16), triflic acid (pKa= -13) or methyl triflate due to the low nucleophilic character of its conjugated base. Conversely, the low acidity of carboxylic acids such as trifluoroacetic acid (TFA, pKa= 0.5) and acetic acid (pKa= 4.7) is not sufficient to promote the reaction. However besides this, it is worth to remark that the thermal stability of the different catalysts may be also an important factor during these reactions due to the high temperatures and long reaction times used.

To get a better understanding of the polymerization mechanism, the effects of (i) the monomer to catalyst ratios and (ii) the reaction temperature were investigated and discussed in the following sections. First, to study the effect

TABLE 2. Effect of catalyst content and temperature on the ROP of ε-caprolactam (ε-CLa).

Entry	Catalyst	Temp. (°C)	ε-CLa:Cat	Conv (%).[a]	Mη(g/mol) [b]
1	$[(CH_2)_4SO_3HMIm]$ $[HSO_4]$	180	100:2.5	67	5600
2	p-toluenesulfonic acid (PTSA)	180	100:2.5	51	1100
3	Methanesulfonic acid (MSA)	180	100:2.5	85	1300
4	$[(CH_2)_4SO_3HMIm]$ $[HSO_4]$	180	100:5	95	2800
5	p-toluenesulfonic acid (PTSA)	180	100:5	89	1700
6	Methanesulfonic acid (MSA)	180	100:5	98	1000
7	$[(CH_2)_4SO_3HMIm]$ $[HSO_4]$	180	100:10	84	1800
8	p-toluenesulfonic acid (PTSA)	180	100:10	85	1200
9	Methanesulfonic acid (MSA)	180	100:10	65	861
10	$[(CH_2)_4SO_3HMIm]$ $[HSO_4]$	160	100:5	83	1800
11	$[(CH_2)_4SO_3HMIm]$ $[HSO_4]$	200	100:5	98	3200

[a] As determined by ^{1}H NMR in *d*-TFA (see Figure S1 in the Supporting Information) .
[b] Determined by viscosimetric measurements.

of catalyst content on the rate of polymerization, three different catalyst concentrations (2.5, 5.0 and 10.0 mol %) were screened at 180 °C using the three different sulfonic acid (BAIL, PTSA and MSA) for 72 h. It can be noted, that increasing the amount of sulfonic acid, lower molecular weight polyamides were obtained specially when the Brønsted acid ionic liquid (BAIL) was used (Table 2, entry 1,4,7). In this case, molecular weights of 1.8 kg mol^{-1} were obtained with 10 mol% of catalyst, in comparison to 5.6 kg mol^{-1} with a 2.5 mol% of catalyst (Table 2). This fact indicated that besides acting as a catalyst, sulfonic acids had a role in the initiation process as confirmed in the model reaction. To clarify the presence of the BAIL acid ionic liquid in the chain ends, we analyze the ^{1}H NMR of the polyamide 6 after purification (SI, Figure S2). The ^{1}H NMR spectroscopy revealed signals that were attributed to acid ionic liquid (BAIL), which suggested that the acid ionic liquid take part in the initiation process of the polymerization generating a primary amine (sulfonic-carboxylic anhydride) that starts the propagation process.

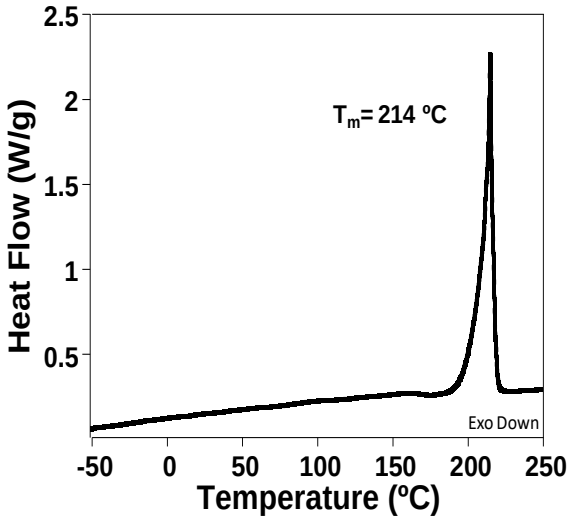


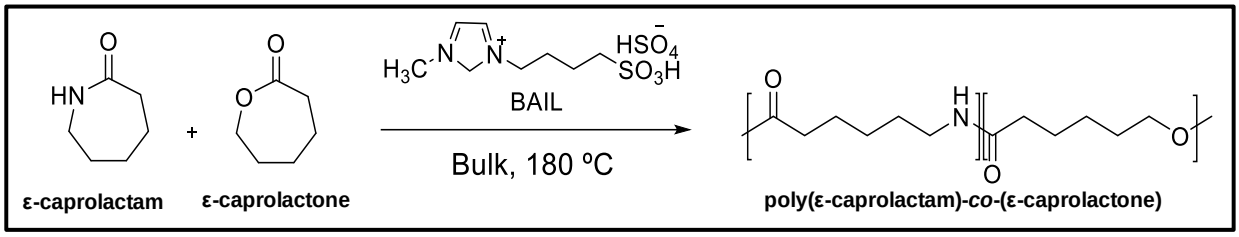
FIGURE 1. DSC of poly(ε-caprolactam) corresponding to the sample of entry 2 in Table 1.

Then we investigated the effect of temperature on the polymerization process. Reactions were carried out at three different temperatures (160, 180 and 200 °C) using BAIL, PTSA and MSA (Table 2 and SI, Table S1). As expected, the highest temperatures resulted in the fastest polymerizations. At 200 °C, higher monomer

conversion and higher molecular weights (Table 2, entry 4, 10, 11) were achieved in 72 h. It can be assumed that lower viscosities at higher temperatures allow for higher mobility of the growing chains in the polymerization mass, and consequently lead to higher conversions in less time. On the other hand, at 160 ˚C after 72 h low monomer conversions were achieved and consequently low molecular weight polyamides were obtained (SI, Table S1).

acids at these elevated temperatures must also be considered as an important factor.

Finally, thermal properties of poly (ε-caprolactam) prepared with 5 mol % BAIL at 180 °C were studied by DSC (Figure 1) and thermal stability by TGA (SI, Figure S7). As shown in DSC trace , poly (ε-caprolactam) showed a melting temperature of 214 °C which is in good agreement with literature values (T_m=219 °C).[35] In TGA analysis, the weight loss of poly(ε-caprolactam) started around 306 °C and the



SCHEME 3. Ring opening copolymerization of ε-caprolactam (ε-CLa) and ε-caprolactone (ε-CLo) using the Brønsted acid ionic liquid (BAIL) (5 mol%) in bulk at 180 °C.

TABLE 3. Reaction Conditions and Results of ε-caprolactam/ε-caprolactone (CLa/CLo) copolymerization using BAIL as Catalyst at 180 °C for 72 h.

Entry	Feed CLa/CLo	Monomer Conv(%)[a]	Poly[(ε-caprolactam)$_x$-*co*-(ε-caprolactone)$_y$]	Mw(g/mol)[b]	Đ[b]	T_m (°C)	ΔH_m (J/g)	R
1	100/0	95	poly(ε-caprolactam)	2800[c]	-	214	97	-
2	80/20	95/98	Poly[(ε-caprolactam)$_{75}$-*co*-(ε-caprolactone)$_{25}$]	900	1.2	167	45	0.92
3	50/50	58/100	Poly[(ε-caprolactam)$_{45}$-*co*-(ε-caprolactone)$_{55}$]	1400	1.5	147	26	0.74
4	20/80	89/98	Poly[(ε-caprolactam)$_{19}$-*co*-(ε-caprolactone)$_{81}$]	800	1.2	55	80	1
5	0/100	100	poly(ε-caprolactone)	3200	1.9	51	71	-

[a] As determined by ^{1}H NMR in *d*-TFA.
[b] As determined by GPC in THF according to PS standards.
[c] Determined by viscosimetric measurements in formic acid.

To conclude, for the homopolymerization of ε-caprolactam distinctly best results were obtained using the BAIL: 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate due to its thermal stability. In fact, higher molecular weights (Table 2, entry 1, 2, 3) were obtained when BAIL was used. It should be pointed out that the other sulfonic acids (PTSA and MSA) also performed well. It should be kept in mind that the reaction conditions at 180 °C are harsh compared to what usually applied for organic acids. Thus, the thermal stability of organic

remaining weight of the sample reached zero at around 500 °C. These thermal analysis confirm the nature of our polymer PA6.

Copolymerization of ε-caprolactam and ε-caprolactone with Brønsted acid ionic liquid

As the Brønsted acid ionic liquid is the most effective catalyst in ROP of ε-caprolactam, we investigated the copolymerization of ε-caprolactam (CLa) and ε-caprolactone (CLo) in bulk conditions at 180 °C using 1-(4-sulfobutyl)-

3-methylimidazolium hydrogen sulfate as catalyst, (Sheme 3) to obtain poly(ester-amide) (PEA) copolymers. For this purpose, five different copolymers were synthesized with varying the ε-caprolactam (CLa) / ε-caprolactone (CLo) ratio (Table 3). In order to obtain full conversion the reactions were carried out for 72 h. Quantitative conversions were measured by ^{1}H NMR spectroscopy (SI, Figure S8) and the molecular weights were determined by gel permeation chromatography (GPC) in THF.

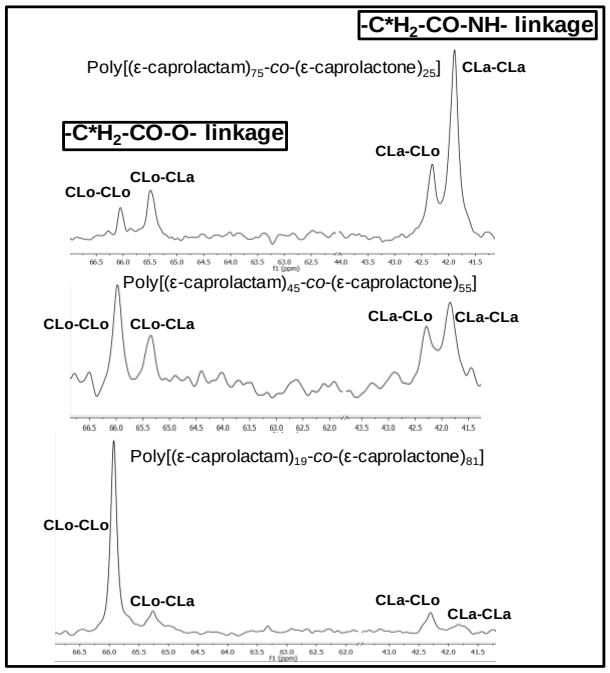


FIGURE 2. Expansion of ^{13}C NMR spectra, showing α-methylene group resonance, representing the copolymer dyads and the corresponding linkages between units for poly(ε-caprolactam)-*co*-(ε-caprolactone) copolymers with different compositions.

In order to determine the distribution of ε-caprolactam (CLa) and ε-caprolactone (CLo) comonomer units along the poly(ester-amide) sequence, the copolymers were further characterized by ^{13}C NMR spectroscopy to determine the copolymers chain microstructure.[36] In the case of the poly(ester-amide) based on caprolactam (CLa) and ε-caprolactone (CLo) units, the carbon atom of the methylene group in α position to the amide and ester groups (-C*H_2-CO-NH- and –C*H_2-CO-O-), respectively, shows four resonance peaks which are monitorized in terms of ^{13}C NMR dyads (CLa-CLa, CLa-CLo, CLo-CLa, CLo-CLo) (Figure 2). This means that the ^{13}C NMR chemical shift is mainly determined by whether the adjacent repeating unit originates from a CLo unit (CLo-CLo and CLo-CLa dyads) or a CLa one (CLa-CLa and CLa-CLo dyads). A schematic representation of copolymer dyads of the poly(ε-caprolactam-*co*-ε-caprolactone) copolymers and the corresponding linkages between units are shown in Figure 2. The peak at δ 65.9 ppm corresponds to the –C*H_2-CO-O- linkage between two CLo units, whereas the –C*H_2-CO-NH- linkage between two CLa units appeared at 42.3 ppm. The linkages between alternating units, CLo and CLa have resonances at 65.2 ppm (CLo-CLa) and 41.9 ppm (CLa-CLo), respectively. The reduction of ε-caprolactam (CLa) content in the copolymer composition led to an intensity drop of the CLa-CLa resonance and conversely and increase in CLo-CLo resonance.

Based on the relative integrated areas of the ^{13}C resonances from the carbon atoms in α position of amide and ester functions, the randomness character (R) of the poly(ester-amide) copolymers were determined using equation 2. Where (CLa) and (CLo) are the two comonomer molar fractions and (CLa-CLo) is the average dyad relative molar fraction.[37]

$$R = \frac{(CLa-CLo)}{2\,(CLa)(CLo)} \quad (2)$$

Considering that in a block copolymer R =0 while in a random copolymer R =1. It can be observed in Table 3, that all the poly(amide-ester) copolymers presented in this work took the value between 0.74 and 1, which confirmed the random nature of the poly (ε-caprolactam-*co*-ε-caprolactone) copolymers.

Thermal properties of the poly(ε-caprolactam-*co*-ε-caprolactone) poly(CLa-*co*-CLo) copolymers

were determined by DSC. As can be observed in Figure 3, when ε-caprolactam (CLa) is copolymerized with ε-caprolactone (CLo) all samples exhibit a single melting peak, confirming the statistical microstructure of poly(CLa-CLo) copolymers.[38]

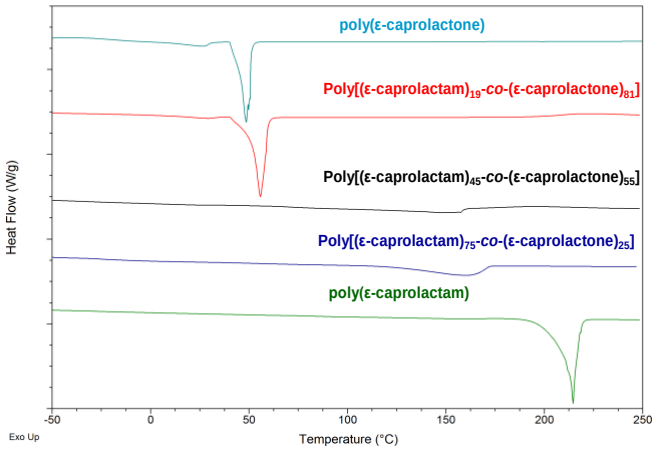


FIGURE 3. DSC heating curves of poly(ε-caprolactone) and poly(ε-caprolactam) homopolymers and poly(ε-caprolactam)-*co*-(ε-caprolactone) random copolymers.

The melting temperature (T_m) of poly(CLa-*co*-CLo) copolymers showed a gradual decrease with increasing ε-caprolactone (CLo) content in the copolymer. This decrease in T_m can be attributed to the random microstructure of the poly(ε-caprolactam-*co*-ε-caprolactone) copolymers.[36] As the ε-caprolactam (CLa) /ε-caprolactone (CLo) sequences are incorporated randomly, they interrupt the linear sequences of ε-caprolactam (CLa) or ε-caprolactone (CLo), breaking the structural order and causing the melting temperature decrease.

However, as reported before for poly(ε-caprolactam-*ran*-ε-caprolactone) poly(CLa-*ran*-CLo) random copolymers[36] a thermodynamic dilution effect (coming from plasticization effect of the ε-caprolactone (CLo) units) could also be a factor that contributes to the melting point. In fact, a melting temperature decrease can also be expected since the ε-caprolactam (CLa) crystals will be surrounded by a macromolecular "solvent" (i.e., molten caprolactone (CLo) sequences) at the moment of their fusion.

Similarly, the enthalpies associated with the melting phenomena decrease as increasing ε-caprolactone (CLo) content (Table 3), except in one case: poly[(ε-caprolactam)$_{19}$-*co*-(ε-caprolactone)$_{81}$]. These results suggest that as have been reported before for analogous copolymers, the ε-caprolactam (CLa) sequences were able to crystallize up to a certain point, and the ε-caprolactone (CLo) sequences did not crystallize (decreasing the enthalpy of melting). On the other hand, in the case of, poly[(ε-caprolactam)$_{19}$-*co*-(ε-caprolactone)$_{81}$] both monomers the ε-caprolactam (CLa) and ε-caprolactone sequences crystallized increasing the enthalpy of melting.

CONCLUSIONS

In this work, the ability of several organic acids for promoting the ring-opening polymerization (ROP) of ε-caprolactam at 180 °C was demonstrated, being sulfonic acids the most effective ones. Due to its high thermal stability the Brønsted acid ionic liquid: 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate was the fastest one. Model reactions and nuclear magnetic resonance (NMR) studies confirmed that the sulfonic acids could take part in the initiation process of the polymerization generating a primary amine that starts the propagation step of the polymerization. The proposed reaction mechanism suggested that the sulfonic acids had a dual role and confirming that the strength of a given acid as well as the nucleophilicity of its conjugated base were crucial for the synthesis of poly (ε-caprolactam).

Finally, after establishing the best polymerization conditions random poly(ε-caprolactam-*co*-ε-caprolactone) were synthesized to combine the outstanding thermal and mechanical properties of polyamides with the biodegradation capacity of aliphatic polyesters. As expected for the

random copolymers, both the melting temperature and melting enthalpy strongly varied with the copolymer composition.

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GRAPHICAL ABSTRACT

Ana Sanchez-Sanchez [1], Andere Basterretxea[1], Daniele Mantione[1], Agustin Etxeberria[1,2], Cristina Elizetxea[3], Amaia de la Calle[3], Sonia García-Arrieta[3], Haritz Sardon[1], David Mecerreyes[1,4]

Organic-acid mediated bulk polymerization of ε-Caprolactam and its Copolymerization with ε-Caprolactone

In this work, organic acids were explored for the ring-opening polymerization (ROP) of ε-caprolactam in bulk at 180 °C (below the polymer's melting point) to give the commercially important product polyamide 6 (PA 6). Among organic acids investigated, sulfonic acids were found the most effective for the polymerization of ε-caprolactam being the Brønsted (sulfonic) acid ionic liquid: 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate the most active one. Under optimum conditions, ε-caprolactam (CLa) was copolymerized with ε-caprolactone (CLo) to obtain biodegradable poly(ester amide)s. It is found that poly (ε-caprolactam-*co*-ε-caprolactone) copolymers with considerably randomness are formed.