

# A novel route to $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diols, precursors of biodegradable polyurethanes, using catalysis by decamolybdate anion

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## Abstract

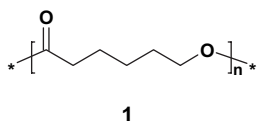
A new convenient route for the synthesis of poly( $\epsilon$ -caprolactone) (PCL) with  $\alpha,\omega$ -telechelic diols' end-groups is presented. Synthesis of  $\alpha,\omega$ -telechelic PCL diols (HOPCLOH) was achieved by ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone (CL) catalyzed with ammonium decamolybdate  $(\text{NH}_4)_8[\text{Mo}_{10}\text{O}_{34}]$  and using diethylene glycol (DEG) as initiator. Obtained HOPCLOH was characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, FT-IR, GPC and MALDI-TOF. Comparative studies demonstrate that ammonium decamolybdate  $(\text{NH}_4)_8[\text{Mo}_{10}\text{O}_{34}]$  is better catalyst than Sn-octanoate ( $\text{SnOct}_2$ ) toward CL polymerization in presence of DEG, under the conditions tested. A biodegradable poly(ester-urethane-urea) derivative was efficiently prepared from synthesized HOPCLOH. Obtained polymer shows minor differences with respect to the properties recorded for a poly(ester-urethane-urea) obtained from commercial HOPCLOH.

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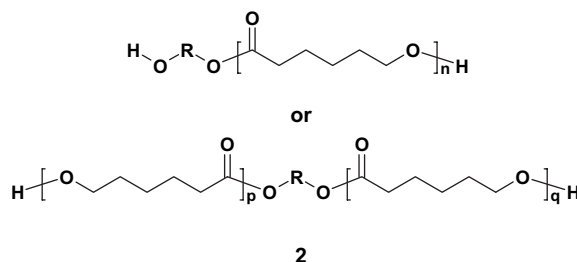
**Keywords:** Ring-opening polymerization;  $\alpha,\omega$ -Telechelic poly( $\epsilon$ -caprolactone) diols; Decamolybdate anion

## 1. Introduction

Biodegradable polymers — such as poly( $\epsilon$ -caprolactone) (PCL) **1** — are receiving increasing attention due to their applications in the biomedical area. Biodegradation of PCL films by pure strains of microorganisms isolated from industrial compost induces a weight loss of 95 wt% (with respect to the initial mass) after 200 h of incubation [1]. It is expected that derivatives obtained by chain extension reactions of PCL also show similar biodegradable properties. Most of these derivatives have also potential uses in surgery and as drug delivery agents.



One of the more important factors to consider for PCL chain extension reactions is the chemical nature of the polyester end-groups. Diol derivatives ( $\alpha,\omega$ -telechelic diols) are specially targeted, due to the feasibility of the hydroxyl end-groups to react with different functional groups [2–9]. Some examples are: (1) synthesis of  $\alpha,\omega$ -telechelic PCL diols (HOPCLOH) **2** [10–15] as precursors of polyurethanes, (2) synthesis of HOPCLOH [16–19] which acts as macroinitiators in the synthesis of triblock copolymers.



The more convenient route for the synthesis of HOPCLOH (with respect to polycondensation) is the ring-opening

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polymerization (ROP) of  $\epsilon$ -caprolactone (CL) using a diol as initiator/chain-transfer agent in the presence of a catalyst. Derivatives from Ge [2], Nd [3], Bi [4,6], Sn [10], Zn [15] and Al [20], have been tested as catalysts to obtain HOPCLOH. However, these synthetic routes are plagued with some inconveniences, such as the use of toxic metals as catalysts [3,10], long reaction times (24–264 h) [2,10,15] and inefficient catalyst systems (CL/catalyst molar ratios of 50–1000 are needed to induce lactone polymerization) [2–4,6,10,15].

Molybdenum is an environmentally friendly element. In the scope of bioinorganic chemistry, molybdenum is considered as a biologically important transition metal. It is the heaviest atomic number element to have a wide range of functions in living organisms. At the present time, activity of over a dozen known enzymes rely on the presence of molybdenum, which is usually absorbed as the molybdate ion,  $[\text{MoO}_4]^{2-}$  [21,22].

We recently reported the synthesis of aliphatic polyesters using decamolybdate anion  $[\text{Mo}_{10}\text{O}_{34}]^{8-}$  as catalyst. Primary and secondary alcohols can be used as initiator/chain-transfer agents. Resulting polyesters possessed two different end-groups: one ester end-group (with the alkyl group of the alcohol linked to the polymer through an ester functionality), and a hydroxyl end-group [23]. When water was used as initiator, a control of the molecular weight of the resulting  $\alpha$ -hydroxyl- $\omega$ - (carboxylic acid) PCL could be achieved [24]. Effectiveness of decamolybdate anion in the synthesis of lactone copolyesters with controlled end-group architecture was also demonstrated [25]. Decamolybdate anion is obtained in the solid state as the ammonium salt  $(\text{NH}_4)_8[\text{Mo}_{10}\text{O}_{34}]$  by thermal decomposition of ammonium heptamolybdate  $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]$  [26].

In this investigation, we report a new synthetic route to obtain  $\alpha,\omega$ -telechelic PCL diols (HOPCLOH), with the use of decamolybdate anion as catalyst and diethylene glycol ( $\text{HO}-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-\text{OH}$ ) (DEG) as initiator. A CL/catalyst molar ratio of 20,000 was used. The amount (in mmol) of catalyst was lower than that commonly used for ROP of lactones with tin(II) 2-ethylhexanoate ( $\text{Sn}(\text{Oct})_2$ ) catalysis [6,10]. This synthetic route represents a convenient alternative to obtain HOPCLOH. On the basis of its particular macromolecular architecture given by the presence of two hydroxyl end-groups, the HOPCLOH was successfully used for the synthesis of a poly(ester-urethane-urea).

## 2. Experimental

### 2.1. Materials

CL (Aldrich Chemicals Co.) was dried over calcium hydride and distilled under reduced pressure before use. Ammonium heptamolybdate tetrahydrate  $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$  (Fluka) was grounded in a mortar and passed through a 100 mesh sieve. The grounded catalyst was dried in an oven at 80 °C overnight before use.

Polycaprolactone diol 530, 1250 and 2000, L-lysine monohydrochloride, DEG and stannous 2-ethylhexanoate were purchased from Aldrich Chemical Company. L-Lysine diisocyanate (LDI, diisocyanate of the L-lysine methyl ester or

methyl-2,6-diisocyanatohexanoate) was a gift from Kyowa Hakko Kogyo Co., Ltd., Japan. Triethylamine and *N,N*-dimethylacetamide (DMAc) were supplied by Scharlau. *N,N*-dimethylacetamide was vacuum distilled from isocyanates (commercial polymeric diisocyanate–diphenylmethane), keeping the distillation temperature below 60 °C to avoid solvent decomposition, and stored in an amber flask blanketed with nitrogen for not more than a week before use. The rest of the reagents were used as received. L-Lysine dihydrochloride ethyl ester (LYS) was synthesized following the procedure reported in literature [14].

### 2.2. Synthesis of $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diols (HOPCLOH) **3a** and **3b**

In a typical run, CL (5.70 g, 50 mmol), DEG (1.53 g, 3.45 mmol) and  $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$  (3 mg) in a CL/ammonium heptamolybdate tetrahydrate molar ratio of 20,000 were placed in a 25 ml flask. The flask was stoppered at room temperature and placed in a thermostated bath at 150 °C and the mixture was stirred for 4 h. No inert atmosphere was used. Ammonium decamolybdate  $(\text{NH}_4)_8[\text{Mo}_{10}\text{O}_{34}]$  was formed in situ at this temperature by thermal decomposition of ammonium heptamolybdate  $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]$  [23,26,27]. Progressive solubilization of ammonium decamolybdate in the reaction media was visually observed. Final polymer was characterized by FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, GPC and MALDI-TOF. IR ( $\text{cm}^{-1}$ ): 3545 ( $\nu_{\text{OH}}$ ), 2943 ( $\nu_{\text{CH}}$ ), 1721 ( $\nu_{\text{C=O}}$ ), 1187 ( $\delta_{\text{O-C=O}}$ ). NMR data for HOPCLOH (**3a** and **3b**) homopolymer,  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ , ppm) (Fig. 2):  $\delta$  173.53 (g), 173.32 (a'), 173.19 (a), 72.18 (5), 68.94 (3), 68.88 (1), 63.92 (f), 63.14 (4), 63.09 (2), 62.27 (l), 61.47 (6), 34.03 (h), 33.91 (b'), 33.76 (b), 32.12 (k), 28.14 (e), 25.32 (d), 25.13 (j), 24.51 (i), 24.37 (c'), 24.28 (c).

### 2.3. Synthesis of $\alpha,\omega$ -trifluoroacetate poly( $\epsilon$ -caprolactone) (TF-PCL-TF) by derivatization of HOPCLOH with trifluoroacetic anhydride (TFA)

Due to the low resolution obtained for some peaks, HOPCLOH was derivatized for NMR characterization. An excess amount of trifluoroacetic anhydride (TFA) was added to a solution of HOPCLOH in  $\text{CDCl}_3$  (100 mg/0.75 ml) at ambient temperature. Full derivatization of the sample was confirmed when the acidic proton of the trifluoroacetic acid by-product appeared as a sharp peak at around 11 ppm. NMR data for TF-PCL-TF (Fig. 1),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  4.49 (3, 2H,  $\text{CH}_2\text{OCOCF}_3$ ), 4.33 (f, 2H,  $\text{CH}_2\text{OCOCF}_3$ ), 4.26 (2, 2H,  $\text{CH}_2\text{O}$ ), 4.09 (d, 2H,  $\text{CH}_2\text{O}$ ), 3.81 (4, 2H,  $\text{CH}_2\text{O}$ ), 3.74 (1, 2H,  $\text{CH}_2\text{O}$ ), 2.35 (a, 2H,  $\text{CH}_2\text{CO}$ ), 1.76 (e, 2H,  $\text{CH}_2$ ), 1.65 (b, 4H,  $(\text{CH}_2)_2$ ), 1.65 (b', 2H,  $\text{CH}_2$ ), 1.37 (c, 2H,  $\text{CH}_2$ ).

### 2.4. Synthesis of poly(ester-urethane-urea) **4** prepared from $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diol (HOPCLOH)

The synthesis of a poly(ester-urethane-urea) **4** was carried out in a 25 ml flask at  $T = 80$  °C. One gram (0.4664 mmol)

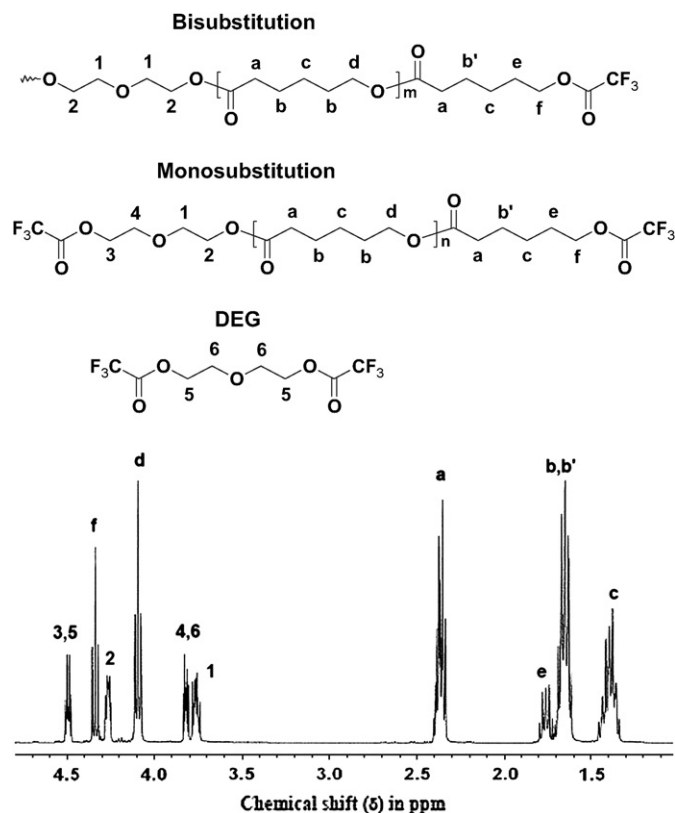


Fig. 1.  $^1\text{H}$  NMR (400 MHz) spectrum of  $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diols (HOPCLOH) ( $M_n(\text{NMR}) = 534$ ) in  $\text{CDCl}_3$ , after derivatization with trifluoroacetic anhydride (TFA).

of PCL ( $M_n(\text{NMR}) = 2140$ ) was dissolved in 1.85 ml of *N,N*-dimethylacetamide.  $\text{Sn}(\text{Oct})_2$  (1.89 mg) and 172.92 mg (1.166 mmol) of *L*-lysine diisocyanate (diisocyanate of *L*-lysine methyl ester) (LDI) were added. After prepolymerization for 3 h at 80 °C, *L*-lysine dihydrochloride ethyl ester (LYS) (172.92 mg, 0.6996 mmol) and triethylamine (0.2919 ml) were added and the reaction mixture was stirred for further 3 h at 80 °C, and then left overnight at room temperature. Reaction mixture was poured into an excess of distilled water/ice, the resulting solid separated, and dried under vacuum. IR ( $\text{cm}^{-1}$ ): 3361 ( $\nu_{\text{NH}}$ ), 2937 ( $\nu_{\text{CH}}$ ), 1729 ( $\nu_{\text{C=O}}$ ), 1652 ( $\nu_{\text{NH-CO-NH}}$ ), 1557 ( $\delta_{\text{NH-CO-NH}}$ ), 1160 ( $\delta_{\text{O-C=O}}$ ).

A polymer film was obtained from an approximately 10% w/v solution in chloroform by casting in a leveled glass within a fume cupboard. The cast solution was covered by a conical funnel to protect it from dust and to avoid an excessively fast solvent evaporation, and allowed to stand at ambient temperature for 48 h. After this time, the polymer film was released and dried for further 24 h in vacuum. Samples for physical characterization were obtained by cutting the film. Film thickness was 260  $\mu\text{m}$ .

### 2.5. Measurements

Solution  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at room temperature on a Varian Gemini 200 (200 MHz  $^1\text{H}$  and 50 MHz  $^{13}\text{C}$ ) and a Varian Mercury 400 (400 MHz for  $^1\text{H}$ )

spectrometers. Chloroform-*d* ( $\text{CDCl}_3$ ) was used as solvent. Spectra were referenced to the residual solvent signals at  $\delta$  7.26 and 77.0 ppm in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, respectively. FT-IR spectra were obtained with the ATR technique on films deposited over a selenium sulfide (SeS) crystal on a Perkin–Elmer 1600 spectrometer. GPC measurements were determined using a Waters 244 gel permeation chromatograph equipped with a refractive index detector. A set of  $10^4$ ,  $10^3$  and 100 Å Waters columns conditioned at 25 °C were used to elute samples at the flow rate of 1 ml/min HPLC-grade chloroform. Polystyrene standards (Polymer Laboratories) were used for calibration. Differential scanning calorimetry (DSC) was performed in a Mettler Toledo DSC822e instrument. Samples were sealed in aluminium pans with perforated lid. Two scans (25–80 °C and –90 to 80 °C) were performed by using a heating rate of 10 °C/min and the fastest cooling rate of the instrument between runs under nitrogen purge. The melting points ( $T_m$ ) are given as the maximum of the endothermic transition, and the data reported are taken from the second scan.

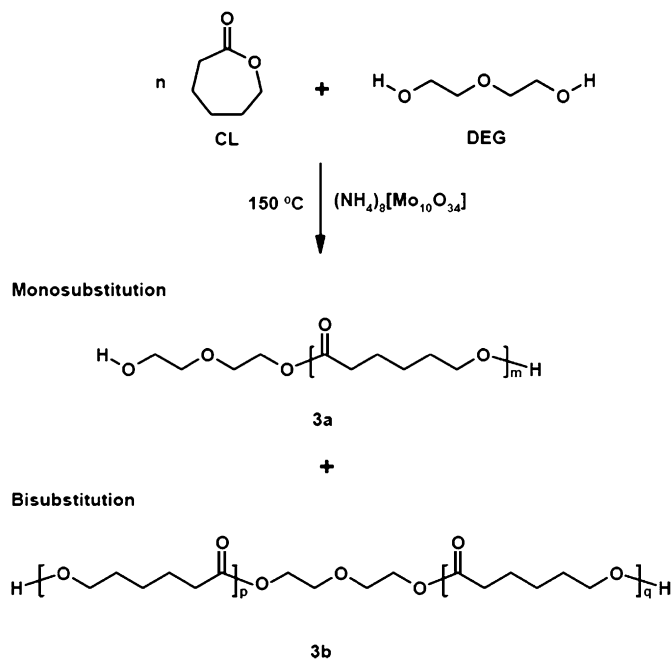
Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectra were recorded on a Voyager DE-PRO time-of-flight mass spectrometer (Applied Biosystems) equipped with a nitrogen laser emitting at  $\lambda = 337$  nm with a 3 ns pulse width and working in positive ion mode and delayed extraction. A high acceleration voltage of 20 kV was employed. 2,5-Dihydroxybenzoic acid (DHB) at a concentration of 10 mg/ml in acetonitrile was used as matrix. Samples were dissolved in acetonitrile and mixed with the matrix at a molar ratio of approximately 1:100.

Tensile properties were measured in a MTS Synergie 200 testing machine equipped with a 100 N load cell. Type 3 dumb-bell test pieces (according to ISO 37) were cut from the film. A crosshead speed of 200 mm/min was used. Strain was measured from crosshead separation and referred to 12 mm initial length. Six samples were evaluated.

## 3. Results and discussion

### 3.1. Synthesis and characterization of $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diols (HOPCLOH) **3a** and **3b**

Molybdenum compounds such as chloride, bromide and oxides have been previously reported as catalysts for ring-opening polymerization of  $\epsilon$ -caprolactone [25]. From all the molybdenum compounds tested, ammonium decamolybdate ( $(\text{NH}_4)_8[\text{Mo}_{10}\text{O}_{34}]$ ) was found to be the best catalyst for the synthesis of the asymmetric telechelic  $\alpha$ -hydroxyl- $\omega$ -(carboxylic acid) PCL (HA-PCL) [24]. This conclusion was based on its selectivity, short reaction times and high conversions. Synthesis of HA-PCL by catalysis with decamolybdate anion was performed in the presence of water as initiator/chain-transfer agent. From these results, it was decided to investigate the use of diols such as diethylene glycol ( $\text{HO}-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-\text{OH}$ ) (DEG) in the CL/ammonium decamolybdate system to obtain the symmetric  $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diols (HOPCLOH, **3a** and **3b**) (Scheme 1).

Scheme 1. Synthesis of  $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diols (HOPCLOH).

$\epsilon$ -Caprolactone (CL) reacted quantitatively by ring-opening in the presence of DEG. Bulk polymerization of CL by ammonium decamolybdate (obtained in situ by thermal decomposition of ammonium heptamolybdate) with a CL/ammonium heptamolybdate feed molar ratio of 20,000 was carried out at 150 °C. CL was quantitatively incorporated into the polymer chains and 100% CL conversion was achieved. For a CL/DEG feed molar ratio of 3.45, a polymer with  $M_n(\text{GPC}) = 1170$  and  $M_w/M_n = 1.39$ , with a conversion of 100% CL, was obtained after 4 h (no. 1, Table 1). An increase in polymer molecular weight at higher CL/DEG molar ratios is found. Analysis of the MWD curve line shapes of final polymers obtained by GPC reveals that unimodal distributions are present, and for sample no. 1 (Table 1), for high elution times, fractionation of oligomers with lower molecular weights is observed.

Number-average molecular weight obtained by GPC (no. 1, Table 1),  $M_n(\text{GPC}) = 1170$  ( $M_w/M_n = 1.39$ ), differs from that calculated by  $^1\text{H NMR}$ ,  $M_n(\text{NMR}) = 534$ . However, theoretical number-average molecular weight (recorded from the CL/DEG ratio,  $M_n(\text{calcd}) = 500$ ) is similar to  $M_n$  obtained by NMR. McLain and Drysdale [28] proposed a factor of 0.45 to convert  $M_n(\text{GPC})$  values into the actual number-average molecular weight for poly( $\epsilon$ -caprolactone). In Table 1 we report this ratio ( $M_n(\text{calcd})/M_n(\text{GPC})$ ) for our samples. Values between 0.46 and 0.51 are recorded. Similar observations were previously reported by our group for  $\alpha$ -hydroxyl- $\omega$ -(aliphatic esters) PCL [23] and  $\alpha$ -hydroxyl- $\omega$ -(carboxylic acid) PCL [24]. As it was stated before, number-average molecular weight obtained by NMR corresponds to the actual  $M_n$  of the sample.

A common route to derivatize PCL with hydroxyl end-groups involves its reaction with trifluoroacetic anhydride (TFA). Reaction between the HOPCLOH diol end-groups and TFA to form an ester occurs. The  $^1\text{H NMR}$  spectrum analysis (Fig. 1) for HOPCLOH with  $M_n(\text{NMR}) = 534$  (no. 1, Table 1)

Table 1

Synthesis of  $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diols (HOPCLOH) **3a** and **3b**<sup>a</sup> by ring-opening polymerization of  $\epsilon$ -caprolactone (CL) with decamolybdate in the presence of diethylene glycol (DEG)

No.	CL/DEG	$M_w/M_n$	$M_n(\text{GPC})^b$	$M_n(\text{calcd})^c$	$M_n(\text{NMR})^d$	Ratio <sup>e</sup>	% $\text{CO}_2\text{H}^f$
1	3.45	1.39	1170	500	534	0.46	$\leq 1$
2	7.84	1.67	2130	1000	1089	0.51	$\leq 1$
3	16.61	1.56	4360	2000	2054	0.47	2
4	34.15	1.73	7000	4000	3570	0.51	5

<sup>a</sup> A CL/ammonium heptamolybdate molar ratio of 20,000 (CL = 50 mmol) was used. Polymerizations were carried out at 150 °C for 4 h (conversion (%) = 100).

<sup>b</sup> Determined by gel permeation chromatography (GPC) using polystyrene standards.

<sup>c</sup> Obtained from equation  $M_n(\text{calcd}) = (M_w(\text{CL})(\text{CL}/\text{DEG}) + M_w(\text{DEG}))$ , where  $M_w$  is the molecular weight of  $\epsilon$ -caprolactone (CL) or diethylene glycol (DEG).

<sup>d</sup> Obtained by  $^1\text{H NMR}$ .

<sup>e</sup>  $M_n(\text{calcd})/M_n(\text{GPC})$  ratio.

<sup>f</sup> Mole percentage of  $\alpha$ -hydroxyl- $\omega$ -(carboxylic acid) poly( $\epsilon$ -caprolactone) (HA-PCL) in samples obtained by  $^1\text{H NMR}$ .

after derivatization with TFA shows the existence of three different chemical species [14]: (a) those formed from bisubstitution of DEG with PCL, (b) those formed from monosubstitution of DEG with PCL and (c) unreacted DEG. The ratio of peak 1 area [ $-\text{CH}_2-\text{O}-$ ,  $\delta$  3.74] to that of peak *f* [ $-\text{CH}_2-\text{OCOCF}_3$ ,  $\delta$  4.33] is 2:2, which confirms that the main reaction product is HOPCLOH, which has a functionality of two. The other peaks observed in the spectrum are assigned to the other methylenes of the CL [ $-\text{CO}-(\text{CH}_2)_5-\text{O}-$ ] and DEG [ $-\text{O}-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-\text{O}-$ ]. The observation of a weak signal at  $\delta$  2.60 can be assigned to the methylene adjacent to an anhydride [ $\text{CH}_2\text{CO}_2\text{COCF}_3$ ] formed from the reaction between one carboxylic acid end-group and TFA, evidencing the formation of the  $\alpha$ -hydroxyl- $\omega$ -(carboxylic acid) PCL (HA-PCL). In the last column of Table 1, we report the percentage of HA-PCL present in our samples. A simple calculation shows that, for the HOPCLOH with theoretical  $M_n(\text{calcd}) = 4000$ , the expected molar ratio [water coming from heptamolybdate/DEG] is 1:146, which is too low to explain the carboxylic acid content found by NMR. This means that some additional water molecules are present in the reaction, and they can come from (a) DEG and CL or (b) humidity present in the air, or both.

$^{13}\text{C NMR}$  spectrum in Fig. 2 also evidences the chemical nature of the HOPCLOH end-groups. In the carbonyl zone, peaks for the ester carbonyl of the hydroxyl end-group [g,  $-\text{O}-\text{CO}-(\text{CH}_2)_5-\text{OH}$ ,  $\delta$  173.53], ester carbonyl of the main chain [a',  $(-\text{CO}-(\text{CH}_2)_5-\text{O}-)_n$ ,  $\delta$  173.32] and ester carbonyl adjacent to DEG [a,  $(-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-)_n$ ,  $\delta$  173.19] are clearly distinguished. Signals for methylene close to the hydroxyl end-group of PCL [l,  $-\text{CH}_2-\text{OH}$ ,  $\delta$  62.27] are seen. In the methylenes linked to oxygen zone, signals for: (a) bisubstituted DEG [1,  $\delta$  68.88 and 2,  $\delta$  63.09], (b) monosubstituted DEG [3,  $\delta$  68.94 and 4,  $\delta$  63.14] and (c) unreacted DEG [5,  $\delta$  72.18 and 6,  $\delta$  61.47] are seen. The  $^{13}\text{C NMR}$  spectrum in Fig. 2 shows also the direct evidence of mono- and bisubstitution in the initiator (DEG). The synthesis of

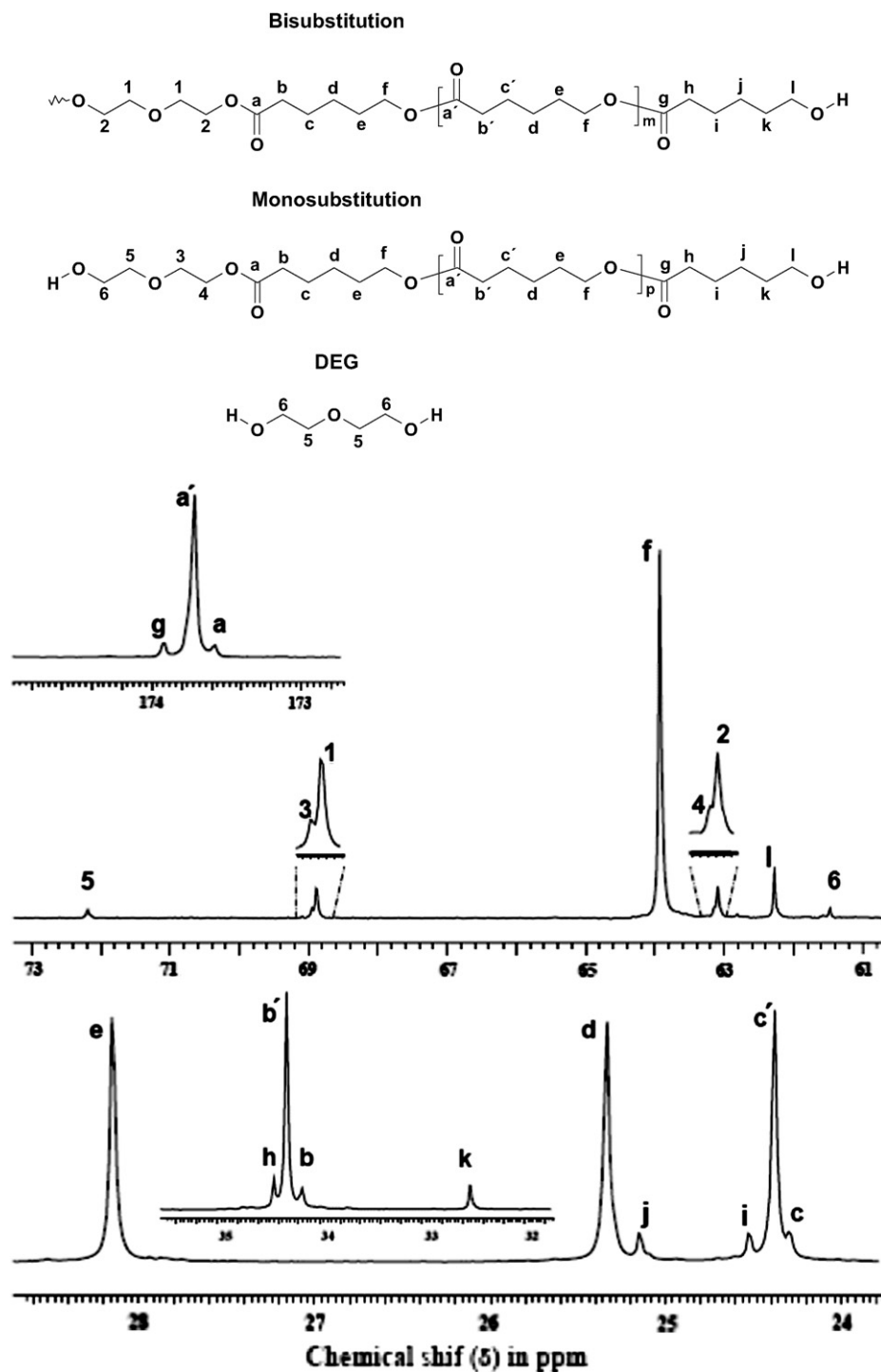


Fig. 2.  $^{13}\text{C}$  NMR (50 MHz) spectrum of  $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diol (HOPCLOH) in  $\text{CDCl}_3$ , ( $M_n(\text{NMR}) = 2054$ ).

HOPCLOH, as reported by Duda [20] using  $\text{Al}[\text{OCH}(\text{CH}_3)_2]_3$  as catalyst and 1,5-pentanediol as initiator, shows mono- and bisubstitution in the initiator glycol. This fact was corroborated by  $^{13}\text{C}$  NMR spectroscopy for a polymer with  $M_n(\text{GPC}) = 400$  ( $M_w/M_n = 1.17$ ). Storey and Sherman [29] reported the synthesis of HOPCLOH with  $\text{Sn}(\text{Oct})_2$  as catalyst and ethylene glycol (or 1,3-propanediol) as initiator; however, proportion of mono- and bisubstitution in the formed polymers ( $M_w/M_n \leq 1.15$ ) is not reported.

CL/DEG ratio versus  $M_n(\text{NMR})$  and versus percent of bisubstituted DEG are plotted in Fig. 3 (Table 2). A linear relationship between  $M_n(\text{NMR})$  and CL/DEG is observed. This result indicates that control of molecular weight can be achieved, that is, a certain  $M_n$  can be targeted by using the proper amount of DEG in the feed reaction. On the other hand, an increase in the percentage of DEG bisubstitution (% Bi (OH)) with the increase in CL/DEG ratio is observed. This result is expected, as higher amounts of CL favor the

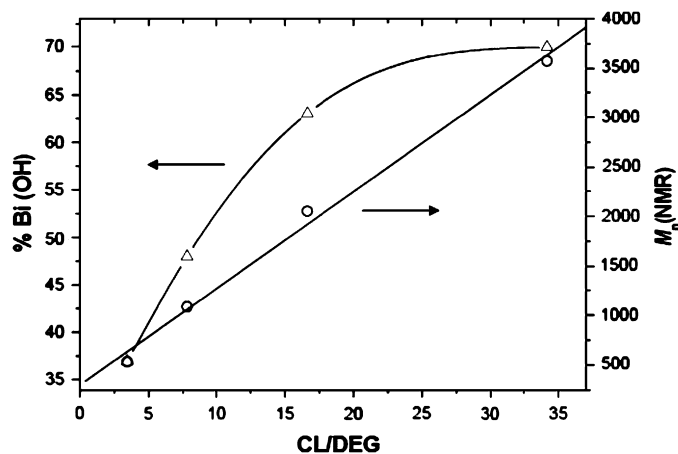


Fig. 3. Polymerization of  $\epsilon$ -caprolactone (CL) in the presence of diethylene glycol (DEG) catalyzed by decamolybdate at 150 °C. Dependence of  $M_n$ (NMR) and % bisubstitution of DEG (% Bi(OH)) on CL/DEG molar ratio feed.

Table 2

Percent of bisubstitution (% Bi(OH)) **3b**, monosubstitution (% MonoOH) **3a** and unreacted diethylene glycol (% DEG) in the synthesized  $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diol (HOPCLOH)

No.	CL/DEG	$M_n$ (NMR) <sup>a</sup>	% Bi(OH) <sup>b</sup>	% MonoOH <sup>b</sup>	% DEG <sup>b</sup>
1	3.45	534	37	42	21
2	7.84	1089	48	39	13
3	16.61	2054	63	33	4
4	34.15	3570	70	28	2

<sup>a</sup> Obtained by <sup>1</sup>H NMR.

<sup>b</sup> Due to peak merging, values are approximate.

probability of DEG bisubstitution. Polydispersity is moderate, from 1.39 to 1.73, similar to the SnOct<sub>2</sub>/butyl alcohol system [30] and higher than that for SnOct<sub>2</sub>/ethylene glycol system [29].

The MALDI-TOF mass spectrum for HOPCLOH ( $M_n$ (NMR) = 534, CL/DEG = 3.45) is shown in Fig. 4. The curve profile indicates a unimodal distribution, with a curve profile similar to that observed in the GPC chromatogram. In Fig. 5 an expansion of the zone between 911 and 1055 amu is shown. This region corresponds to the fragments with 7–8 CL repeating units. Three types of signals (a, b and c) can be distinguished in the spectrum: the first and most intense peaks (a) are due to HOPCLOH species with mono- and bisubstituted DEG. The second and third series of peaks come from (b)  $\alpha$ -hydroxyl- $\omega$ -(carboxylic acid) PCL (HA-PCL) and (c)  $\alpha,\omega$ -telechelic PCL diols, which form from the polymerization of PCL with ethylene glycol (EG) as initiator (PCLEOH; DEG contains small amounts of EG as impurity). Signals for macrocyclic species (CL)<sub>n</sub> are not observed, which indicates that intramolecular transesterification reactions do not occur under these conditions in a detectable amount. Molecular weight distribution obtained by MALDI-TOF for ROP of CL in presence of DEG and with ammonium decamolybdate as catalyst is similar to that for HOPCLOH obtained using Sn(Oct)<sub>2</sub> as catalyst (under the same experimental conditions).

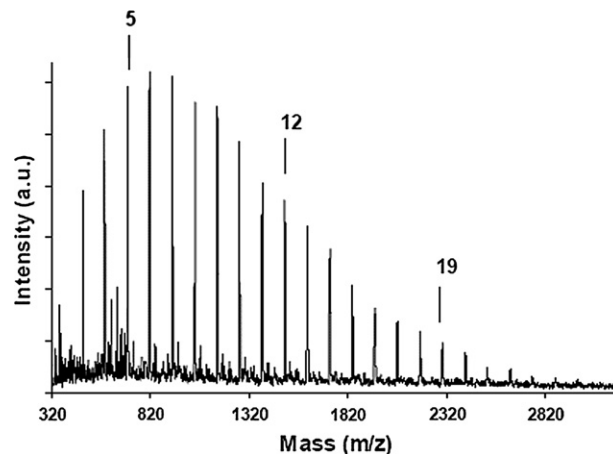


Fig. 4. MALDI-TOF spectrum (linear mode) of  $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diol (HOPCLOH) with  $M_n$ (NMR) = 534. Numbers indicate the degree of polymerization (DP).

Both products show narrower molecular weight distributions compared to that measured for a commercial sample of HOPCLOH from Aldrich. The  $\alpha,\omega$ -telechelic diols' structure architecture was confirmed by NMR and MALDI-TOF, with a low content of carboxylic end-groups coming from initiation by water.

DSC results show, as expected, crystallization due to CL segments, with an increase in melting point when oligomer length increases. Degree of crystallinity increases with length up to 2000 Da, and then a slight decrease takes place for oligomer with  $M_n$  = 4000 Da. When compared with commercial samples, degrees of CL crystallinity are alike for oligomers with similar chain lengths. In the case of oligomer with nominal  $M_n$  = 2000, used in the poly(urethane-urea) synthesis, melting temperature ( $T_m$ ) and CL segments crystallinity were slightly superior for the synthesized oligomer compared to that of commercial oligomer.

Tin(II) 2-ethylhexanoate, Sn(Oct)<sub>2</sub>, is the most widely used catalyst in the synthesis of polylactones [31,32]. A comparative study on the performance of Sn(Oct)<sub>2</sub> and ammonium decamolybdate anion was carried out using the following experimental conditions: bulk polymerization of CL (50 mmol) in the presence of DEG (CL/DEG = 20) as initiator at 150 °C for 25 min, using different CL/catalyst molar ratios (Table 3).

Polymerization of CL by Sn(Oct)<sub>2</sub> proceeded with high conversions (100%) with CL/Sn(Oct)<sub>2</sub> molar ratio = 200. However, the catalytic activity of Sn(Oct)<sub>2</sub> dramatically decreased when molar ratios of 2000 and 4000 were used. On the other hand, ammonium decamolybdate showed an optimal activity even though the amount of catalyst was very low (CL/catalyst = 20,000).

Using decamolybdate catalysis for the synthesis of HOPCLOH, a control of the final molecular weight can be exerted, and polymers with moderate polydispersity ( $M_w/M_n \leq 1.73$ ) can be obtained. Moderate PDIs are typical of decamolybdate system [23–25]. However, catalyst efficiency observed for decamolybdate is very good and higher than that observed for tin derivative systems. This is clearly seen

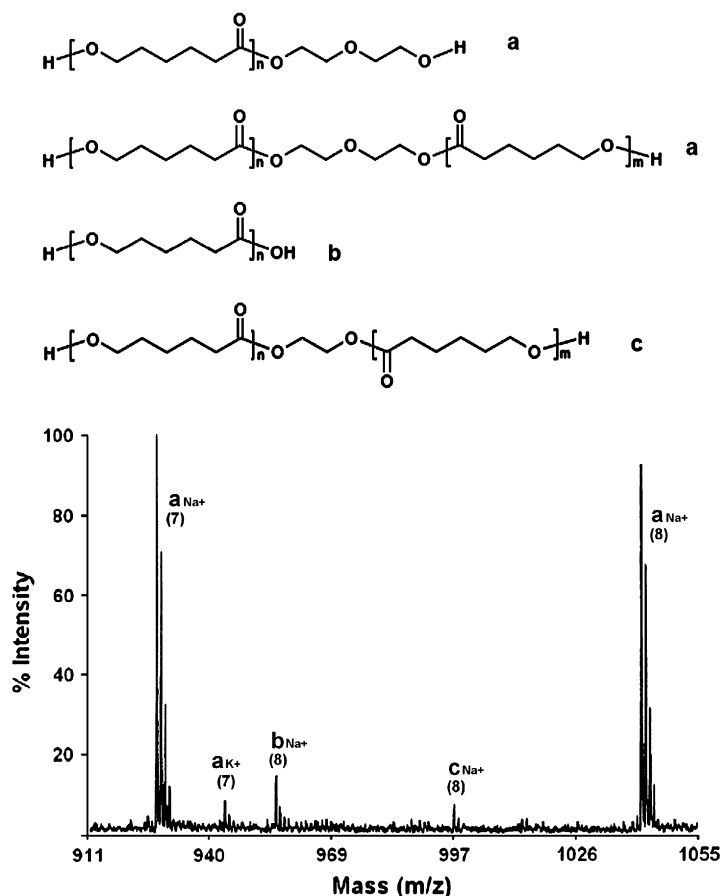


Fig. 5. MALDI-TOF spectrum of  $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diol (HOPCLOH) ( $M_n(\text{NMR}) = 534$ ). Expanded view of the 911–1055  $m/z$  fragments (reflectron mode). In brackets, the degree of polymerization (DP) is specified.

in Table 3, where effect of metal weight percent (Sn vs Mo) in polymerization is shown (no. 3 and 6). For a weight percent of 0.02, obtained CL conversion using molybdenum catalysis is 100%; instead, when this amount of tin catalyst is used, no polymerization occurs after several hours. Also, short reaction times are needed for molybdenum catalysis. These results demonstrate that decamolybdate is a very efficient catalyst for ROP of CL in the presence of diols such as DEG.

Table 3

Synthesis of  $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diol (HOPCLOH) by ring-opening polymerization of  $\epsilon$ -caprolactone (CL) with  $\text{Sn}(\text{Oct})_2$  and decamolybdate  $[\text{Mo}_{10}\text{O}_{34}]^{8-}$  as catalyst, in the presence of diethylene glycol (DEG) as initiator

No.	Catalyst	CL/catalyst	Weight of metal in reaction (%)	Conversion <sup>a</sup> (%)
1	$\text{Sn}(\text{Oct})_2$	200	0.48	100
2	$\text{Sn}(\text{Oct})_2$	2000	0.04	1
3	$\text{Sn}(\text{Oct})_2$	4000	0.02	0
4	$[\text{Mo}_{10}\text{O}_{34}]^{8-}$	200 <sup>b</sup>	2.67 <sup>b</sup>	100
5	$[\text{Mo}_{10}\text{O}_{34}]^{8-}$	2000 <sup>b</sup>	0.27 <sup>b</sup>	100
6	$[\text{Mo}_{10}\text{O}_{34}]^{8-}$	20,000 <sup>b</sup>	0.02 <sup>b</sup>	100

Polymerizations were carried out at 150 °C for 25 min, molar ratio CL/DEG = 20, 50 mmol of CL and 2.5 mmol of DEG.

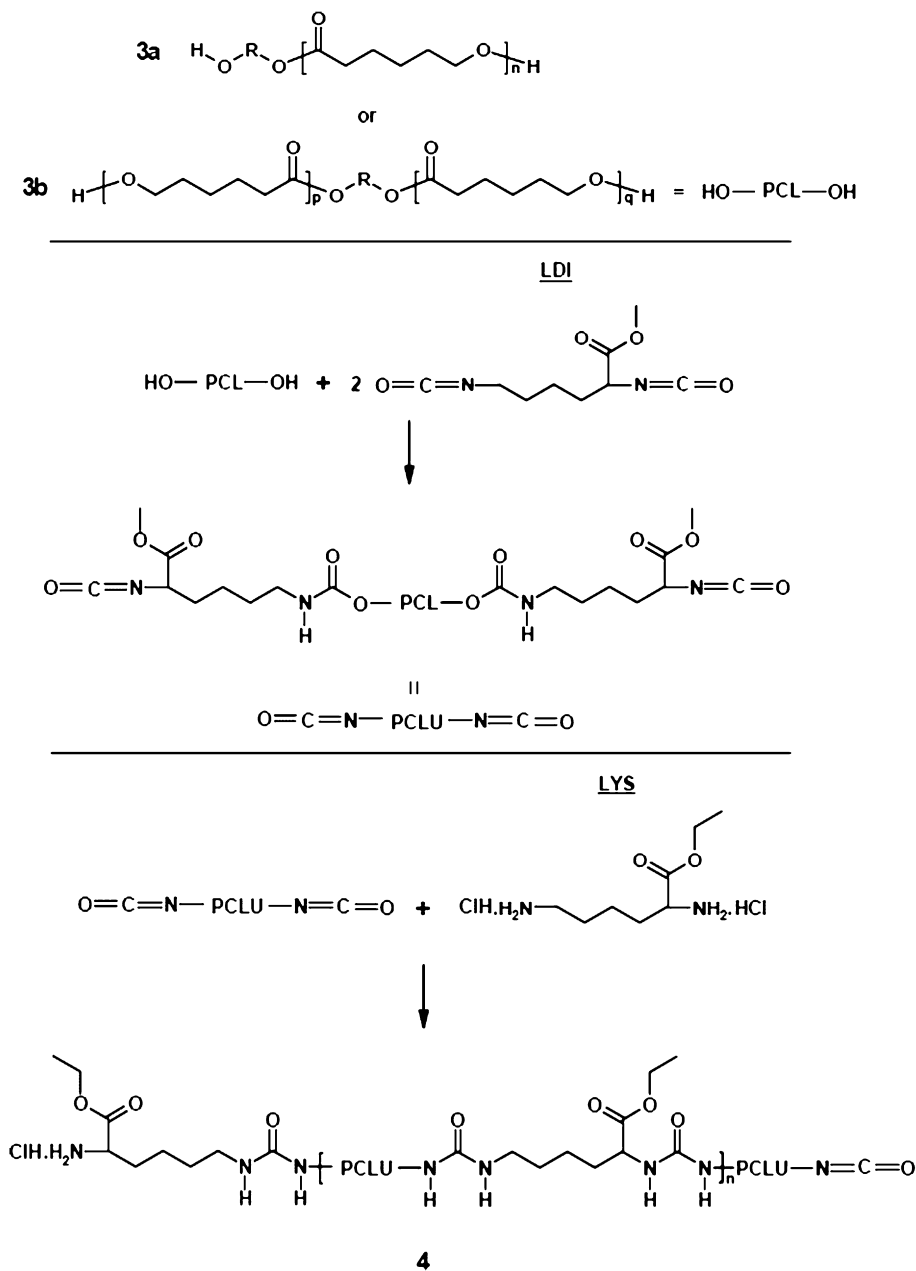
<sup>a</sup> Obtained by  $^1\text{H}$  NMR.

<sup>b</sup> Obtained from precursor feed, ammonium heptamolybdate  $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O}$ .

### 3.2. Synthesis of poly(ester-urethane-urea) 4

A poly(ester-urethane-urea) **4** derivative was prepared in order to test the usefulness of the synthesized diols as precursors for the synthesis of polyurethanes. Poly(ester-urethane-urea) [14] was synthesized by end-capping HOPCLOH with L-lysine diisocyanate (LDI), followed by a reaction with L-lysine dihydrochloride ethyl ester (LYS) (Scheme 2, see Section 2). Growth of the polymeric chain was observed by GPC ( $M_n(\text{GPC}) = 16,890$ ,  $M_w/M_n = 2.96$ ; vs.  $M_n(\text{GPC}) = 4360$ ,  $M_w/M_n = 1.56$  for HOPCLOH with  $M_n(\text{NMR}) = 2054$ ). In the FT-IR spectrum of HOPCLOH (Fig. 6A) bands at 2943, 1721 and 1187, corresponding to the stretching vibration of  $-\text{CH}_2-$ ,  $-\text{CO}-$  and  $-\text{COO}-$  groups, respectively, are seen. In Fig. 6B, FT-IR spectrum of poly(ester-urethane-urea) is depicted. Formation of urea is corroborated by the presence of a band at  $1652\text{ cm}^{-1}$ , corresponding to the  $-\text{CO}-$  stretching vibration of the urea group.

LDI and LYS were chosen as isocyanate and chain extender in order to obtain a biodegradable polymer, taking advantage of the lower toxicity of Mo. Also, a comparative study of the properties of the obtained polymer with those of the corresponding polymer synthesized from a commercial PCL diol [14] was pursued. Tin(II) octoate was used as catalyst.



Scheme 2. Synthesis of poly(ester-urethane-urea) **4** from  $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diols (HOPCLOH) **3a** and **3b**.

PCL segment crystallinity was reduced with respect to the PCL diol as a consequence of the decrease in mobility when hydroxyl end-groups are chemically substituted, but still a substantial amount of these groups was able to crystallize (around 31% of CL units, second DSC scan). Degree of crystallinity is approximately double than that observed for polymer prepared from commercial PCL diol (2000LYS). In Fig. 7, the curves for the second DSC scan for both polymers are displayed. In addition to a higher degree of crystallinity, the CL segments for the synthesized PCL diol melt at higher temperature and crystallize at lower temperatures. Polymer morphology for this polymer must induce a favorable environment for crystallization, and this also may be linked to the narrower molecular weight distribution of the PCL diol, as observed in the MALDI-TOF spectrum.

In Table 4, the mechanical properties of the prepared polymer and those for the corresponding polymer synthesized from commercial PCL diol are listed. In Fig. 8, the stress–strain curves are illustrated. From the results, it is evident that poly(ester-urethane-urea) is more rigid than 2000LYS, reaching a higher stress value at yield, a higher modulus and a lower strain value at break. It has been shown by DSC that poly(ester-urethane-urea) has a higher degree of crystallinity. This fact can be responsible for the observed differences in mechanical properties.

#### 4. Conclusions

We report the synthesis of  $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diols (HOPCLOH), obtained by ring-opening polymerization



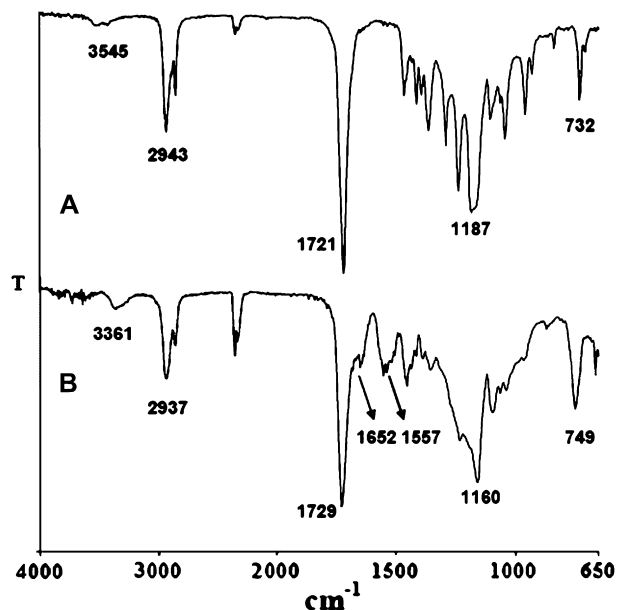


Fig. 6. FT-IR spectrum for (A)  $\alpha,\omega$ -telechelic poly( $\epsilon$ -caprolactone) diols (HOPCLOH) and (B) poly(ester-urethane-urea).

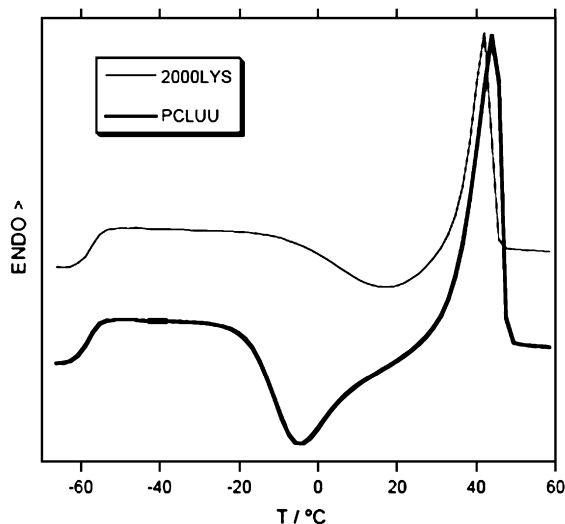


Fig. 7. DSC traces of the prepared poly(ester-urethane-urea) (PCLUU) polymer and of the polymer prepared from commercial PCL2000 (2000LYS, [14]).

of  $\epsilon$ -caprolactone (CL) with diethylene glycol (DEG) as initiator and ammonium decamolybdate as catalyst. This route involves lower amounts of ammonium decamolybdate catalyst, being catalysis efficient even at CL/catalyst molar ratio feed of 20,000. The molecular weight of HOPCLOH oligomers can be

Table 4  
Mechanical properties of the synthesized poly(urethane-urea) 4

Polymer	Stress at yield (MPa)	Strain at yield (%)	Stress at break (MPa)	Strain at break (%)	Modulus (MPa)
PCLUU	13.3 $\pm$ 0.3	12.4 $\pm$ 0.5	16.2 $\pm$ 0.5	1000 $\pm$ 30	242 $\pm$ 19
2000LYS <sup>a</sup>	9.3 $\pm$ 0.6	11.3 $\pm$ 1.8	34.0 $\pm$ 1.8	1460 $\pm$ 50	153 $\pm$ 13

<sup>a</sup> Corresponding polymer prepared from commercial PCL2000 (Aldrich). Data from Ref. [14].

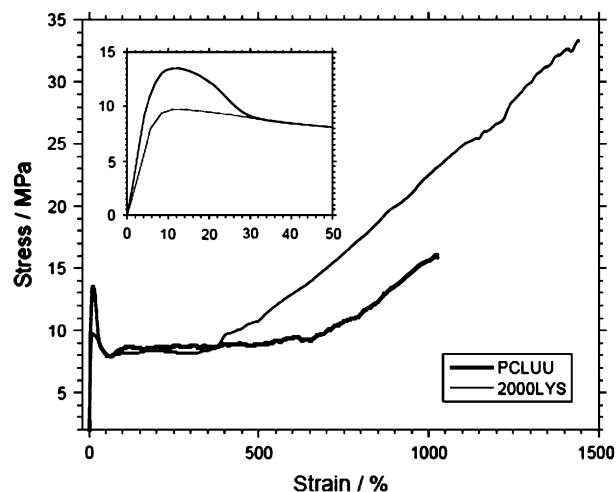


Fig. 8. Stress–strain graph for the prepared poly(ester-urethane-urea) (PCLUU) polymer and for the corresponding polymer prepared from commercial PCL2000 (2000LYS, [14]). In the inset, an expansion of the first part of the curves is shown.

controlled based on the initial CL/DEG ratio up to molecular weights of around 3600 Da. Comparative studies demonstrate that ammonium decamolybdate is a more efficient catalyst than tin(II) octanoate ( $\text{Sn}(\text{Oct})_2$ ), as lower amounts are needed to induce ROP of lactones. Presence of hydroxyl end-groups gives versatility to PCL, and allows the preparation of derivatives by the appropriate coupling reaction. In that regard, a high-molecular weight poly(ester-urethane-urea) was prepared from HOPCLOH, with similar properties to those recorded for a polymer obtained using commercial HOPCLOH.

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