Available online at www.sciencedirect.com
SCIENCE DIRECT
Polymer 46 (2005) 12118–12129
polymer
www.elsevier.com/locate/polymer

Synthesis and characterization of poly(ε-caprolactone) and copolyesters by catalysis with molybdenum compounds: polymers with acid-functional asymmetric telechelic architecture

José E. Báez, Antonio Martínez-Richa *

Facultad de Química, Universidad de Guanajuato, Noria Alta S/N, 36050 Guanajuato, Gto, México

Received 19 May 2005; received in revised form 13 October 2005; accepted 14 October 2005
Available online 8 November 2005

Abstract

Eight different molybdenum compounds were tested in the catalysts of ring-opening polymerization (ROP) of ε-caprolactone (CL). All homopolymerizations were conducted in bulk at 150 °C using a CL/molybdenum compound molar ratio of 200. Ammonium decamolybdate $(NH_4)_8[Mo_{10}O_{34}]$ comes to be the best catalyst for ROP, based on its selectivity, short reaction times (2 h) and high conversions (98%). Aliphatic copolyesters with acid-funtional asymetric telechelic architecture α-hydroxyl-ω-(carboxylic acid) (HA) were synthesized from lactones -such as CL, δ-valerolactone (VL) and γ-butyrolactone (BL)- by ring-opening copolymerization. HA-copolyesters, namely HA-poly(ε-caprolactone-*co*-γ-butyrolactone) (HA-PCB), HA-poly(δ-valerolactone-*co*-γ-butyrolactone) (HA-PVB) and HA-poly(ε-caprolactone-*co*-δ-valerolactone) (HA-PCV), were obtained at 150 °C in 2 h using ammonium decamolybdate as catalyt and water as initiator. A control of the degree of polymerization (DP, measured by NMR) can be achieved in the range between 6 and 24 for HA-PCB and HA-PCV, based on the initial monomer/initiator ratio. DP shows a linear dependence with M/H_2O ratio (where M = CL + (BL or VL)) in this range. The nature of hydroxyl and carboxylic acid end groups of HA-copolyesters was determined by ^1H and ^{13}C NMR. Finally, HA-poly(ε-caprolactone-*block*-δ-valerolactone) (HA-PCbV) was successfully prepared by sequential copolymerization of HA-poly(ε-caprolactone) with VL and characterized by ^1H and ^{13}C NMR, GPC and MALDI-TOF.

Keywords: Ring-opening polymerization; Decamolybdate anion; Aliphatic copolyesters from lactones

1. Introduction

Ring-opening polymerization of lactones provides a convenient route to obtain biodegradable aliphatic polyesters, being poly(ε-caprolactone) (PCL) the most important member of this family. In the case of copolymers derived from CL such as poly(ε-caprolactone-*co*-δ-valerolactone) (PCV) and poly(ε-caprolactone-*co*-γ-butyrolactone) (PCB), the appearance of new physical properties and the observance of a higher rate of degradation make them amenable for tailored applications as biodegradable materials [1,2]. Storey et al. have synthesized poly(ε-caprolactone-*co*-δ-valerolactone) (PCV) copolymer by ring-opening polymerization (ROP) of CL with δ-valerolactone (VL) initiated with stannous octoate [1]. PCB has also been synthesized by ring-opening copolymerization of CL with γ-butyrolactone (BL) using samarium derivatives as catalysts [3–5].

One of the factors that accelerate PCL degradation is the percentage of acidic end groups present in the polyester. Carboxylic acid end groups show a higher hydrophilic character than ester groups. At the same time, biodegradability of polylactones increases as the content of –COOH groups is higher [6]. Some examples found in the recent literature follow: (1) polylactide [7] and poly(trimethylene carbonate) [8] with carboxylic acid end groups; (2) block copolymer of CL and 2-methyl-2-carboxyl-propylene carbonate, with pendant carboxyl groups [9].

Molybdenum is a versatile element present in many catalytic systems used for polymerization, such as those utilized for the polymerization of norbornenes [10,11] and phenylacetylene [12]. However, there are few reports related to the use of molybdenum derivatives in ROP of lactones. In that sense, it has been reported that Mo(VI) acetylacetonate and tetrapropoxide $Mo(OPr)_4$ produce high molecular weight

* Corresponding author. Tel./fax: +52 473 7320006x8111.
E-mail address: richa@quijote.ugto.mx (A. Martínez-Richa).

0032-3861/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2005.10.076

polyesters with high conversions [13]. Molybdenum is also 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 relies on molybdenum, which is usually absorbed in the form of molybdate anion, $[MoO_4]^{2-}$ [14].

End-group functionalization of polymers has been investigated in order to induce new properties such as biocompatibility [15] and hydrophilicity [16]. Recently, research efforts in our group have been focused on the synthesis and characterization of PCL and poly(δ-valerolactone) (PVL) using catalysis with ammonium decamolybdate $(NH_4)_8[Mo_{10}O_{34}]$. Effectiveness of primary alcohols as initiators/chain transfer agents is an important feature of this polymerization process. Final polymers contain ester (RO–CO–) and hydroxyl end-groups. In this way, different ester end-groups can be created, depending on the nature of the alcohol [17].

Hedrick and co-workers carried out the synthesis of asymmetric acid-functional α-hydroxyl-ω-carboxylic acid PCL (HA-PCL) by hydrogenolysis of benzyl esters [18]. However, this synthetic route involves a two-step process in order to obtain HA-PCL's. Stevels and co-workers prepared PCL's functionalized with carboxylic acid end-group from the reaction of hydroxyl terminated PCL's with succinic anhydride [19]. On the other hand, if water is used as initiator/chain transfer agent in the catalysis with decamolybdate anion, HA-PCL with controlled molecular weight can be obtained by a one-step synthetic method. As final polymers possess an asymmetric architecture, having a hydrophilic carboxylic acid end-group, they are bifunctional polymers able to further react to produce a variety of useful derivatives [20].

We report herein a comparative study of the catalytic behavior of eight different molybdenum compounds (all with Lewis acid character) to ROP of CL. The scope of the ring-opening polymerization of lactones (CL, VL and BL) using decamolybdate ammonium is presented and discussed. When water is used as initiator/chain-transfer agent, an asymmetric telechelic α-hydroxyl-ω-(carboxylic acid) copolyester with controlled molecular weight can be obtained using an efficient one-step route. To our knowledge, this is the first report on the synthesis of acid-functional asymmetric telechelic copolyesters derived from lactones. Final polymers and copolymers were characterized by FT-IR, ^{1}H and ^{13}C NMR, GPC and MALDI-TOF.

2. Experimental

2.1. Materials

CL (Aldrich Chemicals Co.), BL (Aldrich) and VL (Fluka) were dried over calcium hydride and distilled under reduced pressure before used. Distilled water was purchased from Baker. $MoCl_3$, $MoCl_5$, $MoBr_3$, MoO_2Cl_2, MoO_2, MoO_3, and $Na_2MoO_4 \cdot 2H_2O$ were purchased from Aldrich and used without further purification. Ammonium heptamolybdate tetrahydrate $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (Hep) (Fluka) was grounded in a mortar and passed through a 100 mesh sieve before used [17].

2.2. Hopolymerization of CL by molybdenum compounds

Polymerizations were carried out in 5 mL vials previously dried and purged with dry nitrogen. In a typical run, monomer (CL, 50 mmol), molybdenum compounds (CMo) and CL (molar ratio CL/CMo = 200) were added under nitrogen atmosphere. Vials were stoppered with a rubber septum and placed in a thermostated bath at 150 °C. In the case of the Ammonium decamolybdate $(NH_4)_8[Mo_{10}O_{34}]$ (Dec), catalyst is formed in situ at this temperature by thermal decomposition of ammonium heptamolybdate $(NH_4)_6[Mo_7O_{24}]$ (Hep) [17]. Final polymer was crystallized from chloroform/methanol and dried under vacuum. Conversion and molecular weight was monitored by ^{1}H NMR. The crystallized polymer was analyzed by MALDI-TOF.

2.3. Synthesis of α-hydroxylic-ω-(carboxylic acid) poly (ε-caprolactone-co-γ-butyrolactone) (HA-PCB) random copolymer

Copolymerizations were carried out in 5 mL vials previously dried and purged with dry nitrogen. In a typical run, ε-caprolactone (CL, 23.75 mmol), γ-butyrolactone (BL, 23.7 mmol), catalyst (Hep, 3 mg) and water (2.5 mmol) were added under nitrogen atmosphere. Vials were stoppered with a rubber septum and placed in a thermostated bath at 150 °C for 2 h. Final copolymer was recrystallized from chloroform/-methanol and dried under vacuum. Crystallized copolymer was also analyzed by FT-IR, ^{1}H and ^{13}C NMR. IR(cm^{-1}): 2942 (ν_{CH}), 1720 ($\nu_{C=O}$), 1166 ($\delta_{O-C=O}$). NMR data for HA-PCB copolymer: ^{1}H NMR (300 MHz, $CDCl_3$, ppm) (Fig. 5): δ 4.12 (t, 2H, [–CH_2O–], BL), 4.06 (t, 2H, [–CH_2O–], CL), 3.68 (t, 2H, [–CH_2OH], BL), 3.64 (t, 2H, [–CH_2OH], CL), 2.39 (t, 2H, [–CH_2CO_2–], BL), 2.31 (t, 2H, [–CH_2CO_2–], CL), 1.96 (q, 2H, [–CH_2–], BL), 1.65 (m, 4H, [–$(CH_2)_2$–], CL), 1.38 (q, 2H, [–CH_2–], CL). ^{13}C NMR (50 MHz, $CDCl_3$, ppm) (Fig. 7): δ 176.80 (a), 173.60 (j), 173.41 (g), 173.25 (s), 172.70 (1), 64.19 (r), 63.96 (f), 63.14 (4), 62.29 (q), 61.68 (5), 34.04 (k), 33.92 (h), 33.83 (t), 33.46 (b), 32.08 (p), 30.58 (2), 28.14 (e), 25.33 (d), 25.12 (m), 24.50 (l), 24.38 (i), 24.18 (c), 23.87 (3).

2.4. Synthesis of α-hydroxylic-ω-(carboxylic acid) poly (δ-valerolactone-co-γ-butyrolactone) (HA-PVB) random copolymer

This copolymer was prepared and isolated in the same manner as described in the HA-PCB synthesis section. Crystallized copolymer was also analyzed by FT-IR, ^{1}H and ^{13}C NMR. IR (cm^{-1}): 2955 (ν_{CH}), 1723 ($\nu_{C=O}$), 1166 ($\delta_{O-C=O}$). NMR data for HA-PVB copolymer: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 4.08 (t, 2H, [–CH_2O–], BL), 4.06 (t, 2H, [–CH_2O–], VL), 3.66 (t, 2H, [–CH_2OH], BL), 3.63 (t, 2H, [–CH_2OH], VL), 2.36 (t, 2H, [–CH_2CO_2–], BL), 2.32 (t, 2H, [–CH_2CO_2–], VL), 1.93 (q, 2H, [—(CH_2)–], BL), 1.65 (m, 4H, [–$(CH_2)_2$–], VL). ^{13}C NMR

(50 MHz, $CDCl_3$, ppm): δ 176.8, 173.53, 173.11, 172.99, 172.64, 63.87, 63.72, 63.20, 61.89, 61.63, 33.70, 33.49, 33.11, 31.79, 30.54, 27.86, 23.84, 21.23, 21.07, 20.97.

2.5. Synthesis of α-hydroxylic-ω-(carboxylic acid) poly (ε-caprolactone-co-δ-valerolactone) (HA-PCV) random copolymer

This copolymer was prepared and isolated in the same manner as described in the HA-PCB synthesis section. Crystallized copolymer was also analyzed by ^1H and ^{13}C NMR. NMR data for HA-PCV copolymer: ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 4.08 (t, 2H, [–CH_2O–], VL), 4.06 (t, 2H, [–CH_2O–], CL), 3.65 (t, 2H, [–CH_2OH], VL), 3.64 (t, 2H, [–CH_2OH], CL), 2.31 (t, 2H, [–CH_2CO_2–], CL), 2.33 (t, 2H, [–CH_2CO_2–], VL), 1.65 (m, 4H, [–$(CH_2)_2$–], CL), 1.60 (m, 4H, [–$(CH_2)_2$–], VL), 1.38 (q, 2H, [–CH_2–], CL).

2.6. Synthesis of α-trifluoroacetate-ω-(trifluoroacetanhydride) PCB (TF-PCB), trifluoroacetate-ω-(trifluoroacetanhydride) PVB (TF-PVB) and α-trifluoroacetate-ω-(trifluoroacetanhydride) PCV (TF-PCV) by derivatization of HA-PCB, HA-PVB and HA-PCV with trifluoroacetic anhydride (TFA)

An excess amount of TFA was added to a solution of HA-PCB in $CDCl_3$ (100 mg/0.75 mL) at ambient temperature. Full derivatization of the sample was confirmed by NMR. NMR data for TF-PCB: ^1H NMR (300 MHz, $CDCl_3$, ppm) (Fig. 6): δ 4.41 (t, 2H, [–CH_2OCOCF_3], BL), 4.36 (t, 2H, [–CH_2-$OCOCF_3$], CL), 4.12 (t, 2H, [–CH_2O–], BL), 4.08 (t, 2H, [–CH_2O–], CL), 2.65 (t, 2H, [–$CH_2CO_2COCF_3$], CL), 2.41 (t, 2H, [–CH_2CO_2–], BL), 2.33 (t, 2H, [–CH_2CO_2–], CL), 1.97 (q, 2H, [–CH_2–], BL), 1.66 (m, 4H, [–$(CH_2)_2$–], CL), 1.39 (q, 2H, [–CH_2–], CL). NMR data for TF-PVB: ^1H NMR (300 MHz, $CDCl_3$, ppm) (Fig. 8): δ 4.38 (t, 2H, [–CH_2OCOCF_3], BL), 4.34 (t, 2H, [–CH_2OCOCF_3], VL), 4.12 (t, 2H, [–CH_2O–], BL), 4.08 (t, 2H, [–CH_2O–], VL), 2.70 (t, 2H, [–$CH_2CO_2COCF_3$], BL), 2.66 (t, 2H, [–$CH_2CO_2COCF_3$], VL), 2.40 (t, 2H, [–CH_2CO_2–], BL), 2.35 (t, 2H, [–CH_2CO_2–], VL), 1.95 (q, 2H, [–CH_2–], BL), 1.67 (m, 4H, [–$(CH_2)_2$–], VL). NMR data for TF-PCV: ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 4.37 (t, 2H, [–CH_2OCOCF_3], VL), 4.36 (t, 2H, [–CH_2OCOCF_3], CL), 4.09 (t, 2H, [–CH_2O–], VL), 4.08 (t, 2H, [–CH_2O–], CL), 2.69 (t, 2H, [–CH_2CO_2-$COCF_3$], VL), 2.65 (t, 2H, [–$CH_2CO_2COCF_3$], CL), 2.35 (t, 2H, [–CH_2CO_2–], VL) 2.34 (t, 2H, [–CH_2CO_2–], CL), 1.66 (m, 4H, [–$(CH_2)_2$–], CL), 1.39 (q, 2H, [–CH_2–], CL).

2.7. Synthesis of α-hydroxylic-ω-(carboxylic acid) poly (ε-caprolactone-block-δ-valerolactone) (HA-PCbV) by copolymerization with comonomer feeding sequentially

Polymerizations were carried out in 10 mL vials previously dried and purged with dry nitrogen. In a typical run, ε-caprolactone (CL, 47.5 mmol), catalyst (Hep, 3 mg) and H_2O (2.5 mmol) were added under nitrogen atmosphere. Vials were stoppered with a rubber septum and placed in a thermostated bath at 150 °C for 2 h. After 2 h of reaction, δ-valerolactone (VL, 47.5 mmol) were injected on the vial using a syringe under nitrogen atmosphere. The mixture was vigorously stirred and placed in a thermostated bath at 150 °C by 2 h. Final polymer was recrystallized from chloroform/-methanol and dried under vacuum. Crystallized copolymer was also analyzed by ^1H and ^{13}C NMR and MALDI-TOF. NMR data for HA-*P*CbV copolymer: ^{13}C NMR (50 MHz, $CDCl_3$, ppm) (Fig. 10): δ 176.28 (a), 173.48 (j), 173.33 (g), 173.06 (g′), 63.92 (f), 63.70 (e′), 63.61 (e″), 62.25 (q), 61.89 (q′), 33.90 (h), 33.70 (k), 33.47 (h′), 33.39 (b), 31.83 (m), 28.12 (e), 27.86 (d′), 25.31 (d), 24.35 (i), 24.17 (c), 21.22 (i′), 20.97 (l).

2.8. Measurements

Solution ^1H and ^{13}C NMR spectra were recorded at room temperature on a Varian Gemini 200 (200 MHz ^1H and 50 MHz ^{13}C) and Varian Unity Plus 300 (300 MHz ^1H and 75.47 MHz ^{13}C). Chloroform-*d* ($CDCl_3$) was used as the solvent. Spectra were referenced to the residual solvent protons at δ 7.26 for $CDCl_3$ in the ^1H NMR spectrum, and the residual solvent carbons at δ 77.0 for $CDCl_3$ in the ^{13}C NMR spectrum. Number-average molecular weight (measured by NMR) was obtained from the equation $M_n(NMR) = (M_w(M)DP(NMR)) + M_w(H_2O)$; $DP(NMR) = I_{pol}/I_{ter} + 1$, where M_w is the molecular weight of lactone monomer or water. I_{pol} and I_{ter} represent the integrals obtained by ^1H NMR from the polymer (4.0 ppm [–CH_2O–]) and hydroxyl end group (3.6 ppm [–CH_2OH]) peaks, respectively. GPC measurements were made in a Waters model 1525 at 40 °C. THF was used as the mobile phase at a flow rate of 1 mL min^{-1}. Commercial polystyrene standards were employed for calibrations to calculate the molecular weight of polyesters. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectra were recorded in the linear mode by using 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.

3. Results and discussion

3.1. Homopolymerization of CL by molybdenum compounds

We have previously reported that ammonium decamolybdate $(NH_4)_8[Mo_{10}O_{34}]$ (Dec) is able to successfully effect and sustain the ring-opening polymerization (ROP) of lactones such as ε-caprolactone (CL) and δ-valerolactone (VL). End-groups functionalization and control of number-average molecular weight (M_n) can be achieved using the appropriate initiator/transfer agent system [17,20]. However, it is convenient to compare the catalytic activity of ammonium decamolybdate with respect to other molybdenum derivatives. With this in mind, experiments were carried out in order to

Table 1
Ring-opening polymerization of the ε-caprolactone (CL) catalyzed by different molybdenum compounds

No.	Molybdenum compound	*t* (*h*)	Conv. (%)[a]
1	$(NH_4)_8[Mo_{10}O_{34}]$[b]	2	98
2	Na_2MoO_4	24	55
3	MoO_3	48	58
4	MoO_2	48	81
5	MoO_2Cl_2	0.4	92
6	$MoCl_5$	0.5	94
7	$MoCl_3$	0.5	52
8	$MoBr_3$	5	62

Bulk polymerization were carried out at 150 °C, a CL/molybdenum compound molar ratio of 200 (with 50 mmol of CL) was used.

[a] Obtained from the equation conv.(%) = $(I_{pol}/I_{mon}+I_{pol})\times 100$, where I_{pol} and I_{mon} represent the integrals by ^{1}H NMR from the polymer (4.0 ppm [–CH_2O–]) and monomer (4.1 ppm [–CH_2O–]) peaks.

[b] Obtained in situ by thermal descomposition of ammonium heptamolybdate $(NH_4)_6[Mo_7O_{24}]$.

compare the effectiveness of Dec with respect to molybdenum chloride, bromide and oxides.

A series of experiments was carried out using the following experimental conditions: bulk polymerization of CL (50 mmol) by different molybdenum derivatives (CMo), using a CL/CMo molar ratio of 200 at 150 °C (Table 1). It is expected that a good catalyst for ROP leads to short reaction times (0.5–3 h), selectivity and quantitative conversions.

Polymerization of CL by $MoCl_5$ (No. 6) proceeded with high conversion (94%) and short reaction times (ca. 0.5 h). On the other hand, in the same period of time (0.5 h), lower conversion (52%) was observed when $MoCl_3$ was used. This result can be attributed to the harder Lewis acid power of molybdenum in $MoCl_5$. A similar behavior was observed for $MoBr_3$. Fig. 1(A) shows the ^{1}H NMR spectrum for the end-group zone (δ 3.3–3.7) for PCL obtained when $MoCl_5$ is used. Peaks correspond to different end-groups (Scheme 1): (1) a singlet corresponding to a methoxy end-group –CO–O–CH_3 (a, δ 3.65 ^{1}H and 51.3 ^{13}C). This methoxy end group comes from methanol, which was used for recrystallization of the polymer. Acylation of methanol apparently requires the presence of an acid chloride end group (R–CO–Cl) in the original polymer chains, (2) –CH_2–OH (b, δ 3.63 ^{1}H and 62.2 ^{13}C) formed by reaction with water [21], (3) –CH_2–Cl (c, δ 3.52 ^{1}H and 44.5 ^{13}C) formed by chlorination of methylene attached to oxygen [22], (4) –CH_2–O–CH_2– (d, δ 3.37 ^{1}H and 70.4 ^{13}C) probably formed by a nucleophilic attack of an alkoxide to the methylene in the epsilon position of CL [23]. Also, peaks for olefinic protons –CH=CH_2 (δ 5.75 and 4.98) due to a dehydration reaction of hydroxyl end groups were observed. Final polymer shows broad polydispersity, as determined by GPC analysis (M_n(GPC) = 6740, M_w/M_n = 2.28). This observation suggests that parallel reactions (such as those leading to the formation of ether linkages) are responsible for observed broad polydispersity. It has been reported that $MoCl_5$ provide an efficient catalyst system in the C–O bond cleavage reaction of ethers [23].

MALDI-TOF spectrum shows the formation of cyclic species, as a consequence of backbiting degradation. This feature is observed for all halide derivatives studied (No. 5–8).

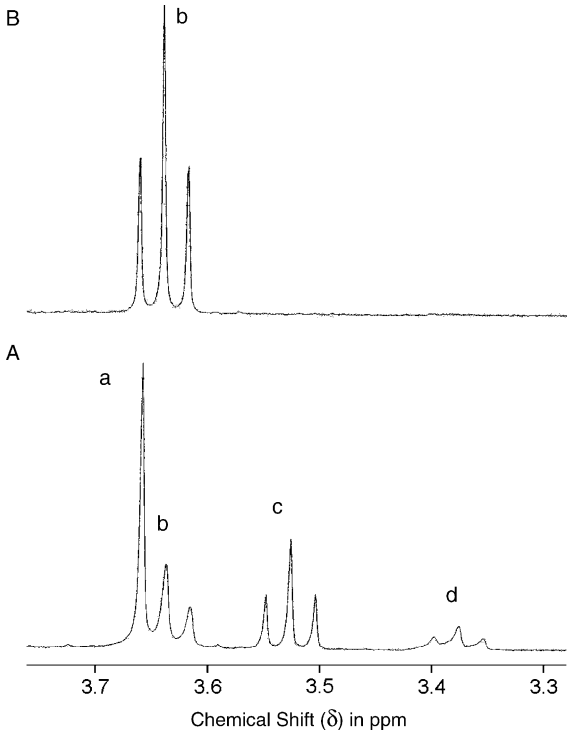
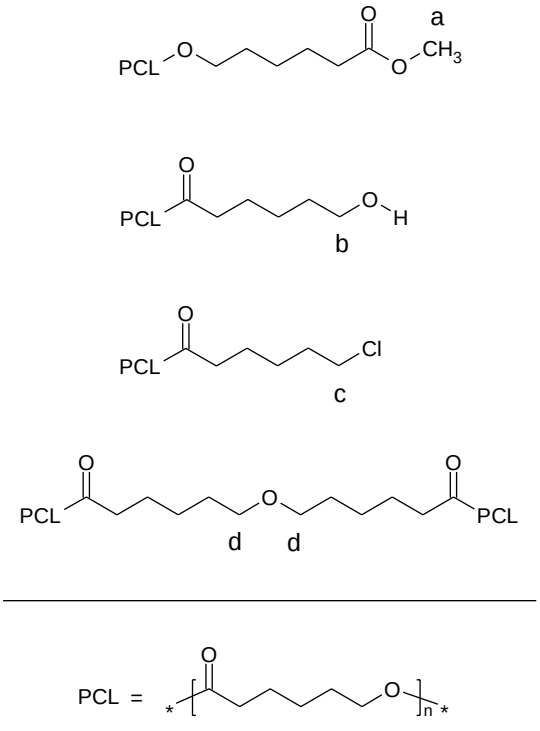


Fig. 1. Three hundred megahertz ^{1}H NMR spectra for poly(ε-caprolactone) PCL in $CDCl_3$. Expanded zone for the end-groups is shown. Polymers were obtained by catalysis with (A) $MoCl_5$ (No. 6, Table 1, Scheme 1), a (–CO–OCH_3), b (–CH_2OH), c (–CH_2Cl), d (–CH_2–O–CH_2–), and (B) Na_2MoO_4 (No. 2, Table 1), b (–CH_2OH).

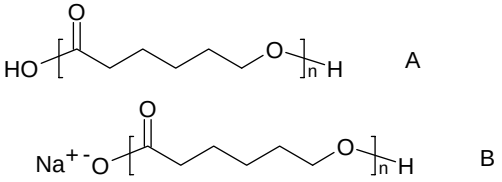


Scheme 1. Different functional groups observed for poly(ε-caprolactone) PCL obtained by ROP of CL catalyzed by $MoCl_5$ (Fig. 1).

In general, reaction times using molybdenum halides derivatives to get quantitative conversions are short (0.4–5 h). However, many side reactions occur in all cases and the polymerization is non-selective.

Other family of molybdenum compounds that shows a high Lewis acid character is that of oxides derivatives (Table 1, no. 3 and 4). End-group analysis by ^{1}H NMR indicates that the formation of asymmetric telechelic α-hydroxyl-ω-(carboxylic acid) PCL (HA-PCL) is mainly achieved when these catalysts are used. However, observed reaction times to obtain quantitative conversions are relatively long (ca. 48 h). As in the case of oxides, molybdates also have oxygens in the chemical structure that are chemically bonded to molybdenum. Catalysis by sodium molybdate (Na_2MoO_4) shows selectivity to the formation of HA-PCL (Fig. 1(B)). However, for reactions times in the order of 24 h, only a 55% conversion is attained. In Fig. 2(a), a unimodal distribution is observed for a polymer with M_n(MALDI) = 3690, M_n(NMR) = 3880. In a previous article, it was demonstrated that molecular weight obtained by NMR is lower than that obtained by GPC (for calibration curve obtained using polystyrene standards) [17]. However, M_n obtained by NMR is close to that measure by MALDI-TOF. This technique is more sensitive to low-molecular weights species, so better information can be derived for this polymer from MALDI-TOF compared to that obtained with GPC [20].

In Fig. 2(b), an expansion of the zone between 2726 and 3307 uma is shown. This region corresponds to fragments with 24–26 CL repeating units. The most intense peaks are due to HA-PCL (structure **A**) fragments. A series of weak peaks was found to originate from the sodium salt (structure **B**). Both series are doped with sodium ions. The species **B** in the MALDI-TOF spectrum must have been formed in situ during MALDI sample preparation. In contrast with PCL obtained with $MoCl_5$, final polymer obtained with Na_2MoO_4 shows moderate polydispersity, as determined by GPC analysis (M_n(GPC) = 6800, M_w/M_n = 1.28).



In contrast with molybdate anion MoO_4^{-2}, CL polymerization by decamolybdate anion $Mo_{10}O_{34}^{-8}$ (Dec) (formed in situ by thermal conversion of ammonium heptamolybdate $(NH_4)_6[Mo_7O_{24}]$ (Hep) at 150 °C [17,24,25]) showed high conversions (98%) in a short reaction time (2 h, No. 1, Table 1). Selectivity in the formation of HA-PCL was confirmed by ^{1}H and ^{13}C NMR and MALDI-TOF. In Fig. 3(a), MALDI-TOF spectrum of HA-PCL obtained by catalysis with decamolybdate is shown. A broader curve

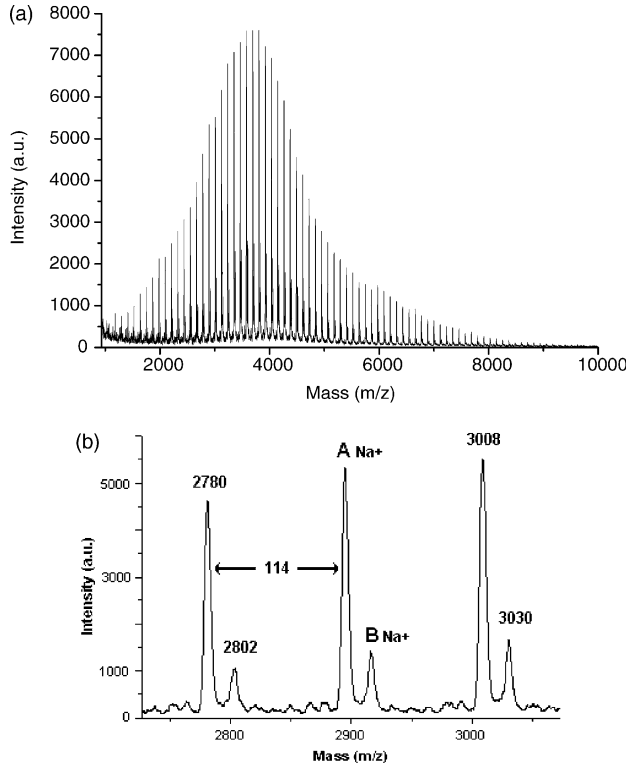


Fig. 2. (a) MALDI-TOF spectrum of the HA-PCL (M_n(NMR) = 3880, M_n(MALDI) = 3690) catalyzed by molybdate (MoO_4^{2-}), t = 24 h. (b) Expanded view for the 2726–3074 m/z fragments.

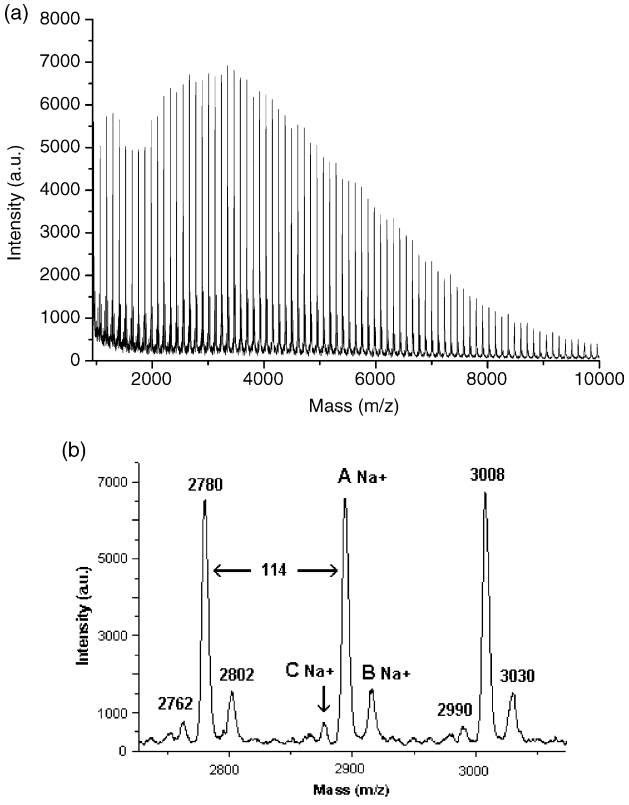
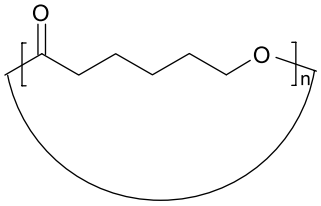


Fig. 3. (a) MALDI-TOF spectrum of the HA-PCL (M_n(NMR) = 4400) obtained by catalysis with decamolybdate anion ($Mo_{10}O_{34}^{8-}$), t = 2 h. (b) Expanded view for the 2726–3074 m/z fragments.

compared to that obtained for HA-PCL synthesized using sodium molybdate is seen. This profile is due to the difference in the number of active species, as $Mo_{10}O_{34}^{-8}$ has 10 active species that potentially can initiate ROP. Curve profiles also reflect differences in catalytic activity between octahedral and tetrahedral species.



C

In Fig. 3(b), the same species observed in the spectrum of the polymer obtained using sodium molybdate, along with macrocyclic species (structure C), are seen. This feature indicates that intramolecular condensation reactions are occurring during CL polymerization by decamolybdate. Molybdates such as sodium molybdate are used as ester-exchange and polycondensation catalysts [26]. Due to this behavior, it is clear that Dec shows the highest reactivity toward ROP of lactones, compared to the other set of molybdenum derivatives hereby studied.

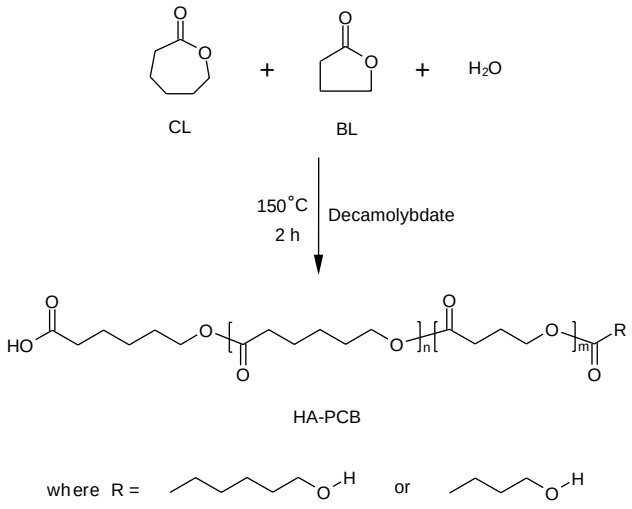
When water is used as initiator in the ROP of CL, production of asymmetric telechelic α-hydroxyl-ω-(carboxylic acid) PCL (HA-PCL) is anticipated. However, not all the catalysts can tolerate the presence of water, for example: (1) aluminum isopropoxide ($Al(O\text{-}iPr)_3$) catalyst was hydrodegraded by water, obtaining an Al compound without polymerization activity to CL [27]; (2) tin octoate (tin(II) 2-ethylhexanoate, ($Sn(Oct)_2$)) in the presence of water leads to the formation of macrocyclic species of PCL [28]. In contrast, in the catalysis with molybdate (MoO_4^{2-}) and decamolybdate ($Mo_{10}O_{34}^{8-}$), hydration water present in the catalysts ($Na_2MoO_4\cdot 2H_2O$ and $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$) acts as initiator/chain transfer agent, leading to the formation of HA-PCL.

Based on the observed selectivity, short reaction times (ca. 2 h) and good yields (98%) obtained when Dec is used as catalyst, we can conclude that $Mo_{10}O_{34}^{-8}$ is the best choice among the other molybdenum derivatives studied to be used in ROP of CL.

Table 2
Copolymerization of CL with BL catalyzed by decamolybdate anion

No.	Ratio feed CL/BL (%)	Unit ratio[a] CL/BL (%)	Conv. (%)[a]	DP(NMR)[a]
1	95/5	99/1	96	490
2	90/10	98/2	88	340
3	80/20	96/4	86	200
4	70/30	95/5	77	150
5	60/40	93/7	70	130
6	50/50	90/10	58	110

Bulk copolymerization were carried out at 150 °C for 2 h (without addition of H_2O), M/Hep = 20,000.
[a] Obtained by ^1H NMR.



Scheme 2. Copolymerization of ε-caprolactone (CL) and γ-butyrolactone (BL) catalyzed by decamolybdate anion in the presence of H_2O. Synthesis of the α-hydroxyl-ω-(carboxyl acid) poly(ε-caprolactone-*co*-γ-butyrolactone) (HA-PCB).

3.2. α-Hydroxylic-ω-(carboxylic acid) poly(ε-caprolactone-co-γ-butyrolactone) (HA-PCB) asymmetric telechelic copolyester

Copolymerization of lactones was studied using decamolybdate anion (Dec) as catalyst, by the above mentioned reasons. As expected, γ-butyrolactone (BL) does not homopolymerize after 2 h in the presence of Dec (reaction conditions: temperature = 150 °C (BL/Hep = 19,000, $BL/H_2O = 20$)). It is well known that, in contrast with CL, VL and other lactones and lactides, polymerization of BL is very difficult to achieve due to thermodynamic considerations. Low yields and oligomers have been reported for PBL when non-extreme reaction conditions are used [29]. It has been reported that some organolanthanides form adducts with BL [30], and in some cases linear diolate

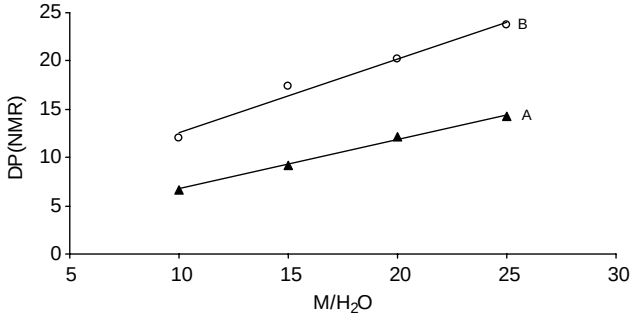


Fig. 4. Dependence of DP(NMR) on M/H_2O ratio for the copolymerization of (A) ε-caprolactone (CL) with the γ-butyrolactone (BL) where M = CL + BL with CL:BL ratio molar of 50:50, and (B) ε-caprolactone (CL) with the δ-valerolactone (VL) where M = CL + VL with CL:VL ratio molar of 80:20. Polymerizations were catalyzed by decamolybdate anion in the presence of H_2O at 150 °C by 2 h.

Table 3
Ring-opening copolymerization de CL with BL catalyzed by decamolybdate anion

No.	M/H_2O	DP(NMR)[a]	DP(NMR)[a,b]	M_n(GPC)[c]	M_w/M_n[c]	%BL[a]	Conv. (%)[a]
1	10	6.7	11.1	2900	1.32	10	48
2	15	9.2	13.5	–	–	10	48
3	20	12.1	18.5	4310	1.52	10	47
4	25	14.3	21.0	–	–	10	47

Effect of M/H_2O ratio on DP(NMR). Bulk copolymerizations were carried out at 150 °C for 2 h, M/Hep = 19,000 where M = CL + BL = 47.5 mmol, a CL:BL molar ratio of 50:50 was used.

[a] Determined by ^{1}H NMR.

[b] After recrystalization with chloroform/methanol.

[c] Determined by gel permeation chromatography (GPC) using polystyrene standards.

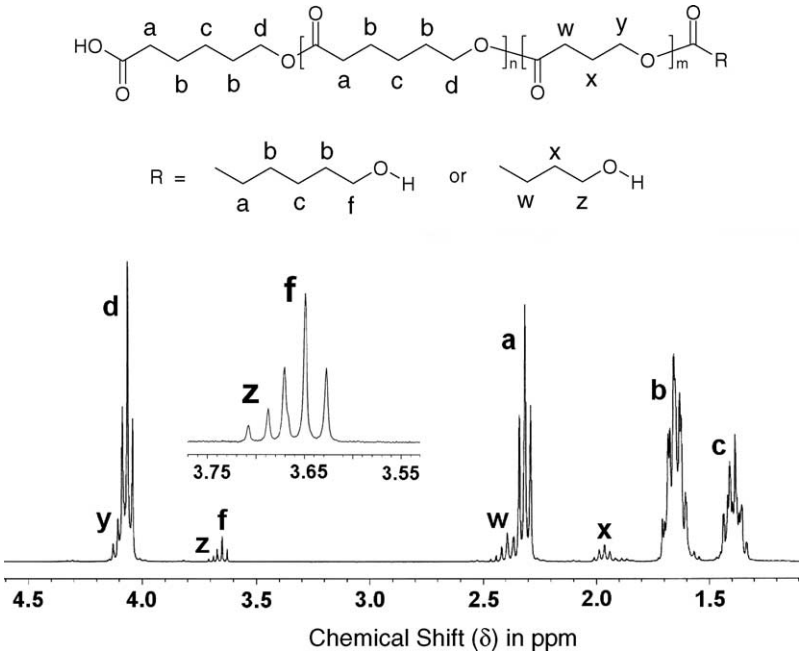


Fig. 5. Three hundred megahertz ^{1}H NMR spectrum for the α-hydroxyl-ω-(carboxyl acid) poly(ε-caprolactone-*co*-γ-butyrolactone) (HA-PCB) in $CDCl_3$, DP(NMR) = 21 with 10% in mol of BL.

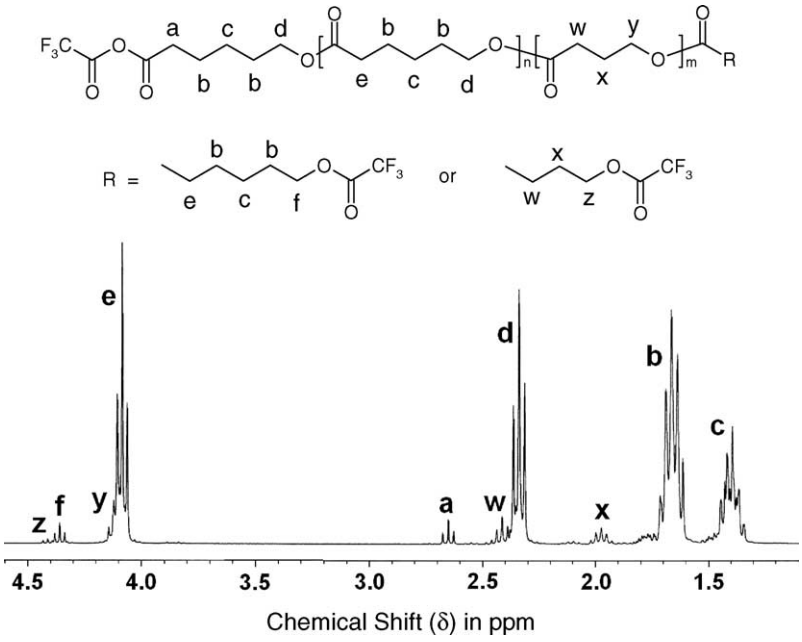


Fig. 6. Three hundred megahertz ^{1}H NMR spectrum for the α-hydroxyl-ω-(carboxyl acid) poly(ε-caprolactone-*co*-γ-butyrolactone) (HA-PCB) after derivatization with trifluoroacetic anhydride (TFA) in $CDCl_3$, DP(NMR) = 21 with 10% in mol of BL.

species ($^{-}O(CH_2)_4O^{-}$) formed by reduction/ring-opening reactions with tetranuclear rare earth polyhydride complex have been obtained [31]. For copolymerization of BL and CL, Kunioka found that addition reactions of BL (comonomer) cause deactivation of yttrium catalyst to ROP of CL [27].

Bulk copolymerization of CL with BL was achieved using ammonium decamolybdate (obtained in situ, Section 2) as catalyst with a M/Hep = 20,000 (where M = CL + BL) at 150 °C by 2 h. Copolymers with different compositions, as a function of the used feed ratio CL:BL, were obtained (Table 2). For a feed ratio 50:50 CL:BL, a copolymer with an insertion of 10% BL was obtained (No. 6, Table 2). Conversions decrease as the amount of BL increases in the feed ratio. This is expected as CL possesses a higher reactivity toward ROP than BL, and this fact also affects the final copolymer molecular weight. A similar behavior was observed for the ring-opening polymerization of CL and BL by SmI_2/Sm [5].

The effect of water in the copolymerization of CL and BL was studied using the same polymerization conditions (Scheme 2). In Fig. 4(A), the dependence of CL + BL/H_2O ratio on DP(NMR) for HA-PCB oligomers is plotted (Nos. 1–4, Table 3). A linear relationship between these variables is observed. These results indicate that the final degree of polymerization can be controlled. Also, the degree of BL insertion is 10% when a feed ratio CL:BL of 50:50 is used, eventhough different final molecular weights are obtained

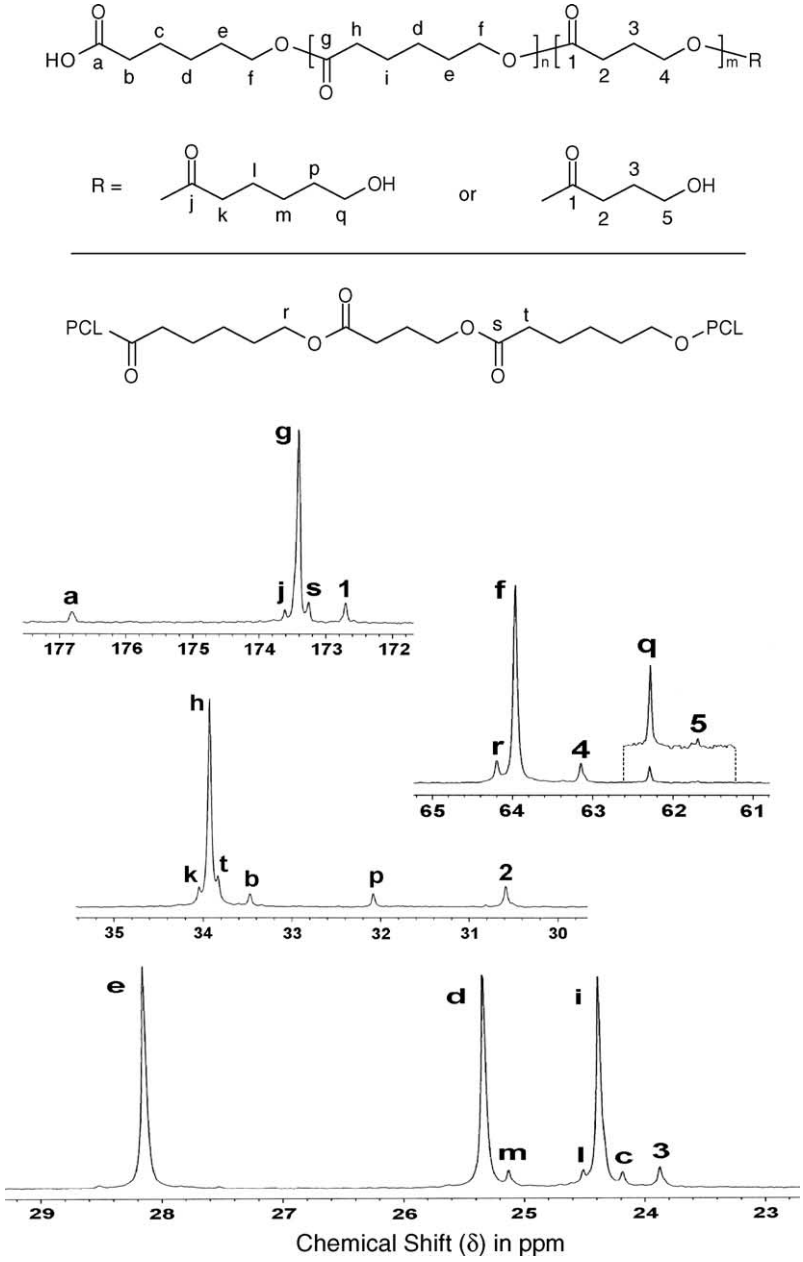


Fig. 7. Fifty megahertz ^{13}C NMR spectrum for the α-hydroxyl-ω-(carboxyl acid) poly(ε-caprolactone-*co*-γ-butyrolactone) (HA-PCB) in $CDCl_3$, DP(NMR) = 21 with 10% in mol of BL.

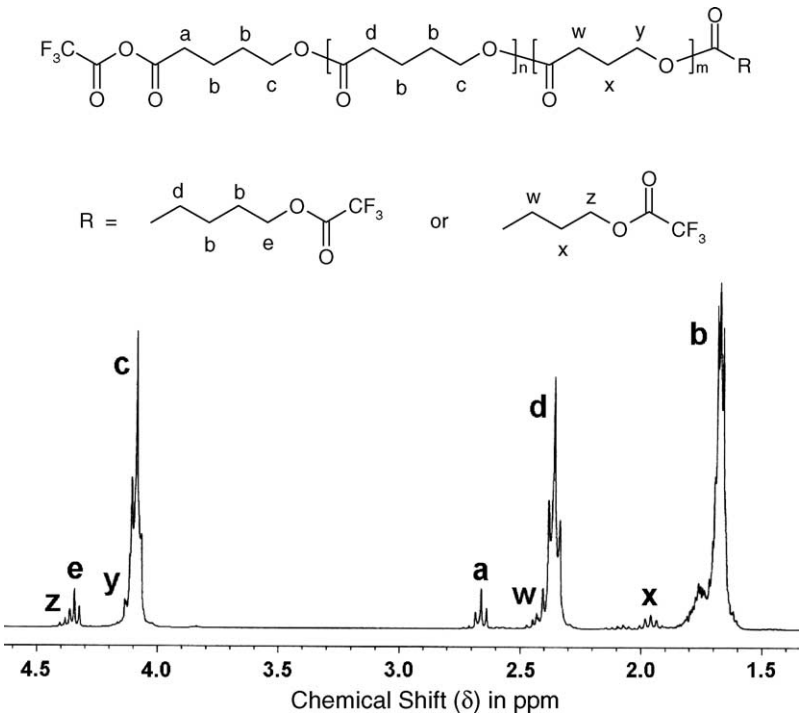


Fig. 8. Three hundred megahertz ^{1}H NMR spectrum for the α-hydroxyl-ω-(carboxyl acid) poly(δ-valerolactone-*co*-γ-butyrolactone) (HA-PVB) after derivatization with trifluoroacetic anhydride (TFA) in $CDCl_3$, DP(NMR) = 12, with 9% in mol of BL.

(Table 3). GPC was used to elucidate molecular weights and PDIs, Table 3 lists the molecular weight characteristics of two samples of HA-PCB.

To verify that the copolymer possesses the structure of an asymmetric telechelic α-hydroxyl-ω-(carboxylic acid) poly(ε-caprolactone-*co*-γ-butyrolactone) (HA-PCB), ^{1}H and ^{13}C NMR spectra were recorded. In Fig. 5, the end-group hydroxyl methylene zone (–CH_2–OH) for PCB copolymer is shown. Two triplets are clearly seen: the more intense, centered at δ 3.65 ppm, corresponds to CL end-groups, whereas the other triplet (centered at δ 3.68 ppm) is due to BL end-groups. Fig. 6 shows the ^{1}H NMR spectrum for PCB after being treated with trifluoroacetic anhydride (ATF). Two different spectral patterns can be distinguished. The most intense peaks corresponds to PCL homopolymer (peaks at δ 4.08 (e), 2.33 (d), 1.66 (b), 1.39 (c)). The other peaks are due to BL units, at δ 4.12 (y), 2.41 (w), 1.97 (x). Peaks due to the formation of two ester end-groups (–CH_2–$OCOCF_3$) from the reaction of CL and BL end-groups with ATF are also observed at δ 4.36 (f) and δ 4.41 (2), respectively. A signal at δ 2.65 (–$CH_2CO_2COCF_3$, a) for a mixed anhydride formed from the reaction between CL end-group (–CH_2–CO_2H) and ATF is also present. Observation of only one peak for the CL end-group carboxylic acid demonstrates that initiation step is mainly induced by the reaction of water with CL.

In Fig. 7, carbon-13 NMR spectrum of HA-PCB copolymer is shown. In the carbonyl zone, five peaks can be clearly distinguished. One signal corresponds to the carbonyl of the carboxylic acid end group (a, –CO_2H, δ 176.8). The other four peaks are due to ester groups: (1) CL carbonyl for hydroxyl-terminated esters (j, –O–CO–$(CH_2)_5$–OH, δ 173.6), (2) CL carbonyl for main-chain repeating unit carbonyl (g, δ 173.41), (3) CL carbonyl adjacent to BL unit (s, δ 173.25) and (4) BL carbonyl (1, δ 172.70). BL units are inserted between CL units [4]. In the methylene attached to

Table 4
Copolymerization of CL with VL catalyzed by decamolybdate anion

No.	Feed ratio CL/VL (%)	Unit ratio[a] CL/VL (%)	Conv. (%)[a]	DP(NMR)[a]
1	95/5	96/4	99	320
2	90/10	92/8	98	300
3	80/20	82/18	98	260
4	70/30	73/27	97	240
5	60/40	62/38	96	–
6	50/50	51/49	94	200

Bulk copolymerizations were carried out at 150 °C for 2 h (without addition of H_2O), M/Hep = 20,000.
[a] Obtained by ^{1}H NMR.

Table 5
Ring-opening copolymerization de CL with VL catalyzed by decamolybdate anion

No.	M/H_2O	DP(NMR)[a,b]	%VL[a]	Conv. (%)[a]
1	10	12.0	17	98
2	15	17.4	18	98
3	20	20.2	20	96
4	25	23.7	20	97

Effect of M/H_2O ratio on DP(NMR). Bulk copolymerizations were carried out at 150 °C for 2 h, M/Hep = 19,000 where M = CL + VL = 47.5 mmol, a CL:VL molar ratio of 80:20 was used.
[a] Determined by ^{1}H NMR.
[b] After recrystalization with chloroform/methanol.

Table 6
Block copolymerization of CL with VL

No.	Monomer	M/H_2O	t (h)	DP(calcd)[a]	DP(NMR)[b]	Conv. (%)[c]	% VL[d]	% VL[e]
1	CL	19	2	19	19.2	100	–	–
2	CL(VL)	19(9.5)[f]	4	28.5	24.5	94	33	18
3	CL(VL)	19(19)[f]	4	38	39.4	91	50	35

A CL/ammonium heptamolybdate ratio of 19,000 (47.5 mmol of CL) was used. Bulk hopolymerization were carried out at 150 °C for 2 h.
[a] Obtained for homopolymer from the equation: DP(calcd) = M/H_2O, and for copolymer using the equation: $DP(calcd) = DP_{CL} + DP_{VL}$.
[b] Obtained from the equation $DP(NMR) = I_{pol}/I_{ter} + 1$. I_{pol} and I_{ter} represent the integrals obtained by ^1H NMR from the polymer (4.0 ppm [–CH_2O–]) and hydroxyl end group (3.6 ppm [–CH_2OH]) peaks, respectively.
[c] Obtained from the equation $conv.(\%) = (I_{pol}/I_{mon} + I_{pol}) \times 100$, where I_{pol} and I_{mon} represent the integrals by ^1H NMR from the polymer (4.0 ppm [–CH_2O–]) and monomer (4.1 ppm [–CH_2O–]) peaks.
[d] Calculated from feed ratio.
[e] Obtained by NMR.
[f] After 2 h an amount VL was added and the system was left at 150 °C for an additional 2 h.

hydroxyl (–CH_2OH) zone, two intense peaks due to CL (q, δ 62.29) and BL (5, δ 61.68) end-groups are distinguished. The other peaks correspond to HA-PCL homopolymer [20] and PCB copolymer [4,5]. All these features corroborates that HA-PCB possesses an asymmetric telechelic architecture. Also, it should be pointed out that the copolymerization route presented here represents a good synthetic alternative to obtain HA-PCB copolymer with short reaction times (2 h). The use of other catalysts to obtain this copolymer, such as SmI/Sm [5] and tetraphenyl tin [32], involve longer reaction times (48 and 96 h, respectively).

3.3. α-Hydroxylic-ω-(carboxylic acid) poly(δ-valerolactone-co-γ-butyrolactone) (HA-PVB) asymmetric telechelic copolyester

A similar procedure to that above described was followed to obtain copolymers of VL and BL (Section 2). For a VL:BL 50:50 feed ratio and $M/H_2O = 20$, a copolymer with a 9% of BL insertion and DP = 12 (conv. = 30%) was obtained. End-group asymmetry was corroborated by ^1H NMR. In Fig. 8, signals for methylenes attached to oxygen of the ester groups –CH_2–OCOCF_3 (δ 4.38 and 4.34 for BL and VL, respectively) and mixed anhydride –CH_2CO_2-COCF_3 (δ 2.66, VL), formed from the reaction with TFA of both end-goups, are observed.

3.4. α-Hydroxylic-ω-(carboxylic acid) poly(ε-caprolactone-co-δ-valerolactone) (HA-PCV) asymmetric telechelic copolyester

Copolymerization between CL and VL by ammonium decamolybdate was carried out at 150 °C by 2 h. Copolymers with different content of CL and VL were synthesized (Table 4). Unlike lactone copolymerization between CL and BL, a good insertion of both monomers is observed. In Fig. 4(B), the relationship between M/H_2O (M = CL + VL) with DP(NMR) (feed ratio CL:VL = 80:20) is shown (No. 1–4, Table 5). A linear dependence is observed, which indicates a controlled copolymerization reaction. End-group asymmetry was corroborated by ^1H NMR (similar to that described in the HA-PVB, Section 2). Final copolymer HA-PCV shows moderate polydispersity (No. 3, Table 5), as determined by GPC analysis ($M_n = 6120$, $M_w/M_n = 1.60$).

3.5. α-Hydroxylic-ω-(carboxylic acid) poly(ε-caprolactone-block-δ-valerolactone) (HA-PCbV), an asymmetric telechelic block copolyester

To find out if the chains preserve their capacity of growing after CL conversion has been completed, a second monomer was added to the reaction mixture without isolation of PCL. Sequential copolymerization of HA-PCL ($M_n = 4300$ $M_w/M_n =$

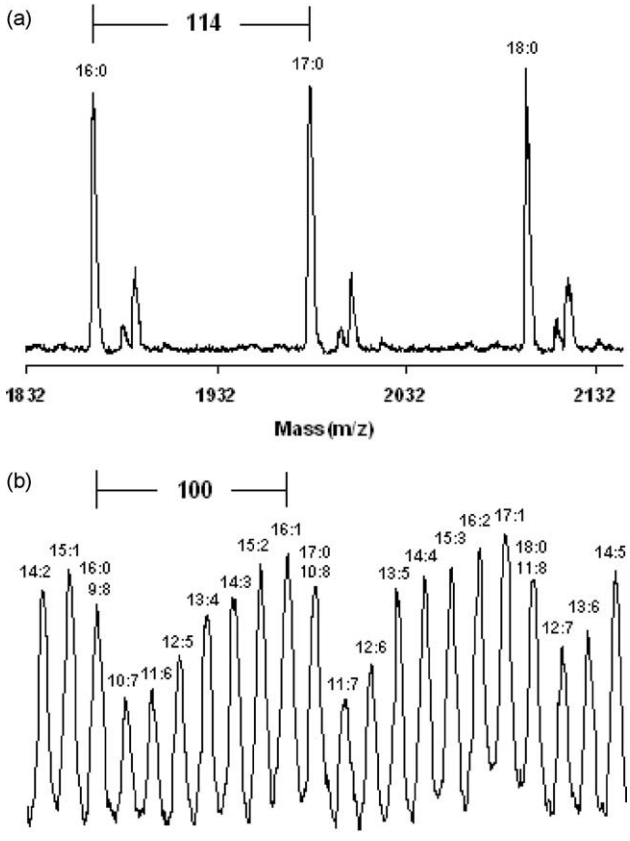


Fig. 9. MALDI-TOF spectra of (a) homopolymer: α-hydroxyl-ω-(carboxylic acid) poly(ε-caprolactone) (HA-PCL) and (b) block copolymer: α-hydroxyl-ω-(carboxylic acid) poly(ε-caprolactone-*block*-δ-valerolactone) (HA-PCbV) with 18% in mol of VL.

1.63) with VL was carried out by adding VL monomer (CL:VL = 50:50 molar ratio) into a prepolymerized HA-PCL (initial CL = 47.5 mmol, CL/Dec = 19,000, 150 °C, 2 h). Reaction mixture was allowed to react for additional 2 h (Table 6). A diblock asymmetric telechelic α-hydroxylic-ω-(carboxylic acid) poly(ε-caprolactone-*block*-δ-valerolactone) HA-PCbV (conv. = 91%) with $M_n = 5500$ ($M_w/M_n = 1.80$) was obtained (an AB type copolymer). Copolymer chain architecture was also identified by MALDI-TOF. Spectra of HA-PCL recorded before and after VL was added corroborate that AB diblock copolymer has been formed (Fig. 9). In Fig. 9(a), the more intense signals can be assigned to HA-PCL homopolymer, whereas the less intense are due to species doped with potassium ion and species with sodium carboxylate end-groups formed during the ionization process [20]. In Fig. 9(b), new peaks are now present. All peaks are due sodium-doped species, and correspond to contributions of species with different VL units in the copolymer (CL:VL). The signals for HA-PCL homopolymer overlap with those due to copolymer with 8 VL units. To our knowledge, this is the first time that a MALDI-TOF spectrum for aliphatic copolyester derived from lactones is reported.

In order to corroborate the presence of HA-PCL homopolymer in the sample, the copolymer was analyzed by ^{13}C NMR. In the spectrum shown in Fig. 10 for HA-PCbV (with a CL:VL molar ratio of 65:35 as determined by NMR), the presence of a peak for HA-PCL hydroxylic carbon q indicates the presence of residual polymer that has not reacted with VL (observed conversion was 91%). Other important feature in the spectrum is the signal for carbon e″ attributed to the VL $–CH_2O–$ groups attached to a CL carbonyl. This signal is also present in the carbon-13 NMR spectra of random PCV copolymers. In this case, the presence of this signal (e″) is due to intermolecular condensation reactions between VL hydroxylic end groups and CL carboxylic acid end groups. Intermolecular reactions only occur after the copolymer has been quantitatively formed (Scheme 3).

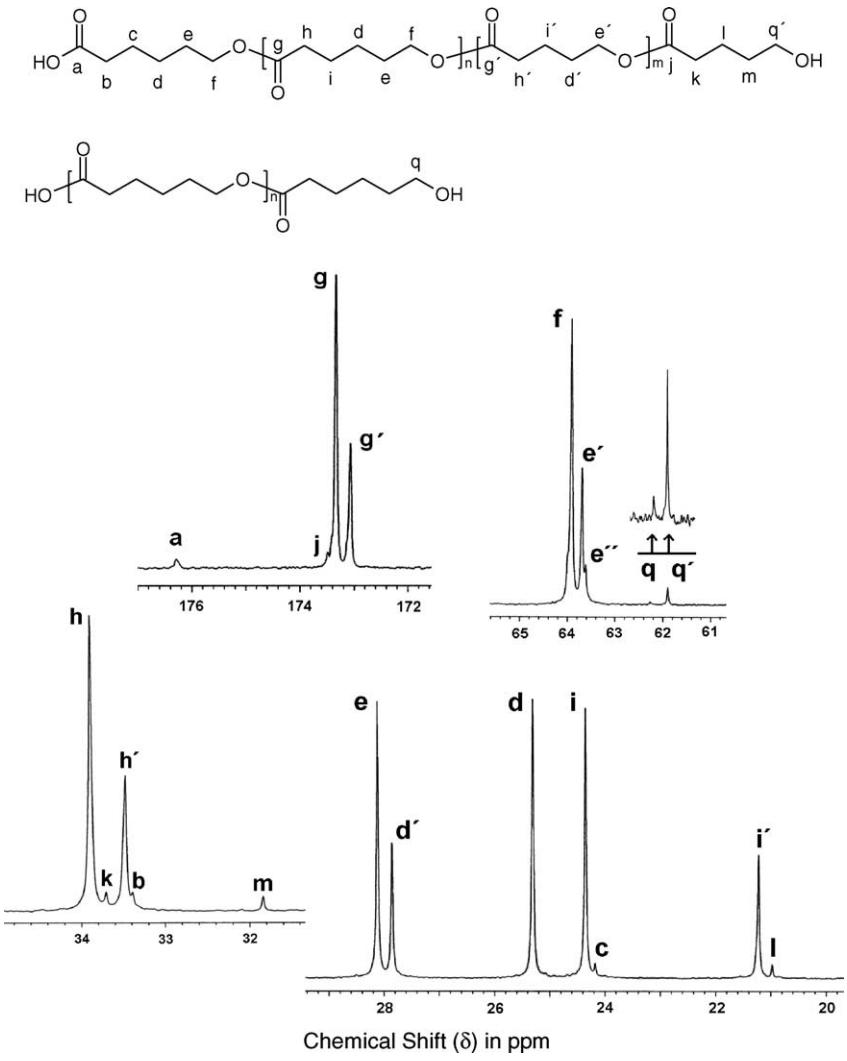
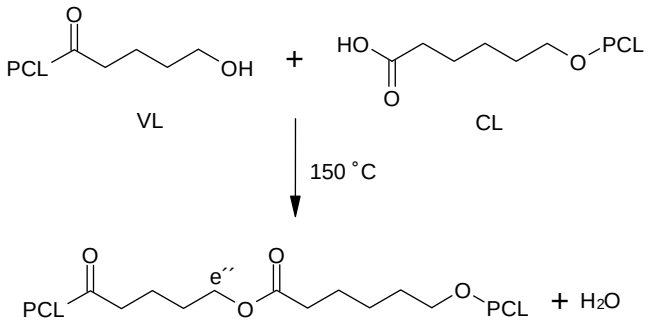


Fig. 10. Fifty megahertz ^{13}C NMR spectrum for α-hydroxyl-ω-(carboxyl acid) poly(ε-caprolactone-*block*-γ-valerolactone) (HA-PCbV) in $CDCl_3$, DP(NMR) = 39.4 with 35% in mol of VL.



Scheme 3. Intermolecular condensation reaction between end-groups VL-OH and HO_2C-CL.

4. Conclusions

It was found that ring-opening polymerization (ROP) of ε-caprolactone (CL) is catalyzed by different molybdenum derivatives. Halides and oxides in general show low selectivity and long reaction times, respectively. However, decamolybdate anion shows selectivity to the formation of α-hydroxyl-ω-(carboxylic acid) PCL (HA-PCL), with short reaction times (2 h) and quantitative conversions (98%). In all the molybdenum derivatives investigated, molybdenum has a Lewis acid character, and this fact is related with its catalytic action in this kind of polymerization.

We have shown that asymmetric telechelic α-hydroxyl-ω-(carboxylic acid) copolyesters can be successfully obtained by the use of decamolybdate anion as catalyst in the ring-opening copolymerization (in bulk) of lactones such as ε-caprolactone (CL), δ-valerolactone (VL) and γ-butyrolactone (BL), in the presence of H_2O as initiator.

Copolymerization of CL with BL occurs, by proceeds with low degree of BL insertion. Characterization by ^1H NMR shows the presence of methylenes groups close to a –COOH (CL) functionality in the α-hydroxyl-ω-(carboxylic acid) poly(ε-caprolactone-*co*-γ-butyrolactone) (HA-PCB), indicating that initiation process by water occurs at a higher rate in CL than in BL molecules, due to the low reactivity of BL to ROP. On the other hand, in the copolymerization of CL and VL a good insertion of both monomers is observed. Formation of α-hydroxyl-ω-(carboxyl acid) poly(ε-caprolactone-*co*-δ-valerolactone) (HA-PCV) copolymer is quantitatively achieved. Copolymer obtained by sequential copolymerization of HA-PCL with VL was analyzed by MALDI-TOF spectrum, and this technique corroborates that the HA-PCL-*block*-PVL block copolymer have been formed.

The presence of carboxylic acid end-groups in the HA-PCB, HA-PCV and HA-PVB copolymers is expected to enhance the biodegradability of the copolymer. The achieved copolymer architecture gives versatility to further derivatization, such as the incorporation of an alfa aminoacid moiety through the carboxylic acid end-group.

Acknowledgements

Financial support by Universidad de Guanajuato is acknowledged. We wish to thank Dr Angel Marcos Fernandez for helpful discussions and for hosting the stay of J.E.B. at Instituto de Ciencia y Tecnología de Polímeros, CSIC, Madrid, Spain. Authors are indebted to Dra. Rosa Lebrón Aguilar (Instituto de Química-Física 'Rocasolano', CSIC) for obtaining MALDI-TOF spectra. J.E.B. thanks Consejo Nacional de Ciencia y Tecnología (CONACYT) for a PhD scholarship.

References

[1] Storey RF, Herring KR, Hoffman DC. J Polym Sci, Part A: Polym Chem 1991;29:1759–77.
[2] Lin W. J Biomed Mater Res 1999;47:420–3.
[3] Agarwal S, Karl M, Anfang S, Dehnicke K, Greiner A. Polym Prepr (Am Chem Soc, Div Polym Chem) 1998;39:361–2.
[4] Nishiura M, Hou Z, Koizumi T, Imamoto T, Wakatsuki Y. Macromolecules 1999;32:8245–51.
[5] Agarwal S, Xie X. Macromolecules 2003;36:3545–9.
[6] Middleton JC, Tipton AJ. Biomaterials 2000;21:2335–46.
[7] Lee S, Kim SH, Ham Y, Kim YH. J Polym Sci, Part A: Polym Chem 2001;39:973–85.
[8] Yu F, Zhuo R. Polym J 2003;35:671–6.
[9] Guan H, Xie Z, Tang Z, Xu X, Chen X, Jing X. Polymer 2005;46:2817–24.
[10] Miyamoto Y, Fujiki M, Nomura K. J Polym Sci, Part A: Polym Chem 2004;42:4248–65.
[11] Hayano S, Kurakata H, Tsunogae Y, Nakayama Y, Sato Y, Yasuda H. Macromolecules 2003;36:7422–31.
[12] Gal Y. Eur Polym J 2000;36:2059–62.
[13] Kubo M, Nakanishi M, Kimura M. Patent No. DE 2947978, Germany; 1980.
[14] Rayner-Canham G. Descriptive inorganic chemistry. 2nd ed. New York: Freeman and Company; 2000 p. 468.
[15] Liu J, Liu L. Macromolecules 2004;37:2674–6.
[16] Nederberg F, Bowden T, Hilborn J. Macromolecules 2004;37:954–65.
[17] Báez JE, Martínez-Rosales M, Martínez-Richa A. Polymer 2003;44:6767–72.
[18] Trollsås M, Hedrick JL, Dubois Ph, Jérôme R. J Polym Sci, Part A: Polym Chem 1998;36:1345–8.
[19] Stevels WM, Stéphane P, Slaghek TM. Polym Bull 1999;42:257–64.
[20] Báez JE, Marcos-Fernández A, Martínez-Richa A. Macromolecules 2005;38:1599–608.
[21] Shen Y, Shen Z, Zhang Y, Hang Q. J Polym Sci, Part A: Polym Chem 1997;35:1339–52.
[22] Abraham GA, Gallardo A, Lozano AE, San Roman J. J Polym Sci, Part A: Polym Chem 2000;38:1355–65.
[23] Guo Q, Miyaji T, Hara R, Shen B, Takahashi T. Tetrahedron 2002;58:7327–34.
[24] Sykes AG. Advances in inorganic chemistry. vol. 49. California: Academic Press; 2000 p. 157.
[25] Fuchns J, Hartl H, Hunnius WD, Mahjour H. Angew Chem Int Ed 1975;14:664.
[26] Tamura Y, Kobayashi I. Patent No. JP 46027546, Japan; 1971.
[27] Kunioka M, Wang Y, Onozawa S. Polym J 2003;35:422–9.
[28] Kowalski A, Duda A, Penczek S. Macromolecules 2000;33:689–95.
[29] Moore T, Adhikari R, Gunatillake P. Biomaterials 2005;26:3771–82.
[30] Yamashita M, Takemoto Y, Ihara E, Yasuda H. Macromolecules 1996;29:1798–806.
[31] Cui D, Tardif O, Hou Z. J Am Chem Soc 2004;126:1312–3.
[32] Nakayama A, Kawasaki N, Aiba S, Maeda Y, Arvanitoyannis I, Yamamoto N. Polymer 1998;39:1213–22.