One-Step Route to α-Hydroxyl-ω-(carboxylic acid) Polylactones Using Catalysis by Decamolybdate Anion

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ABSTRACT: Asymmetric telechelic α-hydroxyl-ω-(carboxylic acid) poly(ϵ-caprolactone) (HA-PCL) and α-hydroxyl-ω-(carboxylic acid) poly(δ-valerolactone) (HA-PVL) were synthesized by ring-opening polymerization of ϵ-caprolactone (CL) and δ-valerolactone (VL), respectively. HA-PCL oligomers were obtained at 150 °C in 2 h using ammonium decamolybdate $(NH_4)_8[Mo_{10}O_{34}]$ as catalyst and water as initiator. A control of the number-average molecular weight (measured by NMR) can be achieved in the range between 212 and 2198 Da, based on the initial monomer/initiator ratio. Number-average molecular weight (M_n) shows a linear dependence with CL/H_2O ratio in this range. The nature of hydroxyl and carboxylic acid end groups of HA-PCL and HA-PVL was studied by MALDI-TOF and ^1H and ^{13}C NMR. Changes in the chemical shifts observed in the NMR spectra as a function of molecular weight were explained in terms of hydrophobic interactions. Formation of macrocyclic species was studied by MALDI-TOF. It was found that macrocyclic species are favored at longer reaction times. Insertion of alcohols and polycondensation reactions occurring after complete monomer conversion were also studied. Alcohol insertion for this system depends on the nature of alcohol. Polycondensation reactions vary with reaction times and affect the polymer molecular weight in a nonlinear manner. Finally, the α-hydroxyl-ω-(sodium carboxylate) PCL salt (HC-PCL) was prepared from HA-PCL and characterized by FT-IR and solution and solid-state NMR. Important differences between CP-MAS and MAS spectra are observed and discussed in terms of morphology and polarization transfer.

Introduction

One of the more important applications of aliphatic polyesters, such as poly(ϵ-caprolactona) (PCL), is their use as a biodegradable material in medicine. Degradation with lipase of PCL microparticles (13.4 ± 4.7 μm) for 5 weeks reduces its number-average molecular weight from 30 000 to 22 800 Da.[1] Degradation by bacteria of solutions containing PCL as the sole source of carbon induces a loss of 55 wt % (with respect to the initial mass) after 7 days of incubation.[2] In the scope of local drug delivery applications, PCL has been successfully tested as a vehicle for slow release of drugs at tumor reactions sites.[3] It has also been applied as a surgical paste compounded with the antitumor drug taxol.[4]

Recently, synthesis of PCL's with specific end groups has been targeted in order to obtain materials with properties tailored to specific uses, including biodegradability. Some examples found in the recent literature follow: (1) α,ω-telechelic PCL diols[5,6] with potential uses as precursors of polyurethanes or as macroinitiators in the synthesis of block copolymers; (2) macromonomers such as the α-hydroxyl-ω-(pyrrolyl or thienyl) PCL;[7] (3) PCLs obtained using initiators such as amino acids[8] and carbohydrates,[9] and these derivatives contain end groups with biological molecules essential for the human nutrition; (4) polyesters and copolyesters with pendant carboxylic acid end groups synthesized from CL and other monomers, which show enhanced hydrophilicity and degradation rates.[10]

The long degradation times observed for PCL limit their spectrum of applications as biodegradable polymer. One of the factors that accelerate the degradation of PCL is the percentage of acidic end groups present in the polyester. Carboxylic acid end groups show a more hydrophilic character than ester groups, and biodegradability of polylactones increases as the content of −COOH groups is higher.[11] Amount of carboxylic acid end groups influences the interaction of the polymer with water and is directly related with acid- and base-catalyzed hydrolysis rates of polylactides (PLA).[12] Polylactide (PLA)[12] and poly(trimethylene carbonate)[13] with carboxylic acid end groups have been synthesized by selective oxidation of the $-CH_2OH$ terminal groups in the presence of succinic anhydride.

The use of initiators in the ring-opening polymerization (ROP) of ϵ-caprolactone (CL) is one of the more convenient routes to produce end- functionalized PCL. Primary and secondary alcohols (such as benzyl alcohol, methanol, and butanol among others) have been successfully used as initiators/chain-transfer agents in the presence of a variety of catalysts.[14−16] This route leads only to the formation of α-hydroxyl-ω-(aliphatic or aromatic esters) PCL. The same type of end group is found when metal alkoxides are used as initiators instead.[17,18] When water is used as initiator, production of α-hydroxyl-ω-(carboxylic acid) PCL (HA-PCL) is anticipated. However, in the presence of alkoxides (such as those derived from tin), formation of metal−OH bonds is thermodynamically favored and the efficiency of water as initiator decreases.[19,20]

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Alternative routes to obtain HA-PCLs have been reported by several authors: Hedrick and co-workers carried out the synthesis of asymmetric acid-functional HA-PCL in two steps by hydrogenolysis of benzyl esters.[21] Storey and co-workers prepared HA-PCL from the reaction of glycolic acid with CL in the presence of stannous octoate catalyst. However, polymerization is plagued with the insertion of glycolic acid within the main chain due to condensation side reactions.[22]

As mentioned earlier, polymerization of CL using H_2O as initiator/chain-transfer agent and alkoxide as catalysts to produce asymmetric telechelic HA-PCL in a single step has many disadvantages due to the formation of hydroxides. Moreover, in general, long reaction times are needed to achieve complete polymerization, as is the case for scandium trifluorometanesulfonate[23] and mesoporous zeolite[15] catalysts (120 and 237 h respectively). In that regard, chemical routes to obtain HA-PCLs are generally inefficient. Alternatively, HA-PCL oligomers are formed by enzyme-catalyzed ring-opening polymerization of CL.[24,25] They are also produced in the enzymatic degradation of PCL by cholesterol esterase.[26] In general, enzymatic polymerizations take place under mild conditions and at low reaction temperatures, making this an attractive route to obtain carboxylic-acid-functionalized PCL. However, the use of high monomer/enzyme ratios and the need of complicated purification procedures limit the usefulness and efficiency of this method for the medium- and large-scale production of HA-PCLs.

We recently reported the use of ammonium decamolybdate ($(NH_4)_8[Mo_{10}O_{34}]$, an isopolymolybdate) as an efficient catalyst for the ring-opening polymerization of lactones. By means of this synthetic procedure, bulk polymerization of CL by heterogeneous catalysis in the presence or absence of hydroxylic compounds can be achieved with high yields. This method also allows a proper control of the final polymer molecular weight, based on the initial monomer/ROH ratio.[27] Another important advantage of this route is that the use of solvents as a reaction medium, such as benzene,[28] chlorobenzene,[29] toluene,[14,30] pyridine,[30] or THF,[30] is avoided. Moreover, use of molybdenum derivatives, such as molybdates, as catalyst is environmentally friendly as they are considered low-toxicity compounds.[31] This feature is particularly important when use of this polymer as a biodegradable material is pursued.

We present here a one-step synthetic method to obtain HA-PCL and α-hydroxyl-ω-(carboxylic acid) poly(δ-valerolactone) HA-PVL using ammonium decamolybdate as catalyst and water as an initiator in ROP of CL and δ-valerolactone (VL). High conversions and short reaction times (2 h, bulk polymerization) are observed. This synthetic route probably represents the best alternative to obtain HA-PCL and HA-PVL. Final polymers and oligomers were characterized by FT-IR, GPC, nuclear magnetic resonance spectroscopy, and MALDI-TOF. Additional experiments were conducted in order to monitor side reactions such as autocondensation and transesterification during polymerization and after monomer conversion had been completed.

Experimental Section

Materials. CL (Aldrich Chemicals Co.) and VL (Fluka) were dried over calcium hydride and distilled under reduced pressure before use. Benzyl alcohol (BzOH) and octyl alcohol (OctOH) were purchased from Aldrich and used without further purification. Distilled water was purchased from J. T.Baker. Ammonium heptamolybdate tetrahydrate $(NH_4)_6[Mo_7O_{24}]\cdot 4\ H_2O$ (Hep) (Fluka) was ground in a mortar and passed through a 100 mesh sieve before use.

Synthesis of α-Hydroxylic-ω-(carboxylic acid) Poly(ε-caprolactone) (HA-PCL) and Poly(δ-valerolactone) (HA-PVL). Polymerizations were carried out in 5 mL vials previously dried and purged with dry nitrogen. In a typical run monomer (CL, 47.5 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. Ammonium decamolybdate $(NH_4)_8[Mo_{10}O_{34}]$ (Dec) was formed in situ at this temperature.[27] Final polymer was crystallized from chloroform/methanol and dried under vacuum. Molecular weight and conversion during reaction were monitored by ^{1}H NMR. The crystallized polymer was analyzed by MALDI-TOF. Polymerizations of VL were carried out in a similar way. NMR data for HA-PCL: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 4.05 (t, 2H, [CH_2O]), 3.64 (t, 2H, [CH_2OH]), 2.35 (t, 2H, [CH_2CO_2H]), 2.31 (t, 2H, [CH_2CO_2]), 1.64 (m, 4H, [$(CH_2)_2$]), 1.37(q, 2H, [CH_2]). ^{13}C NMR (50 MHz, CD_3CN, ppm) δ 175.34, 174.52, 174.36, 64.83, 62.39, 34.86, 34.70, 34.20, 33.20, 29.14, 26.20, 25.64, 25.40, 25.28. ^{13}C NMR ($CDCl_3$, ppm) δ 176.84 (a), 173.62 (j), 173.41(g), 63.99 (f), 62.34 (q), 34.07 (k), 33.95 (h), 33.49 (b), 32.11 (p), 28.17 (e), 25.36 (d), 25.15 (m), 24.53 (l), 24.41 (i), 24.21 (c). NMR data for HA-PVL: ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 4.00 (t, 2H, [CH_2O]), 3.57 (t, 2H, [CH_2OH]), 2.27 (t, 2H, [CH_2CO_2]), 1.60 (m, 4H, [$(CH_2)_2$]). ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ 176.30 (a), 173.53 (j), 173.11 (g), 63.73 (e), 61.94 (q), 33.72 (k), 33.51 (h), 33.06 (b), 31.85 (m), 27.89 (d), 21.24 (i), 21.11 (c), 20.98 (l).

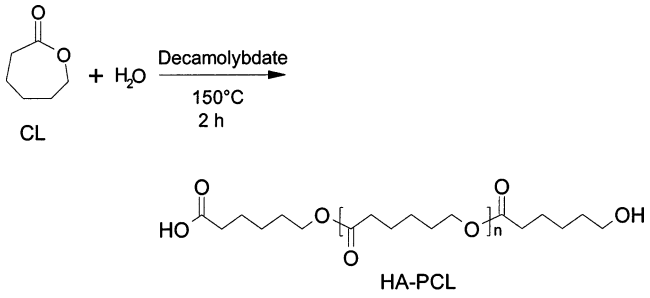
Synthesis of α-Trifluoroacetate-ω-(trifluoroacetanhydride) PCL (TF-PCL) and α-Trifluoroacetate-ω-(trifluoroacetanhydride) PVL (TF-PVL) by Derivatization of HA-PCL and HA-PVL with Trifluoroacetic Anhydride (TFA). An excess amount of TFA was added to a solution of HA-PCL in $CDCl_3$ (100 mg/0.75 mL) at ambient temperature. Full derivatization of the sample was confirmed by NMR. NMR data for TF-PCL: ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ 4.30 (t, 2H, [CH_2OCOCF_3]), 4.02 (t, 2H, [CH_2O]), 2.60 (t, 2H, [$CH_2CO_2COCF_3$]), 2.28 (t, 2H, [CH_2CO_2]), 1.60 (m, 4H, [$(CH_2)_2$]), 1.33 (q, 2H, [CH_2]). NMR data for TF−PVL: ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ 4.32 (t, 2H, [CH_2OCOCF_3]), 4.05 (t, 2H, [CH_2O]), 2.64 (t, 2H, [$CH_2CO_2COCF_3$]), 2.32 (t, 2H, [CH_2CO_2]), 1.62 (m, 4H, [$(CH_2)_2$]).

Condensation of HA-PCL with Alcohols. Reaction of HA-PCL with alcohols was performed under similar conditions as those used for ROP of CL. After 2 h of reaction, 6 mmol of benzyl alcohol was injected in the vial using a syringe under nitrogen atmosphere. The mixture was vigorously stirred and placed in a thermostated bath at 150 °C for 2.6 h. Final polymer was recrystallized three times from chloroform/methanol and dried under vacuum. Evidence of transesterification was observed in the ^{1}H and ^{13}C NMR spectra. Crystallized polymer was also analyzed by MALDI-TOF.

Synthesis of Hydroxycaproic Acid Oligomer Salt Derivative (oligomer HC-PCL). HA-PCL oligomer with M_n(NMR) = 212 (10 mmol) was reacted with an equimolar amount of NaOH previously dissolved in a minimum amount of water. The reaction mixture was slowly brought to boiling and maintained until complete water evaporation. Final product was dried under air flow. The resulting sodium carboxylate derivative is soluble in water and characterized by FT-IR and ^{1}H and ^{13}C NMR. IR (cm^{-1}): 3330, 2935, 1730, 1561, 1187. NMR data for HC-PCL: ^{1}H NMR (200 MHz, D_2O, ppm) δ 4.11 (t, 2H, [CH_2O]), 3.58 (t, 2H, [CH_2OH]), 2.39 (t, 2H, [CH_2CO_2]), 2.17 (t, 2H, [$CH_2CO_2^-Na^+$]), 1.55 (m, 4H, [$(CH_2)_2$]), 1.35 (q, 2H, [CH_2]). Solid-state MAS ^{13}C NMR (75.47 MHz, ppm) δ 181.73 (a), 174.17 (g), 64.70 (f), 62.23 (i), 39.07 (b), 34.59 (h), 33.05 (e), 29.03 (d), 25.94 (c). Solid-state CP-MAS ^{13}C NMR (75.47 MHz, ppm) δ 182.20 (a), 174.32 (g), 62.23 (f,i), 39.07 (b), 33.05 (e,h), 28.88 (d), 25.94 (c).

Measurements. Solution ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Varian Gemini 200 (200 MHz ^{1}H and 50 MHz ^{13}C), Varian Unity *Plus* 300 (300 MHz ^{1}H and 75.47 MHz ^{13}C) and Varian Unity Inova 500 (500 MHz

Scheme 1



^{1}H). Chloroform-*d* ($CDCl_3$), Acetonitrile-*d*3 (CD_3CN), and deuterium oxide (D_2O) were used as solvents. Spectra were referenced to the residual solvent protons at δ 7.26, 1.94, and 4.80 for $CDCl_3$, CD_3CN, and D_2O, respectively, in the ^{1}H NMR spectrum and the residual solvent carbons at δ 77.0 and 1.39 for $CDCl_3$ and CD_3CN, respectively, in the ^{13}C NMR spectrum. Solid-state NMR spectra were recorded under proton decoupling on a Varian Unity *Plus* 300 NMR spectrometer. Approximately 150 mg of sample was packed into a 7 mm diameter zirconia rotor with Kel-F packs. The spectra were obtained under Hartmann−Hann matching conditions at a spinning rate of 4.25 kHz. For CP-MAS spectra, a contact time of 2.5 ms and a repetition time of 8 s were used. For MAS spectra, a repetition time of 30 s was used. The measurements were made using spin-lock power in radio frequency units of 60 kHz, and typically 10 000 transients were recorded. Elimination of spinning sidebands was accomplished by the TOSS sequence. Chemical shifts were referenced to the upfield peak of adamantane at 29.5 ppm (with respect to TMS) determined on a separate sample. 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 made in a Varian HPLC 9012Q equipped with two gel columns, Styragels HR 3 and HR 5E, connected in series and a refractive index detector (Waters 2410). THF was used as the mobile phase at a flow rate of 1 mL min^{-1}. Measurements were made at 30 °C, and 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.

Results and Discussion

Preparation of α-hydroxyl-ω-(carboxylic acid) PCL's (HA-PCL's) was carried out by bulk polymerization at 150 °C using water as co-initiator (see Scheme 1). "In situ" thermal conversion of ammonium heptamolybdate $(NH_4)_6[Mo_7O_{24}]$ (Hep) to ammonium decamolybdate (the actual catalytic species $(NH_4)_8[Mo_{10}O_{34}]$, (Dec)) takes place at this temperature.[27,32,33] It is important to note that under these reaction conditions (a) reaction times are reasonable (on the order of 2 h) and (b) monomer diffusion is promoted, as the reaction product (namely, poly(ϵ-caprolactone)) remains melted during polymerization.

Polymerization of CL (47.5 mmol) by ammonium decamolybdate (produced in situ by thermal decomposition of Hep) with a monomer/heptamolybdate feed molar ratio of 19 000 in the presence of water (H_2O) (CL/H_2O feed molar ratio of 19) proceeds with 100% conversion

Table 1. Ring-Opening Polymerization of the ϵ-Caprolactone (CL) and δ-Valerolactone (VL) by Decamolybdate in the Presence of H_2O[a]

no.	monomer	M/H_2O	M_n(calcd)[b]	M_n(NMR)[c]	conv (%)[d]
1	CL	0.66[e]	132	212	100
2	CL	2[e]	246	383	100
3	CL	4[e]	474	577	100
4	CL	6[e]	703	782	100
5	CL	9	1045	1193	100
6	CL	13	1502	1593	100
7	CL	16	1844	1878	100
8	CL	19	2186	2198	100
9	CL	29	3328	2670	100
10	CL	39	4469	3104	99
11	CL	49	5611	3430	98
12	VL	9	919	1168	88
13	VL	19	1920	1908	92
14	VL	29	2921	2748	91
15	VL	39	3922	3248	91
16	VL	49	4924	3988	89

[a] A monomer/ammonium heptamolybdate ratio of 47.5 mmol/3 mg was used. Polymerizations were carried out at 150 °C for 2 h. [b] Obtained from the equation $M_n(\text{calcd}) = (M_w(\text{M}))(\text{M}/H_2O) + M_w(H_2O)$, where M_w is the molecular weight of lactone monomer or water. [c] Obtained from the equation $M_n(\text{NMR}) = (M_w(\text{M}))(\text{DP}_{(\text{NMR})}) + M_w(H_2O)$; $\text{DP}_{(\text{NMR})} = I_{pol}/I_{ter} + 1$, where M_w is the molecular weight of lactone monomer or water. I_{pol} and I_{ter} represent the integrals obtained by ^{1}H NMR from the polymer (4.0 ppm [$-CH_2O-$]) and hydroxyl end group (3.6 ppm [$-CH_2OH$]) peaks, respectively. [d] 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. [e] A monomer/ammonium heptamolybdate ratio of 23.75 mmol/3 mg was used. Polymerizations were carried out at 150 °C for 2 h.

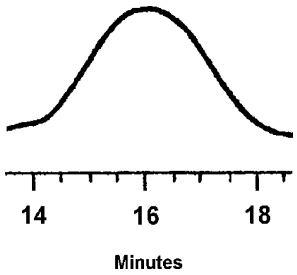


Figure 1. GPC profile for HA-PCL, M_n(GPC) = 5900, M_w/M_n = 1.46 (see no. 8, Table 1).

at 150 °C in 2 h (no. 8, Table 1). Degree of polymerization (determined by ^{1}H NMR) was ∼19, in agreement with the initial feed ratio ($CL/H_2O = 19$). Final polymer shows moderate polydispersity, as determined by GPC analysis (M_n(GPC) = 5900, M_w/M_n = 1.46). A unimodal distribution is observed in the GPC chromatogram (see Figure 1). This result is similar to that reported (in two-step) for α-hydroxyl-ω-(carboxylic acid) PCL obtained when $Al(Et_3)$ was used as catalyst (M_n(GPC)= 3000, M_w/M_n = 1.42).[21] Other authors have reported the synthesis of α-hydroxyl-ω-(carboxylic acid) PCL under conditions near to a living polymerization (M_n(GPC) = 7700, M_w/M_n = 1.10).[23]

Number-average molecular weight obtained by GPC (M_n(GPC) = 5900) differs from that calculated by ^{1}H NMR, M_n(NMR)= 2198 (see no. 8, Table 1). Theoretical number-average molecular weight (recorded from the CL/H_2O ratio, M_n(calcd) = 2186) is equal to M_n obtained by NMR and close to that obtained by MALDI-TOF (M_n(MALDI) = 2410). MacLain and Drysdale[34] proposed a factor of 0.45 to convert M_n(GPC) values into the actual number-average molecular weight of poly(ϵ-caprolactone). This factor accounts for the differences in hydro-

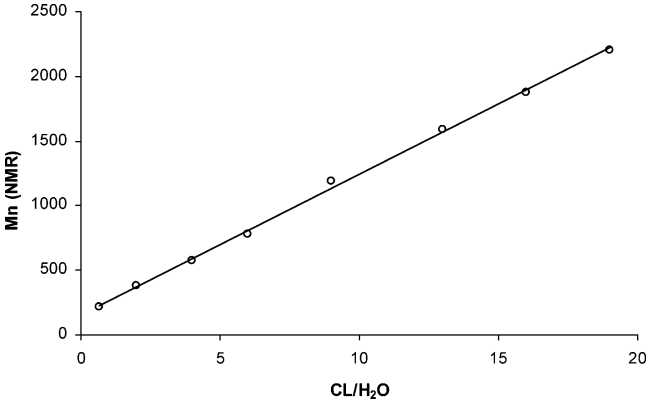


Figure 2. Polymerization of the ϵ-caprolactone (CL) catalyzed by decamolybdate anion in the presence of H_2O at 150 °C. Dependence of M_n(NMR) on CL/H_2O (see nos. 1−8, Table 1).

Table 2. Bulk Polymerization of CL at 150 °C with CL/H_2O = 19. Effect of the CL/Hep Ratio

no.	CL/Hep	t (min)	M_n (NMR)[a]	conv (%)[a]
1	190	50	1556	98
2	1900	60	2056	93
3	19 000	90	2030	90
4	19 000	120	2198	100

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

dynamic volume between polystyrene and aliphatic polyester derived from lactones.[35] Kricheldorf[36] reported that M_n(GPC) values are larger than the M_n values obtained from end-group analyses by 15−25% for PCL.

In Figure 2 the dependence of CL/H_2O ratio with M_n(NMR) for HA-PCL oligomers is plotted (nos. 1−8, Table 1). A linear relationship between these variables is observed. Results indicate that this polymerization method allows the proper control of the final molecular weight of HA-PCL oligomers in the range of 212−2198 Da. When a CL/H_2O ratio of 0.66 is used (water excess, no. 1, Table 1), formation of mainly monomeric hydroxycaproic acid is, in principle, expected. However, formation of hydroxycaproic acid and oligomeric species with a DP of 1.7 (measured by ^{1}H NMR) occurs. It is also observed that for low M/H_2O ratios (≤16), M_n(NMR) is usually higher than the expected molecular weight (M_n(calcd), see Table 1). This result can be explained in terms of condensations reactions. This means that reactivities of functional groups present in the monomeric and low molecular weight oligomeric species are higher than those for higher molecular weight species. As a consequence, a nonzero intercept is obtained in the M_n vs CL/H_2O plot (see Figure 2). In contrast, when the feed CL/H_2O ratio is higher or equal to 29, a negative deviation from linearity is observed (nos. 9−11, Table 1). A similar behavior is observed for VL (nos.12−16, Table 1). A similar trend has been reported for the plot of M_n vs [CL-VL]/[OH] ratio, observed during the copolymerization of lactones catalyzed by stannous octoate.[37] Other authors have reported that a similar trend is observed in the ROP of 1,3-dioxenepan-2-one catalyzed by water−hydrogen chloride[38]

The effect of CL/Hep ratio on the reaction time and molecular weight was also studied (see Table 2). At low CL/Hep ratios reaction times to obtain complete conversion are shorter. For a CL/Hep ratio of 190 (no. 1), a conversion of 98% is attained in only 50 min. On the other hand, for CL/Hep = 19 000 (no. 3) it takes 90 min in order to obtain a conversion of 90%. An increment in the amount of catalyst in the reaction medium also increases the number of active sites, which in turn leads to shorter reaction times. However, when a CL/Hep ratio of 190 (no. 1, Table 2) is used, a molecular weight lower than expected is attained (M_n(NMR) = 1556 Da, M_n(calcd) = 2186). At this stage efficient control of the oligomer molecular weight is no longer possible. This behavior can be attributed to the effect that hydration water from Hep ($(NH_4)_6[Mo_7O_{24}]\cdot 4.H_2O$) has in the initiation step. If this amount of catalyst is used, the total amount of water present in the reaction medium increases from 2.5 to 3.5 mmol. The molecular weight expected when 3.5 mmol of water is used (M_n(calcd) = 1567) is consistent with the observed molecular weight (vide supra).

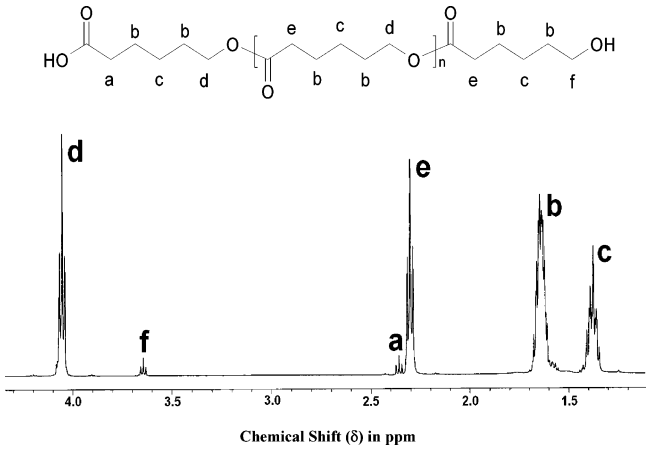


Figure 3. ^{1}H NMR (500 MHz) spectrum for α-hydroxyl-ω-(carboxylic acid) PCL (HA-PCL) in $CDCl_3$, M_n(NMR) = 2198 (see no. 8, Table 1).

In the ^{1}H NMR spectrum for HA-PCL (see Figure 3, no. 8, Table 1), signals for methylene end groups *a* [$-CH_2$COOH, δ 2.35] and *f* [$-CH_2$OH, δ 3.64] are clearly seen. The ratio of the signal intensity of *a* to that of *f* is 2:2. The other peaks in the spectrum are assigned to the other methylenes of the [−CO−$(CH_2)_5$−O−] repeating unit. Thus, the obtained *asymmetric telechelic* polymer has carboxyl $-CO_2H$ and hydroxyl −OH end groups, indicating that H_2O acts as both initiator and chain-transfer agent in the polymerization of CL by decamolybdate. No signals are observed in the olefinic region, which indicates that dehydration of the alcohol functionality does not occur under these conditions.[39]

A common procedure to derivatize the PCL hydroxyl end group is based on its reaction with trifluoroacetic anhydride (TFA).[40,41] The ^{1}H NMR spectrum for HA-PCL (see Figure 4A) shows peaks for the hydroxylic methylene [*f*, $-CH_2$OH, δ 3.64] and the methylene adjacent to the acid carboxylic group [*a*, $-CH_2CO_2H$, overlapping]. In Figure 4B the ^{1}H NMR spectrum of the adduct obtained after addition of TFA to HA-PCL is shown. Formation of an ester group leads to the upfield shift for methylene f from δ 3.64 to 4.31 ppm [*f'*, $-CH_2$-$OCOCF_3$]. Reaction between the HA-PCL carboxylic acid end group and TFA to form an anhydride [*a'*, $-CH_2$-CO_2COCF_3, δ 2.60] also occurs. The ratio of the signal intensity of *a'* to that of *f'* is 2:2. End-group peaks for this adduct are better resolved than those observed in the ^{1}H NMR spectrum of HA-PCL in Figure 3. Therefore, derivatization of both PCL end groups in one step can be achieved with the use of trifluoroacetic anhydride. Addition of an excess amount of trifluoroacetic

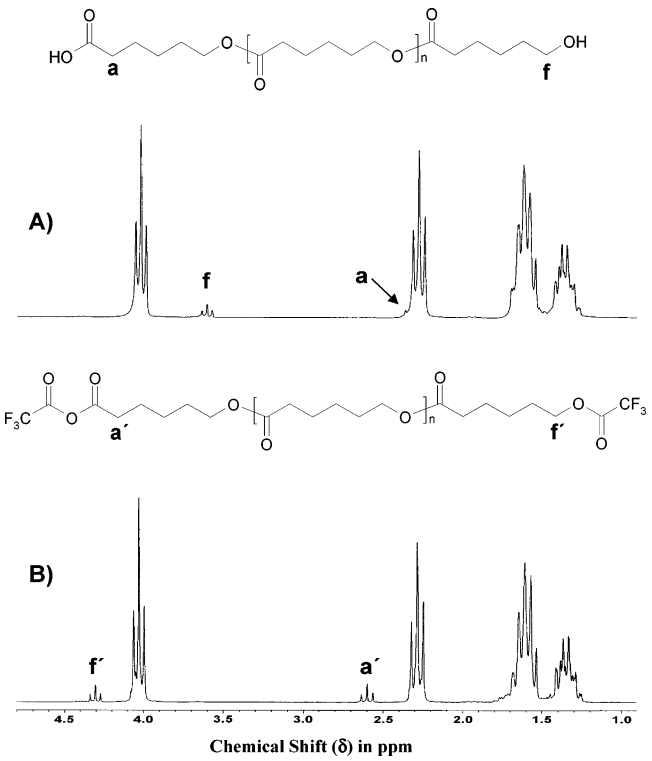


Figure 4. ^{1}H NMR spectrum (200 MHz)for the HA-PCL in $CDCl_3$: (A) HA-PCL (see no. 8, Table 1); (B) after derivatization with trifluoroacetic anhydride (TFA).

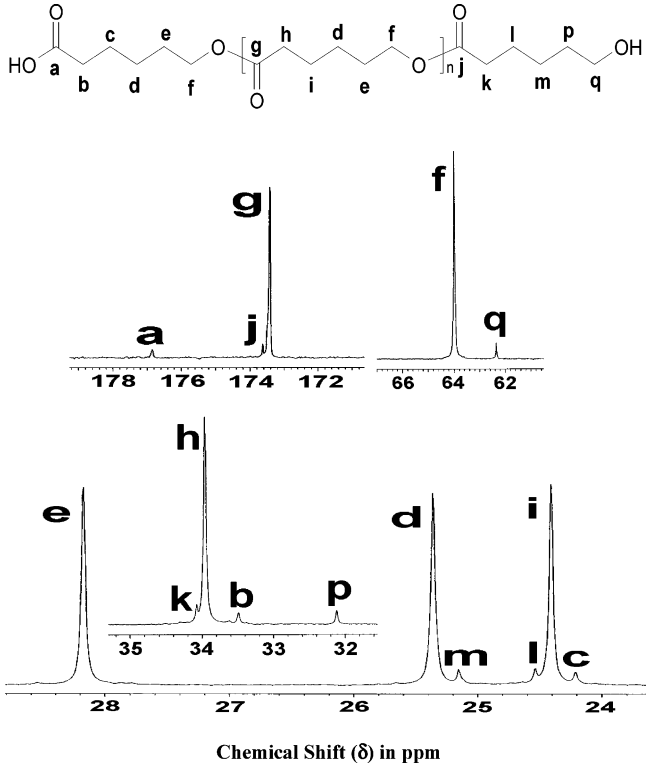


Figure 5. ^{13}C NMR (50 MHz)spectrum for the HA-PCL (see no. 8, Table 1) in $CDCl_3$, M_n(NMR) = 2198.

acid only leads to the acylation of the hydroxyl end group.

The ^{13}C NMR spectrum in Figure 5 also evidences the chemical nature of the HA-PCL end groups. In the carbonyl zone peaks for the carboxylic acid end group [a, $-CO_2H$, δ 176.84] and ester carbonyl of the hydroxyl end group [j, $-O-CO-(CH_2)_5-OH$, δ 173.62] are clearly

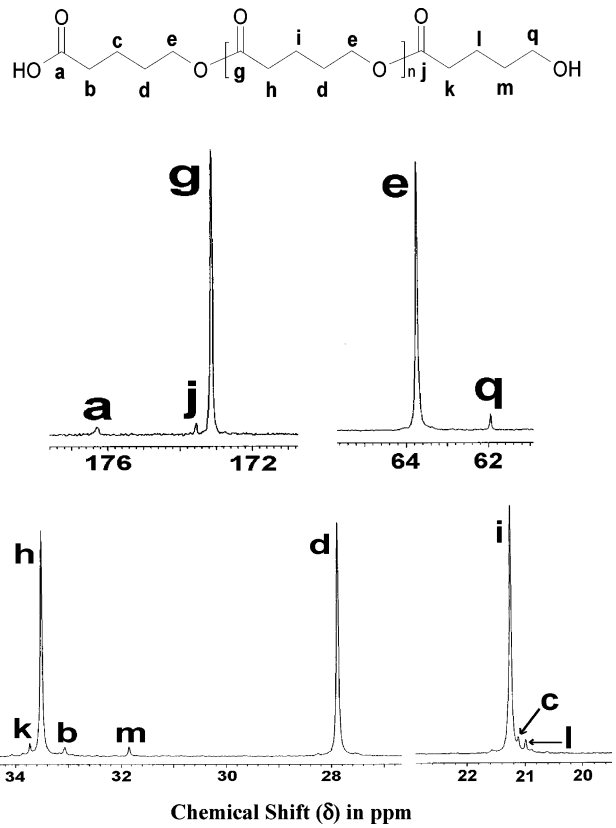


Figure 6. ^{13}C NMR (50 MHz)spectrum for the HA-PVL (see no. 13, Table 1) in $CDCl_3$, M_n(NMR) = 1908.

distinguished. Signals for methylene close to the hydroxyl end group [q, $-CH_2-OH$, δ 62.34] and carboxylic acid end group [b, $-CH_2-COOH$, δ 33.49] are also seen. Assignment for methylene carbon close the carboxylic end group was made by comparison with the observed peak pattern in the ^{13}C NMR spectrum for α-hydroxyl-ω-(octyl ester) PCL (HO-PCL).[27] In the ^{13}C NMR spectrum for HO-PCL peaks for carbons *a* (carboxyl) and *b* and *c* (alpha and beta carbons) of HA-PCL carboxylic acid end groups are not seen, as an octyl end group is present. The chemical shifts for the other three methylene carbon signals of the carboxylic end group (carbons *d*, *e,* and *f*) are similar to those observed for the methylenes of the main chain in the ^{13}C NMR spectrum for HO−PCL. The other weak signals in the spectrum were assigned to the methylenes of the hydroxylic end group. A similar peak pattern is also observed in the ^{13}C NMR spectra of other low molecular weight HA-PCLs. Some of the assignments for end groups of HA-PCL presented here are new and have not been shown in the ^{13}C NMR spectra published in the literature.[21,42]

The chemical nature of HA-PVL end groups is evidenced in Figure 6, where signals for carboxylic acid carbon end groups [a, $-CO_2H$, δ 176.30] and hydroxylic carbon end groups [q, $-CH_2-OH$, δ 61.94] can be distinguished.

Peaks for carbons beta (carbon *i*) and gamma (carbon *d*) to the ester carbonyl of PCL main chain have been incorrectly assigned by some authors.[6,21,42] Using substituent additivity rules and literature data,[43] the chemical shifts predicted for carbons *i* and *d* based on pentane are as follows:

δ(C-*i*) = 22.8 + 2 = 24.8 ppm (obsd 24.4 ppm);

δ(C-*d*) = 34.7 − 2 − 3 = 29.7 ppm (obsd 25.3 ppm).

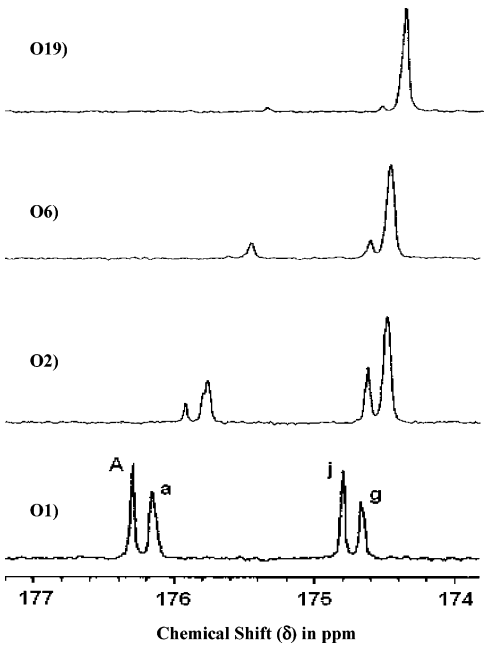
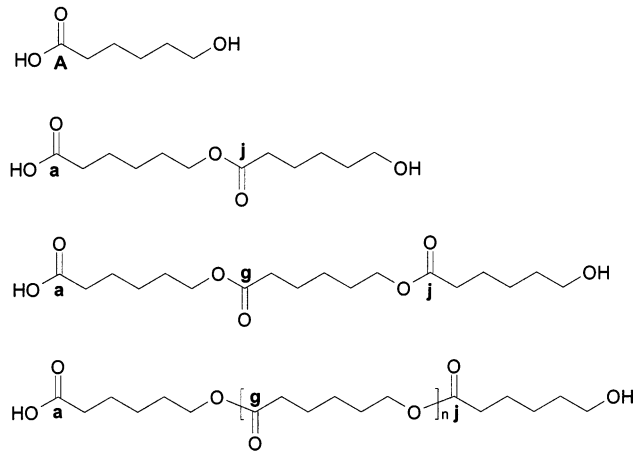


Figure 7. ^{13}C NMR (75.47 MHz)spectrum for HA-PCL. Only the carbonyl zone is shown. Peaks for [$-CO-$O$-$] and [$-CO-$OH] groups in CD_3CN for different CL:H_2O feed ratios: (O1) 1:1.5 (M_n(NMR) = 212), (O2) 2:1 (M_n(NMR) = 383), (O6) 6:1 (M_n(NMR) = 782), (O19) 19:1 (M_n(NMR) = 2198) are shown.

Scheme 2



Using two-dimensional NMR techniques Bovey and Mirau[44] and Nishiura[45] demonstrated that carbon *d* appears at a lower field than carbon *i*.

In Figure 7 the carbonyl region for four samples of HA-PCL with different molecular weights is shown. The peak pattern of the carbonyl zone for high molecular weight sample in CD_3CN is similar to that observed in $CDCl_3$ (see Figure 5). Assignments were made based on the spectra of HA-PCL oligomers and polymers (see Scheme 2).

The observed peak pattern depends strongly on the chain length. In the inset O1 of Figure 7 four peaks at δ 176.29, 176.16, 174.80, and 174.67 can be seen. Signals can be ascribed to carboxylic acid carbonyls (A and *a*, $-CO_2H$) and ester carbonyls (*j* and *g*, $-COO-$). On the other hand, only three signals are distinguished for HA-PCL with higher molecular weight (see inset O19). In inset O1 the carboxylic acid carbonyls are the most intense with the signal for carbonyl A being the highest. Chemical shift and intensity for carboxylic acid carbonyls strongly depends on molecular weight. The peak

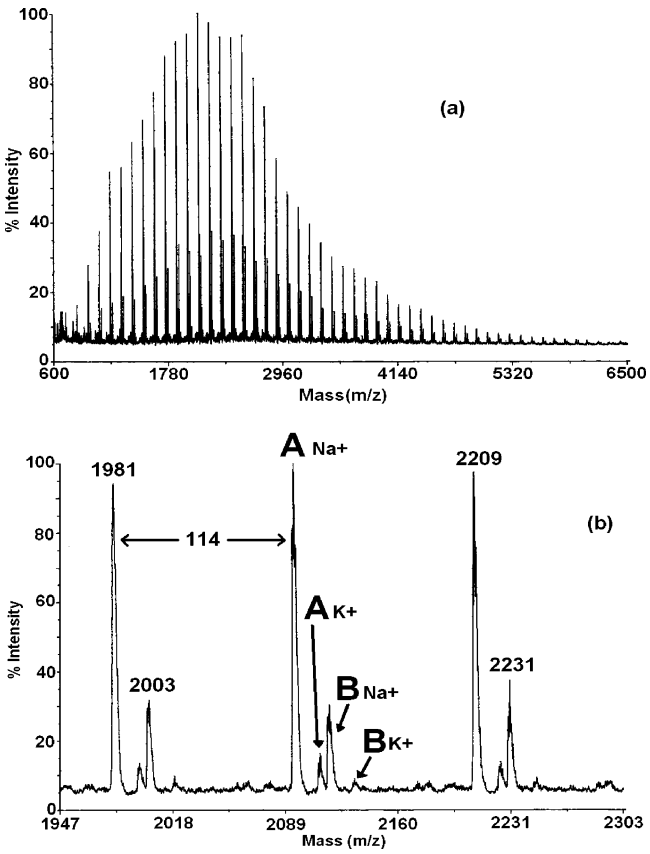
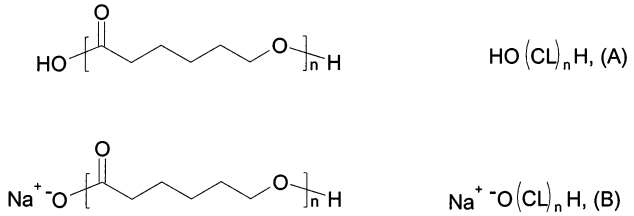


Figure 8. (a) MALDI-TOF spectrum of the HA-PCL (M_n-(NMR) = 2198, M_n(MALDI) = 2410). Polymerization conditions: CL = 47.5 mmol, CL/H_2O = 19 (molar ratio), CL/Hep = 19000, 2 h at 150 °C (see no. 8, Table 1). (b) Expanded view for the 1947−2303 *m/z* fragments.

for carbon A is barely seen for HA-PCL with higher M_n values (see inset O19). On the basis of the differences between the hydrophilic character of −COOH and COOR groups, it is expected that a more *hydrophobic* environment is formed as chain length increases. The observed upfield shifts for carboxylic acid carbons A and *a* reveal that the presence of more monomeric units creates a shielding environment to the carboxylic acid end groups. Progressive increase of chain length also involves a reduction of hydrogen-bonded molecules. Analysis of the oligomer structures shown in Scheme 2 indicates that the only carboxylic acid carbon of the sequence having a different chemical environment is that for hydroxycaproic acid, as it does not have a neighboring ester group. On this basis we assigned the signal for carbon A to the carboxylic acid carbon for this monomeric species. As number-average molecular weight increases, it is expected that the amount of monomeric species is lower. In this regard, the relative intensity of A decreases as the chain length of HA-PCLs increases. The peak pattern shown in O1 is similar to that observed in the ^{13}C NMR spectrum of a commercial sample of hydroxycaproic acid from Aldrich.

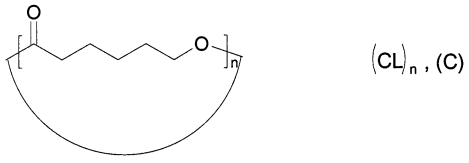
In Figure 8a the MALDI-TOF mass spectrum for HA-PCL (M_n(NMR) = 2198, M_n(MALDI) = 2410, CL/H_2O = 19, reaction time = 2 h) is shown. The curve profile indicates a unimodal distribution, in agreement with the curve observed in the corresponding GPC chromatogram (see Figure 1). Two types of signals (A and B) can be distinguished in the spectrum: one due to linear neutral polymer (A) species and the other to the sodium salt (B).



It is well known that for broad molecular weight distributions (>1.5) the molecular weight obtained with MALDI is generally lower than the actual value. In this case, the spectrum only reflects the low molecular weight part of the distribution.[46] For our HA-PCL oligomer the polydispersity index as obtained by GPC is 1.46, and the calculated M_n from MALDI spectrum is slightly superior to the value obtained with ^{1}H NMR, which lead us to think that the molecular weight distribution obtained with MALDI reflects quite fairly the actual distribution of the sample.

In Figure 8b an expansion of the zone between 1947 and 2303 uma is shown. This region corresponds to fragments with 17−19 CL repeating units. The most intense peaks are due to HA-PCL (A) fragments, whereas the less intense peaks come from α-hydroxyl-ω-(sodium carboxylate) PCL (B) species. Both series are doped with sodium ions. Fragments doped with potassium ions are also present but to a lower extent. As carboxylate end groups are not detected in the carbonyl region (180−190 ppm) of the ^{13}C NMR spectrum for this sample and its oligomers, species B in the MALDI-TOF spectrum should form in situ during MALDI sample preparation.

The nature of the carboxylic acid end groups is related with the condensation reactions occurring after 100% of conversion. As previously mentioned, maximum conversion is achieved after 2 h of reaction. A series of samples was obtained at reaction times above 2 h (see Table 3). The increment in molecular weight is due to polycondensation. From 2 to 48 h, molecular weight increases from 2198 to 3270 Da. In Figure 9 the MALDI-TOF spectrum for HA-PCL obtained after 48 h of reaction is shown. Comparison of the macrocyclic species content observed at 2 and 48 h of reaction indicates that the amount of cyclic species increases with longer residence times (see peak for C_{Na+} in Figure 9).



Cyclic oligomers were produced after long polymerization times from the linear polymer already formed. At conversions lower than 100%, formation of cyclic oligomers is not detected in the MALDI-TOF mass spectrum. In this kind of polymerization it is known that macrocyclic formation by transesterification reaction and/or backbiting degradation is only possible at long reaction times and high degree of conversion.[47] In the ROP of CL by spirocyclic germanium alkoxide (at 140 °C in bulk), an increment in the amount of cyclic species is observed when the reaction time is increased from 24 to 48 h. Likewise, the percent of cyclic oligomers increased when the reaction temperature was increased from 120 to 180 °C.[17] Intramolecular condensation leads to the formation of macrocyclic species and has been reported for other systems such as CL/(SnOct)$_2$/H$_2$O.[48]

Table 3. Bulk Polymerization of CL at 150 °C with CL/H$_2$O = 19 and CL/Hep= 19 000[a]

no.	t (h)	M_n (NMR)[b]
1	2	2198
2	4.6	2415
3	24	3858
4	48	3270

[a] Effect of the reaction time. [b] Determined by ^{1}H NMR.

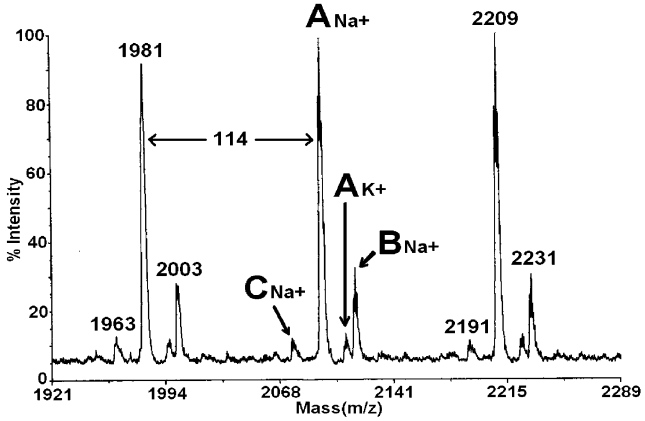


Figure 9. MALDI-TOF spectrum of HA-PCL (M_n(NMR) = 3270). Polymerization conditions: CL = 47.5 mmol, CL/H$_2$O = 19 (molar ratio), CL/Hep = 19 000, reaction time = 48 h at T = 150 °C (see no. 4, Table 2).

Table 4. Insertion of Different Alcohols in the HA-PCL Carboxylic Acid End Group[a]

no.	alcohol	insertion	% insertion	^{13}C NMR[b] (ppm)	M_n (NMR)[c]
1	d				2198
2	e				2415
3	*n*-octanol (OctOH)[a]	yes	49	64.3	2016
4	benzyl alcohol (BzOH)[a]	yes	28	65.9	2640

[a] Polymerization conditions for HA-PCL: 150 °C, CL/H$_2$O = 19, CL/Hep = 19 000, reaction time = 2 h. After 2 h an excess of alcohol was added, and the system was left at 150 °C for an additional 2 h and 40 min. Final products were recrystallized three times from CHCl$_3$/CH$_3$OH. [b] Observed chemical shift in CDCl$_3$ for the methylene alfa to the ester end group (R−*CH*$_2$−O−CO−PCL, R = heptyl or phenyl group). [c] Determined by ^{1}H NMR. [d] In the absence of alcohol, total reaction time = 2 h. [e] In the absence of alcohol, total reaction time = 4 h and 40 min.

Polymerization mechanism involves the following steps: (a) initiation (where ring opening of cyclic ester CL occurs through a nucleophilic attack by water) and propagation by the ROP of CL; (b) afterward a polycondensation and intramolecular condensation at longer time. Molybdates such as sodium molybdate are used as ester-exchange and polycondensation catalysts.[49]

To learn more on the reactivity of the end groups toward hydroxylic compounds, a primary alcohol was added to system CL/Dec/H$_2$O after complete conversion of CL to PCL has occurred (see no. 1, Table 4). In that regard, to the HA-PCL prepared from a CL/H$_2$O ratio of 19 (reaction time = 2 h, M_n = 2198) an excess of octyl or benzyl alcohol (6 mmol) was added. The reaction time between HA-PCL and alcohol was 2.6 h. Final product was recrystallized three times from chloroform/methanol. Analysis by ^{1}H and ^{13}C NMR showed that insertion of octanol (46%) and benzyl alcohol (28%) had occurred (see Table 4, nos. 3 and 4). In the ^{13}C NMR spectra of

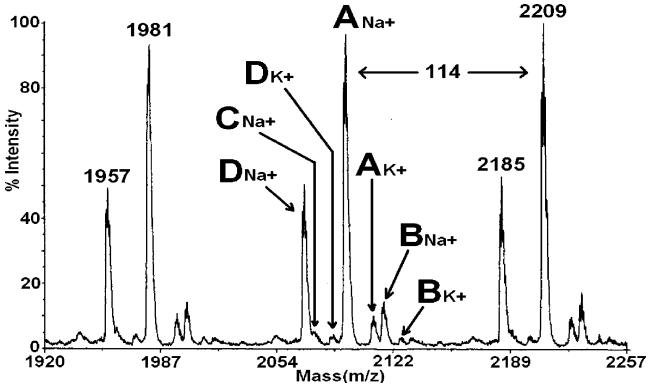
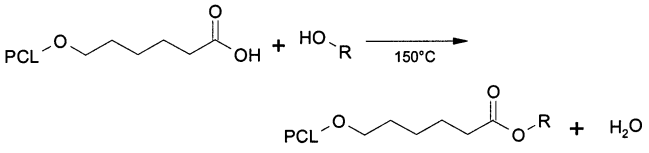


Figure 10. MALDI-TOF spectrum of the HA-PCL (M_n(NMR) = 2640). Polymerization conditions: CL = 47.5 mmol, CL/H_2O = 19 (molar ratio), CL/Hep = 19 000, reaction time = 2 h at 150 °C. After 2 h an excess amount of benzyl alcohol (6 mmol) was added, and the mixture was allowed to react for an additional 2.6 h at 150 °C. Final polymer was recrystallized three times from chloroform/methanol (see no. 4, Table 4).

these derivatives signals for the methylene group bonded to the terminal ester end groups (R−CH_2−O−CO−PCL, where R is heptyl or phenyl group) are seen at δ 64.3 and 65.9, respectively.

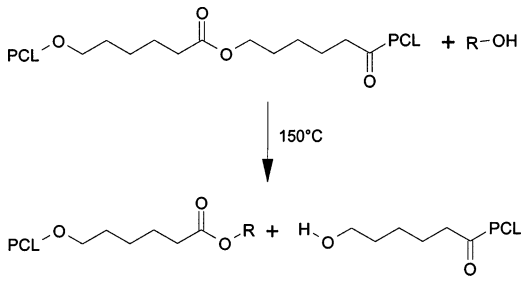
Reaction of alcohols with polymer in the presence of a catalyst can (a) form an ester end group from the reaction between carboxylic acid end groups and the alcohol (see Scheme 3) and (b) produce chain scission

Scheme 3



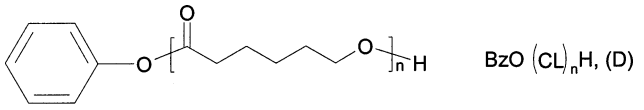
along the polymeric backbone by random nucleophilic addition of R−OH to the ester groups (transesterification reactions, see Scheme 4). In the two cases formation

Scheme 4



of an ester end group (R−OCO−) would be observed. However, Transesterification reactions produce chain fragmentation with a decrease in the polymer molecular weight (Scheme 4). Addition of octanol to HA-PCL produces a polymer with lower molecular weight (M_n = 2016, no. 3 in Table 4), which indicates that transesterification reactions are mainly occurring. On the other hand, after addition of benzyl alcohol a polymer with M_n = 2640 was isolated after 4.6 h. This fact indicates that benzyl alcohol tends to react with the carboxylic acid end groups of the polymer (see Scheme 3).

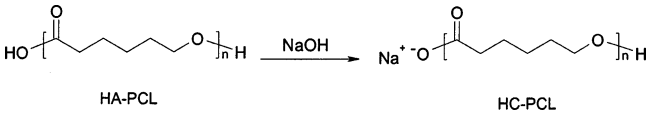
Evidence of addition of the benzyl group to carboxylic acid end groups was obtained by MALDI-TOF. In Figure 10 peaks due to α-hydroxyl-ω-(benzyl ester) PCL species doped with Na^+ and K^+ are observed.



In Table 5 the effect of tempeature, reaction time, and amount of catalyst on the insertion of octyl alcohol is shown. When the reaction temperature is decreased from 150 to 80 °C, alcohol insertion decreases from 49% to 1% (nos. 1−3, Table 5). This indicates that alcohol insertion strongly depends on reaction temperature. On the other hand, the number-average molecular weight increases from 2016 to 2517, which indicates that intermolecular condensation reactions are more favored than octanol insertion (see Schemes 3 and 4). Studies on the effect of increasing the reaction time (from 3 to 7 h, reaction temperature = 150 °C, nos. 1, 4, and 5) show that HA-PCL molecular weight decreases from 2210 to 1767. Alcohol insertion occurs through a chain-scission mechanism (see Scheme 4). The amount of catalyst used increases the observed octyl alcohol insertion from 49% to 66% (nos. 1 and 6). At the same time, intermolecular condensation is also favored, as number-average molecular weight increases from 2016 to 2377, when CL/Hep = 19 000 and 1900 respectively were used.

HA-PCLs have functionalities of 2 and possess reactive functional carboxylic and hydroxylic end groups that can be used for subsequent chain-extension reactions. Physical and chemical properties are complementary to those observed for their α,ω-telechelic PCL diols counterparts.[5,6] On the basis of its particular architecture, selective reactions to obtain carboxylic acid derivatives can be attempted. Thus, the carboxylic acid end group can be converted to the salt derivative (HC-PCLs) under mild conditions (see Scheme 5). HA-PCL (M_n =

Scheme 5



212, no. 1 in Table 1) was converted to its sodium salt α-hydroxyl-ω-(sodium carboxylate) PCL (HC−PCL, see Experimental Section), and the product was characterized by FT-IR spectroscopy. In the FT-IR spectrum of the HA-PCL (Figure 11A) bands at 3345, 2937, 1704, and 1163 cm^{-1}, corresponding to the stretching vibrations of −COOH, $-CH_2-$, −CO−, and −COO− groups, respectively, are seen. In Figure 11B a new band due to the C=O stretching band associated with the sodium carboxylate salt group $-CO_2^-Na^+$ at 1561 cm^{-1} is now present. The peak at 3335 cm^{-1} corresponds to water of crystallization associated to the solid HC-PCL.

HC−PCL was also analyzed by solid-state ^{13}C NMR (see Figure 12A). Assignments were made based on the chemical shifts observed in solution for HA-PCL and literature data. Two signals are observed in the carbonyl zone: one assigned to the carboxylate functionality [a, $-CO_2^-Na^+$, δ 182.2], and the other due to the ester group [g, $-CO_2-$, δ 174.3]. An important feature is the relative low intensity observed for the carboxylate carbon signal (MAS spectrum, Figure 12B) with respect to that observed in the CP-MAS experiments (Figure 12A). This indicates that polarization is effectively transferred from the protons to the carboxylate group in the HC-PCL. One important source for the transfer

Table 5. Insertion of Octyl Alcohol in the HA-PCL[a]

no.	CL/Hep	T (°C)	t (h:min)	% insertion[d]	M_n(NMR)[d]
1[a]	19 000	150	4:40	49	2016
2[b]	19 000	115	4:40	38	2449
3[b]	19 000	80	4:40	1	2517
4[c]	19 000	150	3:00	48	2210
5[c]	19 000	150	7:00	78	1767
6[a]	1900	150	4:40	66	2377

[a] Polymerization conditions: 150 °C, CL/H_2O = 19, CL/Hep = 19 000, reaction time = 2 h. Effect of the temperature, time, and ratio CL/Hep. After 2 h an excess amount of octyl alcohol was added, and the system was left at 150 °C for an additional 2 h and 40 min. Final products were recrystallized three times from $CHCl_3/CH_3OH$. [b] Similar to *a*, with different temperature. [c] Similar to *a*, with different total reaction time. [d] Determined by ^1H NMR.

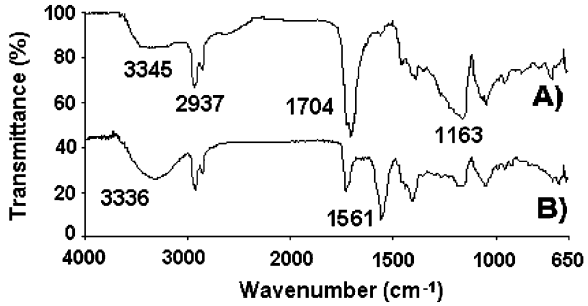


Figure 11. FT-IR spectra of (A) α-hydroxyl-ω-(carboxyl acid) PCL oligomer (HA-PCL) ,M_n(NMR) = 212 (see no. 1, Table 1). (B) After treatment with NaOH to form the α-hydroxyl-ω-(sodium carboxylate) PCL (HC−PCL).

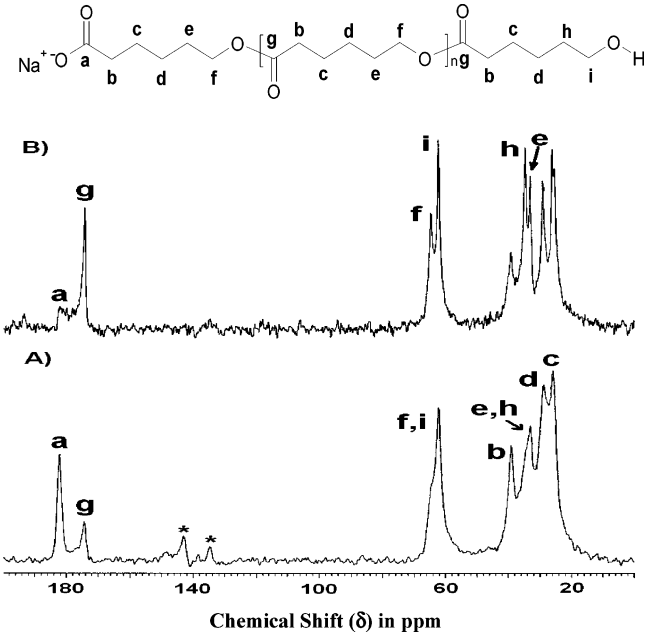


Figure 12. Solid-state ^{13}C NMR (75.47 MHz) spectrum for α-hydroxyl-ω-(sodium carboxylate) PCL (HC−PCL): (A) CP-MAS spectrum, contact time = 2.5 ms, repetition time = 8 s; (B) MAS spectrum with a repetition time of 30 s. Spinning sidebands are indicated by an asterisk.

process can come from the protons of the water of crystallization present in the molecule. Resolution in the HC-PCL MAS spectrum allows the observation of all expected signals, in particular for carbons in the beta and gamma positions with respect to the carbonyl group (*c* and *d*). These peaks are not resolved in either the CP-MAS spectrum or the spectra reported in the literature for PCL.[44,50−52]

Conclusions

Ammonium-decamolybdate-catalyzed ring-opening polymerization of lactones with water as initiator allows the synthesis of functionalized oligomers at 150 °C. Quantitative conversions (on the order of 100%) and short reaction times (2 h) are involved. The molecular weight of oligomers can be controlled based on the initial CL/H_2O ratio up to approximately 2000 Da.

Two stages can be recognized during the ring-opening polymerization of CL and VL in the system lactone/Dec/H_2O. In the initiation step ring opening of lactone with water acting as initiator occurs, followed by addition of more lactone molecules through the hydroxyl end groups (propagation step). When low monomer/H_2O ratios (low M_n oligomers) are used, some condensation occurs. Once the α-hydroxyl-ω-(carboxylic acid) PCL is formed, intermolecular condensation takes place. Intramolecular condensation (to give cyclic species) is another possible reaction and is observed to a very low extent during polymerization. For longer reaction times the cyclization reaction becomes more important.

Alcohol addition confirms the possibility of condensation reactions taking place. Furthermore, benzyl alcohol tends to condensate with carboxylic end groups, whereas octyl alcohol also produces transesterification reactions.

Synthesis of an asymmetric telechelic architecture in α-hydroxyl-ω-(carboxylic acid) PCL and α-hydroxyl-ω-(carboxylic acid) PVL allows many options to the derivatization of the oligomers. Potential uses of HA-PCL derivatives, such as their carboxylic acid salts, need to be explored.

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