Ring-Opening Polymerization of Lactones Using $RuCl_2(PPh_3)_3$ as Initiator: Effect of Hydroxylic Transfer Agents

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ABSTRACT: ε-Caprolactone and δ-valerolactone were polymerized in bulk at 150°C using the ruthenium(II) complex $RuCl_2(PPh_3)_3$ as initiator in the presence of 1,3-propanediol (PD) with a series of alcohols as coinitiators. Polymerization of lactones proceeds via ruthenium(II) alkoxide active centers. ^{1}H-NMR analysis revealed that the ruthenium complex reacted with the alcohol, generating in situ a ruthenium alkoxide. This species became a more active initiator of ring-opening polymerization than was $RuCl_2(PPh_3)_3$. The obtained polylactones were characterized by ^{1}H- and ^{13}C-NMR and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF). The results showed the formation had occurred of α,ω-telechelic PCL and PVL diols, in which PD had been incorporated into the polymer backbone. Depending on the nature of the alcohol used as coinitiator, PCLs with different end groups could be synthesized. Insertion of an alcohol as an end group (benzyl alcohol, *n*-octanol, or isopropanol) or into the polymeric backbone (propanediol) provided support for the conclusion that a classical coordination–insertion mechanism was operating during lactone polymerization. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2737–2745, 2006

Key words: polyesters; ring-opening polymerization; initiator; metal-organic catalysts

INTRODUCTION

In the last few decades, the need for materials with biodegradable properties has increased the interest in biodegradable polymers such as polylactones.[1] Poly(ε-caprolactone) (PCL) and poly(δ-valerolactone) (PVL) are two important polylactones. They are currently obtained by ring-opening polymerization (ROP) of their corresponding precursors, ε-caprolactone (CL) and δ-valerolactone (VL), respectively.

The initiators most commonly used in ROP of cyclic esters are metal alkoxides. Many groups of researchers[2–6] have reported using alkoxides derived from alkaline metals and rare earth elements containing unoccupied p, d, and f orbitals (such as Mg, Zn, Al, Sn, Ti, Zr, Sm, and Y alkoxides) as initiators in the polymerization of cyclic esters. The effectiveness of these compounds has mainly relied on the ability of the particular alkoxide to induce formation of the initiation species, which involves the complexation of the monomer with the initiator via free p or d orbitals, followed by cleavage of the lactone acyl-oxygen bond.

The final morphology and other properties of low-molecular-weight polylactones are closely related to the end-group functionalities. The architecture of the end groups allows versatility in the chemistry of these polymers, as many derivatives with potential new properties can be obtained by proper derivatization. The most common route for obtaining functionalized polylactones involves use of a primary or secondary alcohol as coinitiator. Some recent reports have taken up this approach, and functionalized PCL[7–9] and PVL[9,10] can be obtained in quantitative yields.

Ruthenium derivatives have found widespread use as catalysts in the hydrogenation and oxidation of olefins, in the decarbonylation and dehydration of alcohols, and in hydrogen transfer reactions, among others.[11] Ruthenium catalysts mainly have been used for ring-opening metathesis polymerization of cyclic olefins.[12–15] The main oxidation states for ruthenium are II and III. Ruthenium complexes have a variety of useful characteristics including high electron transfer ability, high Lewis acidity, low redox potentials, and stabilities of reactive metallic species such as oxometals, metallocycles, and metal–carbene complexes. Thus, a large number of novel, useful reactions have begun to be developed using both stoichiometric and catalytic amounts of ruthenium complexes.

Catalytic systems for ROP of lactones are generally composed of derivatives of the transition metals that are on the left side of the d block of the periodic table.

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TABLE I
Polymerization of CL with $RuCl_2(PPh_3)_3$ as Initiator and 1,3-Propanediol (PD) as Coinitiator

No.	CL/PD[a]	Coinitiator/initiator PD/$RuCl_2(PPh_3)_3$	Time (h)	Conv. (%)[b]	DP[b]	$M_{n(calcd)}$[c]	$M_{n(NMR)}$[b]
1	50	20	38	100	35	5780	4070
2	20	50	30	100	22	2360	2590
3	10	100	26	100	14	1220	1670
4	5	500	24	100	8	650	990

Experimental conditions: Temperature/150°C, CL/initiator = 1000.
[a] CL/PD molar ratio, calculated from (CL mol)/PD mol.
[b] Obtained by ^{1}H-NMR.
[c] Obtained from the equation M_n = (MW(L)(M]/PD) + MW(PD), where MW is the molecular weight of lactone monomer or 1,3-propanediol.

However, the use of derivatives of the transition metals from the center to the right side of *d* block has not been investigated. To our knowledge, there have been no reports in the literature regarding the use of ruthenium derivatives in ROP of lactones. On the basis of the aforementioned properties of ruthenium derivatives, we decided to study their effectiveness in inducing ROP of cyclic esters. The aim of this work was to test the effectiveness of dichlorotris(triphenylphosphine)ruthenium(II) $RuCl_2(PPh_3)_3$ (**I**) as a catalyst for ROP of VL and CL. Also, the feasibility of using this catalyst to obtain polyesters with specific end groups, using alcohol and water as coinitiators, was explored. The results indicated that ruthenium derivatives catalyze ROP of lactones, but long reaction times are required to achieve quantitative polymerization. The presence of alcohols involves the formation of a more active initiator species, which shortened the polymerization reaction time and also led to the formation of specific end groups as a function of the alcohol used.

EXPERIMENTAL

Materials

ε-Caprolactone (CL; Aldrich Chemicals Co., Mexico) and δ-valerolactone (VL; Fluka, Mexico) were dried over calcium hydride and distilled under reduced pressure before use. Benzyl alcohol (BzOH), 2-propanol, *t*-butanol, and octyl alcohol (OctOH) were purchased from Aldrich and dried with Na metal for 48 h at room temperature and distilled under a reduced pressure. 1,3-Propanediol (PD; Aldrich Co.) was used without further purification. Distilled water was purchased from J. T. Baker. Ruthenium(II) complexes dichlorotris(triphenylphosphine)ruthenium(II) $RuCl_2(PPh_3)_3$, **I** (Strem Chemical for Research, Newburyport, MA) was used as received).

Synthesis of α,ω-telechelic poly(ε-caprolactone) diols (D-PCL) and α,ω-telechelic poly(δ-valerolactone) diols (D-PVL)

Polymerization was carried out in the presence of 1,3-propanediol (PD) and initiator complex **I** in 5-mL vials previously dried and purged with dry nitrogen. In a typical run, monomer (CL, 15.0 mmol), initiator (complex **I**, 0.015 mmol, 14.3 mg), and PD (0.75 mmol) were added under a nitrogen atmosphere. Vials were stoppered with a rubber septum and placed in a thermostated bath at 150°C for 30 h. The final polymer was crystallized from chloroform/methanol and dried under vacuum. Varying the feed molar ratio of CL monomer to PD controlled the number-average molecular weight (M_n). In this study, the feed molar ratios of CL to the hydroxyl (OH) of PD were 5 : 1, 10 : 1, 20 : 1, and 50:1 (Table I). Molecular weight and conversion during reaction were monitored by ^{1}H-NMR. The crystallized polymer was analyzed by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF). Polymerization of VL was carried out in a similar way. NMR data for D-PCL—^{1}H-NMR (300 MHz, $CDCl_3$, ppm): δ 4.10 [t, 4H, — ($CH_2O)_2$—] of propanediol in D-PCL, 4.00 (t, 2H, —CH_2O—), 3.52 (t, 2H, —CH_2OH), 2.25 (t, 2H, —CH_2CO_2—), 1.90 (q, 2H, —CH_2CH_2O—) of propanediol in D-PCL, 1.54 [m, 4H, —($CH_2)_2$—], 1.30 (q, 2H, —CH_2—); ^{13}C-NMR (50 MHz, $CDCl_3$, ppm): δ 173.57 (8′), 173.37 (8), 173.23 (8″), 63.96 (3), 62.27 (3′), 60.68 (2), 34.06 (4′), 33.85 (4″), 33.94 (4), 32.15 (5′), 28.17 (5), 27.83 (1), 25.35 (7), 25.16 (7′), 24.54 (6′), 24.40 (6). NMR data for D-PVL—^{1}H-NMR (300 MHz, $CDCl_3$, ppm): δ 4.15 [t, 4H, —($CH_2O)_2$—] of propanediol in D-PVL, 4.02 (t, 2H, —CH_2O—), 3.62 (t, 2H, —CH_2OH), 2.20 (t, 2H, —CH_2CO_2—), 1.95 (q, 2H, —CH_2CH_2O—) of propanediol in D-PVL, 1.56 (m, 4H, [—($CH_2)_2$—]; ^{13}C-NMR (50 MHz, $CDCl_3$, ppm): δ 173.20, 173.12, 173.00, 63.74, 61.98, 60.74, 33.74, 33.51, 32.98, 31.90, 27.88, 21.25, 20.98.

Synthesis of α,ω-trifluoroacetate D-PCL (TF-DPCL) and α,ω-trifluoroacetate D-PVL (TF-DPVL) by derivatization of D-PCL and D-PVL with trifluoroacetic anhydride

An excess of trifluoroacetic anhydride (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. ^{1}H-NMR data for TF-DPCL (300 MHz, $CDCl_3$, ppm): δ 4.30 (t, 2H,

TABLE II
Polymerization of CL with $RuCl_2(PPh_3)_3$ as Initiator and Different Hydroxylic Transfer Agents (ROH) as Coinitiators

No.	Coinitiator (ROH)	CL/ROH	M_w/M_n[a]	M_n (GPC)[a]	Conv. (%)[b]	$M_{n(calcd)}$[c]	DP[b]	$M_{n(NMR)}$[b]	Ratio[d]
1	*n*-octanol	20	—	—	100	2410	21	2530	—
2	Benzyl alcohol	20	1.47	5310	100	2390	18	2160	0.45
3	Isopropanol	20	—	—	100	2340	18	2120	—
4	Tert-Butanol	20	—	—	100	2300	29	3330	—
5	Water	20	1.45	4900	100	2300	25	2870	0.47
6	1,3-Propanediol	20	1.49	5390	100	2360	22	2590	0.48

Experimental conditions: temperature, 150°C; CL/initiator, 1000; reaction time, 30 h.
[a] Determined by gel permeation chromatography using polystyrene standards.
[b] Obtained by ^{1}H-NMR.
[c] Obtained from the equation M_n = (MW(L)([M]/RO) + MW(ROH), where MW is the molecular weight of lactone monomer or ROH.
[d] $M_{n(calcd)}/M_{n(GPC)}$ ratio.

—CH_2OCOCF_3), 4.10 [t, 4H, — ($CH_2O)_2$—] of propanediol in D-PCL, 4.02 (t, 2H, —CH_2O—), 2.28 (t, 2H, —CH_2CO_2—), 1.90 (q, 2H, —CH_2CH_2O—) of propanediol in D-PCL, 1.60 [m, 4H, —$(CH_2)_2$—], 1.33 (q, 2H, —CH_2—); ^{1}H-NMR data for TF-DPVL (300 MHz, $CDCl_3$, ppm): δ 4.32 (t, 2H, —CH_2OCOCF_3), δ 4.15 [t, 4H, —($CH_2O)_2$—] of propanediol in D-PVL, 4.05 (t, 2H, —CH_2O—), 2.32 (t, 2H, —CH_2CO_2—), 1.95 (q, 2H, —CH_2CH_2O—) of propanediol in D-PVL, 1.62 [m, 4H, —$(CH_2)_2$—].

Synthesis of PCL with different end groups as a function of the nature of the hydroxylic transfer agents (ROH) used as coinitiators

Polymerization was carried out in the presence of different alcohols (Table II) and initiator complex **I** in 5-mL vials previously dried and purged with dry nitrogen. In a typical run, monomer (CL, 15.0 mmol), initiator (complex **I**, 0.015 mmol, 14.3 mg), and alcohol (0.75 mmol) were added under a nitrogen atmosphere. Vials were stoppered with a rubber septum and placed in a thermostated bath at 150°C for 30 h. The final polymer was crystallized from chloroform/methanol and dried under vacuum. Changing the nature of the alcohol used was a versatile way to modify the end groups in the polymer and to contribute to the macromolecular engineering of PCL. The nature of the PCL end groups was determined by ^{1}H- and ^{13}C-NMR spectroscopy.

Synthesis of α-hydroxylic-ω-(carboxylic acid) poly(ε-caprolactone) (HA-PCL) and α-hydroxylic-ω-(carboxylic acid) poly(δ-valerolactone) (HA-PVL)

Polymerization was carried out in 5-mL vials previously dried and purged with dry nitrogen. In a typical run, monomer (CL, 15.0 mmol), initiator (complex **I**, 0.015 mmol, 14.3 mg), and water (0.75 mmol, 13.5 mg) were added under a nitrogen atmosphere. Vials were stoppered with a rubber septum and placed in a thermostated bath at 150°C for 30 h. The 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. Polymerization of VL was carried out in a similar way. NMR data for HA-PCL—^{1}H-NMR (300 MHz, $CDCl_3$, ppm): δ 4.00 (t, 2H, —CH_2O—), 3.52 (t, 2H, —CH_2OH), 2.25 (t, 2H, —CH_2CO_2—), 1.54 [m, 4H, —$(CH_2)_2$—], 1.30 (q, 2H, —CH_2—); ^{13}C-NMR (50 MHz, $CDCl_3$, ppm): δ 176.00, 173.45, 173.26, 63.83, 62.17, 33.80, 33.92, 33.29, 31.99, 28.03, 25.21, 25.01, 24.26, 24.39, 24.10. NMR data for HA-PVL—^{1}H-NMR (300 MHz, $CDCl_3$, ppm): δ 4.02 (t, 2H, —CH_2O—), 3.62 (t, 2H, —CH_2OH), 2.20 (t, 2H, —CH_2CO_2—), 1.56 [m, 4H, —$(CH_2)_2$—]; ^{13}C-NMR (50 MHz, $CDCl_3$, ppm): δ 176.30, 173.53, 173.11, 63.74, 61.94, 33.74, 33.51, 32.98, 31.90, 27.90, 21.25, 20.98.

Measurements

Solution ^{1}H- and ^{13}C-NMR spectra were recorded at room temperature on a Varian Gemini 2000 (200-MHz ^{1}H- and 50-MHz ^{13}C-NMR) and on a Varian Unity Plus 300 (300-MHz ^{1}H- and 75.47-MHz ^{13}C-NMR) using chloroform-*d* ($CDCl_3$) as solvent. Spectra were referenced to the residual solvent protons at δ 7.27 for $CDCl_3$ in the ^{1}H-NMR spectrum and to the residual solvent carbons at δ 77.0 for $CDCl_3$ in the ^{13}C-NMR spectrum. GPC measurements were made in a Varian HPLC 9012Q equipped with two gel columns, Styragel® HR 3 and Styeagel® 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. Measurements were made at 30°C, and commercial polystyrene standards were employed for calibration to calculate the molecular weight of the polyesters. MALDI-TOF spectra were recorded in the linear mode using a Voyager DE-PRO time-of-flight mass spectrometer (Applied Biosystems) equipped with a nitrogen laser emitting at λ = 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 THF was used as the matrix. Samples were dissolved in THF and mixed with the matrix at a molar ratio of approximately 1 : 100.

RESULTS AND DISCUSSION

Ring-opening polymerization of ε-caprolactone and δ-valerolactone by $RuCl_2(PPh_3)_3$

Bulk polymerization of CL was carried out using $RuCl_2(PPh_3)_3$ (**I**) as initiator. Polymerization of CL (15 mmol) at 150°C initiated by **I** with a monomer/initiator ratio of CL/**I** = 1000 showed a 100% conversion after 85 h. A polyester with a number-average molecular weight, M_n (recorded from NMR data) of 11,460 was obtained. This result indicates that long reaction times were required to obtain quantitative conversions. The dependence of molecular weight on the monomer/initiator ratio was studied. It was found that the M_n did not linearly depend on the CL/**I** ratio. This implies that proper control of the molecular weight cannot be achieved using this initiator. Analysis by MALDI-TOF of this sample showed that mainly HA-PCL was formed, indicating that the polymerization initiation step—which involves the ring-opening of the cyclic ester—occurred by (1) a nucleophilic attack of chloride and/or (2) a nucleophilic attack of water, present in very small amounts.

It has been demonstrated that the use of coinitiators such as alcohols can reduce the observed reaction times in ROP of cyclic esters. However, a decrease in the molecular weight of the obtained polymer also was observed.[16] The use of alcohols in the reaction system investigated in this study was justified by three assumptions: (1) the presence of alcohols (that, in turn, generate metal alkoxides) accelerates the overall reaction rate (by activating the acyl-oxygen cleavage during the initiation step), (2) coinitiators act as a chain transfer agent and can control the final molecular weight, and (3) a functionalized polymer can be obtained, depending on the nature of the alcohol used. With respect to the first assumption, the formation of in situ ruthenium alkoxide was expected by the reaction of complex **I** with the alcohol.

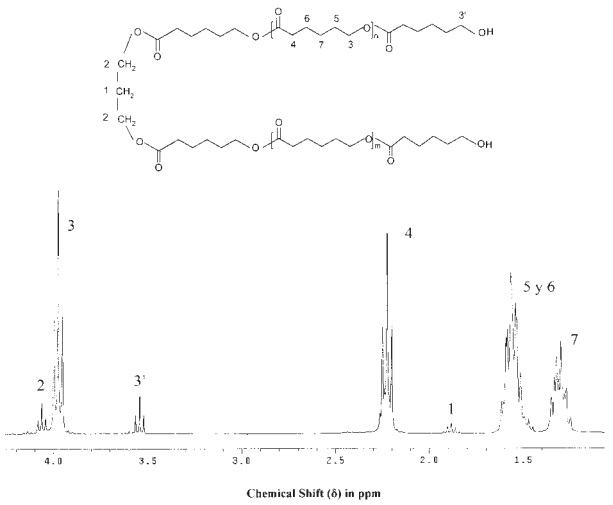

Figure 1 The 300-MHz ^{1}H-NMR spectrum of α,ω-telechelic poly(ε-caprolactone) diol, D-PCL, in $CDCl_3$ obtained using $RuCl_2(PPh_3)_3$(I) as initiator [CL/1,3-propanediol = 20; see Table I(2)].

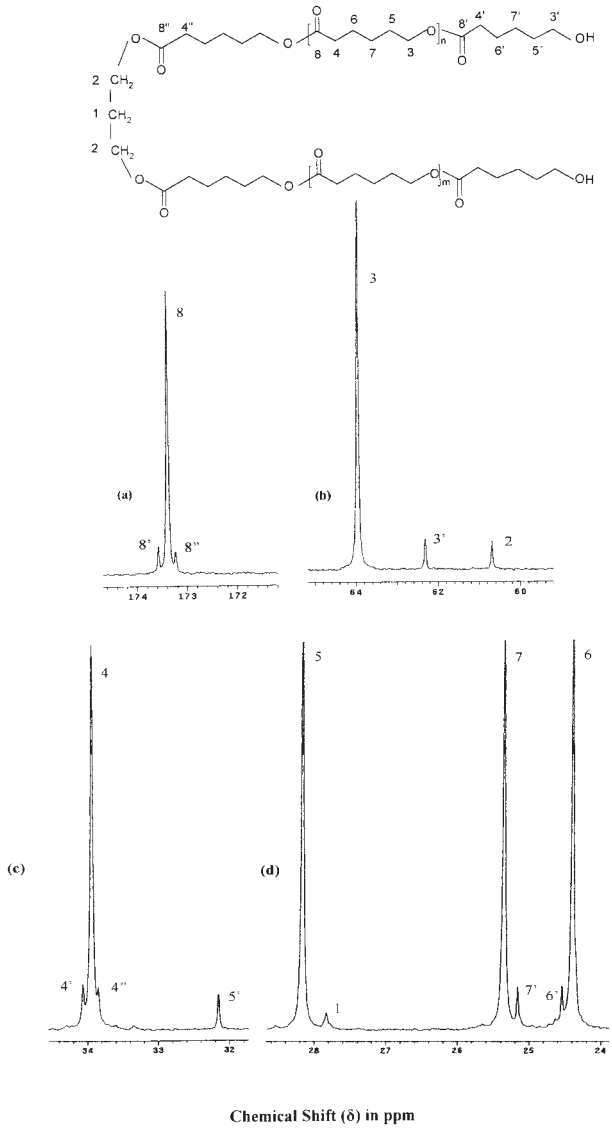

Figure 2 The 75-MHz ^{13}C-NMR spectrum of α,ω-telechelic poly(ε-caprolactone) diol, D-PCL, in $CDCl_3$ obtained using $RuCl_2(PPh_3)_3$(I) as initiator [CL/1,3-propanediol = 20; see Table I(2)]: (a) carbonyl region; (b) methylene carbon —CH_2—O—; (c) methylene carbon α to carbonyl —CO—CH_2—; (d) methylene carbons β, γ, and δ.

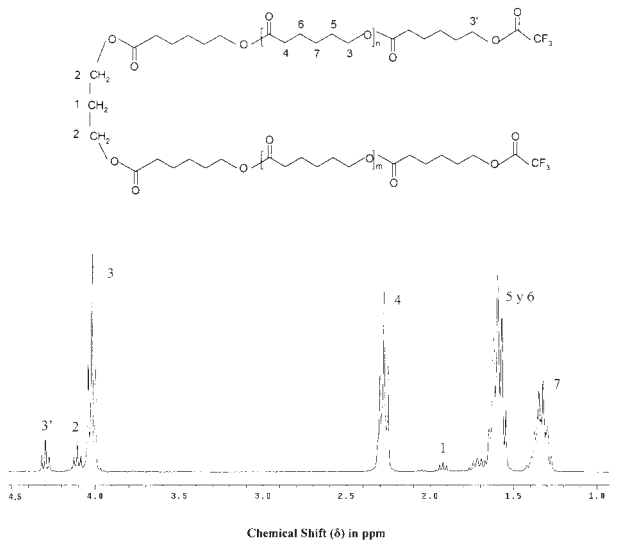

Figure 3 The 300-MHz ^{1}H-NMR spectrum of α,ω-telechelic poly(ε-caprolactone) diol, D-PCL, in $CDCl_3$ obtained using $RuCl_2(PPh_3)_3$(I) as initiator [CL/1,3-propanediol = 20; see Table I(2)], after derivatization with trifluoroacetic anhydride (TFA) an α,ω-trifluoroacetate D-PCL (TF-DPCL).

Polymerization of CL (15 mmol) at 150°C initiated by **I** (CL/**I** = 1000) in the presence of 1,3 propanediol (CL/PD = 20) produced a polymer with a molecular weight calculated by NMR of 2590 and a reaction time of 30 h (100% conversion, see Table I). It was evident that the presence of PD affected the polymerization rate, apparently because of the formation of a more active catalytic species formed from the interaction between the PD and complex **I**. The ^{1}H-NMR spectrum of the final polyester showed that complete incorporation of PD into the polymeric backbone was attained (see Fig. 1). It was also evident that both polymer end groups were hydroxyl groups (HO—CH_2—, δ 3.60). The final polymer architecture of D-PCL also was supported by the observed ^{13}C-NMR peak pattern (Fig. 2). Peaks for hydroxylic methylene (—CH_2OH, δ 62.31), for PD ether methylene inserted in the polymer (—CH_2O—, δ 60.69), and for the central PD methylene (—CH_2—CH_2 —CH_2O—, δ 27.84) were present in the spectrum. Similar end groups recently have been reported by Guillaume[17] and Kricheldorf.[18]

A common procedure to derivatize PCL with hydroxylic end groups consists of treatment with trifluoroacetic acid (TFA) in order to obtain the corresponding ester derivatives. Ester formation causes an upfield shift of the triplet methylene end groups, from 3.5 ppm (CH_2OH) to 4.3 ppm (—CH_2—OCOCF_3; see Fig. 3). The insertion of a PD group in the polymer main chain could be a consequence of the in situ formation of ruthenium alkoxide by the reaction of complex **I** and PD (see above). Polymerization would proceed via monomer insertion into the metal–alkoxide bond, with simultaneous acyl-oxygen bond cleavage. A similar behavior was reported for the polymerization of CL by bismuth(III) acetate.[18]

End-group functionality depends on the nature of the transfer agent. Table II shows the characteristics of the polymers obtained by ROP of CL by **I** in the presence of different coinitiators. For D-PCL, a polymer with a number-average molecular weight of 5390 (determined by GPC) and moderate polydispersity (M_w/M_n = 1.49) was obtained [see Table II(6)]. It was observed that the recorded DP was proportional to the CL/ROH molar ratio, which indicates that proper control of polymer molecular weight can be achieved using the appropriate amount of alcohol in the initial feed.

Polydispersity (M_w/M_n) in the range of 1.45–1.49 was recorded by GPC (see Fig. 4). The number-average molecular weight obtained by GPC (M_n = 5390) differs from that calculated by ^{1}H-NMR (M_n = 2590). The theoretical number-average molecular weight recorded from the CL/PD ratio (M_n = 2360) was close to that obtained by NMR. Overestimation of the M_n obtained by GPC for PCL is common because polystyrene standards are used in the construction of the calibration curve. MacLain and Drysdale found that the M_n(calcd)/M_n(GPC) ratio was approximately 0.45 for PCL.[19] Values between 0.36 and 0.6 were recorded by Báez et al.[8]

The nature of PCL end groups (ε) of PCL in the obtained samples was determined by ^{1}H- and ^{13}C-NMR. The end-group methylene protons obtained when *n*-octanol or benzyl alcohol were used showed a triplet at 3.96 ppm and a singlet at 5.1 ppm, respectively. When isopropyl alcohol was used, a septet for —C*H* end group functionality centered at 4.9 ppm was observed. Benzyl alcohol led to α-hydroxyl-ω-(benzyl ester) PCL (Fig. 5).

Number-average molecular weight (M_n) was recorded by NMR from the ratio of the intensity of the main-chain methylene peak, —CH_2—O—CO—, to the intensity of the end group, —CH_2OH ($M_{n\ \mathrm{NMR}}$). The recorded values were close to those calculated from the M/ROH ratio ($M_{n\ \mathrm{calcd}}$, see Table II).

Chemical shift data for the carbonyl and methylene carbons attached to oxygen (Cα) are shown in Table III. In the carbonyl region, three signals resulting from different ester carbonyl species were seen [see Fig. 2(a)]. The most intense peak corresponded to the carbonyl of the repeating unit C8, whereas the other two signals were ascribed to the ester carbonyl end groups. The chemical shift for the end-group carbon C8″ depended on the nature of the alkyl group of the alcohol in ROH. In that regard, the differences observed in the chemical shifts of the C8″ carbonyl carbons and in the methylene carbons linked to oxygen (Cα) resulted from the differences in the chemical environments of the end groups.

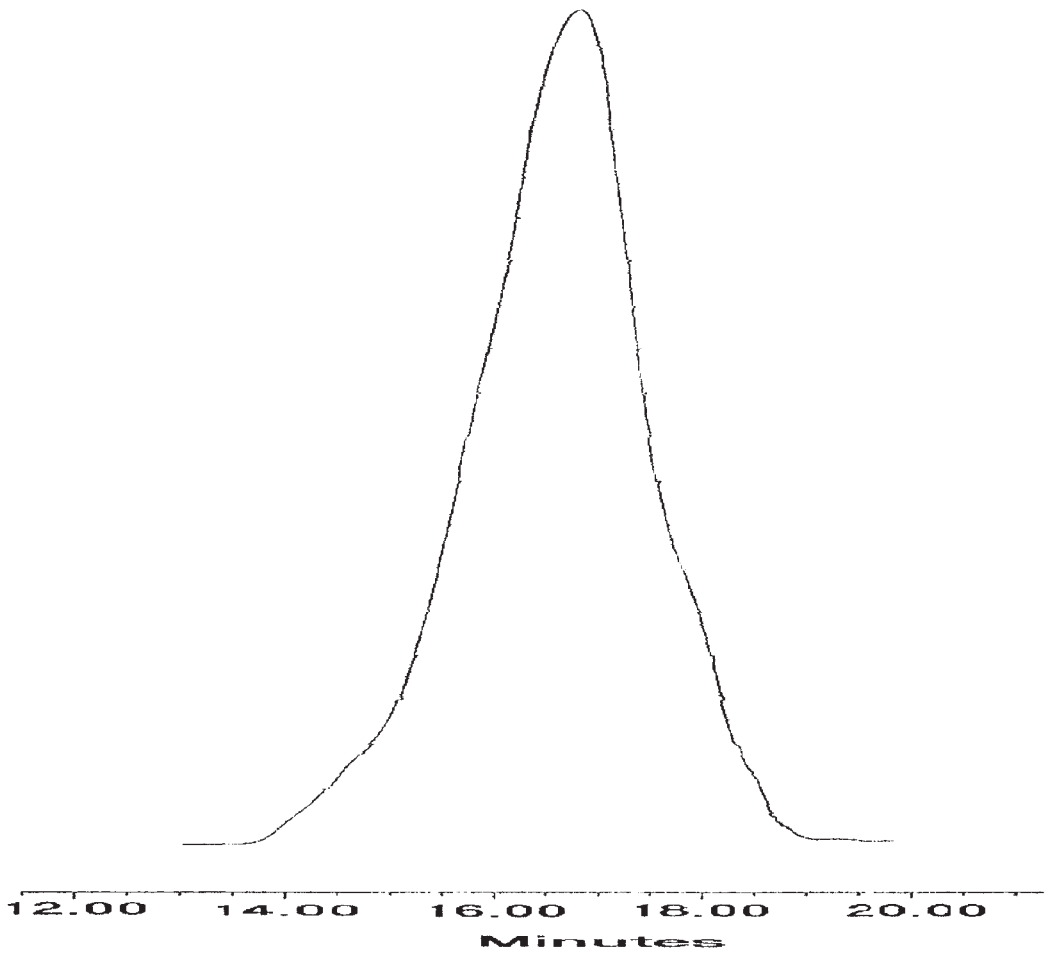

Figure 4 GPC profile of PCL [M_n(GPC) = 4900, M_w/M_n = 1.45; see Table II(5)].

When water was used as a coinitiator, formation of a polyester (HA-PCL) with hydroxyl and carboxylic acid end groups was achieved. In the ^{13}C-NMR spectrum, signals for CO_2H (δ 176.00) and —CH_2OH (δ 62.17) end groups were present. This synthetic procedure constitutes an alternative route to asymmetric telechelic α-hydroxyl-ω-(carboxylic acid) PCL.

When *tert*-butyl alcohol was used as a coinitiator, the formation of hydroxyl-ω-(*tert*-butyl ester) PCL did not occur. Instead, formation of HA-PCL was observed. It is well known that ruthenium derivatives catalyze the dehydration of tertiary alcohols, resulting in the formation of water and the corresponding alkene.[20] This is the basis for the explanation of why HA-PCL was formed, as complex **I** could catalyze the dehydration of *tert*-butyl alcohol before ROP of CL occurred. Water obtained from this reaction acted as the real coinitiator in the polymerization reaction.

Polymerization of VL was carried out under conditions similar to those for CL. VL (15 mmol) was polymerized at 150°C using **I** as initiator (VL/**I** = 1000) in the presence of water (VL/H_2O = 20), and 100% conversion was observed after 48 h. Obtained was α-hy-

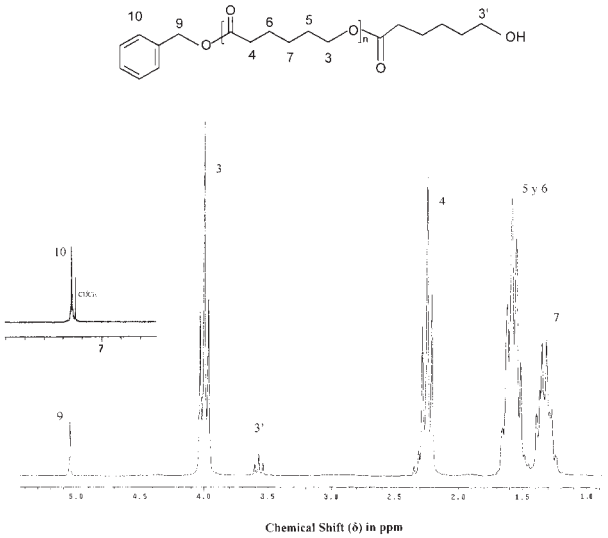

Figure 5 The 300-MHz ^{1}H-NMR spectrum of α-hydroxyl-ω-(benzyl ester) PCL in $CDCl_3$ obtained using $RuCl_2(PPh_3)_3$(I) as initiator [CL/benzyl alcohol = 20; Table II(2)].

TABLE III
Observed ^{13}C-NMR Chemical shifts in $CDCl_3$ for Carbonyl Carbons and Methylene Carbons Linked to Oxygen (Cε) for PCL Obtained from ROP of CL Initiated by $RuCl_2(PPh_3)_3$ and Different Hydroxylic Transfer Agents (ROH) as Coinitiators

R-OH	8′ (δ) ppm	8 (δ) ppm	8″ (δ) ppm	3 (δ) ppm	R—CH_2—O— (δ) ppm	3′ (δ) ppm
n-Octanol	173.49	173.29	173.29	63.91	64.25	62.17
Isopropanol[a]	173.49	173.29	172.79	63.87	67.21[a]	62.20
Benzyl alcohol	173.49	173.30	173.05	63.89	65.88	62.22
Tert-butanol	173.78	173.58	176.30	64.16	—	62.49
1,3-Propanediol	173.57	173.37	173.23	63.96	60.68	62.27
Water	173.45	173.26	176.00	63.83	—	62.17

[a] (CH_3)—CH—O—.

droxyl-ω-(carboxylic acid) PVL (HA-PVL), whose molecular weight (NMR) was 6300. The existence of hydroxyl and carboxylic acid end groups was corroborated by ^{13}C-NMR and MALDI-TOF. Figure 6 shows the MALDI-TOF spectrum for HA-PVL. Only the peak pattern expected for HA-PVL doped with Na^+ can be seen, as the separation between fragments equaled 100 uma.

Polymerization of VL initiated by **I** in the presence of PD (VL/PD = 20) showed 100% conversion in 42 h. A polymer with two hydroxyl end groups whose molecular weight (NMR) was; 2540 was obtained. Figure 7 shows the MALDI-TOF spectrum for D-PVL. It is clear that only one series of peaks (corresponding to a linear polymer, HO—$(VL)_n$—O—$(CH_2)_3$—O—$(VL)_n$—OH, doped with Na^+ ions) was present, and backbiting and formation of cyclic species was negligible.

Initiation mechanism for the polymerization of lactones

To learn more about the reactivity of complex **I** with alcohols, the interaction of benzyl alcohol (BzOH) with complex **I** was investigated as a reaction model by ^{1}H-NMR spectroscopy. Figure 8 shows two ^{1}H-NMR spectra of the CL/BzOH/complex **I** reaction mixture in the methylene-linked-to-oxygen region at different reaction times. Figure 8(a) shows the spectrum observed after 8 h at 25°C. Signals from a unresolved AA′XX′ system centered at 4.1 ppm (3, —CH_2O—, CL), a singlet at 5.0 ppm (1, —CH_2OH, BzOH), and another singlet at 4.84 ppm (2, —OH, BzOH) were present. The observed chemical shifts for the methylene and hydroxyl protons of benzyl alcohol indicated the formation of a strong hydrogen-bonded species. The reaction temperature was increased to 120°C and kept there for 15 h. After this, a ^{1}H-NMR spectrum was recorded, which showed new peaks in the methylene-linked-to-oxygen region: a triplet at 3.82 ppm (5, —CH_2ORu) and a singlet at 5.38 ppm (4, —CH_2OCO), indicating the formation of a ruthenium alkoxide, namely, 5-(benzyloxycarbonyl)-pentyloxy ruthenium(II), complex **II** [see Fig. 8(b)].

The signal observed for the proton attached to carbon 4 in complex **II** split after long reaction times (see

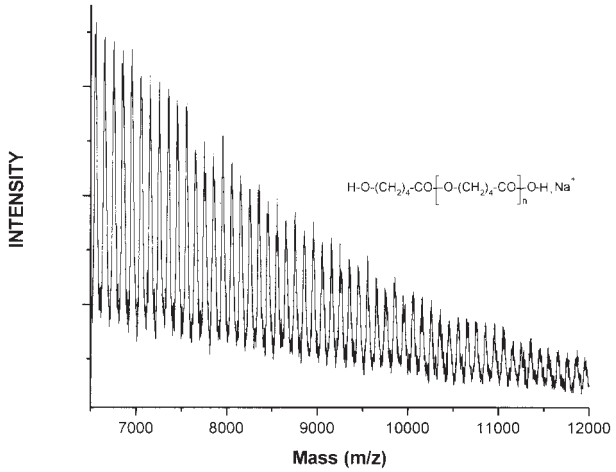

Figure 6 MALDI-TOF mass spectrum of α-hydroxyl-ω-(carboxylic acid) PVL, HA-PVL [M_n(NMR) = 6304]. Polymer was obtained using I as initiator (VL/I = 1000) in the presence of H_2O (VL/H_2O = 20).

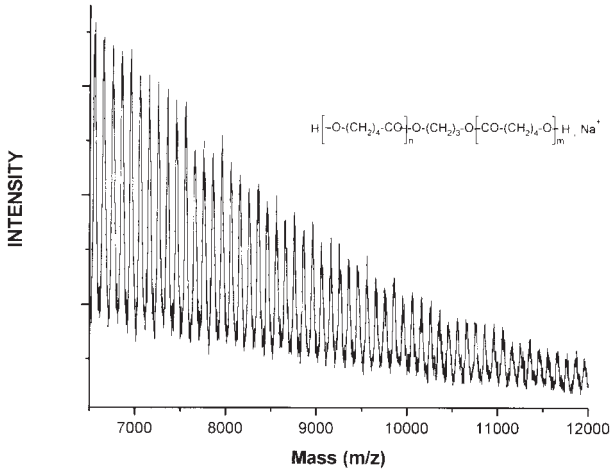

Figure 7 MALDI-TOF mass spectrum of α,ω-telechelic poly(δ-valerolactone) diol PVL, D-PVL [M_n(NMR) = 2536]. Polymer was obtained using I as initiator (VL/I = 1000) in the presence of 1,3-propanediol (VL/PD = 20).

Fig. 9). A new peak at 5.40 ppm appears (6, —CH_2OCO, PCL). This peak can be ascribed to the BzO_2C end group of the oligomer formed.

The above findings provide evidence of the in situ formation of an alkoxide ruthenium derivative (see Scheme 1 for proposed mechanism). A similar observation was made during the polymerization of CL with a samarium(III) complex, $SmMe(C_5Me_5)_2(THF)$,[21] where the formation of 7-hydroxy-2-heptanone (a keto alcohol) occurred.

The maximum lactone conversions for polymerization with complex I in the presence of a coinitiator were attained after approximately 30 h. These reaction times are similar to those reported for polymerization catalyzed by germanium(IV) alkoxides[22] and tin(II) alkoxides and carboxylates.[23,24]

CONCLUSIONS

It has been demonstrated that $RuCl_2(PPh_3)_3$ catalyzes ROP of lactones, but long reaction times are required to achieve quantitative conversions (85 h). Reaction times were shorter when a hydroxylic coinitiator (alcohol or water) was used (30 h). Evidence of the insertion of alcohol as an end group in the polymer (benzyl alcohol, *n*-octanol, and isopropanol) or within the polymeric chain (propanediol) and the evidence obtained by ^{1}H-NMR of the reaction between benzyl alcohol, complex **I,** and ε-caprolactone supports the in situ formation of an alkoxide ruthenium derivative, complex **II**. The synthetic route described here constitutes a new pathway for obtaining PCL and PVL with specific end groups.

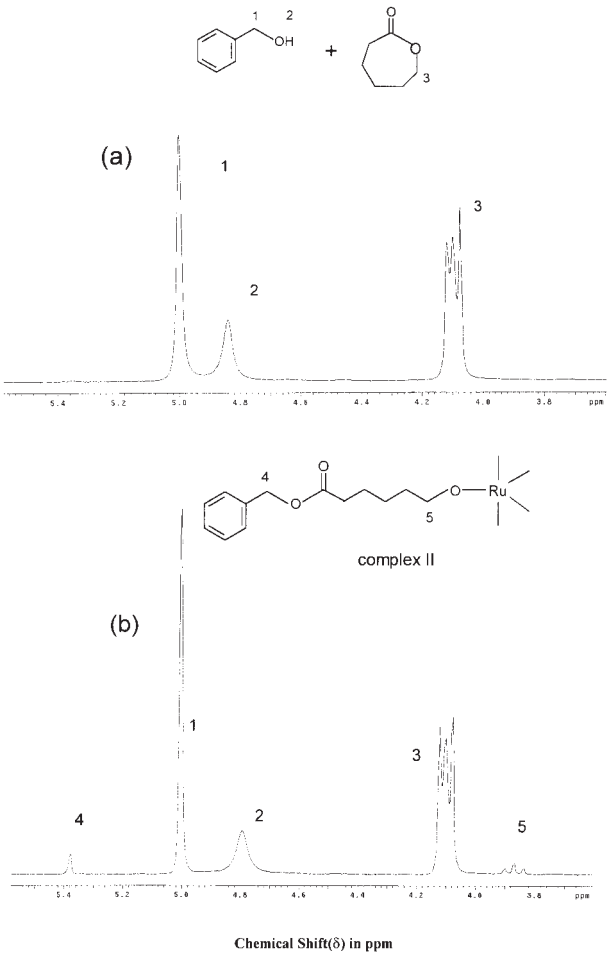

Figure 8 The 200-MHz ^{1}H-NMR spectra of the CL/benzyl alcohol/$RuCl_2(PPh_3)_3$ reaction mixture in C_6D_6 [CL = 4.0 mmol, BzOH = 3.0 mmol, $RuCl_2(PPh_3)_3 = 2.6 \times 10^{-3}$ mmol] after: (a) 8 h at 25°C, (b) 15 h at 120°C.

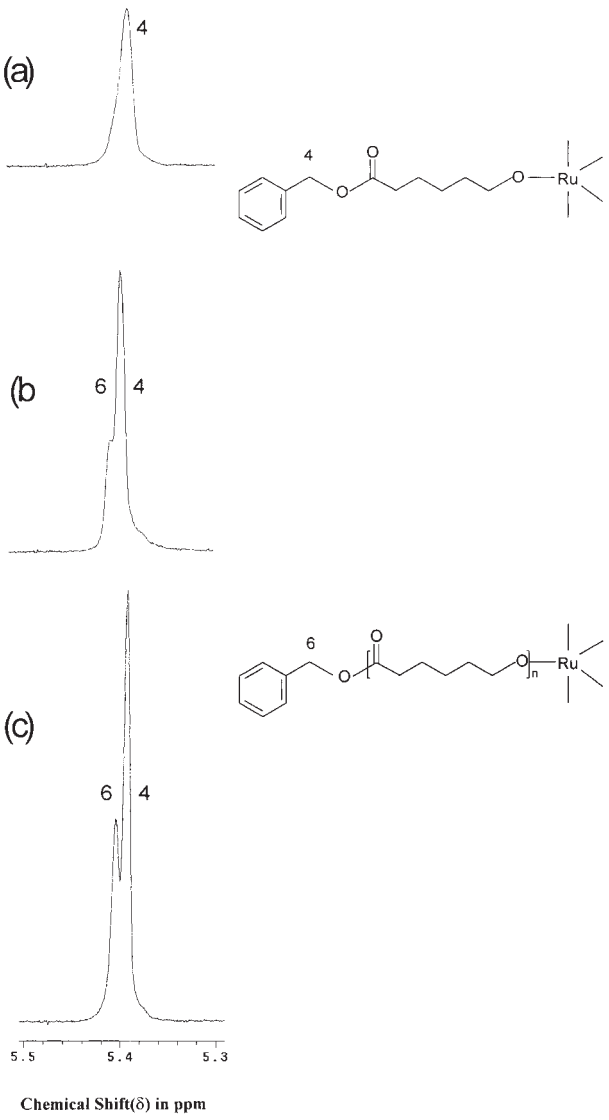

Figure 9 The 200-MHz ^{1}H-NMR spectra of the CL/benzyl alcohol/$RuCl_2(PPh_3)_3$ reaction mixture in C_6D_6 [CL = 4.0 mmol, BzOH = 3.0 mmol, $RuCl_2(PPh_3)_3 = 2.6 \times 10^{-3}$ mmol] at 120°C after: (a) 25 h, (b) 45 h, and (c) 50 h.

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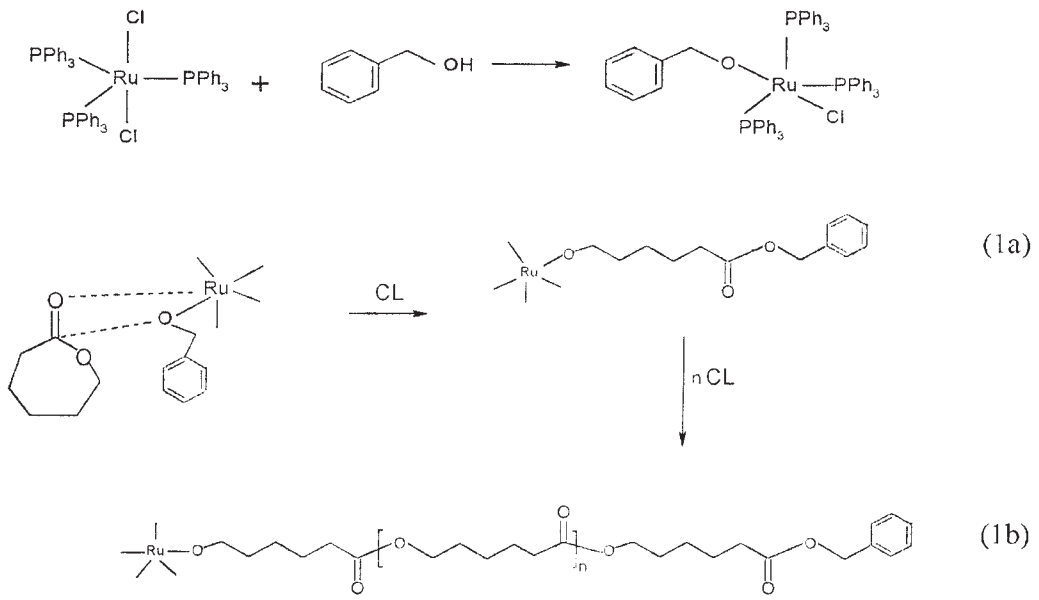

Scheme 1

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