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Oligomerization of ε-caprolactone and δ-valerolactone using heteropolyacid initiators and vanadium or molybdenum complexes

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Abstract

Lactones are efficiently oligomerized by heteropolyacids $H_3[PM_{12}O_{40}]\cdot aq$ with M = Mo or W, "$H_{3+n}[PMo_{12-n}V_nO_{40}]\cdot aq$" (HPA-*n*) and molybdenum(VI) acetylacetonate, vanadium(V) sulfate initiators in the presence of dioxygen. The resulting linear oligomers display relatively low polydispersity (≤1.7) and high monomer conversion (≥99%), and are obtained with relatively short reaction times (1–24 h, 20–60 °C). The products were analysed by various physicochemical methods: size-exclusion chromatography (SEC) (to determine the molecular weight properties); IR; ^{1}H and ^{13}C NMR; matrix-assisted laser desorption ionization-time-of-flight mass spectrometry (MALDI-TOFMS). Lactone oligomerization is proposed to proceed by a coordination-insertion mechanism via cationic species (VO_2^+ and/or MO_2^{2+}; M = Mo or W) with chain growth involving acyl-oxygen bond cleavage and an activated monomer. Brönsted acids catalyse the reaction. These reactions are the first examples of the ring-opening oligomerization of lactones catalysed by heteropolyacids and the inexpensive "$VOSO_4\cdot xH_2O$/THF–H_2O/O_2" system.

Keywords: Heteropolyacids; Lactones; Oligomers; Vanadyl sulfate; Acid catalysis; MALDI-TOF mass spectrometry

1. Introduction

Heteropolyacids "$H_{3+n}[PMo_{12-n}V_nO_{40}]\cdot aq$" (denoted HPA-*n*), having the Keggin structure, are used as precursors for acid- or redox-catalysed reactions [1–8]. They have a very high Brönsted acidity and are efficient oxidants, exhibiting fast reversible multi-electron redox transformations under rather mild conditions. These properties make HPA-*n* bifunctional catalysts in both homogeneous and heterogeneous systems. Thus, heteropolyacids are highly suitable precursors for the oxidative cleavage of cycloalkanones: we described the preparation of keto-acids or α,ω-diacids involving oxidation of α-substituted cycloalkanones and of cyclohexanone in the presence of HPA-*n* (*n* = 2, 3, 4 or 5) or copper(II) salts under dioxygen [6,8–20]. Treatment of the latter with HPA-2/O_2 in AcOH–H_2O or MeOH leads to the formation of adipic acid as the major product, together with glutaric and succinic acids [11,12,14]. Although some oxovanadium complexes induce such oxidations [9], the heteropolyacids are better due to the redox properties of VO_2^+ species and the Brönsted acidity, which is essential for the enolization process [8,14,15,19,20]. In addition to oxidative ring-opening, GC–MS coupling experiments indicate the formation of δ-valerolactone (δ-

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VL) and ε-caprolactone (ε-CL) which can be subsequently oligomerized. We developed the transformation of lactones to oligolactones (OLL), under nearly identical experimental conditions, with the goal of controlling this side-reaction and exploring novel properties of HPA-*n* and of molybdenum and/or vanadium complexes. (These HPA-*n* are easy to prepare from cheap reagents $MoO_3/V_2O_5/H_3PO_4/H_2O_2$ [6,12,17,18], and are thermally very stable.)

The field of biodegradable materials is a fast-growing area of polymer science because they have potential for a variety of therapeutic and technical uses [21]. For example, oligo (ε-caprolactone) is used as a telechelic oligomer, providing soft blocks for polyurethane elastomers. It has a number of potential applications in the biomedical and agricultural fields. It has been obtained with various initiators: organolanthanide complexes and initially frequently with tin, aluminium, early transition metal alkoxides or carboxylates, etc. [22–25]. The use of stannic/stannous compounds is somewhat controversial because they are relatively toxic and complete removal from synthesized materials is difficult. Nitrogen-based organolanthanide complexes are very efficient initiators; the hapticity of the nitrogen-based ligand may be related to the formation of cyclic oligomers [22]. ε-CL can be polymerized in solution with ytterbium and samarium benzimidinates and related complexes as initiators [23]. Trivalent rare-earth metal alkoxides initiate living polymerization of several monomers such as ε-CL, lactide, β-butyrolactone (β-BL) and δ-VL with outstanding reactivity at room temperature [26–31]. The polymerization of ε-CL and δ-VL, based on lanthanide tris[2,6-di(*tert*-butyl)phenolate] and various alcohols, allows excellent control over molecular weight and end-group identity [31].

β-Propiolactone (β-PL) and ε-CL can be cyclo-oligomerized under unusually mild conditions with a catalytic system: "2,2-di-*n*-butyl-1,3,2-dioxastannolane/di-*n*-butyltin dichloride" [32]. Dibutyl- and tributyltin methoxides are also very active in the polymerization of β-PL, β-BL and ε-CL [33]. The polymerization of these lactones proceeds by the so-called "coordination-insertion" mechanism where chain growth involves cleavage of the acyl-oxygen bond and yields polyester chains with a methyl ester end-group [33,34].

Matsumara and co-workers reported that ε-CL is polymerized in toluene, using Lipase CA at 70 °C; the M_n depends of the water content. A strategy for increasing the molecular weight of a polyester by lipase-catalysed polymerization of lactone (ε-CL) was developed using azeotropic dehydration with toluene and a Dean-Stark trap packed with molecular sieves; the structure is clearly macrocyclic, while considerable amounts of linear oligomer are produced by reaction in the presence of water [35]. Various cationic zirconocene complexes catalyse polymerization of ε-CL at ambient temperature to afford poly(ε-caprolactone) with a narrow molecular weight distribution [36]. The efficiency of the catalyst depends on the structure of the cyclopentadienyl ligands. Ring-opening polymerization of ε-CL initiated by $[Nd(BH_4)_3(THF)_3]$ occurs rapidly and quantitatively at room temperature to give polymers in high yield [37]. Some preparation methods have focused on using zwitterionic titanoxanes to catalyse the ring-opening polymerization of ε-CL in toluene solution and in bulk [38]; these are the first examples with zwitterionic group 4 metallocenes (the rate of the polymerization is not very high even under optimal conditions, and tetrahydrofuran (THF) is also polymerized by these complexes (vide infra)). Finally, many organo-lanthanide complexes are active at low temperature, giving very fast living polymerization of lactones [39]. These reactions depend both on the metal compounds used as initiator and on the high-cost ligands surrounding them. It appears that heteropolyacids, vanadium(V) and/or molybdenum(VI) and/or tungsten(VI) are not known as active precursors of the oligomerization of lactones.

In this paper, we report on the ability of heteropolyacids to catalyse the ring-opening oligomerization of lactones and on the search for novel low-cost initiators. The effects of solvent, temperature, reaction times and the absence or presence of dioxygen on polymerization are briefly considered.

2. Experimental

2.1. General

The heteropolyacids HPA-*n* ($n = 2, 3$) were prepared according to the described oxoperoxo procedures [6,12,17,18]. The solids were in some cases dried over P_4O_{10} to minimise the water content. These HPA-*n* are multicomponent systems: they contain several polyanions, positional isomers of these, as well as monomeric metallo species such as the *cis*-dioxo cation $[VO_2(H_2O)_4]^+$, usually written as $[VO_2]^+$, and often traces of V(IV) ($[VO]^{2+}$ species) [14]. $VOSO_4{\cdot}5H_2O$ and $[MoO_2(acac)_2]$ (Prolabo) are ≥99% pure. ε-Caprolactone (99%, Aldrich) and δ-valerolactone (99%, Acros Organics) were purified by distillation over CaH_2 and kept over 3 Å molecular sieves or used without further purification (conversion and selectivity did not vary significantly whatever the products). Anydrous solvents (THF, MeOH, MeCN, MeCOOH, C_6H_5Me) were used as received for catalysis tests.

GC analyses were run on a Girdel chromatograph (FID) fitted with a SPB^{TM} 1701 capillary column with helium as carrier gas, and temperature programming from 70 to 200 °C (5 °C min^{-1}, $P_{He} = 0.16$ MPa). GC–MS analyses were performed on a Trace GC 2000 series (ThermoQuest) coupled to a Trace MS mass spectrometer (EI or CI/NH_3). The IR spectra were measured in the transmission mode, on a Fourier transform infrared (FTIR) Bruker Vector-22 apparatus with samples in Nujol suspension between two cesium bromide plates or using the KBr pressed pellet technique. The ^{1}H NMR (300 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on Bruker AC 300 and 200 spectrometers at 25 °C using TMS as reference. Elemental analyses were carried out at the Service Central d'Analyses CNRS, Lyon.

2.2. MALDI-TOF measurement

The matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) mass spectra were recorded with a Voyager Elite PerSeptive Biosystems mass spectrometer. The pulsed N_2 laser beam (337 nm) is focused onto the target at an angle of 45°. In all experiments, the mass spectrometer was tuned in the reflectron mode using delayed extraction and an acceleration voltage of +20 kV. All mass spectra were recorded and averaged over 256 laser shots. The samples were prepared as follows: the polymer and the matrix (2,5-dihydroxybenzoic acid), 2 and 15 g l^{-1}, respectively, were dissolved in THF freshly distilled from CaH_2. One microliter of polymer solution was added to 50 μl of the matrix solution and 1 μl of the mixture deposited onto the MALDI stainless steel sample slide and allowed to dry in air at RT. External calibration of the instrument with a POE 5000 standard was used.

2.3. Size-exclusion chromatography

Size-exclusion chromatography analysis (SEC) was performed using dry THF eluent-HPLC grade (5 ml min^{-1}) and an equipment consisting of a Rheodyne injector, a Waters 515 pump, a Waters 410 differential refractometer, a set of ultrastyragel columns (19 mm × 300 mm; with pore sizes of 500, 10^3 and 10^4 Å) and the Waters Millenium software. Two hundred microliters of a polymer solution (40 g l^{-1}) were injected. Fractions were taken every 15 s (1.25 ml) using a Waters fraction collector. Selected fractions are then analysed by MALDI-TOF MS and subjected to SEC to obtain a calibration curve against absolute molecular weights. To established the SEC calibration curve ($\ln M = V_e$, where V_e is the elution volume), the molecular weight of each fraction was taken at the peak maximum of the MALDI-TOF mass spectra.

2.4. Solution ring-opening oligomerization with HPA-n or V(IV) precursors

A typical experiment was performed in a Schlenk tube (40 ml), attached to a vacuum line with a manometer and a gas inlet, or in a glass reactor with a reflux condenser. The tube or reactor was charged with HPA-*n* ($n = 2$ or 3) (see Tables 1 and 2) and MeOH, THF or THF–H_2O (10 ml, see Tables 1 and 2) and the mixture was stirred magnetically under dioxygen at room temperature. The lactone (usually 10 mmol) was added and the system equilibrated at RT. The tube or reactor was immersed in a 60 °C thermostated oil-bath. The deep brown mixture was then vigorously stirred for the time indicated (see tables). After adding monomer, the kinetics were monitored by gas chromatography. The mixture was cooled and the oligomers formed after slow evaporation of the solvent were filtered out, washed thoroughly with water and Et_2O and dried over P_4O_{10}. In all cases, the oligomerization medium was homogeneous.

Table 1
Oligomerization of ε-caprolactone promoted by various precursors[a]

Entry	Precursor (mmol)	Time (h)	Conversion[b] (%)	Oligomer yield[c] (%)
1	HPA-2 (0.075)	12	99	98
2	H_3PO_4 (85%) (0.125)	24	99	98
3	H_2SO_4 pure (0.187)	24	99	98
4[d]	HPA-2 (0.075)	24	30	26
5	$H_3[PMo_{12}O_{40}]$·aq (0.062)	24	99	79
6	$H_3[PW_{12}O_{40}]$·aq (0.062)	24	98	98
7	$[MoO_2(acac)_2]$ (0.75)	24	99	96
8	$Mo(CO)_6$ (0.075)	24	0	0
9	$[VO(acac)_2]$ (0.150)	24	Low	Low
10	$VOSO_4{\cdot}5H_2O$ (0.075)	24	99	99
11	HPA-2 (0.075)	18	99	99
12[e]	HPA-2 (0.075)	12	99	99
13	HPA-2 (0.075)	6	70	69
14	HPA-3 (0.075)	12	99	98

[a] General procedure for oligomerization of ε-caprolactone: ε-CL (1.1 ml; 10 mmol); MeOH (10 ml); $T = 60$ °C; $p(O_2) = 10^5$ Pa, HPA-2 = $H_5[PMo_{10}V_2O_{40}]$·aq.
[b] Conversion based on ε-CL was determined by GC using an internal standard.
[c] OCL identified by FTIR, ^1H and ^{13}C NMR, MALDI-TOF MS and SEC. The yield of OCL was determined in the crude reaction products after precipitation from methanol.
[d] Reaction was carried out in dinitrogen (10^5 Pa).
[e] Reaction was carried out in air (10^5 Pa).

The oligomers obtained are white or light yellow powdery materials.

In a typical experiment with vanadyl sulfate, THF (7 ml) and H_2O (≤3 ml) were mixed at RT; $VOSO_4{\cdot}5H_2O$ (18.9 mg, 0.075 mmol) was dissolved and dioxygen uptake (≃ 6.6 ml; 24 h; 25 °C) led to the formation of an orange-red solution with V(V) species by intermediate peroxidation of THF [40]. The dioxygen uptake was 22.2 ml for a 12 h reaction at 60 °C. At the end of the reaction with the monomer, blue $VOSO_4{\cdot}xH_2O$ crystallized out with the white OLL material after slow evaporation of the solvent; washing with water to remove the water-soluble precursor led to analytically pure oligomers.

3. Results and discussion

3.1. Oligomerization of ε-caprolactone

Various results obtained with selected precursors and/or reaction times or concentrations are summarized in Table 1. The oligomerization of ε-caprolactone in the presence of HPA-2/O_2 in methanol gives oligo(ε-caprolactone) denoted OCL, having a weight-average molecular weight of 4900 and relatively low polydispersity ($I_p = M_w/M_n \leq 1.7$) for a 12 h reaction at 60 °C (Table 2, entry 1). The average degree of oligomerization is about 25; the distribution parameters depend on the reaction conditions.

Several experiments show that OCL can be obtained in 98–99% yield and that monomer conversion is total. Vana-

Table 2
Oligomerization of ε-caprolactone using "HPA-2/solvent/O_2", "$VOSO_4{\cdot}5H_2O$/THF–H_2O/O_2" or in the presence of Brönsted acids and in the absence of HPA-*n* under various conditions[a]

Entry	Substrate *g* (mmol)	Solvent (ml)	Time (h)	Conversion[b] (%)	Oligomer yield[b] (%)
1	1.145 (10)	MeOH (10)	12	99	99
2	1.145 (10)	THF (10)	1	99	98
3[c]	1.145 (10)	THF (10)	9	99	99
4[d]	1.145 (10)	THF (10)	8	99	99
5[e]	0	THF (10)	24	0	0
6	1.145 (10)	AcOH–H_2O (9–1)	24	90	86
7	1.145 (10)	MeCN (10)	24	90	87
8	1.145 (10)	Toluene (10)	24	99	96
9	0.62 (5.45)	MeOH (10)	24	99	98
10	0.92 (8.1)	MeOH (10)	24	90	87
11	1.83 (16)	MeOH (10)	24	99	88
12	2.29 (20)	MeOH (10)	24	90	88
13	3.43 (30)	MeOH (10)	24	90	88
14[f]	1.145 (10)	THF–H_2O (7–3)	24	99	98

[a] For a typical procedure, see Section 2; HPA-2 ≃ 0.075 mmol.
[b] cf. Table 1.
[c] In the presence of concentrated H_2SO_4 (3.75 mmol) and in the absence of HPA-2.
[d] In the presence of H_3PO_4 (85%) (3.75 mmol) and in the absence of HPA-2.
[e] Without substrate: THF is not polymerized; see text and [44,45].
[f] "$VOSO_4{\cdot}5H_2O$/THF–H_2O/O_2" system.

dium(IV) acetylacetonate or vanadyl sulfate has little or no catalytic effect under anaerobic conditions (not shown). Under identical conditions (dinitrogen atmosphere) the heteropolyacid is less efficient (Table 1, entry 4). The conversion (30%) and yield (26%) were lower than those obtained under dioxygen (Table 1, entry 1). In an inert atmosphere, an intense green colour was observed. This corresponds to the conversion of HPA-2 to reduced species containing V(IV) and/or Mo(V) in the presence of any organic substrate. However, the reduced forms are re-oxidized when dioxygen is added to the acidic reaction medium. Blank experiments under the same conditions, in the absence of HPA-2, showed that OCL can also be prepared by ring-opening oligomerization of ε-CL catalysed by sulfuric acid or phosphoric acid (Table 1, entries 2, 3) although the oligomerization rate decreases dramatically (not shown). HPA-2 is more effective than H_2SO_4 or H_3PO_4 in this process (Table 1, entries 1, 2, 3, 11, 12). This phenomenon was again observed with other solvents (THF or THF–H_2O, vide infra). Three molybdenum-based precursors were tested (Table 1, entries 5, 7, 8); those with oxo groups are active but the recycling of the Mo(VI) species of $H_3[PMo_{12}O_{40}]{\cdot}$aq and of $[MoO_2(acac)_2]$ was difficult due to the formation of reduced heteropolyanions [1–8] or "insoluble molybdenum(V) blues". The $H_{3+n}[PMo_{12-n}V_nO_{40}]$ ($n = 3$, 4, etc.) also oligomerize ε-CL: HPA-3 initiates the ring-opening oligomerization of ε-CL in MeOH with high activity. The reaction was complete within 6–12 h at 60 °C (Table 1, entry 14), depending on the water content. Monomeric molybdenum(VI) or vanadium(V/IV) precursors show the same chemistry as the heteropolyacids [9,14,15]; we shall consider these observations in a proposed mechanism (vide infra, Scheme 3).

3.2. Characterization of oligo(ε-caprolactone)

The oligomerization products were characterized by physicochemical analysis, Fourier transform infrared spectroscopy, ^{1}H and ^{13}C NMR, MALDI-TOF mass spectrometry and by size-exclusion chromatography.

The IR spectra of the oligomer (Fig. 1, corresponding to Table 1, entry 1) show the characteristic bands at 1244 and 3430–3500 cm^{-1} which may be assigned to C–O (stretching) and O–H groups. Obviously, there is a strong C=O stretching band of aliphatic ester or acid groups at 1724 cm^{-1}. Other IR data (solid, cm^{-1}): 2861, 2926 (CH_2 stretching mode) and 957 (CH_2 rocking mode).

The ^{1}H NMR spectrum of the oligomer prepared in THF (Table 2, entry 2) HO–$^{f'}CH_2{}^{e'}CH_2{}^{d}CH_2{}^{c}CH_2{}^{b}CH_2{}^{a}CO$–$[O^{f}CH_2{}^{e}CH_2{}^{d}CH_2{}^{c}CH_2{}^{b}CH_2{}^{a}CO]_{n-2}O^{f}CH_2{}^{e}CH_2{}^{d}CH_2{}^{c}$–$CH_2{}^{b'}CH_2{}^{a'}$COOH shows five main signals at 4.0, 3.6, 2.3, 1.6 and 1.35 ppm with respect to TMS (Fig. 2). The peaks at 4.0 and 2.3 ppm are assigned to $-O^{f}CH_2$ and $-{}^{b}CH_2COO$ groups, respectively. The peak at 1.35 ppm is attributed to $^{d}CH_2$. The spectrum shows the CH_2OH resonances at 3.6 ppm. The intensity of the multiplet at 1.6 ppm was in all cases about twice that of the other methylene protons, and was therefore assigned to $^{c}CH_2$ and $^{e}CH_2$. The assignment of the NMR signals was in agreement with the literature data [22,34,41]. Only oligomers prepared in THF, with a COOH end-group on one side (COOMe due to esterification in the presence of HPA-*n* in dry methanol) and a hydroxyl group on the other side, are obtained in major amounts. This indicates that the oligomerization of ε-caprolactone proceeds by cleavage between the carbonyl carbon and the oxygen of the lactone ring [33].

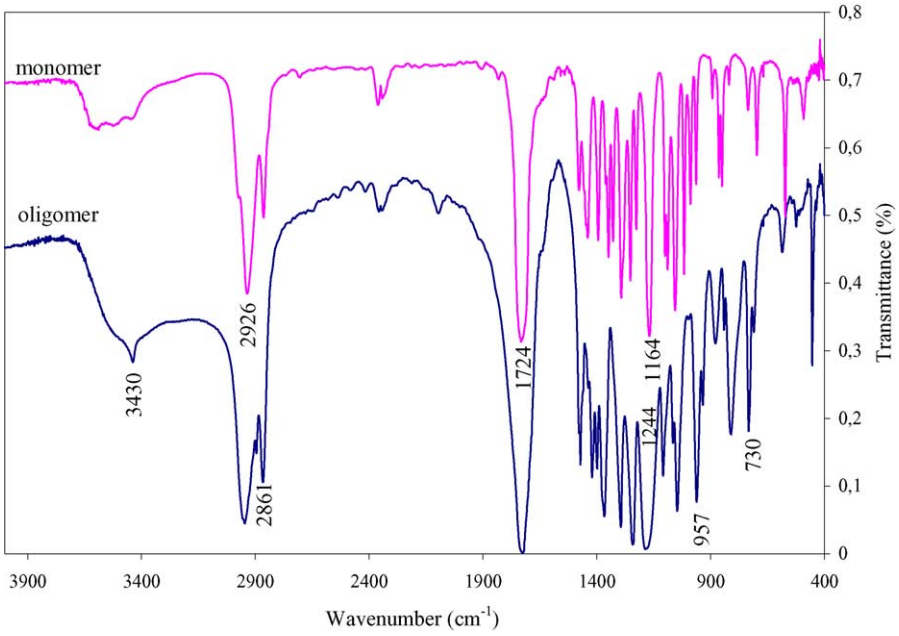


Fig. 1. IR spectra of ε-caprolactone and the oligomer prepared in MeOH.

The ^{13}C NMR spectrum in $CDCl_3$ of the OCL (Table 2, entry 2) obtained with "HPA-2/O_2/THF" is presented (Fig. 3): 176.7 (**C**OOH), 173.3 (**C**O), 63.9 (**C**H_2OC(O)), 62.2 (**C**H_2OH), 33.8 (**C**H_2CO) and 28.1–25.2–24.3 (**C**H_2).

In order to confirm the structure, the products were analysed by MALDI-TOF MS, a very useful method for characterizing oligomers [42–43]. The MALDI-TOF mass spectra (performed on many reaction products for example Table 2, entry 1, solvent: MeOH) showed two main series of peaks with a repeat unit of 114.07 u (Fig. 4). Each peak of the spectrum can be assigned to the linear oligomer $H[O(CH_2)_5CO]_nOR$ (R = H or Me) associated with Na^+. The repeat unit has the same chemical composition as the monomer. The formation of cyclic oligomers occurs but only to a small extent and essentially in the *m*/*z* range 2000–3000. They are produced by intramolecular transesterification reactions that become significant at high monomer conversions. The abundance of the oligomer with ester terminus decreases relative to that of the oligomer with acid terminus as the mass increases. The MALDI-

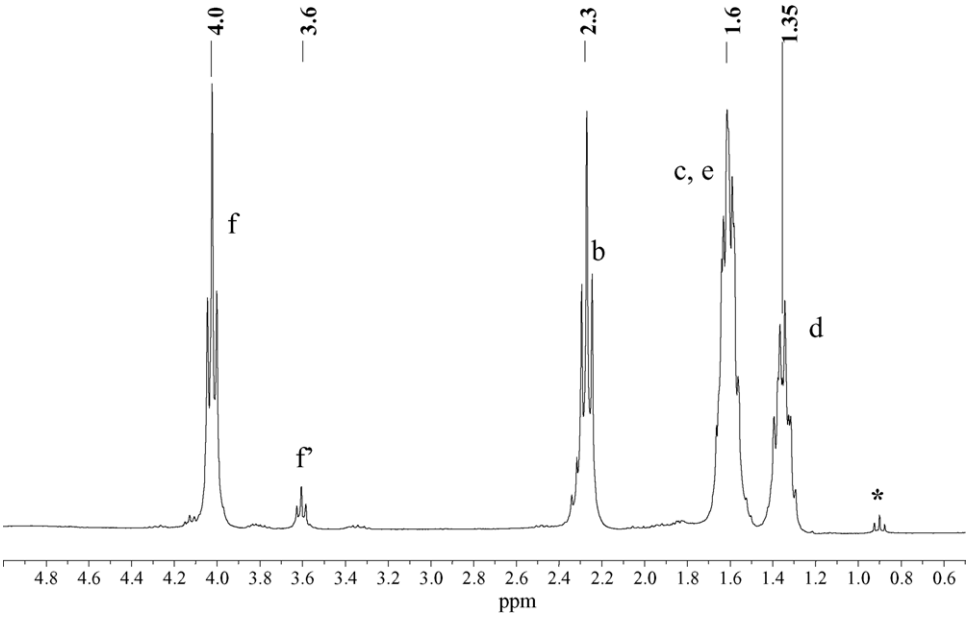


Fig. 2. ^1H NMR spectrum in $CDCl_3$ of oligomer prepared by ring-opening oligomerization of ε-caprolactone (sample: see Table 2, entry 2). HO—$^{f'}CH_2{}^{e'}CH_2{}^{d}CH_2{}^{c}CH_2{}^{b}CH_2{}^{a}CO[O^{f}CH_2{}^{e}CH_2{}^{d}CH_2{}^{c}CH_2{}^{b}CH_2{}^{a}CO]_{n-2}O^{f}CH_2{}^{e}CH_2{}^{d}CH_2{}^{c}CH_2{}^{b'}CH_2{}^{a'}COOH$; (*) minor impurity.

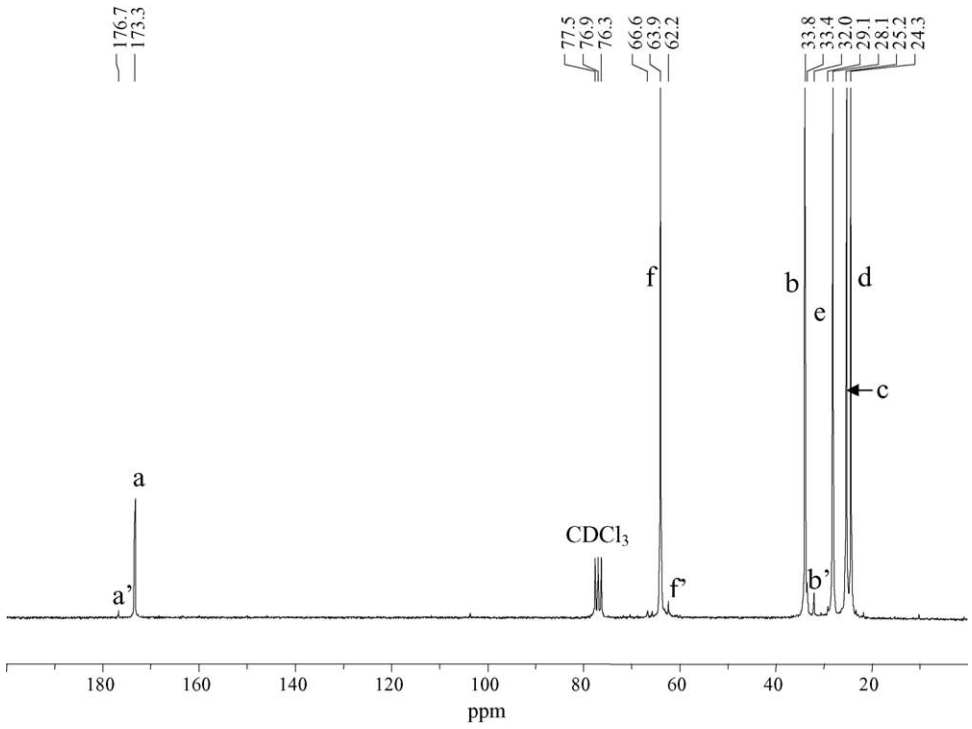


Fig. 3. ^{13}C NMR spectrum in $CDCl_3$ of oligomer prepared by ring-opening oligomerization of ε-caprolactone (see Table 2, entry 2). HO—$^{f'}CH_2{}^{e'}CH_2{}^{d}CH_2{}^{c}CH_2{}^{b}CH_2{}^{a}CO[O^{f}CH_2{}^{e}CH_2{}^{d}CH_2{}^{c}\ CH_2{}^{b}CH_2{}^{a}CO]_{n-2}O^{f}CH_2{}^{e}CH_2{}^{d}CH_2{}^{c}CH_2{}^{b'}CH_2{}^{a'}COOH$. Peaks for the carbon c and carbon d were attributed according to literature data; in fact ^{1}H-detected multiple quantum coherence (^{1}H-^{13}C HMQC NMR) shows that c and d should be permuted.

TOFMS results confirmed that OCL has an essentially linear structure.

With MeOH as solvent, similar mass spectra were observed whatever the precursor and conditions (reaction time and presence or absence of dioxygen; spectra not shown). Thus, the relative abundances of the different oligomers do not depend dramatically upon the vanadium(V), molybdenum(VI) or tungsten(VI) oxo species which is used for the initiation step.

We have previously reported that the selection of solvent is essential in the oxidation of cyclohexanone [11,12]. A significant decrease in the time for completion of the reaction was

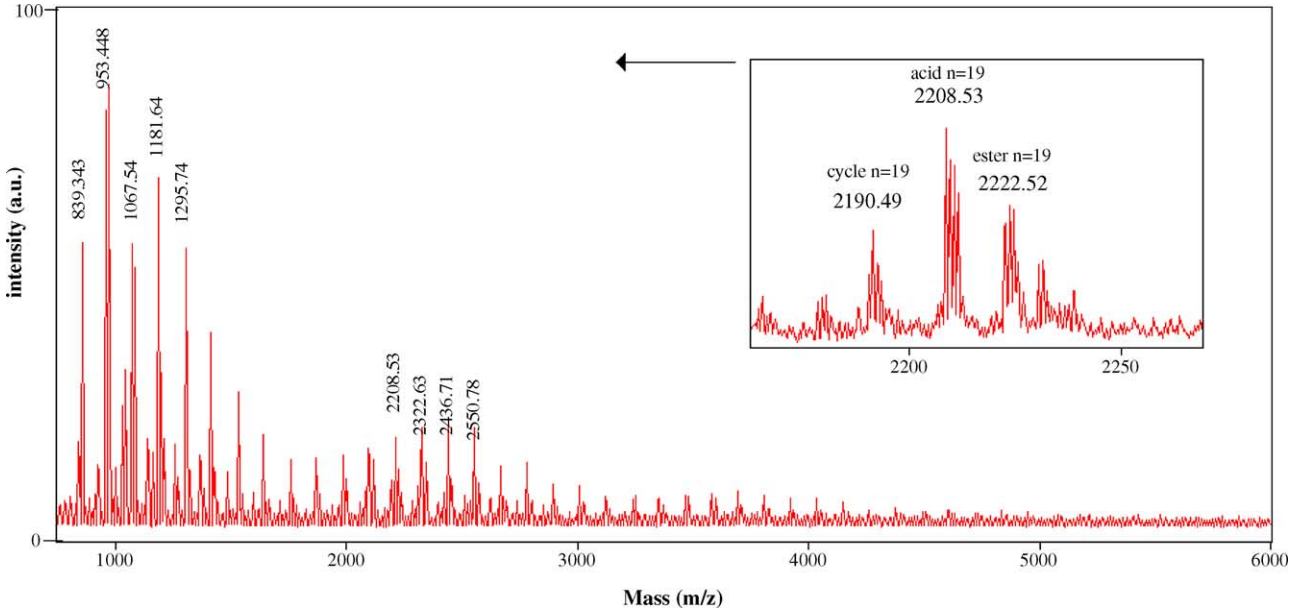


Fig. 4. MALDI-TOF mass spectrum of oligo(ε-caprolactone), $H[O(CH_2)_5CO]_nOR$ (R = H or Me), obtained with the "HPA-2/MeOH/ε-caprolactone/O_2" system (Table 2, entry 1).

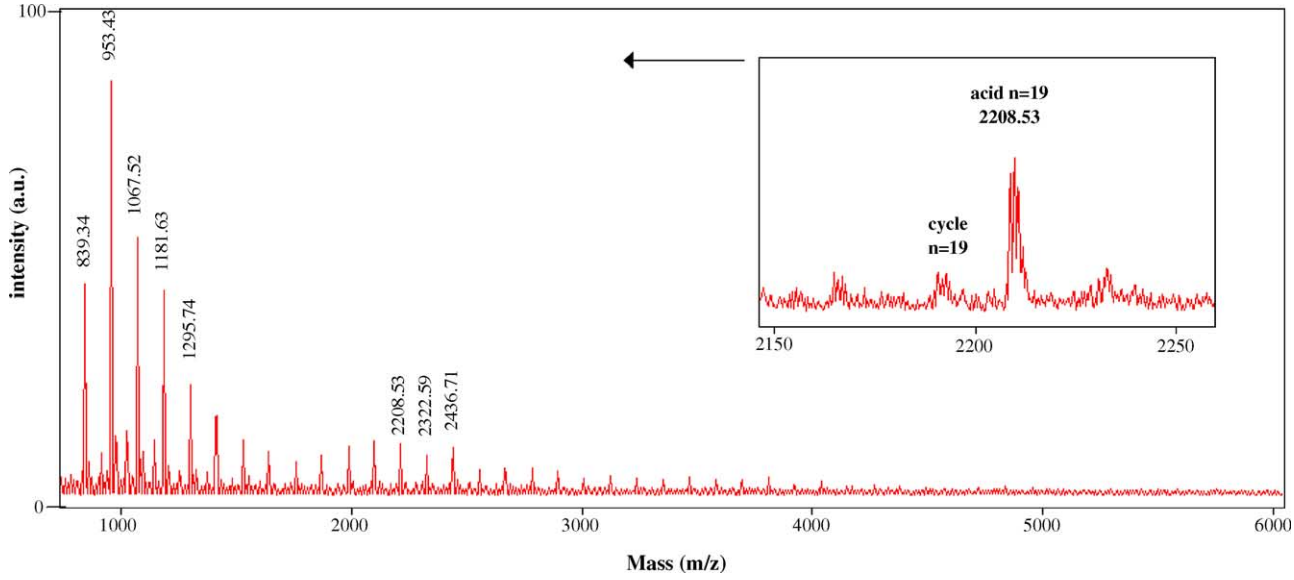
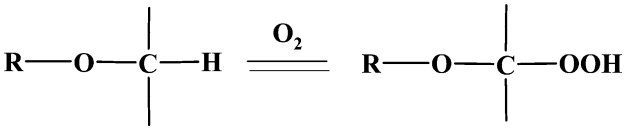


Fig. 5. MALDI-TOF mass spectrum of oligo(ε-caprolactone), $H[O(CH_2)_5CO]_nOH$, obtained with the "HPA-2/THF/ε-caprolactone/O_2" system (Table 2, entry 2).

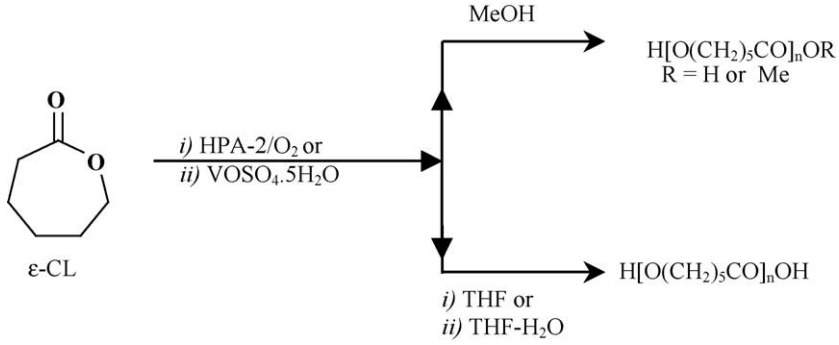
observed with the "HPA-*n*/THF/ε-caprolactone/O_2" system (see Table 2, entries 1 and 2).

With THF as solvent, it was found that OCL was formed quickly with a monomer conversion of almost 100%, and a reaction time much shorter (1 h) than in methanol (12 h). Cyclic oligomers are again very minor (MALDI-TOFMS experiments) (Fig. 5). THF leads to a more selective process than any other solvent used (Scheme 1). Addition of water to this solvent leads to a novel system with $VOSO_4{\cdot}5H_2O$ and dioxygen to produce quickly V(V) species and very pure oligomers; the V(IV) precursors are readily regenerated by slow evaporation of the solvent. With THF the experimental procedure gives protic conditions and it is known that the α positions of ethers are attacked by dioxygen:



The resulting hydroperoxides are seldom isolated, but are known to be proton and alkylhydroperoxide sources. Thus, for the catalytic ketonization of 1-octene, the highest activity at room temperature has been found with the "$Pd^{2+}SO_4^{2-}$/HPA-*n*/THF–H_2O/O_2" system. The peroxidizable solvent seems to favour the reoxidation steps with dioxygen [40]. Here, THF and O_2 lead to orange-red vanadium(V) complex(es) (not isolated) which initiate the oligomerization process, while vanadium(IV) salts are inactive under anaerobic conditions. In dioxygen small amounts of γ-butyrolactone, lactol and 4-hydroxybutyraldehyde are formed. The γ-butyrolactone is not incorporated into the oligomer (^1H and ^{13}C NMR spectra).

In general, the reaction time for completion of the oligomerization of ε-CL is longer when polar solvents are used: compare MeCN with the less polar THF (Table 2, entries 2, 7). It is important to note that, under our conditions, THF is not polymerized in the presence of the catalytic system (Table 2, entry 5) even though polyoxytetramethylene glycol, $HO[(CH_2)_4O]_nH$, has been obtained with $H_3[PW_{12}O_{40}]{\cdot}$aq. at 60 °C [44,45]. The $H_2O/[PW_{12}O_{40}]$ molar ratio is critical in determining the reaction rate and molecular weight of the polymer.



Scheme 1.

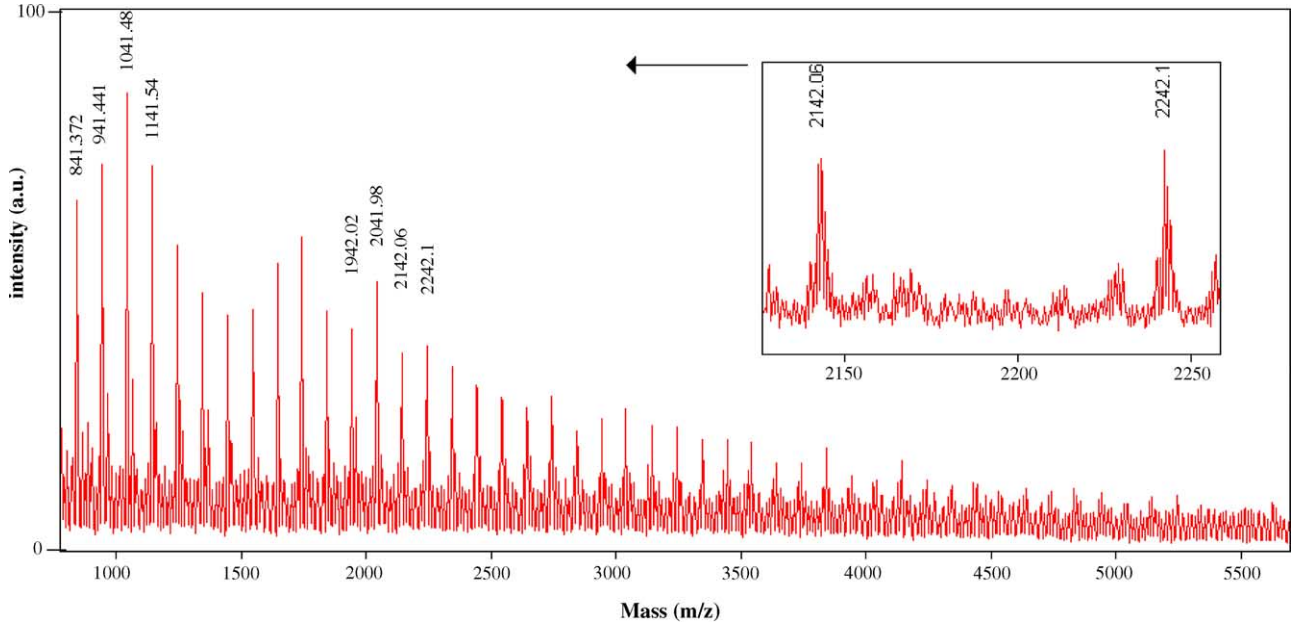


Fig. 6. MALDI-TOF mass spectrum of oligo(δ-valerolactone), $H[O(CH_2)_4CO]_nOH$, obtained with the "HPA-2/THF/δ-valerolactone/O_2" system in 1 h at 60 °C.

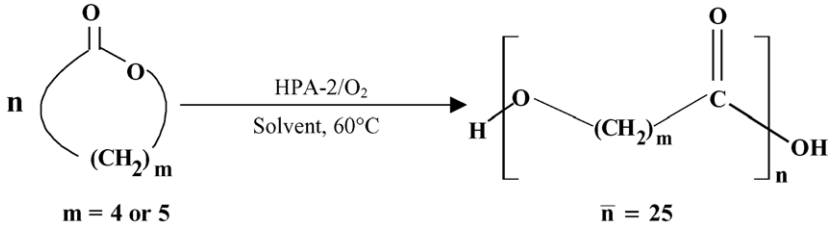
An essential difference between HPA-2 and H_2SO_4 or H_3PO_4 is a considerable decrease in the reaction time when heteropolyacids are used (Table 1, entries 1–3, 11,12). Apparently, the HPA-*n* species are active as Brönsted acids but also as molybdenum(VI)- (entry 7) and/or vanadium(V)-based catalytic centres (Table 1, entry 10). The catalytic activity of HPA-2/O_2 is observed even in AcOH/H_2O (Table 2, entry 6), but was slightly lower than that in the other organic solvents. The presence of water may favour the degradation of the oligomer and modify the concentration of the most likely active species (VO_2^+, MoO_2^{2+}, H_3O^+, etc.) [46]. Material with an average weight molecular weight of order 10,000 was obtained with low moisture content (≤0.02%) of novel vanadium- or molybdenum-based catalytic systems [47].

The effect of the concentration of the starting monomer was studied (Table 2, entries 9–13). Preliminary kinetic studies clearly show that, after an induction period, monomer consumption follows a first-order rate law. The rate law is also first-order in vanadium(V) ("$VOSO_4 \cdot 5H_2O$/THF–H_2O/O_2" system). EPR experiments show that the initial V(IV) is completely oxidized to V(V) with the "THF–H_2O/O_2" system. With methanol, the initial concentration of HPA-2 was kept constant while the ε-CL concentration was varied. The yields obtained at different initial monomer concentrations in the range 0.73–2.27 M did not vary to large extent (98–87%). The concentration of ε-CL is important because, when the concentration is about 0.5 M, the process leads to the formation of liquid oligomers only, whereas at higher concentration the product is solid.

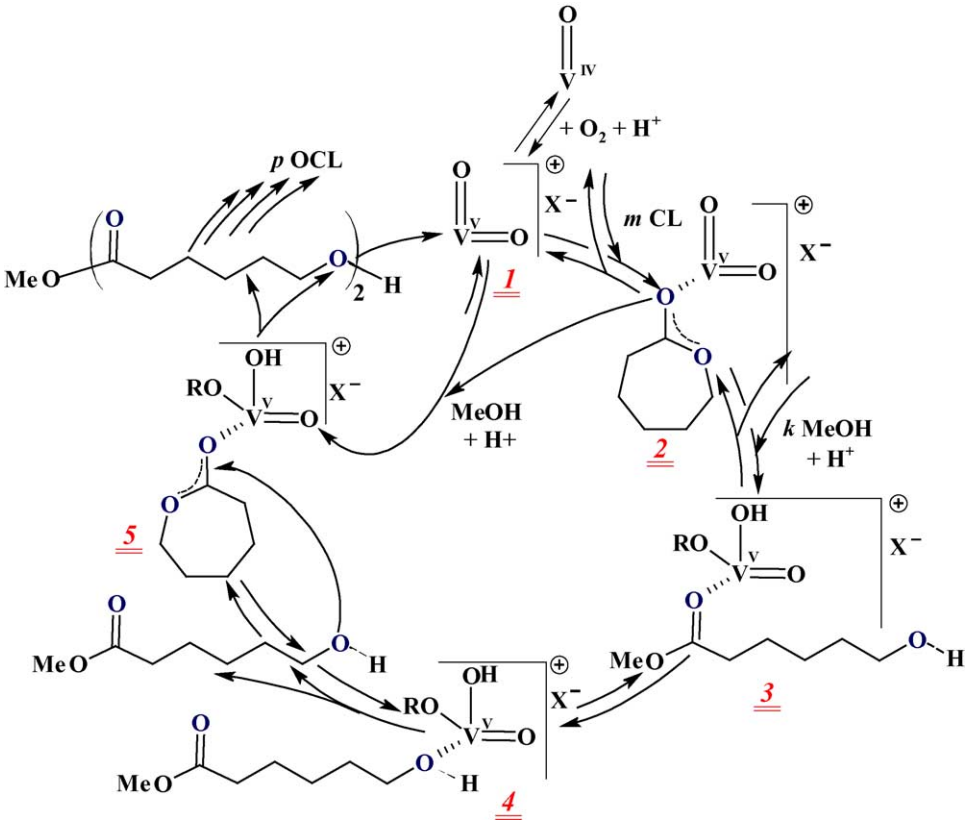
3.3. *Oligomerization of* δ-*valerolactone*

Comparative data have been obtained with δ-valerolactone which is also oligomerized by "HPA-2/MeOH or THF/O_2" systems with the same catalytic activity (Fig. 6, Scheme 2). Linear oligomers are the only reaction products.

Cyclohexanone can be cleaved under not too demanding conditions [6] with copper(II) nitrate and dioxygen. With an efficient promoter, such a pathway would be one of the most economical and clean systems for preparing adipic acid (yield ≥ 75%) [6]. Lactones are also formed among the by-products; surprisingly, preliminary experiments show that ε-caprolactone can be oligomerized by copper(II) precursors [47].



Scheme 2.



Scheme 3. Proposed mechanism for the catalytic oligomerization of ε-caprolactone (CL) catalysed by vanadium(V) species (R = H or Me) and/or MoO_2^{2+} and/or H^+ for the "vanadium(V)/protic solvent/CL/O_2" system.

3.4. Proposed mechanism for the cationic oligomerization of ε-caprolactone

At low pH (≤2), HPA-*n* solutions contain a solvated *cis*-dioxo cation $[VO_2(H_2O)_4]^+$, usually written as $[VO_2]^+$. This is considered to be one of the key-species [5,6,8,14,19]. Moreover, preparations of HPA-*n* obtained by diethyl ether extraction [7] or by the oxo-peroxo route [12,17,18,46] give EPR signals attributable to mononuclear vanadium(IV) species: in the presence of any organic substrate or of hydrogen peroxide, one cannot avoid the V(V)/V(IV) redox process. In acidic medium (slight excess of free H_3PO_4; HPA-*n*/H_3PO_4: 20/1) and in dioxygen, the major part of V(IV) is converted to V(V). The results (Tables 1 and 2) suggest that: (i) vanadium(V) rather than molybdenum(VI) species are, with H^+, the real catalysts (see also [14]); (ii) there is synergy between V(V) and H^+ which was also evidenced in esterification and *trans*-esterification by comparing Zr(O-iPr)$_4$, $[MoO_2(acac)_2]$, $H_3[PM_{12}O_{40}]$·aq and HPA-*n* [7,47]; (iii) the oligomerization process is the main reaction: solvent oxidation has not been observed with MeOH and is a minor path, whereas THF supplies protons (vide supra). A plausible activated monomer mechanism is shown in Scheme 3.

Coordination of CL to **1** affords the cationic complex **2**, followed by electrophilic attack on MeOH (or H_2O in THF–H_2O) to produce mono- or dicoordinated ε-hydroxy ester (or acid) **3**. This is supported by the fact that a different alcohol R′OH (R′ ≠ Me) is consumed at the early stage of oligomerization and also by the formation of ester at one oligomer terminus (TLC analysis and vide supra-MALDI TOF MS). The equilibria between **1**, **2**, **3**, **4**, and **5** are considered; although these catalytic reactions are developed in the presence of water, novel anhydrous complexes are found to be more active. Consequently, they depend on the water content. After coordination of **1**, or of a parent complex by CL, the hydroxy group of the ε-hydroxy ester is attacked by the electrophilic complex. Peroxo species [14,15] can also contribute to maintain the vanadium(V) concentration, but catalytic oxidation does not occur. MeOH/O_2 and THF/O_2 are not initiators because they are inert to CL; the reactive species here are **1** and **2** with or without H^+, but H_2O and MeOH do not suppress the catalytic activity. $\{MO_p\}$ or MO_2^{2+} species (M = Mo, W) responsible for the formation of "$PW_{12-n}Mo_n$" heteropolyacids for equimolar mixtures of $H_3[PM_{12}O_{40}]$·aq (M = Mo and W) would play a similar role [46]. Once more, the precursor that is added is not the active species and counter-ions are rarely unimportant.

4. Conclusion

We have shown that a catalytic system with "HPA-*n* (*n* = 2, 3, etc.)/O_2/solvent" can efficiently induce the oligomerization of two lactones: ε-caprolactone and δ-valerolactone,

which give biodegradable telechelic α-carboxylate, ω-hydroxy functional oligomers [21,24]. Various physicochemical analyses show that the products are linear. This catalytic process is the first example of the linear oligomerization of ε-caprolactone and δ-valerolactone using Keggin-type heteropolyacids, molybdenum(VI), tungsten(VI) and vanadium(V) complexes with dioxygen. We propose that the high effectiveness of HPA-*n* is primarily due the formation of VO_2^+ [14] and/or MO_2^{2+} (M = Mo, W) species and, in part, to their strong Brönsted acidity. The selectivity and activity depend on the solvent. These systems are less water- and air-sensitive than organometallic catalysts and rare-earth and transition metal alkoxides. The advantage of this catalytic oligomerization is the very mild conditions with not too sophisticated precursors but without a strictly anhydrous medium. Furthermore, it is economically and environmentally friendly. One of the major improvements is the reaction with the "$VOSO_4{\cdot}5H_2O$/THF–H_2O/O_2" system which gives quantitative yields of OCL and easy regeneration of the V(IV) precursor by extraction from the pure oligomer. Further work on the synthesis and characterization of novel complexes containing the pervanadyl VO_2^+ core, MO_2^{2+} (M = Mo or W), etc. derived from very strong acids and applications to various monomers is in progress. These catalytic systems involving mononuclear vanadium(V), molybdenum(VI) species or heteropolyacids and the recent discovery of parent nanosized crystallites [1,3,5,7] of formula $[NH_4^+]_{3-x}$ $[H^+]_x$ $[PW_{12}O_{40}]^{3-}$ have opened up new possibilities in the catalysed ring-opening polymerization of lactones. Other lactones which can generate an asymmetric carbon atom and thus chirality at the level of each repeat unit are being studied.

Acknowledgements

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References

[1] Y. Ono, in: J.M. Thomas, K.I. Zamaraev (Eds.), Perspectives in Catalysis, Blackwell Scientific Publications, London, UK, 1992, pp. 431–464.
[2] C.L. Hill, C.M. Prosser-McCartha, Coord. Chem. Rev. 143 (1995) 407.
[3] T. Okuhara, N. Mizuno, M. Misono, Advances in Catalysis, vol. 41, Academic Press, New York, USA, 1996, pp. 113–252.
[4] R. Neumann, Prog. Inorg. Chem. 47 (1998) 317–370.
[5] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171.
[6] J.-M. Brégeault, F. Launay, A. Atlamsani, C. R. Acad. Sci. Paris, Ser. IIc: Chim. 4 (2001) 11, and references therein.
[7] I.V. Kozhevnikov, Catalysis by Polyoxometalates, Wiley, Chichester, UK, 2002, pp. 61–182.
[8] J.-M. Brégeault, Dalton Trans. (2003) 3289.
[9] J.-M. Brégeault, B. El Ali, J. Mercier, J. Martin, C. Martin, C. R. Acad. Sci. Paris, Ser. II: Chim. 307 (1988) 2011.
[10] B. El Ali, J.-M. Brégeault, J. Mercier, J. Martin, C. Martin, O. Convert, J. Chem. Soc., Chem. Commun. 1989 (1989) 825.
[11] A. Atlamsani, J.-M. Brégeault, M. Ziyad, J. Org. Chem. 58 (1993) 5663.
[12] A. Atlamsani, M. Ziyad, J.-M. Brégeault, J. Chim. Phys. 92 (1995) 1344.
[13] L. El Aakel, F. Launay, A. Atlamsani, J.-M. Brégeault, Chem. Commun. 2001 (2001) 2218.
[14] M. Vennat, P. Herson, J.-M. Brégeault, G.B. Shul'pin, Eur. J. Inorg. Chem. 2003 (2003) 908.
[15] M. Vennat, J.-M. Brégeault, P. Herson, Dalton Trans. 2004 (2004) 908.
[16] F. Launay, M. Vennat, L. El Aakel, A. Atlamsani, E. Duprey, J.-M. Brégeault, Proceedings of the Fourth World Congress on Oxidation Catalysis, Dechema e.V., Berlin/Potsdam, 16–21 September, 2001, pp. 321–326.
[17] M. Vennat, Ph.D. thesis, Université P. et M. Curie, 2002.
[18] L. El Aakel, Ph.D. thesis, Université P. et M. Curie, 2003.
[19] J.-M. Brégeault, B. El Ali, J. Mercier, J. Martin, C. Martin, O. Mohammedi, Stud. Surf. Sci. Catal. 55 (1990) 205.
[20] L. El Aakel, F. Launay, J.-M. Brégeault, A. Atlamsani, J. Mol. Catal. 212 (2004) 171.
[21] S. Li, M. Vert, in: G. Scott, D. Gilead (Eds.), Biodegradation of Aliphatic Polyesters: Biodegradable Polymers, Principles and Applications, Chapman and Hall, London, UK, 1995, pp. 43–87.
[22] M. Visseaux, C.H. Brachais, C. Boisson, K. Tortosa, C. R. Acad. Sci. Paris, Ser. IIc: Chim. 3 (2000) 631.
[23] D. Barbier-Baudry, A. Bouazza, C.H. Brachais, A. Dormond, M. Visseaux, Macromol. Rapid Commun. 21 (2000) 213.
[24] M. Vert, S.M. Li, G. Spenlehauer, P. Guérin, J. Mater. Sci.: Mater. Med. 3 (1992) 432, and references therein.
[25] A. Löfgren, A.C. Albertsson, P. Dubois, R. Jérôme, J. Macromol. Sci. Rev., Macromol. Chem. Phys. C35 (1995) 379.
[26] S.J. McLain, N.E. Drysdale, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 33 (1992) 174.
[27] S.J. McLain, T.M. Ford, N.E. Drysdale, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 33 (1992) 463.
[28] H. Yasuda, M. Furo, H. Yamamoto, A. Nakamura, S. Miyake, N. Kibono, Macromolecules 25 (1992) 5115.
[29] A. Le Borgne, C. Pluta, N. Spassky, Macromol. Rapid Commun. 15 (1994) 955.
[30] W.M. Stevels, M.J.K. Ankoné, P.J. Dijkstra, J. Feijen, Macromol. Chem. Phys. 196 (1995) 1153.
[31] W.M. Stevels, M.J.K. Ankoné, P.J. Dijkstra, J. Feijen, Macromolecules 29 (1996) 3332.
[32] S. Roelens, J. Chem. Soc., Chem. Commun. 1990 (1990) 58.
[33] H.R. Kricheldorf, M. Berl, N. Scharnagl, Macromolecules 21 (1988) 286.
[34] H.R. Kricheldorf, M.V. Sumbél, I. Kreiser-Saunders, Macromolecules 24 (1991) 1944.
[35] H. Ebata, K. Toshima, S. Matsumara, Chem. Lett. 2001 (2001) 798.
[36] T. Mukaiyama, M. Hayakawa, K. Oouchi, M. Mitani, T. Yamada, Chem. Lett. 1995 (1995) 737.
[37] S.M. Guillaume, M. Schappacher, A. Soun, Macromolecules 36 (2003) 54;
I. Palard, A. Soum, S.M. Guillaume, Chem. Eur. J. 10 (2004) 4054.
[38] V.V. Burlakov, A.V. Letov, P. Arndt, W. Baumann, A. Spannenberg, C. Fischer, L.I. Strunkina, M.K. Minacheva, Y.S. Vygodskii, U. Rosenthal, V.B. Shur, J. Mol. Catal. A: Chem. 200 (2003) 63.

[39] S. Agarwal, C. Mast, K. Dehnicke, A. Greiner, Macromol. Rapid. Commun. 21 (2000) 195.
[40] B. El Ali, J.-M. Brégeault, J. Martin, J. Organomet. Chem. 327 (1987) C9.
[41] H.R. Kricheldorf, T. Mang, J.M. Jonté, Macromolecules 17 (1984) 2173.
[42] U. Bahr, A. Deppe, M. Karas, F. Hillenkamp, Anal. Chem. 64 (1992) 2866.
[43] M. Montaudo, C. Puglisi, F. Samperi, G. Montaudo, Rapid Commun. Mass Spectrom. 12 (1998) 519.
[44] Y. Izumi, M. Matsuo, K. Urabe, J. Mol. Catal. 18 (1983) 299.
[45] A. Aoshima, S. Tonomura, S. Yamamatsu, Polym. Adv. Technol. 2 (1990) 127.
[46] L. Salles, R. Thouvenot, J.-M. Brégeault, Dalton Trans. (2004) 904, and references therein.
[47] A. Atlamsani, J.-M. Brégeault, unpublished results.