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Ring-opening polymerization of lactones catalyzed by decamolybdate anion

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Abstract

An efficient process for the ring-opening polymerization (ROP) of lactones by ammonium decamolybdate $(NH_4)_8[Mo_{10}O_{34}]$ (obtained in situ from thermal decomposition of ammonium heptamolybdate (Hep) $(NH_4)_6[Mo_7O_{24}]$), is reported for the first time. Polymerization of the ε-caprolactone (CL) and δ-valerolactone (VL) proceeds with quantitative conversions, and high molecular weight polyesters (M_n in the order of 10^4) with moderate polydispersity ($M_w/M_n \leq 1.81$) can be obtained at 150 °C in two hours using a CL/Hep molar ratio of 20,000. Hydroxylic compounds can be efficiently used to control the final molecular weight. Hydroxylic compounds act as both co-initiators and chain transfer agents. Incorporation of the hydroxylic compounds as end groups in the polymeric backbone was corroborated by ^1H and ^{13}C-NMR. The molecular weight of poly(ε-caprolactone) (PCL) measured by gel permeation chromatography (GPC) shows a linear dependence on the CL/OctOH ratio. Decamolybdate anion (isolated as a product from the thermal decomposition of heptamolybdate) shows a similar catalytic activity toward polymerization compared to that observed for ammonium decamolybdate obtained in situ. Catalysts recovered after a polymerization batch maintain most of their initial properties, and can be reused to polymerize lactones in an efficient manner.

Keywords: Polyesters; Ammonium decamolybdate; Ring-opening polymerization

1. Introduction

Poly(ε-caprolactone) (PCL) is a biodegradable polymer that found widespread uses in biomedical applications [1–3]. Ring-opening polymerization (ROP) of ε-caprolactone (CL) is the most convenient route to obtain PCL. Different initiators such as Ytrium derivatives [4], Aluminum and tin alkoxides [5], tetrabutyl tin [6], zinc chloride [7] and zeolites [8] among others have been used to polymerize CL. However, long conversion times are observed in all these systems, limiting their application in the synthesis of aliphatic polyesters.

Isopolyanions may be considered to be portions of a closed packed array of oxide ions with metal ions occupying octahedral holes [9]. Isopolymolybdates are isopolyanions with a special crystalline arrangement, mainly composed of octahedric MoO_6 units. In particular, decamolybdate anion $[Mo_{10}O_{34}]^{8-}$ crystal structure is formed of a Mo_8O_{28} unit built up of edge-bridged MoO_6 octahedra, which connects to two tetrahedral MoO_4 units located at the corners [10] (see Fig. 1). Decamolybdate anion is obtained in the solid state as the ammonium salt $(NH_4)_8[Mo_{10}O_{34}]$ by thermal decomposition of ammonium heptamolybdate $(NH_4)_6[Mo_7O_{24}]$ [11].

One of the main advantages of heterogeneous catalysts is their potential of separation and recycling for repeated usage in a reaction. In this connection, the use of ammonium decamolybdate as a catalyst of ROP of lactones has this benefit. To our knowledge, efficient polymerization of lactones initiated by isopolymolybdates has never been reported before. In the present work, the feasibility of ammonium decamolybdate (obtained in situ by thermal decomposition of ammonium heptamolybdate) to induce ROP of lactones in the absence or presence of hydroxylic compounds (water and alcohols) is investigated. Observed bulk polymerization reaction times were in the order of 2 h, which shows the efficiency of this catalyst in the production of aliphatic polyesters. The role of hydroxylic compounds in the polymerization and the control of the molecular weight

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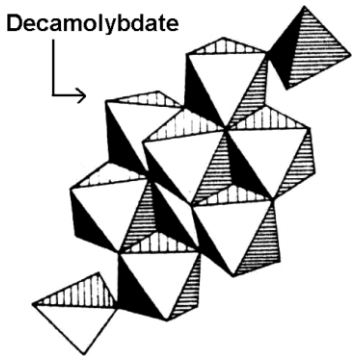

Fig. 1. Crystal structure of the ion $Mo_{10}O_{34}^{-8}$ [10].

is discussed. The use of decamolybdate anion as catalyst represents an alternative and efficient route to obtain biodegradable polyesters such as poly(ε-caprolactone) PCL and poly(δ-valerolactone) PVL.

2. Experimental

2.1. Materials

CL (Aldrich Chemicals Co.) and δ-valerolactone VL (Fluka) were dried over calcium hydride and distilled under reduced pressure before use. *n*-Octanol (OctOH), *n*-Decanol (DecOH) and iso-propanol (IprOH) were purchased from Aldrich and used without further purification. Ammonium heptamolybdate (Fluka) was ground in a mortar and passed through 100 molecular sieve before use. Ammonium decamolybdate was obtained by thermal descomposition of ammonium heptamolybdate at 150 °C for two hours, and characterized by powder X-ray diffraction (XRD) and BET analysis. Analysis by the BET method reveals that this powder has a surface area = 1.47 $m^2\ g^{-1}$ and a pore diameter of 113 Å. Recovered catalyst showed a surface area = 2.68 $m^2\ g^{-1}$ and pore diameter of 116 Å.

2.2. Polymerization procedure

Polymerizations were carried out in 5 ml vials previously dried and purged with dry nitrogen. In a typical run, monomer, catalyst and hydroxylic compound were added under nitrogen atmosphere, vials were stoppered with a rubber septum and placed in a thermostated bath at 150 °C for two hours. Ammonium decamolybdate was formed in situ at this temperature. Final polymer was crystallized from chloroform/methanol and dried under vacuum. Molecular weight and conversion during reaction was monitored by ^{1}H-NMR. Final molecular weight and MWD was determined by gel permeation chromatography (GPC).

2.3. Measurements

Solution ^{1}H and ^{13}C-NMR spectra in $CDCl_3$ were recorded at room temperature on a Varian Gemini 200 and Varian Unity *Plus* 300 spectrometers using tetramethylsilane (TMS) as internal standard. FT-IR spectra were obtained from films deposited over KBr plates on a Perkin–Elmer 1600. GPC measurements were made in a Varian HPLC 9012Q equipped with two gel columns Styragel® HR 3 and Styragel® 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 calibration to calculate the molecular weight of polyesters. Intrinsic viscosity was measured on a Cannon–Fenske viscometer at 30 °C in *N*,*N*-dimethylformamide (DMF). Powder XRD patterns were measured at ambient conditions using a Siemens D-5000 diffractometer and Cu (Kα) radiation. The specific surface areas and pore diameter were measured by the single point BET method using a ASAP 2010 V 4.00 (Micromeritics International Corp.)

3. Results and discussion

Bulk polymerization of ε-caprolactone (CL) by ammonium decamolybdate (obtained in situ by thermal decomposition) with a M/Hep (Monomer/Heptamolybdate molar ratio) of 20,000 was carried out at 150 °C (see Table 1). A polymer with $M_n = 86,190$ and $M_w/M_n = 1.74$, with a conversion of 95%, was obtained after two hours (see No. 2, Table 1). GPC chromatograms for these samples show bimodal peak pattern. If the reaction mixture is left at 150 °C for 24 h, degradation of molecular weight (due mainly to transesterification reactions) yields a polyester with $M_n = 20,430$. Cyclic oligomers are not detected by ^{1}H-NMR. This result indicates that decamolybdate not only catalyzes the polymerization of the CL, but also can induce degradation of the PCL. When a M/Hep ratio of 200 is used instead, a polyester with lower M_n (9730 Da) is obtained.

Table 1
Result for ROP of CL and VL catalyzed by decamolybdate

No.	M	M/Hep[a]	M_w/M_n[b]	M_n(GPC)[b]	Conv (%)[c]
1	CL[d]	200	1.50	9730	98
2	CL[d]	20,000	1.74	86,190	95
3	CL[d,e]	20,000	1.66	20,430	98
4	CL[f]	19,000	1.67	74,420	98
5	VL[f]	19,000	1.64	33,230	100

Polymerizations were carried out at 150 °C for 2 h, except No. 3 (see text for details).

[a] M/Hep = Monomer/ammonium heptamolybdate molar ratio.

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

[c] Obtained by ^{1}H-NMR.

[d] Fifty mmols was used.

[e] For 24 h.

[f] Using 47.5 mmol.

Polymerization of VL (No. 5, Table 1) proceeds with high conversion (100%) and yields a polyester with $M_n = 33,230$ and a polydispersity of 1.64. It can be seen from Table 2 that M/Hep relationship is directly related with the obtained molecular weights. Quantitative conversions (95–99%) are observed for all samples. The molecular weight and intrinsic viscosity values of the PCL linearly increase with the CL/Hep ratio.

Polymerization of 47.5 mmol of ε-caprolactone (CL) by 3 mg of ammonium heptamolybdate in the presence of octanol (OctOH) (CL/OctOH feed molar ratio of 19) was made at 150 °C under N_2. A polymer with $M_n = 5070$ (determined by GPC) and moderate polydispersity ($M_w/M_n = 1.50$) is obtained (see Table 3, No. 2). In general, polyesters with moderate polydispersity ($M_w/M_n \leq 1.81$) were isolated after crystallization. The dependence of number-average molecular weight with CL/OctOH is linear (see Fig. 2, No. 1–7, Table 3), and M_n increased from 2560 to 18,920 almost proportionally to the CL/OctOH ratio. Polydispersities (M_w/M_n) in the range 1.29–1.81 were recorded by GPC. This fact indicates that control of molecular weight can be achieved by using the proper amount of hydroxylic compound in the feed reaction.

Experimental values of M_n calculated from GPC are higher than theoretical values of M_n(calcd) (see Table 3). M_n(calcd) values are similar to those derived from ^{1}H-NMR. Overestimation of M_n obtained by GPC for PCL is a common feature, since polystyrene standards are used in the construction of the calibration curve. MacLain and Drysdale found that M_n(calcd)/M_n(GPC) ratio is around 0.45 for PCL [12]. In the last column of Table 3, we report this ratio for our samples. Values between 0.36 and 0.60 are recorded, which indicate some variation in this ratio. Similar observations were made for polyesters when aluminum thiolates [13] or alkoxides [14] were used as initiators. Also Kricheldorf [15] found that the M_n as obtained from GPC measurements are larger than the values obtained from end-group analyses by 15–25% for PCL. Transesterification reactions and alkene formation are commonly observed during ROP of lactones. One of the consequences is the observation of bimodal molecular weight distributions [16]. Analysis of the MWD curve line shapes of final polymers obtained by GPC reveals that unimodal distributions are present (see Fig. 3). ^{1}H-NMR analysis of intermediates and final product also supports this conclusion. NMR analysis also indicates a quantitative incorporation of RO– as end groups. For the case of octanol, signals for methyl group of $OctO_2C$ moiety ([*a*,CH_3] δ 0.83) and for $HOCH_2$ (*h*, δ 3.59) groups are observed in the ^{1}H-NMR spectrum (see Fig. 4). Formation of macrocycles was not observed. Relative ratio between terminal groups *h* to *a* is around 2:3. In the C-13 NMR spectrum, signals for methylene and methyl terminal groups appear at δ 62.47 and δ 13.97, respectively. Hydroxylic compounds act as initiators/chain transfer agents during polymerization. In the case of water, a polyester with both hydroxyl and carboxylic acid terminal groups is obtained in one step (No. 9, Table 3). Signals for these groups at δ 176.63 [CO_2H] and δ 62.40 [CH_2OH] are observed in carbon-13 NMR spectrum. Polyesters with both terminal groups are an important class of polymer, as they represent bifunctional telechelic α-carboxylic-ω-hydroxyl derivative of PCL [17]. Polymerization in the presence of isopropanol (No. 10, Table 3) yields a polyester with an

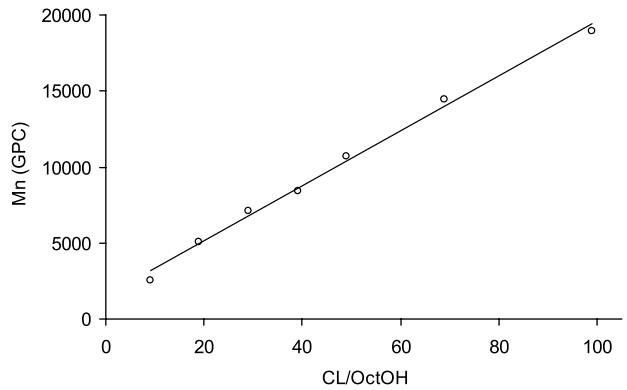

Fig. 2. Dependence of M_n on CL/OctOH ratio for the polymerization of ε-caprolactone (CL) catalyzed by decamolybdate in the presence of octanol (OctOH) at 150 °C.

Table 2
ROP of CL by decamolybdate. Effect of ε-caprolactone/heptamolybdate ratio (CL/Hep)

No.	CL/Hep[a]	Conv (%)[b]	M_n(NMR)[b]	[η][c]
1	200	98	4400	–
2	625	99	12,400	–
3	1250	98	20,600	0.43
4	2500	98	–	0.55
5	5000	98	–	0.60
6	10,000	97	–	0.65
7	20,000	95	–	0.78

Polymerizations were carried out at 150 °C for 2 h (using 50 mmol of CL).
[a] CL/Hep = ε-caprolactone/Ammonium heptamolybdate ratio molar.
[b] Obtained by ^{1}H-NMR.
[c] In DMF at 30 °C.

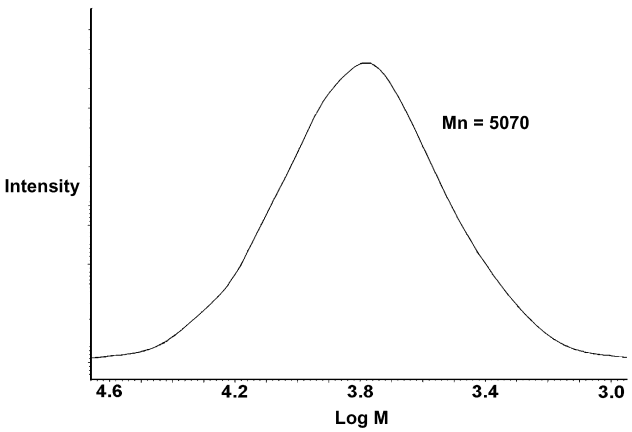

Fig. 3. GPC profile for PCL (see No. 2, Table 3).

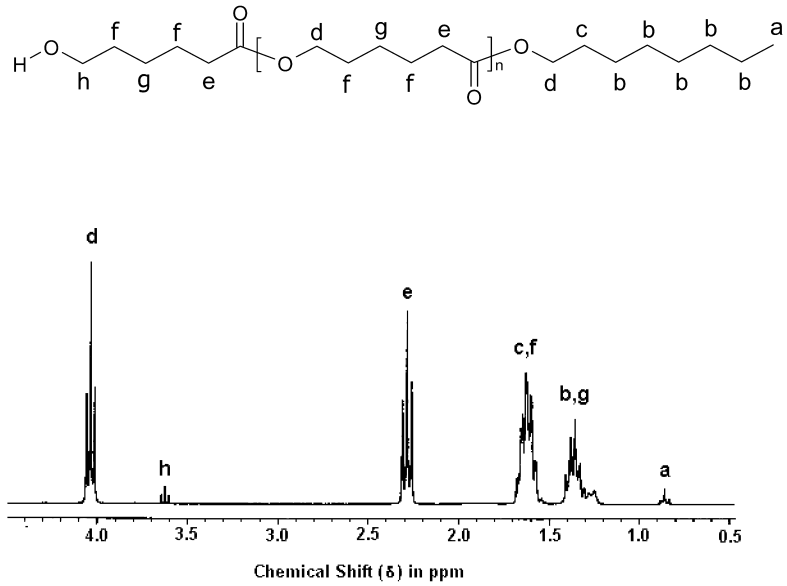

Fig. 4. 300 MHz ^{1}H-NMR spectrum of 300 MHz for PCL (M_n(GPC) = 5070) in $CDCl_3$ (see No. 2, Table 3).

$IprO_2C$ end group. A signal at δ 21.63 for isopropyl methyl groups is observed in the carbon-13 NMR spectrum. The ROP of CL catalyzed for decamolybdate in the presence of an alcohol, is an appropriate route for the obtention of end-functionalized PCL [18].

δ-valerolactone (VL) was polymerized under similar conditions for CL by decamolybdate in the presence of octanol (No. 11, Table 3). Polymerization conversion was 94% in two hours, and a polyester with $M_n = 4740$ and a moderate polydispersity ($M_w/M_n = 1.40$) was obtained. The presence of terminal groups was determined by proton- and carbon-13 NMR spectroscopy as described previously for PCL. FT-IR spectrum of PCL shows bands at 2943, 1721 and 1189 cm^{-1}, corresponding to the stretching vibrations of $-CH_2-$, $-CO-$ and $-COO-$ groups, respectively [19]. Similar bands are observed for PVL at 2955, 1720 and 1165 cm^{-1}.

In order to confirm that the decamolybdate is the active species in polymerization, ammonium decamolybdate was prepared by thermal decomposition of the ammonium heptamolybdate, in a vial at 150 °C for two hours (see Section 2). Formation of decamolybdate was corroborated

Table 3
Results for ROP of CL and VL by decamolybdate in the presence of hydroxylic compounds (ROH)

No.	M	ROH	M/ROH	M_w/M_n	M_n(GPC)[a]	M_n(calcd)[b]	M_n(NMR)[c]	Conv (%)[c]	Ratio[d]
1	CL	OctOH	9	1.29	2560	1160	1110	90	0.45
2	CL	OctOH	19	1.50	5070	2300	2380	100	0.45
3	CL	OctOH	29	1.43	7110	3440	3530	100	0.48
4	CL	OctOH	39	1.47	8430	4580	4470	100	0.54
5	CL	OctOH	49	1.66	10,680	5720	5320	100	0.54
6	CL	OctOH	69	1.81	14,410	8000	6940	100	0.55
7	CL	OctOH	99	1.79	18,920	11,430	8990	100	0.60
8	CL	DecOH	19	1.42	6390	2330	2170	100	0.36
9	CL	H_2O	19	1.46	5900	2190	2220	100	0.37
10	CL	IprOH	19	–	–	2230	2370	100	–
11	VL	OctOH	19	1.40	4740	2030	2110	94	0.42
12	CL[e]	H_2O	19	1.46	5590	2190	2600	98	0.39
13	CL[f]	H_2O	19	–	–	2190	2070	99	–

A Monomer/Ammonium heptamolybdate ratio of 47.5 mmol/3 mg was used (except No. 12 and 13). Polymerizations were carried out at 150 °C for 2 h.

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

[b] Obtained from the equation M_n = (MW(L))([M]/[RO]) + MW(ROH), where MW is the molecular weight of lactone monomer or hydroxylic compound.

[c] Obtained by ^{1}H-NMR.

[d] M_n(calcd)/M_n(GPC) ratio.

[e] Polymerization using ammonium decamolybdate recycled from reaction No. 1, Table 1. Monomer/ammonium decamolybdate ratio was 47.5 mmol/3 mg.

[f] Polymerization using ammonium decamolybdate obtained by thermal decomposition of ammonium heptamolybdate at 150 °C for 2 h. Monomer/ammonium decamolybdate ratio was 47.5 mmol/3 mg.

by its powder XRD pattern (see Fig. 5a). The isolated salt was used to polymerize CL in the presence of water as chain transfer agent ($CL/H_2O = 19$, No. 13 in Table 2) at 150 °C by two hours. A polyester with M_n(RMN) = 2070 was obtained, with a conversion of 99% (based on ^{1}H-NMR). These results are similar to those obtained when decamolybdate was obtained in situ (see No. 9, Table 2), being M_n(RMN) = 2220 and 100% conversion. Reaction of CL and water under similar conditions (without presence of decamolybdate) do not yield polymer formation (determined by ^{1}H-RMN). From this, we can conclude that decamolybdate ion is the catalytic species that operates during the ROP of lactones.

The reusability of the catalyst is one of the main advantages of the heterogeneous catalysis. Decamolybdate can be easily separated after reaction from the polymerization mixture by decanting (see No. 1. Table 1). Before reusing, catalyst was washed out with chloroform and dried. Analysis by powder X-ray diffraction of dried decamolybdate indicates that catalyst has lost some of its initial crystallinity (see Fig. 5b); also, a slight increase in the total surface area (2.68 $m^2\,g^{-1}$) and pore diameter (116 Å) with respect to those values observed for decamolybdate (surface area = 1.47 $m^2\,g^{-1}$ and pore diameter of 113 Å, Fig. 5a) is observed. Catalytic activity and monomer conversion (98%, see No. 12. Table 3) observed for reused catalyst is similar to those obtained for fresh isopolyanions (compare with No. 9 and 13 in Table 3).

It is believed that the mechanism of ROP by metal oxides occurs through the formation of complexes where Lewis acid-base interactions are involved [5]. In some cases, active centers are formed from the reaction of catalyst and alcoholic initiators [20,21]. According to the HSAB (hard and soft acids and bases) principle, formation of Lewis complexes between oxygen (a highly electronegative donor) and metal ions is thermodynamically favored. Also, when ROP of lactones is carried out in the presence of hydroxylic compounds, changes in complexing tendencies among the different species are expected both in the initiation and propagation polymerization steps.

The observance of terminal groups such as $OctO_2C$ and HO_2C suggests a possible nucleophilic attack of a hydroxylic group to the lactone carbonyl is operating in the initiation step. However, experiments to determine the nature of the reaction mechanism and intermediates formed during polymerization are underway in our laboratory.

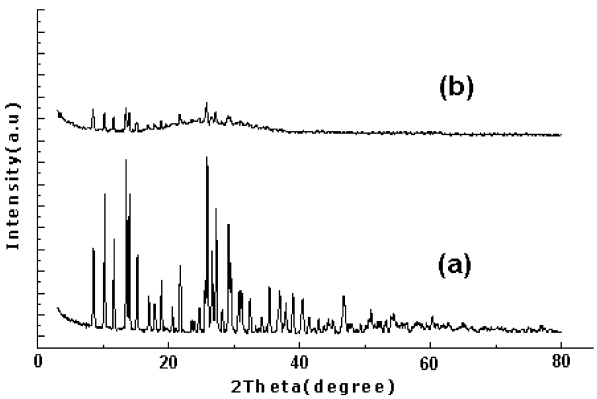

Fig. 5. X-ray diffraction patterns for ammonium decamolybdate obtained in the solid state by thermal descomposition of ammonium heptamolybdate at 150 °C and 2 h. (a) Before and (b) after polymerization of the CL. (CL/Hep = 200, see No. 1 Table 1).

4. Conclusions

It is shown that decamolybdate anion ($Mo_{10}O_{34}^{8-}$) is an effective catalyst for the polymerization of CL and VL in the presence or absence of hydroxylic compounds. ROH act as both initiator and chain transfer agents. This means that a proper control of the final molecular weight can be done in this system. High molecular weight polymers with moderate polydispersity can be obtained within two hours. This method constitutes an appropriate route for the obtention of end-functionalized PCL and PVL. The use of decamolybdate as a catalyst of ROP of lactones has the potential advantages of isolation and recycling for repeated usage in polymerization reactions.

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