

Synthesis and characterization of poly(ϵ -caprolactone) and copolyesters by catalysis with molybdenum compounds

José E. Báez^{1,2}, Antonio Martínez-Richa²

¹ Universidad del Papaloapan, Campus Tuxtepec, Col. Parque Industrial, Circuito Central No. 200, 68301 Tuxtepec, Oax. México.

² Facultad de Química, Universidad de Guanajuato, Noria Alta S/N, 36000 Guanajuato, Gto. México.

e-mail: richa@quijote.ugto.mx

1. Abstract

Novel routes to obtain poly(ϵ -caprolactone) (PCL) by ring-opening polymerization (ROP) of ϵ -caprolactone (CL) using molybdenum compounds (halides, oxides and molybdates) as catalysts are presented in this thesis. Ammonium decamolybdate $(\text{NH}_4)_8[\text{Mo}_{10}\text{O}_{34}]$ (*Dec*) comes to be best catalyst for ROP, based on: (a) selectivity, (b) short reaction time (2 h) and (c) high conversions (98 – 100 %). Different molecular weight were obtained for PCL ($M_n = 212 - 86190$). Control of end groups nature of PCL and copolyesters can be achieved by this method. Final polymers contain ester (RO-CO-) and hydroxyl end-groups. In this way, different ester end-groups can be created, depending on the nature of the alcohol initiator (R-OH, R = alkyl or H). Poly(δ -valerolactone) PVL and copolyesters of CL with δ -valerolactone (VL) and γ -butyrolactone (BL) were synthesized using *Dec* as catalyst. A convenient route to polyurethane-ureas from telechelic α,ω -hydroxyl PCL is described. Evidence support that a coordination-insertion mechanism involving molybdenum (V) species operate during the ROP of CL by *Dec*.

2. Introduction

Molybdenum is a versatile element present in many catalytic systems used for polymerization, such as those utilized for the polymerization of norbornenes [1,2] and phenylacetylene [3]. However, there are few reports related to the use of molybdenum derivatives in the ring-opening polymerization (ROP) of lactones. In that sense, it has been reported that Mo(VI) acetylacetonate and tetrapropoxide $\text{Mo}(\text{OPr})_4$ produce high molecular weight polyesters with high conversions [4]. Molybdenum is also a biologically important transition metal. It is the heaviest atomic number element to have a wide range of functions in living organisms. At the present time, activity of over a dozen known enzymes relies on molybdenum, which is usually absorbed in the form of molybdate anion, $[\text{MoO}_4]^{2-}$ [5].

We recently reported the synthesis of aliphatic polyesters using decamolybdate anion $[\text{Mo}_{10}\text{O}_{34}]^{8-}$ as catalyst. Primary and secondary alcohols can be used as initiator/chain-transfer agents. Resulting polyesters possessed two different endgroups: one ester end-group (with the alkyl group of the alcohol linked to the polymer through an ester functionality), and a hydroxyl end-group [6]. When water was used as initiator, a control of the molecular weight of the resulting α -hydroxyl- ω -(carboxylic acid) PCL could be achieved [7]. Effectiveness of decamolybdate anion in the synthesis of the α,ω -telechelic PCL diols (HOPCLOH), the HOPCLOH was successfully used for the synthesis of a poly(ester-urethane-urea) [8].

We report herein a comparative study of the catalytic behavior of eight different molybdenum compounds (all with Lewis acid character) to ROP of CL [9]. The scope of the ring-opening polymerization of lactones (CL, VL and BL) using decamolybdate ammonium is presented and discussed. When water is used as initiator/chain-transfer agent, an asymmetric telechelic α -hydroxyl- ω -(carboxylic acid) copolyester with controlled molecular weight can be obtained using an efficient one-step route. To our knowledge, this is the first report on the synthesis of acid-functional asymmetric telechelic copolyesters derived from lactones. Final polymers and copolymers were characterized by FT-IR, ^1H and ^{13}C NMR, GPC and MALDI-TOF.

3. Experimental

Polymerizations were carried out in 5 mL vials previously dried and purged with dry nitrogen. In a typical run, monomer (CL, 50 mmol), molybdenum compounds (CMo) and CL (molar ratio CL/CMo = 200) were added under nitrogen atmosphere. Vials were stoppered with a rubber septum and placed in a thermostated bath at 150 °C. In the case of the ammonium decamolybdate $(\text{NH}_4)_8[\text{Mo}_{10}\text{O}_{34}]$ (Dec), catalyst is formed in situ at this temperature by thermal decomposition of ammonium heptamolybdate $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]$ (Hep) [5]. Final polymer was crystallized from chloroform/methanol and dried under vacuum. Conversion and molecular weight was monitored by ^1H NMR. The crystallized polymer was analyzed by MALDI-TOF.

4. Results and Discussion

We have previously reported that ammonium decamolybdate $(\text{NH}_4)_8[\text{Mo}_{10}\text{O}_{34}]$ (Dec) is able to successfully effect and sustain the ring-opening polymerization (ROP) of lactones such as 3-caprolactone (CL) and d-valerolactone (VL). End-groups functionalization and control of number-average molecular weight (M_n) can be achieved using the appropriate initiator/transfer agent system [6,7]. However, it is convenient to compare the catalytic activity of ammonium decamolybdate with respect to other molybdenum derivatives. With this in mind, experiments were carried out in order to compare the effectiveness of Dec with respect to molybdenum chloride, bromide and oxides.

A series of experiments was carried out using the following experimental conditions: bulk polymerization of CL (50 mmol) by different molybdenum derivatives (CMo), using a CL/CMo molar ratio of 200 at 150 °C. It is expected that a good catalyst for ROP leads to short reaction times (0.5–3 h), selectivity and quantitative conversions. Polymerization of CL by MoCl_5 proceeded with high conversion (94%) and short reaction times (ca. 0.5 h). On the other hand, in the same period of time (0.5 h), lower conversion (52%) was observed when MoCl_3 was used. This result can be attributed to the harder Lewis acid power of molybdenum in MoCl_5 . A similar behavior was observed for MoBr_3 . The ^1H NMR spectrum for the end-group zone (δ 3.3–3.7) for PCL obtained when MoCl_5 shows peaks correspond to different end-groups: (1) a singlet corresponding to a methoxy end-group $-\text{CO}-\text{O}-\text{CH}_3$ (δ 3.65 ^1H and 51.3 ^{13}C). This methoxy end group comes from methanol, which was used for recrystallization of the polymer. Acylation of methanol apparently requires the presence of an acid chloride end group ($\text{R}-\text{CO}-\text{Cl}$) in the original polymer chains, (2) $-\text{CH}_2-\text{OH}$ (δ 3.63 ^1H and 62.2 ^{13}C) formed by reaction with water [10], (3) $-\text{CH}_2-\text{Cl}$ (δ 3.52 ^1H and 44.5 ^{13}C) formed by chlorination of methylene attached to oxygen [11], (4) $-\text{CH}_2-\text{O}-\text{CH}_2-$ (d, δ 3.37 ^1H and 70.4 ^{13}C) probably formed by a nucleophilic attack of an alkoxide to the methylene in the epsilon position of CL [13]. Also, peaks for olefinic protons $-\text{CH}=\text{CH}_2$ (δ 5.75 and 4.98) due to a dehydration reaction of hydroxyl end groups were observed. Final polymer shows broad polydispersity, as determined by GPC analysis ($M_n(\text{GPC}) = 6740$, $M_w/M_n = 2.28$). This observation suggests that parallel reactions (such as those leading to the formation of ether linkages) are

responsible for observed broad polydispersity. It has been reported that MoCl_5 provide an efficient catalyst system in the C–O bond cleavage reaction of ethers [13].

5. Conclusions

It was found that ring-opening polymerization (ROP) of 3-caprolactone (CL) is catalyzed by different molybdenum derivatives. Halides and oxides in general show low selectivity and long reaction times, respectively. However, decamolybdate anion shows selectivity to the formation of α -hydroxyl- ω -(carboxylic acid) PCL (HA-PCL), with short reaction times (2 h) and quantitative conversions (98%). In all the molybdenum derivatives investigated, molybdenum has a Lewis acid character, and this fact is related with its catalytic action in this kind of polymerization.

6. References

- [1] Miyamoto Y, Fujiki M, Nomura K. *J Polym Sci, Part A: Polym Chem* **2004**; 42: 4248–65.
- [2] Hayano S, Kurakata H, Tsunogae Y, Nakayama Y, Sato Y, Yasuda H. *Macromolecules* **2003**; 36: 7422–31.
- [3] Gal Y. *Eur Polym J* **2000**; 36: 2059–62.
- [4] Kubo M, Nakanishi M, Kimura M. Patent No. DE 2947978, Germany; 1980.
- [5] Rayner-Canham G. Descriptive inorganic chemistry. 2nd ed. New York: Freeman and Company; 2000 p. 468.
- [6] Báez JE, Martínez-Rosales M, Martínez-Richa A. *Polymer* **2003**; 44: 6767.
- [7] Báez JE, Marcos-Fernández A, Martínez-Richa A. *Macromolecules* **2005**; 38: 1599.
- [8] Báez JE, Marcos-Fernández A, Lebrón-Aguilar R, Martínez-Richa A. *Polymer* **2006**; 47: 8420–8429.
- [9] Báez JE, Martínez-Richa A. *Polymer* **2005**; 26: 12118.
- [10] Shen Y, Shen Z, Zhang Y, Hang Q. *J Polym Sci, Part A: Polym Chem* 1997;35:1339–52.
- [11] Abraham GA, Gallardo A, Lozano AE, San Roman J. *J Polym Sci, Part A: Polym Chem* 2000;38:1355–65.
- [12] Guo Q, Miyaji T, Hara R, Shen B, Takahashi T. *Tetrahedron* 2002;58: 7327–34.