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ScienceDirect
Polymer 47 (2006) 8420–8429
polymer
www.elsevier.com/locate/polymer

A novel route to α,ω-telechelic poly(ε-caprolactone) diols, precursors of biodegradable polyurethanes, using catalysis by decamolybdate anion

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Received 15 June 2006; received in revised form 29 September 2006; accepted 21 October 2006

Abstract

A new convenient route for the synthesis of poly(ε-caprolactone) (PCL) with α,ω-telechelic diols' end-groups is presented. Synthesis of α,ω-telechelic PCL diols (HOPCLOH) was achieved by ring-opening polymerization (ROP) of ε-caprolactone (CL) catalyzed with ammonium decamolybdate $(NH_4)_8[Mo_{10}O_{34}]$ and using diethylene glycol (DEG) as initiator. Obtained HOPCLOH was characterized by ^{1}H and ^{13}C NMR, FT-IR, GPC and MALDI-TOF. Comparative studies demonstrate that ammonium decamolybdate $(NH_4)_8[Mo_{10}O_{34}]$ is better catalyst than Sn-octanoate ($SnOct_2$) toward CL polymerization in presence of DEG, under the conditions tested. A biodegradable poly(ester-urethane-urea) derivative was efficiently prepared from synthesized HOPCLOH. Obtained polymer shows minor differences with respect to the properties recorded for a poly(ester-urethane-urea) obtained from commercial HOPCLOH.

Keywords: Ring-opening polymerization; α,ω-Telechelic poly(ε-caprolactone) diols; Decamolybdate anion

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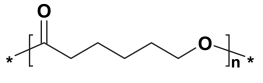
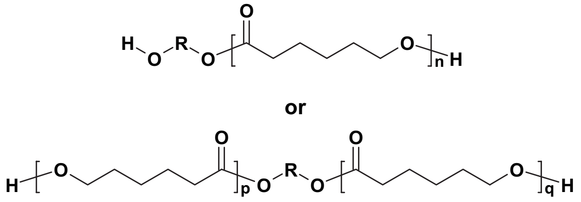
1. Introduction

Biodegradable polymers – such as poly(ε-caprolactone) (PCL) **1** – are receiving increasing attention due to their applications in the biomedical area. Biodegradation of PCL films by pure strains of microorganisms isolated from industrial compost induces a weight loss of 95 wt% (with respect to the initial mass) after 200 h of incubation [1]. It is expected that derivatives obtained by chain extension reactions of PCL also show similar biodegradable properties. Most of these derivatives have also potential uses in surgery and as drug delivery agents.



1

One of the more important factors to consider for PCL chain extension reactions is the chemical nature of the polyester end-groups. Diol derivatives (α,ω-telechelic diols) are specially targeted, due to the feasibility of the hydroxyl end-groups to react with different functional groups [2–9]. Some examples are: (1) synthesis of α,ω-telechelic PCL diols (HOPCLOH) **2** [10–15] as precursors of polyurethanes, (2) synthesis of HOPCLOH [16–19] which acts as macroinitiators in the synthesis of triblock copolymers.



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The more convenient route for the synthesis of HOPCLOH (with respect to polycondensation) is the ring-opening

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doi:10.1016/j.polymer.2006.10.023

polymerization (ROP) of ε-caprolactone (CL) using a diol as initiator/chain-transfer agent in the presence of a catalyst. Derivatives from Ge [2], Nd [3], Bi [4,6], Sn [10], Zn [15] and Al [20], have been tested as catalysts to obtain HOPCLOH. However, these synthetic routes are plagued with some inconveniences, such as the use of toxic metals as catalysts [3,10], long reaction times (24–264 h) [2,10,15] and inefficient catalyst systems (CL/catalyst molar ratios of 50–1000 are needed to induce lactone polymerization) [2–4,6,10,15].

Molybdenum is an environmentally friendly element. In the scope of bioinorganic chemistry, molybdenum is considered as 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 rely on the presence of molybdenum, which is usually absorbed as the molybdate ion, $[MoO_4]^{2-}$ [21,22].

We recently reported the synthesis of aliphatic polyesters using decamolybdate anion $[Mo_{10}O_{34}]^{8-}$ as catalyst. Primary and secondary alcohols can be used as initiator/chain-transfer agents. Resulting polyesters possessed two different end-groups: one ester end-group (with the alkyl group of the alcohol linked to the polymer through an ester functionality), and a hydroxyl end-group [23]. When water was used as initiator, a control of the molecular weight of the resulting α-hydroxyl-ω-(carboxylic acid) PCL could be achieved [24]. Effectiveness of decamolybdate anion in the synthesis of lactone copolyesters with controlled end-group architecture was also demonstrated [25]. 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 $(NH_4)_6[Mo_7O_{24}]$ [26].

In this investigation, we report a new synthetic route to obtain α,ω-telechelic PCL diols (HOPCLOH), with the use of decamolybdate anion as catalyst and diethylene glycol ($HO-(CH_2)_2-O-(CH_2)_2-OH$) (DEG) as initiator. A CL/catalyst molar ratio of 20,000 was used. The amount (in mmol) of catalyst was lower than that commonly used for ROP of lactones with tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) catalysis [6,10]. This synthetic route represents a convenient alternative to obtain HOPCLOH. On the basis of its particular macromolecular architecture given by the presence of two hydroxyl end-groups, the HOPCLOH was successfully used for the synthesis of a poly(ester-urethane-urea).

2. Experimental

2.1. Materials

CL (Aldrich Chemicals Co.) was dried over calcium hydride and distilled under reduced pressure before use. Ammonium heptamolybdate tetrahydrate $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (Fluka) was grounded in a mortar and passed through a 100 mesh sieve. The grounded catalyst was dried in an oven at 80 °C overnight before use.

Polycaprolactone diol 530, 1250 and 2000, L-lysine monohydrochloride, DEG and stannous 2-ethylhexanoate were purchased from Aldrich Chemical Company. L-Lysine diisocyanate (LDI, diisocyanate of the L-lysine methyl ester or methyl-2,6-diisocyanatohexanoate) was a gift from Kyowa Hakko Kogyo Co., Ltd., Japan. Triethylamine and *N*,*N*-dimethylacetamide (DMAc) were supplied by Scharlau. *N*,*N*-dimethylacetamide was vacuum distilled from isocyanates (commercial polymeric diisocyanate–diphenylmethane), keeping the distillation temperature below 60 °C to avoid solvent decomposition, and stored in an amber flask blanketed with nitrogen for not more than a week before use. The rest of the reagents were used as received. L-Lysine dihydrochloride ethyl ester (LYS) was synthesized following the procedure reported in literature [14].

2.2. Synthesis of α,ω-telechelic poly(ε-caprolactone) diols (HOPCLOH) **3a** and **3b**

In a typical run, CL (5.70 g, 50 mmol), DEG (1.53 g, 3.45 mmol) and $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (3 mg) in a CL/ammonium heptamolybdate tetrahydrate molar ratio of 20,000 were placed in a 25 ml flask. The flask was stoppered at room temperature and placed in a thermostated bath at 150 °C and the mixture was stirred for 4 h. No inert atmosphere was used. Ammonium decamolybdate $(NH_4)_8[Mo_{10}O_{34}]$ was formed in situ at this temperature by thermal decomposition of ammonium heptamolybdate $(NH_4)_6[Mo_7O_{24}]$ [23,26,27]. Progressive solubilization of ammonium decamolybdate in the reaction media was visually observed. Final polymer was characterized by FT-IR, ^1H and ^{13}C NMR, GPC and MALDI-TOF. IR (cm^{-1}): 3545 (ν_{OH}), 2943 (ν_{CH}), 1721 ($\nu_{C=O}$), 1187 ($\delta_{O-C=O}$). NMR data for HOPCLOH (**3a** and **3b**) homopolymer, ^{13}C NMR (50 MHz, $CDCl_3$, ppm) (Fig. 2): δ 173.53 (g), 173.32 (a′), 173.19 (a), 72.18 (5), 68.94 (3), 68.88 (1), 63.92 (f), 63.14 (4), 63.09 (2), 62.27 (l), 61.47 (6), 34.03 (h), 33.91 (b′), 33.76 (b), 32.12 (k), 28.14 (e), 25.32 (d), 25.13 (j), 24.51 (i), 24.37 (c′), 24.28 (c).

2.3. Synthesis of α,ω-trifluoroacetate poly(ε-caprolactone) (TF-PCL-TF) by derivatization of HOPCLOH with trifluoroacetic anhydride (TFA)

Due to the low resolution obtained for some peaks, HOPCLOH was derivatized for NMR characterization. An excess amount of trifluoroacetic anhydride (TFA) was added to a solution of HOPCLOH in $CDCl_3$ (100 mg/0.75 ml) at ambient temperature. Full derivatization of the sample was confirmed when the acidic proton of the trifluoroacetic acid by-product appeared as a sharp peak at around 11 ppm. NMR data for TF-PCL-TF (Fig. 1), ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 4.49 (3, 2H, CH_2OCOCF_3), 4.33 (f, 2H, CH_2OCOCF_3), 4.26 (2, 2H, CH_2O), 4.09 (d, 2H, CH_2O), 3.81 (4, 2H, CH_2O), 3.74 (1, 2H, CH_2O), 2.35 (a, 2H, CH_2CO), 1.76 (e, 2H, CH_2), 1.65 (b, 4H, $(CH_2)_2$), 1.65 (b′, 2H, CH_2), 1.37 (c, 2H, CH_2).

2.4. Synthesis of poly(ester-urethane-urea) **4** prepared from α,ω-telechelic poly(ε-caprolactone) diol (HOPCLOH)

The synthesis of a poly(ester-urethane-urea) **4** was carried out in a 25 ml flask at $T = 80$ °C. One gram (0.4664 mmol)