

## Synthesis, characterization and degradation of poly(ethylene-*b*- $\epsilon$ -caprolactone) diblock copolymer

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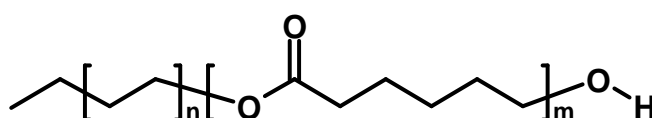
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### 1. Abstract

Poly(ethylene-*b*- $\epsilon$ -caprolactone) (PE-*b*-PCL) diblock copolymers were synthesized by ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone (CL) with  $\alpha$ -hydroxyl- $\omega$ -methyl polyethylene (PE-OH) as macroinitiator and ammonium decamolybdate (NH<sub>4</sub>)<sub>8</sub>[Mo<sub>10</sub>O<sub>34</sub>] as catalyst. Polymerization was conducted in bulk (130-150 °C) with high yield (87-97 %). Block copolymers with different compositions were obtained and characterized by <sup>1</sup>H and <sup>13</sup>C NMR, MALDI-TOF, SAXS and DSC. End-group analysis by NMR and MALDI-TOF indicates the formation of  $\alpha$ -hydroxyl- $\omega$ -methyl PE-*b*-PCL. The PE-*b*-PCL degradation was studied using thermogravimetric analysis (TGA) and alkaline hydrolysis. The PCL block was hydrolyzed by NaOH (4M), without any effect on the PE segment.

### 2. Introduction

Polyethylene (PE) is a thermoplastic polyolefin with important applications in many products such as shopping bags, packaging products and tapes, however it is one of the most chemically inert of all polymers [1,2]. In contrast, poly( $\epsilon$ -caprolactone) (PCL) is a thermoplastic aliphatic polyester with degradable characteristics [3]. Diblock copolymer as the poly(ethylene-*b*- $\epsilon$ -caprolactone) (PE-*b*-PCL) **1** is an interesting macromolecule due to the bond between these two amphiphilics diblocks with potential degradable properties. One of the applications for PE-*b*-PCL is as a compatilizer within polymer blends (PE:PCL) [4]. For other hand, a thermal propriety of PE-*b*-PCL is the melting behavior of double crystalline diblock [5-6].



### 3. Experimental

#### 3.1 Synthesis of $\alpha$ -hydroxyl- $\omega$ -methyl poly(ethylene-*b*- $\epsilon$ -caprolactone) diblock copolymers (PE-*b*-PCL)

Polymerization was carried out in a 50 ml pear shaped flask previously dried. In a typical run,  $\epsilon$ -caprolactone (CL, 0.180 mol, 20 ml),  $\alpha$ -hydroxyl- $\omega$ -methyl polyethylene (PE-OH,  $M_n(\text{NMR}) = 850$  Da, 12.37 mmol, 10.52 g) and ammonium heptamolybdate tetrahydrate  $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O}$  (Hep, 0.0113 mmol, 14 mg) were added and heated to reflux by stirring them in an oil bath at 130-150 °C for 1 h. Ammonium decamolybdate  $(\text{NH}_4)_8[\text{Mo}_{10}\text{O}_{34}]$  was obtained in situ in a solid state by thermal decomposition of ammonium heptamolybdate  $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]$  [7,8]. The diblock copolymer obtained was precipitated from chloroform/methanol, recovered by filtration and left to dry at room temperature in ambient conditions for one night.  $M_n$  of the PCL block ( $M_n = 1480$ ) in the copolymer was estimated by  $^1\text{H}$  NMR. The peak from the methyl ( $\text{CH}_3\text{-CH}_2\text{-}$ ) end group of the polyethylene (PE) block at 0.93 ppm and the peak of the methylene adjacent to the carbonyl group ( $\text{-CH}_2\text{-CO-O-}$ ) of the poly( $\epsilon$ -caprolactone) (PCL) block at 2.33 ppm were used to calculate the number-average degree of polymerization of the PCL block ( $\text{DP}_{\text{PCL}} = 13$ ). The yield was calculated based on weight of monomer at the feed (yield = 87 %).

### 4. Results and Discussion

#### 4.1 Synthesis and Characterization

Ring-opening polymerization (ROP) of the  $\epsilon$ -caprolactone (CL) with  $\alpha$ -hydroxyl- $\omega$ -methyl polyethylene (PE-OH) ( $M_n(\text{NMR}) = 850$ ) as macroinitiator using ammonium decamolybdate as catalyst was an efficient route to obtain  $\alpha$ -hydroxyl- $\omega$ -methyl poly(ethylene-*b*- $\epsilon$ -caprolactone) (PE-*b*-PCL) (Figure 1). The ROP was carried out by bulk polymerization with a CL/ammonium heptamolybdate (Hep) feed molar ratio of 20,000 at 130-150 °C in 1 h (Table 1), with high yield (87-97 %). However the decrement in the yield for sample PE-*b*-PCL1 (87 %, CL/PE-OH = 14.5) with respect to PE-*b*-PCL3 (97 %, CL/PE-OH = 14.5) was observed.

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CL/PE-OH = 85.2) is attributing at the viscosity increment caused by the PE-OH, hindering the monomer diffusion. The number-average degree of polymerization of the PCL block ( $DP_{PCL}$ ) is dependent of molar ratio CL/PE-OH. Diblock copolymers (PE-*b*-PCL) with different compositions, as a function of the feed ratio CL/PE-OH, were obtained (Table 1). For a feed ratio 56/44 (CL/PE-OH), a copolymer with an insertion of 57/43 was obtained. The PE-*b*-PCL structure was corroborated by  $^1H$  and  $^{13}C$  NMR and MALDI-TOF spectroscopies (vide infra).

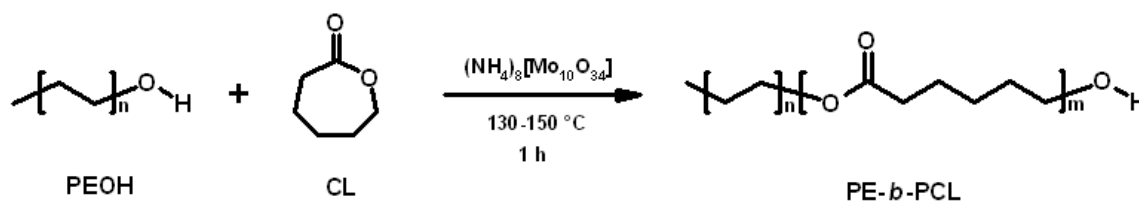


Figure 1. Synthesis of  $\alpha$ -hydroxyl- $\omega$ -methyl poly(ethylene-*block*- $\epsilon$ -caprolactone) (PE-*b*-PCL).

In the  $^1H$  NMR spectrum for the PE-*b*-PCL1, signals for two different blocks are clearly seen. Methyl [*a*,  $-CH_3$ ,  $\delta$  0.93] and methylene [*h*,  $-CH_2-OH$ ,  $\delta$  3.66] end groups can be distinguished for PE and PCL, respectively. The ratio of the signal's intensity of *a* to that of *h* is 3:1.6 (3:2 expected). On the other side, a similar situation is found for the PE-OH macroinitiator, presumably due to micelles. Evidence of micellar aggregation of hydrophilic  $-OH$  group was studied by Kim et al. [9] The hydrophobic tetrachloroethane- $d_2$  solvent is better for methyl end-group in the PE block.

#### 4.2 Degradation

Thermal decomposition of the homopolymers (PE-OH and HA-PCL) and diblock copolymer (PE-*b*-PCL1) is analyzed. TGA analysis shows that PE-OH and HA-PCL started thermal decomposition with an inflection temperature ( $T_{d1}$ ) at 369 and 362  $^\circ\text{C}$ , respectively. The PE-*b*-PCL1 is less stable compared to HA-PCL and PE-OH; in the thermograms, three different thermal degradation steps for the block copolymer at 309, 362 and 430  $^\circ\text{C}$  are shown. Although there is not obvious assignments for the degradation steps in copolymers, due to lower differences between the inflection temperature of the homopolymers (PE-OH and HA-PCL), if we look at the curves of the copolymers, the

relative intensity of the peaks, with the change in the relative content of the blocks, can be taken as evidence to relate the degradation steps with one or another block. On this basis we assigned the PE-*b*-PCL1 the first and third inflection temperature (309 and 430 °C) to the PE block and the second (362 °C) to the PCL block. All diblock copolymer samples show a decrease in the  $T_{d1}$  when the PCL percentages increase. The lower thermal stability of the PE block was interpreted by the decrease in the cristallinity in the PE block [10].

## 5. Conclusions

Poly(ethylene-*b*- $\epsilon$ -caprolactone) (PE-*b*-PCL) can be obtained by ring-opening polymerization of the  $\epsilon$ -caprolactone (CL) catalyzed by ammonium decamolybdate and  $\alpha$ -hydroxyl- $\omega$ -methyl polyethylene (PE-OH) as macroinitiator. Diblock copolymers with different compositions as a function of the used feed ratio were obtained. End-group analysis by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and MALDI-TOF indicates the formation of  $\alpha$ -hydroxyl- $\omega$ -methyl PE-*b*-PCL. PE-*b*-PCL degrades thermally and hydrolytically. In the thermal decomposition both blocks were degraded; however, by basic hydrolysis only PCL block was degraded. This synthesis represents a simple and rapid route for the preparation of the PE-*b*-PCL diblock copolymer.

## 6. References

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