



## Hydrolytic and enzymatic degradation studies of aliphatic 10-undecenoic acid-based polyesters



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### ABSTRACT

The hydrolytic and enzymatic degradations of aliphatic polyesters: poly (10,11-epoxyundecanoic acid) (PEAU) bearing hydroxyl groups along the main chain and poly (11-hydroxyundecanoate)diol (PHU), were studied and compared to that of commercial poly ( $\epsilon$ -caprolactone)diol (PCL). Changes taking place after polyester degradation in sample weight, molecular weight (Mn), chemical constitution, thermal properties, crystallinity and morphology were monitored by size exclusion chromatography (SEC),  $^1\text{H}$  nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), X-Ray diffraction (XRD) and environmental scanning electron and atomic force microscopies (ESEM and AFM). A significant decrease of PEUA Mn in both hydrolytic and enzymatic degradation was detected versus PHU and PCL, and related to its hydrophilic character, by the presence of hydroxyl pendant groups, and the superior amorphous character. An accelerated degradation in acidic media, monitored by SEC and  $^1\text{H}$  NMR spectroscopy to study in detail all residual material of three polyesters, showed the complete degradation only in the case of PEUA and PCL.

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### 1. Introduction

For the last 60 years, synthetic polymeric materials have grown progressively basically due to their low cost, their reproducibility, and their resistance to physical aging and biological attacks. However, the resistance of synthetic polymers to the degrading action of living systems is becoming increasingly problematic in several domains where they are used for a limited period of time before becoming wastes. This is the case in surgery, in pharmacology, in agriculture, and in the environment as well.

Nowadays the open and the patent literature propose a large number of polymers whose main chains can be degraded usefully. Among these degradable polymers, aliphatic polyesters are receiving special attention because they are all more or less sensitive to hydrolytic and enzymatic degradation [1–3]. Aliphatic polyesters containing flexible ester bonds appear to be the most promising because of their excellent biocompatibility and variable degradability and are the most representative examples of environmentally relevant polymeric materials [4–7].

Many aliphatic polyesters biodegrade via a two-step process.

First, polymer backbone bonds must be enzymatically or otherwise hydrolyzed to produce oligomers, which are subsequently broken down in soil to give water, carbon dioxide, and hummus [8]. Generally, polyester degradation rate is impacted by the structure of the polymer backbone, including the electrophilicity of the carbonyl atoms and the presence or absence of bulky substituents. Among the critical factors that affect the degradation rate of polyesters, one is the distance between ester groups in the polymer which determine the polymer character, e.g. hydrophobicity and crystallinity. Molecular weight and crystallinity have been shown to have the largest impact in polyester degradation due to a hindrance in water being able to diffuse into the matrix.

Moreover, the presence of hydrophilic (hydroxyl and carboxyl) end groups also promotes the polyester degradation. It is well known the effect of autocatalysis by the acid ended chain fragments, which leads to a dramatic increase of the rate of degradation as degradation advances [9]. It is established that carboxyl end groups formed by chain cleavage catalyze degradation and that amorphous regions are preferentially degraded [5,10,11].

The introduction of functional groups into commonly used polyesters such as PLA and PCL provides polymers with tuneable degradation behaviour by suppression of crystallinity and enhanced hydrophilicity that also favours cell adhesion to the surfaces important for tissue engineering purposes [12]. Further,

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increased hydrophilicity results in a greater water absorbing capacity of the polymers, thereby increasing the degradation rate and probably preventing a pH drop inside the degrading matrices and hence preventing incomplete release of degraded fragment or encapsulated compounds [13].

Aliphatic polyesters degrade either by bulk erosion or surface erosion [14–16]. Polymer hydrolytic degradation is produced by scission of chemical bonds in the polymer backbone, by water uptake, to form oligomers and finally monomers. In the first step, water molecules attack the water-labile bonds by either direct access to the polymer surface or by imbibition into the polymer matrix followed by bond hydrolysis. This nucleophilic attack by water can be catalysed by acids, bases or enzymes [17].

In this paper we study the hydrolytic and enzymatic degradation of two aliphatic polyesters synthesized from castor oil-derived 10-undecenoic acid: poly (10,11-epoxyundecanoic acid) which contains primary and secondary hydroxyl pendant functions along the main chain and poly (11-hydroxyundecanoate)diol, and compared with commercial poly ( $\epsilon$ -caprolactone)diol. Changes taking place in sample weight, molecular weight, chemical constitution, thermal properties, crystallinity and surface morphology of the polyesters were evaluated and related to the polymer structure and degradation conditions.

## 2. Experimental

### 2.1. Materials

The following chemicals were obtained from the sources indicated and used as received: 1,6-hexanediol (99%), 10-undecenoic acid (98%) (UA), methyl 10-undecenoate (96%), poly ( $\epsilon$ -caprolactone)diol (PCL)  $M_n$  2.000 Da, titanium (IV) isopropoxide (97%), methanesulfonic acid (99.5%), tetrabutylphosphonium bromide (98%) (TBPB), hydrogen peroxide (30%), boron trifluoride diethyl etherate (99%) *Candida Antarctica* immobilized on acrylic resin (5.000 U/g) (CALB), lipase from porcine pancreas (100–500 U/g, pH 8.0, 37 °C) and phosphate buffered saline pH 7.4 (at 25 °C) from Sigma Aldrich. Anhydrous magnesium sulfate and tetramethylsilane (TMS) from Scharlau; citric acid buffer solution pH 2.0 (20 °C) from Fluka, sodium azide and sodium borohydride from Probus; chloroform-D ( $CDCl_3$ ) from euriso-top; toluene, tetrahydrofuran (THF), dimethylformamide (DMF), diethyl ether, dichloromethane (DCM) and methanol (MeOH) from Scharlau. Analytical grade solvents were purified and dried by standard methods. 4 Å powdered molecular sieves were activated 24 h at 220 °C and cooled under vacuum prior use. Flash column chromatography was carried out using neutral silica-gel 60 F254 (from Panreac) and hexane-ethyl acetate as eluent.

### 2.2. Synthesis of monomers

#### 2.2.1. Synthesis of methyl 11-hydroxyundecanoate. (SI.1)

Methyl 11-hydroxyundecanoate was prepared in 72% yield by hydroboration of methyl 10-undecenoate following a reported procedure [18].

#### 2.2.2. Synthesis of 10,11-epoxyundecanoic acid (EUA). (SI.1)

10,11-epoxyundecanoic acid was prepared by enzymatic oxidation of 10-undecenoic acid using CALB and 30%  $H_2O_2$  as previously described [19].

### 2.3. Synthesis of polyesters

#### 2.3.1. Polymerization of EUA: PEUA. (SI.2)

PEUA was synthesized using TBPB as catalyst in toluene as

previously described [19] obtaining a hydroxypolyester with  $M_n$  3650 Da, by  $^{19}F$  NMR, and  $M_n$  8400 Da,  $\bar{D}$  3.9 by SEC.

#### 2.3.2. Preparation of poly(11-hydroxyundecanoate) (PHU) by polymerization of methyl 11-hydroxyundecanoate initiated by 1,6-hexanediol. (SI.2)

In a 50 mL schlenk flask 5.4 g (0.025 mol) of methyl 11-hydroxyundecanoate and 0.25 g (0.0021 mol; molar ratio 12:1) of 1,6-hexanediol were melted with stirring under argon atmosphere at 130 °C. Over the resulting homogeneous clear mixture, 0.07 mL (0.00025 mol, 1% molar) of titanium tetraisopropoxide was added and the temperature raised to 190 °C with the application of vacuum (2 mmHg). After 4 h the mixture was cooled and the resulting solid white mass was dissolved in 25 mL of THF and precipitated twice over 1000 mL of cold diethylether. The resulting white solid was collected by filtration, rinsed with diethyl ether, and dried under vacuum. (Yield: 92%,  $M_n$ : 3520 Da, by  $^1H$  NMR, and 3900 Da,  $\bar{D}$  2.0 by SEC.

$^1H$  NMR ( $CDCl_3$ ,  $\delta$ , ppm): 4.86 (m, 2H,  $CH_2-OH$  (end group)), 4.05 (t, 8H,  $COO-CH_2-CH_2$ ), 3.64 (t, 4H,  $HO-CH_2$  (end group)), 2.29 (t, 4H,  $CH_2-COO$ ), 1.61 (m, 20H,  $-COO-CH_2-CH_2$ ;  $HO-CH_2-CH_2$ ;  $CH_2-CH_2-COO$ ), 1.28 (m, 56H,  $-(CH_2)_n-$ ).

$^{13}C$  NMR ( $CDCl_3$ ,  $\delta$  ppm): 175.1 (s) ( $COO$ ), 64.4 (t) ( $CH_2-OOC$ ), 63.0 (t) ( $CH_2-OH$ ), 34.4 (t) ( $CH_2-COO$ ), 29.4–25.0 (t) ( $CH_2$ )<sub>n</sub>.

#### 2.3.3. Purification of PCL

Commercial PCL-diol was solved in THF and precipitated twice in cold methanol yielding a white solid that was filtered and dried under vacuum. (Yield: 88%,  $M_n$ : 2580 Da, by  $^1H$  NMR, and 3600 Da,  $\bar{D}$  1.9 by SEC.

### 2.4. Polymer solubility

In a 25 mL vial, 0.25 g of finely grounded polymer and 2 mL of each solvent was mixed and stirred, for 2 h at room temperature.

### 2.5. Water uptake

In a closed chamber, accurately weighted disk samples were kept in a constant humidity environment (saturated solution of  $Na_2CO_3 \cdot 10H_2O$ ) at 37 or 45 °C for 48 h. Next, samples were weighted and the water uptake was determined by difference, and was expressed as weight increase percentage. An average of three measurements was taken.

### 2.6. Degradation procedures

Sample disks (12.0 mm x 0.40 mm; surface area to volume ratio equal to  $0.1\text{ cm}^{-1}$ ) weighting about 50 mg, were prepared by compression moulding (4 ton) using a manual hydraulic press 15-ton sample pressing (SPECAC) equipped with a water cooled heater. Finely grounded samples were introduced into the pre-heated (40 °C) mould and after 3 h pressed under vacuum and kept at room temperature for 1 h. Disks were demoulded under cool  $N_2$  and dried under vacuum to constant weight ( $m_0$ ). After incubation in the selected media for the scheduled period of time, three samples of each polymer were rinsed thoroughly with distilled water and weighted immediately after wiping the surface with a filter paper to absorb the surface water to obtain the wet weight ( $m_w$ ). Next, the samples were vacuum-dried for 48 h and weighted again to obtain the dry weight ( $m_d$ ). Finally, samples were grounded and analyzed by  $^1H$  NMR spectroscopy, SEC, DSC, TGA, XRD, ESEM and AFM.

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