



# Versatile post-polymerization modifications of a functional polyester from castor oil

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## ARTICLE INFO

### Article history:

Received 16 July 2015

Received in revised form 4 September 2015

Accepted 5 September 2015

Available online 8 September 2015

### Keywords:

Functionalization of polymers

Renewable resources

Thio-bromo click chemistry

Aliphatic polyesters

Vegetable oils

## ABSTRACT

This work reports a series of versatile post-polymerization modifications of an aliphatic functional polyester obtained by enzymatic polycondensation of dimethyl 2,9-dibromosebacate and 1,10-decanediol, both derived from castor oil. The alkyl halide functionality has shown to react with thiols, amines and carboxylic acids under mild conditions obtaining high modification degrees. Moreover, functionalization using NIPAAm-COOH terminated polymer has been carried out.

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## 1. Introduction

Aliphatic polyesters, including poly( $\epsilon$ -caprolactone), poly(glycolic acid) and poly(lactic acid), are well-known materials that have been extensively used as industrial plastics as well as medical devices. Given their general biocompatibility and biodegradability, they continue receiving significant attention [1]. However, their hydrophobic and semicrystalline properties and the inherent lack of reactive chemical handles for the incorporation of functionalities introduce limitations and reduce the broad applicability of these materials. To widen the versatility of these polymers, special efforts have been devoted to the functionalization of the polyester backbone [2]. Numerous examples of chain-end functionalized aliphatic polyesters have been reported, prepared most commonly by the use of functional nucleophiles to initiate ring-opening lactone polymerization. However, pendent functionalization provides a unique opportunity to alter physical and chemical properties by distributing functionality along polymer backbone. This imparts a structural homogeneity that can assume considerable importance for example in the degradability behavior, where the properties of the degradation products are critically important. Strategies that employ a variety of routes and chemistries for the pendent functionalization of synthetic polyesters via copolymerization with specialty monomers, post-polymerization modification or a combination of the two strategies have emerged. The improved functional group tolerance of controlled radical polymerization techniques when compared with conventional polymerization techniques allowed the preparation of well-defined polymers bearing a wide variety of functional groups that can be quantitatively and selectively modified using relatively mild conditions without any side reactions [3]. The application of click chemistry to aliphatic polyesters is particularly valuable, given the sensitivity of the polyester backbone to the conditions required for many organic transformations and couplings. Many examples of

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incorporation of double bonds [4,5], triple bonds [6,7], thiols [8] and azides [9] onto polyesters backbone, amenable to react under the well known click reactions conditions, have been described.

Renewable resources are of strong interest in materials research [10] and fatty acids are highly valuable platform chemicals for the development of sustainable alternatives to depleting fossil oil reserves [11]. There are two major pathways to prepare polymers from fatty acids. The first one involves the use of the original functional groups to prepare polymers by various polymerization techniques and the second route is the chemical functionalization of the fatty acids before polymerization. Most of the conversions of fatty acids towards renewable monomers have been reported for the low reactivity carbon–carbon double bond of the aliphatic chain to be replaced with new functional groups, which are then readily polymerized [12,13]. Among the different reactive positions of fatty acid derivatives, the  $\alpha$ -halocarbonyl positions offer the possibility of rapid and quantitative nucleophilic displacement. The synthesis of halogenated polyesters based on renewable resources has been described due to the synthetic possibilities they offer. Thus,  $\epsilon$ -caprolactones substituted mainly in the  $\alpha$  and  $\gamma$  positions with pendant halogen groups have been prepared and further ring-opened polymerized by aluminum or tin alkoxides, into functionalized aliphatic polyesters [1]. Polycondensation of bromosuccinic or 2-bromoadipic acids and diols using scandium catalysts at room temperature has been also described [14,15]. The substitution of the pendant halogen groups by azide is one of the most widely employed strategies for the post-polymerization modification of these functional groups via click chemistry [16,17].

Here, we describe an approach to functional aliphatic polyesters by enzymatic polymerization of two monomers derived from castor oil: dimethyl 2,9-dibromosebacate (DMBS) and 1,10-decanediol (DCD) [18]. Enzymatic preparation of polyesters has been regarded as an environmentally friendly synthetic process due to its special features: high catalytic activity, mild reaction conditions and high selectivity [19–21]. This catalytic system is an attractive alternative when the polymer bears labile functional groups and also when it is targeted to biomedical applications, as no toxic metal catalysts are used. To take advantage of the  $\alpha$ -brominated polyesters reactivity, we studied the nucleophilic substitution of the alkyl bromide functions with thiols, amines and carboxylic acids.

## 2. Experimental

### 2.1. Materials

Chemicals and solvents were used, unless otherwise noted, as received. Sebacic acid (95%), thionyl chloride (97%) and diphenyl ether (99%) were purchased from Fluka. The following chemicals were purchased from Sigma–Aldrich: 1,10-decanediol (DCD) (99%), triethylamine (99%), bromine (99%), lipase acrylic resin from *Candida Antarctica* (specific activity 5000 U/g), 2-mercaptoethanol (99%), 2-aminoethanol (98%), propylamine (99%), glycolic acid (99%), propionic acid (99.5%), poly-(*N*-isopropylacrylamide)-carboxylic acid terminated ( $M_n$  2000 g/mol) (NIPAAm COOH) and potassium fluoride (KF) (99%). Diphenyl ether (DPE) was dried under molecular sieves before use. Lipase was dried under vacuum for 24 h before use.

### 2.2. Instrumentation

NMR spectra were recorded on Varian VNMRs400. The samples were dissolved in deuterated solvent, and  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained at room temperature with tetramethylsilane (TMS) as internal standard. Kinetic studies were carried out by dissolving the reactants in DMF- $d_7$ . Size exclusion chromatography (SEC) analysis was carried out with different systems using as solvents THF (flow rate of 1.0 mL/min) at 35 °C or DMF/LiBr 0.1 M (flow rate of 0.8 mL/min) at 60 °C. THF soluble polymers were analyzed with an Agilent 1200 Series system equipped with an Agilent 1100 Series refractive index detector on the following columns system: PLgel 20  $\mu\text{m}$  MIXED-A (20  $\mu\text{m}$ , 7.5 mm  $\times$  300 mm), PLgel 5  $\mu\text{m}$  MIXED-D (5  $\mu\text{m}$ , 7.5 mm  $\times$  300 mm), PLgel 3  $\mu\text{m}$  MIXED-E (3  $\mu\text{m}$ , 7.5 mm  $\times$  300 mm). DMF soluble polymers were analyzed with an Agilent 1260 Infinity system equipped with a Shimadzu RID 6A series refractive index detector on the following columns system PLgel 5  $\mu\text{m}$  MIXED-C (5  $\mu\text{m}$ , 7.5 mm  $\times$  300 mm), PLgel 5  $\mu\text{m}$  MIXED-D (5  $\mu\text{m}$ , 7.5 mm  $\times$  300 mm), PLgel 3  $\mu\text{m}$  MIXED-E (3  $\mu\text{m}$ , 7.5 mm  $\times$  300 mm). The calibration curves for SEC analysis were obtained with narrow polystyrene standards from Agilent ranging from 162 to 483,400 Da.

### 2.3. Synthesis of dimethyl 2,9-dibromosebacate (DMBS)

To a 250-mL round-bottom flask fitted with a reflux condenser and  $\text{CaCl}_2$  tube, 18 mL (234.86 mmol) of thionyl chloride were added and heated to 80 °C. Then 20 g (93.94 mmol) of sebacic acid were added in portions and reacted for 2 h. Bromine (12.0 mL, 234.86 mmol) was added dropwise during 6 h. Finally, the flask was cooled down and the solution was added dropwise to 500 mL of cold methanol and stirred overnight at room temperature. Then, the methanol was removed under reduced pressure, the product was dissolved in chloroform, washed with aqueous solutions of  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{NaHCO}_3$ , and finally dried over anhydrous magnesium sulfate. The product was obtained as a clear oil and purified by vacuum distillation (180 °C, 0.45 mmHg, 85% yield).

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