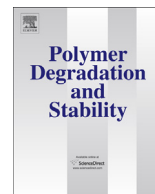




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## Biodegradable polyesters based on star-shaped lactic acid oligomers

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## ABSTRACT

Catalytic polymerization of  $\epsilon$ -caprolactone and copolymerization of maleic anhydride and propylene or ethylene oxide carried out in the presence of star-shaped *L*-lactic acid oligomers were studied. The analysis of the reaction products by means of GPC, MALDI ToF and  $^1\text{H}$  NMR show that the applied processes allowed to combine oligomers with polyesters produced by ring opening polymerization and obtain a new type of lactic acid copolymers of relative molar masses in the range 15–60 kg/mol. DSC studies revealed that the formed polyesters segments were fully or partially miscible with poly(lactic acid) core causing the reduction of its glass transition temperature. Selected copolymers were subjected to enzymatic degradation, which indicated that all of these compounds underwent partial decomposition. An analysis of weight loss showed, however, that the degradation occurred more slowly than in the case of poly(lactic acid) of similar molar masses and chain architecture.

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## 1. Introduction

Biodegradable polyesters have become the object of intensive studies due to environment issues and biomedical applications. One of the most widely used starting material for their synthesis is *L*-lactic acid (*L*-Lac) which is derived from renewable resources such as corn, potatoes and sugar beets [1–3]. The self-condensation of lactic acid yields typically polymers of moderate molar masses which found main use in the lactide (3,6-dimethyl-1,4-dioxane-2,5-dione, LA) production [4–10]. Introduction of the small amount of diols or dicarboxylic acids results in obtaining telechelic prepolymers (terminated by hydroxyl or carboxyl groups) [5,6] which can be linked together using chain extenders e.g. diisocyanates [11–16], oxazolines [15–19], diepoxides [20,21], diols [22]. Several attempts were also made to obtain star-shaped lactic acid oligomers (SLAO) by adding the multifunctional hydroxyl or carboxyl compounds as core molecules [4,23–27]. Although these processes are not fully selective and the final product is typically contaminated by small fraction of linear chains, some of these materials are regarded as promising candidates for medical application because

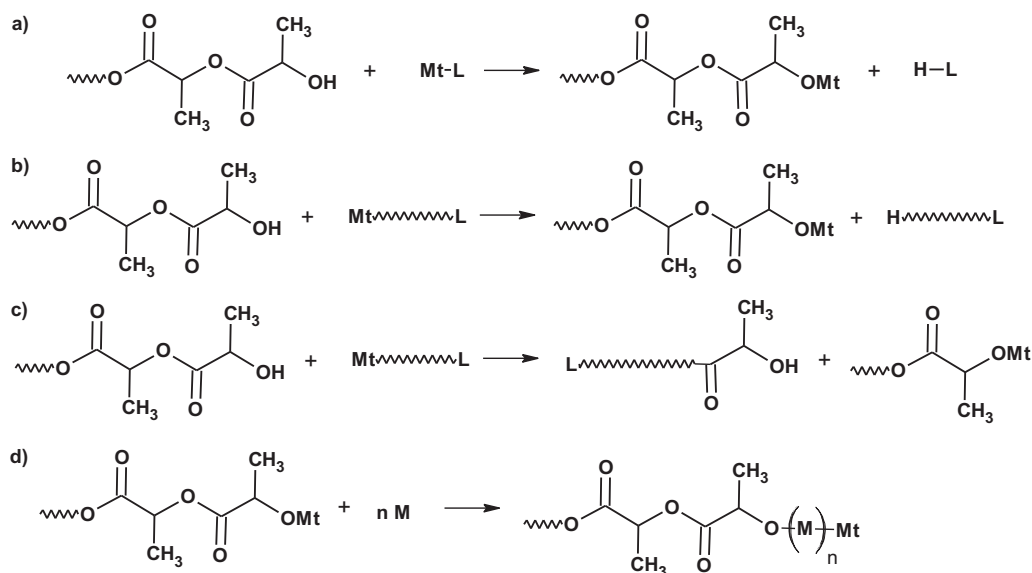
the rate of their biodegradation can be tailored by the kind and concentration of terminal groups [4,26,27].

However, polymers based on lactic acid (LAC), especially those with low molar masses, show high brittleness and poor impact strength [28,29]. Therefore, in order to extend its application, a number of methods of modification have been applied, among which the synthesis of copolymers is one of the most commonly used approach [30–34]. These products are obtained mainly through the catalytic copolymerization of LA and another cyclic monomers e.g.  $\epsilon$ -caprolactone (CL) [35–42], glycolide [43–48], trimethylene carbonate [49–52] or polymerization of LA in the presence of polyestrodioles [53–55] e.g. poly(butylene succinate), poly(butylene adipate-co-terephthalate). As results from the first method, random or block copolymers can be obtained while the second approach in most cases leads to obtaining of a mixture of triblock copolymers and polylactide (PLA).

The aim of these studies was to use SLAO as a building block in copolymer synthesis and combine them with more flexible polyesters obtained by catalytic polymerization processes. We assumed that SLAO can react with catalytic centers either in initiation (Eq. 1a) or chain transfer step (Eq. 1b, 1c) producing metal-oxygen bonds active in ring opening polymerization (Eq. 1d) and give rise to the formation of star-shaped copolymers.

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Equation 1.

We tested the applicability of this approach in the polymerization of CL and copolymerization of maleic anhydride (MA) and propylene oxide (PO) or ethylene oxide (EO). One of the key issues was to limit the occurrence of elementary steps leading to linear or cyclic oligomers and isolate copolymers with high yield. We report here also some preliminary data concerning the susceptibility of the product obtained to enzymatic degradation.

## 2. Experimental

### 2.1. Materials

L-LA (Aldrich) was recrystallized consequently from dry isopropanol, then toluene and vacuum dried before polymerization. Toluene and isopropanol were dried with sodium and distilled. CL (Aldrich), PO (Chemapol) were dried over calcium hydride and distilled under reduced pressure. MA (Aldrich) was sublimed under reduced pressure. Tin(II) 2-ethylhexanoate [Sn(EH)<sub>2</sub>], magnesium ethoxide, N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride [Cr(salen)Cl], calcium hydride, sodium azide, proteinase K (lyophilized powder, ≥30 U/mg protein), proteinase K (lyophilized powder, 3–15 U/mg protein) (all of Aldrich) and EO (Fluka), were used without further purification. The synthesis and characterization of SLAO were previously reported [27]. In this work we used hydroxyl-terminated oligomers of M<sub>w</sub> in the range 8.0–14.6 kg/mol and carboxyl-terminated oligomer of M<sub>w</sub> equal 18.7 kg/mol. Dichloromethane and methanol were used without purification.

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### 2.2. Procedures

#### 2.2.1. Homopolymerization of LA and CL

ROP of LA or CL in the presence of SLAO was catalyzed by 0.01 wt % Sn(EH)<sub>2</sub> (with respect to the batch). Monomer, oligomer and catalyst were placed in a three-necked round-bottom flask equipped with a magnetic stirrer and condenser. The reaction was carried out under nitrogen atmosphere. After polymerization, the final product was cooled to room temperature and dissolved in methylene chloride and then poured into excess methanol. The

precipitated product was filtered and washed with methanol and dried in a vacuum oven at 40 °C for 48 h.

#### 2.2.2. Copolymerization of MA and oxiranes

SLAO, MA, oxirane and catalyst of [MA]/[oxirane]/[SLAO]/[catalyst] = 200/200/1/1) were placed in a tubular glass reactor equipped with a magnetic stirrer. Ring-opening copolymerization of MA and oxirane in the presence of SLAO was catalyzed by magnesium ethoxide or Cr(salen)Cl. The reaction was carried out for 15 h in toluene solution. The remaining mixture was cooled to room temperature and dissolved in methylene chloride and then precipitated from methanol. The precipitated product was filtered and washed with methanol and dried in a vacuum oven to constant weight.

### 2.3. Measurements

<sup>1</sup>H NMR measurements were performed on Varian Mercury 400 MHz spectrometer using DMSO-*d*<sub>6</sub> as solvent. The compositions of the obtained copolymers were determined from <sup>1</sup>H NMR spectra. The molar mass and molar mass distribution were determined by GPC using RI detector and PS calibration on a Viscotek TDA 305 apparatus equipped with one guard and two DVB Jordi gel columns (10<sup>2</sup>–10<sup>7</sup>, linear, mix bed) in methylene chloride as eluent at 30 °C at a flow rate of 1.0 mL/min. The sample of block copolymer was fractionated using a LabAlliance GPC system equipped with one DVB Jordi gel column in chloroform as eluent at 25 °C at a flow rate of 0.75 mL/min. MALDI-ToF mass spectrometry was performed on Bruker Daltonics UltrafleXtreme™ instrument. *Trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile was used as MALDI matrix. The DSC measurements were performed using a DSC Q200 V24.2 Build 107 apparatus. The first heating run from 0 °C to 200 °C was performed at a heating rate of 5–10 °C/min in order to study crystallinity, then cooling at the rate of 20 °C/min was applied. The second heating run was measured at the rate of 20 °C/min to determine glass transition temperatures. TGA measurements were conducted using a TA Instruments SDT Q600 instrument, at heating rate of 5 °C/min under air atmosphere.

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