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Modification of properties of poly(butylene succinate) by copolymerization with tartaric acid-based monomers



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ABSTRACT

The two cyclic acetals, 2,3-di-*O*-methylene-*L*-threitol and dimethyl 2,3-di-*O*-methylene-*L*-threarate, were used for the synthesis of two series of PBS copolyesters differing in which unit, butylene or succinate, was replaced, in addition of the corresponding parent homopolyesters. Polycondensation reactions were carried out in the melt affording polymers with satisfactory molecular weights. Copolyesters were prepared with contents in tartaric acid-based units over the whole range of compositions and they all had a random chemical microstructure. The physical properties of the novel copolyesters varied widely depending not only on their composition but also on the type of unit that was replaced. They showed higher glass transition (T_g), lower melting temperatures (T_m), and lower crystallinity compared to the parent PBS homopolyester. Regarding mechanical properties, the presence of the stiff cyclic acetal units in the PBS chain caused an increase in the elongation at break and also a reduction in both elastic modulus and tensile strength of the polyester. Upon copolymerization the PBS notably increased its hydrolytic degradability and more slightly its susceptibility to be degraded by lipases.

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1. Introduction

The replacement of traditional plastics by bio-based plastics is today the preferred route to diminish their pollutant effect in the environment and to disengage the production of these materials from the uncertain future of oil-based resources [1–3]. Good examples of this are the bio-polyesters, in particular poly(lactic acid) and poly(3-hydroxyalkanoate)s, which are being object of great attention and increasing use due to their bio-accessibility, biodegradability, and nontoxic character of their degradation products. Poly(alkylene alkanate)s are aliphatic polyesters that although mostly produced by chemical synthesis from petrochemical monomers are gaining interest due to their innocuousness and good properties

for selective applications. Thus poly(ethylene sebacate) has been shown to be a safe carrier for drug delivery systems due to its good hydrolytic stability and low cost [4,5].

Recently, poly(butylene succinate) (PBS) has received high interest because of a balanced performance in thermal and mechanical properties as well as a satisfactory thermoplastic processability [6]. The replacement of 1,4-butanediol by another diol of renewable origin that is able to increase the too low glass transition temperature of the polyester, would be highly desirable for increasing the sustainability of PBS and expanding its applications portfolio at the same time. Utilization of carbohydrate derivatives as building blocks for polymer synthesis is currently receiving much attention not only due to their huge abundance and easy accessibility of resources but also because of the wide variety of structures that they can provide. *L*-Threic acid ((2*R*,3*R*)-(+)-2,3-dihydroxybutanedioic acid), more commonly known as *L*-tartaric acid, is the

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aldaric acid derived from *L*-threose. It is a naturally-occurring compound frequently used as starting material for the production of an amazing array of products by well-developed synthetic procedures [7]. It has also attracted a great deal of interest as a substrate for the synthesis of fully or partially bio-based polycondensation polymers such as polyamides [8,9], polyesteramides [10,11], and polyesters [12], and also for polyurethanes [13]. In most of cases, the two hydroxyl groups of tartaric acid are methylated in order to avoid cross-linking reactions and the protected compound is used as either diacid, or diol after reduction of the carboxylate groups.

The use of cyclic sugar derivatives in polycondensation has attained a high impact in these last years. The outstanding interest in these monomers lies in their exceptional capability to rise the glass transition temperature of the polymers. In the context of this paper the works reported by Koning et al. [14,15] on the use of cyclic dianhydrides isosorbide (Is) and isoidide dicarboxylic acid (IIDC) in the polycondensation with succinic acid and 1,4-butanediol respectively to prepare polyesters related to PBS with enhanced T_g are noteworthy. On the other hand, Muñoz-Guerra et al. have extensively reported on polyesters, both aliphatic and aromatic, made of cyclic acetalized carbohydrate monomers derived from *D*-galactose [16], *D*-glucose [17] and *D*-mannose [18]. *L*-Tartaric acid is able to provide after convenient acetalization both the cyclic diol and diacid counterparts required for linear polycondensation. Whereas acetals in general afford protection only under basic conditions, cyclic methylene acetals distinguish in being largely stable in both basic and acid media. The 2,3-di-*O*-methylene-*L*-threitol (Thx-diol) can be directly obtained from the dimethyl 2,3-di-*O*-methylene-*L*-tartrate (Thx-diester) by reduction with LiAlH_4 . The Thx-diester is a readily accessible compound that can be obtained in high purity from the dimethyl ester of *L*-tartaric acid by acetalization with paraformaldehyde in one single step. These compounds (Thx-diol and Thx-diester) have been previously used successfully in the synthesis of polyesters [19,20] and polyurethanes [13b]. The purpose of this paper is to explore the use of these compounds as comonomers of 1,4-butanediol, and dimethyl succinate respectively for the synthesis of PBS copolyesters with enhanced properties. The stiff nature of the cyclic acetalized compounds is expected to increase the glass transition temperature of PBS without too much detriment of other properties. Furthermore, given the bio-based nature of Thx compounds, the sustainability of PBS will be increased and its biodegradability very likely enhanced.

2. Experimental part

2.1. Materials

The reagents 1,4-butanediol (BD) (97%), dimethyl succinate (DMS) (>99%), dimethyl *L*-threarate (99%), lithium aluminium hydride (95%), paraformaldehyde (>95%), sodium hydroxide (>97%) and the dibutyl tin oxide catalyst (DBTO, 98%), were purchased from Sigma–Aldrich. Solvents used for purification, synthesis and characterization, such as chloroform, methanol, acetone, diethyl ether,

ammonia (25%), sulphuric and dichloroacetic acids and sodium trifluoroacetate, all of either technical or high-purity grade, were purchased from Panreac and hexafluoroisopropanol was purchased from Apollo Scientific. All these products were used as received without further purification.

The procedure applied to obtain 2,3-di-*O*-methylene-*L*-threitol (Thx-diol) was that recently described by Marín and Muñoz-Guerra [13b]. To an ice bath cooled dispersion of LiAlH_4 (11 g) in dried diethyl ether (200 mL), a solution of dimethyl 2,3-di-*O*-methylene-*L*-tartrate (25 g) in the same solvent (130 mL) was added dropwise under energetic stirring under an inert atmosphere. The mixture was left under stirring overnight at room temperature and then the flask was reintroduced in the ice bath to add dropwise successively water (10 mL), 15% NaOH solution (10 mL) and water (60 mL). The mixture was left stirring for one hour further at room temperature, filtered and extensively washed with warm acetone. The filtrates were pooled, concentrated, and distilled under vacuum (100–110 °C, 0.01 mBar) to render the 2,3-di-*O*-methylene-*L*-threitol as a yellowish oil (9.5 g, 53% yield). Dimethyl 2,3-di-*O*-methylene-*L*-threarate (Thx-diester) was synthesized by reaction of dimethyl threarate (40 g) at 60 °C with paraformaldehyde (40 g) dissolved in 40 mL of 98%- H_2SO_4 [13b]. The reaction mixture was shaken for 6–8 h at the same temperature and then extracted with chloroform. The extract was concentrated, washed extensively with water and ammonium hydroxide, distilled (84–86 °C, 0.05 mm) to give 16 g of dimethyl 2,3-di-*O*-methylene-*L*-threarate as a transparent liquid (40% yield). The NMR spectra of Thx compounds are provided in the [Supporting Information \(SI\)](#) file linked to this paper.

2.2. General methods

^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer at 25.0 °C operating at 300.1 and 75.5 MHz, respectively. Polyesters were dissolved either in deuterated chloroform or in a mixture of deuterated chloroform/trifluoroacetic acid (TFA) (9/1), and spectra were internally referenced to tetramethylsilane (TMS). About 10 and 50 mg of sample dissolved in 1 mL of solvent were used for ^1H and ^{13}C NMR, respectively. Sixty-four scans were acquired for ^1H and 1000–10,000 for ^{13}C with 32 and 64-K data points as well as relaxation delays of 1 and 2 s, respectively. Viscosities of polyesters were measured in dichloroacetic acid at 25.00 ± 0.01 °C, using a capillary viscosimeter at concentrations ranging from 9 to 12 mg mL $^{-1}$. Gel permeation chromatograms were acquired at 35.0 °C with a waters equipment provided with a refraction-index detector. The samples were chromatographed with 0.05 M sodium trifluoroacetate–hexafluoroisopropanol (NaTFA–HFIP) using a polystyrene–divinylbenzene packed linear column at a flow rate of 0.5 mL min $^{-1}$. Chromatograms were calibrated against poly(methyl methacrylate) (PMMA) monodisperse standards. Thermogravimetric analyses were performed under a nitrogen flow of 20 mL min $^{-1}$ at a heating rate of 10 °C min $^{-1}$, within a temperature range of 30–600 °C, using a Perkin Elmer TGA 6 Thermogravimetric Analyzer. Sample weights of about

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