



Fully bio-renewable multiblocks copolymers of poly(lactide) and commercial fatty acid-based polyesters polyols: Synthesis and characterization



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ABSTRACT

The present work deals with the synthesis and characterization of novel multiblock copolymers containing poly(lactide) (PLA) and fatty acid dimer-based polyols. Notably, both blocks are bio-renewable. PLA segments are rigid and crystallizable, while the polyol-blocks are amorphous and possess low glass transition temperature. The synthetic procedure consists of two successive steps. In the first, PLA oligomers terminated with hydroxyl groups, having a molar mass of about 8000 g/mol, are prepared and characterized with NMR and GPC. The second step involves the coupling of PLA and the (commercially available) polyol by means of 1,6-hexamethylene diisocyanate. The product of the chain-extension reaction is subsequently characterized by NMR, FT-IR spectroscopy, GPC, TGA and DSC. These analyses allowed us to confirm the occurrence of chain coupling and the total inclusion of the fatty acid-based polyol in the copolymer. The chain architecture is thus characterized by a multiblock structure, with random arrangement of PLA and polyol segments. The two blocks are immiscible, poly(lactide) segments preserve their crystallizability, notwithstanding the covalent linkage with amorphous polyol. Blends of multiblocks based on oppositely configured L- and D-poly(lactide) exhibit complete stereocomplexation, independent of soft block content in the copolymer. The inclusion of fatty acid dimer-based polyols in PLA modifies its surface wettability, increasing the hydrophobicity of the material.

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1. Introduction

Recently, driven by increasing environmental concerns regarding oil-based polymers and plastic products, polymer research has been focused on the synthesis and characterization of bio-renewable materials [1–5]. Among the bio-renewable polymers already commercially available, poly(lactic acid) or polylactide (PLA) is surely one of the most promising [6–9]. PLA is an aliphatic polyester obtained either from the polymerization of lactic acid or of its cyclic dimer, lactide. In turn, the monomer is readily produced by microbial fermentation, using various carbohydrate-rich biomasses as carbon source.

Both lactic acid and lactide monomers are chiral, therefore, chiral polymers can be obtained, *i.e.*, poly(L-lactic acid) (PLLA) or poly(D-lactic acid) (PDLA). The two enantiopure polymers are able to co-crystallize in a particular structure, called

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“stereocomplex” [10], which presents faster crystallization, higher melting temperature (230 °C vs. 170 °C), higher stiffness and yield strength with respect to the homochiral PLLA (or PDLA) crystals [11].

Thanks to the high tensile strength, elastic modulus, and good thermal properties of PLA or stereocomplex PLA, the potential application range of this material can be largely broadened, to include durable products. However, the substitution of oil-based materials by PLA is presently hindered by its inferior impact strength or toughness, typically reflected in extremely low elongations at break [12,13].

Several strategies to circumvent this problem have been proposed [12–15]. Among these, direct modification of the polymer chain architecture affords a tailoring of the final material properties via the synthesis step. A relevant example is that of block copolymers, in which chemically distinct segments are covalently linked in the same chain, giving rise to multiphase materials. By combining in the same polymer glassy or semicrystalline regions (“hard” blocks) with rubbery or liquid segments (“soft” blocks), a wide tunability of mechanical properties can be achieved. In particular, while the rigid segments provide relatively high modulus and strength, an improved ductility is conferred by the high extensibility of the rubbery phase.

Different arrangements of the constituents along the chains are possible for such block copolymers: from “precision” tri-block copolymers (hard-soft-hard) to multi-blocks or “segmented” chains, where multiple blocks or block sequences are connected. Both types of chain architecture have been adopted for PLA-based block copolymers [16–44]. Amorphous or semicrystalline PLA always constitutes the rigid block, while for the rubbery segments, several different polymers (either oil- or bio-based) have been used.

The preparation of PLA based triblocks copolymers usually requires two sequential synthetic steps. At first the soft block is synthesized, using reaction conditions which lead to a α,ω -dihydroxyl polymer. The dihydroxyl terminated polymer is then used as a macro-initiator for the subsequent ring-opening polymerization of lactide.

A variety of polymers can be used as soft block [16,17,21,27,31,38,41], provided that they have a suitably low glass transition temperature, and that they can be obtained with proper terminal functional groups. Recently, the research focused on the development of fully biobased PLA-containing triblocks copolymers, by employing biorenewable soft blocks, such as amorphous polyhydroxyalkanoates [18,26], polymethide [28] and polyesters derived from castor oil [44].

Multiblocks copolymers are known to exhibit superior mechanical properties in comparison with analogous triblocks, because in these systems a single segmented polymer chain can span over several nanophase domains [35,42,45–47]. Two main synthetic approaches have been adopted to prepare PLA-based multiblocks copolymers, typically belonging to the polyurethanes family.

In one case, telechelic PLA diols are chain extended with one (or more) dihydroxyl terminated soft segments, by means of reaction with di-isocyanate [20,29,32–34,37,39,43].

The second commonly adopted synthetic strategy is also based on chain extension with di-isocyanate, but the diol in this case consists of a dihydroxyl-terminated PLA-softblock-PLA triblock copolymer, synthesized in advance following the above mentioned procedure [23,30,35,40,42]. Despite the fact that this second approach leads to a rigorously controlled length of the different blocks in the multiblock copolymer, a more complex synthetic procedure is required. Soft blocks employed so far to build this class of multiblocks copolymers based on PLA are not derived from bio-renewable feedstocks, although some of them are bio-degradable [19,23–25,30,33,35,36,42].

In this work we present the synthesis of a fully biobased segmented multiblock copolymer, using PLA diols as hard segments and a polyester polyols derived from vegetable oils as soft blocks. These latter segments are produced by polymerization of fatty acid dimers containing 36 carbon atoms, and have the advantage of being commercially available, with the tradename of Priplast [48]. This feature, together with the choice of segmented chain architecture, resulted in a simpler synthetic procedure of the presented multiblocks copolymers, with respect to the one which exploits the coupling of triblocks copolymers. The novel materials were able to develop PLA stereocomplex crystals, when blends of PLA/Priplast multiblocks copolymers containing enantiomeric polylactides were prepared, and revealed an enhanced hydrophobicity with respect to PLA homopolymer.

2. Experimental

2.1. Materials

L-lactide (L-la) and D-lactide (D-la) (purity >98%) were kindly supplied by Purac Biochem. Before polymerization, both monomers were purified by three successive recrystallizations from 100% (w/v) solution in anhydrous toluene and dried under vacuum at room temperature. Ethylene glycol, a commercial product from Sigma-Aldrich (here simply referred to as ETG), was dried under vacuum at 40 °C for one night prior to use.

Priplast 3196, a polyester polyol with an average molecular weight 3000 g/mol, kindly supplied by Croda, was used as received. The polyol has been synthesized from C36 fatty acid dimers derivative, in turns obtained by dimerization of unsaturated C18 fatty acids (such as oleic, linoleic and linolenic acids).

Tin(II) 2-ethylhexanoate [Sn(Oct)₂] (95%) and 1,6-hexamethylene diisocyanate (HDI) ($\geq 99\%$) were purchased from Sigma-Aldrich and used without further treatments. All the solvents (*i.e.*, anhydrous toluene ($\geq 99.7\%$), chloroform, hexane, methanol, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and dichloromethane) were purchased from Sigma-Aldrich and used as received.

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