



# Titanium-catalyzed transesterification as a route to the synthesis of fully biobased poly(3-hydroxybutyrate-co-butylene dicarboxylate) copolyesters, from their homopolyesters



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## ABSTRACT

Fully biobased poly(3-hydroxybutyrate-co-butylene adipate) (poly(HB-co-BA)) and poly(3-hydroxybutyrate-co-butylene succinate) (poly(HB-co-BS)) copolyesters were synthesized by transesterification between small chain length PHB and poly(butylene dicarboxylate)s (PBS or PBA) with different molar masses, different HB/BA (or HB/BS) molar ratios, in solution or in bulk, using titanium (IV) isopropoxide (TTIP) as an effective catalyst. All synthesized copolyesters were fully characterized by different chemical and physicochemical techniques including NMR, SEC, FTIR, WAXS, DSC and TGA. The influence of (i) the reaction process (ii) the nature of poly(butylene dicarboxylate) used, (iii) the molar masses of the starting homopolymers, (iv) the reaction temperature, (v) the catalyst amount and (vi) the HB/BS (or HB/BA) molar ratio on the transesterification reaction and copolyester properties were investigated. The transesterification in bulk with 1 mol.% of TTIP at 175 °C from low molar mass starting homopolyesters permitted to quickly obtain random copolyesters with final composition similar to the feeds and without thermal degradation. Random poly(HB-co-BA) copolyesters were amorphous at room temperature, whereas poly(HB-co-BS) copolyesters melted at temperatures higher than 40 °C. Poly(HB-co-BS) copolyesters exhibited only a PBS crystalline phase, except for copolyesters with a low degree of randomness and a significant HB content. The melting and crystallization temperatures as well as their respective enthalpies decreased with the randomization and the HB content.

## 1. Introduction

Polyhydroxyalkanoates (PHA) are a family of biopolymers synthesized by several bacteria as intracellular carbon and energy storage granules. A wide variety of prokaryotic organisms can accumulate PHA from 30 to 80% of their cellular dry weight. PHAs can be produced from various renewable resources by fermentation, to develop environmentally friendly materials consistent with a more sustainable development. PHAs are biodegradable but exhibit also biocompatibility in contact with living tissues, suitable for biomedical applications, e.g., tissue engineering [1,2]. Poly[(R)-3-hydroxybutyrate] (PHB) is commercially available and it is one of the most prominent PHAs. However, its application as a thermoplastic material is rather limited, mainly due to its high melting temperature ( $T_m$ ) of approx. 175 °C, high glass transition temperature ( $T_g$ ) of approx. 4 °C, high crystallinity ( $X_c$ ) (approx. 60%) and high thermal sensitivity [2]. Indeed, PHB possesses a low thermal stability with a degradation initiation close to the  $T_m$  [1] and decomposes easily by random cis-elimination chain scission at temperatures above 150 °C, thus limiting its usage [3–5].

Different approaches have been tested to overcome the above drawbacks and then obtain efficient PHB-based materials such as (i)

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the elaboration of multiphase systems, e.g., by blending with other polymers [6–8] or plasticizers [9], or (ii) the bio- or chemosynthesis of 3-hydroxybutyrate (HB)-based copolymers. Bacterial syntheses with varying substrates and strains have allowed the (bio) synthesis of random copolyesters based on HB units [10–12]. Varying the chemical structure of the co-monomeric unit and its amount in the copolymer afford copolyesters with a wide range of  $T_m$ ,  $X_c$  and behaviors. Moreover, block copolyesters based on HB segments were successfully bioproduced with improved properties over random copolyesters [10]. However, despite their important and varied potential applications, studies of such macromolecular architectures still remain limited, mainly because of their lacks of availability in large quantities and their costs.

The chemosynthesis of PHA-based copolymers required first the production of controlled PHA oligomers. These oligomers can be synthesized by anionic- [13,14], chemical- [15,16] and enzymatic [17,18] ring-opening polymerization (ROP) of lactones, or by the enzymatic [19] and chemical [20,21] esterification of hydroxyacids. PHA molar mass reduction with functionalization to obtain hydroxyl-terminated PHA (PHA-diol) oligomers can be performed by either organometallic- [22] and acid-catalyzed [23] alcoholysis or sodium borohydrate reduction [24,25]. From PHA oligomers, different tailored materials can be obtained including block poly(ester-urethane)s, block poly(ester-ether)s and block or random copolyesters based on PHB blocks with others blocks, such as poly( $\epsilon$ -caprolactone) (PCL), poly(ethylene glycol) (PEG) or poly(butylene adipate) (PBA) [26,27]. PHB-based block copolyesters were synthesized *via* the chemical [28,29] or enzymatic [30] ROP of  $\epsilon$ -CL and lactide initiated from PHB-diol oligomers. PEG-PHB-PEG triblock copolymers can be obtained by chain-end esterification [31]. Micro-block and random poly(HB-*co*-CL) and poly(HB-*co*-BA) copolyesters with different compositions have also been synthesized by acid-catalyzed transesterification in solution [32,33].

In a recent study [34], lipase-catalyzed synthesis of biobased micro-block and random copolyesters from PHB-diol oligomers and poly(butylene succinate) (PBS), a well-known biobased, biodegradable and biocompatible aliphatic polyester suitable for packaging and biomedical applications [35–37], has been investigated. More than lipases, organometallic catalysts have been widely used to synthesize high molar mass aliphatic (co)polyesters from diacid and diol building blocks [38–40]. Recently, poly(lactic acid) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) have been slightly transesterified by zinc acetate to improve the compatibility of the blend [41]. However, the efficiency of the transesterification was not analyzed. Whilst these metal-based catalysts showed a remarkable transesterification capacity, especially for titanium-based catalysts [42], to the best of our knowledge, no organometallic transesterification between PHB and PBS or PBA has been reported so far.

The aim of this study was, thus, to synthesize poly(HB-*co*-BA) and poly(HB-*co*-BS) copolyesters by two different transesterification processes (solution or bulk) from PHB and PBA or PBS with titanium (IV) isopropoxide (TTIP) as an effective catalyst. Impallomeni et al. demonstrated that the transesterification between two homopolyesters occurred at a correct rate only when homopolyesters molar mass are not too high [32,33]. Then, small chain length PHB, and PBA or PBS with limited molar masses, were used. The effect of (i) the catalytic process, (ii) the temperature, (iii) the catalyst amount, (iv) the starting homopolyesters molar masses, (v) the HB/BS molar ratio and others factors on the architecture of the synthesized copolyesters were studied. The macromolecular architectures (e.g., composition and sequence distribution) of the resulting copolyesters were determined by NMR, FTIR and SEC. The crystalline structure, thermal stability and thermal properties of the corresponding architectures were studied by WAXS, TGA and DSC, respectively. Finally, the bulk transesterification pathway has been compared to the enzymatic one which had been previously described [34].

## 2. Experimental part

### 2.1. Materials

Small chain length poly([R]-3-hydroxybutyrate) (PHB) of different molar masses ( $M_n$ : 4000, 7000 and 15,000 g/mol, as determined by SEC) were synthesized by tin-catalyzed alcoholysis of high molar mass PHB with 1,4-butanediol, according to a protocol based on previous reports [22] and detailed in the [supporting information SI.1](#). Poly(butylene adipate) (PBA) and poly(butylene succinate) (PBS) with different molar masses were synthesized according to a protocol based on previous reports [38–40] and also detailed in the [supporting information SI.2](#). PBA of  $M_n = 8000$  and 20,000 g/mol and PBS of 10,800 and 28,000 g/mol (from SEC determinations) were used. Before the reaction, small chain length PHB, PBA and PBS were dried at 40 °C under vacuum in an oven for 16 h. Titanium (IV) isopropoxide (TTIP) (98 + %) was supplied by Acros. Anhydrous 1,2-dichlorobenzene (99%) and chloroform were supplied by Sigma-Aldrich. Petroleum ether was supplied from Fisher. All solvents for the analytical methods were of analytical grade, and used without further purifications.

### 2.2. Titanium-catalyzed transesterification in solution

In a round-bottom reactor, dried small chain length PHB and PBA (or PBS) were dissolved in a small amount of anhydrous 1,2-dichlorobenzene (~1.5 mL/g of homopolyester) at 150–175 °C under an argon atmosphere. After 15 min, the proper amount of TTIP (from a 20 wt.% solution of TTIP in 1,2-dichlorobenzene) was added into the reaction mixture. The reaction continued for 4 h at atmospheric pressure under argon. At the end of the reaction, the mixture was precipitated into a large volume of vigorously stirred cold petroleum ether and the copolyester was recovered by filtration. The copolyester was then purified by first a dissolution step in a minimum of chloroform, and then a second precipitation step into a large volume of vigorously stirred cold petroleum ether followed by a filtration. The recovered final product was dried under reduced pressure in an oven at 50 °C for 24 h.

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