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Fully biobased triblock copolyesters from L-lactide and sulfurcontaining castor oil derivatives: Preparation, oxidation and characterization

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ABSTRACT

The synthesis and characterization of fully biobased ABA triblock copolyesters from PLA and castor oil derivatives are described. The synthetic strategy uses a dihydroxy telechelic polyester as a macroinitiator for the ring opening polymerization of L-lactide. This macroinitiator was obtained from a sulfur-containing hydroxyacid derivative of 10-undecenoic acid, which undergoes self-polycondensation with low amounts of biobased 1,4-butanediol, enables the obtention of two prepolymers of different weight. Two series of triblock copolyesters with different percentage of PLA contents were prepared and the resulting thioether-bearing copolyester oxidized to polysulfones. Both series of copolyesters showed improved thermal stability, decrease of crystallinity and a similar hydrophilicity with respect to the PLA homopolymer.

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1. Introduction

A significant increase of interest in biobased polymers has been observed in the last years due to at least two important reasons. The first one is related to the availability of raw materials for the synthesis of polymers. Currently, the majority of polymers is produced from crude oil with the problems associated with the high prices and rapid fluctuations. The second reason of interest is related to waste management. Expected solution to this problem cannot rely on only one approach but rather on combination of a variety of them. Taking advantage of chemistry, the efficient transformation of renewable resources avoiding the use of fossil reserves that contributes negatively to the planet's energy problem is an useful approach [1]. Moreover, the obtention of degradable polymers is also pursued, decreasing the negative environmental impact of huge amounts of plastic waste generation [2].

Aliphatic polyesters represent one of the most relevant groups of polyesters, which are obtained via condensation reactions of alkanediols with α,ω -alkanedioic acid or diesters (or alternatively derived from hydroxyalkanoic acids or hydroxyalkanoates) readily available from inexpensive renewable resources. The biodegradability of aliphatic polyesters has spotlighted them in practice as only this family of polyesters degrade in a reasonable time scale [3].

Among the aliphatic polyester family, polylactide (PLA) is one of the most promising biopolymers. PLA is polymerized from lactic acid which is obtained from the bacterial fermentation of sugar feed stocks such as cassava starch and corn. Actually, several companies produced PLA by the ring-opening polymerization of lactide that is synthesized from the depolymerization of oligomers or a prepolymer of PLA, on a commercial scale [4]. PLA has been widely used in the biomedical, packaging and textile industries because of its unique properties such as biodegradability and biocompatibility [1,5,6]. PLA is an alternative polymer to conventional polymers such as polyethylene, polypropylene, poly (ethylene terephthalate) and polystyrene because it has many interesting properties including a high modulus, high tensile strength, it is easy to process and is environmentally friendly. Unfortunately, the inherent brittleness of PLA is a major drawback which limits its use in applications where tough mechanical behaviour is required. Therefore many efforts have been made to improve PLA toughness [7] including manipulation of crystallinity [8], plasticization [9,10], blending with other polymers [11–15] and incorporation into block copolymers [16–20].

A recent trend for toughening PLA is to use degradable, renewable polymers including starch [21], poly (butylene succinate) [22,23], poly (hydroxyalcanoates) [24], polymerized soybean oil [25] and polyamide 11 [26], as a challenge to find a





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completely renewable and biodegradable toughening agent that enhances PLA properties. However, most tougheners derived from renewable resources are less effective than those derived from petroleum resources in improving the PLA toughness. Consequently, the obtention of block copolymers is a better approach to develop biocompatible, highly toughened PLA which retains both completely renewable origins and the ultimate degradability [10].

Multiblock polymers attract interest because they are expected to have distinct microstructures, offering alluring opportunities to generate exquisitely tailored materials with unparalleled control over nanoscale-domain geometry, packing symmetry, and chemical composition, thus exhibiting different mechanical behaviour compared to conventional polymers with simple structures [27]. Moreover, advances in synthetic polymer chemistry methods allow access to numerous structures of multiblock copolymers and a considerable number of different strategies have been used. As concerns PLA-based block copolymers, one can distinguish between those synthesized by sequential ring opening polymerization (ROP) when comonomers are cyclic esters or carbonates, and block copolymers synthesized by distinct polymerization methods. In the latter case, most of the time, a macroinitiator is first synthesized by another polymerization method than ROP and then ROP of lactide is initiated by the reactive functions of the macroinitiator.

This article describes the synthesis and characterization of fully biobased triblock copolyesters from PLA and castor oil derivatives. The synthetic strategy selected was to design a dihydroxy telechelic polyester, from 10-undecenoic acid derivative, as a macroinitiator for ROP of L-lactide (LA). This approach consisted of the use of a sulfur-containing hydroxyacid, which self-polycondensation initiated with low amounts of biobased 1,4-butanediol [28], enables the obtention of a dihydroxy terminated prepolymer, which initiates the ROP of LA to reach the targeted triblock copolymer. The introduction of polar sulfur-containing groups by oxidation of the main chain sulfide moiety to sulfone is expected to increase polarity and thus, changes in the thermal behaviour and crystallinity of the polymers are expected.

2. Materials

The following chemicals were used as received: 10-undecenoic acid (Fluka), L-lactide (98%, Aldrich) 2-mercaptoethanol (99%, Aldrich), 2,2-dimethoxy-2-phenylacetophenone (DMPA) (99%, Aldrich), tin(II) 2-ethylhexanoate (Sn(Oct)₂) (95%, Aldrich), dibutyl tin oxide (DBTO) (98% Aldrich) 1,4-butanediol (BD) (99%, Aldrich), 3-chloroperbenzoic acid (mCPBA) (\leq 77%, Aldrich), hydrogen peroxide (50% Aldrich). Solvents were purified by standard procedures.

2.1. Thioether-containing ω -hydroxyacid (TEHA)

An equimolar mixture of 10-undecenoic acid (1.0 g, 5.43 mmol) and 2-mercaptoethanol (0.4 g, 5.43 mmol) was irradiated in dichloromethane solution at $\lambda = 365$ nm in the presence of DMPA (2% mol respect to C=C) as photoinitiator. The completion of the reaction was confirmed after 10 min by the completely disappearance of C=C double bonds from ¹H NMR. The thioether containing ω -hydroxyacid was quickly obtained. (yield % 100, mp: 54 °C, LC-(ESI) MS: m/z calcd: 262.16; found: 262.16).

¹H NMR (CDCl₃, δ, ppm): 3.72 (t, 2H, -CH₂-OH), 2.72 (t, 2H, -CH₂-S-), 2.50 (t, 2H, -CH₂-S-), 2.34 (t, 2H, -CH₂-CO), 1.69–1.27 (m, 16H, -CH₂-).

¹³C NMR (CDCl₃, δ, ppm): 179.9 (s), 60.3 (t), 35.4 (t), 34.1 (t), 31.7 (t), 29.9–29.0 (t), 24.8 (t).

2.2. Dihydroxyl-terminated prepolymers (HO-PTEHA-OH)

Hydroxyacid TEHA (2.000 g, 7.630 mmol), 1,4-butanediol (0.034 g, 0.380 mmol in 1:0.05 M ratio or 0.068 g, 0.763 mmol in 1:0.1 M ratio) and $Sn(Oct)_2$ (0.030 g, 0.076 mmol) in 1% TEHA/catalyt molar ratio) were stirred at 140 °C under argon atmosphere. After 1 h, dynamic vacuum was applied during 6 h. The resulted polyester was obtained as a white solid and was dissolved in dichloromethane, precipitated into methanol, filtered and dried under reduced pressure. (yield % 93). Molar mass are collected in Table 1.

¹H NMR (CDCl₃, δ, ppm): 4.21 (t, 2H, $-CH_2-O-$), 4.09 (t, 2H, $-CH_2-OCO-$), 3.72 (m, 2H, $-CH_2-OH$ terminal unit), 2.73 (t, 2H, $-CH_2-S-$), 2.54 (t, 2H, $-CH_2-S-$), 2.30 (t, 2H, $-CH_2-CO-$), 1.70 (t, 2H, $-CH_2-CH_2-OCO-$), 1.63–1.25 (m, 16H, $-CH_2-$)

¹³C NMR (CDCl₃, δ, ppm): 173.8 (s), 63.5 (t), 34.4 (t), 32.6 (t), 30.7 (t), 29.9–29.0 (t), 25.1 (t)

2.3. Synthesis of triblock copolyesters (P(LA-b-TEHA-b-LA))

The desired amounts of dihydroxyl-terminated prepolymer (HO-PTEHA-OH) and LA (Table 1) were refluxed in dry toluene at 120 °C under argon atmosphere for 4 h with addition of $Sn(Oct)_2$ (1% LA/catalyst molar ratio). After completion of the reaction, toluene was removed under reduced pressure, the copolymer was dissolved in dichloromethane followed by precipitation into methanol and dried under reduced pressure. (yield % 85). Molar masses are collected in Table 1.

¹H NMR (CDCl₃, δ, ppm): 5.17 (q, H, -CH-CH₃), 4.35 (q, H, -CH-CH₃ terminal unit), 4.21 (t, 2H, -CH₂-O-), 4.09 (t, 2H, -CH₂-OCO-), 2.73 (t, 2H, -CH₂-S-), 2.55 (t, 2H, -CH₂-S-), 2.31 (t, 2H, -CH₂-CO-), 1.70 (t, 2H, -CH₂-CH₂-OCO-), 1.58 (d, 3H, CH₃-CH-), 1.50-1.25 (m, 16H, -CH₂-)

¹³C (CDCl₃, δ, ppm): 173.6 (s), 169.8 (s), 69.2 (d), 63.5 (t), 34.4 (t), 32.6 (t), 30.7 (t), 29.9–29.0 (t), 25.1 (t), 16.8 (q)

2.4. Oxidation of thioether-containing triblock copolyesters to polysulfone (PSO(LA-b-TEHA-b-LA))

a) Thioether-containing triblock copolyesters (0.3 g, 1.14 mmol) were dissolved in dicloromethane, 3-chloroperbenzoic acid (mCPBA) (0.5 g, 2.28 mmol) was added and the mixture was stirred at room temperature. After 1 h of reaction, the formed polymer was washed with 5% Na₂S₂O₃ and 5% NaHCO₃ prior to drying under reduced pressure.

¹H NMR (CDCl₃, δ , ppm): 5.17 (q, H, -CH-CH₃), 4.50 (t, 2H, -CH₂-O-), 4.35 (q, H, -CH-CH₃ terminal unit), 4.09 (t, 2H, -CH₂-OCO-), 3.28 (t, 2H, -CH₂-S-), 3.02 (t, 2H, -CH₂-S-), 2.31 (t, 2H, -CH₂-CO-), 1.84 (m, 2H, -CH₂-CH₂-S), 1.70-1.25 (m, 16H, -CH₂-).

¹³C (CDCl₃, δ, ppm): 173.1 (s), 169.8 (s), 69.2 (d), 57.7 (t), 54.4 (t), 51.8 (t), 34.3 (t), 29.9–22.0 (t), 16.8 (q).

b) Thioether-containing triblock copolyester (0.2 g, 0.82 mmol) were dissolved in chloroform and subsequently 50% hydrogen peroxide solution (0.09 ml) was added to the reaction flask. The mixture was stirred at room temperature. After 48 h of reaction, the formed polymer was washed with 5% NaHCO₃ and water prior to drying under reduced pressure.

2.5. Instrumentation

The IR analyses were performed on a FTIR- 680PLUS spectrophotometer with a resolution of 4 cm⁻¹ in the transmittance mode. NMR spectra were recorded on a Varian VNMRS400. The samples were dissolved in deuterated chloroform, and $^{1}\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra were recorded at room temperature with tetramethylsilane as an internal standard. ESI MS were run on an Agilent 1100 Series LC/MSD instrument. Size exclusion chromatography (SEC) analysis was carried out with an Agilent 1200 series system equipped with an Agilent 1100 series refractive-index detector. THF or DMF were used as eluents at a flow rate of 1.0 mL/min. The calibration curves for SEC analysis were obtained with polystyrene standards. Differential scanning calorimetry (DSC) measurements were carried out with a Mettler DSC822e thermal analyzer with N₂ as the purge gas. Samples, 6-12 mg, were used for DSC analysis. Nonisothermal crystallization behaviours were evaluated by cooling the samples from the melt. The samples were heated from -80 to 200 °C with a heating rate of 20 °C/min, cooled down to -80 °C with a cooling rate of -20 °C/min, and then heated again to 200 °C at the same heating rate. Tm and enthalpy values were obtained from the second heating curves. Crystallization was performed heating all samples from room temperature to 200 °C, cooled from 200 °C to 120 °C and heated at this temperature for 3 h followed by cooling to -50 °C. Melting points and enthalpies were then recorded while heating at 10 °C/min from -50 °C to 200 °C. Thermal stability studies were carried out with a Mettler TGA/ SDTA851e/LF/1100 with N₂ as the purge gas at a scanning rate of 10 °C/min. The studies were performed in the 30-800 °C temperature range at a scan rate of 10 °C/min. Wide-angle X-ray diffraction (WAXD) measurements were made on powder samples using a Siemens D5000 diffractometer (Bragg-Brentano parafocusing geometry and vertical θ - θ goniometer) fitted with a curved graphite diffracted-beam monochromator. incidentand diffracted-beam Soller slits, a 0.06° receiving slit, and a scintillation counter as a detector. The angular 2θ diffraction range was between 1° and 40°. Samples were dusted onto a low background Si(510) sample holder. The data were collected with an angular step of 0.05° at 3 s per step. Cu KR radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA. The contact angle of deionized water against polymer surfaces was measured by the water drop method (3 mL) at 25 °C, using the OCA15EC contact angle setup (Neurtek Instruments).

3. Results and discussion

3.1. Synthesis of HO-PTEHA-OH prepolymers

Thiol-ene coupling of 2-mercaptoethanol and 10-undecenoic acid leads to an AB monomer containing both hydroxyl and carboxylic functionalities. Synthesis of this monomer was previously described by simply stirring mercaptoethanol and 10-undecenoic acid for 1.5 h at 60 °C. Moreover, reaction has also been described to take place when UV irradiated [29]. We carried out the mercaptoethanol addition to obtain the thioether-containing ω hydroxyacid (TEHA, Scheme 1) under irradiation at room temperature in presence of 2,2-dimethoxy-2-phenylacetophenone (DMPA) as photoinitiator. This monomer was obtained using equimolar amounts of mercaptoethanol, in short reaction times (10 min) with quantitative yield and characterization was carried out by spectroscopic techniques.

To explore the reactivity of the TEHA in the polyesterification reaction, tin (II) 2-ethyl-hexanoate $(Sn(Oct)_2)$ and dibutyl tin



Fig. 1. Mn versus time for TEHA self-condensations.

oxide (DBTO) were tested under similar reaction conditions. Oligomerization of TEHA was performed in bulk under nitrogen atmosphere at 140 °C for 1 h and further vacuum. The reaction was conducted for 24 h and molar masses values on non fractionated products were determined by SEC relative to PS standards. As can be seen in Fig. 1, the highest Mn values were obtained for Sn(Oct)₂ while using DBTO resulted in lower Mn. Moreover, increasing catalyst percentage from 1 to 2 % mol decreases Mn.

Two dihydroxyl-terminated prepolymers were obtained by selfpolycondensation of TEHA with two amounts of biobased 1,4butanediol (BD) and 1% of $Sn(Oct)_2$ as catalyst, at 140 °C (Table 1, Scheme 2). Reactions were carried out under the above described conditions for 6 h.

¹H NMR spectroscopy allowed monitoring the polymer formation by the appearance of new signals in comparison to the starting TEHA (Fig. 2). The characteristic peak of the proton linked to the carbon bearing the hydroxyl group in TEHA (Fig. 2a, H_a) is shifted downfield as the conversion of TEHA increases, confirming the formation of ester functions. Also, the peak of the proton linked to the carbon bearing the carboxylic group in TEHA (Fig. 2a, H_d) undergoes a slight shift upfield confirming the formation of ester. Furthermore, the appearance of a new signal H_x (Fig. 2b) at 4.09 ppm, characteristic of the oxymethylene protons linked to the carbon adjacent to the ester function in the BD unit, clearly confirms that the hydroxyl functions of BD efficiently reacted with the carboxylic acid moieties of TEHA. The ratio of BD to TEHA was determined from signals corresponding to oxymethylene units of BD at 4.10 ppm (H_x) and to one of the methylenes linked to sulfur at 2.73 (H_c) from TEHA moiety, and the obtained values approaches well to theoretical values (Table 1). A high yield (93%) of dihydroxyl-terminated prepolymers was obtained allowing the use of these prepolymers for the ring opening of the LA.

¹H NMR analysis, signals at 3.75 ppm corresponding to endgroup ($H_{a'}$) and at 2.73 ppm corresponding to the repeating unit (H_b), was used to determine the molar mass of the HO-PTEHA-OH samples which was also characterized by SEC. As can be seen (Fig. 1 and Table 1) when using BD as initiator (1:0.05 and 1:0.1 TEHA/BD molar ratio) lower Mn's than in absence of initiator were obtained. Moreover, as expected, higher Mn was obtained when using a 1:0.05 M ratio. Significant differences were noticed between the



Scheme 1. Synthesis of thioether-containing ω-hydroxyacid (TEHA).

Table 1
Molar composition and molar masses of HO-PTEHA-OH prepolymers and P(LA-b-TEHA-b-LA) _x copolyesters.

Polymer	Composition TEHA/BD/LA					Molar masses (g mol ⁻¹)		
	Molar ratio	Feed ratio ^a	¹ H NMR feed ratio	W (%) ^b	W (%) ^c	Mn NMR ^d	Mn SEC ^e	D
НО-РТЕНА-ОН1	1:0.05:0	20	17.0	_	_	4679	15,900	1.39
HO-PTEHA-OH2	1:0.1:0	10	9.5	_	_	2690	10,400	1.43
P(LA-b-TEHA1-b-LA) ₂	1:0.05:2	2	1.6	54	48	4176	15,100	1.22
P(LA-b-TEHA1-b-LA)3	1:0.05:3	3	2.6	63	60	5102	13,200	1.23
P(LA-b-TEHA1-b-LA)5	1:0.05:5	5	4.0	74	70	5583	16,100	1.49
P(LA-b-TEHA1-b-LA)10	1:0.05:10	10	8.4	85	83	9163	13,200	1.58
P(LA-b-TEHA2-b-LA) ₂	1:0.1:2	2	1.6	54	48	4119	14,600	1.26
P(LA-b-TEHA2-b-LA)3	1:0.1:3	3	2.2	63	57	3514	14,500	1.26
P(LA-b-TEHA2-b-LA)5	1:0.1:5	5	3.9	74	69	7898	13,400	1.34
P(LA-b-TEHA2-b-LA)10	1:0.1:10	10	8.5	85	83	11,652	12,800	1.62

^a TEHA/BD molar ratio for prepolymers and LA/TEHA molar ratio for block copolymers.

^b Theoretical weight percentage of PLA.

^c Weight percentage of PLA in block copolymers by ¹H NMR (from LA signal at 5.17 ppm and TEHA signal at 4.21 ppm).

^d Mn values were calculated from LA signal at 5.17 ppm and TEHA signal at 2.73 ppm related to the end group signal at 4.35 ppm.

^e THF as solvent.

absolute molar masses calculated by ¹H NMR and the molar masses evaluated by SEC using THF as solvent, giving an indication that the polystyrene standards calibration of our system over represents the molar masses values.

3.2. Synthesis of P(LA-b-TEHA-b-LA) triblock copolyesters

These macroinitiators, α, ω -dihydroxypolyesters (HO-PTEHA-OH) were used for the ring opening of LA thus obtaining triblock copolymers (Scheme 2). Polymerizations were carried out in toluene due to the high viscosity of the hydroxyl-terminated prepolymer. Four copolymers from each initiator were prepared by changing the monomer to initiator molar feed as shown in Table 1. This enabled the preparation of block copolymers with various compositions ranging from 54 to 85% of PLA. Polymerizations were carried out using 1% of Sn(Oct)₂ at 120 °C to avoid transesterification reaction for 4 h. The ¹H NMR spectra (Fig. 2c) shows

the appearance of a quadruplet at 5.17 ppm (H_e) confirming the ring opening of LA. Moreover, the peak of the terminal unit of macroinitiator at 3.75 ppm ($H_{a'}$) disappears according to initiation of LA polymerization. The composition of the copolymers was evaluated by ¹H NMR spectroscopy using signals corresponding to both repeating units, 5.17 ppm (H_e) and 4.21 ppm (H_a), and fits well to the theoretical values only for the lower feed ratios. This can be due to a lower number of growing chains when this ratio increases and to the viscosity increase with time that limits the accessibility of the monomer to the growing chain.

Molar masses were evaluated from NMR analysis, using end group signal ($H_{e'}$) at 4.35 ppm and repeating LA unit signal at 5.17 ppm (H_e), and TEHA signal at 2.73 ppm (Table 1). Mn values increase as the percentage of PLA in the copolymer increases as can be expected from the higher reactivity of LA. Mn values obtained by SEC are significantly different from ¹H NMR according to the above mentioned behaviour.



Scheme 2. Two step procedure to P(LA-b-TEHA-b-LA) triblock copolymers: obtention of HO-PTEHA-OH and further ring opening of LA, and oxidation to PSO(LA-b-TEHA-b-LA).



Fig. 2. ¹H NMR spectra of a) monomer TEHA; b) macroinitiator HO-PTEHA-OH1 (a' stands for TEHA terminal unit); c) triblock copolyester P(LA-*b*-TEHA1-*b*-LA)₅; d) polysulfone analogue PSO(LA-*b*-TEHA1-*b*-LA)₅ (e' stands for LA terminal unit in c) and d).

3.3. Synthesis of PSO(LA-b-TEHA-b-LA) triblock copolyesters sulfones

It is known that thioethers can easily be oxidized to sulfones (via sulfoxides) by several oxidation reagents. Sulfones exhibit a high polarity and thus, changes in thermal behaviour and crystallinity of the related polymers are expected [30]. It was found that hydrogen peroxide is able to selectively oxidize the thioether to sulfoxide or to sulfone groups depending on the reaction temperature [31]. Thus, the sulfoxide intermediate oxidation product can be obtained when the reaction is carried out at room temperature while the sulfone derivative is obtained by heating at higher temperatures. Oxidation was carried out using H_2O_2 (50 vol %) in a thioether: H_2O_2 molar ratio 1:2, with CHCl₃ as solvent at 25 °C. The reaction progress was followed by ¹H NMR spectroscopy. Signals at 2.72 ppm and 2.96 ppm attributable to α -protons of the sulfoxide moiety appear after 6 h of reaction. After 24 h of reaction, when signals of the thioether can still be observed, signals at 3.02 ppm and 3.28 ppm attributable to the α -protons of sulfone moiety appears. Only after 48 h of reaction signals of thioether completely disappear, when a mixture of sulfoxide and sulfone is present, thus selective oxidation does not take place and long reaction time would be necessary to obtain fully conversion to sulfone. Oxidation with H₂O₂ at high temperature has been described to produce hydrolysis of ester groups that would lead to polymer degradation [32], so alternative oxidants were considered. The oxidation process was finally performed in dichloromethane using m-chloroperbenzoic acid at room temperature [33]. Complete oxidation was achieved in 1 h.

¹H NMR spectroscopy showed full conversion of the thioether functions by the appearance of unique signals for protons H_a , H_b and H_c (Fig. 2d), at higher chemical shifts than for the parent

polymer, indicating that only sulfone oxidation product is formed. It is known that sulfones give two characteristic bands in IR spectroscopy between 1160-1130 cm⁻¹ and 1340-1300 cm⁻¹, whereas sulfoxides give only one band between 1060 and 1040 cm⁻¹. Fig. 3 shows IR spectra of triblock copolymer P(LA-*b*-TEHA1-*b*-LA)₃ parent and its oxidized analogue. Several bands appear at the region between 1160-1130 cm⁻¹ and 1060-1040 cm⁻¹ for the nonoxidized polymer but a new band at 1300 cm⁻¹ is only observed for the oxidized sample, thus indicating the formation of sulfone.

Molar masses of the polysulfones were obtained by ¹H NMR spectroscopy using signals of LA units (H_e) at 5.17 ppm and of oxidized TEHA units (SOTEHA) at 3.28 ppm (H_b) related to end group signal at 4.35 ppm (H_e) (Table 2).

Moreover, SEC analyses were carried out in DMF as polysulfones resulted insoluble in THF. As can be seen, no significant differences among Mn values previous and after oxidation were found, thus indicating that no degradation or crosslinking processes took place. It is noticeable the great difference among values obtained by the two techniques, even higher when using THF as solvent in SEC. The composition of the polysulfones was calculated by ¹H NMR (from LA signal at 5.17 ppm and SOTEHA signal at 4.50 ppm) and approaches better to the theoretical values for the higher LA contents.

Water contact angle measurements were carried out on PLA and copolyesters $P(LA-b-TEHA1-b-LA)_3$ and $P(LA-b-TEHA1-b-LA)_{10}$. The obtained contact angles were 83° , 91° and 91° respectively, showing the more hydrophobic character of the triblock copolyesters related to PLA. The contact angles of corresponding polysulfones $PSO(LA-b-TEHA1-b-LA)_3$ and $PSO(LA-b-TEHA1-b-LA)_{10}$ were 78° and 80° confirming the more hydrophilic character of polysulfones related to the parent copolymers.



Fig. 3. FT-IR spectra of a) triblock copolyester P(LA-*b*-TEHA1-*b*-LA)₃ and b) polysulfone analogue PSO(LA-*b*-TEHA1-*b*-LA)₃.

3.4. Thermal properties

The thermal behaviour of triblock copolyesters under nitrogen atmosphere has been comparatively studied by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), taking as reference HO-PTEHA-OH and PLA homopolymers. The weight loss versus temperature plots registered for the two series of copolyesters and their corresponding derivative curves were very similar in both cases and only P(LA-*b*-TEHA1-*b*-LA)_x triblock copolyesters are shown in Fig. 4 a) and b), respectively.

The temperatures at the decomposition onset and for maximum decomposition rate, together with the weight remaining after heating at 600 °C are listed in Table 3. As can be seen, PLA and HO-PTEHA-OH1 have a unique degradation step with very different temperatures at the decomposition onset and for maximum rate, thus showing a noticeable higher stability for the dihydroxylterminated prepolymer. All the copolyesters started to decompose above 200 °C with the maximum rate taking place in the proximities of 250 °C to leave less than 5% of the initial mass after heating at 600 °C. A common pattern of behaviour is followed by all them and slight differences associated to composition are noticeable. As expected, all copolymers present a multi-step thermal decomposition. A first weight loss is observed at a temperature about 250 °C which correspond to the degradation of PLA, followed by a two step thermal decomposition weight losses centred at 325–350 °C and around 400 °C, which seems to correspond to the decomposition of prepolymers HO-PTEHA-OH. The amount of the material degraded at these temperatures increases with the OH-PTEHA-OH content. This thermal decomposition pattern allows



Fig. 4. a) TGA weight loss curves and b) TGA derivative curves of HO-PTEHA-OH1, PLA and $P(LA-b-TEHA1-b-LA)_x$ triblock copolyesters.

calculating the weight percentage of each block in the copolymer. As can be observed in Table 3, these weight percentages of PLA approach to the theoretical values (in brackets).

In spite of the higher initial degradation temperature of HO-PTEHA-OH, the effect of their incorporation into PLA is lowering the initial degradation temperature of copolymer and the higher the weight fraction of HO-PTEHA-OH in the copolymer, the higher the temperature corresponding to the 5% weight loss.

The DSC heating scans recorded for copolyesters coming directly from synthesis showed two melting endotherms characteristic of melting of (HO-PTEHA-OH) and PLA and a small exotherm (Fig. 5a). In the cooling scans, only the exotherm attributed to the prepolymer crystallization at temperatures around 40 °C can be seen (Fig. 5b). A second heating run showed the two melting endotherms and a crystallization exotherm attributed to PLA crystallization by comparison to the second heating scan of PLA (Fig. 5c).

In block copolymers containing only crystallizable components, the competition between crystallization of the different crystalline

Table 2

Molar masses of P(LA-b-TEHA1-b-LA)x copolyesters and corresponding polysulfones PSO((LA-b-TEHA1-b-LA)x.

Sample Copolyester		Polysulfone						
	Mn NMR	Mn SEC ^a	PDI	Mn NMR	Mn SEC ^a	PDI	W (%) ^b	W (%) ^c
P(LA-b-TEHA1-b-LA) ₂ P(LA-b-TEHA1-b-LA) ₃ P(LA-b-TEHA1-b-LA) ₅	4176 5102 5583	30,265 36,940 35,592	1.06 1.14 1.06	5990 6100 6160	36,467 37,582 41 281	1.17 1.10 1.11	51 61 72	44 55 68
$P(LA-b-TEHA1-b-LA)_{10}$	9163	37,803	1.10	8980	39,670	1.13	84	80

^a SEC values were obtained using DMF as solvent.

^b Theoretical weight percentage of PLA.

^c Weight percentage of PLA in polysulfones by ¹H NMR (from LA signal at 5.17 ppm and SOTEHA signal at 4.50 ppm).

Table 3

Thermogravimetric properties of PLA, HO-PTEHA-OH and $P(\text{LA}-b\text{-TEHA}-b\text{-LA})_{\rm x}$ copolyesters.

Polymer	T5% (°C) ^a	Td (°C) ^b	R (%) ^c	Wt PLA (%) ^d
PLA	230	272	1.5	
HO-PTEHA-OH1	329	372	2.9	
HO-PTEHA-OH2	335	373	2.8	
P(LA-b-TEHA1-b-LA)2	216	249-334-410	3.2	45 (54)
P(LA-b-TEHA1-b-LA)3	215	255-334-411	2.7	55 (63)
P(LA-b-TEHA1-b-LA)5	213	252-324-398	3.2	66 (74)
P(LA-b-TEHA1-b-LA)10	204	254-345-413	4.3	83 (85)
P(LA-b-TEHA2-b-LA)2	204	245-334-409	3.4	44 (54)
P(LA-b-TEHA2-b-LA)3	202	248-332-406	4.7	53 (63)
P(LA-b-TEHA2-b-LA)5	204	250-326-402	2.9	68 (74)
P(LA-b-TEHA2-b-LA)10	198	248-352-397	4.0	83 (85)

^a Temperature at which 5% weight loss was observed.

^b Temperature for maximum degradation rate.

^c Remaining weight at 600 °C.

^d Weight percentage of PLA from TGA (Theoretical values in brackets).



Fig. 5. DSC plots of a) first heating b) cooling and c) second heating of PLA, HO-PTEHA-OH1 and P(LA-*b*-TEHA1-*b*-LA)₅ triblock copolyester.



Fig. 6. DSC plots after annealing PLA, HO-PTEHA-OH1 and P(LA-*b*-TEHA1-*b*-LA)_x triblock copolyesters.

blocks plays an important role and crystallization of one block may affect the crystallization and morphology of the other [34,35]. In our case, melting temperatures of the two blocks are far from each other and the crystallization behaviour is very different. To study the effect of the lower melting temperature block on the crystallization of the PLA block, the polymers were heated at 120 °C, a temperature around 40 °C below the melting temperature of PLA. All samples were heated from room temperature to 200 °C, cooled from 200 °C to 120 °C and heated at this temperature for 2 h, in order to produce maximum PLA block crystallinity, followed by cooling to -50 °C. Melting points and enthalpies were then recorded while heating at 10 °C/min from -50 °C to 200 °C. The obtained DSC heating scans are shown in Fig. 6 and data are collected in Table 4. PLA showed a melting endotherm at 167 °C which enthalpy increase from 53 J/g (second heating in Fig. 5c) to 69 J/g. Moreover, an increase of the melting enthalpy of HO-PTEHA-OH1 from 70 to 91 J/g is observed, indicating an increase of crystallinity in both cases.

For the block copolymers, while melting temperatures of the PTEHA block show slight variations, a decrease of the Tm related to the parent polymer is observed in all cases. Moreover, Tm of PLA block decreases as the weight percent of TEHA increases and copolyesters containing high weight percentages of PLA melt at temperatures close to the PLA homopolymer.

The crystallinity of the PLA block in the copolymers was calculated using the equation $Xc = (\Delta H_m/W\Delta H^0_m) \times 100$, where ΔH_m is the melting enthalpy of PLA given by DSC, ΔH^0_m the enthalpy of fusion of the completely crystalline state (93 J/g for PLA) and W the weight fraction obtained from ¹H NMR data. Considering the degree of crystallization, both series show a decrease of crystallinity with respect to the PLA homopolymer according to the influence of the molten PTEHA chains on the crystallization of the PLA. The crystallinity increases as the weight percentage of PLA increases.

Table 4
DSC properties of PLA, HO-PTEHA-OH and P(LA-b-TEHA-b-LA)_x copolyesters.

Polymer	Tm_1 (°C)	ΔHm_1 (J g ⁻¹)	Tm ₂ (°C)	ΔHm_2 (J g ⁻¹)	Xc ^a
PLA	_	_	167	68	74
HO-PTEHA-OH1	61, 68	91	-	_	
HO-PTEHA-OH2	59, 67	84	-	-	
P(LA-b-TEHA1-b-LA)2	60	22	146	24	54
P(LA-b-TEHA1-b-LA)3	60	13	161	33	59
P(LA-b-TEHA1-b-LA)5	56	10	158	43	66
P(LA-b-TEHA1-b-LA)10	57	5	160	48	62
P(LA-b-TEHA2-b-LA)2	65	25	142	21	47
P(LA-b-TEHA2-b-LA)3	64	25	155	27	51
P(LA-b-TEHA2-b-LA)5	62	10	158	41	64
P(LA-b-TEHA2-b-LA)10	63	7	159	45	58

^a Degree of crystallinity.

The crystallinity of both blocks was confirmed by wide angle Xray experiments. Fig. 7 compares WAXS intensity profile of copolyester with that of PLA and HO-TEHA-OH1 homopolymers recorded after annealing. PLA can crystallize in different forms depending on the processing conditions, being the most stable the α -form with a 10³ helical chain conformation where two chains interact in a orthorhombic unit cell [36]. Typical reflections at (010), (110/200), (203) and (015) corresponding to this form are identified at $2\theta = 14.7^{\circ}$, 16.7°, 19.1° and 22.3°. Moreover, reflections corresponding to PTEHA unit at $2\theta = 19.5^{\circ}$, 21.5° and 23.7° can be seen. Both characteristic homopolymer reflections are visible in the block copolymer sample and the most significant trend is the increase of the amorphous halo which can be related to the crystallinity decrease.

The thermal behaviour of polysulfone derivatives under nitrogen atmosphere has been comparatively studied by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) taking as reference PLA, HO-PSOTEHA-OH1 and the parent triblock copolyesters. Thermogravimetric analysis show that the



Fig. 7. WAXS patterns of a) PLA b) P(LA-*b*-TEHA1-*b*-LA)₂ c) PSO(LA-*b*-TEHA1-*b*-LA)₂ d) HO-PTEHA1-OH.



Fig. 8. a) TGA weight loss curves and b) TGA derivative curves of PLA, HO-PSOTEHA-OH1, P(LA-*b*-TEHA1-*b*-LA)₁₀ and PSO(LA-*b*-TEHA1-*b*-LA)₁.

Table 5

Thermogravimetric properties of HO-PSOTEHA-OH1 and $PSO(LA-b-TEHA-b-LA)_x$ polysulfones.

Sample	$T_{5\%}^{a}$ (°C)	Td ^b (°C)	W ^c (%)	Wt PLA ^d (%)
HO-PSOTEHA-OH1	278	358-435	5.3	_
PSO(LA-b-TEHA1-b-LA)2	235	273-316-423	6.1	38 (51)
PSO(LA-b-TEHA1-b-LA)3	243	289-310-413	5.4	40 (61)
PSO(LA-b-TEHA1-b-LA)5	255	292-413	5.4	72 (72)
PSO(LA-b-TEHA1-b-LA)10	241	316-412	6.2	84 (84)

^a Temperature at which 5% weight loss was observed.

^b Temperature for maximum degradation rate.

^c Remaining weight at 600 °C.

^d Weight percentage of PLA (Theoretical values in brackets).





DSC properties of HO-I	PSOTEHA-OH1 and PSO(LA- <i>b</i> -TEHA- <i>b</i> -LA) _x po	olysulfones.	
Sample	Tm ₁ (°C)	ΔHm_1 (J g ⁻¹)	

Sample	Tm ₁ (°C)	ΔHm_1 (J g ⁻¹)	Tm ₂ (°C)	$\Delta Hm_2 (J g^{-1})$	Xc ^a
HO-PSOTEHA-OH1	114	45	_	_	_
PSO(LA-b-TEHA1-b-LA)2	114	16	148	18	44
PSO(LA-b-TEHA1-b-LA)3	114	10	156	28	55
PSO(LA-b-TEHA1-b-LA)5	105	10	157	32	51
PSO(LA-b-TEHA1-b-LA)10	103	4	158	44	59

^a Degree of crystallinity.

Table C

synthesized polysulfones are stable until at least a temperature of 235 °C, so the oxidation process increases the thermal stability of the block copolymers (Fig. 8 and Table 5). While the polysulfones containing the lowest percentage of LA show the same pattern as copolyester precursors on the derivative curves, the copolymers containing higher LA percentages show only two degradation steps. The first degradation step, that can be attributed to PLA degradation, appears at higher temperatures than in the parent copolymers, according to the increased thermal stability and overlaps to the second degradation step for PSO(LA-*b*-TEHA1-*b*-LA)₅ and PSO(LA-*b*-TEHA1-*b*-LA)₁₀. The weight percentages of each block calculated from these degradation patterns approach well the theoretical values only in the last two cases.

Oxidation of the thioether to sulfone resulted in a significant increase of the melting temperature of the PSOTEHA block of around 40 °C, but not significant differences with the PTEHA block melting enthalpies were found (Fig. 9, Table 6).

Regarding the PLA block, the melting temperatures do not differ significantly from the parent copolymers and lower crystallinities can be observed, showing the influence of the oxidized melting chains on the PLA crystallization. WAXS intensity profile of PSO(LA*b*-TEHA1-*b*-LA)₂ (Fig. 7c) show a similar pattern to the parent copolyester with the above mentioned reflections but different relative intensities.

4. Conclusions

Fully biobased ABA triblock copolyesters from PLA and castor oil derivatives were synthesized. The synthetic strategy used a dihydroxy telechelic polyester, from a sulfur-containing hydroxyacid derivative from 10-undecenoic acid, which self-polycondensation with low amounts of biobased 1,4-butanediol, enables the obtention of a macroinitiator for the ROP of LA. Two series of triblock copolyesters with different LA/HO-PTEHA-OH ratio were prepared and characterized by ¹H NMR spectroscopy and Mn determined by NMR and SEC. DSC results of the triblock copolyesters showed a significant decrease on the melting temperature of PLA block related to percentage of PTEHA in the polymer chain. Both series of copolyesters showed a decrease of crystallinity with respect to the PLA homopolymer. The thermal stability of the copolymers was found to increase as TEHA units increased in the copolymer. Triblock copolyesters were modified to polysulfone analogues by the oxidation of thioether functionality. After oxidation a decrease of crystallinity was observed and thermal analysis demonstrated improved stability of these oxidized polymers compared to the copolyester parents. From water contact angle measurements a higher hidrophobic character of the triblock copolyester and a similar hidrophilicity of the polysulfone analogues related to PLA is observed.

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