# High Tg Bio-Based Aliphatic Polyesters from Bicyclic D-Mannitol

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S *Supporting Information*

ABSTRACT: The carbohydrate-based diol 2,4:3,5-di-*O*-methylene-D-mannitol (Manx) has been used to obtain aliphatic polyesters. Manx is a symmetric bicyclic compound consisting of two fused 1,3-dioxane rings and bearing two primary hydroxyl groups. In terms of stiffness, it is comparable to the widely known isosorbide, but it affords the additional advantages of being much more reactive in polycondensation and capable of producing stereoregular polymers with fairly high molecular weights. A fully bio-based homopolyester (PManxS) has been synthesized by polycondensation in the melt from dimethyl succinate and Manx. The high thermal stability of PManxS, its relatively high glass transition temperature (T_g = 68 °C) and elastic modulus, and its enhanced sensitivity to the action of lipases point to PManxS as a polyester of exceptional interest for those applications where biodegradability and molecular stiffness are priority requirements. In addition, random copolyesters (PB_xManx_yS) covering a broad range of compositions have been obtained using mixtures of Manx and 1,4-butanediol in the reaction with dimethyl succinate. All PB_xManx_yS were semicrystalline and displayed T_g values from −29 to +51 °C steadily increasing with the content in Manx units. The stress−strain behavior of these copolyesters largely depended on their content in Manx and they were enzymatically degraded faster than PBS.
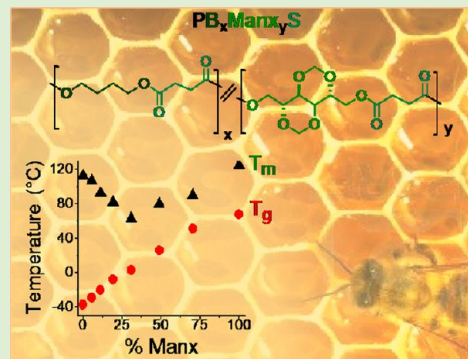
INTRODUCTION

As a result of increasing concerns on sustainable development and minimizing the impact of materials on the environment, biodegradable polymers have attracted a great deal of interest in the last decades.[1−4] Aliphatic polyesters such as poly(butylene succinate) (PBS), poly(L-lactic acid), poly(ε-caprolactone) and poly(3-hydroxy butyrate), among others, constitute a distinguished bunch of biodegradable polymers that are commercially available in several forms. Some of these aliphatic polyesters have found intensive use in a broad variety of medical applications such as bioresorbable surgical sutures, prosthesis, dental implants, bone screw and plates for temporary internal fracture fixation, and controlled drug delivery systems.[5,6] Nowadays PBS is receiving exceptional attention as a polymeric material suitable for replacing conventional commodity plastics in injection-molded articles (cutlery, brushes), tubular films (composting bags, shopping bags), flexible packaging and food tray since it has a melting temperature similar to that of low density polyethylene, satisfactory mechanical properties and can be processed with the conventional equipment commonly used for polyolefins.[7,8] However, PBS has a glass-transition temperature (T_g) of −37 °C, not high enough for its use in rigid packaging and cosmetic and beverage bottles where stiffness and thermal resistance are priority requisites. In this regard, various approaches such as blending and copolymerization with aromatic polyesters as poly(butylene terephthalate) (PBT) and poly(ethylene terephthalate) (PET) have been recently explored.[9,10] The interest for cyclic monomers arises from their capacity for adding stiffness to the polymer chain with the subsequent increase in T_g; the disadvantage of using aromatic

units for such purpose is that they are originated from fossil feedstocks and are reluctant to biodegradation.

The use of carbohydrate-based monomers with a cyclic structure constitute a scarcely explored approach for the preparation of renewable aliphatic polyesters with improved physical properties, especially those related to polymer chain stiffness.[11,12] Moreover, carbohydrate-derived polycondensates typically display enhanced hydrophylicity, lower toxicity and higher susceptibility to hydrolytic degradation and biodegradation than those coming from petrochemical feedstocks. Thus, 2,3-*O*-isopropylidene-L-tartaric acid[13,14] and 2,5-furandicarboxylic acid[15−17] have been polymerized with several diols to obtain bio-based aliphatic cyclic polyesters. 1,4:3,6-Dianhydro-D-glucitol, known as isosorbide, which is prepared by dehydration of D-glucose coming from cereal starch, is the only bicyclic carbohydrate-based monomer industrially available today. Isosorbide, along with their two less accessible stereoisomers isomannide and isoidide, are currently drawing an enormous interest in the polymer science field as bio-based monomers able to provide enhanced stiffness into the polymer chain they are incorporated.[18] These three isohexides are composed of two fused tetrahydrofuran rings, with two secondary hydroxyl groups remaining free for reaction. Because of their fused bicyclic structure, 1,4:3,6-dianhydrohexitols and their diacid derivatives are able to increase the glass-transition temperature of common aliphatic polyesters.[19−23] Nevertheless,

the main shortcoming of isosorbide and its isomers is the limited reactivity of their secondary hydroxyl groups; in fact, this feature seriously hampers the polycondensation reaction in the melt, so aliphatic polyesters from 1,4:3,6-dianhydrohexitols and aliphatic dicarboxylic acids or dicarboxylic esters obtained by this method display rather limited molecular weights.[19,20] Higher molecular weights are achievable via polycondensation with aliphatic dicarboxylic chlorides,[21,22] but this method is not appropriate for industrial application.[24]

Recently, we have reported the synthesis and characterization of aliphatic polyesters made from dimethyl 2,3:4,5-di-*O*-methylene-galactarate (Galx), which is a bicyclic monomer obtained by internal acetalization of galactaric acid.[25,26] This monomer has been shown to be very suitable for the preparation of aliphatic polyesters by polycondensation with aliphatic diols in the melt, since it is able to react at a rate similar to that of other acyclic conventional monomers. In contrast with dianhydrohexitols, Galx is composed of two independent 1,3-dioxolane rings linked by a single C−C bond, and thence, they were found to confer lower rigidity to the polyester backbone than a fused bicyclic structure is able to do. To our knowledge, the bicyclic diester Galx is the only bicyclic diacetalized carbohydrate-based monomer that has been used up to date to obtain aliphatic polyesters.

In this work, bicyclic 2,4:3,5-di-*O*-methylene-D-mannitol, abbreviated as Manx, has been used to obtain aliphatic polyesters. Manx is obtained by internal acetalization of D-mannitol in a manner similar to the way the bicyclic diester Galx is obtained from mucic acid. Nevertheless, unlike Galx, Manx is a rigid structure composed of two fused 1,3-dioxane rings, which will confer to the polymer chain higher stiffness than the two nonfused rings of Galx. Manx is therefore a diol very adequate for the synthesis of bio-based aliphatic polyesters with T_g much higher than usually found in these compounds; in fact, too low T_g is widely recognized to be one of the main shortcomings of most of common aliphatic polyesters. In contrast with isosorbide, which has been previously exploited with the same purpose, the use of Manx as a monomer or comonomer for polyesters will lead to stereoregular chains because of the 2-fold axis of symmetry present in the molecule. Furthermore, the high reactivity of the two primary hydroxyl groups of Manx, which are able to react more efficiently than the secondary hydroxyl groups of isosorbide, will be able to render higher molecular weight polyesters. Here, we present a fully bio-based polysuccinate (PManxS) made from the renewable diol Manx and the dimethyl ester of succinic acid (SA), which has been synthesized by melt polycondensation; its thermal and mechanical properties and its ability to be biodegraded have been evaluated and compared with those displayed by PBS. We also present an exploratory account of new bio-based aliphatic copolyesters obtained by partially replacing 1,4-butanediol in PBS by Manx. An assortment of products with properties grading between those of PBS and PManxS have been obtained and characterized. These copolyesters are called PB$_x$Manx$_y$S, with the subscripts x and y standing for their molar contents in butanediol and Manx units, respectively. The combination of Manx with SA has been proven to be satisfactory to afford bio-based polysuccinates with T_g much higher than most of those known so far and comparable to those prepared from isosorbide.

■ EXPERIMENTAL SECTION

Materials. 2,4:3,5-Di-*O*-methylene-D-mannitol was synthesized following the procedure recently reported by Lavilla et al.[27] Dimethyl succinate (98+%) was purchased from Merck-Schuchardt. 1,4-Butanediol (99%) and the catalyst dibutyl tin oxide (DBTO, 98%) were purchased from Sigma-Aldrich. Solvents used for purification and characterization were purchased from Panreac and they all were of either technical or high-purity grade. All the reagents and solvents were used as received without further purification.

General Methods. ^{1}H 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. Samples were dissolved in a mixture of deuterated chloroform and trifluoroacetic acid (9:1) or in deuterated water, and spectra were internally referenced to tetramethylsilane (TMS). About 10 and 50 mg of sample dissolved in 1 mL of solvent was used for ^{1}H and ^{13}C NMR, respectively. Sixty-four scans were acquired for ^{1}H 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. 2D [1]H−^{1}H homonuclear (COSY) and [13]C−[1]H heteronuclear shift correlation (HETCOR) spectra were recorded by means of the *cosy* and *hxco*, respectively, pulse sequences implemented in the Bruker NMR instrument package. Intrinsic viscosities of polyesters dissolved in chloroform were measured in an Anton Paar AMVn Automated Micro Viscosimeter at 25.00 ± 0.01 °C, using the VisioLab for AMVn software. Gel permeation chromatograms were acquired at 35.0 °C with a Waters equipment provided with a refraction-index detector. Samples were chromatographed with 0.05 M sodium trifluoroacetate-hexafluoroiso-propanol (NaTFA-HFIP) using a polystyrene-divinylbenzene packed linear column with a flow rate of 0.5 mL·min⁻¹. Chromatograms were calibrated against poly(methyl methacrylate) (PMMA) monodisperse standards. The thermal behavior of polyesters was examined by DSC using a Perkin-Elmer DSC Pyris 1. DSC data were obtained from 3 to 5 mg samples at heating/cooling rates of 10 °C·min⁻¹ under a nitrogen flow of 20 mL·min⁻¹. Indium and zinc were used as standards for temperature and enthalpy calibration. The glass-transition temperatures were determined at a heating rate of 20 °C·min⁻¹ from rapidly melt-quenched polymer samples. The treatment of the samples for isothermal crystallization experiments was the following: the thermal history was removed by heating the sample up to 200 °C and left at this temperature for 5 min, and then it was cooled at 20 °C·min⁻¹ to the selected crystallization temperature, where it was left to crystallize until saturation. For morphological study, isothermal crystallizations conducted under the same conditions were carried out in an Olympus BX51 Polarizing Optical Microscope coupled to a THMS LINKAM heating plate and a cooling system LNP (Liquid Nitrogen Pump). 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 equipment. Sample weights of about 10−15 mg were used in these experiments. Films for mechanical testing and contact angle measurements were prepared with a thickness of ~200 μm by casting from chloroform solution at a polymer concentration of 100 g·L⁻¹. For tensile essays, the films were then cut into strips with a width of 3 mm while the distance between testing marks was 10 mm. The tensile strength, elongation at break and Young's modulus were measured at a stretching rate of 30 mm·min⁻¹ on a Zwick 2.5/TN1S testing machine coupled with a compressor Dalbe DR150, at 23 °C. Contact angles were measured in an equipment OCA 20 (DataPhysics Instruments GmbH, Filderstadt) provided with the SCA20 software for image and data treatment. Angle values were registered after 45 s of dropping 1.5 μL of water onto the polyester surface at 23 °C. X-ray diffraction patterns were recorded on the PANalytical X'Pert PRO MPD θ/θ diffractometer using the Cu Kα radiation of wavelength 0.1542 nm from powdered samples coming from synthesis. Scanning electron microscopy (SEM) images were taken with a field-emission JEOL JSM-7001F instrument (JEOL, Japan) from platinum/palladium coated samples.

Polymer Synthesis. PManxS homopolyester was obtained from 2,4:3,5-di-*O*-methylene-D-mannitol and dimethyl succinate.

PB$_x$Manx$_y$S copolyesters were obtained from a mixture of 1,4-butanediol, 2,4:3,5-di-O-methylene-D-mannitol and dimethyl succinate with the selected composition. PBS was obtained from 1,4-butanediol and dimethyl succinate. The reactions were performed in a three-necked, cylindrical-bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a vacuum distillation outlet. An excess of diol mixture to dimethyl succinate was used and dibutyl tin oxide (DBTO, 0.6% molar respect to monomers) was the catalyst of choice. The apparatus was vented with nitrogen several times at room temperature in order to remove air and avoid oxidation during the polymerization. Transesterification reactions were carried out under a low nitrogen flow at the selected temperature. Polycondensation reactions were left to proceed at the selected temperature under a 0.03–0.06 mbar vacuum. Then, the reaction mixture was cooled to room temperature, and the atmospheric pressure was recovered with nitrogen to prevent degradation. The resulting polymers were dissolved in chloroform and precipitated in excess of methanol in order to remove unreacted monomers and formed oligomers. Finally, the polymer was collected by filtration, extensively washed with methanol, and dried under vacuum. These powdered samples coming directly from synthesis, i.e., without any further treatment other than reprecipitation and washing, were used throughout for the characterization performed in this work unless otherwise stated.

PManxS Homopolyester. Five percent molar excess of 2,4:3,5-di-O-methylene-D-mannitol to dimethyl succinate. Transesterification reactions at 160 °C for 3 h under a low nitrogen flow. Polycondensation reactions at 160 °C for 5 h under a 0.03–0.06 mbar vacuum. ^{1}H NMR (300.1 MHz, CDCl$_3$/TFA), δ (ppm): 5.1–4.9 (m, 4H, OCH$_2$O), 4.6–4.4 (m, 4H, OCH$_2$CH), 4.6–4.4 (m, 2H, OCH$_2$CH), 4.3–4.1 (m, 2H, OCH$_2$CHCH), 2.8 (s, 4H, COCH$_2$CH$_2$CO). ^{13}C NMR (75.5 MHz, CDCl$_3$/TFA), δ (ppm): 175.2 (CO), 88.5, 71.6, 66.7, 63.9, 29.2.

PBS Homopolyester. Twenty percent molar excess of 1,4-butanediol to dimethyl succinate. Transesterification reactions at 160 °C for 2.5 h and at 180 °C for 0.5 h under a low nitrogen flow. Polycondensation reactions at 180 °C for 3.5 h under a 0.03–0.06 mbar vacuum. ^{1}H NMR (300.1 MHz, CDCl$_3$/TFA), δ (ppm): 4.2 (t, 4H, OCH$_2$CH$_2$CH$_2$), 2.8 (s, 4H, COCH$_2$CH$_2$CO), 1.8 (t, 4H, OCH$_2$CH$_2$CH$_2$). ^{13}C NMR (75.5 MHz, CDCl$_3$/TFA), δ (ppm): 175.7 (CO), 66.3, 29.6, 25.2.

PB$_x$Manx$_y$S Copolyesters. The copolyesters were obtained by a similar procedure, with polymerization conditions slightly differing for each composition feed.

PB$_{95}$Manx$_5$S and PB$_{90}$Manx$_{10}$S. Five percent molar excess of the diol mixture to dimethyl succinate. Transesterification reactions at 160 °C for 2.5 h and at 180 °C for 0.5 h and under a low nitrogen flow. Polycondensation reactions at 180 °C for 3.5 h under a 0.03–0.06 mbar vacuum.

PB$_{80}$Manx$_{20}$S and PB$_{70}$Manx$_{30}$S. Five percent molar excess of the diol mixture to dimethyl succinate. Transesterification reactions at 160 °C for 2.5 h and at 170 °C for 0.5 h and under a low nitrogen flow. Polycondensation reactions at 170 °C for 4 h under a 0.03–0.06 mbar vacuum.

PB$_{50}$Manx$_{50}$S and PB$_{30}$Manx$_{70}$S. Five percent molar excess of the diol mixture to dimethyl succinate. Transesterification reactions at 160 °C for 3 h and under a low nitrogen flow. Polycondensation reactions at 160 °C for 5 h under a 0.03–0.06 mbar vacuum.

NMR Characterization of PB$_x$Manx$_y$S Copolyesters. ^{1}H NMR (300.1 MHz, CDCl$_3$/TFA), δ (ppm): 5.1–4.9 (m, y·4H, OCH$_2$O), 4.6–4.4 (m, y·4H, OCH$_2$CH), 4.6–4.4 (m, y·2H, OCH$_2$CH), 4.3–4.1 (m, y·2H, OCH$_2$CHCH), 4.2 (t, x·4H, OCH$_2$CH$_2$CH$_2$), 2.8 (s, 4H, COCH$_2$CH$_2$CO), 1.8 (t, x·4H, OCH$_2$CH$_2$CH$_2$). ^{13}C NMR (75.5 MHz, CDCl$_3$/TFA), δ (ppm): 175.7 (CO), 175.2 (CO), 88.5, 71.6, 66.7, 66.3, 63.9, 29.6, 29.2, 25.2.

Biodegradation and Hydrolytic Degradation. Films for polyester biodegradation and hydrolytic degradation studies were prepared with a thickness of ∼200 μm by casting from chloroform solution at a polymer concentration of 100 g·L^{-1}. The films were cut into 10 mm diameter, 20–30 mg weight disks and dried in vacuum to constant weight. For hydrolytic degradation, samples were immersed

in vials containing 10 mL of either citric acid buffer (pH 2.0) or sodium phosphate buffer (pH 7.4) at 37 °C. After incubation for the scheduled period of time, the samples were rinsed thoroughly with distilled water and dried to constant weight. The enzymatic degradation was carried out at 37 °C in vials containing 10 mL of the enzymatic medium, consisting of a pH 7.4 buffered sodium phosphate solution containing lipase from porcine pancreas (10 mg). The buffered enzyme solution was replaced every 72 h to maintain the enzyme activity. At the end of the scheduled incubation periods, the disks were withdrawn from the incubation medium, washed thoroughly with distilled water, dried to constant weight and analyzed by GPC chromatography, NMR spectroscopy and SEM microscopy.

For hydrolytic degradation studies of 2,4:3,5-di-O-methylene-D-mannitol, samples of this diol (80 mg) were immersed in NMR tubes containing 1 mL of citric acid buffer (pH 2.0), sodium phosphate buffer (pH 7.4) or sodium carbonate buffer (pH 10.5), all of them prepared in D$_2$O, and were incubated at 37 °C for 12 weeks. The residue left after incubation was analyzed by NMR spectroscopy.

■ RESULTS AND DISCUSSION

Synthesis and Chemical Structure. The synthesis of the bio-based homopolyester PManxS was carried out by reaction of 2,4:3,5-di-O-methylene-D-mannitol (Manx) with the dimethyl ester of succinic acid. The reaction was performed in the melt and in the total absence of solvents to imitate as far as possible the conditions usually applied in the industry, in two successive stages at 160 °C and under a progressively diminishing reaction pressure to facilitate the removal of released byproducts. Dibutyl tin oxide (DBTO) was the catalyst of choice instead of the commonly used titanium(IV) tetrabutoxide (TBT); our previous results in the synthesis of aliphatic homopolyesters from the bicyclic nonfused diester dimethyl 2,3:4,5-di-O-methylene-galactarate demonstrated the higher activity of DBTO catalyst compared to TBT, which allowed to proceed at lower temperatures without increasing reaction times. Using mild conditions for polymerization, decomposition of thermally sensitive sugar compound was minimized and higher molecular weights could be attained. The M_w of the resulting PManxS homopolyester was higher than 30 000 g·mol^{-1}, with a 2.3 dispersity value. It is worthy to note that M_w of PManxS here obtained by melt polycondensation from the bicyclic diol Manx and succinic dimethyl ester is much higher than those reported for melt polycondensation of 1,4:3,6-dianhydrohexitols with aliphatic diesters or diacids.[19,20] The higher reactivity of the primary hydroxyl groups of acetalized alditols compared to the secondary hydroxyl groups of 1,4:3,6-dianhydrohexitols is doubtlessly the reason for the observed differences. In fact, a recent study carried out by us comparing aromatic polyesters made from either acetalized alditols or alditol dianhydrides showed a much easier synthesis of the formers when obtained by melt polycondensation.[28]

The synthesis of PB$_x$Manx$_y$S copolyesters was carried out from 1,4-butanediol, 2,4:3,5-di-O-methylene-D-mannitol and dimethyl succinate also by a two-step melt polycondensation process, at temperatures between 160 and 180 °C (Scheme 1); lower temperatures and longer reaction times were used for copolyesters with higher contents in Manx units. The homopolyester PBS, used in this study for comparison purposes, was prepared from 1,4-butanediol and dimethyl succinate following a similar procedure. The resulting PB$_x$Manx$_y$S copolyesters had M_w in the 33 000 to 48 000 g·mol^{-1} range, with dispersities between 2.3 and 2.5, and intrinsic viscosities ranging from 0.6 to 0.9 dL·g^{-1} (Table 1).

Scheme 1. Polymerization Reactions Leading to PB$_x$Manx$_y$S Copolyesters
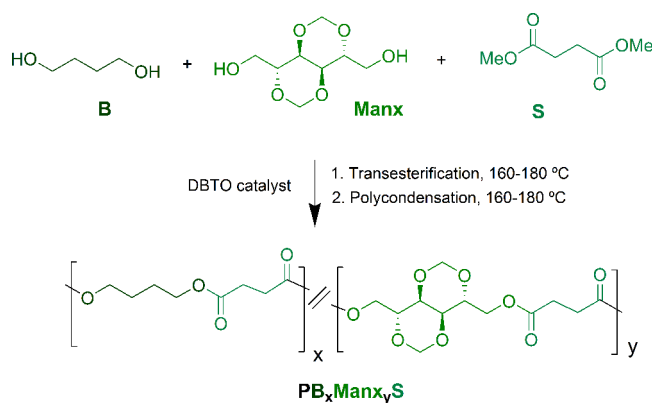
Both the ^{1}H and ^{13}C NMR analysis ascertained the chemical constitution and composition of the polyesters. They are detailed in the Experimental Section, and a selection of the illustrative spectra is provided in the Supporting Information (SI) material associated with this paper. The assignment of the signals arising from the sugar units was supported by COSY and HETCOR spectra, which are included in the SI file. Integration of the proton signals arising from B and Manx units led to quantify the composition of the copolyesters in such units, which appeared to be very close to those of their respective feeds (Table 1). The microstructure of PB$_x$Manx$_y$S copolyesters was determined by ^{13}C NMR analysis. As it is depicted in Figure 1, the ^{13}C NMR spectra of copolyesters show one of the succinic signals with resolution enough as to make possible the elucidation of the copolyester microstructure as far as distribution of B and Manx units along the copolyester chain is concerned. As a consequence of the occurrence of different dyad types (BB, BManx, ManxB and ManxManx), this signal appears split into four peaks that spread within the 29.2–29.7 ppm chemical shift interval. By integration of these peaks, the dyad contents, the number-average sequence lengths and the degree of randomness were estimated (Table 1), leading to the conclusion that the microstructure of the copolyesters was random in all cases.

The solvent affinity of Manx containing polysuccinates was similar to that displayed by PBS. All they continue to be nonsoluble in water but readily soluble in chloroform. The contact angle between water and polyester films was measured to estimate their hydrophilicity (Table 1); no significant differences were observed in the θ_{water} of PBS (~113°) with the incorporation of Manx units except for the case of the homopolyester where the contact angle decreased to near 75° indicating the much higher hydrophilic character of this compound.

Thermal and Mechanical Properties. The thermal behavior of PManxS homopolyester and PB$_x$Manx$_y$S copolyesters has been comparatively studied by TGA and DSC; the thermal parameters resulting from these analyses are given in Table 2, where the corresponding data for the homopolyester PBS are also included for reference. First, the thermal stability was evaluated by TGA under inert atmosphere. The TGA traces of PManxS and PBS homopolyesters together with their derivative curves are shown in Figure 2a, and those recorded from the whole set of PB$_x$Manx$_y$S copolyesters are comparatively depicted in Figure 2b. Thermal decomposition of PManxS occurs in a single stage with maximum rate taking

Table 1. Molar Composition, Molecular Weight, Microstructure, and Contact Angle

copolyester	yield (%)	feed X_B	feed X_{Manx}	copolyester[a] X_B	copolyester[a] X_{Manx}	$[\eta]$[b]	M_n[c]	M_w[c]	D[c]	BB	BManx/ManxB	Manx/Manx	n_B	n_{Manx}	R	θ_{water} (deg)[e]
PBS	90	100	0	100	0	0.97	19,500	49,100	2.5							113 ± 4
PB$_{95}$Manx$_5$S	87	95	5	94.3	5.7	0.90	19,900	47,800	2.4	87.9	11.4	0.7	16.4	1.1	0.96	114 ± 5
PB$_{90}$Manx$_{10}$S	89	90	10	88.7	11.3	0.72	16,900	39,100	2.3	78.0	20.5	1.5	8.6	1.1	0.99	114 ± 4
PB$_{80}$Manx$_{20}$S	88	80	20	80.7	19.3	0.69	14,600	35,200	2.4	66.3	30.8	3.0	5.3	1.2	1.03	117 ± 3
PB$_{70}$Manx$_{30}$S	86	70	30	69.1	30.9	0.70	14,200	35,000	2.5	47.0	44.3	8.8	3.1	1.4	1.04	113 ± 2
PB$_{50}$Manx$_{50}$S	87	50	50	51.1	48.9	0.61	13,900	33,400	2.4	26.1	50.0	24.0	2.0	2.0	1.00	114 ± 4
PB$_{30}$Manx$_{70}$S	89	30	70	29.7	70.3	0.60	13,500	33,500	2.5	8.4	43.4	48.2	1.4	3.2	1.03	116 ± 8
PManxS	85	0	100	0	100	0.56	13,300	30,800	2.3							74 ± 7

^{a}Molar composition determined by integration of the ^{1}H NMR spectra. ^{b}Intrinsic viscosity in dL·g^{-1} measured in chloroform at 25 °C. ^{c}Number and weight-average molecular weights in g·mol^{-1} and dispersities measured by GPC in HFIP against PMMA standards. ^{d}Randomness index of copolyesters statistically calculated on the basis of the ^{13}C NMR analysis. ^{e}Contact angle measured after 45 s of dropping 1.5 μL of water.
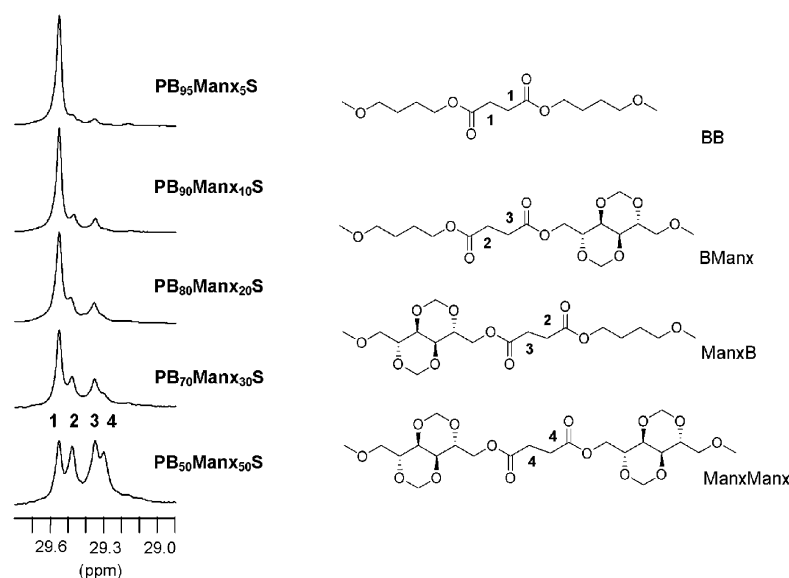
Figure 1. ^{13}C NMR signals used for the microstructure analysis of PB$_x$Manx$_y$S copolyesters with indication of the dyads to which they are assigned.

Table 2. Thermal Properties

	TGA			DSC								
					first heating[e]		cooling[e]		second heating[e]			
copolyester	$^\circ T_{5\%}{}^{a}$	$T_d{}^{b}$	W^c	$T_g{}^{d}$	T_m	ΔH_m	T_c	ΔH_c	T_c	ΔH_c	T_m	ΔH_m
	(°C)	(°C)	(%)	(°C)	(°C)	(J·g^{-1})	(°C)	(J·g^{-1})	(°C)	(J·g^{-1})	(°C)	(J·g^{-1})
PBS	320	384	4	−37	111/114 (113)	75.0 (103.1)	81	60.7	-	-	113	61.1
PB$_{95}$Manx$_5$S	320	386	6	−29	107 (107)	62.9 (69.3)	64	59.5	-	-	107	60.7
PB$_{90}$Manx$_{10}$S	322	387	5	−20	94 (93)	45.3 (48.4)	42	16.9	35	18.7	95	36.2
PB$_{80}$Manx$_{20}$S	323	410	4	−8	50/74/84 (51/82)	44.7 (47.3)	-	-	59	16.0	85	16.1
PB$_{70}$Manx$_{30}$S	322	413	4	3	52/64 (49/63)	30.1 (38.7)	-	-	-	-	-	-
PB$_{50}$Manx$_{50}$S	323	413	4	26	64/85 (62/80)	10.1 (10.9)	-	-	-	-	-	-
PB$_{30}$Manx$_{70}$S	321	413	5	51	91 (90)	3.8 (4.6)	-	-	-	-	-	-
PManxS	320	413	5	68	- (125)[f]	- (14.0)[f]	-	-	-	-	-	-

[a]Temperature at which 5% weight loss was observed. [b]Temperature for maximum degradation rate. [c]Remaining weight at 600 °C. [d]Glass-transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 °C·min^{-1}. [e]Melting (T_m) and crystallization (T_c) temperatures, and melting (ΔH_m) and crystallization (ΔH_c) enthalpies measured by DSC at heating/cooling rates of 10 °C·min^{-1} of powdered samples coming directly from synthesis (without parentheses) and of films prepared by casting from solution (in parentheses). [f]After annealing for 1 h at 60 °C, T_m increased to 127 °C and ΔH_m to 21.5 J·g^{-1}.

place at 413 °C ($^{max}T_d$), and only 5% of the initial weight remains at 600 °C; the maximum decomposition rate of PBS homopolyester occurs at 384 °C ($^{max}T_d$), the residual weight left upon heating at 600 °C being 4%. Decomposition of PB$_x$Manx$_y$S copolyesters takes place also in one stage, at temperatures ranging between $^{max}T_d$ of their two corresponding homopolyesters PBS and PManxS and steadily increasing as butanediol units are replaced by Manx units. The valuable conclusion drawn from this comparative thermogravimetric study is that the insertion of Manx in aliphatic polyesters instead of reducing their decomposition temperatures contributes significantly to increasing their thermal stability, which can

broaden even more the application window of aliphatic polyesters. Since the melting in these copolyesters decreases with composition, a wider range of temperatures between melting and decomposition exists, allowing a more comfortable melt processing.

Another thermal property of prime importance in connection with the potential application of these polyesters is the glass-transition temperature (T_g). For instance, an increase in the T_g of aliphatic polyesters such as PBS could open their use in the rigid packaging field. The DSC analyses revealed that the T_g steadily increased as butanediol was replaced by Manx units going from −29 °C for PB$_{95}$Manx$_5$S up to 51 °C for
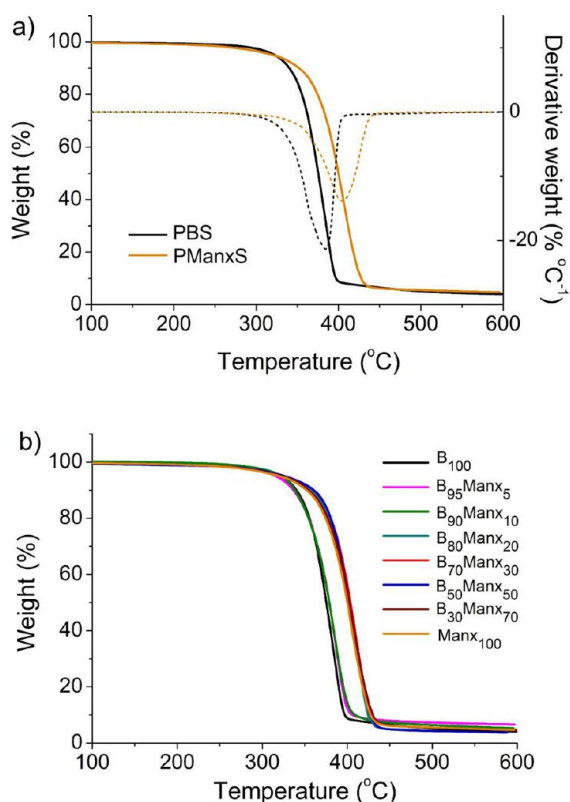
Figure 2. (a) TGA traces (solid lines) and derivative curves (dashed lines) of PBS and PManxS homopolyesters. (b) TGA traces of PB$_x$Manx$_y$S copolyesters.

PB$_{30}$Manx$_{70}$S (Figure 3a). These results are fully consistent with the T_g values of −37 and 68 °C observed for the PBS and PManxS homopolyesters, respectively, provided that the microstructure of the copolyesters is random. Such a remarkable positive effect of the incorporation of Manx on T_g makes this compound a bio-based comonomer very suitable for the preparation of aliphatic polyesters with enhanced T_g.

DSC traces of polyesters coming directly from synthesis are depicted in Figure 3b. All PB$_x$Manx$_y$S copolyesters as well as PBS homopolyester gave heating traces with melting endotherms indicating that they were semicrystalline, whereas PManxS appeared to be amorphous. Comparison of melting temperatures and enthalpies of PB$_x$Manx$_y$S copolyesters with that of PBS leads to the conclusion that the insertion of Manx units gives place to a significant decrease in both T_m and ΔH_m. The T_m did not follow a continuous trend with composition but it fell into a minimum for copolyester compositions around 30% of Manx units (Figure 4). This behavior suggested the occurrence of two different crystal structures depending on the unit, butanediol or Manx, that is predominant in the copolyester.

To complement DSC data, powder X-ray diffraction analyses were performed for PB$_x$Manx$_y$S copolyesters as well as for PBS and PManxS homopolyesters coming directly from synthesis. The X-ray diffraction profiles recorded from powders are compared in Figure 5, and the most prominent Bragg spacings present therein are listed in Table 3. Essentially, the same diffraction pattern regarding both spacing and intensities is shared by PBS homopolyester and copolyesters containing up to 30% of Manx units. This pattern is distinguished by the presence of three sharp strong reflections at 4.5, 4.1, and 3.9 Å
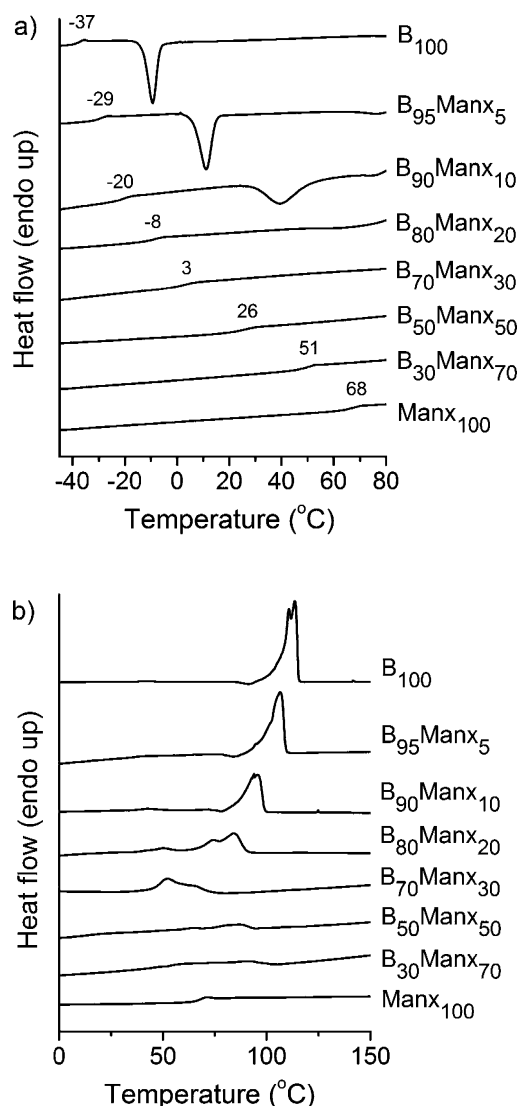
Figure 3. (a) DSC heating traces of PB$_x$Manx$_y$S copolyesters quenched from the melt. (b) DSC heating traces of PB$_x$Manx$_y$S copolyesters coming directly from synthesis.

indicating that the monoclinic crystal structure of PBS[29] is retained in such copolyesters. It must be assumed that the bicyclic structure in these copolyesters is segregated from the crystal lattice which is made of homogeneous sequences of butylene succinate units. Since the average length of these sequences diminishes with the content in Manx, the crystallite thickness decreases and consequently T_m goes down. Conversely, both PB$_{50}$Manx$_{50}$S and PB$_{30}$Manx$_{70}$S produced a scattering profile with a clearly different shape where the three most prominent reflections corresponding now to 4.7, 4.5, and 4.0 Å which also coincides with that exhibited by the PManxS homopolyester. The larger values observed for these spacings, which presumably arise from the interplanar distances that are defined by the side-by-side packing of the chains, are consistent with the bigger size of Manx compared to butanediol. In addition, several weaker reflections are observed at higher spacings in the 6−8 Å range, which might be associated to the axial repeat of the polyester chain. Apparently a second crystal form different from that of PBS, which is able to accommodate the bicyclic structure in the lattice, seems to be adopted by both the homopolyester and the copolyesters containing major

Figure 4. Glass-transition and melting temperatures versus composition plot for PB_xManx_yS copolyesters.

Figure 5. Powder WAXS profiles of PBS, PManxS and PB_xManx_yS copolyesters coming directly from synthesis. *The PManxS profile at the bottom was obtained from a film casted from chloroform that was annealed for 1 h at 60 °C.

amounts of Manx. In this case the butylene succinate would be the unit that is segregated from the crystalline phase; accordingly, the T_m in the Manx-enriched interval should be expected to increase with the content in Manx, as it is experimentally observed.

Crystallinity was found however to decay steadily along the whole series as the content in Manx units increased, to the point that no discrete scattering could be detected for the homopolyester PManxS coming directly from synthesis. These observations are in full agreement with DSC results and reveal the depressing influence that the bicyclic structure has on crystallizability, which may be due to the opposite effect that it has on T_m and T_g. Increasing amounts of Manx led to polyesters with narrower crystallization window (T_m-T_g) and therefore exhibiting less crystallinity because the melt becomes frozen

Table 3. Powder X-ray Diffraction Data and Mechanical Properties

copolyester	d^a (Å)												X_c^b	elastic modulus (MPa)	tensile strength (MPa)	elongation at break (%)
PBS					4.5 m	4.1 m	3.9 s	3.4 w	3.1 w			2.6 w	0.52	351 ± 11	20 ± 2	19 ± 4
PB$_{95}$Manx$_5$					4.5 m	4.1 m	3.9 s	3.4 w	3.1 w			2.6 w	0.48	355 ± 13	22 ± 2	14 ± 3
PB$_{90}$Manx$_{10}$					4.5 m	4.1 m	3.9 s	3.4 w	3.1 w			2.6 w	0.45	372 ± 14	22 ± 2	9 ± 2
PB$_{80}$Manx$_{20}$					4.5 m	4.1 m	3.9 s	3.4 w	3.1 w			2.6 w	0.43	403 ± 15	24 ± 2	7 ± 3
PB$_{70}$Manx$_{30}$					4.5 m	4.1 m	3.9 s	3.4 w	3.1 w			2.6 w	0.37	428 ± 12	24 ± 3	5 ± 2
PB$_{50}$Manx$_{50}$	7.0 w	6.2 w	5.6 w	4.7 s	4.5 m	4.2 w	4.0 m	3.4 w	3.1 w	2.9 w	2.8 w		0.28	471 ± 15	26 ± 2	3 ± 1
PB$_{30}$Manx$_{70}$	7.0 w	6.2 w	5.6 w	4.7 s	4.5 m	4.2 w	4.0 m	3.4 w	3.1 w	2.9 w	2.8 w		0.17	515 ± 14	28 ± 3	2 ± 1
PManxS	(7.0 w)	(6.2 w)	(5.6 w)	(4.7 s)	(4.5 m)	(4.2 w)	(4.0 m)	(3.4 w)	(3.1 w)	(2.9 w)	(2.8 w)		(0.31)	573 ± 15	31 ± 3	2 ± 1

^{a}Bragg spacings measured in powder diffraction patterns. Intensities visually estimated as follows: m, medium; s, strong; w, weak. Data from samples coming directly from synthesis (without parentheses) and from PManxS film annealed for 1 h at 60 °C (in parentheses). ^{b}Crystallinity index calculated as the quotient between crystalline area and total area quantified in the X-ray diffraction profiles using the PeakFit v4.12 software.

before the chains can crystallize upon supercooling. Nevertheless, PManxS was able to crystallize by casting from a chloroform solution. After annealing the cast film showed a melting peak at 127 °C with an enthalpy of 21.5 J·g^{-1}, and produced a WAXS profile identical to those recorded from the enriched Manx copolyesters (Figure 5). These results suggest that rather than hampering the close side-by-side packing of the polyester chains required to form the crystal lattice, the main repressing effect of Manx on crystallization should be due to the restricted mobility that the presence of the bicyclic structure confers to the polyester chain. This is in full agreement with the high delay that is observed in the isothermal crystallization time of PB$_x$Manx$_y$S for slight rises in Manx contents, more than 10-fold for a 5% of increment in Manx (see below).

The cooling DSC traces obtained from molten samples revealed that PB$_x$Manx$_y$S copolyesters with molar contents in Manx below or equal to 10%, as well as PBS homopolyester, were able to crystallize from the melt. After crystallization upon cooling at a constant rate of 10 °C·min^{-1}, PBS homopolyester and PB$_{95}$Manx$_5$S copolyester recovered about 80−97% of their initial crystallinity and displayed almost the same melting temperatures. Conversely PB$_{90}$Manx$_{10}$S copolyester crystallized under such conditions recovering only 37% of its original crystallinity. However, it presented cold crystallization at the second heating run with recovering about 80% of the initially crystallized material, and melting at nearly the same initial temperature. Given the relevance of the ability for crystallizing from the melt regarding polymer processing, the isothermal crystallization of PB$_{95}$Manx$_5$S and PB$_{90}$Manx$_{10}$S copolyesters and PBS homopolyester was comparatively studied in the 70−100 °C interval. Unfortunately, not all of them could be compared at exactly the same crystallization temperature due to large differences in crystallization rates displayed by them; nevertheless, crystallization conditions were chosen as close as possible in order to be able to draw out meaningful conclusions. Avrami log$[-\ln(1 - X_c)]$ versus log$(t - t_0)$ data plots and the evolution of the relative crystallinity, X_c, versus crystallization time for some illustrative crystallization experiments are shown in Figure 6. Data afforded by the experiments carried out are gathered in Table 4, where the observed onset and half-crystallization times, as well as the corresponding calculated Avrami parameters, are given for each case. It is seen that for each copolyester the crystallization half-time as well as the Avrami exponent n increase with temperature, the values of the latter being in the 2.2−2.8 range corresponding to a complex axialitic-spherulitic crystallization as was observed by polarizing optical microscopy (illustrative pictures shown in the SI file). The double-logarithmic plot indicates that only primary crystallization takes place in the selected time intervals and that the presence of Manx units depresses the crystallizability in succinate copolyesters. The valuable conclusion that can be drawn from this study is that PB$_{95}$Manx$_5$S and PB$_{90}$Manx$_{10}$S copolyesters continue displaying the ability of crystallizing from the melt although at lower crystallization rates than their parent homopolyester PBS.

Mechanical tests and biodegradation essays of PManxS and PB$_x$Manx$_y$S copolyesters were performed on films prepared by casting from solution as described in the Experimental Section. For comparison purposes, PBS was tested as well. DSC analysis were also carried out on these films to evaluate if great differences regarding thermal properties exist between powdered and film samples. DSC data recorded for films showed that melting enthalpies from PBS and all PB$_x$Manx$_y$S
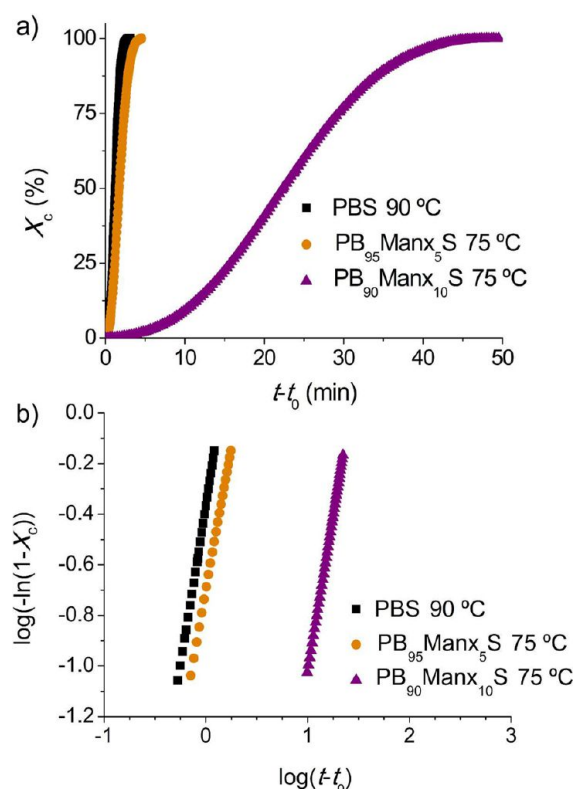
Figure 6. Isothermal crystallization of PBS, PB$_{95}$Manx$_5$S and PB$_{90}$Manx$_{10}$S at the indicated temperatures. Relative crystallinity versus time plot (a) and log−log plot (b).

Table 4. Isothermal Crystallization Data

copolyester	T_c (°C)	t_0 (min)	$t_{1/2}$ (min)	n	$-\log k$	T_m (°C)
PBS	90	0.17	1.37	2.44	0.37	111.9
	95	0.59	5.24	2.69	1.99	113.0
	100	0.95	20.33	2.76	3.73	113.8
PB$_{95}$Manx$_5$S	75	0.29	2.03	2.22	0.70	105.0
	80	0.53	4.82	2.65	1.85	105.9
PB$_{90}$Manx$_{10}$S	70	0.73	8.98	2.41	2.35	95.8
	75	1.21	23.54	2.46	3.48	96.6

films were slightly higher than those displayed by powdered samples coming directly from synthesis (Table 2), with values steadily decreasing with the increasing content of the copolyester in Manx units. On the contrary, no significant differences in melting temperature were observed between films and powdered samples. The case of PManxS deserves particular mention since it was amorphous when coming directly from synthesis but able to crystallize by casting. In fact, the DSC trace of the PManxS film showed a melting peak at 125 °C and a melting enthalpy of 14.0 J·g^{-1}, which is higher than those observed for films of PB$_{50}$Manx$_{50}$S and PB$_{30}$Manx$_{70}$S copolyesters. These results bring out the capability of the homopolyester to crystallize under conditions favoring chain mobility.

The stress−strain curves resulted from tensile essays are depicted in Figure 7, and the mechanical parameters measured in these tests are compared in Table 3. PManxS homopolyester displayed higher modulus and tensile strength than PBS and accordingly PB$_x$Manx$_y$S copolyesters present a nearly steady trend consisting of a continuous increase in both elastic modulus and tensile strength and a decrease in ductility when
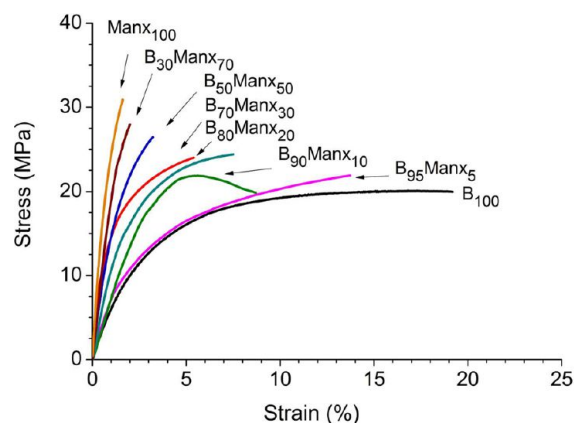
Figure 7. Stress–strain curves of PB_xManx_yS copolyesters.

their content in Manx units increase. This behavior is in full accordance with what should be expected from the trend observed for glass-transition temperatures along the polyester series. It should be noticed however that the molecular weight of polyesters decreases steadily with the Manx content along the series whereas chain stiffness increases. For a rigorous comparison of their mechanical properties, longer chain lengths would be required for stiffer polyesters in order to undergo comparable entanglement effects upon stretching. It is probable therefore that the differences observed in the mechanical parameters would become even greater if Manx-rich polyesters with higher molecular weights were used for this comparative study.

Biodegradation and Hydrolytic Degradation. To evaluate the effects that the incorporation of Manx units exerts on biodegradability and hydrolytic degradability of aliphatic polyesters, PManxS homopolyester and $PB_{70}Manx_{30}S$ copo-

lyester were incubated under a variety of conditions. For comparison purposes, PBS was also tested in parallel. First, they were incubated in pH 7.4 buffer at 37 °C, both in the presence and in the absence of porcine pancreas lipase. The changes taking place in sample weight and molecular weight of PBS, $PB_{70}Manx_{30}S$ and PManxS polyesters at increasing incubation times under these conditions are presented in Figure 8. Upon 8 weeks of incubation with enzymes, PManxS lost 32% of the initial weight, whereas the weight loss undergone by PBS was 24%. Under such conditions, $PB_{70}Manx_{30}S$ lost 29% of weight, a value intermediate between those observed for the two homopolyesters. Conversely, the weight losses observed for these polyesters when incubated in the absence of lipase was only between 10 and 15%. Accordingly, a slight decay in M_w and M_n was observed for the three polyesters when incubated without enzymes, whereas changes were much more noticeable in the presence of lipase. Melting enthalpies displayed by PBS, $PB_{70}Manx_{30}S$ and PManxS polyesters after incubation are compared in Figure 9. It was noteworthy to observe that crystallinity of the three polyesters increased as degradation proceeded, and that the raise in crystallinity was higher when samples were incubated in the presence of lipase. Such increase in crystallinity is indicative that hydrolysis has taken place preferably in the more permeable amorphous phase, as it is usually observed in semicrystalline polymers.

Selected SEM micrographs of PBS, $PB_{70}Manx_{30}S$ and PManxS polyesters before and after incubation are shown in Figure 10 and a wider selection is afforded in the SI material. This morphological analysis confirmed that the surface of the three polyesters displayed apparent physical alterations when they were incubated in the presence of lipase, whereas much less perceivable changes took place after incubation without enzymes. The conclusion derived from these observations is that degradation of PManxS and $PB_{70}Manx_{30}S$ polyesters under
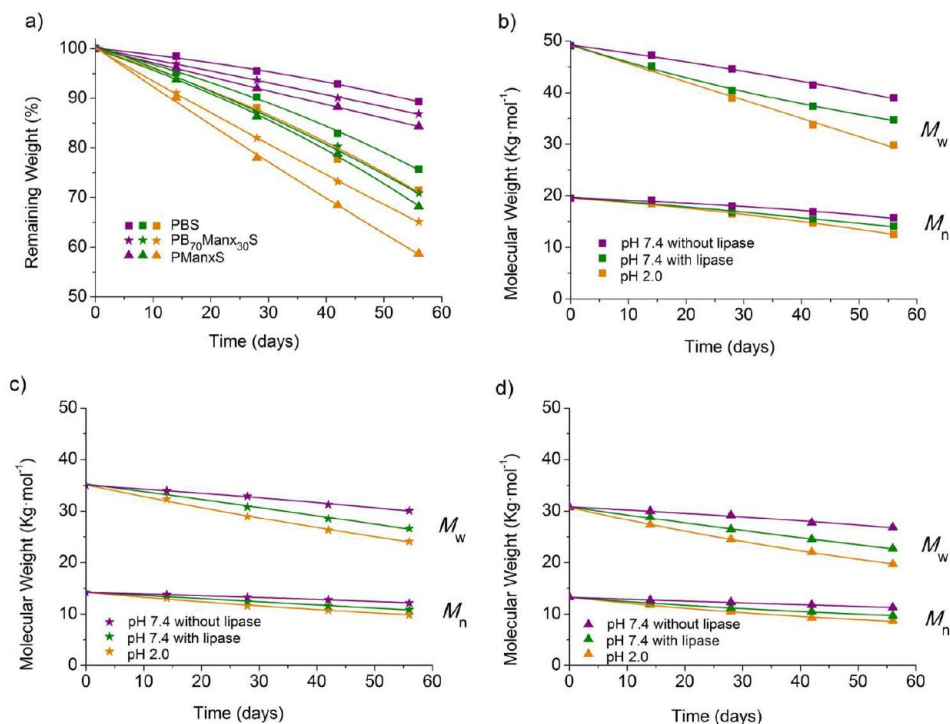
Figure 8. Degradation of PBS, $PB_{70}Manx_{30}S$ and PManxS at pH 2.0 (orange) and at pH 7.4 at 37 °C with (green) and without (purple) porcine pancreas lipase. Remaining weight (a) and molecular weight of PBS (b), $PB_{70}Manx_{30}S$ (c) and PManxS (d) versus degradation time.
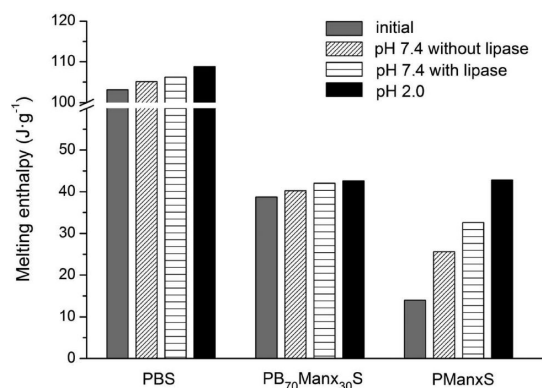
Figure 9. Melting enthalpies of PBS, PB$_{70}$Manx$_{30}$S and PManxS after 56 days of incubation and initial samples.

physiological conditions was clearly enhanced by the action of enzymes, a property that points to Manx as a potential comonomer for the preparation of biodegradable aliphatic polyesters.

To gain insight into the degradation of the polyester chain at the molecular level, PBS, PB$_{70}$Manx$_{30}$S and PManxS polyesters were incubated at 37 °C in aqueous buffer at pH 2.0. Under these conditions, the hydrolysis process will be speeded and the detailed analysis of both releasing fragments and residual polymer will be feasible within reasonable periods of time. Changes taking place in sample weight, M_w and M_n of the three polyesters upon hydrolysis are depicted in Figure 8. The weight losses undergone by PBS, PB$_{70}$Manx$_{30}$S and PManxS were 30–40% after 8 weeks of incubation. A substantial decrease in M_w and an increase in melting enthalpy were also observed under such conditions (Figure 9), and SEM analysis showed very apparent alterations in the surfaces of the three polyesters (see SI). According to the relatively greater changes observed in sample weight, molecular weight and morphology in these essays as compared to those observed at pH 7.4, it is concluded that the hydrolytic degradation of PB$_x$Manx$_y$S copolyesters and homopolyesters was boosted under acidic conditions.

^{1}H NMR spectra of the products released to the aqueous medium and the residual polymer resulting after 8 weeks of incubation in acidic water are depicted in Figure 11 and in the SI document. All the spectra recorded from the supernatant solution showed signals corresponding to succinic acid and soluble oligomers, in addition to either 1,4-butanediol or 2,4:3,5-di-*O*-methylene-D-mannitol signals for PBS and PManxS, respectively. On the contrary, and as it could be expected, signals of both diols were seen for the PB$_{70}$Manx$_{30}$S copolyester. The spectra recorded from the residue of the three cases displayed, in addition to the signals characteristic of the polymer, another one arising from CH$_2$OH end groups; this signal is indicative of the presence of reduced molecular weight fragments in full agreement with data provided by the GPC analysis. The NMR analysis of the residual polymer afforded in addition two remarkable indications: (a) A progressive decrease in the Manx to B ratio in the PB$_{70}$Manx$_{30}$S copolyester along the degradation process, which was estimated by integration of the corresponding NMR signals. (b) A full stability of the bicyclic structure against hydrolysis as it could be inferred from the total absence in the spectra of any signal indicative of hydrolysis of the acetal group.

NMR results have demonstrated therefore that PManxS and PB$_{70}$Manx$_{30}$S polyesters were degraded by water through splitting of the ester group, preferably through that involving the sugar diol, whereas the acetal group remained stable against hydrolysis. This result is really striking because acetals are known to be sensitive to acidic conditions[30] and the opening of the dioxane rings might be therefore expected to happen in some extend. To corroborate the stability of the bicyclic dioxane structure against hydrolysis observed in Manx containing copolyesters, compound 2,4:3,5-di-*O*-methylene-D-mannitol was incubated in aqueous buffer at pH 2.0, 7.4, and 10.5 for 12 weeks. The spectra recorded at the end of incubation period are shown in Figure 12; all correspond to the structure of the original diol without exhibiting any sign indicative of hydrolysis of the acetal group.

Main Features of PManxS Polyester. PManxS is a singular polyester since it is fully bio-based, is more stable to heating than PBS, displays a T_g comparable to aromatic polyesters and is semicrystalline. The chemical structure of PManxS is depicted in Scheme 2.

The onset decomposition temperature of PManxS is around 320 °C and its maximum decomposition rate happens at 413 °C, about 30 °C above that of PBS. It is able to crystallize by casting from solution showing a T_m = 125 °C. Its glass transition temperature is quite high (T_g = 68 °C), especially if
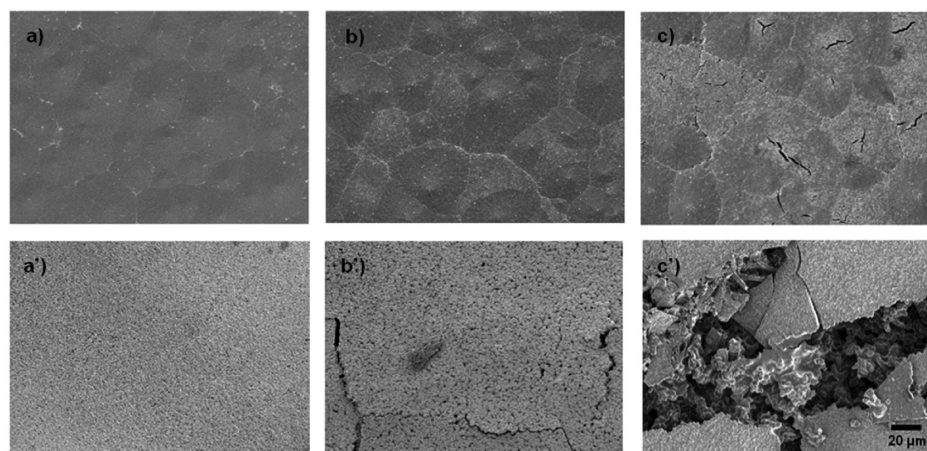
Figure 10. SEM micrographs of PB$_{70}$Manx$_{30}$S (top) and PManxS (bottom): Initial sample (a, a′). After incubation at pH 7.4 for 56 days without (b, b′) and with (c, c′) porcine pancreas lipase.
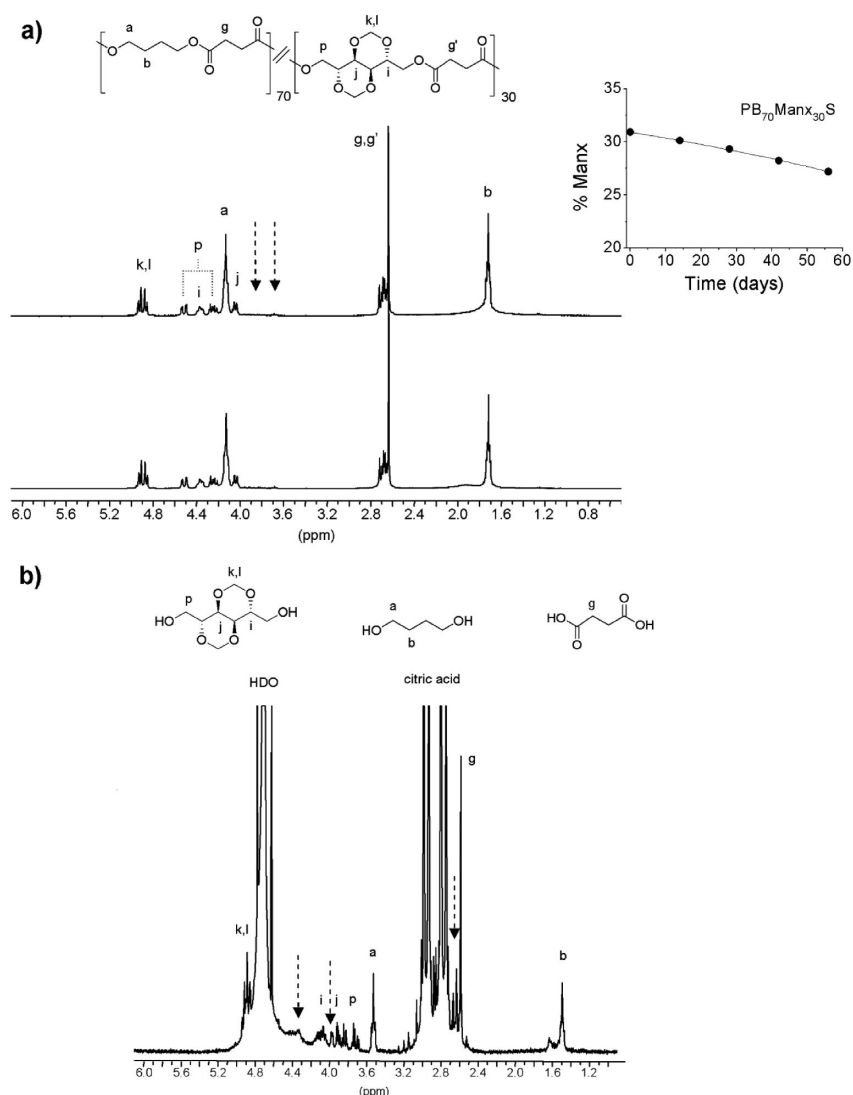
Figure 11. (a) Compared ^{1}H NMR spectra in CDCl$_3$ of PB$_{70}$Manx$_{30}$S after incubation at pH 2.0 for 56 days (top) and initial sample (bottom); the arrows indicate the signals arising from −CH$_2$OH end groups that appear upon hydrolysis of the main chain ester group. The evolution of the content in Manx units of the residual polyester along incubation time is represented on the right. (b) ^{1}H NMR spectrum in D$_2$O of the products released to the aqueous medium after incubation. The arrows indicate signals corresponding to oligomers generated upon hydrolysis of the main chain ester group.

compared with that of PBS (T_g = −37 °C). As expected from the bicyclic structure of the Manx unit, the T_g of PManxS is higher than that of the polyesters made from 1,4-butanediol and the cyclic diacids 2,3-O-isopropylidene-L-tartrate[13] and 2,5-furandicarboxylic acid,[17] whose T_g values are −9 and 45 °C, respectively. Since the two rings of Manx are fused, the T_g of PManxS is even higher than that of the polyester made from 1,4-butanediol and the bicyclic nonfused dimethyl 2,3:4,5-di-O-methylene-galactarate[31] (T_g = 18 °C); in fact, it is much higher than that of the polyester made from 1,4-butanediol and bicyclic fused isoidide dicarboxylic acid[23] (T_g = 0 °C). Regarding 1,4:3,6-dianhydrohexitols, the T_g reported for the polyester from succinic acid and isomannide[21] (T_g = 75 °C) is very close to that of PManxS, whereas T_g values ranging from 36 to 68 °C have been reported for polyesters obtained from succinic acid and isosorbide.[20−22] The main advantage of PManxS over polysuccinates made from dianhydrohexitols is that, having nearly the same T_g, it is obtained more easily by melt polycondensation. PManxS is a biodegradable polyester

which exhibits a sensitivity to the action of lipases comparable to the commonly used PBS. PManxS is degraded through splitting of the relatively weak ester group and without alteration of the diacetal group forming part of the carbohydrate-based Manx unit.

The renewable origin of PManxS polyester, its good thermal stability, its biodegradability, and its relatively high glass-transition temperature make it a bio-based polyester of exceptional interest as an potential alternative to PBS in those applications where thermal and mechanical properties are matters of utmost importance.

■ CONCLUSIONS

Fully and partially bio-based aliphatic polyesters have been obtained from the bicyclic carbohydrate-based diol 2,4:3,5-di-O-methylene-D-mannitol (Manx) and succinic acid. The synthesis of the homopolyester PManxS was carried out by polycondensation in the melt to imitate as closely as possible the conditions usually applied in the industry, and using DBTO
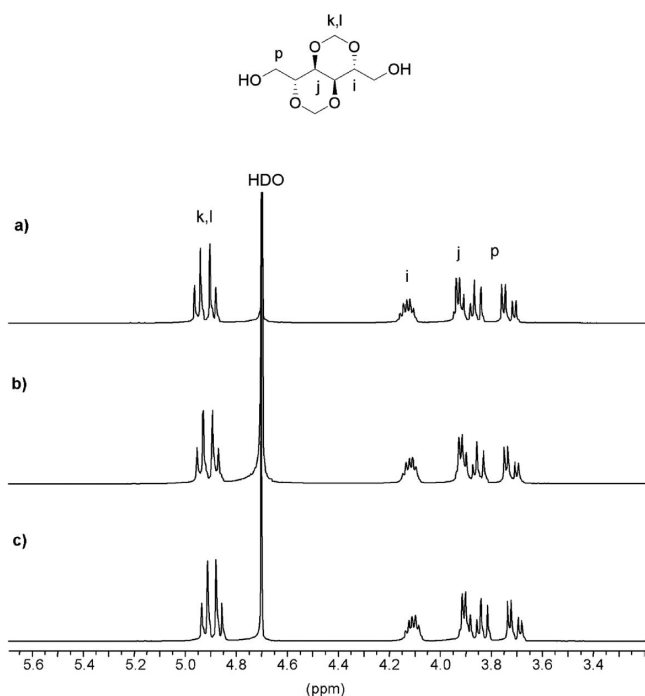
Figure 12. ^{1}H NMR spectra in D$_2$O of 2,4:3,5-di-*O*-methylene-D-mannitol after incubation for 90 days at pH 2.0 (a), 7.4 (b) and 10.5 (c).

Scheme 2. Chemical Structure of PManxS (left) and PBS (right) Polyesters
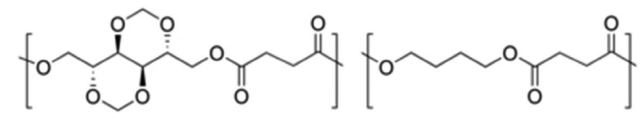
as catalyst. This novel polyester melts at 127 °C and its T_g is 68 °C, which is more than 100 °C higher than the T_g of PBS and comparable to those displayed by aliphatic polyesters obtained from 1,4:3,6-dianhydrohexitols; the advantage of PManxS is that it can be obtained more easily and with higher molecular weight by melt polycondensation. The higher reactivity of primary hydroxyl groups of the diol Manx compared to the secondary ones of 1,4:3,6-dianhydrohexitols is responsible for such benefit. PB$_x$Manx$_y$S copolyesters made from Manx, 1,4-butanediol and dimethyl succinate were semicrystalline with melting temperatures lower than that of the parent homopolyester PBS. Since the thermal stability increases with the content in Manx, a wider range of temperatures between melting and decomposition exists in these copolyesters. Their T_g and, consequently, their elastic modulus and tensile strength increased with the content in Manx units. Hydrolytic degradation of Manx containing polyesters happened through hydrolysis of the main chain ester group without modification of the diacetal structure. Degradation of both PManxS and the copolyester PB$_{70}$Manx$_{30}$S under physiological conditions was clearly favored by the action of enzymes. This exploratory study of Manx containing polyesters and copolyesters points to 2,4:3,5-di-*O*-methylene-D-mannitol as a potential comonomer for obtaining biodegradable aliphatic polyesters with enhanced T_g.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
COSY and HETCOR spectra of PManxS; compared ^{1}H NMR spectra of PB$_x$Manx$_y$S. ^{13}C NMR spectra of PBS, PManxS and PB$_{70}$Manx$_{30}$S; compared polarizing optical micrographs and crystallization rate plots of PBS, PB$_{95}$Manx$_5$S and PB$_{90}$Manx$_{10}$S; compared SEM micrographs of PBS, PManxS and PB$_{70}$Manx$_{30}$S along degradation; ^{1}H NMR spectra of PBS and PManxS along degradation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Engelberg, I.; Kohn, J. *Biomaterials* **1991**, *12*, 292−304.
(2) Okada, M. *Prog. Polym. Sci.* **2002**, *27*, 87−133.
(3) Albertsson, A. C.; Varma, I. K. *Adv. Polym. Sci.* **2002**, *157*, 1−40.
(4) Nair, L. S.; Laurencin, C. T. *Prog. Polym. Sci.* **2007**, *32*, 762−798.
(5) Wang, H. Y.; Xu, M.; Wu, Z. W.; Zhang, W.; Ji, J. H.; Chu, P. K. *ACS Appl. Mater. Interfaces* **2012**, *4*, 4380−4386.
(6) Coutinho, D. F.; Gomes, M. E.; Neves, N. M.; Reis, R. L. *Acta Biomater.* **2012**, *8*, 1490−1497.
(7) Papageorgiou, G. Z.; Bikiaris, D. N. *Biomacromolecules* **2007**, *8*, 2437−2449.
(8) Gualandi, C.; Soccio, M.; Saino, E.; Focarete, M. L.; Lotti, N.; Munari, A.; Moroni, L.; Visai, L. *Soft Matter* **2012**, *8*, 5466−5476.
(9) Li, W. D.; Zeng, J. B.; Lou, X. J.; Zhang, J. J.; Wang, Y. Z. *Polym. Chem.* **2012**, *3*, 1344−1353.
(10) Deng, L. M.; Wang, Y. Z.; Yang, K. K.; Wang, X. L.; Zhou, Q.; Ding, S. D. *Acta Mater.* **2004**, *52*, 5871−5878.
(11) Gandini, A. *Green Chem.* **2011**, *13*, 1061−1083.
(12) Galbis, J. A.; García-Martín, M. G. *Top. Curr. Chem.* **2010**, *295*, 147−176.
(13) Dhamaniya, S.; Jacob, J. *Polymer* **2010**, *51*, 5392−5399.
(14) Dhamaniya, S.; Jacob, J. *Polym. Bull.* **2012**, *68*, 1287−1304.
(15) Gomes, M.; Gandini, A.; Silvestre, A. J. D.; Reis, B. *J. Polym. Sci., Polym. Chem.* **2011**, *49*, 3759−3768.
(16) Gandini, A.; Coelho, D.; Gomes, M.; Reis, M.; Silvestre, A. J. D. *J. Mater. Chem.* **2009**, *19*, 8656−8664.
(17) Wu, L.; Mincheva, R.; Xu, Y.; Raquez, J. M.; Dubois, P. *Biomacromolecules* **2012**, *13*, 2973−2981.
(18) Fenouillot, F.; Rousseau, A.; Colomines, G.; Saint-Loup, R.; Pascault, J. P. *Prog. Polym. Sci.* **2010**, *35*, 578−622.
(19) Braun, D.; Bergmann, M. *J. Prakt. Chem.* **1992**, *334*, 298−310.
(20) Noordover, B. A. J.; van Staalduinen, V. G.; Duchateau, R.; Koning, C. E.; van Benthem, R. A. T. M.; Mak, M.; Heise, A.; Frissen, A. E.; van Haveren, J. *Biomacromolecules* **2006**, *7*, 3406−3416.
(21) Okada, M.; Okada, Y.; Tao, A.; Aoi, K. *J. Appl. Polym. Sci.* **1996**, *62*, 2257−2265.
(22) Okada, M.; Tsunoda, K.; Tachikawa, K.; Aoi, K. *J. Appl. Polym. Sci.* **2000**, *77*, 338−346.
(23) Wu, J.; Eduard, P.; Thiyagarajan, S.; Jasinska-Walc, L.; Rozanski, A.; Fonseca Guerra, C.; Noordover, B. A. J.; van Haveren, J.; van Es, D. S.; Koning, C. E. *Macromolecules* **2012**, *45*, 5069−5080.

(24) Fradet, A.; Tessier, M. Polyesters. In *Synthetic Methods in Step-Growth Polymers*; Rogers, M. E., Long, T. E., Eds.; Wiley: Hoboken, NJ, 2003; pp 17−134.

(25) Lavilla, C.; Alla, A.; Martínez de Ilarduya, A.; Benito, E.; García-Martín, M. G.; Galbis, J. A.; Muñoz-Guerra, S. *Biomacromolecules* **2011**, *12*, 2642−2652.

(26) Lavilla, C.; Alla, A.; Martínez de Ilarduya, A.; Benito, E.; García-Martín, M. G.; Galbis, J. A.; Muñoz-Guerra, S. *J. Polym. Sci., Polym. Chem.* **2012**, *50*, 1591−1604.

(27) Lavilla, C.; Martínez de Ilarduya, A.; Alla, A.; García-Martín, M. G.; Galbis, J. A.; Muñoz-Guerra, S. *Macromolecules* **2012**, *45*, 8257−8266.

(28) Lavilla, C.; Muñoz-Guerra, S. *Green Chem.* **2013**, *15*, 144−151.

(29) Ihn, K. J.; Yoo, E. S.; Im, S. S. *Macromolecules* **1995**, *28*, 2460−2464.

(30) Smith, M. B.; March, J. *March's Advanced Organic Chemistry*; Wiley-Interscience: Hoboken, NJ, 2007; pp 523, 1270.

(31) (a) Lavilla, C.; Alla, A.; Martínez de Ilarduya, A.; Benito, E.; García-Martín, M. G.; Galbis, J. A.; Muñoz-Guerra, S. *Polymer* **2012**, *53*, 3432−3445. (b) Lavilla, C.; Muñoz-Guerra, S. *Polym. Degrad. Stab.* **2012**, *97*, 1762−1771.