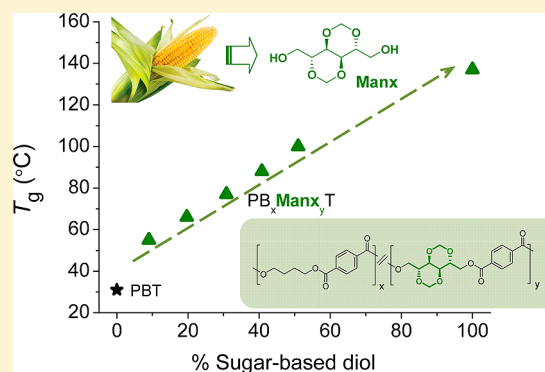


Bio-Based Aromatic Polyesters from a Novel Bicyclic Diol Derived from D-Mannitol

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S Supporting Information

ABSTRACT: 2,4:3,5-Di-O-methylene-D-mannitol, abbreviated as Manx, is a D-mannitol-derived compound with the secondary hydroxyl groups acetalized with formaldehyde. The bicyclic structure of Manx consists of two fused 1,3-dioxane rings, with two primary hydroxyl groups standing free for reaction. A homopolymer made of Manx and dimethyl terephthalate as well as a set of copolymers of poly(butylene terephthalate) (PBT) in which 1,4-butanediol was replaced by Manx up to 50% were synthesized and characterized. The polyesters had M_w in the 30 000–52 000 g mol⁻¹ range and a random microstructure and were thermally stable up to nearly 370 °C. They displayed outstanding high T_g with values from 55 to 137 °C which steadily increased with the content in Manx. Copolymers containing up to 40% of Manx were semicrystalline and adopted the crystal structure of PBT. Their stress-strain parameters were sensitively affected by the presence of carbohydrate-based units with elongation at break decreasing but tensile strength and elastic moduli steadily increasing with the degree of replacement.



INTRODUCTION

Bio-based polymers are nowadays attracting a great deal of interest, not only for their potential to reduce the utilization of petrochemicals but also for increasing the added-value of agriculture products and wastes.^{1–4} Carbohydrates constitute an interesting renewable source for being used as polymer building blocks; they are the most abundant type of biomass feedstock, and they are found in a very rich variety of structures displaying great stereochemical diversity. However, they possess an excess of functional groups that upon polycondensation would lead to undesirable cross-linking reactions unless special precautions are taken. Although some linear polyesters have been synthesized using carbohydrate-based monomers bearing free hydroxyl groups,^{5,6} most syntheses have been carried out with derivatives in which the exceeding functional groups have been appropriately protected.^{7–10}

Among carbohydrate-derived monomers, those with a cyclic structure have achieved a privileged position because, in addition to their natural origin, they are able to provide polycondensates with improved properties, especially those related to polymer chain stiffness, as it is the case of the glass transition temperature. A high T_g is nowadays a greatly appreciated property in polyesters that are addressed to packaging under heating or to the manufacture of containers for pressurized gaseous beverages. Thus, 2,5-furandicarboxylic acid has been reported as a potential alternative to replace terephthalic acid for the preparation of aromatic polyesters based on renewable sources.^{11,12} 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 and other less accessible dianhydrohexitols derivatives are receiving recently a great deal of attention as building blocks for the synthesis of aromatic copolymers with increased T_g .^{13–15} The two hydroxyl groups of isosorbide are secondary, and due to their different spatial position in the molecule, they display different reactivity. These features seriously hamper the polycondensation reaction in the melt, so isosorbide polyesters obtained by this method display rather limited molecular weights.^{16,17} Another type of carbohydrate-based bicyclic monomer is that obtained by internal acetalization, which has been shown to be very suitable to prepare polyesters by polycondensation in the melt since they are able to react at a rate similar to that of other acyclic conventional monomers.^{18–20}

In this work we present a new bicyclic carbohydrate-based monomer useful for the preparation of linear polycondensates. 2,4:3,5-Di-O-methylene-D-mannitol, abbreviated as Manx, is a D-mannitol-derived compound with the secondary hydroxyl groups acetalized with formaldehyde. A set of copolymers of poly(butylene terephthalate) (PBT) in which the 1,4-butanediol has been replaced by Manx have been synthesized

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and characterized. PBT is a well-known thermoplastic aromatic polyester, with a melting temperature near 225 °C and a glass transition temperature around 30 °C, which is used in a wide variety of engineering applications.²¹ Nevertheless, despite being innocuous for humans, PBT and other aromatic polyesters are considered not to be environmentally friendly materials due to their nonrenewable origin.²² In this work special attention is paid to study the effect of the introduction of renewable Manx on the glass transition temperature, thermal stability, and crystallizability of the resulting PBT copolyesters because of the relevance that these properties have not only for the technical use of PBT but also for the potential application that this novel carbohydrate-based monomer may have in the synthesis of other polycondensates. Contrary to isosorbide, the two hydroxyl groups of Manx remaining free for reaction are primary, and since Manx possess a 2-fold axis of symmetry, they display the same reactivity. Moreover, the use of Manx as polycondensation monomer leads to regioregular polymer chains, provided that it is made to react with nondirectional monomers.

EXPERIMENTAL SECTION

Materials. The reagents D-mannitol (ACS reagent grade), benzoyl chloride (99+%), paraformaldehyde (95%), 1,4-butanediol (99%), and dimethyl terephthalate (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. ¹H and ¹³C 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 either deuterated chloroform, deuterated dimethyl sulfoxide, or a mixture of deuterated chloroform and trifluoroacetic acid (9:1), and spectra were internally referenced to tetramethylsilane (TMS). About 10 and 50 mg of sample dissolved in 1 mL of solvent were used for ¹H and ¹³C NMR, respectively. Sixty-four scans were acquired for ¹H and 1000–10 000 for ¹³C with 32K and 64K data points as well as relaxation delays of 1 and 2 s, respectively. For conformational studies ¹H NMR spectra were recorded from 60 to –60 °C in the NMR spectrometer equipped with a variable-temperature unit. Temperatures were selected at 20 °C interval. For each temperature the sample was held for 10 min to reach thermal equilibrium. 2D NOE spectrum (NOESY) was recorded at a fixed temperature ($T = 298.1$ K) with a standard pulse sequence (noesytp) with a mixing time of 2 s over a sweep width of 1397 Hz using 2048 data points in the t_2 dimension and 256 increments in the t_1 dimension. The repetition delay was 2 s, and 256 scans were collected for each t_1 increment. ¹H NMR simulated spectra were obtained with SpinWorks 3.1.8 program (Kirk Marat, University of Manitoba). Intrinsic viscosities of polymers dissolved in dichloroacetic acid were measured in an Ubbelohde viscosimeter thermostated at 25.0 ± 0.1 °C. Gel permeation chromatograms were acquired at 35.0 °C using a Waters equipment provided with a refraction index detector. The samples were chromatographed with 0.05 M sodium trifluoroacetate–hexafluoroisopropanol (NaTFA–HFIP) using a polystyrene–divinylbenzene packed linear column 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 PerkinElmer 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 250 °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 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 PerkinElmer TGA 6 equipment. Sample weights of about 10–15 mg were used in these experiments. Films for mechanical testing measurements were prepared with a thickness of ~200 μm by casting from solution (100 g L⁻¹) in either chloroform or a mixture of chloroform and hexafluoroisopropanol (5:1); 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 at 23 °C on a Zwick 2.5/TNIS testing machine coupled with a compressor Dalbe DR 150. X-ray diffraction patterns were recorded on the PANalytical X'Pert PRO MPD θ/θ diffractometer using the Cu K α radiation of wavelength 0.1542 nm from powdered samples coming directly from synthesis.

Monomer Synthesis. *1,6-Di-O-benzoyl-D-mannitol.* A solution of 28.1 g of benzoyl chloride (200 mmol) in dry pyridine (70 mL) was added dropwise to a dispersion of 36.4 g of D-mannitol (200 mmol) in 70 mL of dry pyridine. The mixture was stirred at room temperature for 5 h and then poured into ice–water. The precipitated solid was filtered, washed with cold water and with chloroform, dried, and recrystallized from ethanol. Yield: 36%; mp 189–193 °C [lit.²³ 188–192 °C]. ¹H NMR (300.1 MHz, DMSO), δ (ppm): 8.1 (m, 4H, *o*-ArH), 7.6 (m, 2H, *p*-ArH), 7.5 (m, 4H, *m*-ArH), 5.1 (bs, 2H, OH), 4.7–4.3 (m, 6H, OCH₂, OH), 3.9 (m, 2H, CH₂CHOH), 3.7 (d, 2H, CH₂CHOHCHOH). ¹³C NMR (75.5 MHz, DMSO), δ (ppm): 166.0 (CO), 133.1, 130.1, 129.3, 128.6, 69.1, 68.3, 67.7.

1,6-Di-O-benzoyl-2,4:3,5-di-O-methylene-D-mannitol. To a mixture of 28.0 g of 1,6-di-O-benzoyl-D-mannitol (72 mmol) and 28.0 g of paraformaldehyde (930 mmol), 22 mL of sulfuric acid 96% was added dropwise, and the mixture was stirred for 3 h at room temperature. The reaction mixture was then repeatedly extracted with chloroform. The combined organic layers were washed with ammonia (12% w/w) and water and dried over anhydrous sodium sulfate. The solution was evaporated to a solid residue, which was recrystallized from ethanol. Yield: 52%; mp 121–122 °C [lit.²⁴ 121 °C]. ¹H NMR (300.1 MHz, CDCl₃), δ (ppm): 8.1 (m, 4H, *o*-ArH), 7.6 (m, 2H, *p*-ArH), 7.4 (m, 4H, *m*-ArH), 5.0–4.8 (dd, 4H, OCH₂O), 4.8–4.3 (m, 4H, COOCH₂), 4.4 (m, 2H, OCH₂CH), 4.2 (m, 2H, OCH₂CHCH). ¹³C NMR (75.5 MHz, CDCl₃), δ (ppm): 166.3 (CO), 133.2, 129.7, 129.6, 128.4, 88.5, 71.1, 66.7, 63.7.

2,4:3,5-Di-O-methylene-D-mannitol. A dispersion of 15.5 g of 1,6-di-O-benzoyl-2,4:3,5-di-O-methylene-D-mannitol (37 mmol) in 200 mL of dry methanol was stirred overnight with a small piece of sodium. The solution was treated with cation exchange resin, the resin was filtered, and the filtrate was concentrated to dryness. The resulting semisolid residue was washed with diethyl ether and recrystallized from ethanol. Yield: 72%; mp 139–140 °C [lit.²⁵ 139 °C]. ¹H NMR (300.1 MHz, CDCl₃), δ (ppm): 5.0–4.8 (dd, 4H, OCH₂O), 4.2 (m, 2H, HOCH₂CH), 4.1 (m, 2H, HOCH₂CHCH), 4.0–3.7 (m, 4H, HOCH₂), 1.9 (bs, 2H, OH). ¹³C NMR (75.5 MHz, CDCl₃), δ (ppm): 87.2, 73.5, 65.8, 59.6.

Polymer Synthesis. PB_xMan_yT copolyesters were obtained from a mixture of 1,4-butanediol, 2,4:3,5-di-O-methylene-D-mannitol, and dimethyl terephthalate with the selected composition. PBT and PManxT homopolyesters were obtained by reacting dimethyl terephthalate with 1,4-butanediol and 2,4:3,5-di-O-methylene-D-mannitol, respectively. 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 terephthalate 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 or in a mixture of chloroform and trifluoroacetic acid (9:1) 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.

PBT Homopolyester. 60% molar excess of 1,4-butanediol to dimethyl terephthalate. Transesterification reactions at 180 °C for 1 h, at 200 °C for 1 h, and at 240 °C for 0.5 h under a low nitrogen flow. Polycondensation reactions at 260 °C for 2 h under a 0.03–0.06 mbar vacuum. ^1H NMR (300.1 MHz, CDCl_3/TFA), δ (ppm): 8.13 (s, 4H, ArH), 4.50 (t, 4H OCH_2CH_2), 2.02 (t, 4H, OCH_2CH_2). ^{13}C NMR (75.5 MHz, CDCl_3/TFA), δ (ppm): 168.0 (CO), 133.7, 129.9, 66.2, 25.1.

PManxT Homopolyester. 5% molar excess of 2,4:3,5-di-*O*-methylene-*D*-mannitol to dimethyl terephthalate. Transesterification reactions at 160 °C for 1 h and at 180 °C for 2 h under a low nitrogen flow. Polycondensation reactions at 180 °C for 5 h under a 0.03–0.06 mbar vacuum. ^1H NMR (300.1 MHz, CDCl_3/TFA), δ (ppm): 8.1 (s, 4H, Ar-H), 5.2–5.0 (m, 4H, OCH_2O), 4.9–4.5 (m, 4H, OCH_2CH), 4.7 (m, 2H, OCH_2CH), 4.3 (m, 2H, OCH_2CHCH). ^{13}C NMR (75.5 MHz, CDCl_3/TFA), δ (ppm): 167.5 (CO), 133.5, 130.3, 88.6, 71.4, 66.7, 64.4.

$PB_x\text{Man}_y\text{T}$ Copolyesters. The copolyesters were obtained by a similar procedure, with polymerization conditions slightly differing for each composition feed.

$PB_{90}\text{Man}_{10}\text{T}$ and $PB_{80}\text{Man}_{20}\text{T}$. 5% molar excess of the diol mixture to dimethyl terephthalate. Transesterification reactions at 160 °C for 1 h, at 200 °C for 1 h, and at 240 °C for 0.5 h under a low nitrogen flow. Polycondensation reactions at 240 °C for 2.5 h under a 0.03–0.06 mbar vacuum.

$PB_{70}\text{Man}_{30}\text{T}$. 5% molar excess of the diol mixture to dimethyl terephthalate. Transesterification reactions at 160 °C for 1 h, at 200 °C for 1 h, and at 230 °C for 0.5 h under a low nitrogen flow. Polycondensation reactions at 230 °C for 3 h under a 0.03–0.06 mbar vacuum.

$PB_{60}\text{Man}_{40}\text{T}$. 5% molar excess of the diol mixture to dimethyl terephthalate. Transesterification reactions at 160 °C for 1 h, at 200 °C for 1 h, and at 220 °C for 0.5 h under a low nitrogen flow. Polycondensation reactions at 220 °C for 3.5 h under a 0.03–0.06 mbar vacuum.

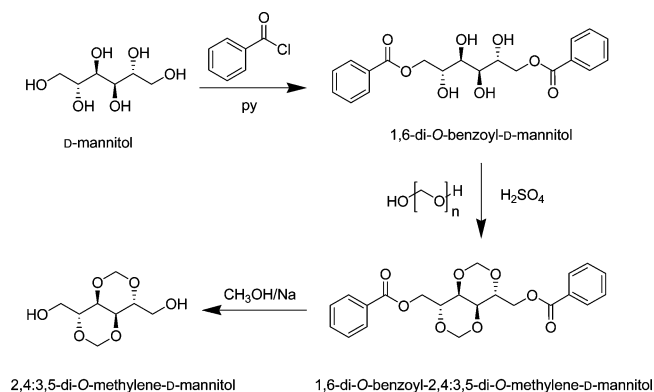
$PB_{50}\text{Man}_{50}\text{T}$. 5% molar excess of the diol mixture to dimethyl terephthalate. Transesterification reactions at 160 °C for 1 h, at 200 °C for 1 h, and at 210 °C for 0.5 h under a low nitrogen flow. Polycondensation reactions at 210 °C for 4 h under a 0.03–0.06 mbar vacuum.

NMR Characterization of $PB_x\text{Man}_y\text{T}$ Copolyesters. ^1H NMR (300.1 MHz, CDCl_3/TFA), δ (ppm): 8.1 (s, 4H, Ar-H), 5.2–5.0 (m, γ -4H, OCH_2O), 4.9–4.5 (m, γ -4H, OCH_2CH), 4.7 (m, γ -2H, OCH_2CH), 4.5 (t, α -4H, OCH_2CH_2), 4.3 (m, γ -2H, OCH_2CHCH), 2.0 (t, α -4H, OCH_2CH_2). ^{13}C NMR (75.5 MHz, CDCl_3/TFA), δ (ppm): 168.3 (CO), 167.5 (CO), 134.2–133.3, 130.4, 130.2, 88.6, 71.4, 66.7, 66.5, 64.4, 25.4.

RESULTS AND DISCUSSION

Monomer Synthesis and Conformation. The bicyclic diol 2,4:3,5-di-*O*-methylene-*D*-mannitol (Manx) was prepared from *D*-mannitol following the chemical synthetic route depicted in Scheme 1. Primary hydroxyl groups of *D*-mannitol were first protected as benzoyl esters, and then the addition of paraformaldehyde led to cyclic acetalization of the secondary hydroxyl groups in the 2,4:3,5 arrangement with the two fused 1,3-dioxane rings. ^1H and ^{13}C NMR spectra of Manx are shown

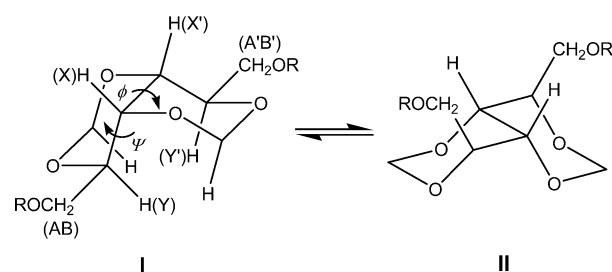
Scheme 1. Synthesis of 2,4:3,5-Di-*O*-methylene-*D*-mannitol



in the Supporting Information and detailed in the Experimental Section. The coupling between the two protons of the methylene acetalic group with a $J = -6.2$ Hz confirms the presence of the two fused six-membered rings and then the 2,4:3,5 arrangement of the bicyclic structure.²⁶ It should be stressed that the synthesis route used for the preparation of Manx, although effective for the purpose of the work, is not environmentally friendly. Obviously, an alternative synthetic route or an improvement of the existing one will need to be developed to make this monomer of fully practical use and to render benefits to the environment.

This bicyclic diol Manx possesses a 2-fold axis of symmetry, and therefore its two hydroxyl groups will display the same reactivity in the polycondensation reaction producing regioregular polymer chains. Since the two rings are fused, a fairly high degree of rigidity should be in principle expected for Manx although it could be largely relieved if interconversion between possible conformers takes place. The rigidity of the monomer is critical for the preparation of polymers with improved thermal and mechanical properties. To appraise the effect that this novel diol monomer will have on the stiffness of the polyesters thence produced, a conformational analysis of 1,6-di-*O*-benzoyl-2,4:3,5-di-*O*-methylene-*D*-mannitol was undertaken. This diester is an adequate model compound for aromatic polyesters and copolyesters made from Manx. The two most probable conformations²⁷ for the 2,4:3,5-di-*O*-methylene-*D*-manno bicyclic structure are depicted in Scheme 2. In order to assess the

Scheme 2. Preferential Conformers of 1,6-Di-*O*-benzoyl-2,4:3,5-di-*O*-methylene-*D*-mannitol



relative preference of Manx for these two conformations, a variable temperature ^1H NMR study was carried out in the +60 to –60 °C range, and 2D-NOESY spectra were recorded at room temperature. In the case that I and II conformers were present, two signals for each proton should appear in the ^1H NMR spectra at low temperatures since no interconversion is

expected to take place under such conditions. On the contrary, single proton signals were observed along the whole interval and the only detected change was an upfield shift of the signals with heating (see Supporting Information). It can be concluded therefore that no conformational interconversion occurs and that only one conformer is present along the whole range of temperatures. The analysis of the coupling constants of the ^1H NMR spectra suggested that conformer I is the preferred one for Manx. In fact, NMR spin simulation using the SpinWorks 3 program provided the spin–spin coupling constants (see Supporting Information) for the ABXY'X'A'B' system, in which small long-range couplings between Y and X' protons were detected. The calculated coupling constants were

$$\begin{aligned} J_{AB} &= J_{A'B'} = -11.98 \text{ Hz}; & J_{AY} &= J_{A'Y'} = 2.91 \text{ Hz}; \\ J_{BY} &= J_{B'Y'} = 6.71 \text{ Hz}; & J_{YY'} &= J_{Y'Y} = 5.3 \text{ Hz}; \\ J_{YX} &= J_{Y'X'} = 8.60 \text{ Hz}; & J_{YX'} &= J_{Y'X} = -0.58 \text{ Hz} \end{aligned}$$

Applying these coupling constants to the Karplus equation derived for alditols,^{28,29} the torsional angles Ψ and Φ could be estimated. The values obtained were 160° and 48° , respectively, which are very close to the angles measured for conformer I but very far from those of conformer II.

The identity of conformer I as the preferred one was strongly supported by 2D NOESY spectrum (Figure 1). As expected for

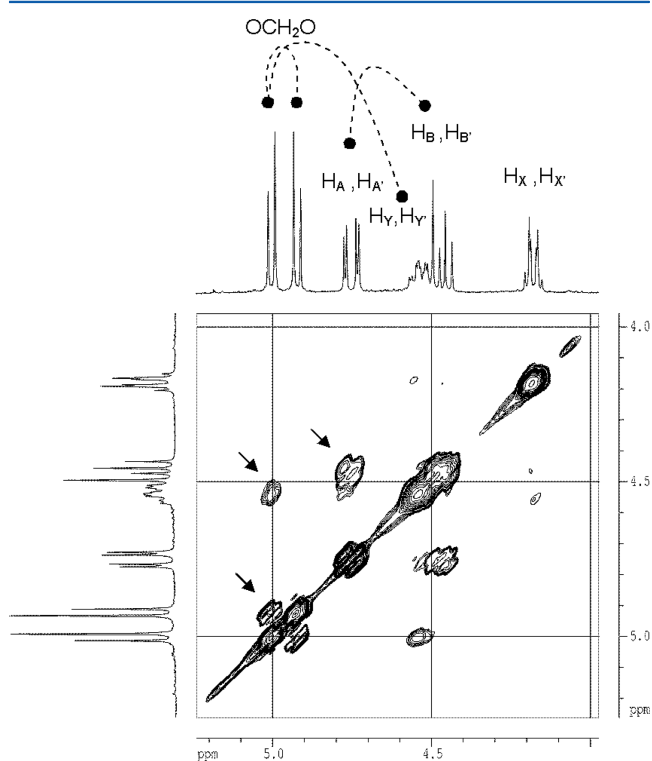


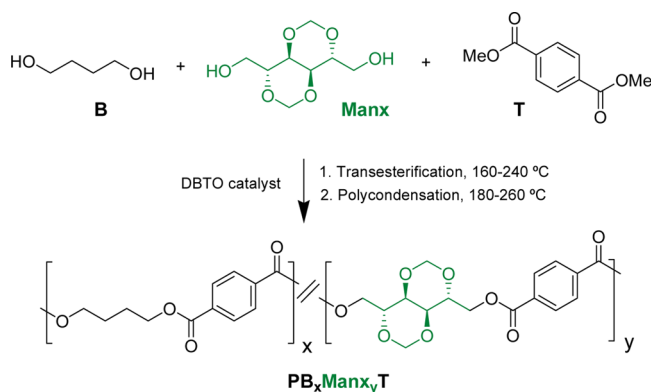
Figure 1. 2D NOESY spectrum of 1,6-di-O-benzoyl-2,4:3,5-di-O-methylene-D-mannitol. Small arrows indicate NOE signals.

conformation I, strong NOE signals were detected for H_Y and one of the acetal methylene protons, whereas no NOE signals were observed for H_X . In conformation II the short distances between H_X and one of the protons of the acetal methylene should be reflected in the 2D spectra with strong NOE signals, which is not the case. It is worthy to note that crystal structure studies on 2,4:3,5-di-O-methylene-D-mannitol-1,6-di-*trans*-cin-

namate³⁰ established a conformation in the solid state for the bicyclic unit similar to which is determined in this work. The conclusion derived from this conformational study is that the preferred conformation of Manx is I and that this conformation is well stable; such features will confer to this monomer an enhancing stiffness effect on the polymer chain in which it is inserted.

Polymer Synthesis and Chemical Structure. The polymerizations involving 2,4:3,5-di-O-methylene-D-mannitol were carried out in the total absence of solvents to imitate as far as possible the conditions usually applied in the industrial practice. PManxT homopolymer, from 2,4:3,5-di-O-methylene-D-mannitol and dimethyl terephthalate, as well as $\text{PB}_x\text{Man}_y\text{T}$ copolyesters from 2,4:3,5-di-O-methylene-D-mannitol, 1,4-butanediol, and dimethyl terephthalate, were prepared by a two-step melt-polycondensation process using DBTO as catalyst (Scheme 3). For comparison purposes, the parent PBT

Scheme 3. Polymerization Reactions Leading to $\text{PB}_x\text{Man}_y\text{T}$ Copolyesters



homopolymer was obtained from 1,4-butanediol and dimethyl terephthalate using the same polycondensation procedure. In the preparation of $\text{PB}_x\text{Man}_y\text{T}$ copolyesters, the incorporation of the diols into the copolyesters was accurately controlled by using a 5% molar excess of the diol mixture to dimethyl terephthalate and by initiating transesterification reactions at mild temperature to prevent volatilization of diols. Temperature was progressively increased to avoid crystallization of oligomers, and polycondensation reactions were performed at temperatures between 210 and 240 °C and under vacuum to facilitate the removal of volatile byproducts; lower temperatures and longer reaction times were used in copolyesters with higher contents in Manx to minimize the decomposition of this sugar compound. When polymerizations were ended, the reaction mixtures were dissolved either in chloroform or in a mixture of chloroform and trifluoroacetic acid and precipitated in methanol to obtain the polymers in yields close to 85–90%. The synthesis results obtained for sugar-based PManxT homopolymer and $\text{PB}_x\text{Man}_y\text{T}$ copolyesters are gathered in Table 1 together with data for the parent PBT homopolymer.

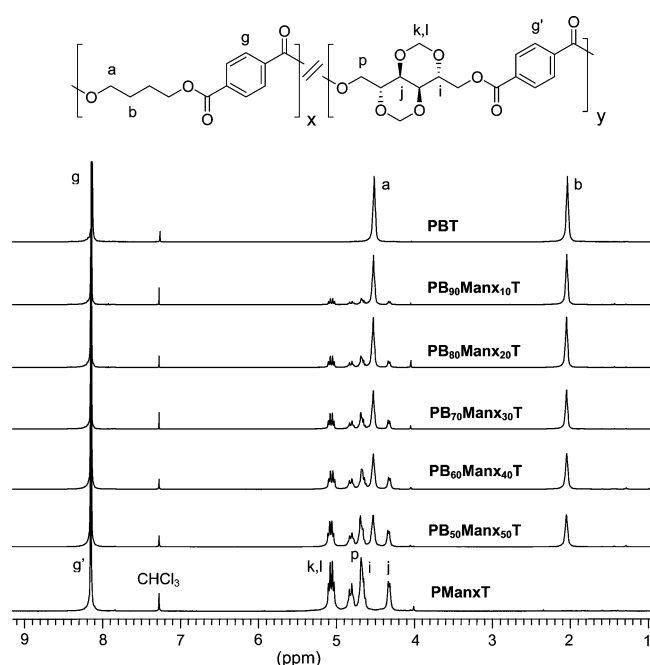
The precipitated $\text{PB}_x\text{Man}_y\text{T}$ copolyesters were obtained with intrinsic viscosities between 0.8 and 1.2 dL g⁻¹, weight-average molecular weights confined in the 38 000–52 000 g mol⁻¹ interval, and dispersities in the 2.3–2.5 range. Molecular weights of $\text{PB}_x\text{Man}_y\text{T}$ copolyesters slightly decay with the content in Manx, in accordance with the values observed for PManxT homopolymer. The GPC analysis of the reaction product (without being subjected to any treatment) afforded

Table 1. Molar Composition, Molecular Weight, and Microstructure of PB_xManx_yT Copolyesters

copolyester	yield (%)	molar composition					microstructure									
		feed		copolyester ^a		[η] ^b	molecular weight			dyads			number-average sequence lengths		randomness ^d	
		X _B	X _{Manx}	X _B	X _{Manx}		M _n ^c	M _w ^c	D ^c	BB	BManx/ManxB	ManxManx	n _B	n _{Manx}		R
PBT	90	100	0	100	0	0.93	17 100 (11 800)	41 300 (40 500)	2.4 (3.4)							
PB ₉₀ Manx ₁₀ T	86	90	10	91.0	9.0	1.18	20 300 (14 200)	51 200 (50 800)	2.5 (3.6)	75.6	21.7	2.7	8.0	1.3	0.92	
PB ₈₀ Manx ₂₀ T	87	80	20	80.3	19.7	0.84	16 500 (11 500)	41 000 (40 200)	2.5 (3.5)	59.9	34.0	6.1	4.5	1.4	0.96	
PB ₇₀ Manx ₃₀ T	86	70	30	69.2	30.8	0.75	16 600 (10 400)	38 500 (37 900)	2.3 (3.6)	44.9	44.0	11.1	3.0	1.5	0.99	
PB ₆₀ Manx ₄₀ T	85	60	40	59.2	40.8	0.83	16 400 (11 600)	40 100 (39 800)	2.4 (3.4)	35.0	47.8	17.2	2.5	1.7	0.99	
PB ₅₀ Manx ₅₀ T	88	50	50	49.0	51.0	0.77	16 300 (10 900)	38 900 (38 400)	2.4 (3.5)	23.1	48.4	28.5	2.0	2.2	0.97	
PManxT	85	0	100	0	100	0.51	12 900 (8100)	30 200 (29 300)	2.3 (3.6)							

^aMolar composition determined by integration of the ¹H NMR spectra. ^bIntrinsic viscosity in dL g⁻¹ measured in dichloroacetic acid at 25 °C. ^cNumber- and weight-average molecular weights in g mol⁻¹ and dispersities measured by GPC in HFIP against PMMA standards after (without parentheses) and before purification (in parentheses). ^dRandomness index of copolyesters statistically calculated on the basis of the ¹³C NMR analysis.

weight-average molecular weights very close to those obtained for the precipitated product but with significantly higher dispersities. Such differences indicate the presence of minor amounts of oligomeric fractions or remaining monomers in the raw product that were then removed by precipitation. The ¹H NMR spectra corroborated the chemical structure of the copolyesters with all signals being correctly assigned to the different protons contained in their repeating units (Figure 2). Integration of the proton signals arising from B and Manx units led to quantify the composition of the copolyesters in such units. Data provided by this analysis are given in Table 1,

Figure 2. Compared ¹H NMR spectra of PB_xManx_yT copolyesters.

showing that all copolyesters had compositions very close to those of their corresponding feeds.

The microstructure of PB_xManx_yT copolyesters was determined by ¹³C NMR analysis. The signals of all the magnetically different carbons contained in the repeating units of the copolyesters appear well resolved in the ¹³C NMR spectra (see Supporting Information) and in particular those arising from the nonprotonated aromatic carbons, which come out to be sensitive to sequence effects at the dyad level. As shown in Figure 3 for the whole set of PB_xManx_yT copolyesters, each resonance of the nonprotonated aromatic carbons appears split so that four peaks are seen in the 133–135 ppm chemical shift interval corresponding to the three types of dyads (BB, BManx and ManxB, ManxManx) that are feasible along the copolyester chain. 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 at random in all cases.

Thermal Properties. 2,4:3,5-Di-O-methylene-D-mannitol is a thermally fairly stable solid compound which starts to volatilize above 150 °C and displays a sublimation temperature of 280 °C without perceivable decomposition. The thermal stability of PManxT homopolyester and PB_xManx_yT copolyesters made from this compound was evaluated by thermogravimetry under inert atmosphere and compared with that displayed by PBT. TGA traces are depicted in Figure 4, and thermal data provided by this analysis are presented in Table 2. The weight loss profiles generated reveal that all polyesters start to decompose well above 360 °C with a thermal degradation mechanism involving one main step with the maximum rate at temperatures steadily increasing with the content in Manx units. The same trend is observed for ^oT_{5%} and these results are in accordance with the high thermal stability observed for PManxT homopolyester, with ^oT_{5%} and ^{max}T_d at 378 and 421 °C, respectively. The valuable conclusion drawn from this

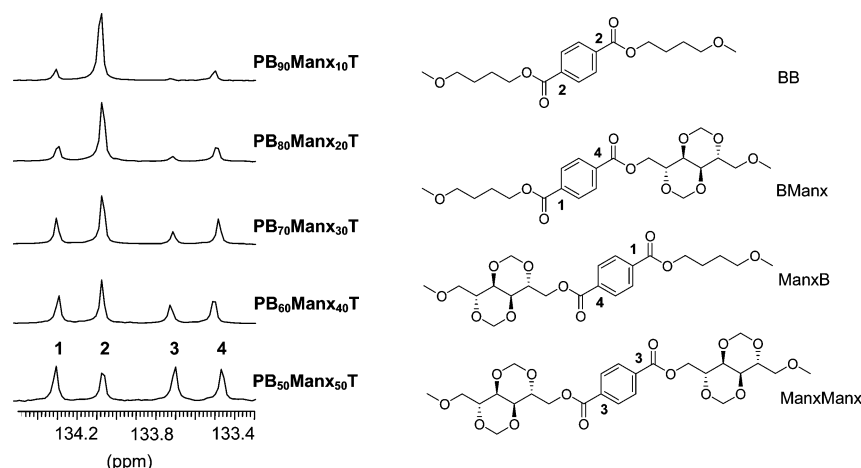


Figure 3. ^{13}C NMR signals used for the microstructure analysis of $\text{PB}_x\text{Manx}_y\text{T}$ copolyesters with indication of the dyads to which they are assigned.

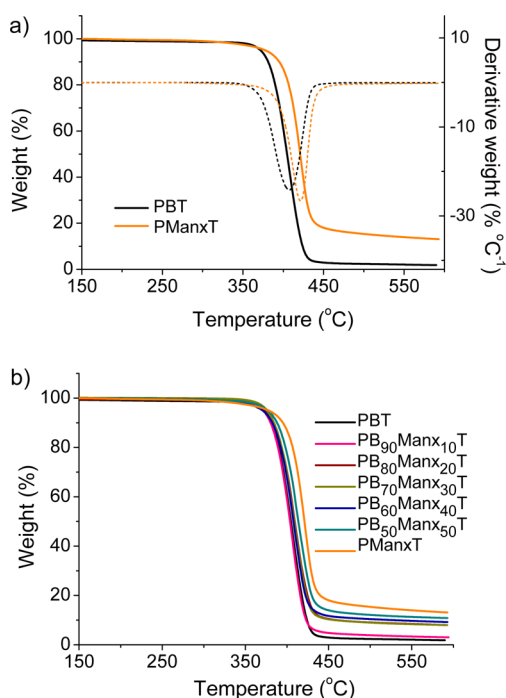


Figure 4. (a) TGA traces (solid lines) and derivative curves (dashed lines) of PBT and PManxT homopolyesters. (b) TGA traces of $\text{PB}_x\text{Manx}_y\text{T}$ copolyesters.

thermogravimetric study is that the insertion of Manx units in aromatic polyesters instead of reducing their thermal stability contributes to a significant increase in their decomposition temperatures. The fact of improving the thermal stability of commonly used aromatic polyesters such as PBT can broaden even more the application window of these materials.

Other thermal properties of prime importance in connection with the potential application of these copolyesters are the glass transition temperature (T_g) and the melting temperature (T_m). For instance, an increase in the T_g of these polyesters could open their use in the hot-filled and pasteurized-container fields. The glass transition temperatures of the PManxT and PBT homopolyesters and $\text{PB}_x\text{Manx}_y\text{T}$ copolyesters were measured as the inflection point of the heating DSC traces of samples quenched from the melt (Figure 6a). A remarkable feature of PManxT homopolyester is that it has a T_g more than 100 °C

higher than the aromatic PBT homopolyester. Regarding $\text{PB}_x\text{Manx}_y\text{T}$ copolyesters, their T_g increase steadily with the content in Manx units, with minimum and maximum values corresponding to their respective PBT and PManxT homopolyesters (Figure 5), as should be expected from their statistical microstructure. As expected from its cyclic stiff nature, the effect of Manx on T_g of PBT is largely greater than that exerted by the incorporation of acyclic sugar units such as trimethoxy xylitol or L-arabinitol.³¹ It has even a much more pronounced effect than 2,3:4,5-di-O-methylene-galactitol, another acetalized sugar diol constituted by two nonfused dioxolane rings, which has been recently reported by us as capable of raising the T_g of PBT by near 30 °C when it replaces 1,4-butanediol in a 40%.²⁰ The effect of Manx turns to be similar to that of isosorbide; in fact, both PBT copolyesters containing 40% of either Manx or isosorbide^{14,16} display a T_g of around 90 °C. No doubt the fused bicyclic structure characteristic of both Manx and isosorbide is unique in providing the polyester chain with a degree of stiffness not achievable with the insertion of rotatable bicyclic units, as it is the case of the acetalized hexitol with galacto configuration.

DSC traces of polyesters in the powdered form registered at first heating are depicted in Figure 6b. $\text{PB}_x\text{Manx}_y\text{T}$ copolyesters with molar contents in Manx below or equal to 40%, as well as PBT homopolyester, gave heating traces with melting endotherms indicating that they are semicrystalline. Comparison of melting temperatures and enthalpies of semicrystalline $\text{PB}_x\text{Manx}_y\text{T}$ copolyesters with that of PBT homopolyester leads to the conclusion that the insertion of Manx units gives place to a significant decrease in both T_m and ΔH_m (Table 2). $\text{PB}_{50}\text{Manx}_{50}\text{T}$ copolyester and PManxT homopolyester appear to be amorphous. DSC data recorded from polyester films prepared by casting from solution are not far from those obtained from powders, the higher coincidence being found for lower contents in Manx units.

Isothermal Crystallization. The cooling DSC traces obtained from molten samples revealed that $\text{PB}_x\text{Manx}_y\text{T}$ copolyesters with molar contents in Manx below or equal to 20%, as well as PBT homopolyester were able to crystallize from the melt. After crystallization from the melt, these polyesters recovered about 75–95% of their initial crystallinity and displayed almost the same melting temperatures. Given the relevance of this property regarding polymer processing, the isothermal crystallization of $\text{PB}_{90}\text{Manx}_{10}\text{T}$ and $\text{PB}_{80}\text{Manx}_{20}\text{T}$

Table 2. Thermal Properties of PB_xMan_xT Copolyesters

copolyester	TGA				DSC					
	$T_{5\%}^a$ (°C)	T_d^b (°C)	W^c (%)	T_g^d (°C)	first heating ^e		cooling ^e		second heating ^e	
					T_m (°C)	ΔH_m (J g ⁻¹)	T_c (°C)	ΔH_c (J g ⁻¹)	T_m (°C)	ΔH_m (J g ⁻¹)
PBT	371	408	2	31	223 (223)	56.2 (54.3)	196	43.3	223	44.0
PB ₉₀ Man ₁₀ T	371	408	3	55	197 (196)	34.1 (33.0)	159	30.4	198	31.3
PB ₈₀ Man ₂₀ T	372	410	8	66	184 (183)	26.0 (27.0)	140	23.4	184	24.1
PB ₇₀ Man ₃₀ T	374	411	8	77	162 (162)	5.5 (16.6)				
PB ₆₀ Man ₄₀ T	376	411	9	88	122 (119)	5.0 (9.8)				
PB ₅₀ Man ₅₀ T	377	412	11	100						
PManxT	378	421	13	137						

^aTemperature at which 5% weight loss was observed. ^bTemperature for maximum degradation rate. ^cRemaining weight at 600 °C. ^dGlass-transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 °C min⁻¹. ^eMelting (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 precipitated samples (without parentheses) and of films (in parentheses).

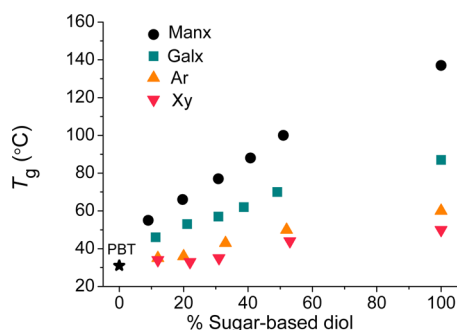


Figure 5. Glass-transition temperature versus composition plot for PBT copolyesters containing 2,4:3,5-di-*O*-methylene-*D*-mannitol (Manx), 2,3:4,5-di-*O*-methylene-galactitol (Galx),²⁰ 2,3,4-tri-*O*-methyl-L-arabinitol (Ar), or 2,3,4-tri-*O*-methylxylylitol (Xy).³¹

copolyesters and PBT homopolymer was comparatively studied in the 150–210 °C interval. Unfortunately, not all of them could be compared at exactly the same isothermal crystallization temperature due to the large differences in crystallization rates displayed by them and to the short ranges of temperature in which crystallization evolution is measurable by DSC. Nevertheless, crystallization conditions were chosen as close as possible in order to be able to draw out meaningful conclusions. The Hoffman–Weeks plot of T_m versus T_c showed a good correlation (see Supporting Information) and provided the equilibrium melting temperatures, which, as expected, continue to display the same trend with composition as was observed for the T_m measured for nonisothermally crystallized samples.

Kinetic data afforded by the Avrami analysis of the results obtained at the selected crystallization temperatures are gathered in Table 3. The evolution of the relative crystallinity, X_c , with crystallization time and the corresponding Avrami data plots $\log[-\ln(1 - X_c)]$ versus $\log(t - t_0)$ for some illustrative crystallization experiments are depicted in Figure 7. The morphological appearance of the crystallized material observed by polarized optical microscopy is shown in the Supporting Information. It is seen that for each polyester the crystallization half-time as well as the Avrami exponent n increase with

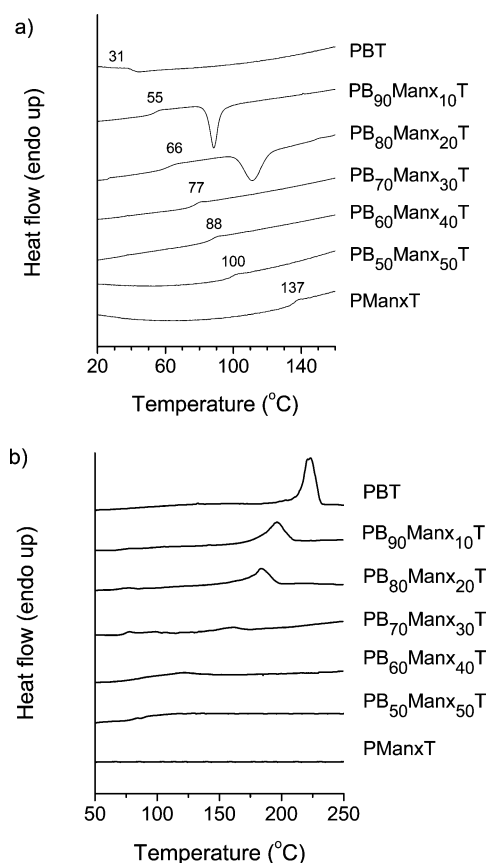
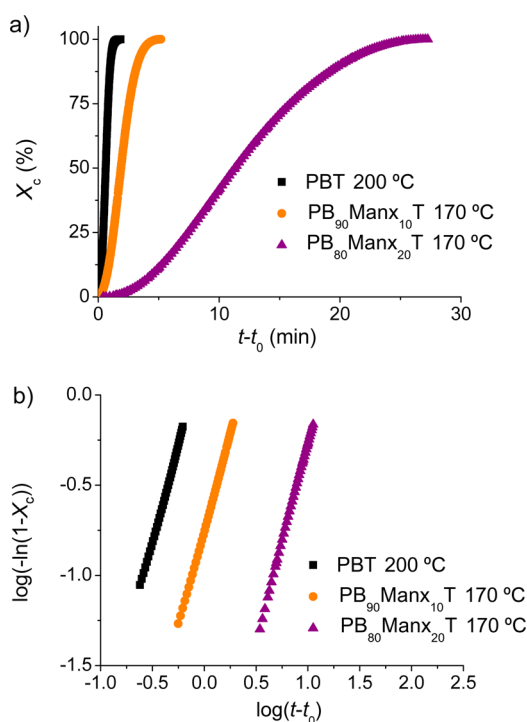


Figure 6. (a) DSC heating traces of PB_xMan_xT copolyesters quenched from the melt. (b) DSC melting traces of the PB_xMan_xT copolyesters without being subjected to any thermal treatment.

temperature, the values of the latter being in the 2.0–2.6 range corresponding to a complex axialitic–spherulitic crystallization as was observed by polarizing optical microscopy. 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 terephthalate copolyesters. The valuable conclusion that can be drawn from

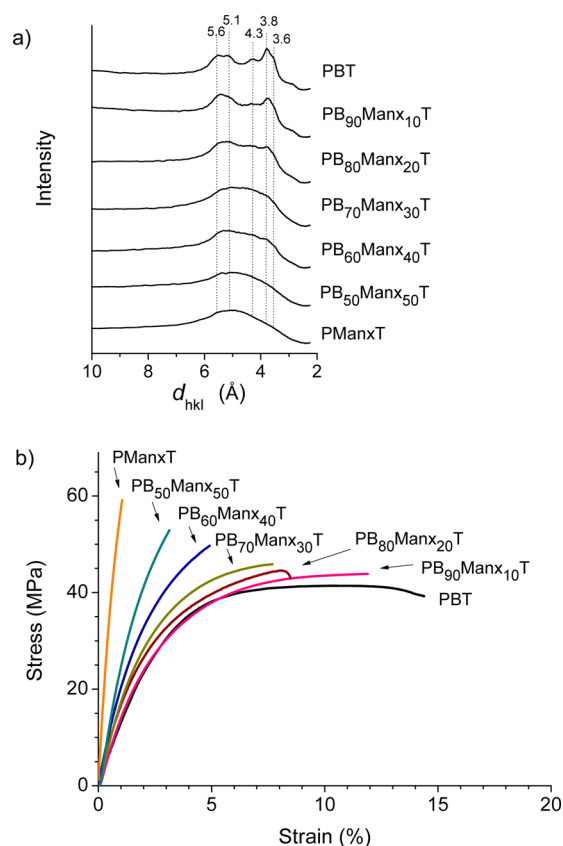
Table 3. Isothermal Crystallization Data of PB_xManx_yT Copolyesters

copolyester	T_c (°C)	t_0 (min)	$t_{1/2}$ (min)	n	$-\log k$	T_m (°C)
PBT	200	0.19	0.82	2.14	-0.25	223.9
	205	0.51	2.68	2.45	1.02	225.5
	210	2.33	12.83	2.56	2.78	226.9
PB ₉₀ Manx ₁₀ T	165	0.15	1.13	2.01	0.15	194.5
	170	0.26	2.14	2.12	0.75	196.3
	175	0.31	4.37	2.43	1.64	198.0
	180	0.59	8.53	2.52	2.42	199.8
	185	1.93	19.43	2.57	3.34	202.1
PB ₈₀ Manx ₂₀ T	150	0.19	1.61	2.02	0.56	184.1
	155	0.23	2.45	2.04	0.93	185.3
	160	0.29	3.50	2.07	1.26	186.9
	165	0.44	5.60	2.13	1.74	188.8
	170	0.98	11.85	2.20	2.46	190.5

**Figure 7.** Isothermal crystallization of PBT, PB₉₀Manx₁₀T, and PB₈₀Manx₂₀T at the indicated temperatures. Relative crystallinity versus time plot (a) and log–log plot (b).

this study is that PB₉₀Manx₁₀T and PB₈₀Manx₂₀T copolyesters continue displaying the ability of crystallizing from the melt as their parent homopolymer PBT although at lower crystallization rates.

Crystal Structure and Stress–Strain Behavior. Powder X-ray diffraction analyses were performed for all PB_xManx_yT copolyesters as well as PManxT and PBT homopolymers. Powder X-ray diffraction profiles are presented in Figure 8a, and Bragg spacings present in such patterns are listed in Table 4. In agreement with DSC results, copolyesters containing up to 40% of Manx produced discrete diffraction scattering distinctive of semicrystalline material, whereas fully plain profiles characteristic of amorphous material were obtained from PB₅₀Manx₅₀T as well as from the PManxT homopolymer. The PBT pattern is characterized by five prominent reflections at 5.6, 5.1, 4.3, 3.8, and 3.6 Å. Essentially the same pattern

**Figure 8.** Powder WAXS profiles (a) and stress–strain curves (b) of PB_xManx_yT copolyesters.

regarding both spacing and relative intensities is shared by PB_xManx_yT copolyesters with low content in Manx, revealing that the triclinic crystal structure of PBT³² must be retained in polyesters. The crystallinity index was estimated as the quotient between crystalline area and total area of the X-ray diffraction pattern, showing that PB₉₀Manx₁₀T, PB₈₀Manx₂₀T, PB₇₀Manx₃₀T, and PB₆₀Manx₄₀T were semicrystalline with crystalline indexes decreasing for increasing contents in Manx units. However, PB₅₀Manx₅₀T copolyester and PManxT copolyester did not show any discrete reflection characteristic of crystalline material. These X-ray diffraction results are in full agreement with DSC results and confirmed that PB_xManx_yT copolyesters with molar contents in Manx below or equal to 40% are semicrystalline.

To evaluate the influence of the presence of Manx in the mechanical properties of copolyesters, tensile assays of PManxT copolyester as well as PB_xManx_yT copolyesters were carried out using the films that were prepared by casting as described in the Experimental Section. For comparison purposes, mechanical properties of PBT were also tested. According to enthalpy values (Table 2), the degree of crystallinity of these films must be close to that displayed by powders with X_c steadily decreasing with the increasing content of the copolyester in Manx units to become 0 for PB₅₀Manx₅₀T and PManxT (Table 4). The stress–strain curves resulting from tensile assays are depicted in Figure 8b, and the mechanical parameters measured in these tests are compared in Table 4. PManxT homopolymer displayed higher elastic modulus and tensile strength than PBT, and accordingly PB_xManx_yT copolyesters present a nearly steady trend consisting of a continuous increase in both elastic modulus and tensile strength and a decrease in ductility when

Table 4. Powder X-ray Diffraction Data and Mechanical Properties of PB_xMan_xT Copolyesters

copolyester	X-ray diffraction data						mechanical properties		
	d^a (Å)						X_c^b	elastic modulus (MPa)	tensile strength (MPa)
PBT	5.6 s	5.1 s	4.3 s	3.8 s	3.6 m	0.48			
PB ₉₀ Man ₁₀ T	5.6 s	5.1 s	4.3 m	3.8 s	3.6 m	0.39	852 ± 13	44 ± 6	12 ± 3
PB ₈₀ Man ₂₀ T	5.6 m	5.1 m	4.3 m	3.8 m	3.6 w	0.32	871 ± 25	45 ± 7	9 ± 2
PB ₇₀ Man ₃₀ T	5.6 w	5.1 w	4.3 w	3.8 w	3.6 w	0.11	888 ± 17	46 ± 5	8 ± 3
PB ₆₀ Man ₄₀ T	5.6 w	5.1 w	4.3 w	3.8 w	3.6 w	0.10	891 ± 19	50 ± 7	5 ± 2
PB ₅₀ Man ₅₀ T						0	909 ± 26	52 ± 5	3 ± 1
PManxT						0	1067 ± 29	59 ± 6	2 ± 1

^aBragg spacings measured in powder diffraction patterns for samples coming directly from synthesis. Intensities visually estimated as follows: m, medium; s, strong; w, weak. ^bCrystallinity index calculated as the quotient between crystalline area and total area. Crystalline and amorphous areas in the X-ray diffraction pattern were quantified using PeakFit v4.12 software.

their content in Manx units increases. The observed variations in the stress–strain behavior are fully consistent with the changes in T_g . Apparently, the mechanical moduli of these copolyesters are mainly determined by the mobility of the chains in the amorphous phase rather than by the structural stiffness induced by the presence of crystalline domains.

CONCLUSIONS

For the first time, polyesters from the biobased 2,4:3,5-di-*O*-methylene-*D*-mannitol monomer, obtained by internal acetalization of the secondary hydroxyl groups of *D*-mannitol, have been successfully synthesized. By taking special care of polycondensation conditions, polyesters and statistical copolyesters with pretty high molecular weights were obtained in good yields. The incorporation of the sugar derived diol improved appreciably the thermal stability of the resulting polyesters. The most remarkable effect of copolymerization was however noticed on the glass-transition temperature which increased with the content in 2,4:3,5-di-*O*-methylene-*D*-mannitol almost linearly with a slope of about of 1 °C/% mol, allowing fine-tuning of T_g of PBT over a wide range. Consequently, the mechanical moduli of the copolyesters also increased significantly in the same sense. Although copolymerization depressed the crystallinity and crystallizability of PBT, those copolyesters containing up to 40% of sugar based units were semicrystalline and adopted the crystal structure of PBT, and those containing up to 20% were able to crystallize from the melt. The 50/50 copolyester and the polyester entirely made of Manx units were amorphous, at least under the crystallization conditions used in this work. The bicyclic sugar-based diol investigated in this work as monomer for polycondensation stands out not only for being a sustainable compound but also for providing polyesters with satisfactory molecular weights and with improved thermal and mechanical properties; nevertheless, the synthesis of this compound will need to be improved in order to make it simpler and to avoid the use of environmentally unfriendly reagents.

ASSOCIATED CONTENT

Supporting Information

Additional figures (Figures 1–7). 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.

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REFERENCES

- (1) Wool, R.; Sun, S. *Biobased Polymers and Composites*; Academic Press: New York, 2005.
- (2) Pillai, C. K. S. *Des. Monomers Polym.* **2010**, *13*, 87–121.
- (3) Gandini, A. *Green Chem.* **2011**, *13*, 1061–1083.
- (4) Chen, G. Q.; Patel, M. K. *Chem. Rev.* **2012**, *112*, 2082–2099.
- (5) Kiely, D. E.; Chen, L.; Lin, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 571–578.
- (6) Kiely, D. E.; Chen, L.; Lin, T. H. *J. Polym. Sci., Polym. Chem.* **2000**, *38*, 594–603.
- (7) Okada, M. *Prog. Polym. Sci.* **2002**, *27*, 87–133.
- (8) Metzke, M.; Guan, Z. *Biomacromolecules* **2008**, *9*, 208–215.
- (9) Williams, C. K. *Chem. Soc. Rev.* **2007**, *36*, 1573–1580.
- (10) Kricheldorf, H. R. *J. Macromol. Sci.* **1997**, *C37*, 599–631.
- (11) Gandini, A.; Coelho, D.; Gomes, M.; Reis, B.; Silvestre, A. J. D. *J. Mater. Chem.* **2009**, *19*, 8656–8664.
- (12) Gomes, M.; Gandini, A.; Silvestre, A. J. D.; Reis, B. *J. Polym. Sci., Polym. Chem.* **2011**, *49*, 3759–3768.
- (13) Fenouillot, F.; Rousseau, A.; Colomines, G.; Saint-Loup, R.; Pascault, J. P. *Prog. Polym. Sci.* **2010**, *35*, 578–622.
- (14) Sablong, R.; Duchateau, R.; Koning, C. E.; de Wit, G.; van Es, D.; Koelewijn, R.; van Haveren, J. *Biomacromolecules* **2008**, *9*, 3090–3097.
- (15) 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.
- (16) Kricheldorf, H. R.; Behnken, G.; Sell, M. *J. Macromol. Sci., Pure Appl. Chem.* **2007**, *44*, 679–684.
- (17) Storbeck, R.; Ballauff, M. *J. Appl. Polym. Sci.* **1996**, *59*, 1199–1202.
- (18) 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.
- (19) 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.
- (20) 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.
- (21) Gallucci, R. R.; Patel, B. R. Poly(Butylene Terephthalate). In Scheirs, J.; Long, T. E., Eds.; *Modern Polyesters, Chemistry and*

Technology of Polyesters and Copolyesters; John Wiley & Sons: Chichester, 2004; pp 293–321.

(22) Tripathy, A. R.; MacKnight, W. J.; Kukureka, S. N. *Macromolecules* **2004**, *37*, 6793–6800.

(23) Brigl, P.; Gruner, H. *Ber* **1932**, *65B*, 641–645.

(24) Haworth, W. N.; Wiggins, L. F. *J. Chem. Soc.* **1944**, 58–61.

(25) Haskins, W. T.; Hann, R. M.; Hudson, C. S. *J. Am. Chem. Soc.* **1943**, *65*, 67–70.

(26) Burden, I. J.; Stoddart, J. F. *J. Chem. Soc., Perkin Trans. 1* **1975**, *7*, 666–674.

(27) Mills, J. A. *Adv. Carbohydr. Chem.* **1955**, *10*, 1–53.

(28) Franks, F.; Dadok, J.; Ying, S.; Kay, R. L.; Grigera, J. R. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 579–585.

(29) Jardetzky, O.; Roberts, G. C. K. *Molecular Biology*; Academic Press: New York, 1981; p 201.

(30) Bernstein, J.; Green, B. S.; Rejtö, M. *J. Am. Chem. Soc.* **1980**, *102*, 323–328.

(31) Alla, A.; Hakkou, K.; Zamora, F.; Martínez de Ilarduya, A.; Galbis, J. A.; Muñoz-Guerra, S. *Macromolecules* **2006**, *39*, 1410–1416.

(32) Hall, I. H. The determination of the structures of aromatic polyesters from their wide-angle X-ray diffraction patterns. In Hall, I. H., Ed.; *Structure of Crystalline Polymers*; Elsevier Applied Science: London, 1984; pp 39–78.