

Bio-based PBS copolyesters derived from a bicyclic D-glucitol

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2,4:3,5-di-O-methylene-D-glucitol (Glux-diol) was used for the synthesis of poly(butylene succinate) (PBS) copolyesters by melt polycondensation. Glux-diol possess a rigid bicyclic asymmetric structure made of two fused 1,3-dioxane rings and two hydroxyl functions at the end positions. Copolyesters were prepared over the whole range of compositions with molecular weights varying from 26,000 to 46,000 g·mol⁻¹ and a random microstructure. The thermal stability of PBS did not significantly alter with the presence of Glux units. The glass transition temperatures (T_g) steadily increased from -28 to 80 °C along the whole copolyester series with the insertion of Glux. On the contrary, melting temperature (T_m) and crystallinity decreased because of lack of regularity of the polymer chain although copolyesters with contents of Glux units up to 30 mole-% were semicrystalline. The stress-strain behavior changed according to variations produced in thermal transitions. The replacement of 1,4-butanediol by Glux-diol slightly increased both the hydrolytic degradability and the biodegradability of PBS. Compared to other bicyclic sugar-based diols reported in the literature, Glux-diol appeared to be more efficient in both increasing the T_g and enhancing the susceptibility to hydrolysis of PBS.

Introduction

A growing interest for chemicals derived from renewable resources which are able to replace oil-based monomers for the production of industrial polymers is noticeable in these last years.^{1,2} Additionally, environmental pollution has recently become a big problem of both social and technical repercussions due largely to the high impact of plastic wastes.³ The most popular approach followed today to give response to these concerns is to replace the commodity synthetic polymers by bio-based polymers.^{4,5,6} In fact, polymers made from monomers derived from non-fossil materials are sustainable and also total or partially susceptible to microbial degradation.⁷ Aliphatic polyesters such as poly(L-lactic acid), poly(butylene succinate), and polyhydroxyalkanoates among others, constitute primary examples of bio-based

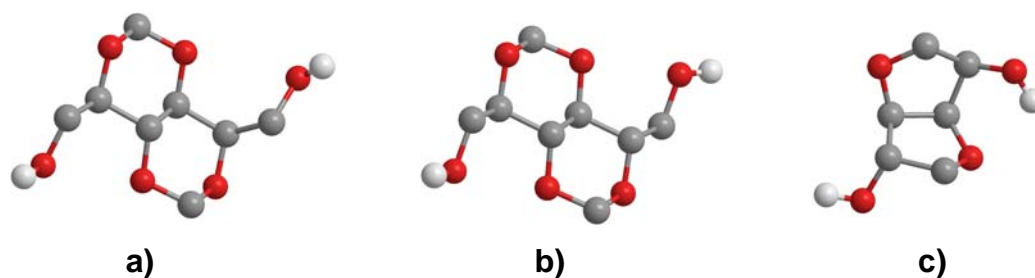
36 polymers that distinguish by being fully renewable and displaying partial or total
37 biodegradability. Such features make aliphatic polyesters especially suitable for large-
38 tonnage applications where large consumption of raw materials and high environmental
39 impact are major concerns, e.g. packaging, disposable items and agricultural mulch
40 films.⁸

41 Poly(butylene succinate) (PBS) is one of the members of the aliphatic polyester
42 family that is receiving greatest attention. This polyester not only may be built by using
43 exclusively renewable feedstock but it also displays mechanical properties comparable
44 to other extensively used conventional polymers.⁹ Furthermore, PBS has been
45 demonstrated to exhibit significant biodegradation in soil, activated sludge and sea
46 water.¹⁰ Due to its outstanding potential, PBS is today in the focus of an intensive
47 research addressed to improve its thermal and mechanical properties without
48 significant detriment to its sustainability and biodegradability. Copolymerization
49 involving cyclic comonomers and blending with nanofillers are the main approaches
50 followed in this regard.^{11,12}

51 Carbohydrates stand out as very convenient raw materials for furnishing
52 polycondensation monomers. They are relatively inexpensive, readily available, and
53 provide broad functional diversity. In recent years, a large number of examples of
54 polycondensation polymers made from carbohydrate derivatives have been reported in
55 the literature.^{13,14} Cyclic carbohydrate-based monomers are particularly relevant
56 because their stiff structures are able to increase the glass transition temperature and
57 hence to improve certain polymer properties such as heat deflection temperature,
58 hardness, tearing resistance and permeability. Isohexides and more specifically
59 isosorbide, are bicyclic dianhydride diols coming from hexoses that have been widely
60 investigated for their potential to enhance the performance of both aliphatic and
61 aromatic polyesters.^{15,16} More recently, carbohydrate-based bicyclic diols and diacids
62 with a diacetal constitution have emerged as a new class of bio-based monomers with
63 a potential at least comparable to that of isohexides.^{17,18} Most exciting results have

64 been those attained with aromatic copolyesters containing fused diacetalized bicyclic
65 units derived from D-mannose and D-glucose.^{19,20} These novel sugar-based
66 copolyesters have been reported to exhibit enhanced thermal properties and
67 biodegradability when compared to PET and PBT.^{19b,20b}

68 The purpose of this work is to explore the effects on properties of PBS caused
69 by the presence of carbohydrate-based diacetalized bicyclic units in the polymer chain,
70 more specifically of 2,4:3,5-di-O-methylene-D-glucitol, abbreviated as Glux-diol. We
71 have very recently reported on PBS copolyesters made from Manx-diol, the
72 stereoisomer of Glux-diol that derives from D-mannose.²¹ Both isomers consist of two
73 fused 1,3-dioxane rings structure sharing a C6-segment backbone that bears two
74 hydroxyl functions at the end positions. At difference with Manx-diol, Glux-diol is
75 asymmetric so its two OH groups are spatially and hence chemically different (Scheme
76 1). Random PBS copolyesters containing Manx units could be obtained with M_w above
77 30,000, they were semicrystalline for the whole range of compositions and displayed
78 enhanced T_g and biodegradability. Since polymerization rate as well as polymer
79 properties are largely depending on monomer symmetry, it is of much conceptual
80 interest to compare Manx and Glux diols as comonomers for the production of PBS
81 copolyesters. Additionally, data obtained from this study can be related to those
82 reported for PBS copolyesters containing isosorbide in order to assess diacetalized
83 and dianhydride bicyclic diols as optional comonomers for their capacity to improve
84 PBS properties. The study is also of practical relevance since Glux-diol is a compound
85 coming from D-glucose, the most available monosaccharide in nature.



Scheme 1 Molecular structures of Manx-diol (a), Glux-diol (b) and isosorbide (c).

89 **Experimental part**

90 **Materials**

91 The reagents 1,4-butanediol (BD) (97%), dimethyl succinate (DMS) (> 99%),
92 1,5-D-gluconolactone (99%), lithium aluminium hydride (95%), paraformaldehyde
93 (>95%), sodium hydroxide (>97%) and the catalyst dibutyl tin oxide (DBTO, 98%), were
94 purchased from Sigma-Aldrich. Lipase from porcine pancreas (activity 15-35 U, 3 mg⁻¹,
95 pH 8.0, 37 °C) was also purchased from Sigma-Aldrich. Solvents used for purification,
96 synthesis and characterization were all of either technical or high-purity grade and they
97 were purchased from Panreac and used as received without further purification.
98 Irganox 1010, Irgafos 126 antioxidants were a generous gift from BASF. The cyclic diol
99 2,4:3,5-di-O-methylene-D-glucitol (Glux-diol) has been prepared following a procedure
100 well described in the recent literature.²²

101 **General methods**

102 ¹H and ¹³C NMR spectra were recorded on a Bruker AMX-300 spectrometer at
103 25.0 °C operating at 300.1 and 75.5 MHz, respectively. Polyesters were dissolved
104 either in deuterated chloroform or in a mixture of deuterated chloroform/ trifluoroacetic
105 acid (TFA) (1/1), and spectra were internally referenced to tetramethylsilane (TMS).
106 About 10 and 50 mg of sample dissolved in 1 mL of solvent were used for ¹H and ¹³C
107 NMR, respectively. Sixty-four scans were acquired for ¹H and 1,000-10,000 for ¹³C with
108 32 and 64-K data points as well as relaxation delays of 1 and 2 s, respectively.
109 Viscosities of polyesters were measured in dichloroacetic acid at 25.00 ± 0.01 °C,
110 using a capillary viscosimeter at concentrations ranging from 5 to 10 mg·mL⁻¹. Gel
111 permeation chromatograms were acquired at 35.0 °C with a Waters equipment
112 provided with a refraction-index detector. The samples were chromatographed with
113 0.05 M sodium trifluoroacetate-hexafluoroisopropanol (NaTFA-HFIP) using a PL
114 HFIPgel 300 × 7.5 mm column with a flow rate of 0.5 mL·min⁻¹. Chromatograms were
115 calibrated against poly(methyl methacrylate) (PMMA) monodisperse standards. The

116 thermal behavior of polyesters was examined by DSC using a Perkin Elmer DSC Pyris
117 1. DSC data were obtained from 3 to 5 mg samples at heating/cooling rates of 10
118 °C·min⁻¹ under a nitrogen flow of 20 mL·min⁻¹. Indium and zinc were used as standards
119 for temperature and enthalpy calibration. The glass-transition temperatures were
120 determined by the tangent method at a heating rate of 20 °C·min⁻¹ from rapidly melt-
121 quenched polymer samples. The treatment of samples for isothermal crystallization
122 experiments was the following: the thermal history was removed by heating the sample
123 up to 200 °C and left at this temperature for 5 min, and then it was cooled at 20 °C·min⁻¹
124 to the selected crystallization temperature, where it was left to crystallize until
125 saturation. Thermogravimetric analyses were performed under a nitrogen flow of 20
126 mL·min⁻¹ at heating rate of 10 °C·min⁻¹, within a temperature range of 30 to 600 °C,
127 using a Mettler Toledo TGA/DSC 1 thermobalance. Sample weights of about 10-15 mg
128 were used in these experiments. Films for mechanical properties with a thickness of
129 ~200 µm were prepared by the hot-pressing method. The tested samples were cut into
130 strips with a width of 3 mm while the distance between testing marks was 10 mm. The
131 tensile strength, elongation at break and Young's modulus were measured at a
132 stretching rate of 30 mm·min⁻¹ on a Zwick 2.5/TN1S testing machine coupled with a
133 compressor Dalbe DR 150. Each sample was measured five times. X-ray diffraction
134 patterns were recorded on the PANalytical X'Pert PRO MPD θ/θ diffractometer using
135 the Cu K α radiation of wavelength 0.1542 nm from powdered samples coming from
136 synthesis.

137 **Polymer synthesis**

138 Copolyesters of PBS containing Glux units (PB_xGlux_yS with subscripts x and y
139 standing for mole-% of BD and Glux units in the feed respectively) were synthesized by
140 reaction of dimethyl succinate with mixtures of 1,4-butanediol and 2,4:3,5-di-O-
141 methylene-D-glucitol at different selected ratios. PBS and PGluxS homopolyesters
142 were obtained by polycondensation of dimethyl succinate with 1,4-butanediol and

143 2,4:3,5-di-O-methylene-D-glucitol, respectively. Since diols were partially streamed off
144 by the nitrogen flow and also volatilized when the high vacuum was applied, a mole-
145 10% excess of the diols respect to the diester monomer was used in all cases. The
146 antioxidants Irganox 1010 (0.2% w/w) and Irgafos 126 (0.6% w/w) were added to
147 minimize degradation of thermally sensitive sugar-based monomers. The same
148 reaction protocol was applied for all compositions. Reactions were carried out in a
149 three-necked, cylindrical bottom flask equipped with a mechanical stirrer, a nitrogen
150 inlet and a vacuum distillation outlet. The reactants were stirred to get a homogeneous
151 mixture and DBTO (0.4-0.6 mole-% respect to the total of monomers) was added as
152 catalyst. The transesterification step was performed for 3-5 h at 160 °C under nitrogen
153 flow, and polycondensation for 7-8 h at 160-180 °C under vacuum (0.03-0.06 mbar).
154 The final reaction mixture was cooled to room temperature under a nitrogen flow to
155 prevent degradation, the resulting solid mass was dissolved in chloroform, and the
156 polymer precipitated with methanol, collected by filtration and dried under vacuum. The
157 NMR data ascertaining their constitution and purity are described below.

158 *PBS homopolyester*: ^1H NMR (300.1 MHz, CDCl_3), δ (ppm): 4.1 (t, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$),
159 2.6 (s, 4H, $\text{COCH}_2\text{CH}_2\text{CO}$), 1.7 (t, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$). ^{13}C NMR (75.5 MHz,
160 CDCl_3/TFA), δ (ppm): 176.7 (CO), 65.1, 29.0, 25.2.

161 *PB_xGlux_yS copolyesters*: ^1H NMR (300.1 MHz, CDCl_3), δ (ppm): 5.2-4.8 (m, y·4H,
162 OCH_2O), 4.6-4.4 (m, y·2H, OCH_2CH), 4.4-4.2 (m, y·4H, OCH_2CH), 4.2-4.1 (m, y·1H,
163 OCH_2CHCH), 4.2-4.0 (t, x·4H, COCH_2CH_2), 3.9 (m, y·1H, OCH_2CHCH), 3.8-3.7 (t,
164 y·1H, OCH_2CHCH), 3.7-3.6 (t, y·1H, $\text{OCH}_2\text{CHCHCHCH}$), 2.7-2.6 (t, x·4H,
165 $\text{COCH}_2\text{CH}_2\text{CO}$), 2.7-2.6 (t, y·4H, $\text{COCH}_2\text{CH}_2\text{CO}$), 1.7 (t, x·4H $\text{OCH}_2\text{CH}_2\text{CH}_2$). ^{13}C NMR
166 (75.5 MHz, CDCl_3/TFA), δ (ppm): 176.7 (CO), 93.2, 88.3, 76.2, 74.5, 71.5, 68.4, 67.0,
167 65.1, 61.8, 29.0, 25.2.

168 *PGluxS homopolyester*: ^1H NMR (300.1 MHz, CDCl_3), δ (ppm): 5.2-4.8 (m, 4H,
169 OCH_2O), 4.6-4.4 (m, 2H, OCH_2CH), 4.4-4.2 (m, 4H, OCH_2CH), 4.2-4.1 (m, 1H,
170 OCH_2CHCH), 3.9 (m, 1H, OCH_2CHCH), 3.8-3.7 (t, 1H, OCH_2CHCH), 3.7-3.6 (t, 1H,

171 OCH₂CHCHCH), 2.7-2.6 (t, 4H, COCH₂CH₂CO). ¹³C NMR (75.5 MHz, CDCl₃/TFA),
172 δ (ppm): 176.7 (CO), 93.2, 88.3, 76.2, 74.5, 71.5, 68.4, 67.0, 61.8, 20.9.

173 **Hydrolytic degradation and biodegradation**

174 Films for hydrolytic degradation and biodegradation studies were prepared with
175 a thickness of ~200 μm by casting from chloroform solution at a polymer concentration
176 of 100 g·L⁻¹. The films were cut into 10 mm diameter, 20–30 mg weight disks and dried
177 under vacuum to constant weight. For hydrolytic degradation, samples were immersed
178 in vials containing 10 mL of either citric acid buffer pH 2.0 or sodium phosphate buffer
179 pH 7.4 at 37 °C. The enzymatic degradation was carried out at 37 °C in vials containing
180 10 mL of a pH 7.4 buffered sodium phosphate solution with added lipase from porcine
181 pancreas (10 mg) and replacing the supernatant every 72 h to maintain the enzyme
182 activity. In both cases, the disks were withdrawn from the incubation medium after
183 scheduled periods of time, washed carefully with distilled water, dried to constant
184 weight, and analyzed by GPC chromatography and NMR spectroscopy.

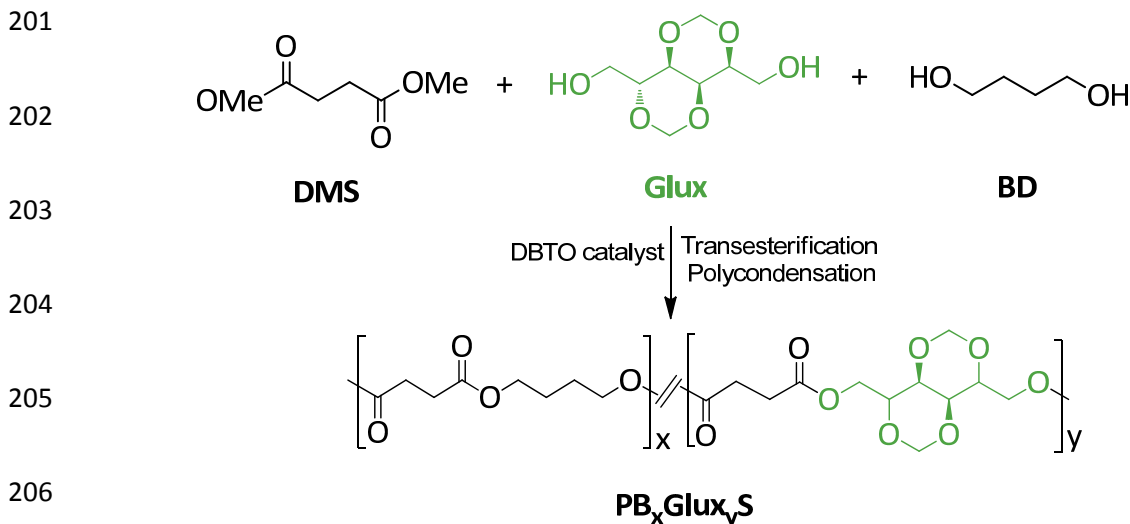
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186 **Results and discussion**

187 **Synthesis and chemical structure**

188 The monomer 2,4:3,5-di-O-methylene-D-glucitol (Glux-diol) with the required
189 purity and in satisfactory yield was prepared from commercially available 1,5-D-
190 gluconolactone as it has been previously reported by us.²² Polycondensation in the melt
191 was the method chosen to prepare both homopolyesters and copolyesters in
192 agreement with that is usual in the industrial practice, and the applied procedure
193 conditions were as close as possible to those reported for the synthesis of Manx-
194 containing PBS copolyesters.²¹ As it is depicted in Scheme 2, the polymerization
195 procedure consisted in two steps, first generation of hydroxyl capped oligoesters by
196 transesterification under a nitrogen flow to prevent decomposition of Glux, and second,
197 polycondensation under vacuum to remove the excess of BD as much as possible.

198 Reaction conditions regarding time and temperature were optimized for each individual
 199 case. Both the homopolyester PGluxS and the series of copolyesters PB_xGlux_yS
 200 containing Glux units from 5 up to 70 mole-% were thus synthesized.



207

208 **Scheme 2** Polycondensation reactions leading to PB_xGlux_yS copolyesters. Only asymmetric
 209 carbons keeping a unique spatial orientation along the copolyester chain (3 and 4 carbons of
 210 the Glux unit) have been stereochemically represented.
 211

212 The chemical constitution of the polyesters was assessed by NMR. As an
 213 example, both ¹H and ¹³C NMR spectra of PB₅₀Glux₅₀S with indication of all signals
 214 assignments are shown in Fig. 1. NMR spectra of PB₉₀Glux₁₀S and PGluxS are
 215 provided in the ESI file (Fig. SI-1 and SI-2). Data regarding composition, molecular
 216 weight and microstructure of PB_xGlux_yS copolyesters and homopolyesters are collected
 217 in Table 1. Copolyester compositions were determined by integration of the proton
 218 signals arising from BD and Glux units in the by ¹H NMR spectra. As it is seen in Table
 219 1, copolyester compositions are very close to those used in their respective feeds with
 220 a slight excess in the Glux content. The GPC analysis revealed that polyesters were
 221 obtained with weight average molecular weights within the 46,000-26,000 range with
 222 dispersity degrees oscillating between 2.2 and 3.1. The general trend is that molecular
 223 weights slightly decrease with the increasing amount of Glux units in the polymer chain

224 so that the minimum value is attained for the PGluxS homopolyester. Intrinsic
 225 viscosities decreased from 1.0 to near 0.4 dL·g⁻¹ in agreement with the trend observed
 226 for molecular weights. According to which has been repeatedly noticed for other
 227 polyesters containing sugar residues,¹⁹ such a trend is very likely determined by the
 228 high sensitivity to heat of 2,4:3,5-di-O-methylene-D-glucitol and the relatively high
 229 temperatures used in the polymerization reaction.

Table 1. Composition, molecular weights and microstructure of polyesters.

Polyester	Composition (mol/mol)		Molecular weight				Microstructure		
	Feed	Copolyester ^a	$[\eta]^b$ (dL·g ⁻¹)	M_n^c	M_w^c	D^c	Average sequence length		R^d
							X_{BD}/X_{Gluc}	n_B	
PBS	100/0	100/0	1.00	17900	45600	2.5	-	-	-
PB ₉₅ Glux ₅ S	95/5	94.4/5.6	0.71	17000	43700	2.6	9.9	1	1.10
PB ₉₀ Glux ₁₀ S	90/10	88.9/11.1	0.65	14900	43400	2.9	6.3	1.2	0.96
PB ₇₀ Glux ₃₀ S	70/30	71.2/28.8	0.60	14000	39300	2.8	2.6	1.7	0.98
PB ₅₀ Glux ₅₀ S	50/50	46.2/53.8	0.59	12900	36700	2.8	1.6	2.6	1.00
PB ₃₀ Glux ₇₀ S	30/70	25.4/74.6	0.60	12600	38500	3.1	1.3	4.8	0.98
PGlucS	0/100	0/100	0.41	12300	26800	2.2	-	-	-

^a Molar composition determined by integration of ¹H NMR spectra.

^b Intrinsic viscosity measured in dichloroacetic acid at 25 °C.

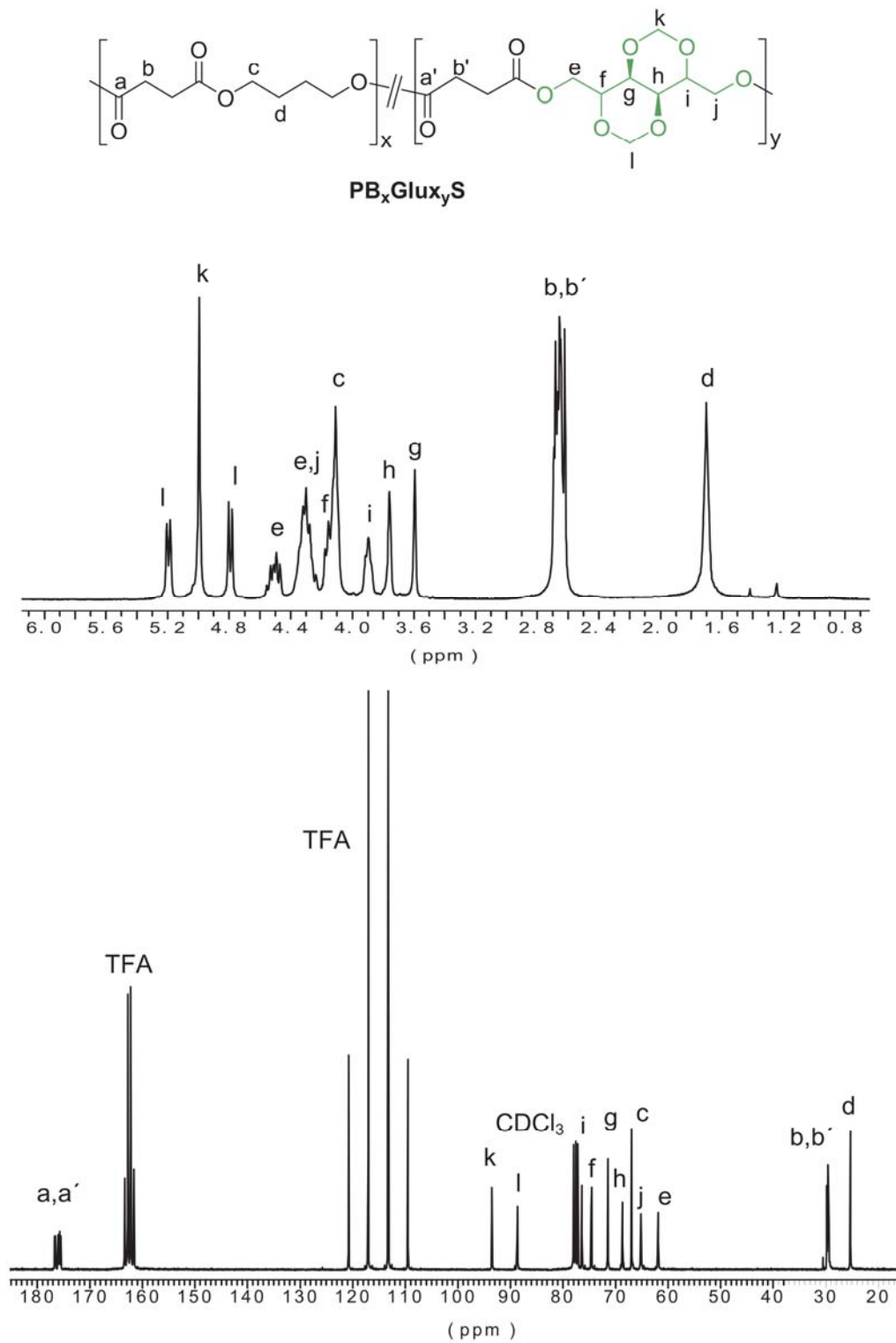
^c Determined by GPC in HFIP against PMMA standards.

^d Randomness degree of copolyesters calculated on the basis of the ¹³C NMR analysis.

230

231 The microstructure of the copolyesters was determined by ¹³C NMR taking
 232 benefit from the sensitiveness of the carbonyl groups to the sequence distribution at
 233 the dyads level (BB, BG, GB, GG). As a consequence of the occurrence of different
 234 dyads and also of the two orientations for the Gluc unit, the CO signal splits into
 235 multiple peaks that appear spread within the 176.8–175.3 ppm interval (Fig. 2).
 236 Nevertheless, three groups of peaks may be discerned in such spectra which are
 237 arising from the four types of diol-dyads present in the copolyester chain. Although it is
 238 known that different carbons frequently have different relaxation times, it is not the case
 239 because the composition calculated using these carbon signals was the same as that
 240 obtained by ¹H NMR. Then, the integration of all the dyad-associated peaks and
 241 application of the equations given below, allowed estimating the number average

242 sequence lengths to evaluate the microstructure of the copolyesters according to the
 243 randomness degree R .



244

245 **Fig. 1** ^1H (top) and ^{13}C (bottom) spectra of $\text{PB}_{50}\text{Glux}_{50}\text{S}$ copolyester.

246 The values resulting from these calculations are given in Table 1 and they indicate that
 247 an almost random microstructure is shared by all the copolyesters ($R \sim 1$).

248

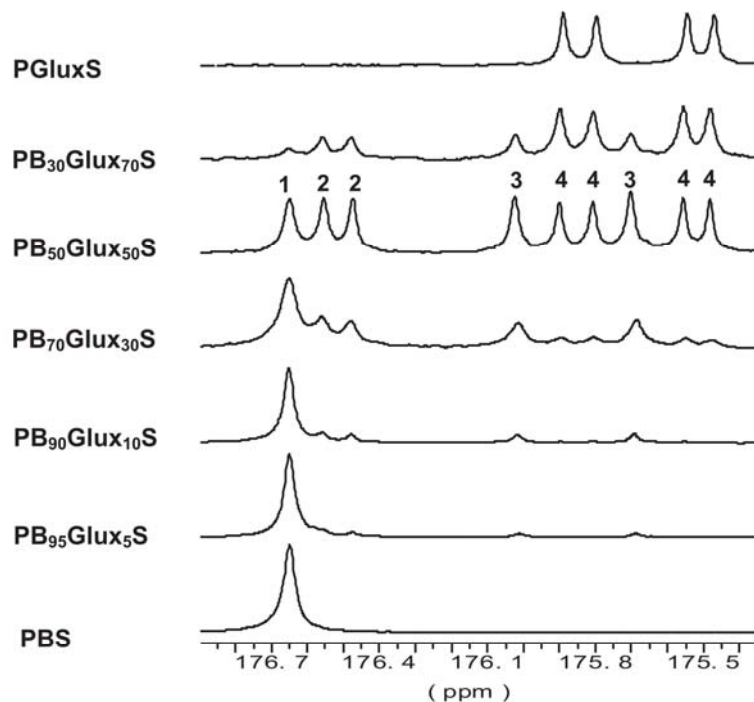
249 $n_B = (BB + 0.5(BG + GB)) / 0.5(BG + GB)$ $n_G = (GG + 0.5(GB + BG)) / 0.5(BG + GB)$

250

$R = 1/n_B + 1/n_G$

251

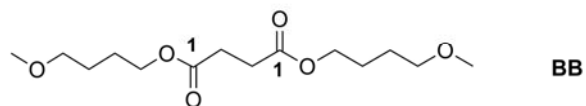
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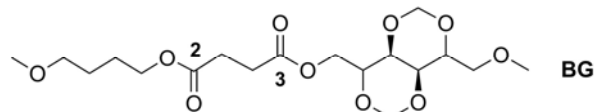
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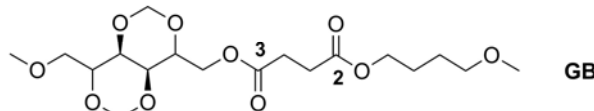
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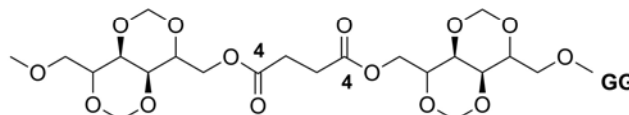


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272 **Fig. 2** ^{13}C NMR spectra showing the changes undergone by the carbonyl signal of $\text{PB}_x\text{Glux}_y\text{S}$
 273 copolyesters with variations in composition.

274

275 **Thermal properties and crystallization**

276 The basic thermal properties of the obtained copolyesters were evaluated by
277 TGA and DSC with special attention to the influence of the presence of the Glux units
278 on decomposition, melting and glass transition temperatures. Data afforded by these
279 analyses are collected in Table 2.

280 The recorded TGA traces for the whole series are compared in Fig. 3. All traces
281 except that of PGluxS obey the same behavior pattern consisting of one only
282 decomposition step that starts around 340 °C, falls down at the proximities of 400 °C
283 (see Fig. SI-3) and leaves less than 10% (w/w) of residual weight. A detailed
284 comparison of the decomposition parameters reveals that the insertion of the Glux
285 units in PBS does not alter significantly the thermal stability of the parent polyester
286 provided that the case for homopolyester PGluxS is excluded. In fact, the maximum
287 change observed for the onset temperature is a decrease in 10 °C whereas the
288 maximum rate decomposition temperature slightly increases with copolymerization.
289 The fact that opposite tendencies are observed for $^{\circ}T_d$ and $^{\max}T_d$ respectively, suggests
290 the presence of small amounts of structural water associated to the Glux units in
291 PB_xGlux_yS copolyesters. The exceptional behavior observed for PGluxS can be
292 explained by assuming that it contains adsorbed water in much larger amounts than
293 copolyesters, a conjecture that makes much sense given the 100 mole-% content of
294 this homopolyester in Glux units. The high heat resistance displayed by PB_xGlux_yS is a
295 really remarkable fact regarding the potential of these copolyesters to be used in
296 applications involving thermal processing.

297

Table 2. Thermal and mechanical properties and X-ray spacings of PB_xGlux_yS polyesters.

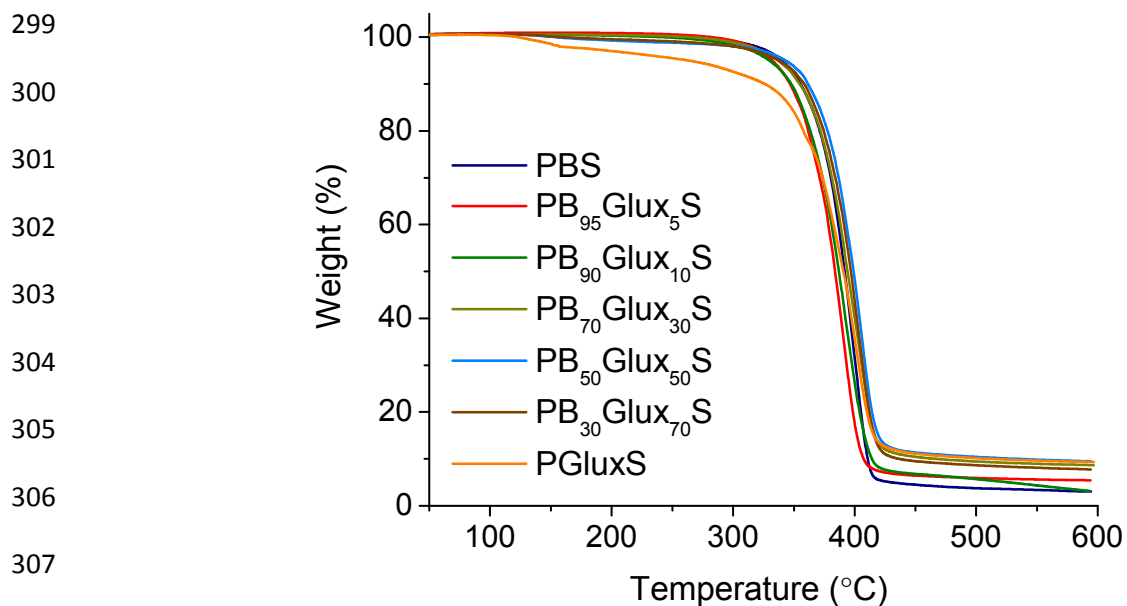
Polyester	TGA ^a			DSC ^b										XRD ^c	Stress-strain essays ^d			
	^o T _d (°C)	^{max} T _d (°C)	RW (%)	First heating			Cooling	Second heating			t _{1/2} (min) (at °C)				d-(nm)	E (MPa)	σ _{max} (MPa)	ε (%)
				T _g (°C)	T _m (°C)	ΔH _m (J·g ⁻¹)	T _c (°C)	T _c (°C)	T _m (°C)	ΔH _m (J·g ⁻¹)	(75)	(80)	(85)	(90)				
PBS	340	396	3	-37	113	78	78	99	114	62	-	-	1.9	5.3	0.45, 0.40, 0.39	545 ± 11	32 ± 2	9 ± 1
PB ₉₅ Glux ₅ S	332	390	5	-28	106	70	62	90	106	63	1.2	2.3	-	-	0.45, 0.40, 0.39	482 ± 10	13 ± 2	4 ± 1
PB ₉₀ Glux ₁₀ S	330	392	3	-20	96	54	33	30	96	48	18.7	28.0	-	-	0.45, 0.40, 0.39	370 ± 13	16 ± 1	10 ± 2
PB ₇₀ Glux ₃₀ S	337	405	7	14	59	33	-	-	-	-	-	-	-	-	0.46, 0.40	348 ± 15	11 ± 1	4 ± 2
PB ₅₀ Glux ₅₀ S	343	407	9	54	-	-	-	-	-	-	-	-	-	-	-	1093 ± 16	15 ± 2	3 ± 2
PB ₃₀ Glux ₇₀ S	338	403	8	80	-	-	-	-	-	-	-	-	-	-	-	1356 ± 19	40 ± 3	6 ± 2
PGluxS	264	403	9	103	-	-	-	-	-	-	-	-	-	-	-	-	-	-

^a Onset decomposition temperature corresponding to 5% of weight loss (^oT_d), temperature for maximum degradation rate (^{max}T_d), and % of weight remaining after heating at 600 °C (RW).

^b Glass-transition temperature (T_g) taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 °C·min⁻¹. Melting (T_m) and crystallization (T_c) temperatures, and melting enthalpy (ΔH_m) measured at heating/cooling rates of 10 °C·min⁻¹. Isothermal crystallization half-time (t_{1/2}) determined at the indicated temperatures.

^c Bragg spacings measured by powder X-ray diffraction.

^d Elastic modulus (E), maximum stress (σ) and elongation to break (ε) measured by tensile testing from hot-pressing films.



309 **Fig. 3** TGA traces of PB_xGlux_yS .

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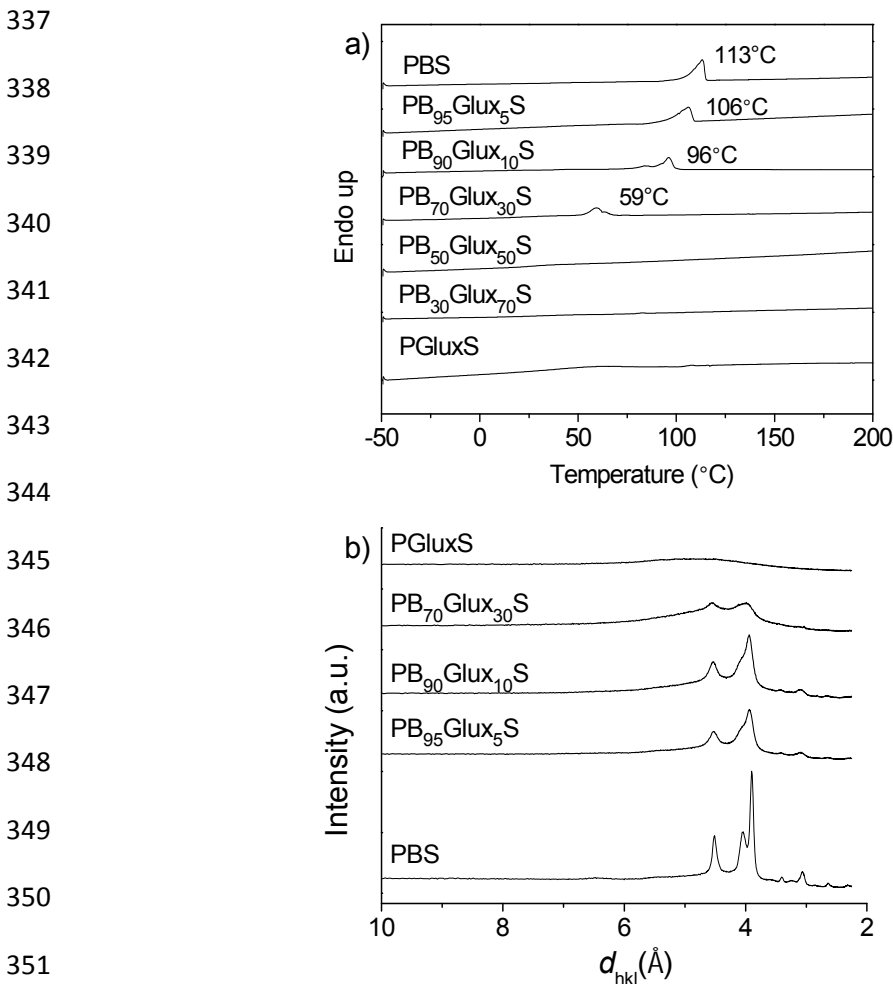
311 The glass transition and melting temperatures of PB_xGlux_yS copolyesters and
312 homopolyesters were measured by DSC. Observation of the slope changes were
313 clearly seen for the whole series on traces recorded from samples quenched from the
314 melt that were exempted of crystallinity (see Fig. SI-5). The T_g observed for
315 copolyesters varied from -28 to 80 °C with values steadily increasing for increasing
316 contents in Glux units (Table 2). This range of values is fully consistent with the T_g
317 values displayed by the parent homopolyesters (-37 °C and 103 °C for PBS and
318 PGluxS, respectively). Such strong enhancing effect is just simply the consequence of
319 the increasing in chain stiffness that is produced when the flexible butylene segment is
320 replaced by the rigid bicyclic Glux structure.

321

322 The influence of copolymerization on the melting/crystallization behavior was
323 brought into evidence by DSC. As it is shown in Fig. 4a, the DSC heating traces of
324 copolyesters with contents in Glux units of 30 mole-% as maximum displayed an
325 endothermic peak characteristic of melting and revealed therefore that they are
326 semicrystalline. Both T_m and ΔH_m decreased as the presence of Glux units increased.
Copolyesters with Glux contents above 30 mole-% as well as the PGluxS

327 homopolymer produced plain traces without any vestige of crystallinity. This tendency
328 is a consequence of the depressing effect on chain regularity that is produced when
329 butylene units are replaced by Glux units.

330 The X-ray diffraction analysis corroborated the DSC results by showing discrete
331 scattering diffraction for PBS and PB_xGlux_yS copolyesters containing up to 30% of Glux
332 units with a peak sharpness and intensity decreasing with the increasing B/Glux ratio
333 (Fig. 4b). Moreover the reflections observed for the semicrystalline copolyesters were
334 coincident in both spacing and intensity with those characteristic of PBS,²³ which is
335 indicative that the crystal structure of the homopolymer is retained after
336 copolymerization.

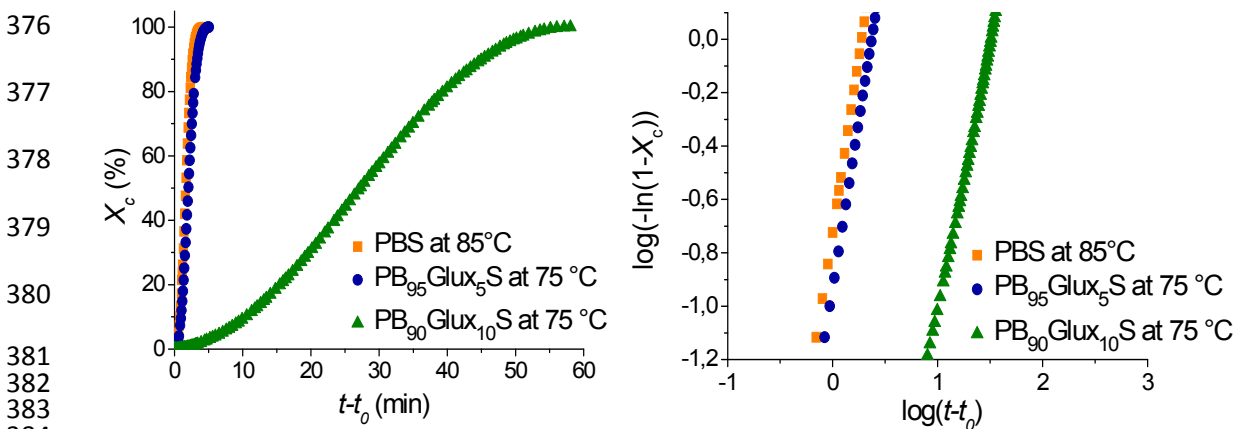


353 **Fig. 4** DSC heating traces of the whole series of PB_xGlux_yS recorded at heating at $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$
354 from samples coming from synthesis (a), X-ray diffraction profiles of the indicated PB_xGlux_yS
355 copolyesters (b).
356

357 The trend to crystallize is a relevant property of semicrystalline polyesters that
 358 has to be considered when they are intended to be used as thermoplastics. As it can
 359 be seen in Table 2 only PB_xGlux_yS copolyesters containing 10 mole-% of Glux as
 360 maximum are able to crystallize from the melt (Fig. SI-4). Although these results
 361 clearly indicated that crystallizability of PBS is strongly depressed by the insertion of
 362 Glux units in the polyester chain, and that such effect has been reported to invariably
 363 occur for other related copolyesters containing sugar units, a comparative
 364 crystallization kinetics study has been undertaken in this work to quantify the influence
 365 of Glux in this regard.

366 PBS, $PB_{95}Glux_5S$ and $PB_{90}Glux_{10}S$ were compared regarding their isothermal
 367 crystallization although a common temperature could not be set for the three
 368 compounds due to their large differences in crystallizability. The study also included the
 369 crystallization of each polymer at two different crystallization temperatures in order to
 370 estimate the influence of temperature on crystallization rate. The graphical
 371 representations of crystallization data as a function of time are depicted in Fig. 5 for the
 372 three compared polyesters. The kinetics was evaluated by the classical Avrami
 373 model,^{24,25} and the crystallization half-times afforded by this analysis are given in Table
 374 2. It is clearly noticeable how $t_{1/2}$ is strongly influenced by composition so it increased

375



386 **Fig. 5** Isothermal crystallization of PBS, $PB_{95}Glux_5S$ and $PB_{90}Glux_{10}S$ at the indicated
 387 temperatures. Relative crystallinity vs. crystallization time (left), Avrami representation of
 388 crystallization data (right).

389

390 more than ten times for an increase in the Glux content of only 5 mole-%. On the other
391 hand, the observed inverse dependence of crystallization rate on temperature indicates
392 that in both PBS and copolyesters, the crystallization process is controlled mainly by
393 nucleating factors rather than by chain mobility.²⁴

395 **Stress-strain behavior**

396 For a preliminary assessment of the mechanical behavior of PB_xGlux_yS, films of
397 the copolyesters were subjected to stress-strain essays testing. Considering the strong
398 influence that crystallinity has on mechanical properties, the samples used for tensile
399 testing were previously checked by DSC. These measurements proved that melting
400 parameters (T_m and ΔH_m) of films were close to those recorded for the powdered
401 samples with the initial PBS crystallinity decreasing about 20, 30 and 50% for 5, 10 and
402 30 mole-% of Glux in the copolyester, respectively, to finally disappear for higher
403 contents. The copolyesters were tested in parallel and compared with PBS. The
404 mechanical parameters obtained in these essays are gathered in Table 2. Results
405 showed that the copolyesters with amounts of Glux units till 30 mole-%, which are
406 those displaying crystallinity, undergo a reduction in Young modulus and tensile
407 strength whereas those with higher contents of Glux exhibit a sustained increasing in
408 these parameters. Although rather wandering values were found for the elongation to
409 break, probably due to sample heterogeneities and divergences in molecular weight, it
410 can be reasonably concluded that ductility is not significantly modified by
411 copolymerization. The ambiguous mechanical behavior exhibited by PB_xGlux_yS
412 copolyesters reflects the ambivalent effect of the insertion of Glux unit in the PBS chain
413 as far as crystallinity and chain mobility in the amorphous phase is concerning. For low
414 contents in Glux, crystallinity is the main factor determining the stress-strain response,
415 and E and σ_{max} decrease with copolymerization. Conversely, for high Glux contents
416 crystallinity disappears and T_g becomes the only property affecting deformation.
417 Consequently the mechanical performance is improved with copolymerization to the

418 point that amorphous PB_xGlux_yS copolyesters arrive to be stiffer and stronger than
419 PBS.

420 **Hydrolytic degradation and biodegradation**

421 In order to evaluate the effect of Glux on the behavior of PBS regarding its
422 degradability and biodegradability, several essays were carried out in parallel using
423 PBS, PGluxS and PB₇₀Glux₃₀S copolyester. Samples were incubated in the appropriate
424 aqueous buffer solution, with or without lipases added, and degradation evolution was
425 followed by monitoring the changes taking place in weight and molecular weight of the
426 residue. Firstly, the degradation at pH 2.0 was performed to evaluate the influence of
427 Glux on the chemical hydrolysis of PBS and results coming out from these essays have
428 been plotted in Fig. 6 (a and a'). According to what should be expected for aliphatic
429 polyesters, a continuous decreasing in both sample weight and polymer molecular
430 weight is observed for the three polyesters along incubation time with the noticeable
431 remark that changes became more accentuated for Glux containing polyesters. In
432 second place the degradation of the three polyesters incubated under approximately
433 physiological conditions both with and without porcine pancreas lipases added, was
434 examined, and results obtained therein are presented also in Fig. 6 (b and b'). As
435 expected, degradation at pH 7.4 took place in much less extent than at pH 2.0 but the
436 changes observed in both W and M_n continued being of the same sign as before for the
437 three tested polyesters. Interestingly, degradation was notably enhanced when lipases
438 were added to the incubation medium to the point that changes taking place in W and
439 M_n were comparable to those observed at pH 2.0. To get insight into the hydrolytic
440 mechanism, the residue left by the PB₇₀Glux₃₀S after incubation at pH 2.0 for 40 days
441 was analyzed by ¹H NMR, which revealed that the content in Glux of this sample had
442 decreased about 10%, *i.e.* about one third of the Glux units were released upon
443 degradation. This result is demonstrative that hydrolysis of PBS containing Glux units
444 mostly happens by breaking those ester groups in which the carbohydrate units are

445 directly implied. Such a difference is also observed when the homopolyesters PGluxS
 446 and PManxS are compared (see Fig. SI-6). All these results lead to conclude that not
 447 only the chemical degradation but also the biodegradability of PBS, becomes
 448 enhanced by the insertion of Glux units in the polyester chain.

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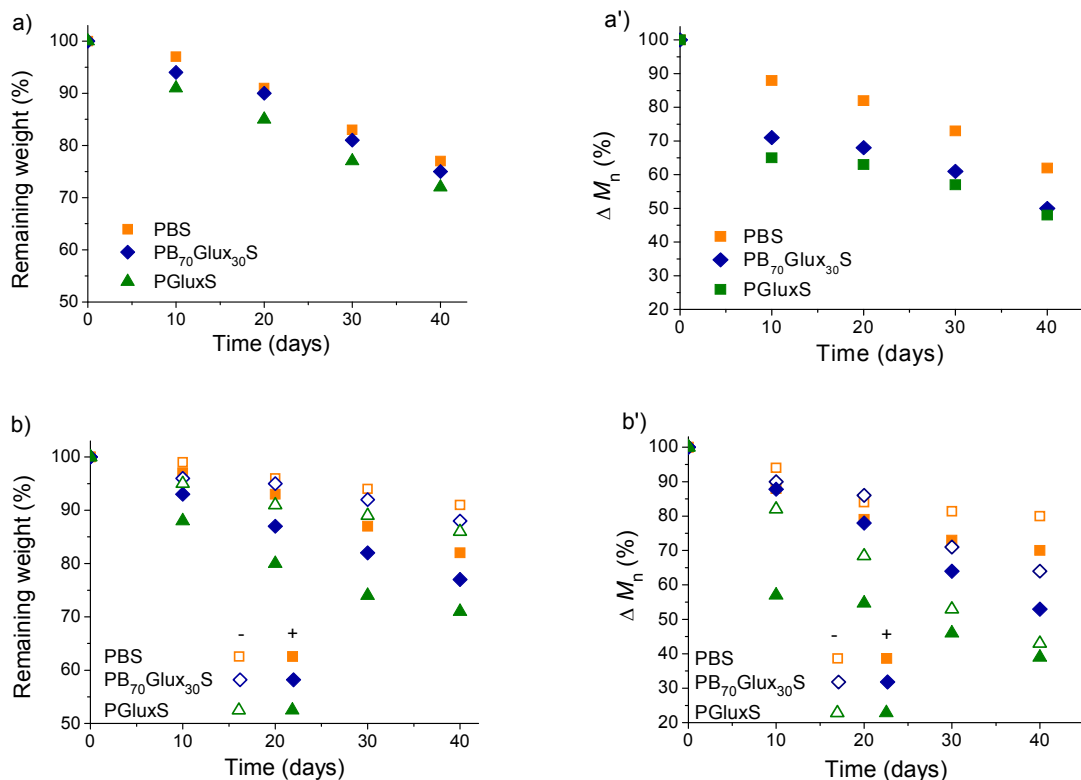
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462 **Fig. 6** Degradation plots of PBS, PB₇₀Glux₃₀S, PGluxS at pH 2.0 (a, a') and pH 7.4 with and
 463 without porcine pancreas enzyme added (b, b').

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467 Sugar-based bicyclic diols compared

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The results achieved in this work have proven the ability of Glux-diol (2,4:3,5-di-
 O-methylene-D-glucitol) to be used as monomer for the preparation of PBS
 copolyesters with conveniently modified properties. A similar work with also satisfactory
 results but using Manx-diol (2,4:3,5-di-O-methylene-D-mannitol) has been recently
 published by us.²¹ It is of interest comparing these two bicyclic diols as comonomers of
 1,4-butanediol for the preparation of PBS copolyesters.

474 PB_xGlux_yS and PB_xMan_xyS copolyesters synthesized by the same
475 procedure have a random microstructure, their compositions are in general close to
476 those used in their respective polymerization feeds, and their divergences regarding
477 molecular weights are less than 15% (Fig. SI-7). The two hydroxymethyl groups of
478 Man_x-diol are indistinguishable and equatorially oriented whereas in the asymmetrical
479 Glux-diol, one CH₂OH group is equatorial and the other one is axial. A recent study on
480 the use of Glux-diol as comonomer in the solid state modification of PBT has shown
481 that the reactivity of the axially oriented hydroxyl function in transesterification reactions
482 was significantly hindered.²⁶ However the slight differences in synthesis results attained
483 for the two PBS copolyester series indicate that such hindering effect must not be
484 significant in this case.

485 Although neither PB_xGlux_yS nor PB_xMan_xyS copolyesters should be expected to
486 be stereoregular due to the random distribution of the comonomers along their
487 respective chains, the disorder will be less severe in the later due to the twofold
488 symmetry of the Man_x configuration. Accordingly PB_xMan_xyS copolyesters show a
489 greater ability to crystallize; they are crystalline over the whole range of compositions
490 with crystallinity degrees oscillating between 50 and 65 mole-%. As it is shown in Fig.
491 7a, T_m values in this series display a parabolic tendency with the minimum placed at
492 comonomer compositions no far from 30 mole-% and the maximum at 100 mole-%
493 (homopolyester PMan_xS). In contrast, only PB_xGlux_yS copolyesters containing 30
494 mole-% of Glux units as maximum were found to be crystalline. Furthermore no sign of
495 crystallinity was detected for PGluxS. Nevertheless practically identical T_m values are
496 displayed by the two series over the interval in which PB_xGlux_yS are able to crystallize.

497 A pronounced increase of T_g is perhaps the most interesting outcome of using
498 bicyclic sugar-based compounds as comonomers in the synthesis of aliphatic
499 polyesters. A close comparison of the T_g values displayed by PB_xGlux_yS and
500 PB_xMan_xyS series is graphically afforded in Fig. 8b. An almost linear trend is followed
501 in both cases with slopes of ~ 1.5 and ~ 1.0 °C·mole-%·sugar unit⁻¹, respectively. The

502 fact that higher T_g 's are displayed by copolyesters containing Glux units is really
 503 amazing since they are less crystalline than their isocompositional Manx analogs.
 504 Apparently it is the more corrugated shape of the Glux structure which additionally
 505 contributes to hindering the mobility of the polyester chain and gives rise to an
 506 exceptionally increase in T_g .

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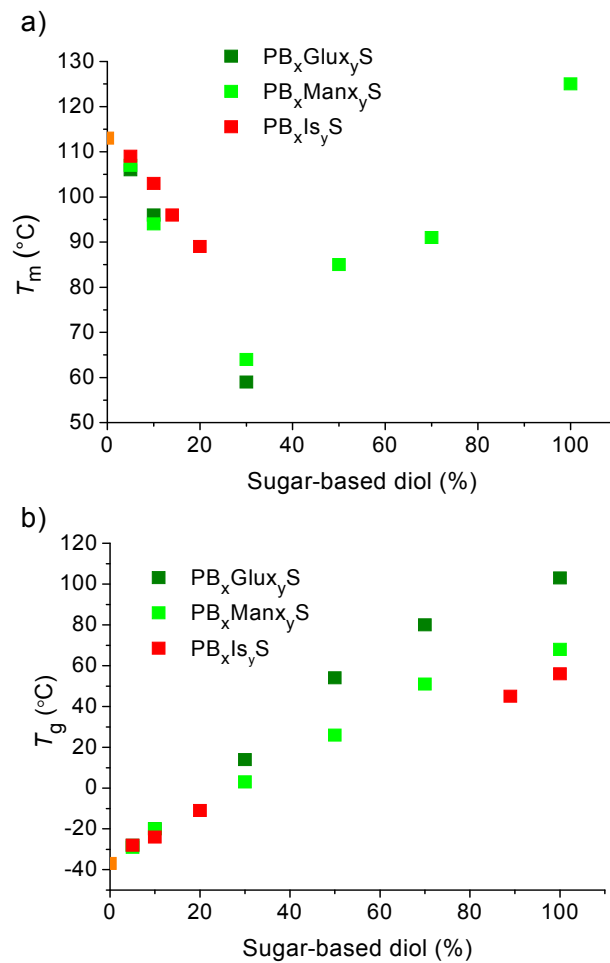
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Fig. 7 Compared melting (a) and glass transition (b) temperatures of PBS copolyesters made from Glux-diol, Manx-diol and isosorbide (Jacquel et al., 2015; Tan et al., 2011). PBS data in orange.

Isosorbide (Is, 1,3:4,6-dianhydride-D-glucitol) is another glucose-derived bicyclic diol that has achieved in these last years wide recognition for the synthesis of bio-based semicrystalline copolyesters with high T_g .^{16,28} It will be worth therefore to compare Is with Glux and Manx regarding thermal properties. Unfortunately only a few

530 papers dealing with PBS copolyesters containing isosorbide are found in the accessible
531 literature,²⁹⁻³¹ and data there afforded are incomplete or not fully suitable for a reliable
532 comparison. Noordover *et al.*^{16b} reported low molecular weight PIsS with T_g between
533 ~ 50 and ~ 70 °C and Tan *et al.*²⁹ described the a PB₁₁Is₈₉S copolyester with M_n 14,000
534 and T_g of ~ 45 °C. More recently, Jacquel *et al.*³⁰ succeeded in preparing PB_xIs_yS
535 copolyesters with astonishingly high molecular weights ($45,000 < M_n < 55,000$) although
536 with compositions restricted to low contents in Is (less than 15 mole-%). These
537 copolyesters were reported to be semicrystalline with T_m decreasing with composition
538 from 130 °C down to 89 °C and T_g increasing from -28 °C up to -11 °C. The T_m and T_g
539 data available on PB_xIs_yS copolyesters have been also plotted in Fig. 8 for comparison
540 with those of Glux and Manx. In spite of being scarce, data are enough to conclude that
541 the effect of Is on PBS thermal properties is in line with that exerted by Manx and Glux.

542 Copolymerization of PBS with bicyclic sugar-based monomers has proven to be
543 not only non-detrimental for its basic properties but favoring both chemical hydrolysis
544 and biodegradation.^{21,27} The presence of the sugar moiety in the polyester chain does
545 not deactivate the enzyme function but enhances its action due to increasing chain
546 hydrophilicity. Both Manx and Glux have an enhancing effect on degradability upon
547 aqueous incubation, either in absence or presence of lipases, but apparently Glux is
548 significantly more efficient than Manx (see comparison in Fig. SI-8). The higher
549 enhancing effect displayed by Glux is most likely due to the strong depressing effect
550 that this unit has on PBS crystallinity.

551 **Conclusions**

552 A series of PBS copolyesters (PB_xGlux_yS) containing bicyclic acetalized units
553 derived from D-glucose (Glux) in addition to the homopolyester PGluxS were
554 synthesized by melt polycondensation from mixtures of 1,4-butanediol, Glux-diol and
555 dimethyl succinate. A complete incorporation of Glux-diol as well as satisfactory
556 molecular weights were in general attained by careful selection of the reaction

557 conditions. As it is usually observed for other sugar-based copolyesters, PB_xGlux_yS
558 had a random microstructure. The presence of Glux in the polyester chain significantly
559 modified the properties of PBS. Melting temperature and crystallinity were severely
560 depressed so copolyesters containing more than 30 mole-% of Glux including the
561 homopolyester were amorphous. Oppositely, the glass transition temperature of PBS
562 dramatically increased with the content in Glux units with a slope not paragoned by any
563 other sugar-based described up to date. Mechanical properties of the PB_xGlux_yS
564 largely varying with composition with good results obtained for copolyesters with high
565 contents in Glux. In line with the effect observed for other sugar-based copolyesters,
566 PB_xGlux_yS display higher sensitivity to both hydrolytic degradation and biodegradation
567 than PBS. All these results lead to finally conclude that Glux-diol is a highly appropriate
568 bio-based comonomer to notably improve the properties of PBS as far as T_g and
569 degradability are concerned. The exceptionally good accessibility of D-glucose as
570 feedstock for Glux-diol is an additional merit of this compound if the modified PBS was
571 intended to be used for industrial purposes.

572

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579 **Electronic Supplementary Information**

580 **Fig. SI-1** 1H NMR (top), ^{13}C (bottom) spectra of $PB_{90}Glux_{10}S$ copolyester with indication of peak
581 assignments. **Fig. SI-2** 1H NMR (top), ^{13}C (bottom) spectra of $PGluxS$ homopolyester with
582 indication of peak assignments. **Fig. SI-3** Derivative curves of PBS, $PB_{90}Glux_{10}S$ and
583 $PB_{50}Glux_{50}S$. **Fig. SI-4** DSC traces for $PB_{95}Glux_5S$. **Fig. SI-5** Heating DSC traces of samples
584 quenched from the melt for T_g observation. **Fig. SI-6** Degradation curves representing the decay
585 in molecular weight against incubation time for $PGluxS$, $PManxS$ at pH 7.4. **Fig. SI-7** Compared
586 weight-average molecular weight of PBS copolyesters made from Glux-diol and Manx-diol. **Fig.**
587 **SI-8** Degradation curves representing the decay in molecular weight against incubation time for
588 isocompositional PBS copolyesters containing Glux and Manx units at pH 7.4.

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