Biodegradable Aromatic Copolyesters Made from Bicyclic Acetalized Galactaric Acid

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ABSTRACT: Random poly(hexamethylene terephthalate-co-galactarate)s and poly(dodecamethylene terephthalate-co-galactarate)s copolyesters covering the whole range of compositions were obtained with weight-average molecular weights of ~30,000–50,000 g mol⁻¹ by melt polycondensation. They were thermally stable above 300 °C, and displayed Tgs in the +20 to –20 °C range with values steadily decreasing with the content in galactarate units. All the copolyesters were semicrystalline with Tms between 50 and 150 °C and those made from dodecanediol were able to crystallize from the melt at a crystallization rate depending on composition. Copolyesters containing up to 50% of galactaric units retained the crystal structure of their respective polyterephthalate homopolyesters, whereas they adopted the structure of the respective polygalactarates when the content in GaIX units reached 70%. Stress-strain essays revealed decay in the mechanical parameters as the aromatic units were replaced by GaIX. Incubation in aqueous buffer revealed that hydrolysis of the copolyesters were largely enhanced by copolymerization and evidenced the capacity of the GaIX unit for making aromatic polyesters susceptible to biodegradation. A detailed NMR analysis complemented by SEM observations indicated that hydrolysis took place by preferred splitting of galactarate ester bonds with releasing of alkanediol and GaIX-diacid. © 2012 Wiley Periodicals, Inc.


KEYWORDS: biodegradable; polyesters; renewable resources

INTRODUCTION Nowadays great attention is given to the development of biobased and biodegradable polymers, to reduce the amount of petroleum that is consumed in the industry as well as to minimize the impact of the use of plastics on the environment.1,2 Aromatic polyesters are high performance thermoplastic materials with excellent mechanical and thermal properties that are massively used in diverse applications. Despite being innocuous for humans, they are considered unfriendly compounds because of their great resistance to degradation by atmospheric and biological agents. Thus, different strategies to obtain modified aromatic polyesters able to be chemically degraded under suitable conditions or biologically degraded are currently drawing an enormous interest.3–6

The incorporation of carbohydrate moieties in polycondensation polymers, such as polyamides and polyesters, is an interesting approach to yield novel sustainable and biodegradable materials.7 The use of carbohydrates as polymer building blocks is motivated by several features: they are easily available, even coming from agricultural wastes, they are found in a very rich variety of structures with large stereochimical diversity, and they constitute a renewable source with good accessibility everywhere. Nevertheless, linear polycondensation of monomers derived from carbohydrates is not straightforward. Carbohydrate-based compounds usually 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 sugar-derived monomers bearing free hydroxyl groups,8,9 most synthesis have been carried out with derivatives in which the exceeding functional groups have been appropriately blocked.10–13

Recently several examples of aromatic polyesters and copolyesters containing sugar-derived units have been described in the literature. Poly(ethylene terephthalate) (PET), poly (ethylene isophthalate) (PEI), and poly(butylene terephthalate) (PBT) were chemically modified by the insertion of different alditols and aldaric acids having D-manno, galacto, L-arabino, and xylo configurations with the secondary hydroxyl groups protected as methyl ether.14,15 Particular attention was paid to

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the sensitivity displayed by these carbohydrate-based polyesters to degradability. Hydrolytic degradation experiments revealed that PET, PEI, and PBT analogs made from pentitiols and hexitols degraded significantly faster than their parent homopolymers at rates depending on the configuration of the sugar units. Conversely, no evaluation of their biodegradability was reported. The state-of-art in this regard is that whereas a fair number of aromatic-aliphatic copolyesters displaying biodegradability have been created along these last decades, no case of biodegradable aromatic copolyester containing sugar residues has been reported so far. However, carbohydrate-based monomers with a cyclic structure constitute an interesting approach to the preparation of polycodensates with improved physical properties, especially those related to polymer chain stiffness. The use of these cyclic monomers has been however scarcely investigated with most of the work carried out up to date having been devoted to bicyclic 1:4;3:6 dianhydroalditols, specifically those made from α-glucitol, α-mannitol, and β-iditol. The former, which is known as isosorbide and that is prepared from β-glucose coming from cereal starch, has been by far the most studied dianhydroalditol. Thus, PET and PBT copolyesters containing isosorbide have been synthesized over the entire range of compositions. As the proportion of isosorbide increased, the copolyesters were less prone to crystallize and their melting temperature steadily decreased. In fact, PET and PBT copolyesters became amor-

EXPERIMENTAL

Materials

Galx was synthesized following the procedure reported by Stacey and coworkers. The reagents 1,6-hexanediol (97%), 1,12-dodecanediol (99%), dimethyl terephthalate (99+%), and the catalyst dibutyltin oxide (DBTO, 98%) were purchased from Sigma-Aldrich. Solvents used for purification and characterization, as chloroform and methanol, as well as solvents used in the solubility essays, were purchased from Panreac and were all of either technical or high-purity grade. The enzyme used in biodegradation experiments, lipase from porcine pancreas (activity 15−35 U mg⁻¹, pH 8.0, and 37 °C) was also purchased from Sigma-Aldrich. One unit (U) was defined as that amount of enzyme that catalyzed the release of fatty acid from triglycerides at the rate of 1 μmol min⁻¹.

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. Polysters and water degradation products were dissolved in deuterated chloroform or deuterated water, and spectra were internally referenced to tetramethylsilane or the sodium salt of 3-(trimethylsilyl)-propanesulfonic acid. 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 1,000–10,000 for 13C with 32 and 64-K data points as well as relaxation delays of 1 and 2 s, respectively. Intrinsic viscosities of polymers dissolved in chloroform were measured in an Anton Paar AMVn Automated microviscometer at 25.00 ± 0.01 °C, using the VisioLab software. Gel permeation chromatograms were acquired at 35.0 °C with 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 polymers 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 200 °C and left at this temperature for 5 min, and then it was cooled at 20 °C min⁻¹ to the selected crystallization temperature, where it was left to crystallize until saturation. 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 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 a chloroform solution at a concentration of 100 g L$^{-1}$. The films were cut into strips with a width of 3 mm while the distance between testing marks was 10 mm. The tensile strength, elongation at break and Young’s modulus were measured at a stretching rate of 30 mm min$^{-1}$ on a Zwick 2.5/TN1S testing machine coupled with a compressor Daie DR 150, at 23 °C. X-ray diffraction patterns were recorded on the PANalytical X’Pert PRO MPD 0/0 diffractometer using the Cu-K$_\alpha$ radiation of wavelength 0.1542 nm from powdered samples coming directly from synthesis. Scanning electron microscopy (SEM) images were taken with a field-emission JEOL JSM-7001F instrument (JEOL, Japan) from Pt/Pd coated samples.

**Polymer Synthesis**

PHT$_x$Gal$_x$, and PDT$_x$Gal$_x$ copolyesters as well as PHT, PDT, PHGal$_x$, and PDGal$_x$ homopolymers were obtained from the chosen aliphatic $\alpha$-hydroxydiol (either 1,6-hexanediol or 1,12-dodecanediol) and a mixture of Gal$_x$ and dimethyl terephthalate with the selected composition. The reaction was performed in a three-necked, cylindrical-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum distillation outlet. With regard to PHT$_x$Gal$_x$ and PDT$_x$Gal$_x$ copolyesters as well as PHGal$_x$ and PDGal$_x$ homopolymers, 5% molar excess of diol to the diester mixture, and DBTO as catalyst (0.8%-mol respect to monomers) were used. The apparatus was vented with nitrogen several times at room temperature to remove the air and avoid oxidation during the polymerization. The transesterification reaction was carried out under a low nitrogen flow at 140 °C for 3 h. The polycondensation reaction was left to proceed at 140 °C for 5 h, under a 0.03–0.06 mbar vacuum. Then, the reaction mixture was cooled to room temperature, and the atmospheric pressure was recovered with nitrogen to prevent degradation. The resulting polymers were dissolved in chloroform and precipitated in excess of methanol to remove unreacted monomers and formed oligomers. Finally, the polymer was collected by filtration, extensively washed with methanol, and dried under vacuum. Since dimethyl terephthalate is not thermally sensitive as Gal$_x$, shorter periods combined with higher temperatures were used for the preparation of both PHT and PDT. A 10% molar excess of the diol to dimethyl terephthalate and DBTO as catalyst was used in this case to compensate expected larger losses of the volatile diol at these higher temperatures. Transesterification reactions were carried out at 180 °C for a period of 3 h under a low nitrogen flow, whereas polycondensation reactions took place for 3 h at 200 °C under vacuum. Polymers were dissolved in chloroform, precipitated, washed with methanol, and dried under vacuum.

PHT$_x$Gal$_x$

$^1$H NMR (300.1 MHz, CDCl$_3$), δ (ppm): 8.09 (s, T, 4CH), 5.25 and 5.05 (2 s, Galx, 2CH$_2$), 4.60 (m, Galx, 2CH$_2$), 4.36 (t, T, 2CH$_2$), 4.27 (m, Galx, 2CH) 4.20 (t, Galx, 2CH$_2$), 1.83 (m, T, 2CH$_3$), 1.69 (m, Galx, 2CH$_3$), 1.54 (m, T, 2CH$_3$), 1.39 (m, Galx, 2CH$_2$). $^{13}$C NMR (75.5 MHz, CDCl$_3$), δ (ppm): 170.3 (CO), 165.8 (CO), 154.2, 134.3, 129.4, 29.2, 29.1, 25.7.

**RESULTS AND DISCUSSION**

**Synthesis and Chemical Structure**

Aromatic copolyesters from dimethyl terephthalate, dimethyl 2,3,4,5-di-o-methylene galactarate, and either 1,6-hexanediol (PHT$_x$Gal$_x$, copolyesters) or 1,12-dodecanediol (PDT$_x$Gal$_x$, copolyesters) at the entire range of molar galactaric/terephthalic compositions were prepared by a two-step melt-polycondensation process as indicated in Scheme 1, using DBTO as catalyst. Transesterification reactions were performed under a low nitrogen flow for a period of 3 h at 140 °C. Polycondensation reactions were carried out for 5 h at the same temperature to minimize the decomposition of thermally sensitive sugar compounds, and under vacuum to facilitate the removal of volatile by-products. When polymerizations were ended, the reaction mixtures were dissolved in chloroform and precipitated in methanol to obtain the copolyesters as white powders in yields close to 90%. The chemical constitution and composition of the resulting copolyesters were ascertained by $^1$H NMR (see Supporting Information), and their molecular weights were estimated by GPC and viscometry. Data provided by these analyses are given in Table 1, where it can be seen that the copolyesters had compositions essentially similar to those of their corresponding feeds.
Intrinsic viscosities of polyesters and copolyesters were between 0.6 and 1.0 dL g\(^{-1}\), with the higher values being generally observed for the whole series of PDT\(_x\)Gal\(_y\) and for PHT\(_x\)Gal\(_y\) with low content in galactaric units. The weight-average molecular weights of copolyesters were found to be within the 30,000–48,000 g mol\(^{-1}\) range, with polydispersities between 2.0 and 2.8. The \(M_n\) was estimated by both GPC and \(^1\)H NMR (end group analysis) and a very good concordance was found between values provided by the two techniques. Nevertheless, the NMR-based \(M_n\)-values were always higher than those obtained by GPC, which could be in principle attributed to the use of GPC standards leading to underestimated molecular weights. However, the presence of endless macrocyclic chains would result in an overestimation of the \(M_n\) values calculated by end-group analysis, and could be also a reason for the observed differences; however, the occurrence of these macrocycles in the polycondensated product cannot be ascertained since they are undistinguishable from linear chains by NMR.

The microstructure of copolyesters was determined by \(^{13}\)C NMR analysis. Complex signals were observed for the carbon atoms of diol units, indicating that these units are sensitive to sequence distribution effects. Thus, as shown in Figure 1, the resonance of the \(c\) and \(c’\) carbon atoms of diol units appeared as four signals in the 25.3–25.8 ppm chemical shift interval corresponding to the four types of dyads (TT, GT, TG, and GG) that are possible along the copolyester chain. The plot of the content in each type of dyad as a function of the copolyester composition reveals that the microstructure of the copolyester is clearly statistical, with randomness quite near unity in all cases. The statistical values obtained from this microstructure analysis are shown in Table 2. Similar results were obtained for the PDT\(_x\)Gal\(_y\) series.

The solubility of both PHT\(_x\)Gal\(_y\) and PDT\(_x\)Gal\(_y\) copolyesters was assessed in an assortment of representative solvents, and results are compared in Table 1. Solubility appears to be insensitive to the length of the diol polymethylene segment, and the incorporation of the acetalized galactarate unit in the polyester only produces a slight increase in solubility so that PHT\(_x\)Gal\(_y\) and PDT\(_x\)Gal\(_y\) copolyesters become additionally soluble in DMF, NMP, and THF. All of them are invariably insoluble in water, ethanol, diethyl ether, and DMSO, and soluble in chloroform, HFIP, and TFA.

**Thermal Properties**

Thermal data of both PHT\(_x\)Gal\(_y\) and PDT\(_x\)Gal\(_y\) copolyesters were recorded by TGA and DSC and they are shown in Table 3, where the corresponding data for the parent homopolymesters PHT, PHGalx, PDT, and PDGalx are also included for comparison.

The TGA traces of PHT\(_x\)Gal\(_y\) and PDT\(_x\)Gal\(_y\) copolyesters registered under an inert atmosphere are comparatively depicted in Figure 2, evidencing the similar behavior among the members of the two series. Decomposition of aromatic homopolymesters PHT and PDT took place in a single step, which initiated above 350 °C, and attained the maximum rate at 410 °C. Both carbohydrate-based homopolymesters PHGalx and PDGalx were decomposed in three different stages, the first one with a maximum rate around 350 °C involving a weight loss of 15%; the second stage at 390–400 °C with a weight loss of 45%, and the final stage at 450–460 °C involving a weight loss of 25–30%, leaving a residual weight of 13% at 600 °C. With regard to PHT\(_x\)Gal\(_y\) and PDT\(_x\)Gal\(_y\) copolyesters, those with galactaric/terephthalic compositions between 30 and 70% showed an intermediate mechanism involving two different stages with maximum decomposition rates at 360 and 410 °C, respectively, leaving a final residue

![Scheme 1](image-url)
### TABLE 1 Molecular Weights and Compositions of PHT<sub>x</sub>Gal<sub>y</sub> and PDT<sub>x</sub>Gal<sub>y</sub> Copolyesters

<table>
<thead>
<tr>
<th>Copolyester</th>
<th>Yield (%)</th>
<th>Feed</th>
<th>Copolyester&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Molar composition</th>
<th>Molecular weight</th>
<th>Solubility&lt;sup&gt;a&lt;/sup&gt;</th>
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<td></td>
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<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
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<tr>
<td>PHT</td>
<td>91</td>
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<td>100</td>
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<td>0.95</td>
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<td>90</td>
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<td>50</td>
<td>49.6</td>
<td>50.4</td>
<td>0.68</td>
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<tr>
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<td>70</td>
<td>30</td>
<td>70.9</td>
<td>29.1</td>
<td>0.66</td>
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<td>0</td>
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<td>0</td>
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<td>22,700</td>
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<tr>
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<td>50</td>
<td>50</td>
<td>51.0</td>
<td>49.0</td>
<td>0.92</td>
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<tr>
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<td>70</td>
<td>30</td>
<td>70.3</td>
<td>29.7</td>
<td>0.74</td>
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<tr>
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<td>93</td>
<td>90</td>
<td>10</td>
<td>89.9</td>
<td>10.1</td>
<td>0.77</td>
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<tr>
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<td>100</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0.81</td>
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</tbody>
</table>

<sup>a</sup> Insoluble, (+) soluble.
<sup>b</sup> Molar composition determined by integration of the 1H NMR spectra.
<sup>c</sup> Intrinsic viscosity in dL g<sup>-1</sup> measured in chloroform at 25 °C.
<sup>d</sup> Number-average molecular weight in g mol<sup>-1</sup> determined by 1H NMR end group analysis.
<sup>e</sup> Number and weight-average molecular weights in g mol<sup>-1</sup> measured by GPC in HFIP against PMMA standards.
of 4–10% of the initial weight. The copolyesters containing amounts of the second comonomer below 10% decomposed by a mechanism similar to those of their respective parent homopolymers. The residual weight at 600 °C of both PHT₉Galₓ and PDT₉Galₓ copolyesters invariably increased with their content in Galₓ units.

The DSC analysis of samples quenched from the melt revealed the occurrence of a unique Tₓ for these copolyesters, with a value decreasing with the content in Galₓ units, and confined between those of their respective parent homopolymers. DSC traces of PHT₉Galₓ and PDT₉Galₓ copolyesters registered at first heating are depicted in Figure 3. All copolyesters coming directly from synthesis, as well as their parent homopolymers, gave heating traces with melting endotherms indicating that all of them were semicrystalline. The trend followed by Tₘ as a function of the copolyester composition is shown in the Supporting Information. In each series, the aromatic homopolyester displayed Tₘ and ΔHₘ higher than their corresponding carbohydrate-based homopolyester. Regarding copolyesters, the Tₘ did not follow a continuous trend with composition but fell into a minimum for copolyester compositions around 70% of Galₓ units. This behavior suggested the occurrence of two different crystal structures in each series according to which unit, galactaric or terephthalic, is predominant in the copolyester. Melting enthalpies displayed a similar behavior to melting temperatures, also falling into a minimum for intermediate compositions.

All PDT₉Galₓ copolyesters and their respective parent PDT and PDGalₓ homopolymers were able to crystallize upon cooling from the melt. On the contrary, in the PHT₉Galₓ series, only PHT₉₀Galₓ₁₀ crystallized from the melt, although PHT₇₀Galₓ₃₀ presented cold crystallization. Moreover, PHT crystallized from the melt, whereas PHGalₓ did not present such behavior. The different results found between the two series regarding crystallization were in accordance with the higher flexibility of the dodecamethylene segment. The copolyesters crystallized from the melt recovered about 75–90% of their initial crystallinity and displayed almost the same melting temperatures. To evaluate quantitatively the effect of composition on crystallizability, the isothermal crystallization

### FIGURE 1

13C NMR signals used for the microstructure analysis of PHTₓGalₓ copolyesters (left) with indication of the dyads to which they are assigned (right).

### TABLE 2

Microstructure Analysis of PHTₓGalₓ Copolyesters

<table>
<thead>
<tr>
<th>Copolyester</th>
<th>Dyads (mol %)</th>
<th>Number Average Sequence Lengths</th>
<th>Randomness</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>TT</td>
<td>TG/GT</td>
<td>GG</td>
</tr>
<tr>
<td>PHT₉₀Galₓ₁₀</td>
<td>80.9</td>
<td>17.6</td>
<td>1.6</td>
</tr>
<tr>
<td>PHT₇₀Galₓ₃₀</td>
<td>48.7</td>
<td>41.5</td>
<td>8.7</td>
</tr>
<tr>
<td>PHT₅₀Galₓ₅₀</td>
<td>26.8</td>
<td>50.8</td>
<td>22.4</td>
</tr>
<tr>
<td>PHT₃₀Galₓ₇₀</td>
<td>9.1</td>
<td>43.5</td>
<td>47.4</td>
</tr>
<tr>
<td>PHT₁₀Galₓ₉₀</td>
<td>1.4</td>
<td>23.6</td>
<td>75.0</td>
</tr>
</tbody>
</table>
of PDTGalx copolyesters in the whole range of compositions was comparatively studied in the 50–105 °C interval. Unfortunately, not all the copolyesters could be compared at the same isothermal crystallization temperature due to large differences in their crystallization rates. Nevertheless, crystallization temperatures were selected as close as possible so that meaningful conclusions could be drawn. For comparative purposes, the isothermal crystallization of PHT10Galx10 and its parent homopolyester PHT was also examined. PDTGalx, PDT10Galx90, and PDT30Galx70 isothermally crystallized at 60 °C revealed that the crystallization of Galx enriched copolyesters was largely delayed by the presence of terephthalate units. The conclusion derived from this study is that crystallization rate is maximum for the homopolyesters PDT and PDGalx and that it decays in both cases upon incorporation of a second comonomer to fall into a minimum for intermediate copolyester compositions.

Crystal Structure and Stress-strain Behavior

DSC results have shown that both PHTGalx and PDTGalx copolyesters are semicrystalline for the whole range of compositions and suggested the existence of two different structures depending on which unit, galactaric or terephthalic, is predominant in the copolyester. To complement DSC data, powder X-ray diffraction analyses were performed for both PHTGalx and PDTGalx copolyesters. Powder X-ray diffraction patterns are presented in Figure 5, and most Bragg spacings present in such patterns are listed in Table 5. Homopolyester PDT and PDT10Galx90, PDT30Galx70, and PDT50Galx50 copolyesters produced the same diffraction pattern, which was distinguished by the presence of four prominent reflections at 5.5, 5.0, 4.3, and 3.8 Å. On their turn, PHT and PHGalx copolyesters displayed the same diffraction pattern with five prominent reflections at 5.0, 4.8, 4.3, 4.0, and 3.6 Å only differing in the degree of sharpness. However, PDT10Galx70 and PDT10Galx90 displayed the same reflection pattern as homopolyester
PDGalx, with three prominent reflections at 4.6, 4.3, and 4.0 Å, whereas PHT10Galx70 and PHT10Galx90 displayed the same reflection pattern as PHGalx, with three prominent reflections at 5.0, 4.3, and 4.0 Å. The valuable conclusion that can be drawn from these results is that PHTxGalxy and PDTxGalxy copolyesters containing up to 50% of galactaric units must share the same crystal structure as PHT and PDT, respectively, whereas they retain the structure of PHGalx and PDGalx homopolymers, respectively, when the content in Galx units arrive to be 70% as minimum.

To evaluate the influence of the presence of Galx units in the terephthalate polyesters, tensile essays of both PHTxGalxy and PDTxGalxy series were carried out using thin films prepared by casting from chloroform solution. The recorded stress-strain curves are shown in Figure 6, and the mechanical parameters measured in such essays are listed in Table 5. PHT was the polyester, which presented the highest elastic modulus and tensile strength with a steadily reduction in these parameters as the terephthalate units were replaced by Galx units, so that all the copolyester values span between those of PHT and PHGalx homopolymers. The same trend was observed for PDTxGalxy copolyesters, with elastic modulus comprised between 430 and 150 MPa and tensile strength values located in the 13–18 MPa range.

**Hydrolytic Degradation and Biodegradation**

The difficulty in hydrolyzing and biodegrading aromatic polyesters is a well-known fact. However, previous studies on the degradability of polyesters containing sugar moieties have revealed that the presence of these units increases the hydrophilicity of polyesters and enhances the attack by water. To investigate the influence of the incorporation of Galx on hydrodegradation and biodegradation of polyterephthalates, a comparative study of the two homopolymers PDT and PDGalx and the intermediate PDT50Galx50 copolyester was made under a variety of conditions.

Degradation results obtained for the copolyester PDT50Galx50, as well as for its parent homopolymers upon incubation in aqueous pH 7.4 buffer at 37 °C, with and without porcine pancreas lipase, are presented in Figure 7. The changes taking place in sample weight, $M_w$ and $M_n$, and...
polydispersity were followed as a function of the incubation time. According to the invariance observed for these parameters in the case of PDT homopolyester, it was concluded that no detectable degradation took place in this polymer, neither in the presence nor in the absence of lipase. On the contrary, the results obtained for both PDT50Galx50 and PDGalx were much more stirring. A substantial decay in sample weight, $M_w$ and $M_n$ was observed for both polyesters when they were incubated in the aqueous buffer, which was more pronounced as the content in Galx increased. Nonetheless, what is remarkable in this study is the fact that degradation was significantly more noticeable when incubation was made adding lipases to the degradation medium. This result evidences the capacity of Galx unit for making aromatic polyester susceptible to biodegradation. Given the random nature of the copolyesters and assuming that aliphatic moieties are first degraded, the remaining aromatic residues will be composed of a few repeating units (their average length will depend on the composition). Earlier studies carried out by us on the degradability of building blocks of aromatic polyesters showed that DMT and BISHET were readily degraded by bacteria. To estimate the hydrodegradability of these copolyesters in a more aggressive medium, copolyester PDT50Galx50 as well as the parent homopolyesters PDT and PDGalx were incubated at 80°C in water at pH 2.0. Results are compared in Figure 8, which clearly reveals a notable influence of the Galx units under such conditions. A fast weight loss of PDT50Galx50 and PDGalx samples took place during the first period of

![Figure 4](https://www.materialsviews.com/journalopolymerscienceparta-2012-50-3393-3406-3401.png)

**FIGURE 4** Isothermal crystallization of PHT, PHT90Galx10, PDT, and PDT90Galx10 at the indicated temperatures. Relative crystallinity versus time plot (a and a’) and log-log plot (b and b’).
incubation, which slowed down in the later stages. In fact, the weight that was lost upon 8 weeks of incubation was about 40 and 85% for PDT50Galx and PDGalx, respectively, whereas the weight of PDT homopolyester was maintained unchangeable through all the process. Even more remarkable was the decrease in molecular weight, particularly if compared with the invariance observed for PDT. In accordance to changes observed in sample weight, \( M_w \) remained invariable corroborating that PDT is fully resistant to the aqueous attack. On the contrary, the decrease in \( M_w \) of PDT50Galx and PDGalx became apparent from the beginning to reach a final value of 11,000 and 5,000 g mol\(^{-1}\) after 8 weeks of incubation.

A NMR study was undertaken to deep insight the degradation of the polyester chain at the molecular level. \(^1\)H NMR spectra of the products released to the aqueous medium and the residual material resulting after 8 weeks of incubation in acidic water at 80 °C are depicted in Figure 9 and in the Supporting Information. As expected, PDT spectra of both the aqueous medium and the residual material did not show differences with the initial spectra. By contrast, the PDGalx spectrum of the incubation medium showed signals corresponding to the released Galx diacid. The fact that no signals corresponding to 1,12-dodecanediol were detected was probably due to the insolubility of 1,12-dodecanediol in water. Furthermore the NMR analysis of the incubation medium of PDT50Galx50 showed only signals characteristic of Galx diacids and the spectrum of residual polymer contained \(-\text{CH}_2\text{OH}\) signals of both oligomers and 1,12-dodecanediol in addition to those arising from aromatic COOH end-groups of oligomers. Integration of galactaric and terephthalic signals indicated that the residual material contained 2.0% of Galx and 98.0% of terephthalic units. Comparison with the \(^1\)H NMR spectrum of initial PDT50Galx50 leads to conclude that degradation of this copolyester occurs mainly by splitting of the Galx ester groups with release of water-soluble Galx diacid and water-insoluble 1,12-dodecanediol to the medium. The residual copolyester showed a continuous reduction in molecular weight and an increase in the terephthalate content as degradation proceeded.

**TABLE 4** Isothermal Crystallization Data for PHT\(_x\)Gal\(_x\) and PDT\(_x\)Gal\(_x\) Copolyesters

<table>
<thead>
<tr>
<th>Copolyester</th>
<th>( T_c ) (°C)</th>
<th>( t_0 ) (min)</th>
<th>( t_{1/2} ) (min)</th>
<th>( n )</th>
<th>(-\log k)</th>
<th>( T_m ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHT</td>
<td>115</td>
<td>0.27</td>
<td>1.64</td>
<td>2.42</td>
<td>0.51</td>
<td>139.6</td>
</tr>
<tr>
<td></td>
<td>117.5</td>
<td>0.29</td>
<td>2.01</td>
<td>2.88</td>
<td>0.82</td>
<td>140.6</td>
</tr>
<tr>
<td>PHT(<em>{90})Gal(</em>{10})</td>
<td>115</td>
<td>0.38</td>
<td>4.44</td>
<td>2.82</td>
<td>1.88</td>
<td>132.2</td>
</tr>
<tr>
<td></td>
<td>117.5</td>
<td>0.44</td>
<td>5.13</td>
<td>3.07</td>
<td>2.19</td>
<td>133.0</td>
</tr>
<tr>
<td>PHT(<em>{120})Gal(</em>{10})</td>
<td>120</td>
<td>0.61</td>
<td>8.39</td>
<td>3.23</td>
<td>3.04</td>
<td>133.9</td>
</tr>
<tr>
<td>PDGalx</td>
<td>100</td>
<td>0.23</td>
<td>1.23</td>
<td>2.27</td>
<td>0.18</td>
<td>118.7</td>
</tr>
<tr>
<td></td>
<td>102.5</td>
<td>0.28</td>
<td>1.77</td>
<td>2.31</td>
<td>0.56</td>
<td>119.4</td>
</tr>
<tr>
<td></td>
<td>105</td>
<td>0.42</td>
<td>4.01</td>
<td>2.69</td>
<td>1.65</td>
<td>120.3</td>
</tr>
<tr>
<td>PDGalx</td>
<td>100</td>
<td>0.31</td>
<td>2.10</td>
<td>2.72</td>
<td>0.87</td>
<td>115.4</td>
</tr>
<tr>
<td></td>
<td>105</td>
<td>0.86</td>
<td>3.70</td>
<td>2.76</td>
<td>1.60</td>
<td>116.2</td>
</tr>
<tr>
<td>PDT(<em>{70})Gal(</em>{30})</td>
<td>80</td>
<td>0.26</td>
<td>1.47</td>
<td>2.50</td>
<td>0.37</td>
<td>100.7</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>0.41</td>
<td>3.08</td>
<td>2.79</td>
<td>1.34</td>
<td>102.2</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>1.41</td>
<td>10.58</td>
<td>2.83</td>
<td>2.85</td>
<td>104.9</td>
</tr>
<tr>
<td>PDT(<em>{50})Gal(</em>{50})</td>
<td>72</td>
<td>0.20</td>
<td>1.12</td>
<td>2.06</td>
<td>0.06</td>
<td>87.1</td>
</tr>
<tr>
<td></td>
<td>74</td>
<td>0.30</td>
<td>1.30</td>
<td>2.13</td>
<td>0.14</td>
<td>88.0</td>
</tr>
<tr>
<td></td>
<td>76</td>
<td>0.45</td>
<td>2.32</td>
<td>2.25</td>
<td>0.73</td>
<td>89.4</td>
</tr>
<tr>
<td>PDT(<em>{50})Gal(</em>{50})</td>
<td>50</td>
<td>0.33</td>
<td>2.58</td>
<td>2.12</td>
<td>0.96</td>
<td>74.2</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.56</td>
<td>6.54</td>
<td>2.75</td>
<td>2.25</td>
<td>75.5</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.94</td>
<td>8.86</td>
<td>3.08</td>
<td>3.03</td>
<td>76.4</td>
</tr>
<tr>
<td>PDT(<em>{10})Gal(</em>{90})</td>
<td>55</td>
<td>0.13</td>
<td>0.64</td>
<td>2.31</td>
<td>-0.53</td>
<td>84.9</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.26</td>
<td>1.16</td>
<td>2.49</td>
<td>0.06</td>
<td>85.4</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>0.45</td>
<td>2.58</td>
<td>2.78</td>
<td>1.07</td>
<td>86.0</td>
</tr>
<tr>
<td>PDGalx</td>
<td>55</td>
<td>0.07</td>
<td>0.38</td>
<td>2.28</td>
<td>-1.03</td>
<td>89.1</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.22</td>
<td>0.94</td>
<td>2.42</td>
<td>0.18</td>
<td>89.6</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>0.37</td>
<td>2.23</td>
<td>2.76</td>
<td>0.88</td>
<td>90.2</td>
</tr>
</tbody>
</table>

**FIGURE 5** Powder WAXS profiles of PHT\(_x\)Gal\(_x\) (a) and PDT\(_x\)Gal\(_x\) (b) copolyesters.
TABLE 5 Powder X-ray Diffraction Data and Mechanical Properties of PHT$_{x}$Gal$_{y}$ and PDT$_{x}$Gal$_{y}$ Copolyesters

<table>
<thead>
<tr>
<th>Copolyester</th>
<th>$d^a$ (Å)</th>
<th>Mechanical Properties</th>
<th>Elastic modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHT</td>
<td>7.2 m</td>
<td>5.0 s 4.8 s 4.3 w 4.0 s 3.6 s</td>
<td>0.41</td>
<td>610 ± 15</td>
<td>24 ± 2</td>
</tr>
<tr>
<td>PHT$<em>{90}$Gal$</em>{10}$</td>
<td>7.2 m</td>
<td>5.0 s 4.8 s 4.3 m 4.1 s 3.6 m</td>
<td>0.40</td>
<td>653 ± 12</td>
<td>22 ± 1</td>
</tr>
<tr>
<td>PHT$<em>{70}$Gal$</em>{30}$</td>
<td>7.2 m</td>
<td>5.0 m 4.8 m 4.3 m 4.1 m 3.6 m</td>
<td>0.37</td>
<td>451 ± 9</td>
<td>19 ± 2</td>
</tr>
<tr>
<td>PHT$<em>{50}$Gal$</em>{50}$</td>
<td>7.2 m</td>
<td>5.0 m 4.8 w 4.3 m 4.1 m 3.6 w</td>
<td>0.34</td>
<td>327 ± 9</td>
<td>17 ± 1</td>
</tr>
<tr>
<td>PHT$<em>{30}$Gal$</em>{70}$</td>
<td>10.4 m</td>
<td>7.1 s 5.0 s 4.3 s 4.0 s 3.6 s</td>
<td>0.30</td>
<td>260 ± 7</td>
<td>15 ± 1</td>
</tr>
<tr>
<td>PHT$<em>{10}$Gal$</em>{90}$</td>
<td>10.4 m</td>
<td>7.1 s 5.0 s 4.3 s 4.0 s 3.6 s</td>
<td>0.33</td>
<td>176 ± 5</td>
<td>14 ± 1</td>
</tr>
<tr>
<td>PHGal$_x$</td>
<td>10.4 m</td>
<td>7.1 s 5.0 s 4.3 s 4.0 s 3.6 s</td>
<td>0.34</td>
<td>158 ± 4</td>
<td>13 ± 1</td>
</tr>
<tr>
<td>PDT</td>
<td>17.8 s</td>
<td>5.5 s 5.0 s 4.3 s 3.8 s 3.8 s</td>
<td>0.50</td>
<td>432 ± 11</td>
<td>18 ± 2</td>
</tr>
<tr>
<td>PDT$<em>{90}$Gal$</em>{10}$</td>
<td>17.8 s</td>
<td>5.5 s 5.0 s 4.3 s 3.8 s 3.8 s</td>
<td>0.48</td>
<td>389 ± 8</td>
<td>17 ± 2</td>
</tr>
<tr>
<td>PDT$<em>{70}$Gal$</em>{30}$</td>
<td>17.8 s</td>
<td>5.5 s 5.0 s 4.3 s 3.8 s 3.8 s</td>
<td>0.45</td>
<td>317 ± 8</td>
<td>16 ± 1</td>
</tr>
<tr>
<td>PDT$<em>{50}$Gal$</em>{50}$</td>
<td>17.9 s</td>
<td>5.5 s 5.0 s 4.3 s 3.8 s 3.8 s</td>
<td>0.42</td>
<td>261 ± 6</td>
<td>16 ± 1</td>
</tr>
<tr>
<td>PDT$<em>{30}$Gal$</em>{70}$</td>
<td>17.9 s</td>
<td>4.6 s 4.3 s 4.0 s 3.8 s 3.8 s</td>
<td>0.40</td>
<td>220 ± 6</td>
<td>15 ± 1</td>
</tr>
<tr>
<td>PDT$<em>{10}$Gal$</em>{90}$</td>
<td>17.9 s</td>
<td>4.6 s 4.3 s 4.0 s 3.8 s 3.8 s</td>
<td>0.41</td>
<td>172 ± 5</td>
<td>14 ± 1</td>
</tr>
<tr>
<td>PDGal$_x$</td>
<td>17.9 s</td>
<td>4.6 s 4.3 s 4.0 s 3.8 s 3.8 s</td>
<td>0.42</td>
<td>155 ± 4</td>
<td>13 ± 1</td>
</tr>
</tbody>
</table>

* Bragg spacings measured in powder diffraction patterns for samples coming directly from synthesis. Intensities visually estimated as follows: m, medium; s, strong; w, weak.

b Crystallinity 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.

FIGURE 6 Stress-strain curves for PHT$_{x}$Gal$_{y}$ (a) and PDT$_{x}$Gal$_{y}$ (b) copolyesters.

FIGURE 7 Degradation of PDT, PDT$_{50}$Gal$_{50}$, and PDGal$_x$ at pH 7.4 in the presence of lipase from porcine pancreas (solid lines) and without lipase (dashed lines) at 37°C. (a) Remaining weight versus degradation time. (b) Changes in $M_w$ and $M_n$ (solid symbols) and polydispersity index (empty symbols) versus incubation time.
The analysis by SEM (Fig. 10 and Supporting Information) of the surface of the incubated material revealed the changes taking place in the micromorphology of the copolyester PDT<sub>50</sub>Gal<sub>x50</sub>, as well as the parent homopolymers PDT and PDGalx due to degradation. The SEM analysis confirmed that the smooth surface of PDT remained unaltered after being incubated under any applied condition confirming the reluctance of this polyester to be hydrolyzed. The surface of the initial sample of PDGalx exhibited a spherulitic texture, which became plenty of cracks after being incubated under physiological conditions in the presence of lipase, a feature that was absent when incubation was carried out in the absence of enzymes. However, when PDGalx was incubated in acidic water at room temperature, some little cracks were
also developed, indicating that hydrodegradation was more active in acidic than in neutral medium. After being incubated at 80°C in water at pH 2.0, the spherulites of PDGalx were almost destroyed, and a second phase was deposited on them, which is thought to be composed of 1,12-dodecanediol that crystallized after being released to the medium. With regard to PDT_{50}Galx_{50}, SEM micrographs of samples incubated at 80°C in water at pH 2.0 showed almost destruction of the polymer surface with features similar to that happening with PDGalx. However, when PDT_{50}Galx_{50} was incubated in the presence of lipase, plenty of tiny holes and cracks appeared in the surface evidencing again a degradation process similar to that undergone by PDGalx. The important conclusion derived from this study is that degradation of PDT_{50}Galx_{50} copolyester under physiological conditions was due to the action of lipase, a property that points to these carbohydrate-based aromatic copolyesters as interesting biodegradable materials.

CONCLUSIONS

The bicyclic diacetal dimethyl 2,3:4,5-di-O-methylene galactarate Galx has been successfully used as comonomer of di-methyl terephthalate to produce random copolyesters by
melt polycondensation with either 1,6-hexanediol or 1,12-
dodecanediol. Two sets of galactarate-terephthalate copo-
lyesters, each one covering the whole range of compositions
and with a random microstructure, were obtained. The copo-
lyesters were thermally stable and semicrystalline with melt-
ing temperatures and enthalpies slightly decreasing as the
content in the second comonomer increased and falling into a
minimum for intermediate compositions, in accordance with
the existence of two different crystal structures in each series.
The copolysters made of dodecanediol were able to crystal-
lize from the melt although the crystallization rate was signifi-
cantly delayed by the presence of Galx. In addition, the glass
transition temperature of the parent terephthalate homopo-
lyesters diminished with the replacement of the aromatic
units by the sugar units. The Galx containing copolyesters dis-
played an accentuated hydrodegradability when compared
with the fully aromatic homopolysters, which is most re-
markable; they appeared to be sensitive to enzymatic action
showing a significant hydrolytic degradability under physio-
logical conditions in the presence of lipases. The hydrolysis of
the copolyesters was found to take place mainly by breaking
of the galactarate ester bonds. It is concluded therefore that
the incorporation of the acetalized galactarate units in aro-
matic polyesters makes them not only more easily degradable
but also biodegradable while retaining their thermal and me-
chanical properties at acceptable values.

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