Isomannide-Containing Poly(butylene 2,5-furandicarboxylate) Copolyesters via Ring Opening Polymerization

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Additional Supporting Information (SI) may be found in the online version of this article.

Abstract: Cyclic oligomers of isomannide 2,5-furandicarboxylate were synthesized using the high dilution condensation method. A mixture of dimer, trimer and tetramer species largely enriched in the dimer was obtained. These cyclic oligomers were copolymerized with those made of butylene 2,5-furandicarboxylate in bulk at 220 °C by ring opening polymerization using Sn(Oct)₂ as catalyst. A series of random poly(butylene 2,5-furandicarboxylate) copolyesters containing isomannide in a range of 5 to 50 %-mole and with weight-average molecular weights between 30,000 and 50,000 g·mol⁻¹ were prepared. These copolyesters started to decompose above 300 °C and only those containing less than 10 %-mole of isomannide showed signs of crystallinity. They displayed glass-transition temperatures in the 40-100 °C range with values increasing steadily with the content in isomannide. At difference with the poly(butylene 2,5-furandicarboxylate) homopolyester that is reluctant to hydrolysis, the isomannide-containing copolyesters were noticeably degraded by water, much more rapidly when exposed to the presence of lipases.

Keywords: Bio-based polyesters, furan-based polyesters, polyfuranoates, FDCA, isohexides, isomannide, poly(butylene furanoate), ring-opening polymerization.
Introduction

Ring Opening Polymerization (ROP) of cyclic monomers is a well-known method in polymer chemistry, in particular when the synthesis of polycondensation polymers is concerned.\cite{1,2} Despite the advantages offered by ROP (milder reaction conditions, absence of subproducts, minimization of side-reactions, etc.), conventional polycondensation continues to be the preferred preparation method for polyesters because of the high difficulty that is generally met in supplying the lactones required for the application of ROP.\cite{3,4} Nevertheless some representatives polyesters such as polylactic acid or poly(ε-caprolactone) are industrially produced by ROP,\cite{5-7} and the expansion of this method, although gradual, appears to be incessant. Both enthalpically and entropically driven processes are known to operate in ROP depending on the size of the lactone that is polymerized.\cite{1,2,8,9}

Aromatic polyesters, most of them poly(phthalate)s, are invariably produced at the industrial scale by polycondensation in the melt of diols and bencendicarboxylic acids or their methyl esters.\cite{10-12} Nonetheless a diversity of cyclic oligophthalates and their ROP to linear polyesters have been reported in the scientific literature.\cite{1,2} The synthesis of these cycles using the so-called high-dilution condensation method and their ROP to poly(alkylene terephthalate)s and poly(alkylene isophthalate)s was firstly described by Brunelle et al.,\cite{14,15} and later extended to other related polyesters by different authors.\cite{16-20} Recently the preparation of cyclic oligo(alkylene 2,5-furandicarboxylate)s by this method has been reported,\cite{21,22} which has opened a new via towards the preparation of furane-based polyesters and copolyesters. Thus random furanoate-terephthalate\cite{23} and furanoate-succinate\cite{24} copolyesters, as well as furanoate copolyesters containing caprolactone\cite{25} have been synthesized by ROP with results comparable to those attained by melt polycondensation.

Polyfuranoates derived from 2,5-furandicarboxylic acid (FDCA) are polyesters of maximum current interest.\cite{26} Poly(ethylene 2,5-furandicarboxylate) (PEF) and poly(butylene 2,5-furandicarboxylate) (PBF) are sustainable aromatic polyesters that
are proposed as potential substitutes of the industrial thermoplastics poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), respectively. In fact, PBF combines a bio-based character with a set of properties that compares or even surpasses those of PBT. Considerable efforts have been made however to modify its physical or chemical behavior, and a number of PBF copolyesters displaying novel properties may be today found in the literature. One usually applied approach has been to design PBF copolyesters with high \( T_g \) or enhanced biodegradability without detriment of the genuine sustainability of the parent homopolyester. This is really challenging since stiff monomers coming from renewable sources and suitable for polycondensation are not frequent. Bicyclic dianhydroalditols and diacetalized alditols are exceptional examples of diols that could be used for such purpose.

Isomannide (Im) together with isosorbide (Is) and isoidide (Id) are 1,4:3,6 dianhydroalditols (commonly known as isohexides), a family of bicyclic diols that have attracted great attention in these last decades as new bio-based monomers for polycondensation. The high interest for isohexides arises not only from their bio-based character but also from their capacity to generate high \( T_g \) polymers due to the great stiffness of the bicyclic structure. Isosorbide (1,4:3,6 dianhydrosorbitol derived from D-glucose) is by far the most widely known and used isohexide. A wide number of polycondensates containing isosorbide have been described and even some of them have achieved industrial realization. Isomannide has certain chemical advantages on isosorbide due to its more symmetrical structure but it has been much less studied because its accessibility is more difficult. Nonetheless, the only isohexide-containing cyclic oligomers suitable for ROP that have been reported in the literature are made from aliphatic dicarboxylic acids.

In this paper we wish to report on Im-containing copolyesters of poly(butylene 2,5-furandicarboxylate) prepared by ROP. Novel cyclic oligo(isomannide 2,5-furandicarboxylate), \( c(\text{ImF})_n \), have been synthesized and copolymerized with
oligo(butylene 2,5-furandicarboxylate), \( c(BF)_n \), to obtain a series of poly(butylene-co-
isomannide 2,5-furandicarboxylate) copolymers, \( (coPB_xIm_yF) \), with Im contents
ranging from 0 up to 50 %-mole. The copolymers are fully characterized and their
thermal properties and degradability are evaluated as a function of the comonomeric
composition. To our knowledge, only isosorbide has been used so far for making
furanoate-based copolymers, and conventional polycondensation was the technique
invariably applied in such cases. Furthermore, this is the first time that aromatic
polyesters containing isohexides are synthesized by ROP, and also that the thermal
properties and biodegradability of PBF have been enhanced without detriment of its
sustainability.

**Experimental**

**Materials.** 2,5-Furandicarboxylic acid (FDCA, 98% purity) was purchased from
Satachem and isomannide (Im, 98%) from TCI Chemicals. Thionyl chloride (SOCl₂,
99%), di-azabicyclo[2.2.2] octane (DABCO, 99%), tin octoate (Sn(Oct)₂, 98%) and
porcine pancreas lipase were purchased from Sigma Aldrich. All solvents were of
high-purity grade and used as received with the exception of tetrahydrofuran (THF)
that was dried on 3Å-molecular sieves and DABCO catalyst that was purified by
sublimation.

**Measurements.** \(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker AMX-300
spectrometer at 25 °C, operating at 300.1 and 75.5 MHz, respectively. All the
compounds were dissolved in deuterated chloroform (CDCl₃) or a mixture of CDCl₃
and trifluoroacetic acid (TFA). The spectra were internally referenced to
tetramethylsilane (TMS). About 10 and 50 mg of sample in 1 mL of solvent were used
for \(^1\)H and \(^{13}\)C NMR, respectively. Sixty-four scans were recorded for \(^1\)H and between
1,000 and 10,000 scans for \(^{13}\)C NMR. High performance liquid chromatography
(HPLC) analyses were performed at room temperature in a Waters apparatus
equipped with a UV detector of Applied Biosystems operating at 254 nm wavelength,
and a Scharlau Science column (Si60, 5 µm; 250 x 4.6 mm). Cyclic oligomers (1 mg) were dissolved in chloroform (1 mL) and eluted with hexane/1,4-dioxane 70/30 (v/v) at a flow rate of 1.0 mL⋅min⁻¹. Molecular weight analyses of polymers were performed by GPC on a Waters equipment provided with RI and UV detectors. 100 µL of 0.1% (w/v) sample solution was injected and chromatographed using 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as mobile phase with a flow of 0.5 mL⋅min⁻¹. HR5E and HR2 Waters linear Styragel columns (7.8 mm x 300 mm, pore size 10³–10⁴ Å) packed with crosslinked polystyrene and protected with a precolumn were used. Average molar masses and dispersities were calculated against PMMA standards. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra were recorded in a 4700 Proteomics Analyzer instrument (Applied Biosystems) of the Proteomics Platform of Barcelona Science Park, University of Barcelona. Spectra acquisition was performed in the MS reflector positive-ion mode. About 0.1 mg of sample was dissolved in 50 µL of DCM and 2 µL of this solution were mixed with an equal volume of an anthracene solution in dichloromethane (DCM) (10 mg⋅mL⁻¹), and the mixture left to evaporate to dryness onto the stainless steel plate of the analyser. The residue was then covered with 2 µL of a solution of 2,5-dihydroxibenzoic acid in acetonitrile/H₂O (1/1) containing 0.1% TFA, and the mixture was left to dry prior to exposition to the laser beam.

Thermogravimetric analysis (TGA) of polymers was performed on a Mettler-Toledo TGA/DSC 1 Star System under a nitrogen flow of 20 mL⋅min⁻¹ at a heating rate of 10 °C⋅min⁻¹ and within a temperature range of 30-600 °C. The non-destructive thermal behaviour was examined by differential scanning calorimetry (DSC) within the 30-200 °C range using a Perking-Elmer Pyris apparatus. Thermograms were obtained from 4-6 mg samples at heating and 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 temperature (T₉) was taken
as the inflection point of the heating traces recorded at 20 °C·min\(^{-1}\) from melt-
quinched samples, and the melting temperature (\(T_m\)) was taken as the maximum of
the endothermic peak appearing on the heating traces recorded from samples
crystallized from the melt.

X-Ray diffraction patterns from powdered samples coming directly from
synthesis were recorded on a PANalytical X’Pert PRO MPD θ/θ diffractometer using
the CuK\(_\alpha\) radiation of wavelength 0.1542 nm. Optical micrographs were taken using an
Olympus BX51 polarizing optical microscope with a Linkam THMS 600 stage attached.
For observation, 10 mg of sample were dissolved in 1 mL of HFIP for PBF or
chloroform for copolyesters, and 0.2 mL aliquots of these solutions were slowly
evaporated on a glass slide.

**Cyclic oligomers synthesis.** Cyclic oligomers \(c(BF)_n\) were synthesized applying the
high dilution condensation method (HDC) previously reported by us.\(^{22}\) Cyclic
oligomers \(c(ImF)_n\) were synthesized applying the same method. Briefly, \(\text{Error! Bookmark not defined.}\)
a three-necked round bottom flask was charged with 250 mL of
THF and cooled to 0°C, and then 12.5 mmol (1.40 g) of DABCO were added under
stirring. 5 mmol (0.96 g) of FDCA-Cl\(_2\) and 5 mmol (0.73 g) of isomannide in 10 mL of
THF were drop-wise added simultaneously for 40 min using two addition funnels in
order to maintain the reagents equimolarity in the reaction mixture. The reaction was
finished by adding 1 mL of water followed by 5 mL of 1M HCl, and after stirring for 5
min, it was diluted with DCM and filtered. The filtrate was washed with 0.1M HCl and
water, dried on MgSO\(_4\), and evaporated to dryness to render a mixture of linear and
cyclic oligomers. Linear oligomers were removed by flash chromatography through a
short column of silica gel using a cold mixture of DCM/diethyl ether 90/10 (v/v) as
eluent. Yield: 60%. \(c(ImF)_n\): \(^1\)H NMR (\(\delta\) ppm, CDCl\(_3\), 300 MHz): 7.34 (1s, 2H), 5.39
(m, 2H), 4.91 (m, 2H), 4.35 (m, 2H); 3.99 (m, 2H); \(^{13}\)C NMR (\(\delta\) ppm, CDCl\(_3\), 75.5
MHz): 157.2, 146.4, 146.3, 146.0, 119.6, 119.4, 80.7, 74.5, 74.4, 73.9, 71.2, 71.1, 70.9.

**Polymer synthesis.** Copolymerization of c(BF)$_n$ and c(ImF)$_n$ was performed in bulk following the procedure previously reported by us.$^{23}$ Briefly, mixtures of c(BF)$_n$ and c(ImF)$_n$ with the selected molar compositions were placed in a three necked round bottom flask provided with a N$_2$ flow and heated at 220 °C. Then Sn(Oct)$_2$ (0.5 % mole) was added to the molten mass and the reaction was left to proceed for 6 h. The reaction mixture was then cooled down to room temperature, diluted with CHCl$_3$, and precipitated with diethyl ether. The precipitated sample was analyzed by NMR.

**Hydrolytic and enzymatic degradation.** Hydrolytic degradation and biodegradation studies were made on PBF and PlmF homopolymesters, and coPB$_{50}$Im$_{50}$F, and coPB$_{70}$Im$_{30}$F copolyesters. Films of these polymers with a thickness of ~200 µm were prepared by casting from either HFIP or chloroform solution at a polymer concentration of 100 g·L$^{-1}$. The films were cut into 10 mm-diameter, 20-30 mg-weight disks and dried under vacuum to constant weight. For hydrolytic degradation, samples were immersed in vials containing 10 mL of either citric acid buffer, pH 2.0 or sodium phosphate buffer, pH 7.4 at 37 °C. Enzymatic degradation assays were carried out at 37 °C in pH 7.4 buffered sodium phosphate solution with 10 mg of porcine pancreas lipase added. In this case the buffered solution was replaced every 72 h in order to maintain the enzyme activity. In both cases, disks were withdrawn from the incubation medium at scheduled periods of time, washed carefully with distilled water, dried to constant weight, and finally analysed by GPC.

**Results and discussion**

The strategy followed to synthesize the cyclic oligoesters c(BF)$_n$, and c(Im)$_n$, and to polymerize them for producing the copolyesters coPB$_x$Im$_y$F is depicted in Scheme 1.
Scheme 1. Synthetic route to poly(butylene-co-isomannide 2,5 furandicarboxylate) copolyesters.

**Cyclic oligomers.** c(BF)$_n$ were synthesized as described in several works recently reported by us$^{22,25}$ following the high dilution (HDC) technique assisted by the organic catalyst DABCO. Characterization details of these cyclic oligomers are provided in the SI file (Figure S1). The same technique was then applied to the synthesis of cyclic oligo(isomannide 2,5-furandicarboxylate) c(ImF)$_n$, which are described in this paper for the first time. The NMR of the crude reaction product revealed that, in analogy with that happens with c(BF)$_n$, it was a mixture of cyclic oligomers of different sizes contaminated by a significant amount of linear species (Figure S2). After removing the linear oligomers by flash chromatography, the eluted sample was analyzed by NMR,
Maldi-Tof and HPLC (Figure 1) which demonstrated that this fraction consisted mainly of dimer (85%) accompanied by minor amounts of trimer and tetramer (10% and 5%, respectively). The thermal analysis of \( c(\text{ImF})_n \) by TGA showed that these cycles are resistant to heat up to temperatures around 350 °C, and the DSC analysis revealed that they are crystalline with melting point at 160 °C (Figure 2). The most relevant

<table>
<thead>
<tr>
<th>Cyclic oligomer</th>
<th>Precursors</th>
<th>Yield(^a) (%)</th>
<th>Composition(^b) ( n = 2,3,4 )</th>
<th>Thermal Properties(^c)</th>
<th>( ^{a}T_d ) (°C)</th>
<th>( ^{\text{max}}T_d ) (°C)</th>
<th>( T_m ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c(\text{BF})_n )</td>
<td>FDCA-Cl (_2) + BD</td>
<td>67</td>
<td>62/30/8</td>
<td></td>
<td>240</td>
<td>378</td>
<td>147</td>
</tr>
<tr>
<td>( c(\text{ImF})_n )</td>
<td>FDCA-Cl (_2) + Im</td>
<td>62</td>
<td>85/10/5</td>
<td></td>
<td>350</td>
<td>410</td>
<td>161</td>
</tr>
</tbody>
</table>

\(^a\) Yields after removing the linear species by flash chromatography.  
\(^b\) Molar ratio of cycle species determined by HPLC.  
\(^c\) Determined by TGA and DSC. \( ^{a}T_d \) is the onset temperature determined for a weight loss of 5%, \( ^{\text{max}}T_d \) is the temperature for maximum decomposition rate, and \( T_m \) is the melting temperature.
characteristics of these cycles compared with those of c(BF)$_n$, are collected in Table 1.

Figure 2. a) TGA (a and b) and DSC (c) of c(BF)$_n$ and c(ImF)$_n$.

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It is noteworthy to report that a series of experiments similar to those carried out for the synthesis of \( c(\text{ImF})_n \), were made using isosorbide, i.e. the isohexide derived from glucose, with the purpose of generating its corresponding cyclic oligoesters. Unfortunately, all the attempts were unsuccessful and apparently only linear oligomers were obtained according to the NMR analysis (Figure S3). The unfavorable relative spatial orientation of the two reactive hydroxyl groups in Is (exo and endo) compared to the two endo positions occupied by the two hydroxyls in Im could be invoked to be responsible for the different behavior observed. An exploratory study on the energy of the cyclic oligofuranoates of the three known isohexides (Is, Im and Id) was comparatively performed by molecular simulations. The results clearly revealed that cyclic oligomers made of Is are less stable than those made of Im (Figure S4), which is fully consistent with the experimental results reached in the attempts of cyclization carried out with isomannide and isosorbide. Simulation results also indicated a relative high energy for the cyclic oligofuranoates containing isoidide, which leads to predict that cyclization involving this diol will be hampered too. Isoidide has the two hydroxyl groups in exo position, which is very favorable for reactivity but not for cyclization due to their opposite orientation in the space.

**Synthesis of copolyesters.** Mixtures of \( c(\text{BF})_n \) and \( c(\text{ImF})_n \) covering the ratio range of 95/5 to 50/50 were copolymerized by ROP in bulk using tin 2-ethylhexanoate as catalyst to produce the \( \text{coPB}_x\text{Im}_y\text{F} \) copolyesters series. The homopolymers PBF and PlmF to be used as references in characterization and properties studies were prepared by this method too. The reaction temperature was fixed by taken into account the meltability of the cyclic fractions and the resulting polymers, as well as its effect on reaction kinetics. To assess this variable, a mixture of \( c(\text{BF})_n \) and \( c(\text{ImF})_n \) with a 60/40 molar ratio was made to react at 200, 220 and 230 °C, and aliquots of the reaction mixture were withdrawn at scheduled times and the molecular weight of the copolyester formed up to that instant was estimated by GPC. Results are plotted in
Figure 3a to show the positive effect of temperature on conversion upon raising it from 200 to 220 ºC whereas not significant change seems to happen after further increasing. According to these results and since the c(BF)ₙ cycles started to decompose around 240 ºC, it was advisable to fix the reaction temperature at 220 ºC for the ROP of the whole series. To complement this study, the evolution of $M_w$ with time in the ROP at 220 ºC of c(BF)ₙ/c(ImF)ₙ mixtures differing in composition was followed by using the same methodology as before, and results obtained therefrom are shown in Figure 3b.

![Figure 3a](image1)

**Figure 3a.** Plots of the evolution of $M_w$ of the resulting copolyesters coPBₓImᵧF against reaction time. a) coPB₆₀Im₄₀F at different temperatures. b) coPBₓImᵧF with different compositions.

The $M_w$ vs time plots showed that the $M_w$ of the copolyesters decreased steadily with the content in ImF which brings out the less reactivity of the c(ImF)ₙ cycles compared to the c(BF)ₙ in the ROP of their mixtures. Nevertheless, all the copolyesters could be obtained in yields and with molecular weights high enough as to validate successfully the suitability of the applied methodology in the synthesis of coPBₓImᵧF.

Yields, molecular weights and compositions of the whole coPBₓImᵧF series are collected in Table 2. Yields were above 80% in all cases with losses being ascribable to the low molecular species that could not be recovered in the precipitation treatment.
to which the final reaction product is subjected. \( M_w \) of copolyesters are roughly in the 
\( \sim 40,000-60,000 \, \text{g} \cdot \text{mol}^{-1} \) range, and the homopolysters PBF and PlmF were obtained
with 65,000 g·mol\(^{-1}\) and 28,000 g·mol\(^{-1}\) respectively, which is according to the trend observed for the copolyesters series. \( D \) values are between 1.5 and 2.0 which is a 
range of molar dispersity values according to expectations, in particular if transesterification reactions took place during ROP, a possibility that cannot be 
neglected given the high temperature used for reaction. The constitution of the polymers was ascertained by \(^1\)H and \(^13\)C NMR spectroscopy, and the spectra recorded
from coPB\(_{60}\)Im\(_{40}\)F with indication of all peak assignments are depicted in Figure 4. The
spectra of the whole series are included in the SI file (Figure S5). The quantitative
analysis of the \(^1\)H NMR spectra based on the integration of group specific signals
provided an accurate estimation of the copolymer composition in BF (butylene
furanoate) and ImF (isomannide furanoate) units. As it is seen in Table 2, differences
in Im contents between the feed and its generated copolyester are kept below 5%
which is a small value perfectly attributable to uncontrolled experimental causes.

<table>
<thead>
<tr>
<th>Polyester</th>
<th>Yield (%)</th>
<th>Composition(^a) ( x(\text{BF}/y(\text{ImF})) ) (mole/mole)</th>
<th>Molecular weight(^b) ( M_w ) (g·mol(^{-1}))</th>
<th>Microstructure(^c) ( D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBF</td>
<td>95</td>
<td>100/0</td>
<td>65,000</td>
<td>1.8</td>
</tr>
<tr>
<td>PB(<em>{93})Im(</em>{6})F</td>
<td>93</td>
<td>95/5 96/4</td>
<td>63,000</td>
<td>1.6</td>
</tr>
<tr>
<td>PB(<em>{90})Im(</em>{10})F</td>
<td>90</td>
<td>90/10 92/8</td>
<td>55,000</td>
<td>1.9</td>
</tr>
<tr>
<td>PB(<em>{85})Im(</em>{20})F</td>
<td>85</td>
<td>80/20 80/20</td>
<td>45,000</td>
<td>1.9</td>
</tr>
<tr>
<td>PB(<em>{85})Im(</em>{30})F</td>
<td>85</td>
<td>70/30 66/34</td>
<td>43,000</td>
<td>1.4</td>
</tr>
<tr>
<td>PB(<em>{85})Im(</em>{40})F</td>
<td>82</td>
<td>60/40 58/42</td>
<td>40,000</td>
<td>1.8</td>
</tr>
<tr>
<td>PB(<em>{85})Im(</em>{50})F</td>
<td>82</td>
<td>50/50 55/45</td>
<td>39,000</td>
<td>2.0</td>
</tr>
<tr>
<td>PlmF</td>
<td>80</td>
<td>0/100</td>
<td>28,000</td>
<td>1.9</td>
</tr>
</tbody>
</table>

\(^a\) % Mole feed and copolymer composition determined by NMR.
\(^b\) Weight-average molecular weight \((M_w)\) and dispersity \((D)\) determined by GPC.
\(^c\) % of dyads (BB, BIm/ImB and ImIm) determined by NMR, number average sequence lengths \((n_{BF}\) and \(n_{ImF}\)) and degree of randomness calculated using the approach reported by Randall.\(^{43}\)
Figure 4. $^{13}$C (top) and $^1$H (bottom) NMR of coPB$_{60}$Im$_{40}$F.

The elucidation of the microstructure of the copolyesters was made by $^{13}$C NMR analysis using the 145.5-147.5 signal arising from the non-protonated aromatic carbon of the furanoate unit that is sensitive to dyads. In consequence the signal appears split into four peaks (Figure 5) corresponding to the feasible dyads BB, ImIm, BIm/ImB. Peak areas were used to calculate, according to the procedure reported by Randall,$^{43}$ the number-average sequence lengths ($n$) and the degree of randomness ($R$) for each composition. $n$ and $R$ values are listed Table 2 indicating that a nearly statistical distribution of BF and Im is present in the coPB$_x$Im$_y$F copolyesters with a random degree that decreases as the content of the copolyester in isomannide increases.
Figure 5. $^{13}$C NMR signals used for microstructure analysis of coPB$_x$Im$_y$F with assignments of the carbons for the different dyads.

Thermal properties

The thermal properties of the coPB$_x$Im$_y$F copolyesters were analyzed by DSC and TGA, and data collected in these analyses are gathered in Table 3.

The thermogravimetric traces of the copolyesters recorded under an inert atmosphere over the 50/600 range, are depicted in Figure 6a and a representative selection of their derivative curves are shown in Figure 6b. PBF and PlmF homopolymers started to decompose around 360 °C and 325 °C, respectively,

Table 3. Thermal Properties of coPB$_x$Im$_y$F Copolyesters Prepared via ROP.

<table>
<thead>
<tr>
<th>Copolyester</th>
<th>TGA</th>
<th>DSC</th>
<th>Crystallization kinetics$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha_T$</td>
<td>$\beta_T$</td>
<td>$\Delta T_{g}$</td>
</tr>
<tr>
<td>PBF</td>
<td>360</td>
<td>400</td>
<td>6</td>
</tr>
<tr>
<td>coPB$<em>{95}$Im$</em>{5}$F</td>
<td>344</td>
<td>390</td>
<td>6</td>
</tr>
<tr>
<td>coPB$<em>{90}$Im$</em>{10}$F</td>
<td>329</td>
<td>390</td>
<td>8</td>
</tr>
<tr>
<td>coPB$<em>{85}$Im$</em>{15}$F</td>
<td>334</td>
<td>388</td>
<td>8</td>
</tr>
<tr>
<td>coPB$<em>{80}$Im$</em>{20}$F</td>
<td>330</td>
<td>390</td>
<td>9</td>
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<tr>
<td>coPB$<em>{75}$Im$</em>{25}$F</td>
<td>330</td>
<td>390</td>
<td>9</td>
</tr>
<tr>
<td>coPB$<em>{70}$Im$</em>{30}$F</td>
<td>362</td>
<td>403</td>
<td>5</td>
</tr>
<tr>
<td>PlmF</td>
<td>325</td>
<td>376</td>
<td>9</td>
</tr>
</tbody>
</table>

$^a$Onset temperature measured for 5% of weight loss.

$^b$Avrami parameters determined from isothermal crystallization at de indicated $T_c$. 
whereas the coPBₓImᵧF copolyesters did it at intermediate values but without following a recognizable trend. Nevertheless, ᵇTₓₐ₁₅% is far above 300 °C for whichever composition, which is a clear indication of the good thermal stability of these copolyesters. A similar pattern is observed for the temperature at which maximum rate decomposition takes place although in this case this temperature is much less fluctuant along the series. In fact, max Tₓ of copolyesters is confined in the ~390-400 °C, which are values very close to that of PBF but clearly above the 376 °C shown by the PlmF homopolyester. It is remarkable that decomposition of all the polyesters takes place through one single step and at a rate that largely depends on the content in Im units. Residual weights after heating at 600 °C oscillated between 5% and 10% of the initial sample weight without showing apparent interrelation with the polyester composition.

![TGA traces of coPBₓImᵧF (a) and a selection of their derivative curves (b).](image)

**Figure 6.** TGA traces of coPBₓImᵧF (a) and a selection of their derivative curves (b).

The DSC traces of coPBₓImᵧF together with those of PBF and PlmF homopolymers, recording at heating and cooling over the 0-200 °C range, are depicted in Figure 7. Only PBF and copolyesters containing as maximum 10% of Im were found to display thermal changes indicative of melting or crystallization. Furthermore, only coPBₓ₉₅Imₓ₅F was able to crystallize clearly from the melt whereas an extremely weak broad crystallization exotherm was hardly seen on the cooling trace of
coPB₉₀Im₁₀F. As expected, both melting temperature and enthalpy decreased with the content in isomannide. It can be said therefore that coPBₓImᵧF copolyesters are essentially amorphous polymers as it is also the case for PlmF homopolyester, a feature that had been earlier reported by Okada et al.³⁶ These results bring into evidence the strong repressing effect that the insertion of Im units into the PBF chain exerts on the genuine crystallinity of this polyester. The occurrence of such effect is by no means surprising since most of homopolymers made of isoheuses are known to be unable to crystallize.⁴⁴-⁴⁶

Figure 7. a) First heating, b) cooling, and c) second heating of coPBₓImᵧF.

The crystallinity of coPB₉₅Im₅F detected by DSC was firmly sustained by XRD analysis (Figure S6). The powder diffraction pattern recorded from this copolyester displayed discrete scattering that was similar in both spacing and intensity to that of PBF. The scattering showed by coPB₉₀Im₁₀F was much poorer but still indicative of a slight crystallinity according to what was observed by DSC. Additionally, the characteristic grainy texture displayed by PBF films when they are observed by POM was also present in the films of these two copolyesters (Figure S7). It can be concluded from these observations therefore that both coPB₉₅Im₅F and coPB₉₀Im₁₀F are semicrystalline and that they crystallize sharing the crystal structure of PBF. The crystallization of copolyesters containing small amounts of one of their comonomers in the crystal lattice of the homopolymer made of the major comonomer is a well-known
common fact. The phenomenon is understood by assuming that upon crystallization the minor comonomer is rejected to the amorphous phase and only homogeneous sequences made of the main comonomer are incorporated in the crystal phase.\textsuperscript{47-49}

Since the capacity of $\text{coPB}_{95}\text{Im}_{5}F$ to crystallize is so severely restricted, the kinetics study addressed to quantify the influence of composition on crystallizability had to be restricted to the $\text{PBF/coPB}_{95}\text{Im}_{5}F$ pair. The isothermal crystallization of these two polyesters was carried out at 146 °C and the evolution of crystallinity with time was compared. The typical sigmoidal curves resulting from these assays are plotted in Figure 8, and the kinetic parameters estimated by application of the Avrami approach to the experimental data are given in Table 3. As it could anticipated, PBF and $\text{coPB}_{95}\text{Im}_{5}F$ crystallized through a similar mechanism (their Avrami exponents are comparable) but the crystallization process is highly delayed for the copolyester ($t_{1/2}$ is almost doubled).

![Figure 8. Relative crystallinity vs time in the isothermal crystallization of PBF and $\text{coPB}_{95}\text{Im}_{5}F$ at 146 °C.](image)

The glass-transition temperature of the copolyesters was measured on the DSC heating traces registered from samples that were rapidly cooled from the melt. These traces showing the inflections indicative of glass-transition may be inspected in the SI file (Figure S8), and the $T_g$ values estimated therefrom are listed in Table 3. It was found that the $T_g$ of PBF appearing at 42 °C raised up to 97 °C as the content of the polymer in Im increased from 0 to 50 %-mole. Obviously, the replacement of the
relatively flexible butylene unit by the much more rigid Im bicyclic structure reduced the
chain mobility triggering a notable increase in $T_g$. The high stiffness of Im is clearly
brought into evidence in the PImF homopolyester itself, which has a $T_g$ of 189 °C. The
variation of $T_g$ with the copolyester composition is plotted in Figure 9 where the
experimentally observed values are compared with those predicted by the Fox and
Gordon-Taylor equations. As it is largely expected from the amorphous nature of
the coPB$_x$Im$_y$F, a good fit is attained with both equations as far as contents in Im are
20% and higher. The deviations detected for PBF, coPB$_{95}$Im$_5$F and coPB$_{90}$Im$_{10}$F are
likely due to the crystallinity present in these polyesters.

![Figure 9. Variation of $T_g$ with composition in the coPB$_x$Im$_y$F series.](image)

**Hydrolytic and enzymatic degradation.** Both hydrolytic degradation and
biodegradation of PBF have been examined by different authors in previous works, the which unanimously reported the high resistance of this polyester to be attacked
by water. This is a behavior characteristic of aromatic polyesters that is commonly
rationalized by taking into account the hydrophobicity and high $T_g$ caused by the
presence of the aromatic units. On the other hand, the incorporation of isohexide units in polyesters has been repeatedly reported to increase their sensitivity to water.\textsuperscript{34,36, 54}

The effect played by the presence of isomannide in the degradability of PBF has been examined in this work in a systematic manner. Both the decrease in sample weight and molecular weight during 30 days of incubation in a phosphate buffer at 7.4 with and without the assistance of porcine pancreas enzyme was monitored for coPB,Im,F copolyesters containing 30 and 40 %-mole of Im as well as for the PBF and PlmF homopolymers, and results are plotted in Figure 10. It is apparent in these plots

![Hydrolytic degradation of coPB,Im,F copolyesters and PBF and PlmF homopolymers.](image)

**Figure 10.** Hydrolytic (a and a') and enzymatic (b and b') degradation of coPB,Im,F upon incubation in water at pH 7.4.
that copolymerization enhances significantly the degradability of PBF. In fact, an essentially invariable function independent of time was obtained in the incubation of PBF for both sample weight and molecular weight, and either with or without enzyme added. On the contrary, PlmF appears to be highly sensitive to hydrolysis undergoing around 20% of degradation after 30 days of incubation, a value that increase up to near 50% in the presence of porcine pancreas lipases. The positive response shown by this polyester to hydrolysis, and in particular when it is mediated by enzymes, is certainly amazing given its very high $T_g$ (~190 °C), and brings into evidence the great sensitivity of Im-containing polyesters to biodegradation. In agreement with the behavior observed for the two reference homopolysters, coPB$_{70}$Im$_{30}$F and coPB$_{60}$Im$_{40}$F copolyesters showed a noticeable hydrolytic degradation at a rate that increased with the content in Im, and that was significantly enhanced in the presence of lipases.

Conclusions

Furanoate-based cyclic oligomers have been demonstrated in several previous reports to be useful monomers for ring opening polymerization and copolymerization. Cyclic oligomers of isomannide 2,5-furandicarboxylate could be successfully synthesized in this work for the first time. As it generally happens, a mixture of dimer, trimer and tetramer species, largely enriched in the dimer, was obtained. This oligomeric mixture was successfully copolymerized with cyclic butylene 2,5-furandicarboxylate oligomers to render random butylene-co-isomannide copolyfuranoates with satisfactory molecular weights and compositions similar to those used for feeding. These novel copolyesters are greatly resistant to heat and they are amorphous except for extremely low contents in isomannide. The most outstanding feature of these Im-containing copolyesters is their high $T_g$, which increases almost monotonically with the content in isomannide to reach a value near to 100 °C for a 50 %-mole of composition. A second merit of these copolyesters is their apparent
sensitivity to hydrolytic degradation whereas the homopolyester entirely made of butylene furanoate is essentially inert to water. Moreover the Im-containing copolyfuranoates become much more rapidly hydrolyzed when subjected to the action of lipases, a certainly amazing behavior given their relatively high $T_g$. The overall conclusions that can be drawn from this work are: a) Polyfuranoates and copolyfuranoates containing isomannide may be prepared via ROP, which constitutes a large step forward the generalization of the ROP technique for the synthesis of furanoate-based polyesters. This methodology would be extensible to other isohexides provided that their cyclic oligofuranoates could be prepared. b) Polyfuranoates containing isomannide are shown to be fully bio-based copolyesters that are distinguished by being amorphous for a wide range of compositions, by having a high $T_g$, and by displaying noticeable biodegradability.

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