

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

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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, polyfuranates, 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.^{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.^{3,4} Nevertheless some representatives polyesters such as polylactic acid or poly(ϵ -caprolactone) are industrially produced by ROP,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.^{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 benzenedicarboxylic acids or their methyl esters.¹⁰⁻¹² Nonetheless a diversity of cyclic oligophthalates and their ROP to linear polyesters have been reported in the scientific literature.^{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.*,^{14,15} and later extended to other related polyesters by different authors.¹⁶⁻²⁰ Recently the preparation of cyclic oligo(alkylene 2,5-furandicarboxylate)s by this method has been reported,^{21,22} which has opened a new way towards the preparation of furane-based polyesters and copolyesters. Thus random furanoate-terephthalate²³ and furanoate-succinate²⁴ copolyesters, as well as furanoate copolyesters containing caprolactone²⁵ 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.²⁶ Poly(ethylene 2,5-furandicarboxylate) (PEF) and poly(butylene 2,5-furandicarboxylate) (PBF) are sustainable aromatic polyesters that

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3 are proposed as potential substitutes of the industrial thermoplastics poly(ethylene
4 terephthalate) (PET) and poly(butylene terephthalate) (PBT), respectively. In fact, PBF
5 combines a bio-based character with a set of properties that compares or even
6 surpasses those of PBT.²⁷⁻³⁰ Considerable efforts have been made however to modify
7 its physical or/and chemical behavior, and a number of PBF copolyesters displaying
8 novel properties may be today found in the literature.^{23-25,29} One usually applied
9 approach has been to design PBF copolyesters with high T_g or/and enhanced
10 biodegradability without detriment of the genuine sustainability of the parent
11 homopolyester. This is really challenging since stiff monomers coming from renewable
12 sources and suitable for polycondensation are not frequent. Bicyclic
13 dianhydroalditols^{31,32} and diacetalized alditols³³ are exceptional examples of diols that
14 could be used for such purpose.

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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.^{31,32} 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.^{34,35} 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.³⁶⁻³⁸ 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^{39,40} are made
from aliphatic dicarboxylic acids.

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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

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3 oligo(butylene 2,5-furandicarboxylate), $c(\text{BF})_n$, to obtain a series of poly(butylene-co-
4 isomannide 2,5-furandicarboxylate) copolyesters, $(\text{coPB}_x\text{Im}_y\text{F})$, with Im contents
5 ranging from 0 up to 50 %-mole. The copolyesters are fully characterized and their
6 thermal properties and degradability are evaluated as a function of the comonomeric
7 composition. To our knowledge, only isosorbide has been used so far for making
8 furanoate-based copolyesters, and conventional polycondensation was the technique
9 invariably applied in such cases.⁴¹⁻⁴² Furthermore, this is the first time that aromatic
10 polyesters containing isohexides are synthesized by ROP, and also that the thermal
11 properties and biodegradability of PBF have been enhanced without detriment of its
12 sustainability.

23 **Experimental**

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25 **Materials.** 2,5-Furandicarboxylic acid (FDCA, 98% purity) was purchased from
26 Satachem and isomannide (Im, 98%) from TCI Chemicals. Thionyl chloride (SOCl_2 ,
27 99%), di-azabicyclo[2.2.2] octane (DABCO, 99%), tin octoate ($\text{Sn}(\text{Oct})_2$, 98%) and
28 porcine pancreas lipase were purchased from Sigma Aldrich. All solvents were of
29 high-purity grade and used as received with the exception of tetrahydrofuran (THF)
30 that was dried on 3Å-molecular sieves and DABCO catalyst that was purified by
31 sublimation.

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33 **Measurements.** ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-300
34 spectrometer at 25 °C, operating at 300.1 and 75.5 MHz, respectively. All the
35 compounds were dissolved in deuterated chloroform (CDCl_3) or a mixture of CDCl_3
36 and trifluoroacetic acid (TFA). The spectra were internally referenced to
37 tetramethylsilane (TMS). About 10 and 50 mg of sample in 1 mL of solvent were used
38 for ^1H and ^{13}C NMR, respectively. Sixty-four scans were recorded for ^1H and between
39 1,000 and 10,000 scans for ^{13}C NMR. High performance liquid chromatography
40 (HPLC) analyses were performed at room temperature in a Waters apparatus
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3 and a Scharlau Science column (Si60, 5 μm ; 250 x 4.6 mm). Cyclic oligomers (1 mg)
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5 were dissolved in chloroform (1 mL) and eluted with hexane/1,4-dioxane 70/30 (v/v)
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7 at a flow rate of 1.0 mL \cdot min⁻¹. Molecular weight analyses of polymers were performed
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9 by GPC on a Waters equipment provided with RI and UV detectors. 100 μL of 0.1%
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11 (w/v) sample solution was injected and chromatographed using 1,1,1,3,3,3-hexafluoro-
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13 2-propanol (HFIP) as mobile phase with a flow of 0.5 mL \cdot min⁻¹. HR5E and HR2 Waters
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15 linear Styragel columns (7.8 mm x 300 mm, pore size 10³–10⁴ Å) packed with
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17 crosslinked polystyrene and protected with a precolumn were used. Average molar
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19 masses and dispersities were calculated against PMMA standards. Matrix-assisted
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21 laser desorption/ionization time of flight (MALDI-TOF) mass spectra were recorded in
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23 a 4700 Proteomics Analyzer instrument (Applied Biosystems) of the Proteomics
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25 Platform of Barcelona Science Park, University of Barcelona. Spectra acquisition was
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27 performed in the MS reflector positive-ion mode. About 0.1 mg of sample was
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29 dissolved in 50 μL of DCM and 2 μL of this solution were mixed with an equal volume
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31 of an anthracene solution in dichloromethane (DCM) (10 mg \cdot mL⁻¹), and the mixture
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33 left to evaporate to dryness onto the stainless steel plate of the analyser. The residue
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35 was then covered with 2 μL of a solution of 2,5-dihydroxybenzoic acid in
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37 acetonitrile/H₂O (1/1) containing 0.1% TFA, and the mixture was left to dry prior to
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39 exposition to the laser beam.

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41 Thermogravimetric analysis (TGA) of polymers was performed on a Mettler-
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43 Toledo TGA/DSC 1 Star System under a nitrogen flow of 20 mL \cdot min⁻¹ at a heating
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45 rate of 10 $^{\circ}\text{C}\cdot$ min⁻¹ and within a temperature range of 30-600 $^{\circ}\text{C}$. The non-destructive
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47 thermal behaviour was examined by differential scanning calorimetry (DSC) within
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49 the 30-200 $^{\circ}\text{C}$ range using a Perking-Elmer Pyris apparatus. Thermograms were
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51 obtained from 4-6 mg samples at heating and cooling rates of 10 $^{\circ}\text{C}\cdot$ min⁻¹ under a
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53 nitrogen flow of 20 mL \cdot min⁻¹. Indium and zinc were used as standards for
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55 temperature and enthalpy calibration. The glass transition temperature (T_g) was taken
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3 as the inflection point of the heating traces recorded at 20 °C·min⁻¹ from melt-
4 quenched samples, and the melting temperature (T_m) was taken as the maximum of
5 the endothermic peak appearing on the heating traces recorded from samples
6 crystallized from the melt.
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10 X-Ray diffraction patterns from powdered samples coming directly from
11 synthesis were recorded on a PANalytical X'Pert PRO MPD θ/θ diffractometer using
12 the CuK α radiation of wavelength 0.1542 nm. Optical micrographs were taken using an
13 Olympus BX51 polarizing optical microscope with a Linkam THMS 600 stage attached.
14 For observation, 10 mg of sample were dissolved in 1 mL of HFIP for PBF or
15 chloroform for copolyesters, and 0.2 mL aliquots of these solutions were slowly
16 evaporated on a glass slide.
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24 **Cyclic oligomers synthesis.** Cyclic oligomers $c(\text{BF})_n$ were synthesized applying the
25 high dilution condensation method (HDC) previously reported by us.²² Cyclic
26 oligomers $c(\text{ImF})_n$ were synthesized applying the same method. Briefly,**Error!**
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29 **Bookmark not defined.** a three-necked round bottom flask was charged with 250 mL of
30 THF and cooled to 0°C, and then 12.5 mmol (1.40 g) of DABCO were added under
31 stirring. 5 mmol (0.96 g) of FDCA-Cl₂ and 5 mmol (0.73 g) of isomannide in 10 mL of
32 THF were drop-wise added simultaneously for 40 min using two addition funnels in
33 order to maintain the reagents equimolarity in the reaction mixture. The reaction was
34 finished by adding 1 mL of water followed by 5 mL of 1M HCl, and after stirring for 5
35 min, it was diluted with DCM and filtered. The filtrate was washed with 0.1M HCl and
36 water, dried on MgSO₄, and evaporated to dryness to render a mixture of linear and
37 cyclic oligomers. Linear oligomers were removed by flash chromatography through a
38 short column of silica gel using a cold mixture of DCM/diethyl ether 90/10 (v/v) as
39 eluent. Yield: 60%. $c(\text{ImF})_n$: ¹H NMR (δ ppm, CDCl₃, 300 MHz): 7.34 (1s, 2H), 5.39
40 (m, 2H), 4.91 (m, 2H), 4.35 (m, 2H); 3.99 (m, 2H); ¹³C NMR (δ ppm, CDCl₃, 75.5
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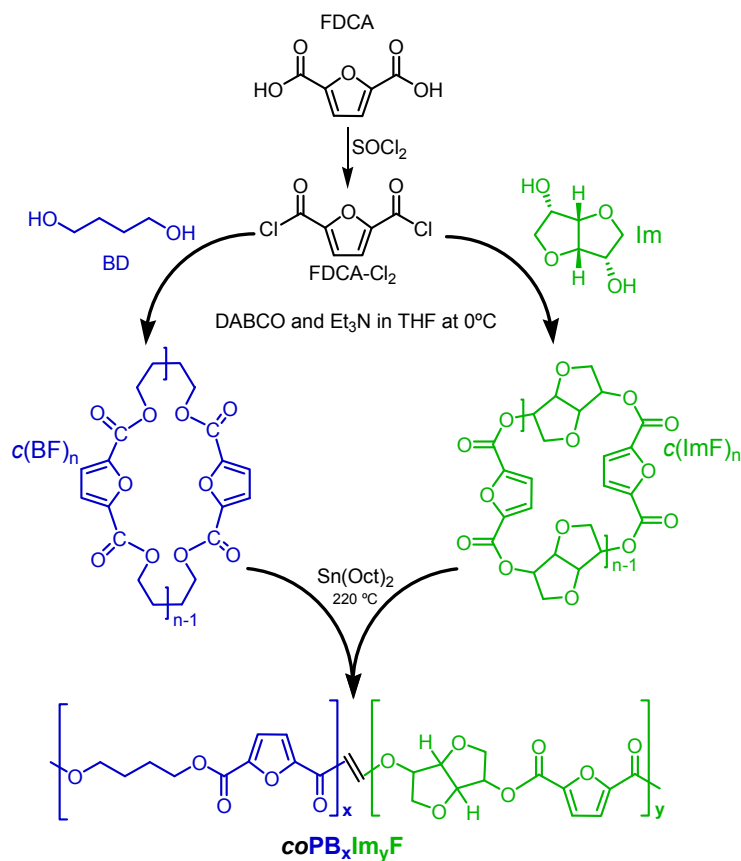
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3 MHz): 157.2, 146.4, 146.3, 146.0, 119.6, 119.4, 80.7, 74.5, 74.4, 73.9, 71.2, 71.1,
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5 70.9.

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7 **Polymer synthesis.** Copolymerization of $c(\text{BF})_n$ and $c(\text{ImF})_n$ was performed in bulk
8 following the procedure previously reported by us.²³ Briefly, mixtures of $c(\text{BF})_n$ and
9 $c(\text{ImF})_n$ with the selected molar compositions were placed in a three necked round
10 bottom flask provided with a N_2 flow and heated at 220 °C. Then $\text{Sn}(\text{Oct})_2$ (0.5 %-mole)
11 was added to the molten mass and the reaction was left to proceed for 6 h. The
12 reaction mixture was then cooled down to room temperature, diluted with CHCl_3 , and
13 precipitated with diethyl ether. The precipitated sample was analyzed by NMR.
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17 **Hydrolytic and enzymatic degradation.** Hydrolytic degradation and biodegradation
18 studies were made on PBF and PImF homopolyesters, and $\text{coPB}_{50}\text{Im}_{50}\text{F}$, and
19 $\text{coPB}_{70}\text{Im}_{30}\text{F}$ copolyesters. Films of these polymers with a thickness of $\sim 200 \mu\text{m}$ were
20 prepared by casting from either HFIP or chloroform solution at a polymer
21 concentration of $100 \text{ g}\cdot\text{L}^{-1}$. The films were cut into 10 mm-diameter, 20-30 mg-weight
22 disks and dried under vacuum to constant weight. For hydrolytic degradation,
23 samples were immersed in vials containing 10 mL of either citric acid buffer, pH 2.0
24 or sodium phosphate buffer, pH 7.4 at 37 °C. Enzymatic degradation assays were
25 carried out at 37 °C in pH 7.4 buffered sodium phosphate solution with 10 mg of
26 porcine pancreas lipase added. In this case the buffered solution was replaced every
27 72 h in order to maintain the enzyme activity. In both cases, disks were withdrawn
28 from the incubation medium at scheduled periods of time, washed carefully with
29 distilled water, dried to constant weight, and finally analysed by GPC.
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49 **Results and discussion**

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

Cyclic oligomers. $c(\text{BF})_n$ 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) $c(\text{ImF})_n$, 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 $c(\text{BF})_n$, 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%,

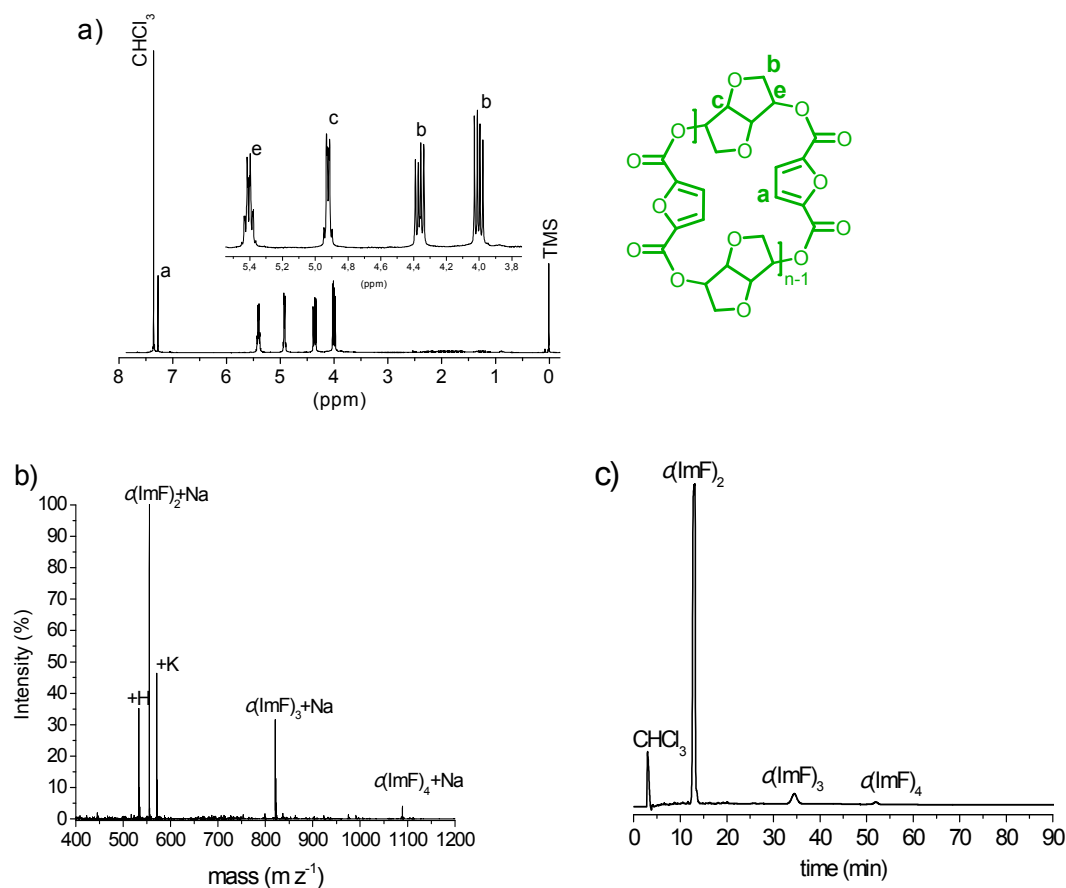


Figure 1. a) ^1H NMR, b) MALDI-ToF, and c) HPLC of $\alpha(\text{ImF})_n$ after purification.

respectively). The thermal analysis of $\alpha(\text{ImF})_n$ 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 1. Cyclic Oligomers Used for the ROP Synthesis of Im-Containing Copolyesters.

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

^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. $^{\circ}T_d$ 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 $c(\text{BF})_n$ are collected in Table 1.

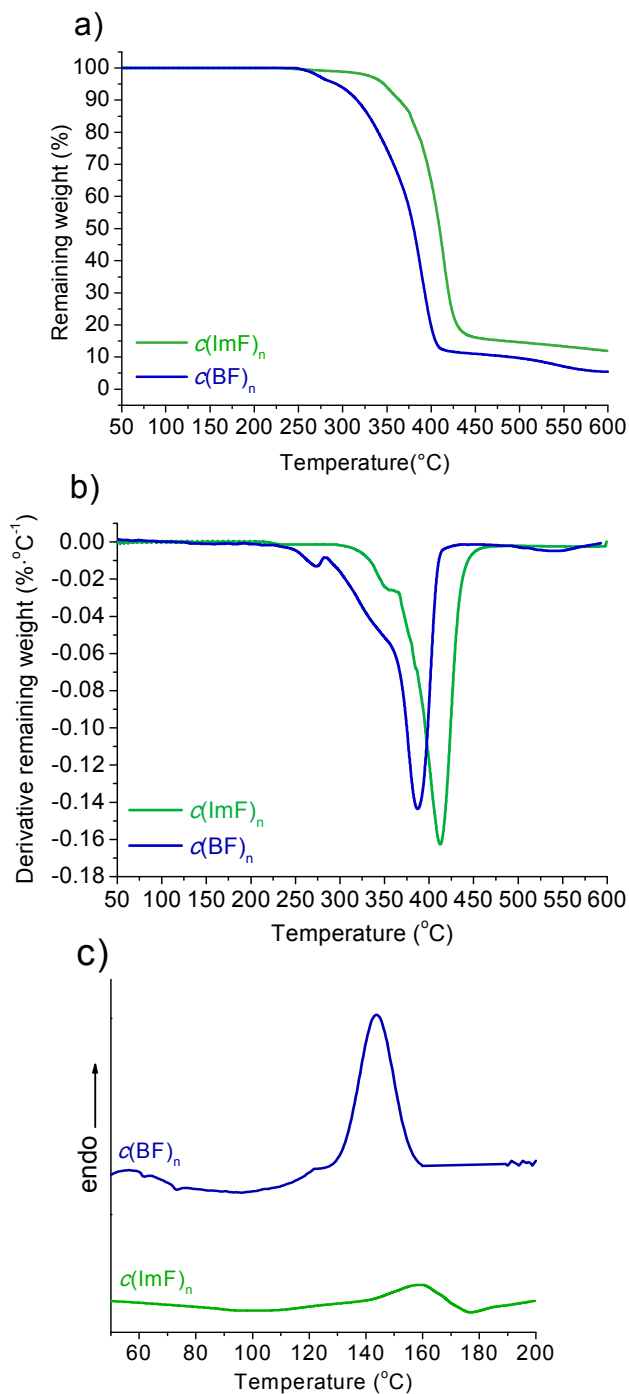


Figure 2. a) TGA (a and b) and DSC (c) of $c(\text{BF})_n$ and $c(\text{ImF})_n$.

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3 It is noteworthy to report that a series of experiments similar to those carried out
4 for the synthesis of $c(\text{ImF})_n$ were made using isosorbide, *i.e.* the isohexide derived from
5 glucose, with the purpose of generating its corresponding cyclic oligoesters.
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7 Unfortunately, all the attempts were unsuccessful and apparently only linear oligomers
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9 were obtained according to the NMR analysis (Figure S3). The unfavorable relative
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11 spatial orientation of the two reactive hydroxyl groups in Is (*exo* and *endo*) compared to
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13 the two *endo* positions occupied by the two hydroxyls in Im could be invoked to be
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15 responsible for the different behavior observed. An exploratory study on the energy of
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17 the cyclic oligofuranoates of the three known isohexides (Is, Im and Id) was
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19 comparatively performed by molecular simulations. The results clearly revealed that
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21 cyclic oligomers made of Is are less stable than those made of Im (Figure S4), which is
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23 fully consistent with the experimental results reached in the attempts of cyclization
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25 carried out with isomannide and isosorbide. Simulation results also indicated a relative
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27 high energy for the cyclic oligofuranoates containing isoidide, which leads to predict
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29 that cyclization involving this diol will be hampered too. Isoidide has the two hydroxyl
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31 groups in *exo* position, which is very favorable for reactivity but not for cyclization due
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33 to their opposite orientation in the space.
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37 **Synthesis of copolyesters.** Mixtures of $c(\text{BF})_n$ and $c(\text{ImF})_n$ covering the ratio range of
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39 95/5 to 50/50 were copolymerized by ROP in bulk using tin 2-ethylhexanoate as
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41 catalyst to produce the $\text{coPB}_x\text{Im}_y\text{F}$ copolyesters series. The homopolyesters PBF and
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43 PImF to be used as references in characterization and properties studies were
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45 prepared by this method too. The reaction temperature was fixed by taken into account
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47 the meltability of the cyclic fractions and the resulting polymers, as well as its effect on
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49 reaction kinetics. To assess this variable, a mixture of $c(\text{BF})_n$ and $c(\text{ImF})_n$ with a 60/40
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51 molar ratio was made to react at 200, 220 and 230 °C, and aliquots of the reaction
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53 mixture were withdrawn at scheduled times and the molecular weight of the
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55 copolyester formed up to that instant was estimated by GPC. Results are plotted in
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Figure 3a to show the positive effect of temperature on conversion upon raising it from 200 to 220 °C whereas not significant change seems to happen after further increasing. According to these results and since the $c(\text{BF})_n$ cycles started to decompose around 240 °C, it was advisable to fix the reaction temperature at 220 °C for the ROP of the whole series. To complement this study, the evolution of M_w with time in the ROP at 220 °C of $c(\text{BF})_n/c(\text{ImF})_n$ mixtures differing in composition was followed by using the same methodology as before, and results obtained therefrom are shown in Figure 3b.

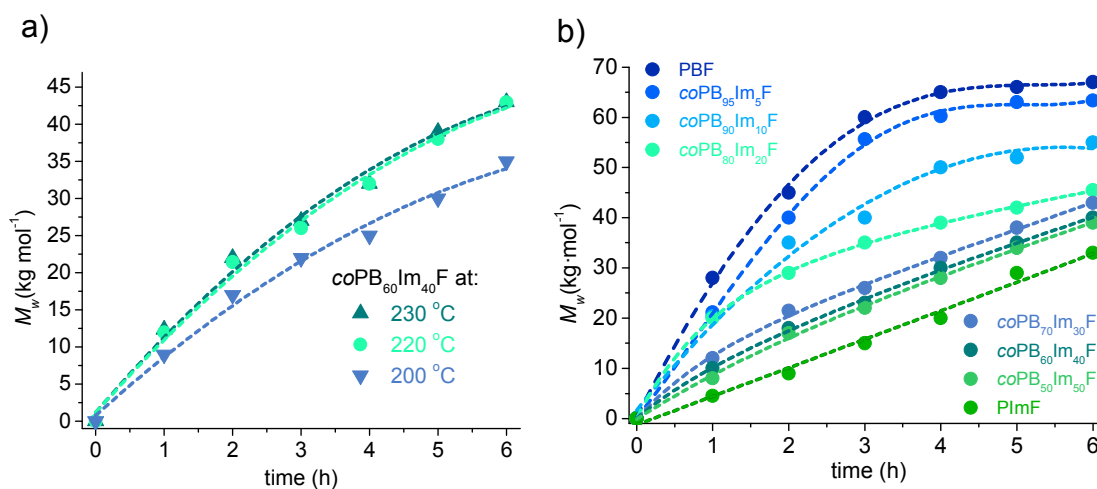


Figure 3. Plots of the evolution of M_w of the resulting copolyesters $\text{coPB}_x\text{Im}_y\text{F}$ against reaction time. a) $\text{coPB}_{60}\text{Im}_{40}\text{F}$ at different temperatures. b) $\text{coPB}_x\text{Im}_y\text{F}$ with different compositions.

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 $c(\text{ImF})_n$ cycles compared to the $c(\text{BF})_n$ 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 $\text{coPB}_x\text{Im}_y\text{F}$.

Yields, molecular weights and compositions of the whole $\text{coPB}_x\text{Im}_y\text{F}$ 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 ~40,000-60,000 $\text{g}\cdot\text{mol}^{-1}$ range, and the homopolyesters PBF and PImF were obtained with 65,000 $\text{g}\cdot\text{mol}^{-1}$ and 28,000 $\text{g}\cdot\text{mol}^{-1}$ respectively, which is according to the trend observed for the copolyesters series. \mathcal{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 ^1H and ^{13}C NMR spectroscopy, and the spectra recorded from $\text{coPB}_{60}\text{Im}_{40}\text{F}$ 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 ^1H 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 2. Yield, Composition, Molecular Weight, and Microstructure of $\text{coPB}_x\text{Im}_y\text{F}$.

Polyester	Yield (%)	Composition ^a x(BF/y(ImF)) (mole/mole)		Molecular weight ^b		Microstructure ^c						
		Feed	Copol	M_w ($\text{g}\cdot\text{mol}^{-1}$)	\mathcal{D}	BB	BIm ImB	ImIm	η_{BF}	η_{ImF}	R	
PBF	95	100	0	65,000	1.8	-	-	-	-	-	-	-
$\text{PB}_{95}\text{Im}_5\text{F}$	93	95/5	96/4	63,000	1.6	91.5	8.5	0	22.4	1.00	1.04	
$\text{PB}_{90}\text{Im}_{10}\text{F}$	90	90/10	92/8	55,000	1.9	80.4	18	1.6	9.9	1.18	0.95	
$\text{PB}_{80}\text{Im}_{20}\text{F}$	85	80/20	80/20	45,000	1.9	66.3	28.5	5.2	5.7	1.37	0.91	
$\text{PB}_{70}\text{Im}_{30}\text{F}$	85	70/30	66/34	43,000	1.4	54.9	35.4	9.7	4.1	1.55	0.89	
$\text{PB}_{60}\text{Im}_{40}\text{F}$	82	60/40	58/42	40,000	1.8	46.8	33.5	19.7	3.8	2.17	0.76	
$\text{PB}_{50}\text{Im}_{50}\text{F}$	82	50/50	55/45	39,000	2.0	37.2	37.0	25.8	3.0	2.39	0.75	
PImF	80	0	100	28,000	1.9	-	-	-	-	-	-	-

^a %-Mole feed and copolymer composition determined by NMR.

^b Weight-average molecular weight (M_w) and dispersity (\mathcal{D}) determined by GPC.

^c % of dyads (BB, BIm/ImB and ImIm) determined by NMR, number average sequence lengths (η_{BF} and η_{ImF}) and degree of randomness calculated using the approach reported by Randall.⁴³

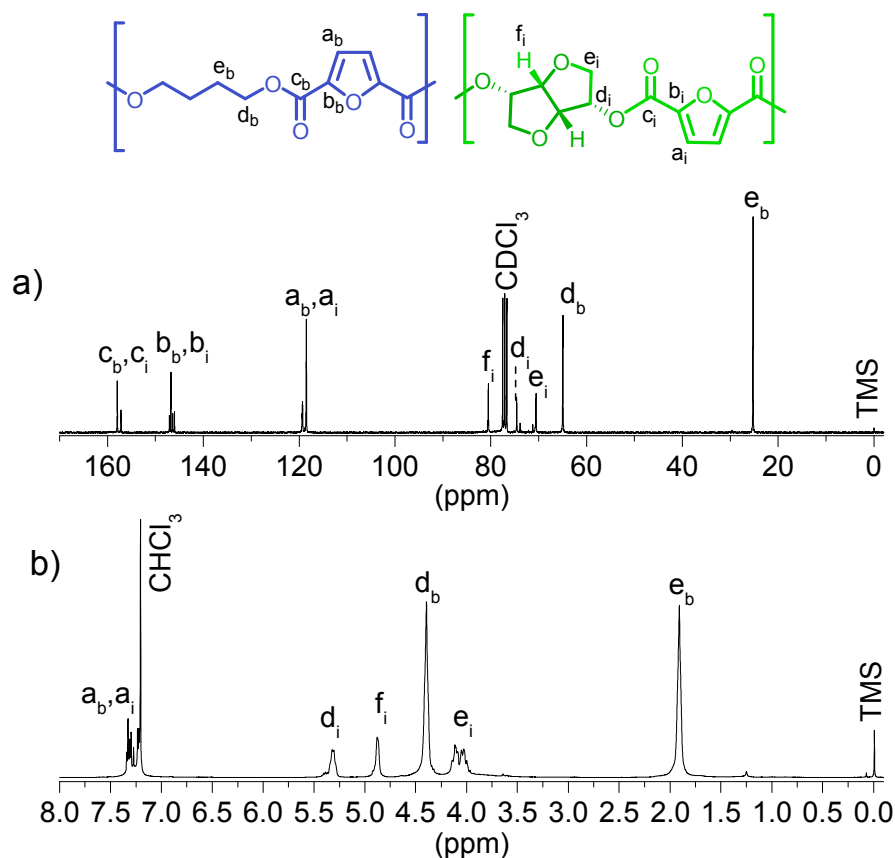


Figure 4. ^{13}C (top) and ^1H (bottom) NMR of $\text{coPB}_{60}\text{Im}_{40}\text{F}$.

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, Blm/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 $\text{coPB}_x\text{Im}_y\text{F}$ copolyesters with a random degree that decreases as the content of the copolyester in isomannide increases.

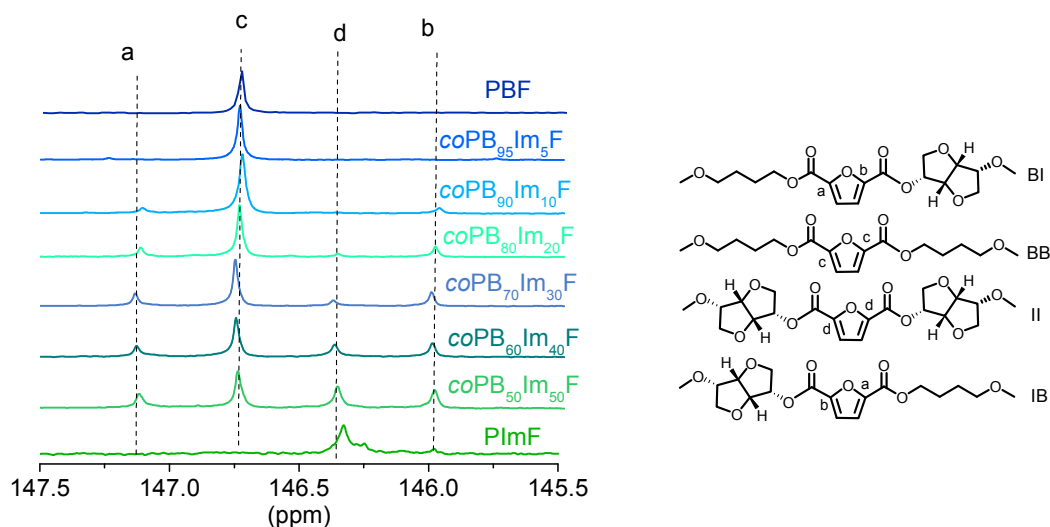


Figure 5. ^{13}C NMR signals used for microstructure analysis of $\text{coPB}_x\text{Im}_y\text{F}$ with assignments of the carbons for the different dyads.

Thermal properties

The thermal properties of the $\text{coPB}_x\text{Im}_y\text{F}$ 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 homopolyesters started to decompose around 360 °C and 325 °C, respectively,

Table 3. Thermal Properties of $\text{coPB}_x\text{Im}_y\text{F}$ Copolyesters Prepared *via* ROP.

Copolyester	TGA			DSC					Crystallization kinetics ^b			
	$^{\circ}T_d^a$ (°C)	$\text{max}T_d$ (°C)	R_w (%)	T_g (°C)	T_m (°C)	ΔH_m (J·mol ⁻¹)	T_m (°C)	ΔH_m (J·mol ⁻¹)	T_c (°C)	n	$\ln K$	$t_{1/2}$ (min)
PBF	360	400	6	42	172	35	172	35	146	2.07	-4.46	7.0
$\text{coPB}_{95}\text{Im}_5\text{F}$	344	390	6	45	169	30	166	28	146	2.49	-6.89	13.4
$\text{coPB}_{90}\text{Im}_{10}\text{F}$	329	390	8	47	160	12	156	7	-	-	-	-
$\text{coPB}_{80}\text{Im}_{20}\text{F}$	334	388	8	56	-	-	-	-	-	-	-	-
$\text{coPB}_{70}\text{Im}_{30}\text{F}$	330	390	9	66	-	-	-	-	-	-	-	-
$\text{coPB}_{60}\text{Im}_{40}\text{F}$	330	390	9	80	-	-	-	-	-	-	-	-
$\text{coPB}_{50}\text{Im}_{50}\text{F}$	362	403	5	97	-	-	-	-	-	-	-	-
PlmF	325	376	9	189	-	-	-	-	-	-	-	-

^aOnset temperature measured for 5% of weight loss.

^bAvrami parameters determined from isothermal crystallization at the indicated T_c .

whereas the $\text{coPB}_x\text{Im}_y\text{F}$ copolyesters did it at intermediate values but without following a recognizable trend. Nevertheless $^{\circ}T_{d,5\%}$ 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, $^{\text{max}}T_d$ of copolyesters is confined in the $\sim 390\text{--}400$ °C, which are values very close to that of PBF but clearly above the 376 °C shown by the PImF 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.

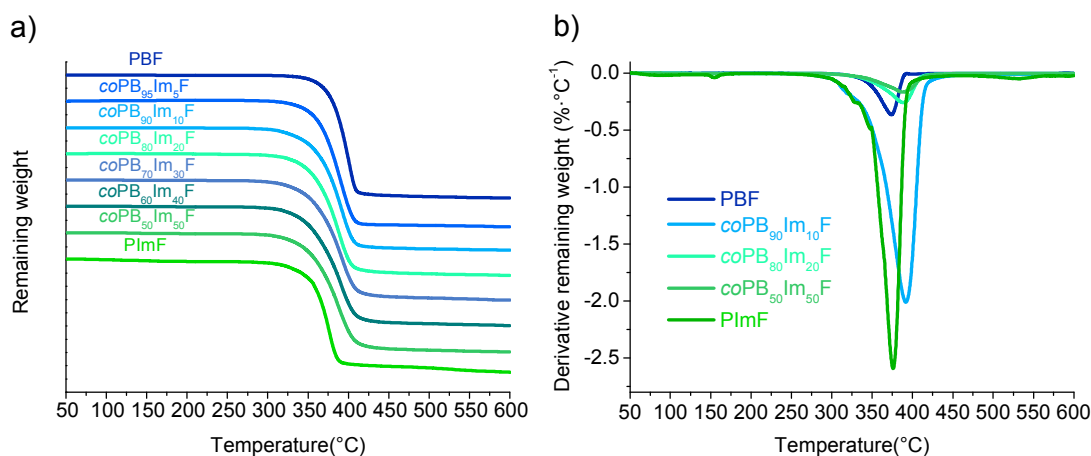


Figure 6. TGA traces of $\text{coPB}_x\text{Im}_y\text{F}$ (a) and a selection of their derivative curves (b).

The DSC traces of $\text{coPB}_x\text{Im}_y\text{F}$ together with those of PBF and PImF homopolyesters, 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 $\text{coPB}_{95}\text{Im}_5\text{F}$ was able to crystallize clearly from the melt whereas an extremely weak broad crystallization exotherm was hardly seen on the cooling trace of

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coPB₉₀Im₁₀F. As expected, both melting temperature and enthalpy decreased with the content in isomannide. It can be said therefore that coPB_xIm_yF copolyesters are essentially amorphous polymers as it is also the case for PImF homopolymer, 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 homopolyesters made of isohexides are known to be unable to crystallize.⁴⁴⁻⁴⁶

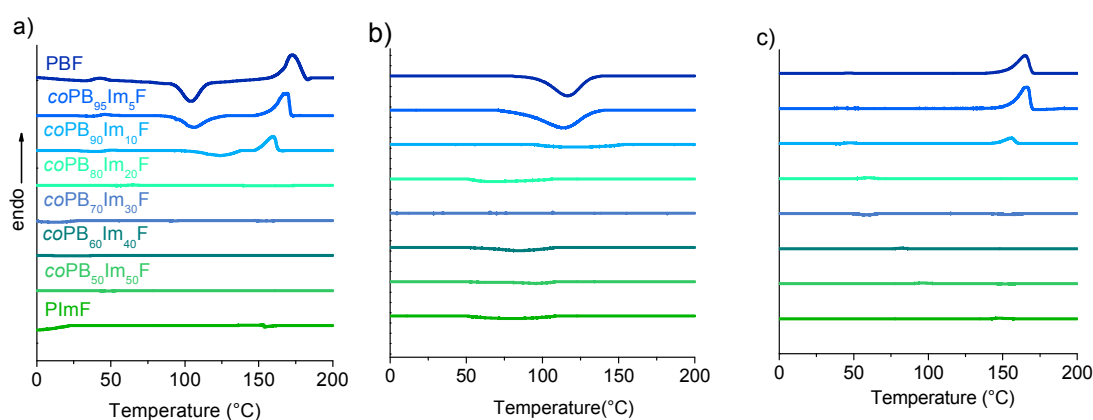
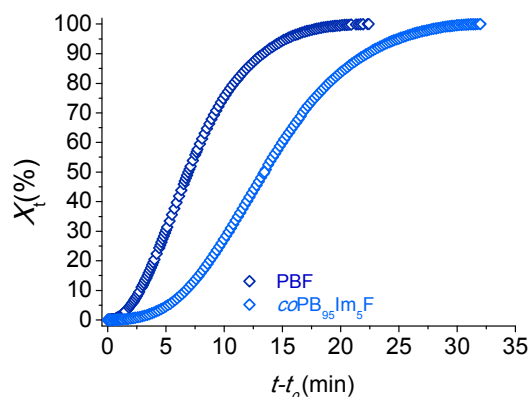


Figure 7. a) First heating, b) cooling, and c) second heating of coPB_xIm_yF.

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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

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3 common fact. The phenomenon is understood by assuming that upon crystallization
4 the minor comonomer is rejected to the amorphous phase and only homogeneous
5 sequences made of the main comonomer are incorporated in the crystal phase.⁴⁷⁻⁴⁹
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7 Since the capacity of $\text{coPB}_x\text{Im}_y\text{F}$ to crystallize is so severely restricted, the kinetics
8 study addressed to quantify the influence of composition on crystallizability had to be
9 restricted to the PBF/ $\text{coPB}_{95}\text{Im}_5\text{F}$ pair. The isothermal crystallization of these two
10 polyesters was carried out at 146 °C and the evolution of crystallinity with time was
11 compared. The typical sigmoidal curves resulting from these assays are plotted in
12 Figure 8, and the kinetic parameters estimated by application of the Avrami approach
13 to the experimental data are given in Table 3. As it could anticipated, PBF and
14 $\text{coPB}_{95}\text{Im}_5\text{F}$ crystallized through a similar mechanism (their Avrami exponents are
15 comparable) but the crystallization process is highly delayed for the copolyester ($t_{1/2}$ is
16 almost doubled).
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43 **Figure 8.** Relative crystallinity vs time in the isothermal crystallization of PBF and $\text{coPB}_{95}\text{Im}_5\text{F}$ at
44 146 °C.

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46 The glass-transition temperature of the copolyesters was measured on the DSC
47 heating traces registered from samples that were rapidly cooled from the melt. These
48 traces showing the inflections indicative of glass-transition may be inspected in the SI
49 file (Figure S8), and the T_g values estimated therefrom are listed in Table 3. It was
50 found that the T_g of PBF appearing at 42 °C raised up to 97 °C as the content of the
51 polymer in Im increased from 0 to 50 %-mole. Obviously, the replacement of the
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3 relatively flexible butylene unit by the much more rigid Im bicyclic structure reduced the
4 chain mobility triggering a notable increase in T_g . The high stiffness of Im is clearly
5 brought into evidence in the PImF homopolymer itself, which has a T_g of 189 °C. The
6 variation of T_g with the copolymer composition is plotted in Figure 9 where the
7 experimentally observed values are compared with those predicted by the Fox and
8 Gordon-Taylor equations.^{50,51} As it is largely expected from the amorphous nature of
9 the $\text{coPB}_x\text{Im}_y\text{F}$, a good fit is attained with both equations as far as contents in Im are
10 20% and higher. The deviations detected for PBF, $\text{coPB}_{95}\text{Im}_5\text{F}$ and $\text{coPB}_{90}\text{Im}_{10}\text{F}$ are
11 likely due to the crystallinity present in these polyesters.

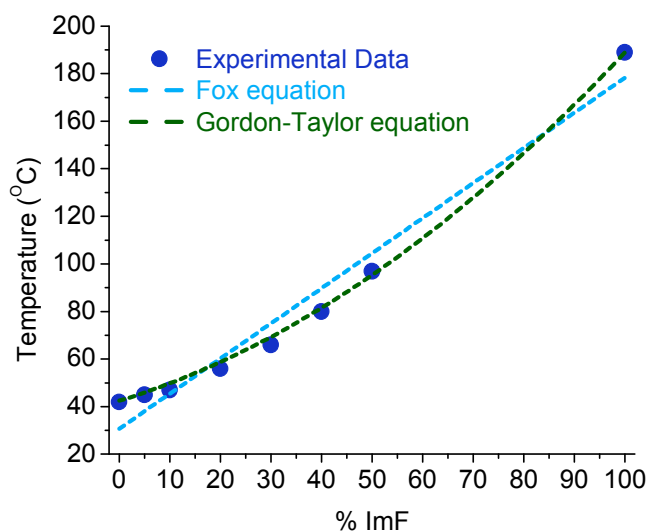


Figure 9. Variation of T_g with composition in the $\text{coPB}_x\text{Im}_y\text{F}$ series.

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45 **Hydrolytic and enzymatic degradation.** Both hydrolytic degradation and
46 biodegradation of PBF have been examined by different authors in previous works,^{23-25,}
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49^{52,53} the which unanimously reported the high resistance of this polyester to be attacked
50 by water. This is a behavior characteristic of aromatic polyesters that is commonly
51 rationalized by taking into account the hydrophobicity and high T_g caused by the
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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.^{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 $\text{coPB}_x\text{Im}_y\text{F}$ copolyesters containing 30 and 40 %-mole of Im as well as for the PBF and PImF homopolyesters, and results are plotted in Figure 10. It is apparent in these plots

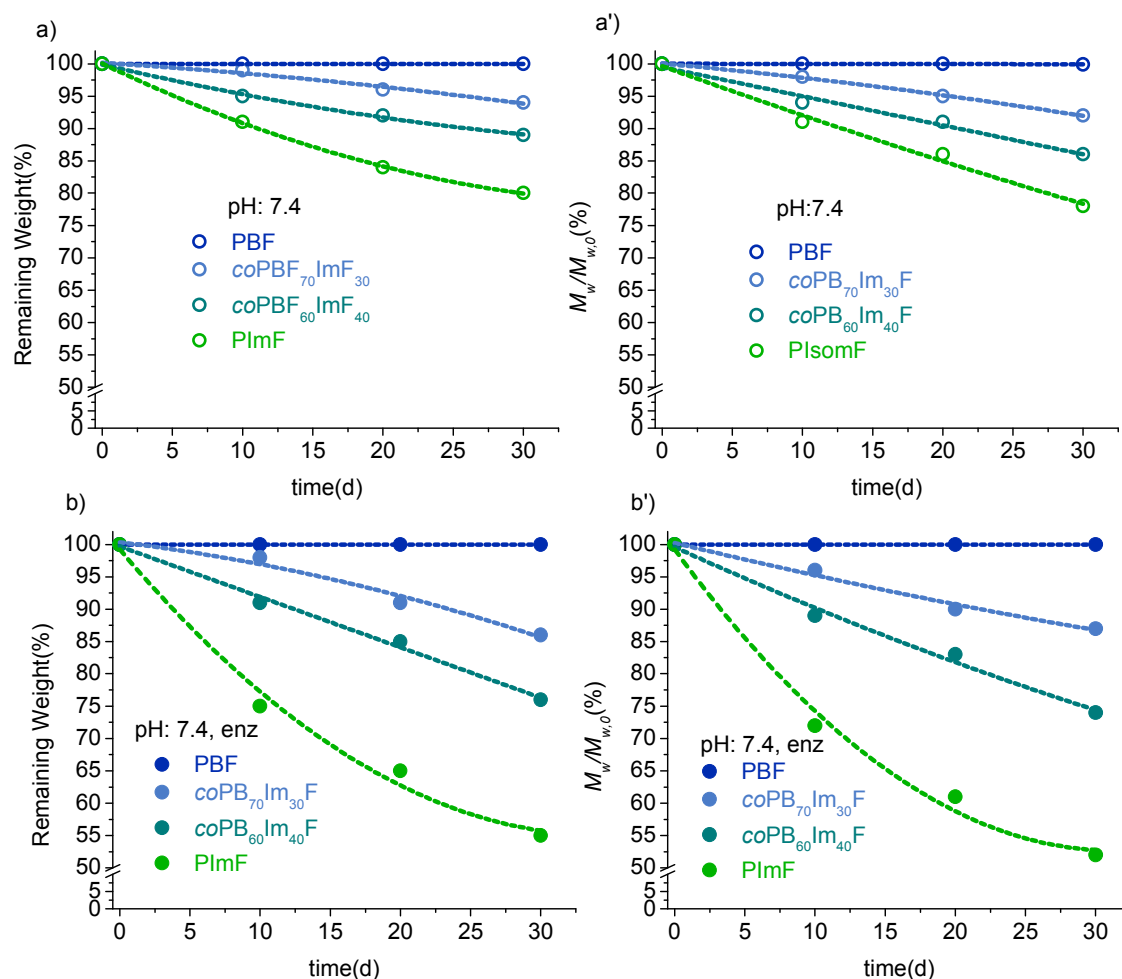


Figure 10. Hydrolytic (a and a') and enzymatic (b and b') degradation of $\text{coPB}_x\text{Im}_y\text{F}$ upon incubation in water at pH 7.4.

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3 that copolymerization enhances significantly the degradability of PBF. In fact, an
4 essentially invariable function independent of time was obtained in the incubation of
5 PBF for both sample weight and molecular weight, and either with or without enzyme
6 added. On the contrary, PImF appears to be highly sensitive to hydrolysis undergoing
7 around 20% of degradation after 30 days of incubation, a value that increase up to near
8 50% in the presence of porcine pancreas lipases. The positive response shown by this
9 polyester to hydrolysis, and in particular when it is mediated by enzymes, is certainly
10 amazing given its very high T_g (~190 °C), and brings into evidence the great sensitivity
11 of Im-containing polyesters to biodegradation. In agreement with the behavior observed
12 for the two reference homopolyesters, $\text{coPB}_{70}\text{Im}_{30}\text{F}$ and $\text{coPB}_{60}\text{Im}_{40}\text{F}$ copolyesters showed
13 a noticeable hydrolytic degradation at a rate that increased with the content in Im, and
14 that was significantly enhanced in the presence of lipases.
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29 **Conclusions**

31 Furanoate-based cyclic oligomers have been demonstrated in several previous
32 reports to be useful monomers for ring opening polymerization and copolymerization.
33 Cyclic oligomers of isomannide 2,5-furandicarboxylate could be successfully
34 synthesized in this work for the first time. As it generally happens, a mixture of dimer,
35 trimer and tetramer species, largely enriched in the dimer, was obtained. This
36 oligomeric mixture was successfully copolymerized with cyclic butylene 2,5-
37 furandicarboxylate oligomers to render random butylene-co-isomannide
38 copolyfuranoates with satisfactory molecular weights and compositions similar to those
39 used for feeding. These novel copolyesters are greatly resistant to heat and they are
40 amorphous except for extremely low contents in isomannide. The most outstanding
41 feature of these Im-containing copolyesters is their high T_g , which increases almost
42 monotonically with the content in isomannide to reach a value near to 100 °C for a 50
43 %-mole of composition. A second merit of these copolyesters is their apparent
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3 sensitivity to hydrolytic degradation whereas the homopolyester entirely made of
4 butylene furanoate is essentially inert to water. Moreover the Im-containing
5 copolyfuranoates become much more rapidly hydrolyzed when subjected to the action
6 of lipases, a certainly amazing behavior given their relatively high T_g . The overall
7 conclusions that can be drawn from this work are: a) Polyfuranoates and
8 copolyfuranoates containing isomannide may be prepared via ROP, which constitutes
9 a large step forward the generalization of the ROP technique for the synthesis of
10 furanoate-based polyesters. This methodology would be extensible to other isohexides
11 provided that their cyclic oligofuranoates could be prepared. b) Polyfuranoates
12 containing isomannide are shown to be fully bio-based copolyesters that are
13 distinguished by being amorphous for a wide range of compositions, by having a high
14 T_g , and by displaying noticeable biodegradability.

25 26 27 28 29 **Acknowledgements**

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