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Polyesters containing cyclic carbohydrate-based units obtained by ring opening polymerization

by

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Polyesters containing cyclic carbohydrate-based units obtained by Ring Opening Polymerization

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Abstract

In recent years, as a result of climate change, the interest in sustainable materials has increased dramatically. The replacement of compounds of petrochemical origin by bio-based ones has spread to all areas of chemistry. Nowadays there is a development of sustainable polymers based on 2,5-furandicarboxylic acid (FDCA) as it may compete in performance with the ones based on terephthalic acid (PTA). On the other hand, the ring opening polymerization (ROP) is an attractive synthesis route whose interest has grown in this last decade because no byproducts are generated and polymers of high molecular weight can be obtained in short reaction times.

This Thesis reports the synthesis and characterization of cyclic oligomers of FDCA with different diols, such as 1,4-butanediol ($c(BF)_n$), ethylene glycol ($c(EF)_n$), resorcinol ($c(RF)_n$) and isomannide ($c(ImF)_n$) using different synthetic routes including high dilution condensation (HDC) and cyclodepolymerization (CD). The cyclic oligomers of butylene isophthalate ($c(BI)_n$) and butylene terephthalate ($c(BT)_n$) have also been synthesized by HDC. Finally, the cyclic oligomers of butylene succinate ($c(BS)_n$) and ethylene succinate ($c(ES)_n$) were obtained by enzymatic cyclization reaction (EC).

The furanic cyclic oligomers were homopolymerized and copolymerized with the aforementioned cyclic oligoesters as well as with ε-caprolactone (ε-CL). The polymerization reactions were catalyzed with tin octanoate ($SnOct_2$), except in the case of homopolyesters and copolyesters with aliphatic units in which the *Candida antarctica* lipase B (CALB) was used. The molecular weights of the polymers obtained ranged between 25,000 and 80,000 g mol^{-1}. The copolymers presented a random microstructure with the exception of the caprolactone derivatives, which presented a blocky microstructure.

Differential scanning calorimetry (DSC) studies revealed that PEF, PBF, PBT, PBI, PBS, PES, and the copolymers containing more than 30% of one or another comonomer, turned out to be crystalline, on the contrary, copolymers with close compositions to 50:50 were usually amorphous. On the other hand, the PRF and the PImF were amorphous and the incorporation of their units in other copolyesters restricted the crystallinity. In addition, the melting temperature (T_m) and the glass transition temperature (T_g) were intermediate to those of the homopolyesters, with a practically linear tendency in the second case. The crystallizability of most copolyesters was also studied, which allowed obtaining different kinetic parameters through the application of the Avrami equation.

Thermogravimetric analysis (TGA) revealed that most polyesters and copolyesters were thermally stable up to 320 °C.

The studies of hydrolytic and enzymatic degradability showed the high resistance to the degradation of PBF, PEF and PRF, which decreased markedly with the incorporation of aliphatic units such as BS, ES, CL or ImF in the copolyesters.

This thesis summarizes the main aspects in the synthesis of cyclic oligomers of FDCA and its homopolymerization and copolymerization with different cyclic oligomers via ROP. According to the results obtained, polyesters based on furanic derivatives could be considered as a viable alternative to polyesters of petrochemical origin for industrial applications.

Key words: polyesters, carbohydrates, bio-based, cyclic oligoesters, ring opening polymerization, furan-based polyesters, poly(butylene 2,5-furandicarboxylate).

Resumen

En estos últimos años, como consecuencia del cambio climático, ha aumentado extraordinariamente el interés por materiales sostenibles. El reemplazo de los compuestos de origen petroquímico por naturales se ha extendido a todos los ámbitos de la química. Se están desarrollando polímeros sostenibles basados en ácido 2.5-furandicarboxílico (FDCA) ya que pueden competir en prestaciones con los basados en el ácido tereftálico (PTA). Por otro lado, la polimerización por apertura de anillo (ROP) es una vía de síntesis atractiva cuyo interés ha crecido en esta última década debido a que en la reacción no se generan subproductos y se puede obtener polímeros de alto peso molecular en cortos tiempos de reacción.

En esta Tesis se reporta la síntesis y caracterización de oligómeros cíclicos de FDCA con diferentes dioles, tales como 1,4-butanodiol ($c(BF)_n$), etilenglicol ($c(EF)_n$), resorcinol ($c(RF)_n$) e isomannide ($c(ImF)_n$) usando diferentes rutas sintéticas incluyendo la condensación en alta dilución (HDC), la ciclodepolimerización (CD). También se han sintetizado mediante HDC los oligómeros cíclicos de butilén isoftalato ($c(BI)_n$) y butilén tereftalato ($c(BT)_n$). Finalmente, se han obtenido los oligómeros cíclicos de butilén succinato ($c(BS)_n$) y etilén succinato ($c(ES)_n$) por reacción de ciclación enzimática (EC).

Los oligómeros cíclicos furánicos se homopolimerizaron y copolimerizaron con los oligoesteres cíclicos mencionados anteriormente así como con la ε-caprolactona (ε-CL). Las reacciones de polimerización fueron catalizadas con el octanoato de estaño ($SnOct_2$), excepto en el caso de los homopoliésteres y copoliésteres con unidades alifáticas en los que se utilizó la enzima lipasa B de Cándida antárctica (CALB). Los pesos moleculares de los polímeros obtenidos oscilaron entre 25,000 y 80,000 g/mol. Los copolímeros presentaban una microestructura al azar con la excepción de los derivados de caprolactona, los cuales presentaron una microestructura en bloques.

Los estudios de calorimetría diferencial de barrido (DSC) revelaron que el PEF, PBF, PBT, PBI, PBS, PES, y sus copolímeros conteniendo más del 30% de uno o de otro comonómero, resultaron ser cristalinos, por el contrario, los copolímeros con composiciones cercanas al 50:50 resultaron ser por lo general amorfos. Por otro lado, el PRF y el PImF eran amorfos y la incorporación de sus unidades en otros copoliésteres restringió la cristalinidad de los mismos. Además la temperatura de fusión (T_m) y la temperatura de transición vítrea (T_g) eran intermedias a las de los homopoliésteres, con una tendencia prácticamente lineal en el segundo caso. También se estudió la cristalizabilidad de la mayoría de los copoliésteres, lo cual permitió la obtención de diferentes parámetros cinéticos mediante la aplicación de la ecuación de Avrami.

El análisis termogravimétrico (TGA) reveló que la mayoría de los poliésteres y copoliésteres eran térmicamente estables hasta 320 ^{o}C.

Los estudios de degradabilidad hidrolítica y enzimática mostraron la alta resistencia a la degradación del PBF, PEF y PRF, la cual decrecía notablemente con la incorporación de unidades alifáticas tales como el BS, ES, CL o ImF.

La presente Tesis resume los principales aspectos en la síntesis de oligómeros cíclicos de FDCA y su homopolimerización y copolimerización con diferentes oligómeros cíclicos vía ED-ROP. De acuerdo con los resultados obtenidos, los poliésteres basados en derivados furánicos podrían considerarse como una alternativa viable a los poliésteres de origen petroquímico para aplicaciones industriales.

Index

Acronyms

a	Mark-Houwink parameter
ArH	Aromatic proton
B	Butylene units
BPA	Bisphenol A
bs	Broad singlet
CALB	Lipase *Candida Antarctica* B
***c*(AF)$_n$**	cyclic oligomers of alkylene 2,5-furandicarboxylate.
***c*(BA)$_n$**	cyclic oligomers of butylene adipate
***c*(BF)$_n$**	cyclic oligomers of butylene 2,5-furandicarboxylate.
***c*(BI)$_n$**	cyclic oligomers of butylene isophthalate.
***c*(BS)$_n$**	cyclic oligomers of butylene succinate
***c*(BT)$_n$**	cyclic oligomers of butylene terephthalate
***c*(CT)$_n$**	cyclic oligomers of cyclohexamethylene terephthalate
***c*(EA)$_n$**	cyclic oligomers of ethylene adipate
***c*(EF)$_n$**	cyclic oligomers of ethylene 2,5-furandicarboxylate.
***c*(EI)$_n$**	cyclic oligomers of ethylene isophthalate
***c*(ES)$_n$**	cyclic oligomers of ethylene succinate
***c*(ET)$_n$**	cyclic oligomers of ethylene terephthalate
***c*(HI)$_n$**	cyclic oligomers of hexamethylene terephthalate
***c*(RF)$_n$**	cyclic oligomers of resorcinol 2,5-furandicarboxylate
***c*(IiF)$_n$**	cyclic oligomers of isoidide 2,5-furandicarboxylate
***c*(ImF)$_n$**	cyclic oligomers of isomannide 2,5-furandicarboxylate
***c*(IsF)$_n$**	cyclic oligomers of isosorbide 2,5-furandicarboxylate
***c*(PT)$_n$**	cyclic oligomers of propylene terephthalate
CD	cyclodepolymerization
***co*PBF$_x$T$_y$**	poly(butylene 2,5-furandicarboxylate-*co*-terpehthalate)
***co*PBF$_x$S$_y$**	poly(butylene 2,5-furandicarboxylate-*co*-succinate)
***co*PBS$_x$RF$_y$**	poly(butylene succinate-*co*-resorcinol 2,5-furandicarboxylate)
***co*PES$_x$RF$_y$**	poly(ethylene succinate-*co*-resorcinol 2,5-furandicarboxylate)
***co*PCL$_x$BF$_y$**	poly(caprolactone-*co*-butylene 2,5 furandicarboxylate)
***co*PES$_x$CL$_y$**	poly(ethylene succinate-*co*-caprolactone)
***co*PES$_x$BS$_y$**	poly(ethylene succinate-*co*-butylene succinate)
***co*PES$_x$LA$_y$**	poly(ethylene succinate-*co*-lactide)
***co*PB$_x$Im$_y$F**	poly(butylene-*co*-isomannide 2,5-furandicarboxylate)
d	Doublet
DABCO	di aza bycyclic octane
DBTO	Dibutyl tin oxide
DCB	Dichlorobenzene
dd	Doublet of doublets

d_{hkl}	Bragg spacings
DCM	Dichloromethane
DMF	*N*,*N*-Dimethyl formamide
DMSO	Dimethyl sulfoxide
DMT	Dimethyl terephthalate
DSC	Differential scanning calorimetry
Đ	molar dispersity
δ	Chemical shift (ppm)
ΔH_c	Crystallization enthalpy
ΔH_m	Melting enthalpy
ΔT ‘	Undercooling values required for crystallization ($\Delta T = Tm - Tc$)
E	ethylene units
ε-CL	ε-caprolactone
EG	Ethylene glycol
Exo	Secondary hydroxyl groups (1,4:3,6-dianhydrohexitols) or methylol groups (bicyclic acetalized alditols) oriented outside the bicyclic structure
F	Furanic units
FDCA	2,5-Furandicarboxylic acid
FDCA-Me$_2$	2,5 furandicarboxylate diester
FDCA-Cl$_2$	2,5-furandicarboxylic dichloride
FTIR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
HER	1,3-bis(2-hydroxylethoxy) benzene
HFIP	1,1,1,3,3,3-Hexafluoroisopropanol
HMF	Hydroxymethylfurfural
HPLC	High performance liquid chromatography
$[\eta]$	Intrinsic viscosity
Im	Isomannide 1,4:3,6-Dianhydro-D-mannitol
IPA	Isophthalic acid
IPA-Cl$_2$	Isophthaloyl chloride
Is	Isosorbide; 1,4:3,6-dianhydro-D-glucitol
Isoidide	1,4:3,6-Dianhydro-L-iditol
Isosorbide	1,4:3,6-Dianhydro-D-glucitol
k	Avrami kinetic constant
LA	Lactic acid
m	In NMR spectra, multiplet signal; in WAXD measurements, medium intensity.
M_n	Number-average molecular weight
m.p.	Melting point
M_w	Weight-average molecular weight
N	Relative molar amount of the dyads as obtained from ^{13}C NMR

n	In isothermal crystallization studies, Avrami exponent; in chemical microstructure analysis by 13C NMR, number average sequence lengths
NaTFAHFIP	0.05 M sodium trifluoroacetate-hexafluoroisopropanol
n.d.	Not determined
NMR	Nuclear magnetic resonance
PBA	Poly(butylene adipate)
PBF	Poly(butylene 2,5-furandicarboxylate)
PBS	Poly(butylene succinate)
PBT	Poly(butylene terephthalate)
PBI	Poly(butylene isophthalate)
PBT	Poly(butylene terephthalate)
PCL	Poly(ε-caprolactone)
PCT	Poly(cyclohexamethylene terephtalate)
PEA	Poly(ethylene adipate)
PEF	Poly(ethylene 2,5-furandicarboxylate)
PEI	Poly(ethylene isophthalate)
PES	Poly(ethylene succinate)
PET	Poly(ethylene terephthalate)
PHI	Poly(hexamethylene isophthalate)
PIiF	Poly(isoidide 2,5-furandicarboxylate)
PImF	Poly(isomannide 2,5-furandicarboxylate)
PIsF	Poly(isosorbide 2,5-furandicarboxylate)
PIsT	Poly(isosorbide terephthalate)
PLA	Polylactic acid
POM	Polarizing optical microscopy
PPF	Poly(propylene 2,5-furandicarboxylate)
PPT	Poly(propylene terephthalate)
PTA	Purified terephthalic acid
R	Randomness index of copolyesters statistically calculated on the basis of the 13C NMR analysis.
ROP	Ring-opening polymerization
s	In NMR spectra, singlet signal; in WAXD measurements, strong intensity
SA	Succinic acid
SEM	Scanning electron microscopy
Sn(Oct)$_2$	Tin Octanoate
SSP	Solid-state polycondensation
t	Triplet signal
T	Terephthalate units
t_0	Onset crystallization time
$t_{1/2}$	Half-crystallization time
°$T_{5\%}$	In TGA, temperature at which 5% weight loss was observed

TBT	Titanium (IV) tetrabutoxide
T_c	Crystallization temperature
T_{cc}	Cold crystallization temperature
${}_\mathrm{max}T_\mathrm{d}$	In TGA, temperature for maximum degradation rate
TFA	Trifluoroacetic acid
TFA-*d*	Deuterated trifluoroacetic acid
T_g	Glass-transition temperature
TGA	Thermogravimetry
THF	Tetrahydrofuran
T_m	Melting temperature
TMS	Tetramethylsilane
TOT	Tetrakis(2-ethylhexyl)-titanate
TPA-Cl$_2$	Terephthaloyl chloride
TPA-Me$_2$	Dimethyl terephthalate
U	One unit (U) was defined as that amount of enzyme which catalyzed the release of fatty acid from triglycerides at the rate of 1 μmol·min-1.
w	In WAXD measurements, weak intensity
W	In TGA, remaining weight at 600 ºC
WAXD	Wide angle X-ray diffraction
X	Molar composition determined by 1H NMR
X_c	Crystallinity index

I. **Aim and structure of the Thesis**

I.1 Introduction

Polymers have arrived to be indispensable materials due to their versatility in structure and properties. Nowadays, a world without polymers cannot be conceived because these materials are present in the development of all new and modern technologies. On the other hand, the concern about environmental problems and limitation of fossil sources has motivated the investigation of new polymeric materials and the innovation of technologies based on renewable and biodegradable compounds. Although the challenge is great, many efforts have been made to attain such objectives.

Bio-based materials are not a new topic in polymer research. Materials, such as casein, rubber or cellulose have been long studied and modified to convert them in useful polymers with novel or/and improved properties. Examples include rubber trees' latex for the fabrication of tires or moldable nitrocellulose as substitute of ivory which is used to make billiard balls. As a result of time, many studies have been performed along the last decades so that a good number of bio-based polymers with interesting features are now under use. Sugar derived monomers are interesting materials for the production of bio-based polymers with an enormous potential because of their easy accessibility, structural diversity as well as their very convenient features as harmlessness for human health and hydrophilic nature.

Carbohydrate-based difunctional compounds with a cyclic molecular structure have special characteristics such as the stiffness of the resultant polymer chain and the increasing of the glass transition temperature, T_g, as well as, their natural origin. Furan derivatives obtained from both C5 and C6 sugars, and in particular 2,5-furan dicarboxylic acid (FDCA) have a large potential for the replacement of purified terephthalic acid (PTA). The structure of FDCA resembles that of PTA, being a viable substitute in the polyesters' production without a significant decrease in the T_g. Although first studies about polyesters of FDCA were reported in 1970´s, dealing with the synthesis of furanoate polyesters have continuously published since then, a trend that is still observed nowadays. [-,]

Furthermore, carbohydrate-based bicyclic monomers, such as 2,4:3,5-di-*O*-methylene-D-mannitol (Manx-diol), 2,4:3,5-di-*O*-methylene-D-glucitol (Glux-diol) or isohexides (isommanide (Im), isosorbide (Is) or isoidide (Id)) have recently attained great interest as bulding blocks in polymer synthesis. These monomers have revealed to be very suitable for the preparation of copolyesters with high T_g values by melt polycondensation. Isosorbide and isomannide are thermally stable and resistant to hydrolysis. They have a rigid structure due to the presence of the fused bicyclic dioxane structure. A traditional polymerization pathway for these polymers is the two-step polycondensation, however, new strategies of synthesis has been explored.

Ring opening polymerization (ROP) is presented as a useful synthetic route for bio-based polymers displaying specific properties. Cyclic monomers can be polymerized due to the decrease of enthalpy or increase of entropy associated with the opening of the ring. A broad range of industrial polymers are produced *via* ROP, such as polylactides, which are becoming important like packaging materials, due to their biocompatibility and biodegradability. Nowadays, ROP has been beginning considered an important alternative to the traditional polycondensation method for the preparation of the most extensively used polyesters such as poly(terephthalate)s and poly(isophthalate)s.

I.2 Aim of the Thesis

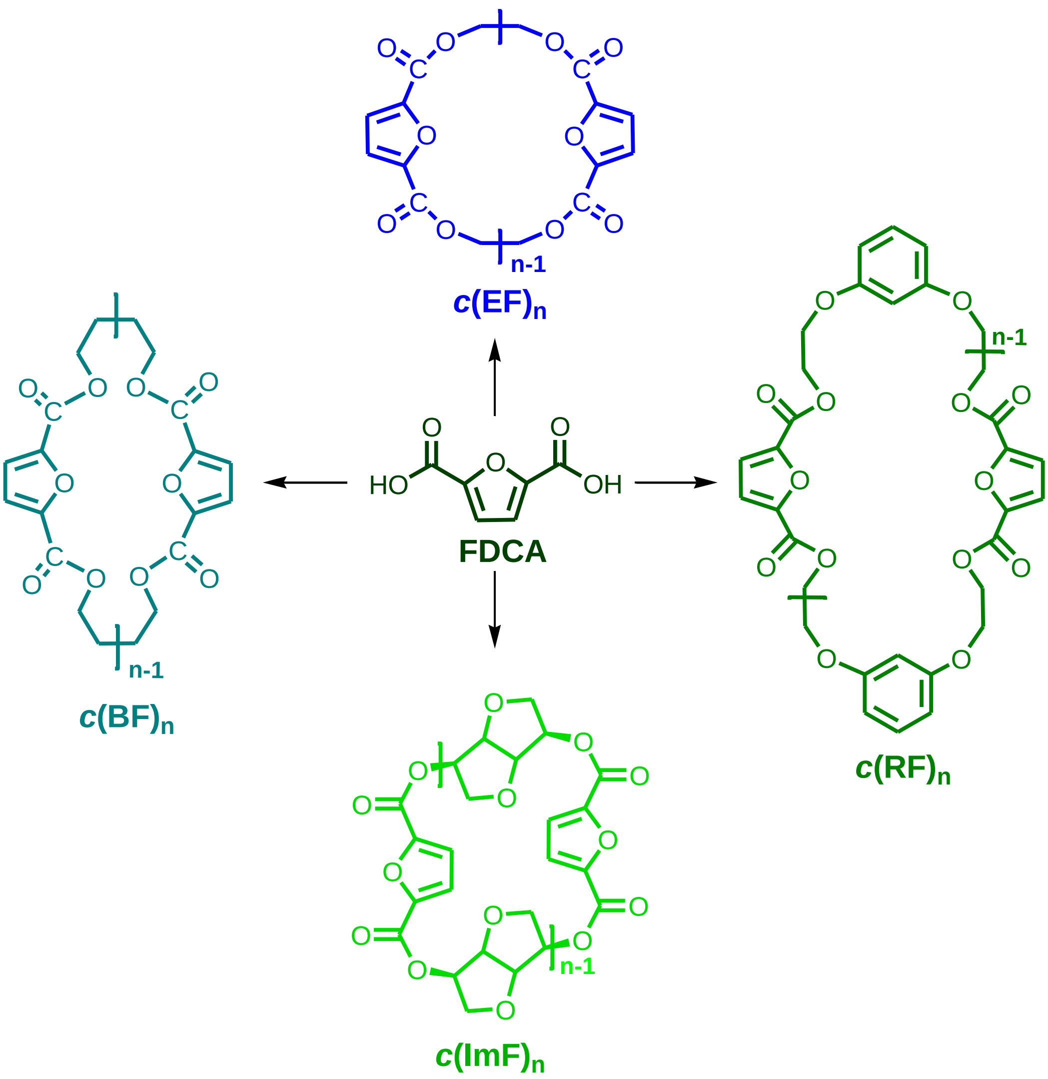
The project objective was to develop new polymeric materials based on the renewable raw materials usages with advantageous properties according to their potential use in industrial applications. The systems which have been studied, were the polyesters and copolyesters prepared *via* Ring Opening Polymerization (ROP). The materials were selected including a broad range of compositions and structures with enhanced thermal and mechanical properties covering the range from elastomeric polymers to those with high crystallinity adequate to the manufacturing of pieces, films and fibers.

This Ph.D. work was addressed to the research and development of polymers of 2,5-furandicarboxylate and different diols such as poly(butylene 2,5-furandicarboxylate) (PBF), poly(ethylene 2,5 furandicarboxylate) (PEF), poly(resorcinol 2,5-furandicarboxylate) (PRF) or poly(isomannide 2,5-furandicarboxylate) (PImF) homopolyesters, as well as, copolyesters with other cyclic oligomers to be used as comonomers such as butylene terephthalate $c(\mathrm{BT})_n$, butylene succinate $c(\mathrm{BS})_n$, ethylene succinate $c(\mathrm{ES})_n$, butylene isophthalate $c(\mathrm{BI})_n$ and others as ε-caprolactone (CL) and lactide (LA).The final objective which is being presented in this thesis achieved the following partial objectives.

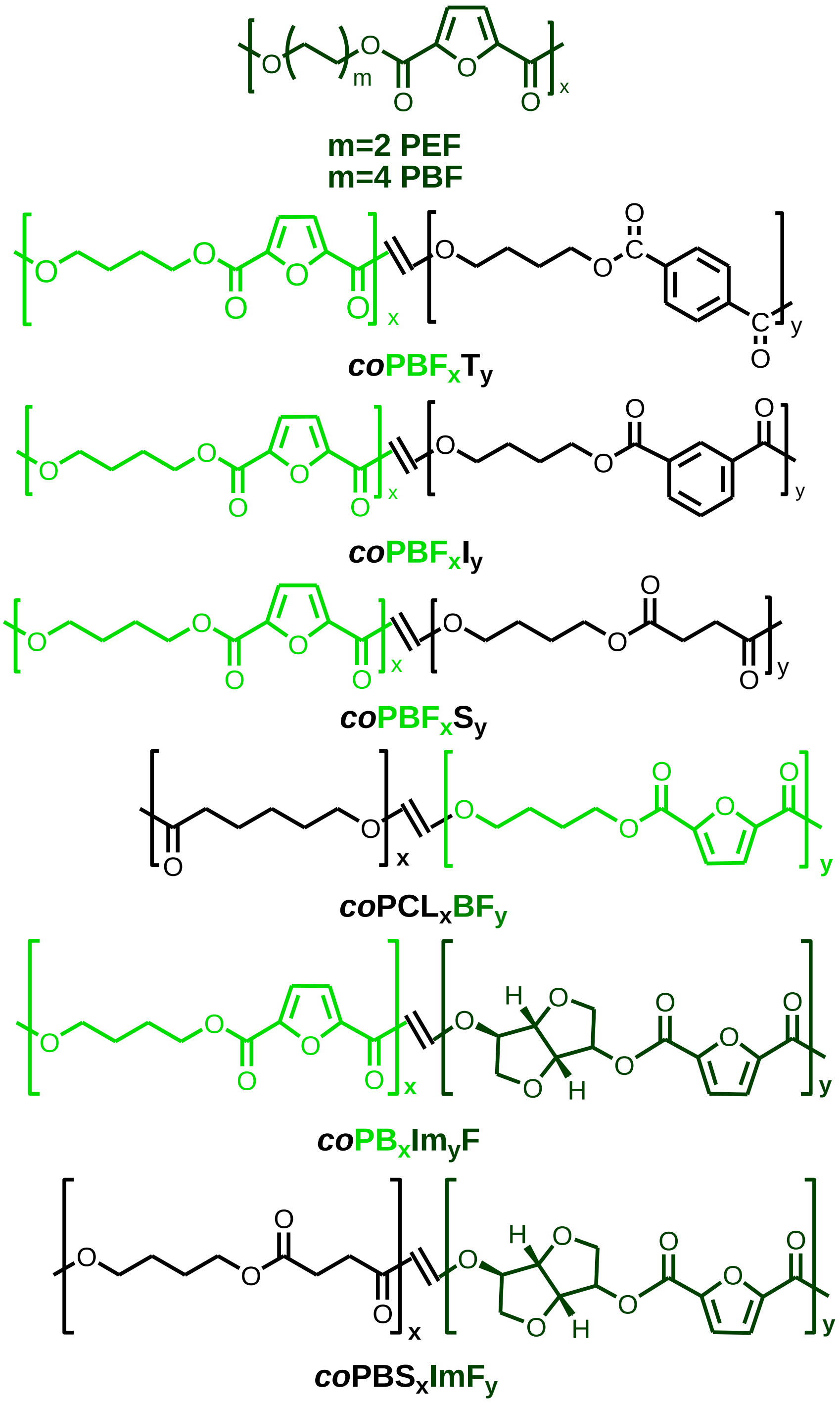
a) Preparation, characterization and optimization of cyclic oligomers from FDCA with different diols, such as 1,4-butanediol $c(\mathrm{BF})_n$, ethylenglycol $c(\mathrm{EF})_n$, 1,3-bis(2-hydroxyethoxy)benzene $c(\mathrm{RF})_n$ or isommanide $c(\mathrm{ImF})_n$ (Scheme 1.1).

b) Synthesis, characterization and property evaluation of homopolyesters obtained by ROP of $c(\mathrm{BF})_n$, $c(\mathrm{EF})_n$, $c(\mathrm{RF})_n$ or $c(\mathrm{ImF})_n$ (Scheme 1.2).

c) Synthesis, characterization and property evaluation of copolyesters obtained by ROP of $c(\mathrm{BF})_n$, $c(\mathrm{RF})_n$, $c(\mathrm{ImF})_n$ and other cyclic oligomers such us $c(\mathrm{BT})_n$, $c(\mathrm{BS})_n$, $c(\mathrm{ES})_n$, $c(\mathrm{BI})_n$, and CL. (Scheme 1.2).



Scheme 1.1 Cyclic oligomers of 2,5-furandicarboxylate with different diols.



Scheme 1.2 Polymers and copolymers of FDCA with different diols.

I.3 Structure of the Thesis

This Thesis includes eight chapters followed by an enumeration of the main conclusions of the work.

Chapter 1 introduces the Thesis that includes its aims and organization.

Chapter 2 overviews polyesters, as well as of the common methods of polymerization including ROP of the furan-based polyesters..

Chapter 3 describes the materials, measurements and synthesis methods applied in this work

Chapter 4 describes the synthesis, characterization, separation and polymerization of cyclic oligomers of 2,5-furan dicarboxylate ($c(BF)_n$ and $c(EF)_n$) obtained by (ROP).

In **Chapter 5**, copolyesters of butylene 2,5-furandicarboxylate and butylene succinate, coPBF$_x$S$_y$, obtained via ROP using either tin octate $Sn(Oct)_2$ and Lipase B: Candida Antarctica (CALB) as catalyst are described.

Chapter 6 describes copolymers of butylene 2,5-furandicarboxylate and butylene terephthalate/isophthalate (coPBF$_x$T$_y$ and coPBF$_x$I$_y$) were performed via ROP. A study of the crystallinity of coPBF$_x$T$_y$ was performed. Furthermore, the synthesis of coPBF$_x$I$_y$ was also reported.

Chapter 7 describes the synthesis of cyclic oligomers of isommanide 2,5 furandicarboxylate and their copolymerization with cyclic oligomers of butylene succinate and butylene 2,5-furandicarboxylate. The incorporation of isommanide units increases the T_g and the biodegradability in the polyesters.

Chapter 8 describes the synthesis of novel cyclic oligomers of ethylene succinate ($c(ES)_n$) using CALB as catalyst, as well as their polymerization and copolymerization with *c*(BS)$_n$, CL and LA. Furthermore, the synthesis of new cyclic oligomers of resorcinol 2,5-furandicarboxylate (*c*(RF)$_n$), their polymerization and copolymerization with cyclic oligomers of alkylene succinate with the modulating of T_g is reported.

II. Introduction

II.1 General aspects

The word polyester represents a wide quantity of polymers containing a group ester in the repeating unit. Since the pioneers experiments made in the 1930's, the applications of the polyesters have been incredible extended, including engineering plastics, high performance and biodegradable materials, etc. It is mainly possible due to the diversity of the monomer structures, making enormous advances in the improvement of their properties. Nevertheless, these advances triggered consequences respecting to the environment. In this context, the polymeric industry is awareness about ecological problems and the scarcity of fossil stocks. Consequently, the pursuit of natural origin alternatives begins to be essential for the fabrication of compounds with optimized properties.[1-3]

Biobased polymer industry is one of the markets with a higher growth.[1-3] Many projects around the world have proposed the use of different natural-origin monomers.[4-8] Actually, there is an expectation that the biobased production of them will be close to 12 millions of tons by the year 2020.[9,10] Replacement of terephthalic acid (PTA) by natural origin monomers is, nowadays, a central topic.[11] Under this scenario, the carbohydrates are notable by their easy accessibility and their diversity in their structure[12] especially, difunctionalized sugar derivatives, which have been recently explored for the synthesis of polycondensates including polyesters, polyamides, polyurethanes and polycarbonates among others.[13-16]

Isohexides, bicyclic diacetalyzed galactaric acid and 2,5-furandicarboxylic acid (FDCA) are the most studied carbohydrate based monomers due to the potential properties in their polymers .[12]

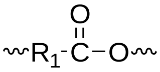
Among them, FDCA has attained great attention because its aromatic character. Actually, it is listed in the “ten bio-based chemicals” of top priority by the US Department of Energy.[17]

Polyesters based on FDCA has been reported since 70 years ago[18], however, the excellence of the polyesters has been recently explored[19]

Most of them have been produced by polycondensation using organometallic catalyst.[20-23] Nevertheless, alternative routes of synthesis such as ROP has been also explored.[24-26] ROP is an excellent technique for the synthesis of high molecular weight polymers without the formation of by-products. ROP implies the rupture of a ring molecule in the presence of a suitable catalyst for the formation of a linear polymer. An advantage of this process is the low melt viscosity prior to polymerization because the melt consist of only small monomers or oligomers, in which no high vacuum is required.[27,28]

II.2 Polyesters

Polyesters are polymers containing ester groups in the main chain. They could be fabricated from different synthetic methods including the dibasic acids with diols and derivatives. A general formula of the polyesters is represented in Scheme 2.1, where due to the nature of R_1, an enormous amount of polyesters can be possible with a great variety of properties.



$$\sim R_1-\overset{\overset{\displaystyle O}{\|}}{C}-O\sim$$

Scheme 2.1. General formula for the polyesters.

In this context, the copolyesters could be classified in aliphatic polyesters and aliphatic-aromatic polyesters. Aliphatic copolyesters include linear low-molar-mass hydroxyl-terminated macromonomers used in the synthesis of polyurethanes, biodegradable thermoplastic linear polyesters, such as polylactides, polylactones and hyperbranched polyesters applied as crosslinkers in coatings. Aliphatic-aromatic polyesters including PBT and PET exhibit better mechanical properties and thermal resistance that could be applied for a widely number of applications as high performance thermoplastics.[29-30]

II.3 Green monomers

The search of eco-friendly alternatives has established the “green chemistry” trend in the polymeric industry. The substitution of the monomers for “greener” ones and convert them into useful products and energy sources is a priority. Lignocellulosic feedstock promises a potential source of bioenergy and biochemicals.[28] The biomass components, such as carbohydrates, lignin, oils, etc. can be transformed into chemical compounds for the synthesis of biobased polymers.[2-5,32] Conventional monomers from natural origin have been recently investigated. Most of them are accessible, however, some of them are only made in lab-scale currently.

II.3.1 Diacids:

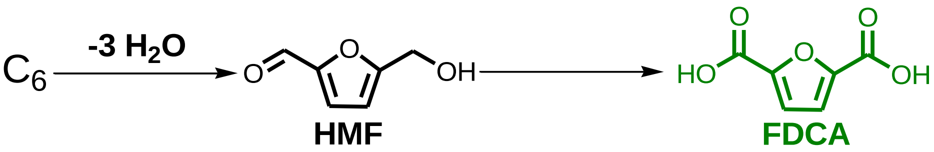
Succinic acid: Succinic acid is a C4-dicarboxylic acid which has a great interest due to its extensive applications in pharmaceuticals, food and chemistry industry.[33,34] Biobased succininc acid is produced by glucose, lactose, sucrose, maltose or fructose using organisms such as *Actinobacilius succiogenes*[33,34,38] or *Anarobiospirillum succinoproducens.*[35-37,39]

Adipic acid: Adipic acid is an important aliphatic dicarboxylic acid, which is used for the production of nylon 6-6.[40] Even though the synthesis of adipic acid from petrochemical resources is more economical than bio-based feedstocks, these routes have been recently studied.[41] They include the fabrication of *cis, cis* muconic acid and D-glucaric acid from lignin-derived aromatics using the metabolisms of the microorganisms.[42,43]

Terephthalic acid (PTA): PTA is one of the most used compounds due to the importance in the fabrication of polymers such as poly(ethylene terephthalate), PET, and poly(butylene terephthalate), PBT.[44] Industrially, PTA is produced by oxidation of p-xylene by oxygen in air using cobalt-manganese-bromide catalyst.[45,46] Nevertheless, many efforts have been made for the production of p-xylene using biomass.[46] The feedstock includes ethanol, hydroxymethylfurfural (HMF), isobutanol, isoprene, limonene and furfural.[45] However, some disadvantages have been found, such as the high-cost process and the limitation of the raw materials in the biomass.[47] These handicaps have been reduced in the recent years, however the production is still in lab-scale.[46]

Isophthalic acid (IPA): IPA is an organic compound that is produced by the oxidation of m-xylene. The m-xylene can be produced with similar methods as p-xylene from furfural with a final separation among the three xylene isomers.[46]

2,5-furandicarboxylic acid (FDCA): FDCA is one of the most studied and valuated compounds in the polymeric industry.[19] Resulting a natural origin molecule from the catalytic oxidation of HMF, which in turn, is obtained from the acid catalyze-dehydration of C6-sugars (Scheme 2.2).[47-57] This molecule has a rigid structure that resembles to the isophthalic acid with high melting point and solubility in DMSO.[48-63] It has been synthesized from more than a century, being the pioneers, the works reported by Fittig and Heinzelman[54] and Sohts and Tollens[55]. Nevertheless, its synthesis has had a great relevance until recent years when the synthesis routes from lignocellulosic feedstocks and a potentially substitution of PTA were explored.[47-53] As the structure suggest, the characteristics of the molecule are similar to the terephthalic counterpart with the advantage of its natural origin.[64-67]



Scheme 2.2. Synthesis of 2,5-furandicarboxylic acid (FDCA)

II.3.2 Diols

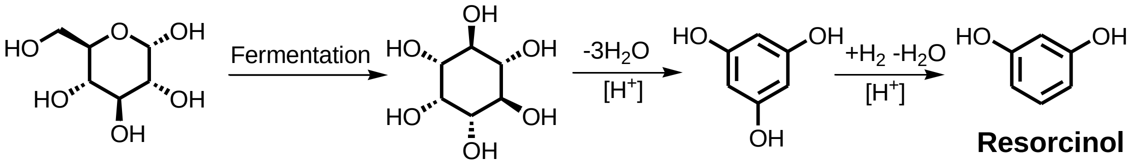
Ethylene glycol (EG): Nowadays, bioethanol is an important biofuel produced at industrial scales from starch and sugar.[68] Likewise, bioethanol can be catalytic dehydrated to ethylene,[68,69] allowing the fabrication of EG via conventional routes of direct oxidation to ethylene oxide followed by thermal hydrolysis[70,71]. In an industrial-scale, Coca Cola and PepsiCo companies have been developed bio-based EG to the subsequent PET production for eco-friendly bottles.[72]

1,3-propanediol: 1,3-propanediol is an important compound because their polyesters are generally biodegradable.[73] Bio-based 1,3-propanediol has been produced from glycerol which can be converted into 1,3-propanediol using different microorganisms, such as citrobacter.[74-76] *Escheria coli,*[77] *Klensiella* species[78,79], *Clostridium*[80-82] are some organisms which have been proven to be effective.

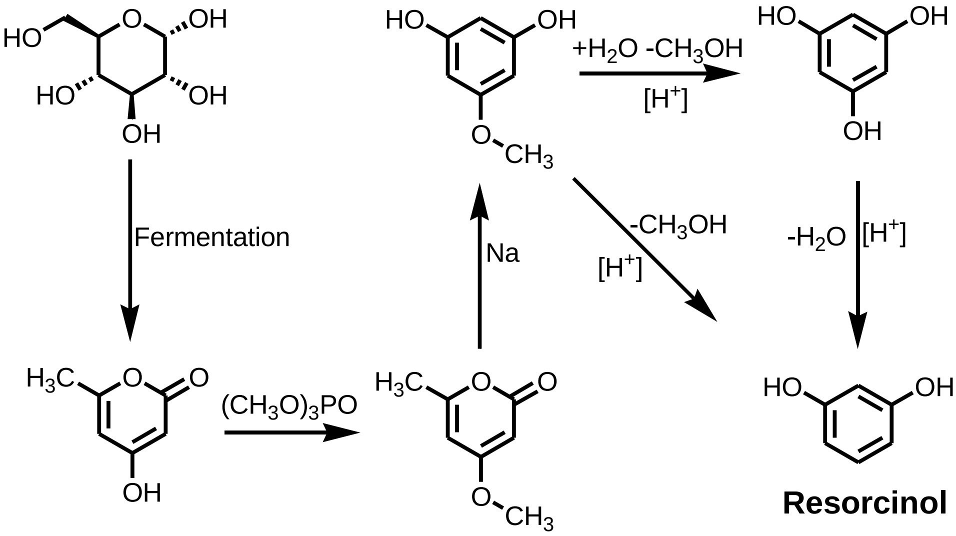
1,4-butanediol (BD): BD is obtained from a sucrose-based process using microorganisms.[82] Additionally, it can be produced from bio-based succinic acid involving three steps: 1) corn-derived glucose is fermented to succinic acid, 2) succinic acid is purified and 3) its reduction to 1,4-butanediol.[83] Although important efforts for the industrial-scale preparation of BD have been made, it is until now mostly synthesized from petroleum-based compounds due to economic reasons.[84]

1,10-decanediol: Important efforts have been made about the bio-based production of 1,10-decanediol. It has been reported by a potential derivative of the castor oil.[85] Until now, it is only produced in a lab-scale.

Resorcinol: Resorcinol is an important natural origin monomer that is produced in several ways. Its structure is the diol-analoge to the isophthalic acid.[67] The biobased synthesis of resorcinol includes the production from catechins by fermentation to be transformed to 1,3,5-benzenetriol and after reduced to resorcinol (Scheme 2.3)[86-88] or more commonly from glucose, where triacetic acid lactone can be prepared from glucose and converted in the methyl ether, which could be transformed into 1,3,5-benzenetriol methyl ether to obtain resorcinol directly or via 1,3,5-benzenetriol as intermediate (Scheme 2.4).[88,89]

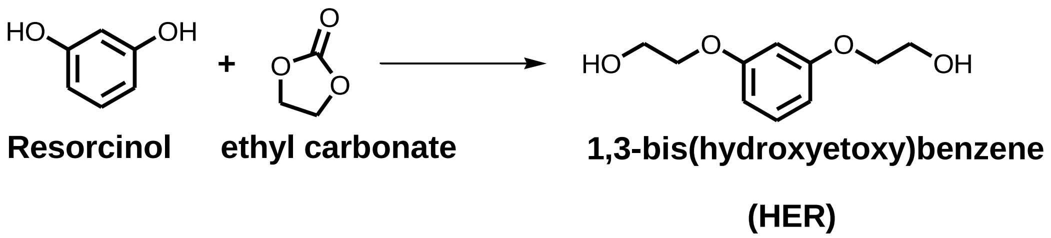


Scheme 2.3. Synthesis of Resorcinol via Inositol.[87]



Scheme 2.4. Synthesis of resorcinol via triacetic lactone.[89]

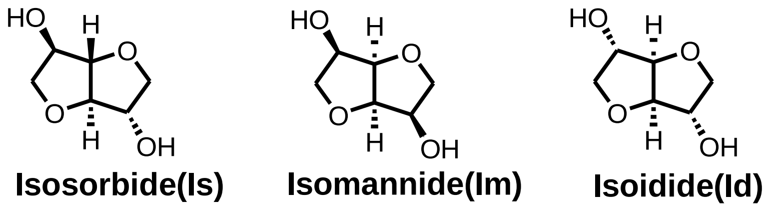
Resorcinol has a low reactivity compared with the aliphatic moieties, consequently, a functionalization is necessary in order to increase the activity. 1,3-bis(hydroxyethoxy)benzene (HER) is a more reactive alternative for resorcinol. It could be obtained by a reaction with ethyl carbonate (Scheme 2.5).[67]



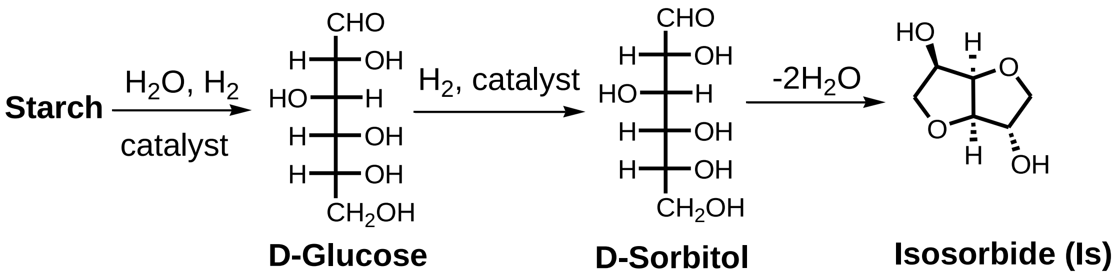
Scheme 2.5. Synthesis of 1,3-bis(hydroxyethoxy) resorcinol (HER).

Few works about the synthesis of polyesters with HER has been reported.[90] Polymerization of HER with different aliphatic and aromatic diacids obtaining mainly amorphous copolymers with high dispersity has been reported by Gioia.[67]

1,4:3,6-dianhydrohexytols: Other alternatives for the substitution of petrochemical compounds are the 1,4:3,6 dianhydrohexitols. They have been recently used for the polymerization systems. The three isomers (Isommanide, Im, Isosorbide, Is and Isoidide, Id,) (Scheme 2.6) have rigid chiral and non-toxic molecules providing a high T_g. The applications of the polyesters can be obtained packaging or medical devices.[91] Initial works in the synthesis of isohexides have reported since 1950s.[92,93] The structure of the molecule is composed of two-fussed tetrahydrofuran rings with an angle of 120 °C between the rings. The location of the secondary hydroxyl groups that are situated in the carbons 2 and 5 positioned either inside or outside is related with the reactivity of the molecule and according to the literature, Is; is the only one produced in an industrial-scale, (Scheme 2.7) isommanide (Im) is the less studied and with the low reactivity and finally, isoidide, Id, is the most reactive of the isomers, however, it is derived from L-idose which rarely exists in nature and it is difficult to extract from biomass.[61] An alternative route of the synthesis of isohexides is the isomerization among them.[93] Although the isohexides have several important features for replacing fossil based compounds, important handicaps require to be solved, such as the high cost of the synthesis and the low reactivity in the secondary alcohol. [61]

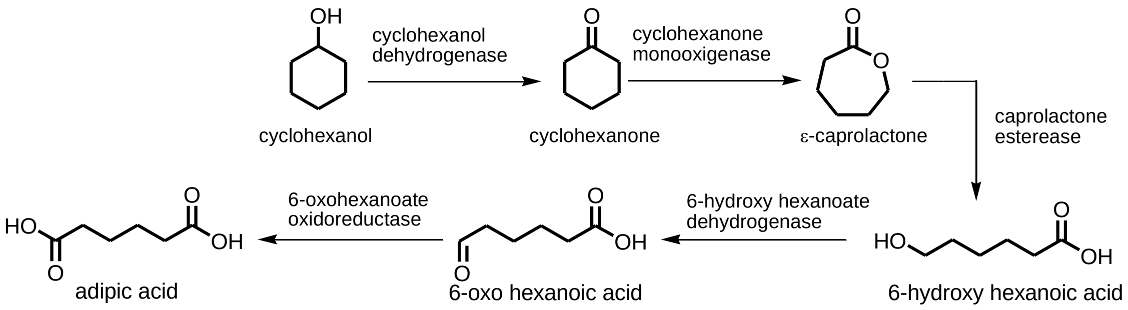


Scheme 2.6. Molecules of 1,4:3,6-dianhydrohexytols.



Scheme 2.7. Green synthesis of isosorbide (Is).

ε-Caprolactone: Industrially, ε-Caprolactone (ε-CL) is produced by the oxidation of cyclohexanone by peracetic acid.[94] Nevertheless, a number of microorganism oxidize cyclohexanol into adipic acid making both ε-CL and 6-hydroxyhexanoic acid as intermediary products (Scheme 2.8).[95]



Scheme 2.8. Oxidation of cyclohexanol to adipic acid in *Actinobacter* reported by Thomas et al. 95

II.4 Methods of polymerization

Among years, several methods for the synthesis of polyesters have been developed, optimizing the process and enhancing their properties. The common methods of polymerization are presented as follows.

Melt polymerization by polycondensation: Polyesters can be obtained by stoichiometric stepwise reaction between difunctional reactants with the formation of low molecular weight and condensates byproducts. Typically, polyesterifications reactions include two steps: 1) esterification with a diol and 2) polycondensation to synthesize of polymers. It is necessary to maintain a proper end group stechiometry and to removal the condensates products in order to obtain high molecular weights.[96] These reactions are performed using an acid or using a dimethyl ester with an excess of 3:1 mol of diol. Vacuum is commonly applied in the second step in order to remove the condensate (water or methanol) and resulting high molecular weights. An organometallic catalyst, such as metal salts and oxides is used with temperatures in a range of 160-290 ºC.[97,98] Many commercial aliphatic and aromatic polyesters, i.e. PET or PBT are produced by this method. Specifically, in the case of PET, the second stage is carried out at 270-290 ºC and applying vacuum.[98] For this reason, alternatives of synthesis have been investigated in the last years.

Solution polymerization: Most of the diols have low reactivity with the direct diacids, therefore, their derivatives, such as diesters and dichlorides are used for the polymerization.[6] These reactions commonly take place in solution at temperature in a range of -10 to 100 ºC.[99] Few works have been reported about aromatic polyesters[100] Common catalysts are the tertiary amines such as pyridine or trimethylamine, which play a role of both: reaction catalyst and HCL acceptor. The main disadvantage of this method is the low molecular weights obtained. [27]

Solid state polymerization (SSP): The solid state polymerization (SSP) consists in a polymerization upper than T_g but lower than T_m. One of the main advantages is the use of low temperatures in order to prevent degradation. The increase in molecular weight is accompanied by raising the crystallinity. Disadvantages are the low reaction rates compared with the polycondensation and the ROP, especially at high temperatures.[102]

SSP is carried out in glass tubes, fluidized and fixed bed reactors. Mechanical agitation provides a good heat and mass transfer and prevents agglomeration, especially for reactions up to 200 °C.[102,103] During the process, by products are removed applying vacuum, convection or passing an inert gas. Despite the reaction proceeds faster when high vacuum is used than under nitrogen atmosphere,[104,105] if the atmospheric pressure returned when high vacuum is used, the polyester could be degraded and discolored. An inert gas is necessary 1) to remove the condensate, 2) to inhibit the polymer oxidation and 3) to heat the reacting mass. The reaction temperature is the most important parameter of the rate variation, due to its influence on all aspects in the reaction progress. An increase in the temperature accelerates the overall rate of the process, as a result of the speeding up of the chemical reaction, the mobility of the functional end groups and the byproduct diffusion.[103] Small size of prepolymer particles can lead the rise of the rate; the surface by-product diffusion is influenced by the flow of the inert gas. Acceleration in the gas flow can increase the mass and heat transfer in the gas-solid system and decrease the resistance of the diffusion of the byproducts from the particle surface into the bulk of the gas phase. [105,106]

Ring Opening Polymerization (ROP): ROP is an excellent polymerization method of synthesis for the preparation of polymers using cyclic monomers, which can be opened by both enthalpical and entropical ways.[27,107] Even though this method has been used for the polymerization of many products, the use in lactones is scarcely explored.[98] Ring sizes between 2 and 8 atoms may be polymerized due to the loss of enthalpy associated with the loss of ring strain. Polymerization via ROP has two objectives in the context of this Thesis: 1) to polymerize at mild temperatures in order to mantain the carbohydrate moieties, and 2) to promote a faster polymerization reactions able to afford higher molecular weights.[108]

Nowadays, ROP is considered an important alternative to the traditional polycondensation method for the preparation of important polyesters such as poly(terephthalate)s and poly(isophthalate)s.[109] The method has been successfully extended to the synthesis of copolyesters composed of aromatic and aliphatic units, i.e. poly(butylene terephthalate-co-caprolactone) copolymers prepared from butylene terephthalate cyclic oligomers and ε-caprolactone.[110.111] The main advantage of ROP of macrocyclic oligomers are the following:[112-115]

1) Allows the polymerization of macrocyclic oligomers, not only small strained rings.
2) Practically, there is not formation of small molecules or by-products.
3) The minimizing of the end groups that permits high molecular weights.
4) The polydispersity is expected less than 2.0.

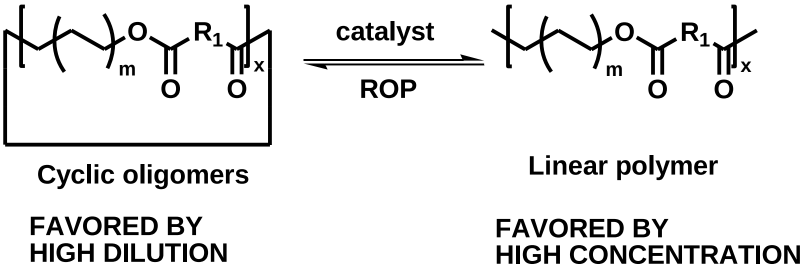
Enzymatic polymerization by ROP: Enzymes can be used for polymerization by ROP. Enzymes are proteins which exhibits a high catalytic efficiency. Lipases are reported to be good catalysts for melt polycondensation[116] and ring opening polymerization.[117,118] Enzymatic polymerization by ROP has been studied in organic solvents such as toluene[119] and diphenyl ether[120] or in bulk.[116-121] The best activity of the enzymes is in hydrophilic solvents, on the contrast, hydrophobic solvents such as DMSO or methanol lead to significant modifications in enzyme conformation and therefore to a dramatic decrease in the enzyme activity.[122,123] The enzymatic synthesis of polyesters is used in the preparation of low-melting point polyesters, mainly aliphatic ones when the polymerization temperature is not upper than maximum accepted by the enzyme.[124] Lipases have been proved to be efficient for polymerizations via ROP, especially, *Candida Antarctica (*CALB) that is widely used in many reaction with different cyclic oligomers and lactones.[125,126]

II.5 Cyclic oligomers

Ring opening polymerization of macrocyclic oligomers is based on the principle of the ring–chain equilibria.[115] (Scheme 2.9) Nowadays, the synthesis of cyclic oligomers of polyesters has gained great interest due to the development of three suitable high efficiently synthesis techniques: 1) the high dilution condensation (HDC)[27], the cyclodepolymerization (CD)[127] and the enzymatic cyclization (EC).[118]

Cyclic oligomers of condensation polymers, such as polycarbonates (PC) and polyesters, have been known for many years, but they were not exploited commercially until the last decade because, in the past, their synthesis and isolation were very difficult. The attraction of cyclic oligomers as monomers for thermoplastics relies on the low melt viscosity and then the ultimate high molecular weight polymer. Furthermore, since cyclic oligomers do not contain end groups, very high molecular weights are obtained without the formation of secondary by-products.[107]

Pioneer works about cyclic oligomers of polyesters were reported by Ross et al.[112] and Schnell and Bottenbruch.[113] They described the tetramer cyclic oligomer carbonate of bisphenol A (BPA), however, their work was only academically important, due to the long reaction time, the extensive purification required, and the low productivity attained. On the other hand, Semylen et al. developed a high dilution method but they obtained low yields.[114] In Table 2.1 are summarized the common cyclic oligomers reported in literature.



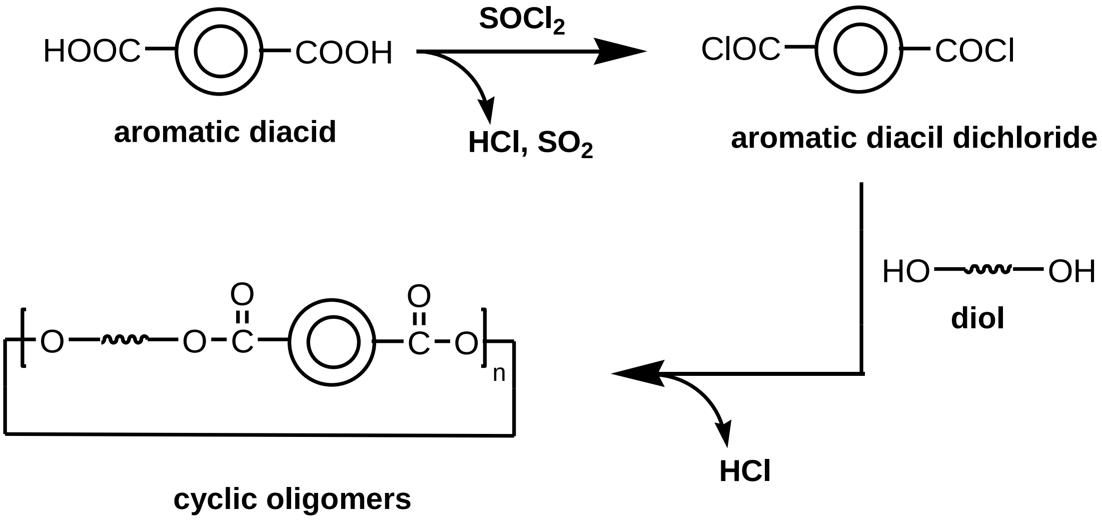
Scheme 2.9. Ring chain equilibrium of cyclic oligomers.

II.5.1 Synthesis of cyclic oligomers

High dilution condensation (HDC): HDC involves the preparation of cyclic oligomers *via* condensation of an acid dichloride with a diol in high dilution conditions (< 0.005 M) using tertiary amines such as quinuclidine or diazabycyclo[2.2.2] octane

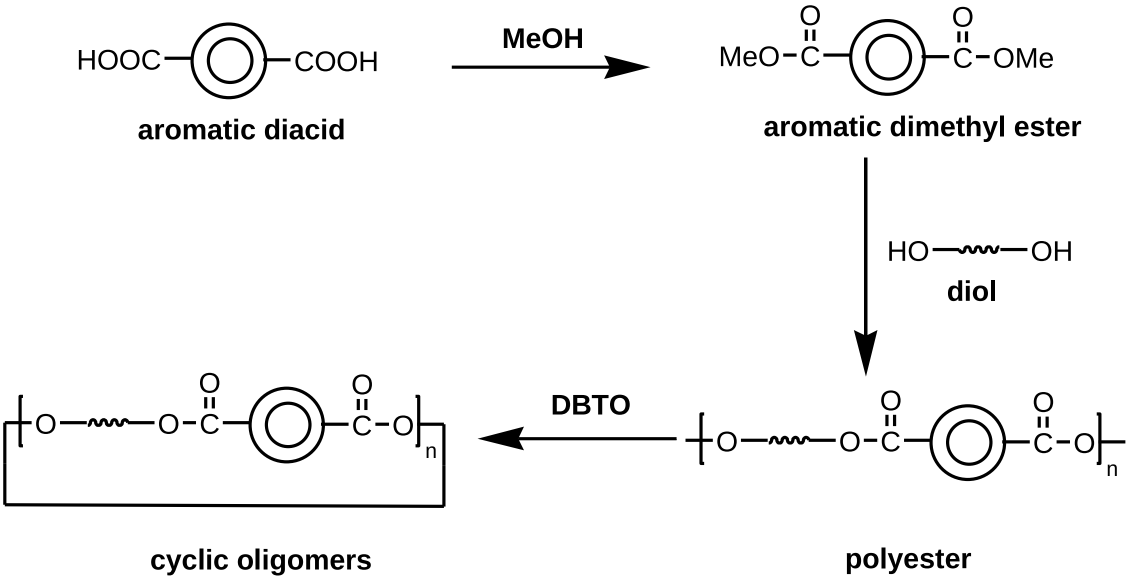
(DABCO) as catalyst. An important factor is the stoichiometry of the reagents in the reaction to avoid the formation of linear oligomers.[27,107,115] (Scheme 2.10)

HDC is a technique cyclization method of aromatics, which was optimized by Brunelle et al.[107]An important advantage of this method is the reaction time, then the formation of cyclic oligomers is practically instantaneous with the contact of the monomers. The removal of catalyst is carried on with concentrated HCL and the final separation from the linear oligomers is normally made it with flash chromatography.[107]



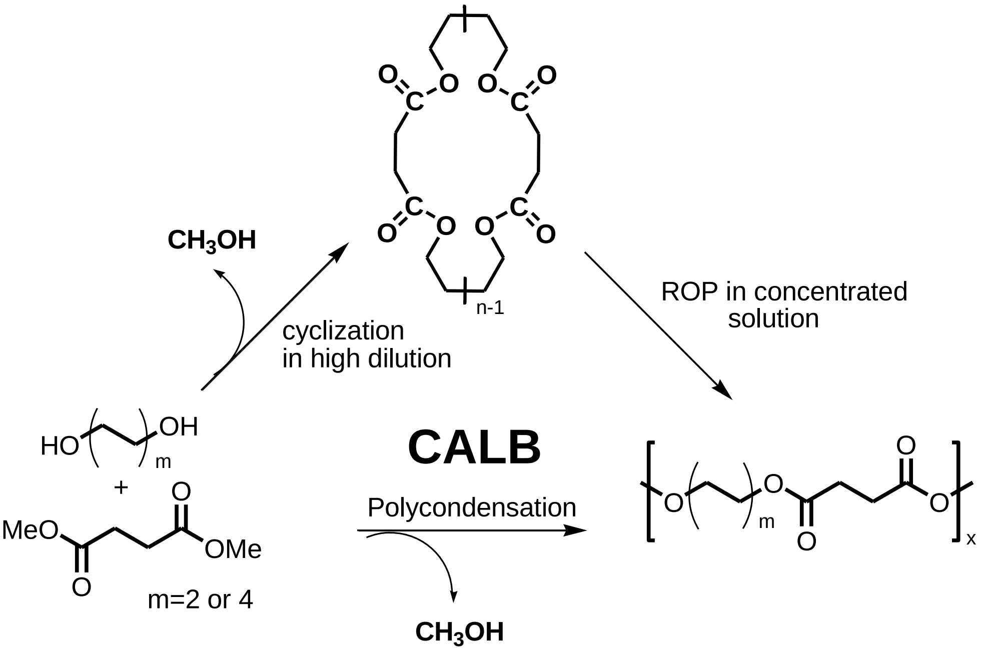
Scheme 2.10. Mechanism for the synthesis of cyclic oligomers by high dilution condensation (HDC).

Cyclodepolymerization (CD): CD consists in a thermal depolymerization of a linear polyester placed in a stable solvent at high dilution in the presence of a transesterification catalyst.[19,115,127,128] This synthesis method could be an important alternative for the polymer recycling.[115] In CD the formation of the polyester is previously synthesised. This method is performed at high temperatures, close to 200 °C because it is necessary the degradation of the polymer. Chlorobenzene and dichlorobenzene (DCB) are common solvents used due to their high T_m allowing the temperature required. The main disadvantage of this method is the time of reaction (5 to 7 days).[115,128]



Scheme 2.11. Mechanism for the synthesis of cyclic oligomers by cyclodepolymerization (CD).

Enzymatic Cyclization (EC): EC involves the formation of cyclic oligomers from a diester (mainly aliphatic diesters) and a diol under high dilution conditions in the presence of enzymes.[121,129] The first work applying this method was reported by Sugihara et al.[121] for the cyclization of butylene succinate (BS) and BD. A crucial purification step is the removal of low-molecular-weight by-products such as water or methanol, then they are the responsible for the reversible reaction. The mechanism in Scheme 2.12 represents two pathways for the PBS; a direct polycondensation and ROP with the previously synthesis of cyclic oligomers. According to the reported in literature, higher molecular weights are obtained with the utilization of ROP synthesis.[121]Typical reactions are conducted at 90 °C for 48 h.



Scheme 2.12. Mechanism of cyclic oligomers performed by enzymatic cyclization.[121]

Synthesis of cyclic oligoesters by distillation from reaction mixtures: Cyclic oligomers can be obtained when the cyclic oligomers are not the central species. Volatility is the key requirement of the cyclic oligomers.[127] Preliminary works about this synthesis method were reported by Carothers for aliphatic polycarbonates,[130] and polyesters[131] at elevated temperatures. A recent paper published by Labruyere[132] describes the preparation of *c*(BS)$_n$ using ZnO as catalyst at higher temperature in a glass oven.

Extraction of the cyclic oligoesters from the products of condensation polymers: When a polymer is obtained via polycondensation reactions, the products of condensation normally contains an small quantity of cyclic oligomers that can be performed with a soxhlet apparatus. Actually, it has been applied for many years,[133,134] including the extraction of cyclic oligomers from poly(ethylene terephthalate), poly(ethylene isophthalate) and combinations between them.[135] A classical example is the extraction of cyclic oligomers from commercial samples of PET extracted with boiling dioxane at 285 °C for 4 h.[135]

Table 2.1. Common cyclic oligomers reported in the literature

Cyclic Oligomer	Cyclization method	Catalyst	Reaction solvent	Yield (%)	Composition (2/3/>4)	Ref.
$c(\mathrm{BF})_n$	HDC	DABCO	CH_2Cl_2	50	5/31/64	26
$c(\mathrm{BT})_n$	HDC	DABCO	CH_2Cl_2	80	51/26/23	107
$c(\mathrm{BT})_n$	CD	DBTO	Clorobenzene	78	50/40/10	136
$c(\mathrm{BT})_n$	EC	CALB	Toluene	85	79/12/9	137
$c(\mathrm{ET})_n$	HDC	DABCO	CH_2Cl_2	60	39/21/40	107
$c(\mathrm{ET})_n$	CD	DBTO	DCB	50	35/30/35	138
$c(\mathrm{ET})_n$	EC	CALB	Toluene	60	34/50/16	137
$c(\mathrm{HT})_n$	HDC	DABCO	CH_2Cl_2	55	63/20/7	107
$c(\mathrm{HT})_n$	CD	DBTO	DCB	76	59/24/17	139
$c(\mathrm{HT})_n$	EC	CALB	Toluene	89	72/19/9	137
$c(\mathrm{PT})_n$	HDC	Et_3N	$CHCl_3$	55	60/25/15	107
$c(\mathrm{PT})_n$	CD	DBTO	DCB	67	55/35/10	135
$c(\mathrm{CT})_n$	CD	DBTO	DCB	50	3/57/40	138
$c(\mathrm{BI})_n$	HDC	DABCO	$CHCl_3$	82	63/19/18	107
$c(\mathrm{BI})_n$	CD	DBTO	Clorobenzene	70	56/31/13	140
$c(\mathrm{BI})_n$	EC	CALB	Toluene	70	81/13/6	137
$c(\mathrm{EI})_n$	HDC	DABCO	$CHCl_3$	80	74/13/13	107
$c(\mathrm{EI})_n$	CD	Stanooxane	DCB	63	70/20/10	128
$c(\mathrm{EI})_n$	EC	CALB	Toluene		72/19/9	137
$c(\mathrm{HI})_n$	HDC	DABCO	$CHCl_3$	75	59/23/18	107
$c(\mathrm{HI})_n$	CD	DBTO	DCB	70	60/30/10	141
$c(\mathrm{HI})_n$	EC	CALB	Toluene	90	72/19/9	137
$c(\mathrm{BS})_n$	HDC	p-toluene sulfonic acid	Toluene	50	70/20/10	142
$c(\mathrm{BS})_n$	CD	ZnO	None	40	70/20/10	132
$c(\mathrm{BS})_n$	EC	CALB	Toluene-	75	60/30/10	121
$c(\mathrm{EA})_n$	HDC	Pyridine	$CHCl_2$	28	22/45/33	143
$c(\mathrm{EA})_n$	CD	DBTO	DCB	80	34/55/11	144
$c(\mathrm{BA})_n$	EC	CALB	Toluene	80	55/45/5	145

A: Adipate; B: 1,4-butylene; C: Cyclohexamethylene; E: Ethylene; F:2,5-furandicarboxylate; H: Hexamethylene; I: Isophthalate; P:2,3-propylene; S: Succinate; T: Terephthalate

II.6 Polymerization of cyclic oligomers

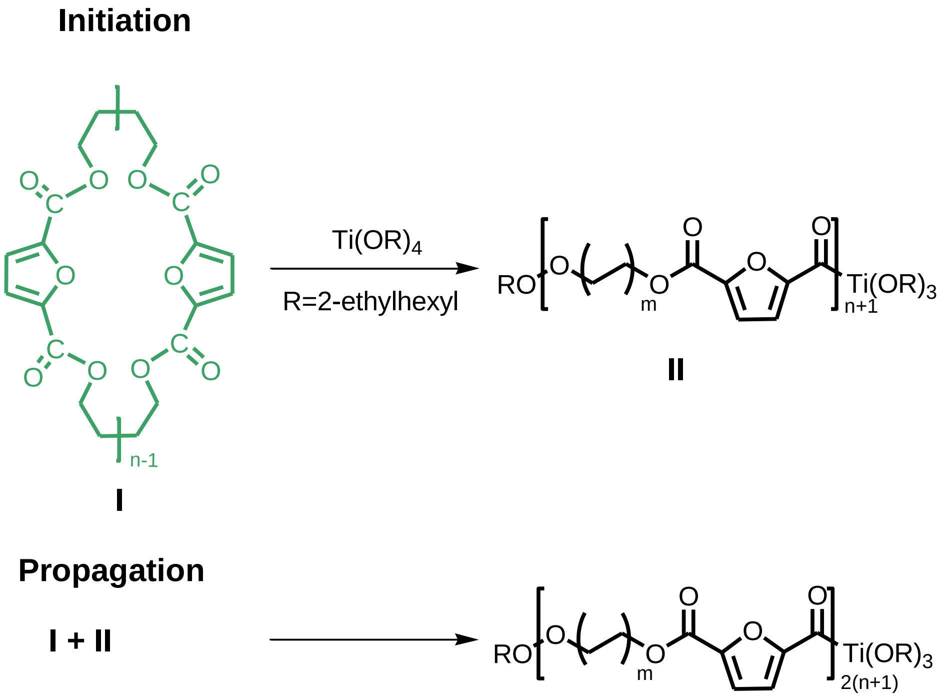
Many advances about the conversion of cyclic oligomers into high molecular weight linear polymer have been performed. ROP offers more advantages respecting the conventional polycondensation process due to the high *Mw,* which can be obtained (as high as 100,000-300,000 g/mol) in short times versus the typically molecular weights by melt polycondensation (40,000 to 60,000 g/mol). The low melt viscosity allows their processability.[147] The low viscosities are also useful for the production of high melting points and high viscosities polymers, such as polyethylene 2,6-naphthalene (PEN).[147]

In an industrial scale, Cyclic Corporation produces mixtures of cyclic dimer, trimer and tetramer of butylene terephthalate ($c(BT)_n$).[148] $c(BT)_n$ can be polymerized in the presence of transesterification catalysts, such as antimony oxide (Sb_2O_3), calcium oxide (CaO), tetrabutyl titanate (TBT) or tin octate ($Sn(Oct)_2$),).[107,109,147] The polymerization can be performed with high molecular weight in only 20 min. Usually, the melting point of the cyclic oligomers is lower than the polymer making conceivable the polymerization at temperatures lower than necessary for polycondensation.

An essential step in the synthesis of high molecular weight is the purification to remove the linear oligomers which affect the reaction kinetics and limit the final molecular weight. Among the purification process the chromatography, precipitation and recrystallization are the most used.[149]

The mechanism of the reaction consists of 2 steps: 1) the initiation to form an active chain end. 2) the propagation reactions continue the consummation of the cyclic oligomers until the ring-chain equilibrium becomes degenerated (Scheme 2.13). The initiator is attached to the polymer, and the chain growth is not finished. Due to their size and flexibility, the cyclic oligomers are nearly strain-free and the polymerization is practically thermoneutral, leading to complete the equilibration of ester groups.[27]

Polydispersities of the final polymers are about 2.0, similar to the obtained with the conventional polycondensation.



Scheme 2.13. Ring opening polymerization of cyclic oligomers.

Copolymerization of cyclic oligomers: Homopolyesters have defined characteristics which are important for industry such as good mechanical and thermal properties and versatility in the process production. Nevertheless, many times it is necessary to improve them for the modification of crystallinity and crystallizability to increase the biodegradability or to the modification of undesired properties such as poor dyeability (due to high T_g) or poor procesability (due to high melting points).[107]

An important number of aliphatic-aromatic copolyesters has been produced modifying their properties like PET/PBS, PET/PCL or PBA/PBS. In Table 2.2, a summary of common polymers performed by the polymerization of cyclic oligomers is shown.

Table 2.2. Common polyesters from cyclic oligomers reported in literature

Polymer	Cyclic source	catalyst	ROP Method	Yield (%)	M_w (kg mol^{-1})	Ref.
PBF	HDC	TOT	Bulk	80	58	26
PBT	HDC	TOT/ Bu_2Sn	Bulk	96	115	107
PBT	CD	Stannooxane	Bulk	88	104	136
PBT	EC	$Sn(Oct)_2$	Toluene	87	85	137
PET	HDC	TOT/ Bu_2Sn	Bulk	98	104	107
PET	CD	Sb_2O_3	Bulk	90	32	139
PET	EC	$Sn(Oct)_2$	Toluene	87	67	137
PHT	HDC	TOT/ Bu_2Sn	CH_2Cl_2	55	98	107
PHT	CD	TBT	Bulk	84	41	138
PHT	EC	$Sn(Oct)_2$	Bulk	87	45	137
PPT	HDC	DBTO	Bulk	78	5.4	107
PPT	CD	DBTO	Bulk	67	5.1	150
PCT	CD	DBTO	Bulk	70	4.6	139
PBI	HDC	TOT/ Bu_2Sn	Bulk	80	94	107
PBI	CD	TOT	Bulk	85	43	140
PEI	HDC	TOT/ Bu_2Sn	Bulk	67	95	107
PHI	HDC	TOT/ Bu_2Sn	Bulk	88	60	107
PBS	HDC	Sb_2O_3	Bulk	90	60	142
PBS	CD	$Sn(Oct)_2$	Bulk	88	65	132
PBS	EC	CALB	Toluene	95	120	121
PEA	HDC	DBTO	Bulk	83	60	143
PBA	EC	CALB	Bulk	89	50	145

A: Adipate; B: 1,4-butylene; C: Cyclohexamethylene; E: Ethylene; F:2,5-furandicarboxylate; H: Hexamethylene; I: Isophthalate; P:2,3-propylene; S: Succinate; T: Terephthalate

II.7 FDCA-based polymers

FDCA-based polymers have been synthesized since 1970’s with the work reported by Moore and Kelly[18] however, the interest augmented in the last ten years when it was proposed as a potential alternative to PTA.[19-24] FDCA-based polymers with high molecular weights and high yields have been obtained since last decade.[22-25,54-58] The field of FDCA can be extended to a more vast number of polyesters from FDCA and its copolymers with different aliphatic diols[54-58] and the dianhydrohexitols.[59,60] The similitudes in the properties of these polymers with the counterparts of the terephthalic acid make them feasible for industrial applications.[54-58] Nonetheless, other furanic-aliphatic polyesters have been synthesized obtaining polymers with biodegradability and good thermal properties including the bicyclic alditols such as the 1.4:3,6 dianhydrohexitols (Isosorbide, isommanide and isoidide).[61,62-66]

Furanic polymers have been widely reported. The interest of them includes the improvement in thermal and mechanical properties. The molecular weights reported for FDCA-polyesters are in a range of 20 to 83 kg mol^{-1}. T_m and T_g are in a range of 140 to 230 ^{o}C and 40 to 90 ^{o}C lower than the analogs with PTA. Generally, these polyesters show low crystallinity and crystallizability.[65] The polymers based on FDCA have been traditionally reported as non-degradables, however, recent works report the enzymatic hydrolysis of PEF[151] using a modified cutinase, which is also used for the degradation of PET[152] and poly(1,20-eicosanediyl 2,5-furandicarboxylate).[58]

On the other hand, the copolymerization of FDCA polyesters have been extensively explored, expecting the improvement of important properties such as the crystallinity, the biodegradability and the T_g.

FDCA-copolyesters containing succinic, adipic and lactic units were fully biobased. Studies reported degradability in the copolymers with a high amount in aliphatic units such as lactates or succinic ones.[64,153,160] Properties, such as crystallinity and crystallizability are improved when aliphatic copolyesters are added. In table 2.3 is presented a summary of the main polyesters and copolyesters based on FDCA and their main properties.

Table 2.3. Molecular weight and thermal properties of polyesters based on 2,5-furandicarboxylic acid reported in the literature.

Polyester/ Copolyester	**M_w (kg mol^{-1})**	**T_g (°C)**	**T_m (°C)**	**T_d (°C)**	**Ref**
PEF	50-83	80-85	210-220	270-290	20, 154, 155
PPF	22-59	50-58	174-175	300-375	20, 22,154
PBF	50-65	31-40	168-173	304-373	20, 22,153, 154
PHF	13-32	7-28	141-148	350-375	18, 154
POF	21-34	-22	140-149	375	154
PNF	40	-30	69	-	156
PDF	37	-8	116	-	156
PRF	25	-65	-	350	67
PImF	27	189	-	380	20, 59
*co*PEF$_x$LA$_y$	7-9	-25-81	120	230-324	157,158
*co*PEF$_x$ES$_y$	26-41	-	21-173	300	153
*co*PBF$_x$BS$_y$	39-89	-31-31	71-159	339-349	64
*co*PBF$_x$CL$_y$	45	-40-42	65-172	391-401	152
*co*PBF$_x$BT$_y$	500	42-51	165-223	400	156

B: 1,4-butylene; C: Cyclohexamethylene; CL: ε-caprolactone D: Decamethylene E: Ethylene; F:2,5-furandicarboxylate; H: Hexamethylene; I: Isophthalate; Im: Isomannide; LA: Lactide N: Nonamethylene O: Octamethylene; P:2,3-propylene; R: Resorcinol S: Succinate; T: Terephthalate

II.8 References

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III. Materials and methods

III.1 Materials

2,5-Furan dicarboxylic acid (FDCA, >99% purity) samples used in this work was a donation of Drs. K. Wilsens and B. Noordover (Technische Universiteit, of Eindhoven, NL) and after it was obtained from Satachem (China). Other reagents as isophthalic acid (IPA, 99%), terephthaloyl chloride ($TPA\text{-}Cl_2$), 1,4-butanediol (BD, 99%), ethylene glycol (EG, 99%), thionyl chloride ($SOCl_2$, 99%), ε-caprolactone (CL, 99%), L-lactide (LA, 99%), titanium (IV) butoxide (TBT, 97%), Lipase *Porcine Pancreas*, as well as catalysts dibutyltin(IV) oxide (DBTO, 98%), di-azabicyclo[2.2.2] octane (DABCO, 99%) and tin(II) ethylhexanoate ($Sn(Oct)_2$, 99%), were purchased from Sigma-Aldrich Co. Resorcinol bis(2-hydroxyethyl)ether (HER) (99%) and Isommanide (Im, 98%) were obtained from TCI Chemicals. Triethylamine (Et_3N, 98%) and dimethyl succinate (DMS, 99%) were purchased from Panreac. Novozym 435 (lipase B *Candida Antarctica* CALB) was a gift of Novozymes. Antioxidants Irganox 1010 and Irgafos 126 used for polycondensation reactions were gifts from BASF. Solvents used for reaction, isolation and purification were of high-purity grade and used as received except dichloromethane (DCM), tetrahydrofurane (THF), diphenyl ether and dichlorobenzene (DCB) that were dried on 3Å-molecular sieves. DABCO catalyst was purified by sublimation.

III.2 Measurements

NMR Spectroscopy: ^1H 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. Compounds were dissolved in deuterated chloroform ($CDCl_3$) or a mixture of trifluoroacetic acid (TFA) and $CDCl_3$, and spectra were internally referenced to tetramethylsilane (TMS). About 10 and 50 mg of sample in 1 mL of solvent were used for ^1H and ^{13}C NMR, respectively. Sixty-four scans were recorded for ^1H and between 1,000 and 10,000 scans for ^{13}C NMR. Molecular weight analysis was 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 with a flow of 0.5 mL·min^{-1}. HR5E and HR2 Waters linear Styragel columns (7.8 mm x 300 mm, pore size 10^3–10^4 Å) packed with crosslinked polystyrene and protected with a precolumn were used. Molar mass average and distributions were calculated against PMMA standards. High-performance liquid chromatography (HPLC) analysis was performed at 25 °C in a Waters apparatus equipped with a UV detector of Applied Biosystems, operating at 254 nm wavelength, and a Scharlau Science column (Si60, 5μm; 250 x 4.6 mm).

HPLC: Cyclic oligomers (1 mg) were dissolved in $CHCl_3$ (1 mL) and eluted with hexane/1,4-dioxane 70/30 (v/v) at a flow rate of 1.0 mL·min^{-1}. Semipreparative HPLC was performed using a Scharlau Science column (Si60, 100 μm x 19 mm) with the cyclic oligomers sample (35 mg) dissolved in $CHCl_3$ (3 mL) and eluted with a mixture of hexane/1,4-dioxane 70/30 (v/v) with a flow rate of 17 mL·min^{-1}. Individual fractions were collected with an UV-monitored Waters Fraction Collector III.

MALDI-ToF spectroscopy: Matrix-assisted laser desorption/ionization time of flight (MALDI-ToF) mass spectra were recorded in a 4700 Proteomics Analyser instrument of Applied Biosystems (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 DCM solution of anthracene (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/H_2O (1/1) containing 0.1% TFA, and the mixture was left to dry prior to exposition to the laser beam.

TGA: Thermogravimetric analysis (TGA) of cyclic oligomers and 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 30-700 °C.

DSC: The non-destructive thermal behaviour was examined by differential scanning calorimetry (DSC) within the 30-200 ºC 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, respectively. The glass transition temperature (T_g) was taken as the inflection point of the heating traces recorded at 20 °C·min^{-1} from melt-quenched 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.

WAXS analysis: X-rays diffraction was made in the Synchrotron ALBA facility (Barcelona) using powder samples which were irradiated with a bean energy corresponding to 0.1 nm wavelength and also was recorded on a PANalytical X'Pert PRO MPD θ/θ diffractometer using the CuKα radiation of wavelength 0.1542 nm.

MOP: Micrographs were recorded using an Olimpus BX51 polarizing optical microscopy with a Linkam THMS 600 stage attached. For observation, 10 mg of sample were dissolved in 1 mL of 1,1,1,3,3-hexafluoro-2-propanol (HFIP) for PBF or chloroform for copolymers, and 0.2 mL aliquots of these solutions were slowly evaporated on a glass slide.

III.3 Synthesis of precursors

2,5-Furandicarbonyl dichloride (FDCA-Cl$_2$) and isophthaloyl chloride (IP-Cl$_2$) preparation: FDCA-Cl$_2$ and IP-Cl$_2$ were prepared according to the method reported by Gomes *et al.*[1] with minor modifications. In brief, 6.4 mmol of FDCA or IPA were made to react with 2 mL of $SOCl_2$ in the presence of 10 μL of dimethyl formamide

(DMF) for 8 hours under reflux. After removing the excess of $SOCl_2$ the residual product was purified by high vacuum sublimation.

FDCA-Cl_2: ^{1}H NMR (δ ppm, $CDCl_3$, 300 MHz): 7.60 (s, 2H). ^{13}C NMR (δ ppm, $CDCl_3$, 75.5 MHz): 155.9, 149.4, 123.3.

IPA-Cl_2:^{1}H NMR (δ ppm, $CDCl_3$, 300 MHz): 7.76 (s, 1H), 7.73 (s, 1H), 7.71 (s, 1H). ^{13}C NMR (δ ppm, $CDCl_3$, 75.5 MHz): 167.2, 136.9, 134.4, 133.8, 129.9.

Synthesis of 2,5-dimethyl 2,5-furandicarboxylate (FDCA-Me_2): Dimethyl 2,5-furandicarboxylate (FDCA-Me_2) was synthetized following the method reported by Gubbels *et al*.[2] based on the Fischer esterification of FDCA with MeOH. A round bottom flask was charged with 25.6 mmol (4 g) of FDCA, 1.38 mol (55.3 g) of MeOH, and 1mL of 12M HCl. The mixture left to react for 18 h under reflux and the reaction was then stopped by adding 0.5M methanol solution of KOH. The solution was then evaporated to dryness and the residue extracted with $CHCl_3$. The extract was then washed with water (200 mL), dried on $MgSO_4$ and evaporated to render a solid that was crystallized from $CHCl_3$ upon adding hexane and cooling.

^{1}H NMR (δ ppm, $CDCl_3$, 300 MHz): 3.94 (s, 6H), 7.23 (s, 2H). ^{13}C NMR (δ ppm, $CDCl_3$, 300 MHz): 52.4, 118.5, 146.9, 158.4.

III.4 Synthesis of cyclic oligomers

Synthesis of cyclic oligomers by pseudo-high dilution cyclization (HDC): Cyclic oligoesters of butylene 2,5 furandicarboxylate, *c*$(BF)_n$, ethylene 2,5-furandicarboxylate, *c*$(EF)_n$, resorcinol 2,5-furandicarboxylate, *c*$(RF)_n$, isomannide 2,5 furandicarboxylate, *c*$(ImF)_n$, butylene isophtalate, *c*$(BI)_n$ and butylene terephthalate, *c*$(BT)_{\mathbf{n}}$, were synthesized by applying the method of HDC[3] for the synthesis of oligo(alkylene phthalates). A three-necked round bottom flask was charged with 250 mL of DCM and cooled to 0°C, and then 12.5 mmol of DABCO were added under stirring. 5 mmol of FDCA-Cl_2 or TPA-Cl_2 in 10 mL of THF and 5 mmol of butanediol, BD, or ethylenglicol, EG, or 1,3-bis(2-hydroxyethoxy) benzene (HER), or isommanide (Im) 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, dried on $MgSO_4$, and evaporated to dryness to render a mixture of linear and cyclic oligomers. Linear oligomers were removed by chromatography through a short column of silica gel using a cold mixture of DCM/diethyl ether 90/10 (v/v) as eluent. For *c*$(BF)_n$ and *c*$(EF)_n$. The cyclic oligomeric mixture was fractionated into individual size species by preparative HPLC using a mixture of hexane/dioxane 60/40 (v/v).

***c*(BF)$_n$:** ^{1}H NMR (δ ppm, $CDCl_3$, 300 MHz): 7.23, 7.24, 7.25 (3s, 2H), 4.40 (m, 4H), 1.92, 1.99 (2m, 4H), ^{13}C NMR (δ ppm, $CDCl_3$, 75.5 MHz): 158.1, 157.9, 146.7, 146.5, 118.7, 118.6, 118.5, 65.0, 64.8, 25.4.

***c*(EF)$_n$:** ^{1}H NMR (δ ppm, $CDCl_3$, 300 MHz): 7.37, 7.23, 7.21 (3s,4H), 4.68, 4.67, 4.65 (3s, 4H). ^{13}C NMR (δ ppm, $CDCl_3$, 75.5 MHz): 157.6, 157.5, 146.5, 119.3, 119.1, 62.8.

***c*(RF)$_n$:** ^{1}H NMR (δ ppm, $CDCl_3$, 300 MHz): 7.26 (d, 1H), 7.23 (s, 2H), 7.14 (t, 1H), 6.65 (dd, 2H), 4.55 (m, 4H), 4.44(m, 4H). ^{13}C NMR (δ ppm, $CDCl_3$, 75.5 MHz): 161.6, 157.6, 145.9, 129.8, 118.3, 111.7, 107.2, 69.2, 64.9.

***c*(ImF)$_n$:** ^{1}H NMR (δ ppm, $CDCl_3$, 300 MHz): 7.28, 7.27 (2s, 2H), 5.43, 5.41, 5.39, 5.38 (m, 4H), 4.94, 4.93, 4.91, 4.89 (2m, 4H), 4.39, 4.37, 4.35, 4.33 (2m, 4H); 4.03, 4.01, 3.99, 3.97 (2m, 4H); ^{13}C NMR (δ 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, 29.7.

***c*(BT)$_n$:** ^{1}H NMR (δ ppm, $CDCl_3$, 300 MHz): 8.10, 8.07, 7.87 (3s, 4H, Ar-H), 4.42 (m, 4H), 2.05, 1.96 (2m, 4H). ^{13}C NMR (δ ppm, $CDCl_3$, 75.5 MHz): 165.7, 165.6, 165.5, 134.0, 133.9, 129.5, 129.4, 65.0, 64.8, 64.6, 25.9, 25.6, 25.5.

***c*(BI)$_n$:** ^{1}H NMR (*δ* ppm, $CDCl_3$, 300 MHz): 8.62, 8.60 (2m, 1H), 8.26, 8.21 (2m, 2H), 7.56, 7.50 (2m, 1H), 4.45 (m, 4H), 2.01, 1.97 (2m, 4H). ^{13}C NMR (*δ* ppm, $CDCl_3$, 75.5 MHz): 165.6, 165.5, 134.2, 133.8, 130.6, 130.5, 130.3 129.7, 128.8, 128.6, 64.8, 64.7, 64.6, 25.5, 25.4.

Synthesis of cyclic oligomers by cyclodepolymerization (CD). *c*(BF)$_n$ and *c*(EF)$_n$ were prepared by cyclodepolymerization of PBF and PEF polyesters. Previously the polyesters were synthesized by melt polycondensation. The procedure used was reported before by us for the preparation of cyclic oligo(hexamethylene terephthalate)s[4]. 0.8 g of PBF or PEF (previously dried overnight in a vacuum oven at 60 °C), 20 mL of dried DCB and 3% mol of DBTO were introduced into a 50 mL round-bottom flask fitted with a magnetic stirrer and a condenser. The mixture was stirred for 7 days under reflux and then it was cooled at room temperature, filtered, and the solvent evaporated under vacuum at 50 °C. In order to remove the linear oligomers the solid residue was chromatographed on a short column of silica gel using a mixture of DCM and diethyl ether 90/10 (v/v) as eluent.

***c*(BF)$_n$:** ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.23, 7.21, 7.20 (3s, 2H), 4.41 (m, 4H), 1.98, 1.92 (2m, 4H). ^{13}C NMR (δ ppm, $CDCl_3$, 75.5 MHz): 158.1, 158.0, 146.7, 146.5, 118.8, 118.6, 118.5, 65.0, 64.9, 64.8.

***c*(EF)$_n$:** ^{1}H NMR (δ ppm, $CDCl_3$, 300 MHz): 7.35, 7.23, 7.21, (3s, 2H), 4.68, 4.67, 4.65 (3s, 4H). ^{13}C NMR (δ ppm, $CDCl_3$, 75.5 MHz): 157.6, 157.5, 146.5, 119.3, 62.8.

Synthesis of cyclic oligomers by enzymatic cyclization (EC). Cyclic butylene succinate *c*(BS)$_n$ and ethylene succinate *c*(ES)$_n$ oligomers were obtained by enzymatic cyclization of BD and DMS following the procedure reported by Sugihara et al.[5] with slight modifications. Briefly, a three necked round bottom flask was charged with 250 mL of toluene, 4.97 mmol of DMS, 5.07 mmol of BD or EG and 1.184 g of CALB (100% w/w of the relative total monomers concentration) and the mixture left to react for 48 h at 96 °C under a nitrogen flow. 4 Å-molecular sieves were placed at the top of the flask to absorb the released methanol. Subsequently, the reaction mixture was then diluted with 50 mL of $CHCl_3$ and the enzyme was removed by filtration. The solvent was evaporated under reduced pressure to obtain the oligomer mixture which was analysed by NMR, and MALDI-TOF.

c**(BS)$_n$:** ^{1}H NMR (δ ppm, $CDCl_3$, 300 MHz): 4.14 (m, 4H), 2.64 (m, 4H), 1.72 (m, 4H). ^{13}C NMR (δ ppm, $CDCl_3$, 75.5 MHz): 171.90, 64.27, 29.37, 26.13.

c**(ES)$_n$:** ^{1}H NMR (δ ppm, $CDCl_3$, 300 MHz): 4.30 (m, 4H), 2.68 (m, 4H). ^{13}C NMR (δ ppm, $CDCl_3$, 75.5 MHz): 172.62, 172.05, 171.55, 62.48, 62.33, 62.15, 29.33, 28.96, 28.80.

III.5 Synthesis of polymers by polycondensation

Synthesis of PBF, PEF and *co*PBF$_{50}$T$_{50}$ by polycondensation in the melt: The synthesis of PBF and PEF homopolypolyesters and *co*PBF$_{50}$T$_{50}$ copolyesters were carried out by polycondensation in the melt following the usual two-steps method repeatedly described in literature.[6] In the first step (transesterification), 10.9 mmol (2.0 g) of FDCA-Me$_2$ or DMT was made to react with 23 mmol of BD or EG in the presence of 5 μL of Sn(Oct)$_2$ as catalyst and Irganox 1010 and Irgafos 126 (0.1% relative of the total amount of the monomer) as antioxidants at 180, 225 and 250 ºC for PBF, PEF and *co*PBF$_{50}$T$_{50}$, respectively, in a three necked flask provided with mechanical stirring and under a nitrogen atmosphere for 4 h. The transesterification process was followed by ^{1}H NMR spectroscopy and when the FDCA-Me$_2$ conversion exceeded 95%, the second step of polycondensation was initiated by increasing the temperature up to 220 and 250 ºC for PBF, PEF and *co*$PBF_{50}T_{50}$, respectively, and reducing the pressure to 0.5-1 mbar. The reaction was left to proceed under such conditions for 4 h. Analysis of the obtained polyesters were performed without previous treatment.

PBF: ^1H NMR (δ ppm, $CDCl_3$/TFA, 300 MHz): 7.34 (s,2H), 4.49 (bm, 4H), 1.97 (bm, 4H) .^{13}C NMR (δ ppm, $CDCl_3$/TFA, 75.5 MHz): 161.1, 147.1, 120.5, 67.2, 25.3.

PEF: ^1H NMR (δ ppm, $CDCl_3$/TFA, 300 MHz): 7.30 (s, 2H), 4.71 (s, 4H).^{13}C NMR (δ ppm, $CDCl_3$/TFA, 75.5 MHz): 159.3, 146.4, 120.2, 63.8.

***co*$PBF_{50}T_{50}$:** ^1H NMR (δ ppm, $CDCl_3$/TFA, 300 MHz): 8.12 (s, 2H), 7.35 (s, 2H), 4.50 (m, 4H), 2.0 (m, 4H), ^{13}C NMR (δ ppm, CDCl3/TFA, 75.5 MHz): 168.2, 158.1, 157.9, 146.7, 146.5, 134.0, 130.2, 120.7, 66.7, 66.6, 66.5, 66.4, 25.4, 25.2, 25.1, 25.0.

III.6 Synthesis of polyesters and copolyester by chemical ROP

Synthesis of PBF, PEF, PRF, PImF, PBI, PBT, PBS and PES by chemical ROP. 2.37 mmol of *c*$(BF)_n$ or *c*$(EF)_n$ or *c*$(RF)_n$ or *c*$(ImF)_n$ or *c*$(BI)_n$ or *c*$(BT)_n$ or *c*$(BS)_n$ or *c*$(ES)_n$ along with 0.5% mol of $Sn(Oct)_2$ were dissolved in 5 mL of DCM in a vial and dried under vacuum at room temperature for 24 h. Subsequently, the mixture was made to react for 2h into a three-necked round-bottom flask provided with mechanical stirring at 180 and 250 °C for homopolymers.

PBF: ^1H NMR (δ ppm, $CDCl_3$/TFA, 300 MHz): 7.30 (s, 2H), 4.46 (m, 4H), 1.93 (m, 4H). ^{13}C NMR (δ ppm, $CDCl_3$/TFA, 75.5 MHz): 160.3, 146.7, 120.0, 66.6, 25.0.

PEF: ^1H NMR (δ ppm, $CDCl_3$/TFA, 300 MHz): 7.29 (s, 2H), 4.70 (s, 4H).^{13}C NMR (δ ppm, $CDCl_3$/TFA, 75.5 MHz): 159.1, 146.3, 120.1, 63.7.

PRF: ^{1}H NMR (δ ppm, CDCl$_3$, 00 MHz): 7.26 (d, 1H), 7.23 (s, 2H), 7.14 (t, 1H), 6.55 (dd, 2H), 4.65 (m, 4H), 4.25 (m, 4H). ^{13}C NMR (δ ppm, CDCl$_3$, 75.5 MHz): 159.60, 157.77, 146.58, 130.08, 118.87, 107.43, 101.97, 69.25, 65.70, 63.8, 61.41.

PImF: ^{1}H NMR (δ ppm, CDCl$_3$, 300 MHz): 7.28, 7.27 (2s, 2H), 5.43, 5.41, 5.39, 5.38 (m, 4H), 4.94, 4.93, 4.91, 4.89 (2m, 4H), 4.39, 4.37, 4.35, 4.33 (2m, 4H); 4.03, 4.01, 3.99, 3.97; ^{13}C NMR (δ 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, 29.7.

PBT: ^{1}H NMR (δ ppm, CDCl$_3$/TFA, 300 MHz): 8.13 (s, 2H), 4.51 (m, 4H), 2.03 (2m, 4H). ^{13}C NMR (δ ppm, CDCl$_3$/TFA, 75.5 MHz): 168.2, 133.8, 130.1, 66.4, 25.3.

PBS: ^{1}H NMR (δ ppm, CDCl$_3$, 300 MHz): 4.12 (m, 4H), 2.63 (m, 4H), 1.71 (m, 4H). ^{13}C NMR (δ ppm, CDCl$_3$, 75.5 MHz): 172.19, 64.10, 28.97, 25.16.

PES: ^{1}H NMR (δ ppm, CDCl$_3$, 300 MHz): 4.29 (m, 4H), 2.66 (m, 4H). ^{13}C NMR (δ ppm, CDCl$_3$, 75.5 MHz):172.01, 61.37, 27.81

Synthesis of PBF from *c*(BF)$_2$, *c*(BF)$_3$ and *c*(BF)$_4$: For the synthesis of PBF from individual *c*(BF)$_m$ species the polymerization reactions were carried out in the DSC. 5 mg of *c*(BF)$_2$, *c*(BF)$_3$ or *c*(BF)$_4$ and 0.5 %-mol of Sn(Oct)$_2$ were dissolved in 1 mL of DCM in a vial and dried under vacuum at room temperature for 24 h. Aliquot amounts of the mixture were then placed in aluminium pans heated at 220 ºC for periods of times going from 5 min up to 2 h. At scheduled times the capsules were opened and the sample analysed by NMR ang GPC.

PBF: ^{1}H NMR (sample obtained from *c*(BF)$_2$) (δ ppm, CDCl$_3$/TFA, 300 MHz): 7.32 (s, 2H), 4.48 (m, 4H), 1.95 (m, 4H). ^{13}C NMR (δ ppm, CDCl$_3$/TFA, 75.5 MHz): 161.1, 147.1, 120.5, 67.2, 25.3.

III.7 Synthesis of polyesters and copolyester by ROP using CALB

Synthesis of PBS and PES by enzymatic ROP: Ring opening polymerization of the *c*(BS)$_n$ and *c*(ES)$_n$ mixtures was performed in the bulk with the concourse of CALB. Briefly, 47 mmol of the cyclic oligomers mixture were placed in a three-necked round bottom flask provided with a nitrogen flow and heated at five different temperatures under stirring. Then CALB (40% w/w) was added to the molten mass and the reaction left to proceed for 24 h. The reaction mixture was then cooled down to room temperature and a large volume of $CHCl_3$ was added to dissolve the polymer. After removing the enzyme by filtration, the solvent was evaporated under vacuum and the solid residue was dried for 24 h before analysis. Aliquots were withdrawn at scheduled times and analysed by GPC.

Enzymatically copolyesters catalysed by ROP in bulk: Ring opening polymerization of the *c*(BF)$_n$ and *c*(BS)$_n$ or ε-CL were performed in the bulk with the concourse of CALB. Briefly, 47 mmol of the cyclic oligomers mixture were placed in a three-necked round bottom flask provided with a nitrogen flow and heated at five different temperatures under stirring. Then CALB (40% w/w) was added to the molten mass and the reaction left to proceed for 24 h. The reaction mixture was then cooled down to room temperature and a large volume of $CHCl_3$ was added to dissolve the polymer. After removing the enzyme by filtration, the solvent was evaporated under vacuum and the solid residue was dried for 24 h before analysis. Additionally, *c*(ES)$_n$ and *c*(BS)$_n$/CL/LA in a ratio of 50:50 were placed in a three necked round bottom flask and the mixture was heated at 125 ºC. CALB (40% w/w) previously dried, was added and the mixture left to react for 24 h.

Enzymatically catalyzed ROP in solution. *co*PBF$_{50}$S$_{50}$ was also synthesised by ROP in solution assisted by CALB. Briefly, a mixture of 0.29 mmol (60.9 mg) of *c*(BF)$_n$ and 0.29 mmol (50 mg) of *c*(BS)$_n$ were dispersed in diphenyl ether (1 g) and the mixture placed in a three-necked round-bottom flask under stirring. When the mixture was solubilized, 40% w/w of CALB was added. The reaction was conducted at 50 °C for 24 h and aliquots were withdrawn at scheduled times to follow the reaction advance by GPC analysis. Finally the reaction mass was diluted by adding $CHCl_3$ and CALB was removed by filtration. The clean solution was concentrated and precipitated with hexane. The recovered copolyester was dried in vacuum for 2 days previous to be subjected to analysis.

Blank essays: Blank essays of PES, *co*$PBS_{50}RF_{50}$, *co*$PES_{50}RF_{50}$ were carried out for comparative purposes. For this, *c*$(ES)_n$ and a mixture of 0.24 mmol of *c*$(BF)_n$ or *c*$(RF)_n$ and 0.24 mmol of *c*$(BS)_n$; and *c*$(ES)_n$ without any catalyst added was made to react at 150-220 °C for 12-24 h. The evolution of the reaction was followed as above and the resulting products were analysed by NMR.

III.8. Transesterification of PCL_xBF_y copolyesters

Transesterification reactions in the copolyesters obtained by e-ROP were accomplished by subjecting them to heating in the presence of TBT. The selected copolyester and TBT (1 %-mole) were dissolved in $CHCl_3$ and the solution dried under vacuum to give a homogeneous residue that was heated at 200 °C for 24 h. After cooling, the treated product was dissolved in $CHCl_3$ and the solution filtered and evaporated to dryness. The residue was analyzed by ^{13}C NMR analysis to ascertain the degree of transesterification attained.

III.9 Hydrolytic degradation and biodegradation

Films for hydrolytic degradation and biodegradation studies were prepared from PBF, PRF, PImF, PBS, PES and selected copolyesters *co*PBFxBSy, *co*PRF_xBS_y, *co*PRF_xES_y, *co*PBF_xImF_y and *co*PBS_xImF_y with a thickness of ~200 μm by casting from either HFIP or chloroform solution at a polymer concentration of 100 $g\cdot L^{-1}$. 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 lipase *Porcine Pancreas* added. In this case the buffered solution was replaced every 72 h in order to maintain the enzyme activity. In both cases, the 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.

III.10 References

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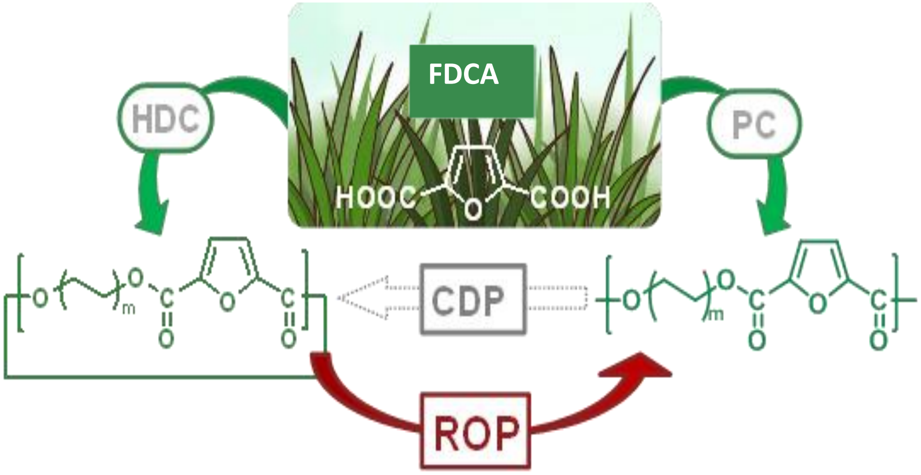
IV. Poly(alkylene 2,5-furandicarboxylate)s

Abstract: The preparation of cyclic ethylene and butylene 2,5-furandicarboxylate oligoesters and their conversion to furan-based polyesters poly(ethylene furanoate) (PEF) and poly(butylene furanoate (PBF) by ring-opening polymerization (ROP) are described. The cyclic oligoesters were obtained in high yields by both high dilution condensation and thermal cyclodepolymerization methods, and they consisted of mixtures of small size species. Cyclic dimer, trimer and tetramer oligoesters were isolated by semipreparative chromatography and found to be crystalline compounds melting within the 140-200 ºC range. ROP catalyzed by $Sn(Oct)_2$ of both mixtures and individual species afforded PEF and PBF with weight-average molecular weights between 50,000 and 60,000 g·mol^{-1}. Polymerization rate was found to be higher for butylene than for ethylene cyclic oligofuranoates, and also to increase slightly as cycle size decreased. The thermal properties of PEF and PBF prepared by ROP were in full agreement with those reported for these polyesters obtained by melt polycondensation.



Publication derived from this work:

J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra, Poly(alkylene 2,5-furandicarboxylate)s (PEF and PBF) by ring opening polymerization. *Polymer*, **2016,** 87,148-158.

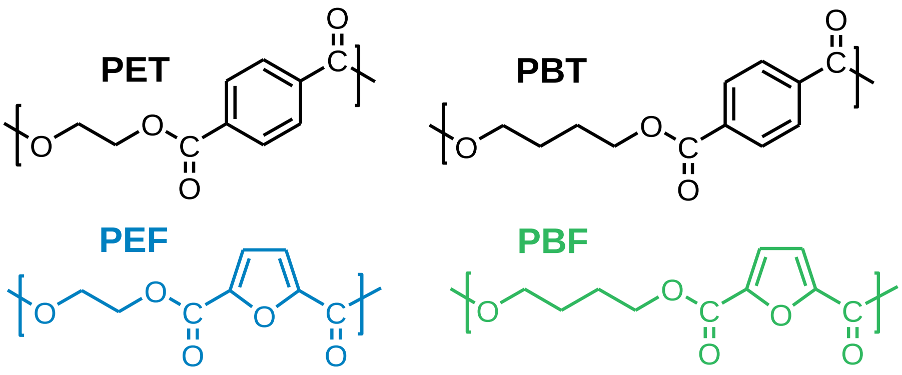
IV.1.1 Introduction

2,5-Furandicarboxylic acid (FDCA) is a sugar-based compound that has attained high notoriety in these last years due to its great potential as a renewable platform for the synthesis of a wide variety of chemicals,[1-3] and in particular of polymers produced by polycondensation.[4-5] The outstanding relevance of FDCA to the development of new bio-based polyesters has been updated in an excellent review published recently by Sousa *et al*.[6] The chemical structure, thermal stability and aromatic nature of FDCA are features that make this diacid specially suitable for replacing terephthalic acid in the preparation of the important engineering thermoplastics poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) (Scheme 4.1.1). In fact, most of efforts made up to date on the development of FDCA as monomer have been addressed to the synthesis of poly(ethylene 2,5-furandicarboxylate) (PEF) and poly(butylene 2,5-furandicarboxylate) (PBF) homopolyesters[7-9] and copolyesters,[10-14] and Avantium in Netherlands started in 2010 the industrial production of PEF on multi-ton scale for fibers and packaging. The aliphatic-furanic polyesters based on FDCA have been shown to have enhanced thermo-mechanical[11,15-17] and biodegradable[18-19] properties over existing terephthalate polyesters.

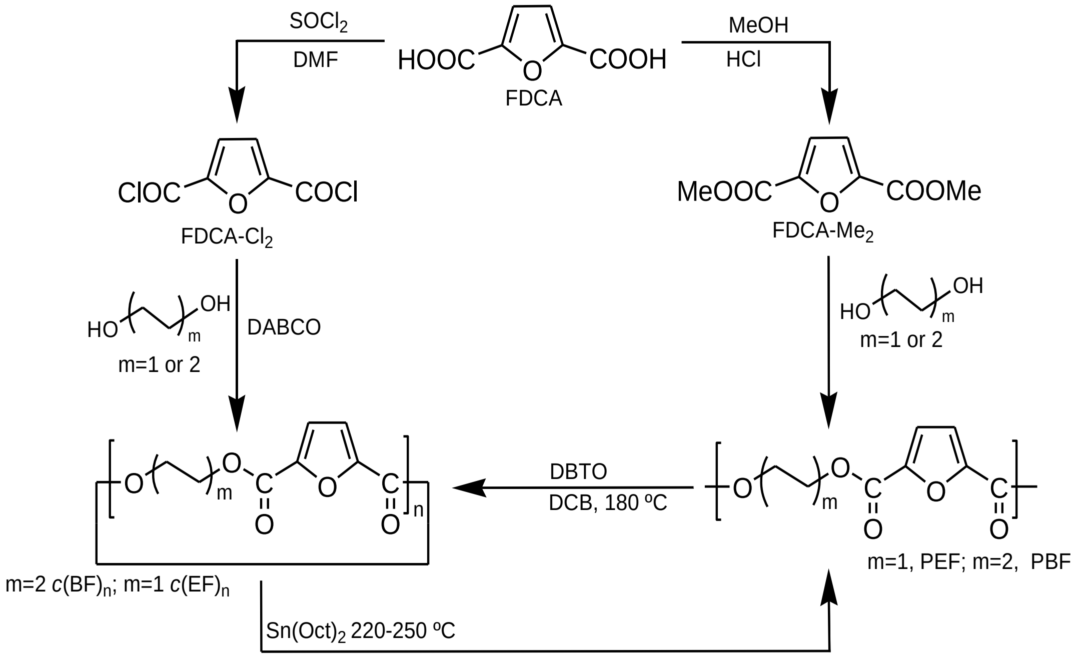
Both PEF and PBF are usually synthesized from either pristine FDCA[7-9] or its dimethyl ester,[15] by polycondensation in the melt through a two-steps process. Organometallic catalysts, temperatures well above the T_m of the resulting polyfuranoate, and periods of times of hours to days are required to attain high conversions. The main processing difficult arises from the high melt viscosity achieved by the reaction mixture that severely hampers mass transfer and makes therefore difficult to remove the volatile condensation products.[20] Post-polycondensation in the solid state is performed as a third-step in order to increase further the molecular weight.[14,15] The severe conditions applied in the polycondensation usually imply some discoloration and eventual generation of minor amounts of secondary products.

Ring opening polymerization (ROP) is a well-stablished technique that has been extensively used for the polymerization of a wide variety of cyclic compounds and in particular of cyclic oligoesters.[21] The relatively soft reaction conditions applied in this method makes feasible to synthesize high molecular weight polymers in good yields without perceivable chemical alteration of the product. Specific advantages of ROP are a high polymerization rate, the absence of reaction coproducts, and the low viscosity retained by the reaction until high conversions are attained. Consequently the formation of secondary by-products is almost insignificant, the remaining monomer can be easily removed, and discoloration is minimized. Both PET[22-24] and PBT[22,25,26] have been successfully synthesized by ROP of cyclic oligo(terephthalate)s applying temperatures between 200 ºC and 300 ºC and times of minutes. The oligoesters required for these syntheses were furnished either by condensation of terephthaloyl dichloride with diols in highly diluted solution (HDC, high dilution condensation) or by thermal depolymerization of the corresponding polyester (CD, cyclodepolymerization) methods. The CD method is particularly interesting with regards to the potential recycling of the polyester.[27]

In the present paper we wish to report on the preparation of high molecular weight PEF and PBF by ROP of the corresponding cyclic oligo(alkylene 2,5-furandicarboxylate)s. Both the HDC and CD methods have been here applied for the synthesis of these cyclic oligoesters, and the influence of cycle size on polymerization rate has been investigated. The characteristics of the resulting PEF and PBF are compared with those reported for the same polyesters obtained by polycondensation. A paper reporting the preparation of PBF by ROP come out just in these last days. In this work polymerization was accomplished using a mixture of cyclic butylene furanoates prepared by HDC to obtain a PBF with moderate molecular weight.[28]



Scheme 4.1.1. Aliphatic-aromatic polyesters from terephthalic acid and 2,5-furandicarboxylic acid.



Scheme 4.1.2. Synthesis of PEF and PBF by ROP of cyclic oligo(alkylene 2,5-furandicarboxylate)s prepared either by condensation in solution or by cyclodepolymerization.

IV.1.2 Results and discussion

Synthesis and characterization of cyclic oligo(alkylene 2,5-furandicarboxylate)s.

The synthesis of the cyclic oligo(alkylene 2,5-furandicarboxylate)s**,** abbreviated *c*(AF)$_n$ with A being ethylene or butylene, was carried out by two well-known cyclization methods, namely pseudo-high dilution (HDC) and cyclodepolymerization (CDP). Results obtained by both methods are compared in Table 4.1.1.

The HDC method was developed by Brunelle et al.[32] for the synthesis of a variety of macrocycles containing carbonate or carboxylate functions. The method consists of mixing carefully highly diluted solutions of the diacyl dichloride and the appropriate diol in the presence of catalytic amounts of DABCO and one equivalent of trimethylamine. The method was later extended to a wide variety of compounds and we have recently made use of it for the synthesis of cyclic oligo(hexamethylene terephthalate)s.[29] The application of this method to the preparation of *c*(AF)$_n$ required previously the preparation of the 2,5-furandicarbonyl dichloride (FDCA-Cl$_2$), which was successfully achieved by reaction of commercial 2,5-furandicarboxylic acid with SOCl$_2$.

The cyclization reaction was conducted in DCM at 0ºC and using reagents concentrations of around 5 mM. The crude reaction product was obtained in ~80% yield and by ^{1}H NMR it was shown to contain both cyclic and linear AF oligomers in an approximate ratio of ten to one (Figure A-1.5). The linear species could be efficiently removed by flash chromatography and the purified product, which was obtained in around 65% yield, consisted of a mixture of cyclic oligomers of varying small size whose ^{1}H NMR spectra did not present detectable signals arising from hydroxyl or carboxylic end groups (Figure 4.1.1).

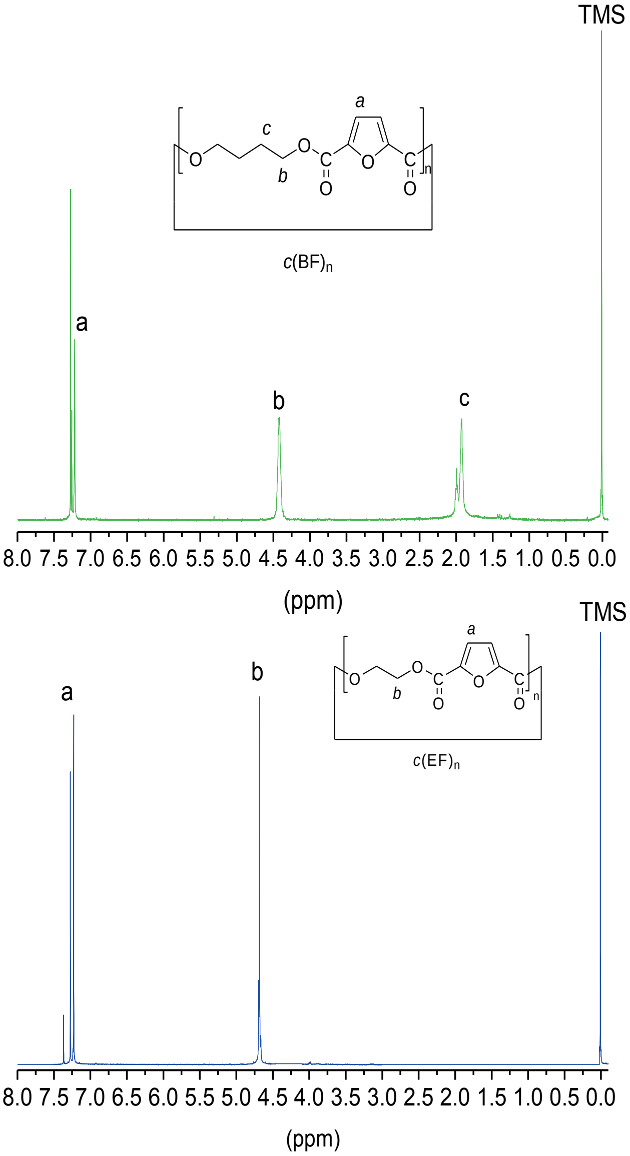


Figure 4.1.1. ^{1}H NMR spectra of cyclic oligomers *c*(BF)$_n$ (top) and *c*(EF)$_n$ (bottom) mixtures prepared by HDC with indication of peak assignments.

As it is shown in Figure 4.1.2, the analysis of the purified (AF)$_m$ mixtures by HPLC chromatography combined with MALDI-ToF spectrometry revealed that they mainly contained dimer, trimer and tetramer cycles together with minor amounts of pentamer and others cycles of larger sizes. Cyclic dimer and trimer together accounted for about 90% of the content of both *c*(BF)$_n$ and *c*(EF)$_n$ mixtures but the ratio of these two species in the two mixtures was almost reversed.

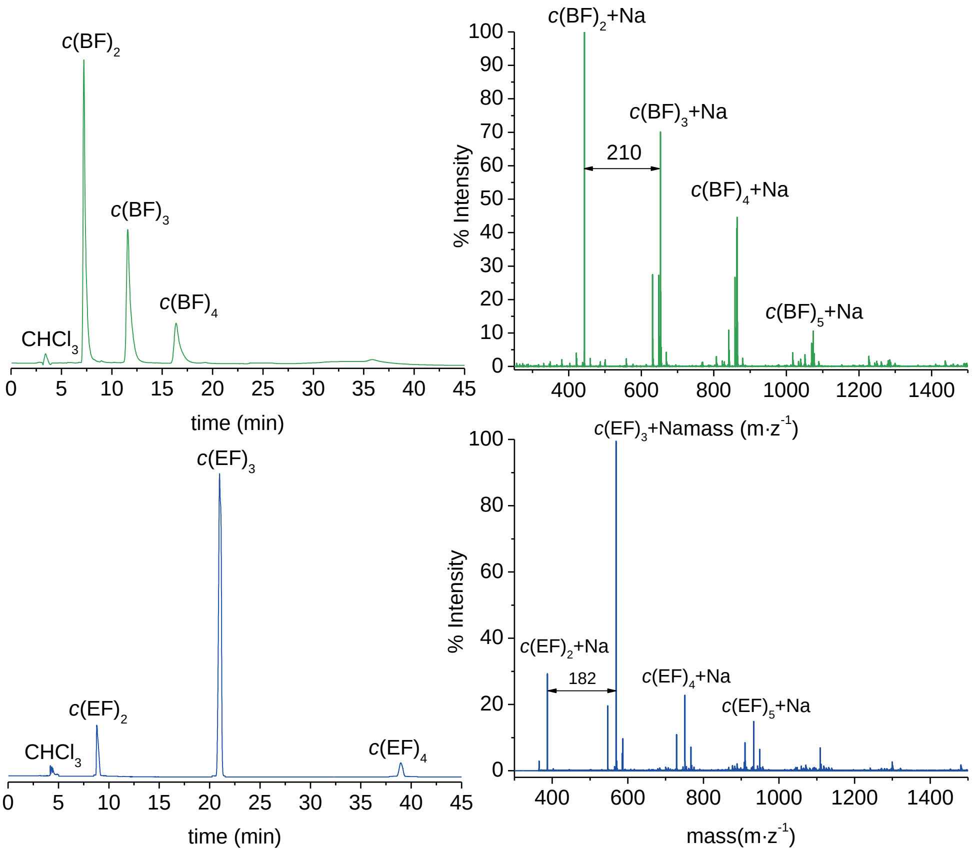


Figure 4.1.2. HPLC chromatograms (left) and MALDI-TOF (right) spectra of cyclic oligomers *c*(BF)$_n$ (top) and *c*(EF)$_n$ (bottom) mixtures obtained by HDC

Table 4.1.1. Cyclic (Alkylene 2,5-furandicarboxylate) Oligomers: Compared Synthesis Results.

Method[a]	*c*(AF)$_n$	Precursors	Yield (%)[b]		Composition (*n*:2/3/4)[c]	
			Crude	Flashed	Mixture	Fractionated
HDC	*c*(BF)$_n$	FDCA-Cl$_2$ + BD	80	67	62/30/8	50/22/9
	c(EF)$_n$	FDCA-Cl$_2$ + EG	78	64	20/74/6	n.d.
CD	*c*(BF)$_n$	PBF	74	60	41/49/10	33/35/9
	c(EF)$_n$	PEF	72	60	24/58/18	n.d.

[a] HDC: High Dilution Cyclization carried out in DCM at 0 ºC in the presence of DABCO/TEA; CD: Cyclodepolymerization reaction carried out in DCB at 180 ºC catalysed by DBTO.

[b] Yields for the crude oligomeric mixture and after removal of the linear species (flashed).

[c] Composition in *c*(BF)$_2$, *c*(BF)$_3$ and *c*(BF)$_4$ before and after fractionation. n.d: not determined.

The *c*(BF)$_n$ mixture was fractionated by semipreparative HPLC with a yield higher than 80% to render homogeneous fractions of *c*(BF)$_2$, *c*(BF)$_3$ and *c*(BF)$_4$ species whose cycle size and purity could be ascertained by MALDI-Tof analysis (Figure 4.1.3).

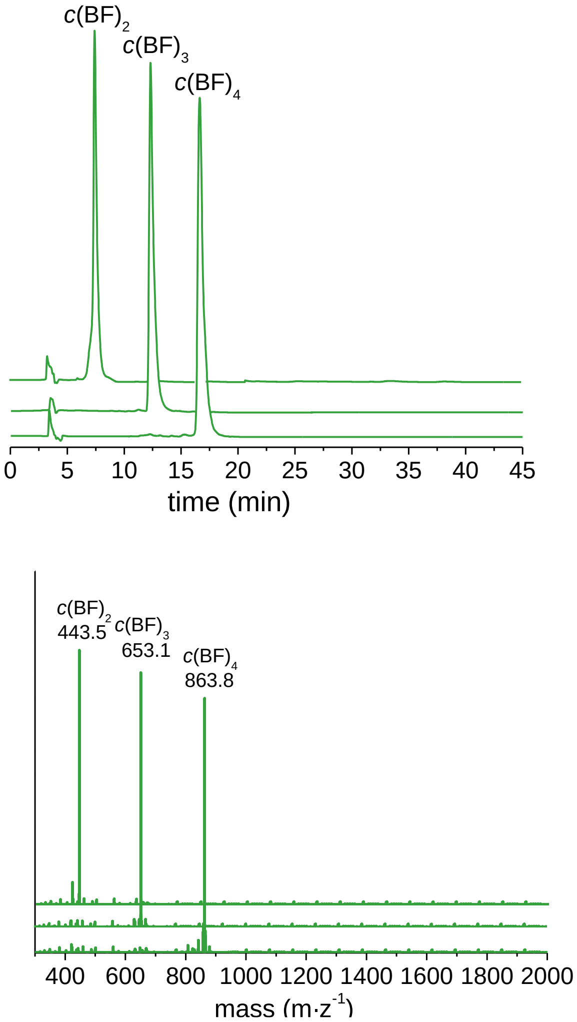


Figure 4.1.3. HPLC chromatograms (top) and MALDI-TOF spectra (bottom) of individual cyclic oligo(butylene 2,5-furandicarboxylate)s obtained by HDC.

The ^{1}H NMR spectra of these fractions showed specific signals according to cycle size so that a clear distinction between dimer and higher size cycles is feasible by comparing to each other. These spectra are shown in Figure A.1.6. The heating DSC traces of these fractions together with those registered for the *c*(BF)$_n$ and *c*(EF)$_n$ mixtures are compared in Figure 4.1.4a. Prominent endothermal peaks arising from melting and appearing at temperatures increasing with cycle size were recorded from the three homogeneous *c*(BF)$_n$ fractions. On the other hand, the DSC trace registered from the *c*(BF)$_n$ mixture displayed a broad peak centered at ~147 ºC and covering the range of temperatures observed for the three isolated fraction peaks. The DSC trace of the *c*(EF)$_n$ mixture displayed a peak of similar features to that of *c*(BF)$_n$ but displaced about 40 ºC higher, which is a result according to the T_m values of their respective derived polymers PBF (~170 ºC) and PEF (~210 ºC). The crystallinity present in both individual and mixed samples was corroborated by powder X-ray diffraction at wide angles which provided patterns containing peaks characteristic of crystalline material that disappeared upon heating at temperatures above melting. (Figure A.1.7). The thermal stability of the *c*(BF)$_n$ and *c*(EF)$_n$ mixtures was examined by TGA under inert atmosphere and the traces registered from the two mixtures are compared in Figure 4.1.4b. The two samples started to lose weight at temperatures near to 300 ºC with the weight fall happening at ~380 ºC and ~390 ºC for *c*(EF)$_n$ and *c*(BF)$_n$, respectively.

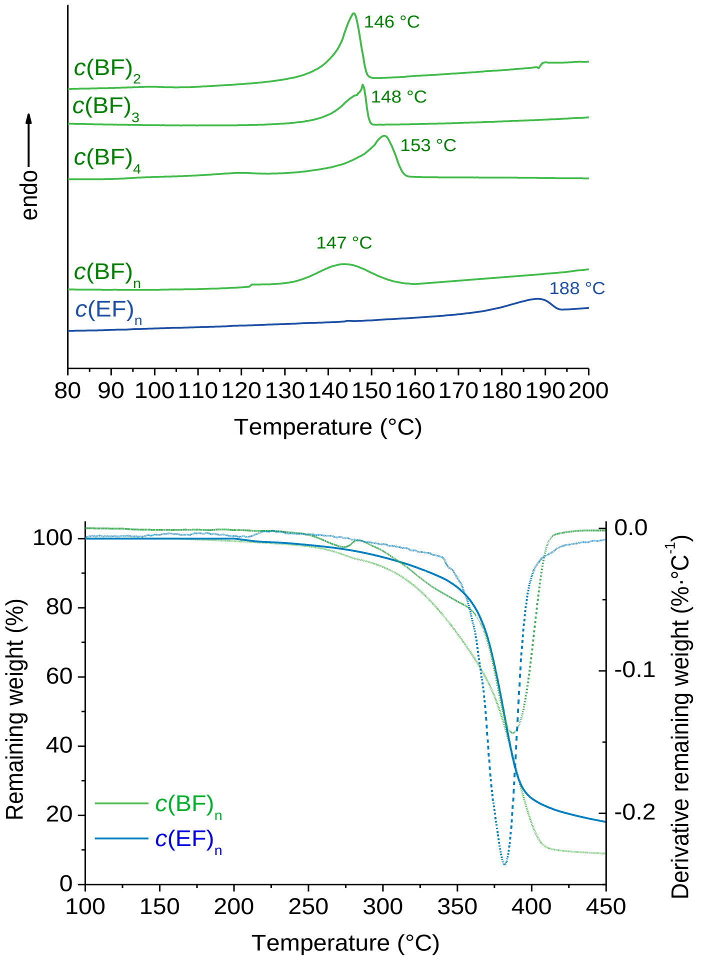


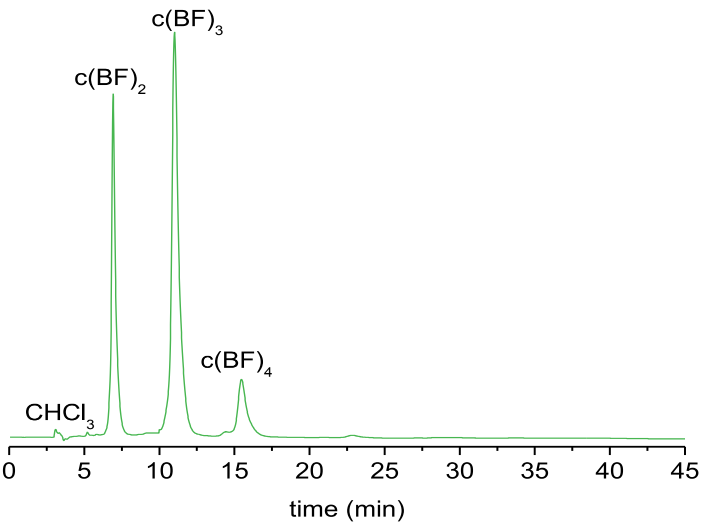
Figure 4.1.4. Top: DSC of individual cyclic oligo(butylene 2,5-furandicarboxylate)s and *c*(BF)$_n$ and *c*(EF)$_n$ mixtures. Bottom: TGA traces of *c*(BF)$_n$ and *c*(EF)$_n$ mixtures and their derivative curves.

The preparation of $c(AF)_n$ by CD was then explored given the relevance that this method has to the potential chemical recycling of PAF polyesters. In this case the previously synthesized PBF and PEF polyesters were dissolved in DCB and subjected to heating at 180 ºC in the presence of DBTO.

Results were no very far from those obtained by the HDC method so that cyclic oligomeric mixtures comprising essentially dimer, trimer and tetramer were obtained in approximate 60% yields for both $c(EF)_n$ and $c(BF)_n$ (Figure 4.1.5). However significant differences in cycle size composition were observed between the two methods with a more equilibrated proportion being obtained by the HDC method. Such differences are particularly noticeable for $c(BF)_n$ where the $c(BF)_2/c(BF)_3$ ratio changed approximately from 2 to 1 according to cyclization was induced either by condensation or depolymerization (Table 4.1.1).

Since CD took place at high temperatures and long times, it is probably that transesterification reactions involving interconversion of cycles of different sizes happened along with cycle formation.

On the contrary, the low temperatures and short times applied for HDC are unfavorable conditions for the occurrence of interconversion reactions so cycle sizes initially generated in the condensation reaction would be preserved. The different compositions observed for the $(AF)_m$ mixtures could therefore respond to which kind of driven factor, thermodynamic or kinetics, is operating in the process.



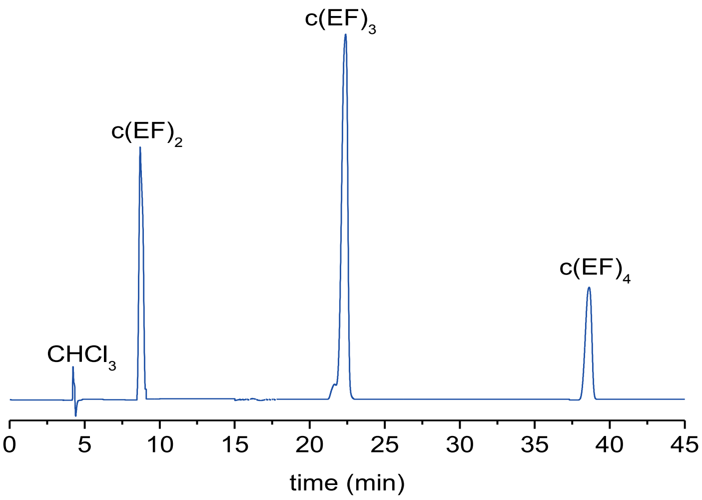


Figure 4.1.5. HPLC of *c*(BF)$_n$ (top) and *c*(EF)$_n$ (bottom) prepared by CD.

Synthesis poly(alkylene 2,5-furandicarboxylate)s by ROP. The synthesis of poly(butylene 2,5-furandicarboxylate) (PBF) and poly(ethylene 2,5-furandicarboxylate) (PEF) was accomplished by ROP of *c*(BF)$_n$ and *c*(EF)$_n$ mixtures respectively, by applying the usual melt procedure catalyzed by Sn(Oct)$_2$. As it is shown in Figure 4.1.6, the chemical constitution and purity of the resulting polyesters was ascertained by ^{1}H NMR. It is worthy to note that no signals arising from diethylene glycol units were detected in the PEF spectrum despite that etherification involving hydroxyl end groups is a undesirable secondary reaction difficult to avoid in melt polycondensation (compare with the ^{1}H NMR spectra recorded from PEF obtained by polycondensation which is shown in Figure A.1.4). In order to investigate the influence of cycle size on the ROP of *c*(AF)$_n$, the homogeneous fractions *c*(BF)$_2$, *c*(BF)$_3$ and *c*(BF)$_4$ were polymerized under identical conditions to that use for the *c*(BF)$_n$ mixture, and polymer growing was compared for the four systems. The study was also extended to the polymerization of the *c*(EF)$_n$ mixture in order to compare results for different alkylene units. Polymer growing was estimated by following the evolution of the molecular weight of the forming polyester with time by GPC analysis of the reaction mass. The changes observed in both weight- and number-average molecular weights along reaction time for polymerizations carried out at different temperatures are shown in Figure 4.1.7.

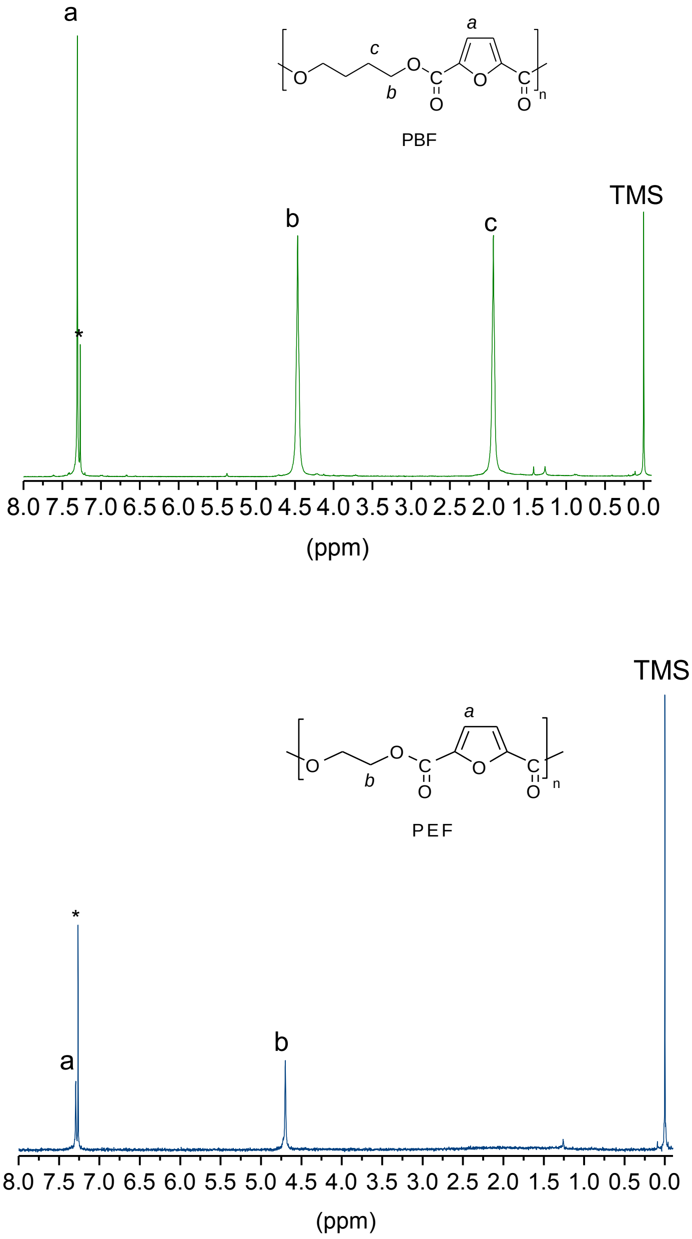


Figure 4.1.6. ^{1}H NMR spectra of PBF and PEF obtained *via* ROP.

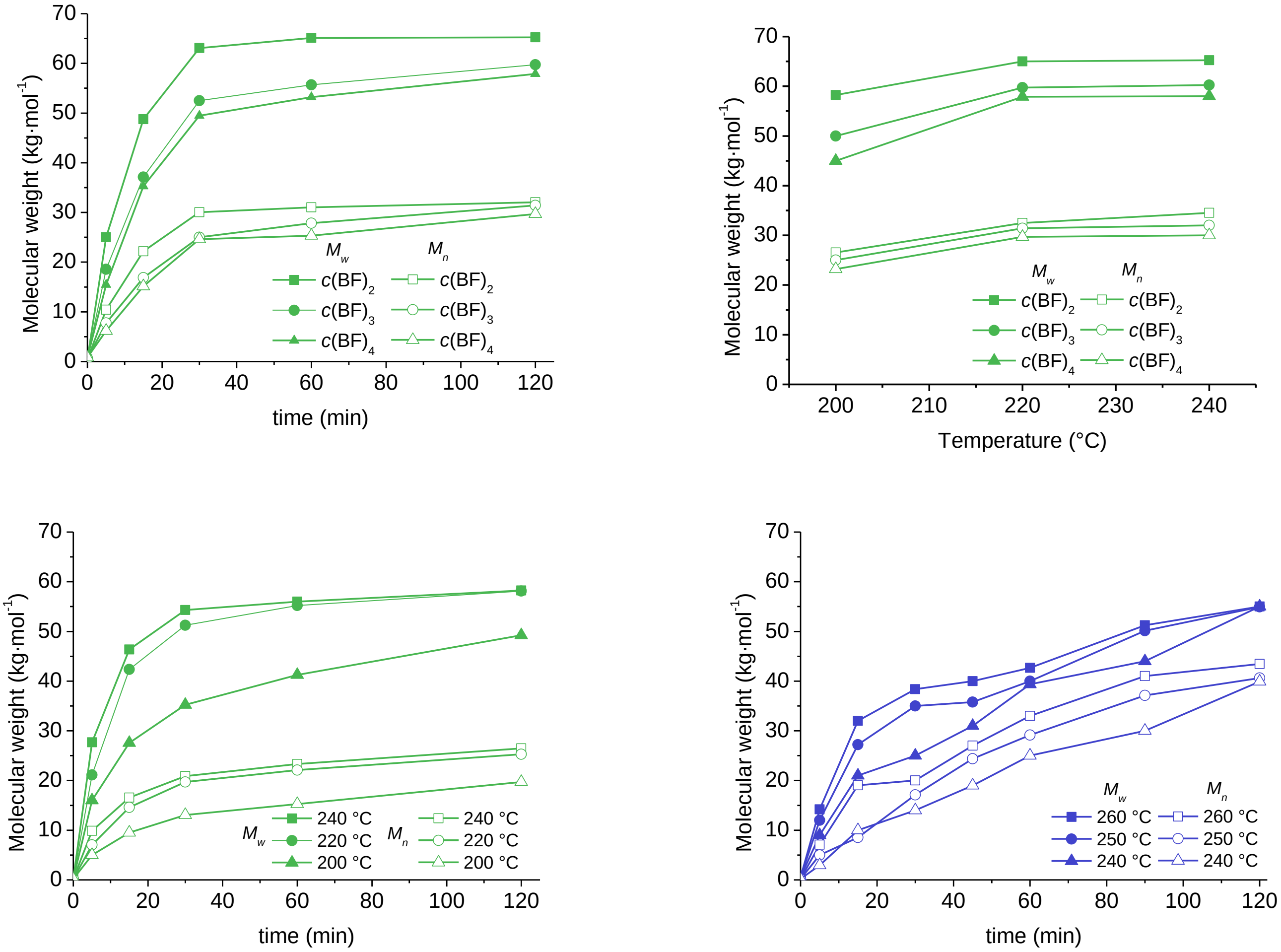


Figure 4.1.7. Evolution of molecular weight in the ROP of cyclic oligo(alkylene 2,5-furandicarboxylate)s as a function of temperature and time. Top: compared individual cyclic oligo(butylene 2,5-furandicarboxylate)s. Bottom: Compared *c*(BF)$_n$ and *c*(EF)$_n$ mixture for different temperatures.

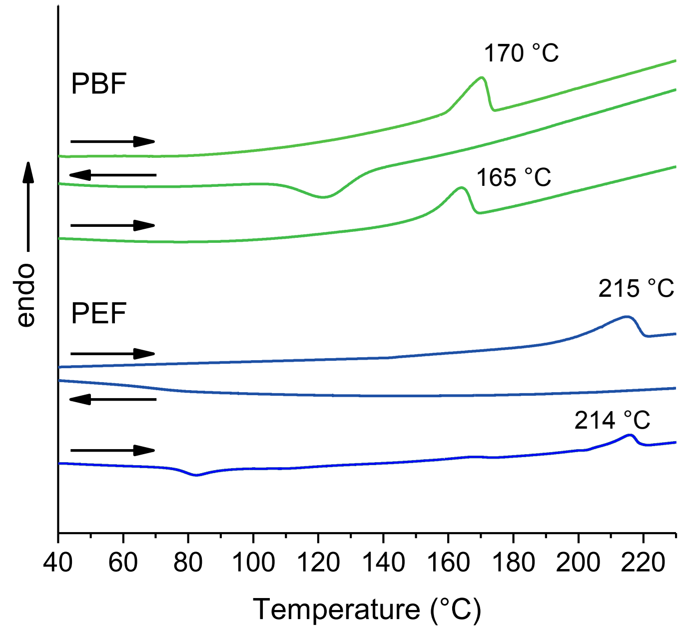
The inspection of these plots leads to conclude the following: a) *c*(BF)$_n$ cyclopolymerized initially faster than *c*(EF)$_n$ but after two hours of reaction similar molecular weights were reached in the two systems. In fact, an asymptotic profile was observed in the first case whereas a tendentiously linear trend was displayed by the second one. b) The molecular weight increasing rate was found to be higher for smaller cycle sizes although such differences are mild and tend to disappear at high conversions. c) The profiles obtained for the *c*(BF)$_n$ mixture were comparable to those of the individual fractions revealing that polymerization proceeded in this case at an approximate average rate. d) As expected, the polymerization rate increased with temperature with variations being larger for *c*(BF)$_n$ than for *c*(EF)$_n$; furthermore polymerization of $c(\mathrm{EF})_n$ required higher temperatures than $c(\mathrm{BF})_n$ to attain similar molecular weights at the end.

The thermal properties of the PBF and PEF polyfuranoates samples obtained after reaction for two hours at 240 ºC were then evaluated. The DSC and TGA traces registered from them are depicted in Figure 4.1.8 and their most characteristic parameters are collected in Table 4.1.2. Ranges of data reported by different authors for these polyesters prepared by melt polycondensation are also included for comparison. As it can be seen, the polyfuranoates obtained by ROP display molecular weights perfectly comparable to those obtained by polycondensation or even higher. The same can be said about the decomposition, glass transition and melting temperatures.

Table 4.1.2. Compared Properties of Poly(alkylene 2,5-furandicarboxylate)s Obtained by ROP and Melt Polycondensation.

Method	PAF	Monomer	M_w[a] (g·mol^{-1})	Đ[a]	T_o[b] (ºC)	T_g[c] (ºC)	T_m[c] (ºC)
ROP							
	PBF						
		$c(\mathrm{BF})_n$	58,000	2.3	430	41	168
		$c(\mathrm{BF})_2$	65,000	1.9	nd	40	171
		$c(\mathrm{BF})_3$	59,900	2.0	nd	42	169
		$c(\mathrm{BF})_4$	57,000	2.1	nd	41	168
	PEF						
		$c(\mathrm{EF})_n$	55,000	1.4	360	80	215
PC[d]							
	PBF						
		FDCA	65,000-34,000	2.8-2.2	310-400	30-39	168-175
	PEF						
		FDCA	47,000-10,000	2.4-1.3	300-390	80-90	200-215
		FDCA-Me_2	80,000[e]	n.d	n.d		239

[a] Weight-average molecular weight and dispersity measured by GPC.
[b] Onset degradation temperature corresponding to 10% of mass loss measured by TGA.
[c] Glass transition and melting temperatures measured by DSC.
[d] PBF and PEF obtained by polycondensation in the melt from FDCA or FDCA-Me_2 and BD or EG; data expressed as ranges of values reported in references 7-15.
[e] After SSP (solid-state postpolycondensation)



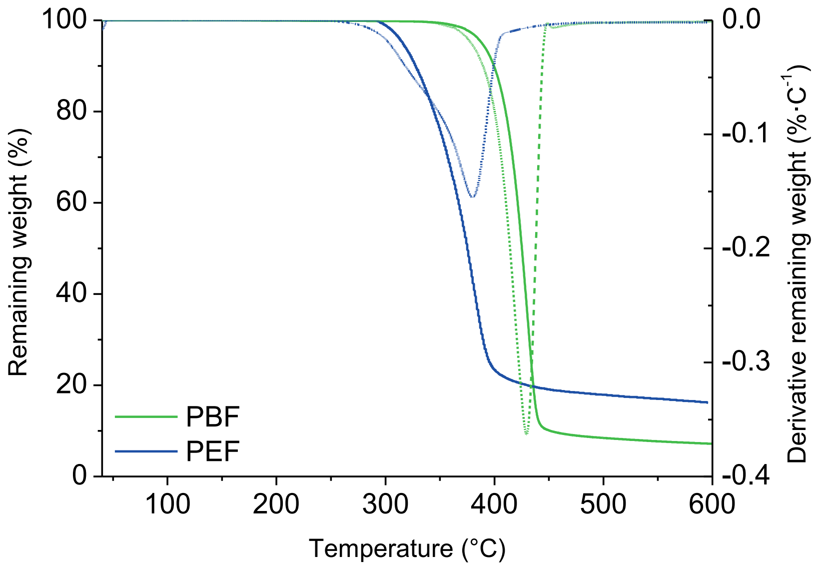


Figure 4.1.8. Top: First heating, cooling and second heating DSC traces of PBF and PEF. Bottom: TGA traces registered under inert atmosphere of PBF and PEF.

A brief comment on the paper recently published on PBF[28] obtained by ROP should be made. In such work, PBF was synthesized from a mixture of cyclic (butylene 2,5-furandicarboxylate)s enriched in trimers and tetramers and with an average cycle size significant larger than that of the mixtures used in the present work. The polymerization was there conducted in a DSC pan with the oligomeric sample mixed with tetrakis(2-ethylhexyl) titanate catalyst and heating at 270 ºC for 15 min. The PBF thus obtained showed a number-average molecular weight about 6,000 g·mol^{-1} and values of T_g and T_m of 35 ºC and 169 ºC, respectively. In the light of our results (Figure 4.1.8) may be reasonably inferred that the relative low molecular weight obtained for PBF in that work is very likely due to the short polymerization time applied and also to the relative larger cycle sizes used for feeding. The low transition temperatures that are observed for the synthesized sample is nothing more than a consequence of its low molecular weight; the strong dependence of thermal parameters on molecular weight in PAF's is a well-known fact.

IV.1.3 Conclusions

In the present work, PBF and PEF were successfully synthesized by ring opening polymerization catalyzed by $Sn(Oct)_2$. The cyclic oligoesters used for feeding could be prepared in high yields by both high-dilution and thermal cyclodepolymerization methods as mixtures containing substantially from dimer to tetramer species. The cyclic oligo(butylene 2,5-furandicarboxylate) mixture could be fractionated by semi-preparative HPLC to provide homogeneous dimer, trimer and tetramer fractions. Polymerization of mixtures and individual fractions under the same conditions revealed that polymerization rate was favored by smaller cycle sizes. The oligo(ethylene 2,5-furandicarboxylate) cycles were more reluctant to polymerize than the butylene ones and required higher temperature to reach similar conversions. In all cases, polyfuranoates of high molecular weight, exempted of detectable chain defects, and displaying thermal parameters in perfect agreement with those reported in the literature were obtained in good yields. The results reported in this papers demonstrate the potential of the ring opening polymerization method as a suitable option for the preparation of poly(alkylene furanoate)s.

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V. Poly(butylene phthalates) containing furanoate units

V.1 Poly(butylene terephthalate) copolyesters

Abstract: A series of poly(butylene 2,5-furandicarboxylate-*co*-terephthalate) copolyesters P(BF-*co*-BT) covering the whole range of compositions has been prepared *via* ring opening polymerization (ROP). Cyclic oligomers of butylene 2,5-furandicarboxylate *c*(BF)$_n$ and butylene terephthalate *c*(BT)$_n$, both mainly consisting of a mixture of dimer, trimer and tetramer species, were synthesized by the high dilution condensation method. Random copolyesters with the targeted compositions and weight-average molecular weights within the 55,000-80,000 g·mol^{-1} range were obtained by ROP of *c*(BF)$_n$/*c*(BT)$_n$ mixtures in periods of time much shorter than those required by melt polycondensation. The thermal properties of these copolyesters were consistent with their compositions and comparable to their isocompositional analogs obtained by polycondensation. A comparative kinetics study of the isothermal crystallization of the homopolyesters and copolyesters differing in composition revealed that the presence of the 2,5-furandicarboxylate units decreased the crystallization rate of PBT. Nevertheless, P(BF-*co*-BT) copolyesters with moderate contents in BF units were still able to crystallized rapidly from the melt.

Publication derived from this work:

J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra. Sustainable aromatic copolyesters via ring opening polymerization: poly(butylene 2,5-furandicarboxylate-*co*-terephthalate) *ACS Sustainable Chem. Eng.* **2016**, 4, 4965-4973. (**ACS Editor's Choice: September 2016**).

V.1.1 Introduction

The attention given to sustainability in polymer science is continuously growing, and the use of renewable resources in industrial polymer synthesis is rapidly increasing in parallel[1-3]. This is mainly due to the fact that society is becoming more and more concerned with environmental problems associated to fossil fuel CO_2 emissions. Also the announced scarcity of petroleum in a not very far future, and the difficulty for controlling the market prices of its derivatives, are additional factors contributing to the increasing interest for sustainable polymers. As a consequence chemicals coming from naturally-occurring compounds of very different nature are incessantly proposed to substitute petrochemicals in the production of industrial polymers [4-6].

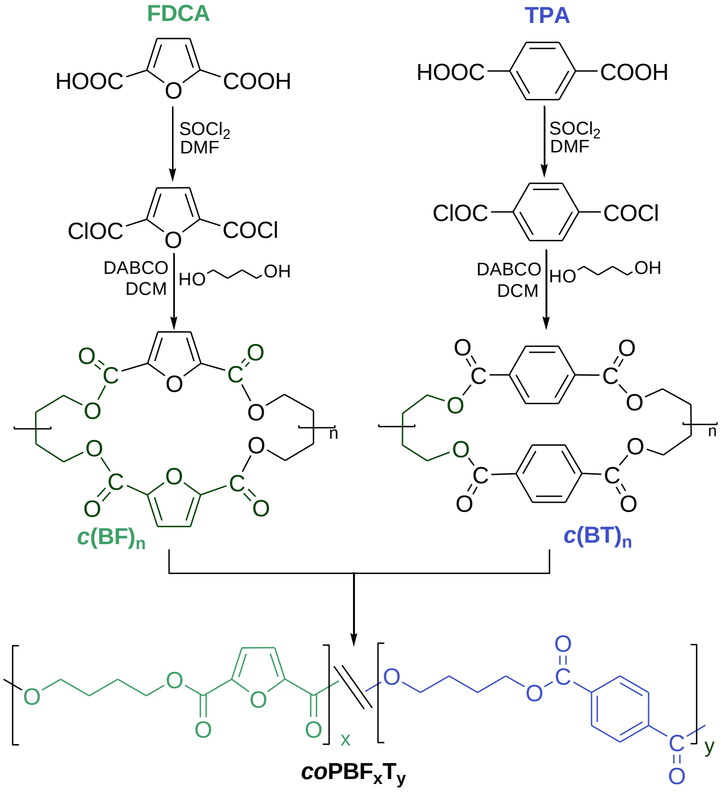
Among the different renewable feedstocks that can be used for building suitable monomers, carbohydrates are distinguished by their easy availability and tremendous structure diversity. The potential of sugar resources in the manufacture of sustainable polymers, and in particular of polycondensation polymers, has been recently reviewed by Galbis et al.[7]. A wide variety of difunctionalized sugar derivatives has been explored in these last years for the synthesis of polycondensates that includes polyesters, polyamides, polyurethanes and polycarbonates among others.[8-11] In this context, aromatic polyesters deserve specific attention. Poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are commercial well known thermoplastics that are produced in huge amounts from terephthalic acid (TPA), a compound of petrochemical origin for which several green alternative syntheses are currently under consideration.[12,13] Nevertheless, partial or even full substitution of TPA by other diacids derived from carbohydrates has been also an extensively investigated approach. Among them, 2,5-furandicarboxylic acid (FDCA) has attained a privileged position due to its aromatic character and easy accessibility. The enormous potential of this compound in the production of aromatic polyesters able to replace PET and PBT, has been rigorously reviewed by Sousa et al.[14] To date a wide variety of poly(alkylene furanoate)s, both homopolyesters and copolyesters, have been reported, although polycondensation in the melt catalyzed by organometallics has been almost invariably the method used for their synthesis.[15-19]

Ring opening polymerization (ROP) of lactones is an interesting technique for the synthesis of polyesters that is currently used for the production of several industrial aliphatic polyesters, *i.e*. polyglycolic and polylactic acids[20], and that has been demonstrated to be also suitable for the synthesis of aromatic polyesters and copolyesters.[21-23] This method offers as distinguishing advantages the possibility of using milder polymerization conditions and no generation of side-products in the polymerization reaction. Moreover the method would attain particular interest regarding chemical recycling in the case that the feed lactones were accessible by thermal depolymerization of polyester wastes. The synthesis of both poly(ethylene 2,5-furandicaboxylate) (PEF)[24] and poly(butylene 2,5-furandicarboxylate) (PBF)[24,25] by ROP of their respective cyclic oligomers has been recently reported. The polyfuranoates thus obtained were perfectly comparable in molecular weights and thermal properties to those prepared by melt polycondensation but they were exempted of the chain defects commonly present in polycondensates.

In this paper we wish to report on the synthesis of poly(butylene 2,5-furandicarboxylate-*co*-terephthalate) copolyesters, abbreviated *co*PBF$_x$T$_y$, by ROP of mixtures of cyclic oligo(butylene 2,5-furandicarboxylate)s and oligo(butylene terephthalate)s, initiated by Sn(Oct)$_2$. A series of *co*PBF$_x$T$_y$ covering the whole range of BF to BT ratios has been prepared and synthesis results are compared to those obtained by melt polycondensation. Zhou et al. published in 2015[26] an extensive and systematic study of several series of aromatic copolyesters derived from FDCA and TPA and different linear alkanediols including 1,4-butanediol. The method of synthesis used therein was polycondensation in the melt with tetrabutyl titanate as catalyst. Data provided by these authors on the PBF/PBT copolyesters have been taken in this work as reference for evaluating the suitability of the ROP method for producing furan-based aromatic copolyesters.

V.1.2 Results and discussion

Synthesis. The route of synthesis followed in this work to produce the copolyesters *co*PBF$_x$T$_y$ is depicted in Scheme 5.1.2. Firstly the cyclic oligoesters *c*(BF)$_n$ and *c*(BT)$_n$ were prepared by cyclization of the mixture of 1,4-butanediol and the respective diacid dichloride following the high dilution method reported by Brunelle et al.[27] The composition of the cyclic fractions were determined by HPLC-MALDI-Tof combined analysis and showed to be a mixture of dimer, trimer and tetramer in both cases (see Figure B.1.3 in the annex). For polymerization, mixtures of the two cyclic fractions at molar ratios covering the whole range of proportions of furanoate to terephthalate units in the copolyester, in addition to the both isolated fractions leading to the parent PBF and PBT homopolyesters, were made to react at 200-250 ºC in the presence of small amounts of Sn(Oct)$_2$.



Scheme 5.1.1. Synthetic route *via* ROP towards aromatic copolyesters containing butylene 2,5-furandicarboxylate and butylene terephthalate units.

The constitution and composition of the ensuing copolyesters were ascertained by ^{1}H and ^{13}C NMR spectroscopy, which differentiated clearly the aromatic proton and carbon signals arising from the 2,5-furandicarboxylate and terephthalate units and did not display detectable signals arising from other structures than those expected for the constitution of the copolyester. For illustrative purposes, the spectra recorded from *co*PBF$_{50}$T$_{50}$ are reproduced in Figure 5.1.1, and the spectra of the remaining whole series are accessible in the annex (Figure B.1.4). The results attained in the synthesis of *co*PBF$_{x}$T$_{y}$ copolyesters are collected in Table 5.1.1. Yields were over 90% in all cases and the compositions of the copolyesters were practically the same as those of the cyclic oligomers mixtures used for feeding with deviations rarely overpassing 5%.

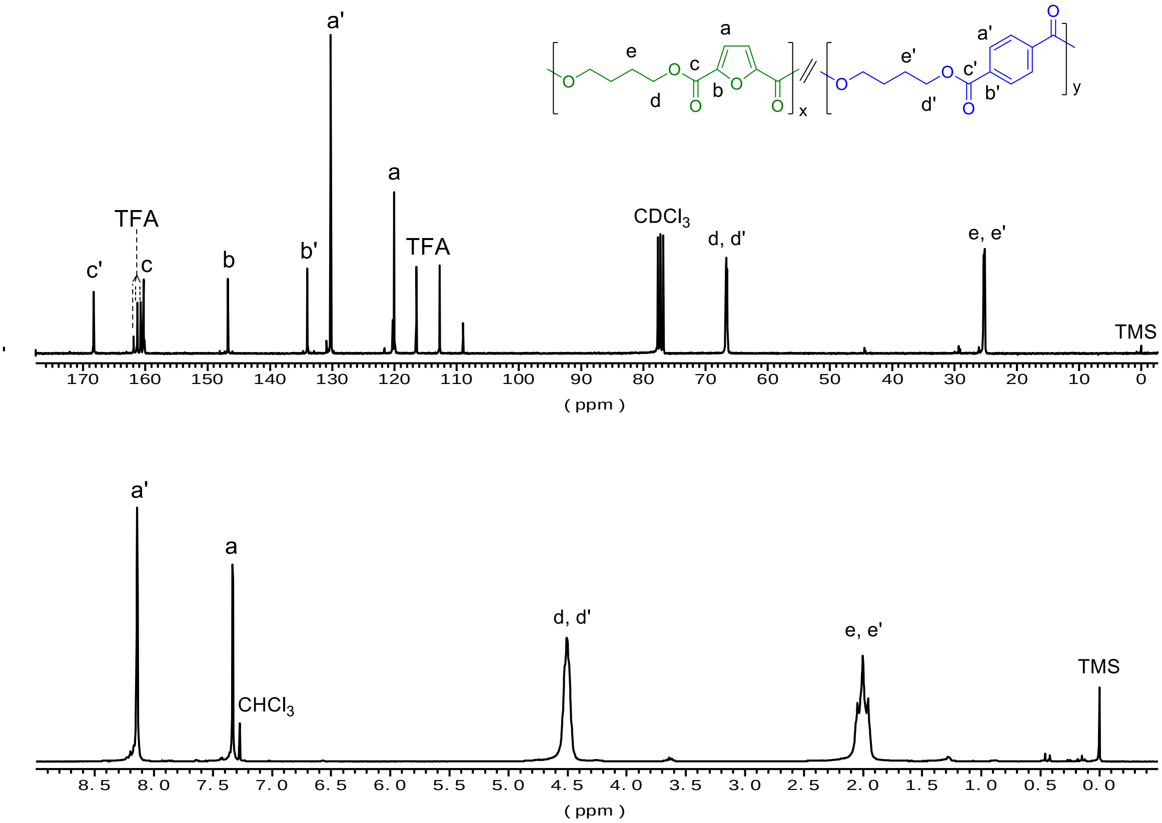


Figure 5.1.1. ^{13}C- (top) and ^{1}H-NMR (bottom) spectra of *co*(PBF$_{50}$T$_{50}$).

Table 5.1.1. Synthesis results for *co*PBF$_x$T$_y$ copolymers obtained *via* ROP.

Copolyester	Yield (%)	x_{BF}/y_{BT}[a] (mol/mol)	Molecular Weight[b]		Dyad content (mol %)[c]			Sequence length[d]		*R* [d]
			M_w	Đ	FBF	FBT+TBF	TBT	n_{BF}	n_{BT}	
PBF	90	100/0	60,000	1.65	-	-	-	-	-	-
*co*PBF$_{90}$T$_{10}$	92	88/12	58,000	1.90	74.1	25.8	1.2	6.90	1.09	1.05
*co*PBF$_{80}$T$_{20}$	91	77/23	55,000	1.54	57.3	37.3	5.4	4.06	1.29	1.02
*co*PBF$_{60}$T$_{40}$	93	59/42	65,000	1.40	34.9	47.3	17.8	2.47	1.75	0.97
*co*PBF$_{50}$T$_{50}$	93	52/48	70,000	1.75	30.1	36.6	34.0	1.98	2.05	1.00
*co*PBF$_{40}$T$_{60}$	92	41/59	69,000	1.80	24.3	49.7	2.0	1.65	2.44	1.02
*co*PBF$_{20}$T$_{80}$	94	21/79	71,000	1.30	16.5	47.9	35.5	1.31	5.36	0.95
*co*PBF$_{10}$T$_{90}$	94	11/89	75,000	1.43	5.5	29.8	64.7	1.17	11.1	0.95
PBT	95	0/100	79,000	1.67	-	-	-	-	-	-

[a] Measured by ^{1}H NMR.
[b] Weight-average molecular weight in g·mol^{-1} determined by GPC.
[c] Determined by deconvolution of the ^{13}C NMR peaks appearing in the 67.0 - 66.5 ppm region.
[d] Number average sequence lengths and degree of randomness (*R*) calculated according to reported in literature [30].

The advance of the reaction in the polymerization of the equimolar mixture of *c*(BF)$_n$ and *c*(BT)$_n$ was followed by GPC, and the plots showing the evolution of molecular weight with time at two different reaction temperatures, *i.e*. 230 and 250 ºC are depicted in Figure 5.1.2.

These plots reveal that no significant differences are appreciated in the reaction rate for the two chosen temperatures and that polymer growing ceased after one hour of reaction. A clearly different profile was generated when the same study was carried out for the polycondensation reaction of BD with an equimolar mixture of the dimethyl esters of FDCA and TPA.

In this case polymerization seems to slow down also after one hour, but the molecular weight of the ensuing copolyester was now much lower with a value of M_W around 40,000 g·mol^{-1} against the near 70,000 g·mol^{-1} attained by ROP.

It is worthy to remark that these results prove not only the suitability of ROP for producing high molecular weight copolyesters containing furanoate units but also that they may be obtained by this method in shorter times than by polycondensation.

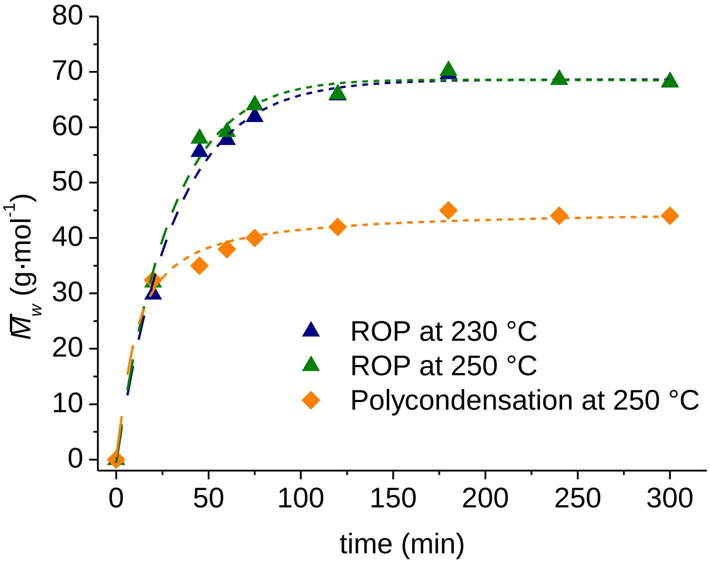


Figure 5.1.2. Evolution in M_w of *co*PBF$_{50}$T$_{50}$ produced by ROP and by melt polycondensation.

The microstructure of the copolymers was examined by ^{13}C NMR. As it is shown in Figure 5.1.3, the ^{13}C resonance signal appearing within the 65.5-67.5 ppm range and arising from the α-carbon of the butylene segment was sensitive to sequence effects at the level of dyads.

Four peaks are therefore present in the spectra of the copolyesters which correspond to the four feasible dyad arrangements of the furanoate and terephthalate units (FBF, FBT, TBF, TBT) along the polymer chain. Integration of these peaks and application of equations reported for sequence determination,[30] which takes into account the copolyester composition, led to determine the number-average sequence lengths (*n*) and the degree of randomness (*R*) of *co*PBF$_x$T$_y$.

Results are given in Table 5.1.1 and indicate that the arrangement of the two aromatic units in the copolyesters is near to random whichever is their composition.

The homogeneous distribution of the BF and BT units attained in the copolyesters could be taken as indicative of the similar relative reactivity displayed by the two comonomeric cyclic species when they are made to react via ROP. This interpretation is however questionable since the occurrence of transesterification reactions, which would lead to homogenization of the initially blocky copolyester, is very likely occurring at the temperatures applied for polymerization.

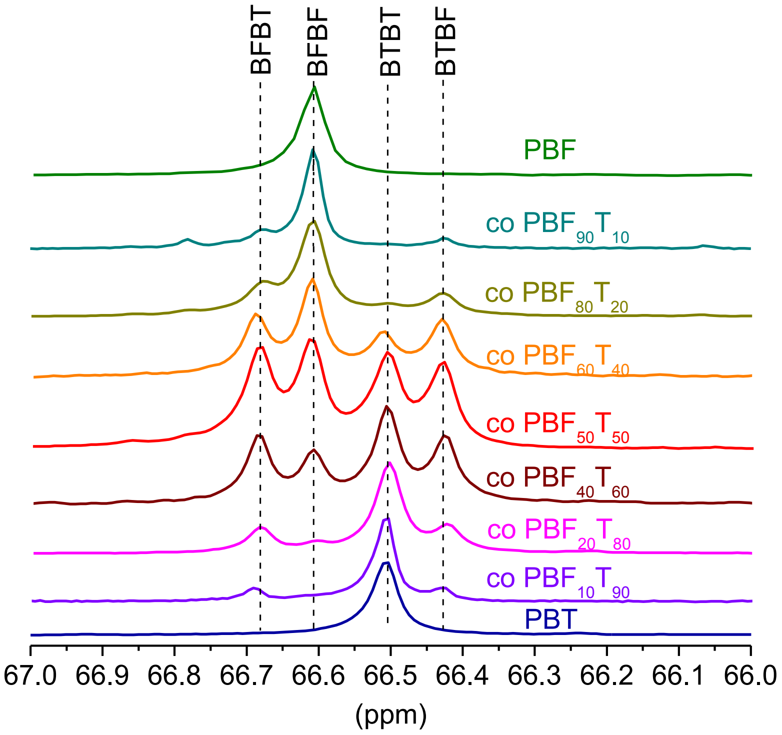


Figure 5.1.3. Enlarged ^{13}C NMR spectra (65.5 - 67.5 ppm region) of *co*PBF$_x$T$_y$ obtained by ROP.

Thermal properties. The data afforded by TGA and DSC analyses of *co*PBF$_x$T$_y$ are collected in Table 5.1.2. These data revealed that the basis thermal behavior of these copolyesters obtained by ROP is similar to that displayed by those prepared by polycondensation in the melt. The reference we have used for comparison is the paper recently published by Zhou et al.[26], which is the only one describing these copolyesters that may be found by now in the accessible literature. However it must be noted that molecular weights up to 500,000 g·mol^{-1} for furan containing polyesters were obtained by these authors, which are indeed astonishing values without precedent in the available literature of polyesters made by polycondensation.

Both the onset ($^{o}T_d$) and maximum degradation rate ($^{max}T_d$) temperatures of PBT decreased with the incorporation of BF units but the decay is not so large as to impair the furanoate-terephthalate copolyesters for thermal processing. In fact, onset temperatures measured for 5% of mass loss were above 330 ºC and massive decompositions started around 400 ºC and proceeded along one main decomposition step. The residue left after heating at 600 ºC was about 4-7% for the whole series. It should be noticed that variations in decomposition temperatures with composition do not follow a consistent trend but they oscillate up and down with some values overpassing those of PBT and PBF. ${}^{o}T_d$ display deviations from PBT up to near 40 ºC which must be attributed to the destabilizing effect of the furanic structure. On the contrary, differences in ${}^{max}T_d$ are hardly greater than 10 ºC, a low deviation that cannot be discarded to be due to experimental error.

Table 5.1.2. Thermal properties and crystallizability of *co*PBF$_x$T$_y$ copolyesters prepared *via* ROP.

Copolyester	**TGA**			**DSC**					**Crystallization kinetics**			
					First heating		Second heating					
	${}^{o}T_d{}^{a}$ (°C)	${}^{max}T_d$ (°C)	R_w (%)	T_g (°C)	T_m (°C)	ΔH (J·mol^{-1})	T_m (°C)	ΔH (J·mol^{-1})	Tc (ºC)	n^b	lnK^b	$t_{1/2}$ (min)
PBF	360	400	6	42	165	35	165	35	146	2.2	-4.42	6.91
*co*PBF$_{90}$T$_{10}$	337	400	7	35	157	33	155	5	-	-	-	-
*co*PBF$_{80}$T$_{20}$	338	395	6	29	143	12	140	1	-	-	-	-
*co*PBF$_{60}$T$_{40}$	348	394	7	32	135	1	-	-	-	-	-	-
*co*PBF$_{50}$T$_{50}$	342	397	6	35	132	8	138	2	-	-	-	-
*co*PBF$_{40}$T$_{60}$	357	398	4	39	155	11	155	11	-	-	-	-
*co*PBF$_{20}$T$_{80}$	362	403	5	45	194	22	194	25	175	2.7	-4.46	5.12
*co*PBF$_{10}$T$_{90}$	367	410	6	50	207	31	205	32	186	2.7	-3.02	3.72
PBT	375	408	5	51	227	52	223	39	204	2.8	-2.42	2.72

[a] T_d obtained at 5% of weight lost.

[b] Avrami parameters.

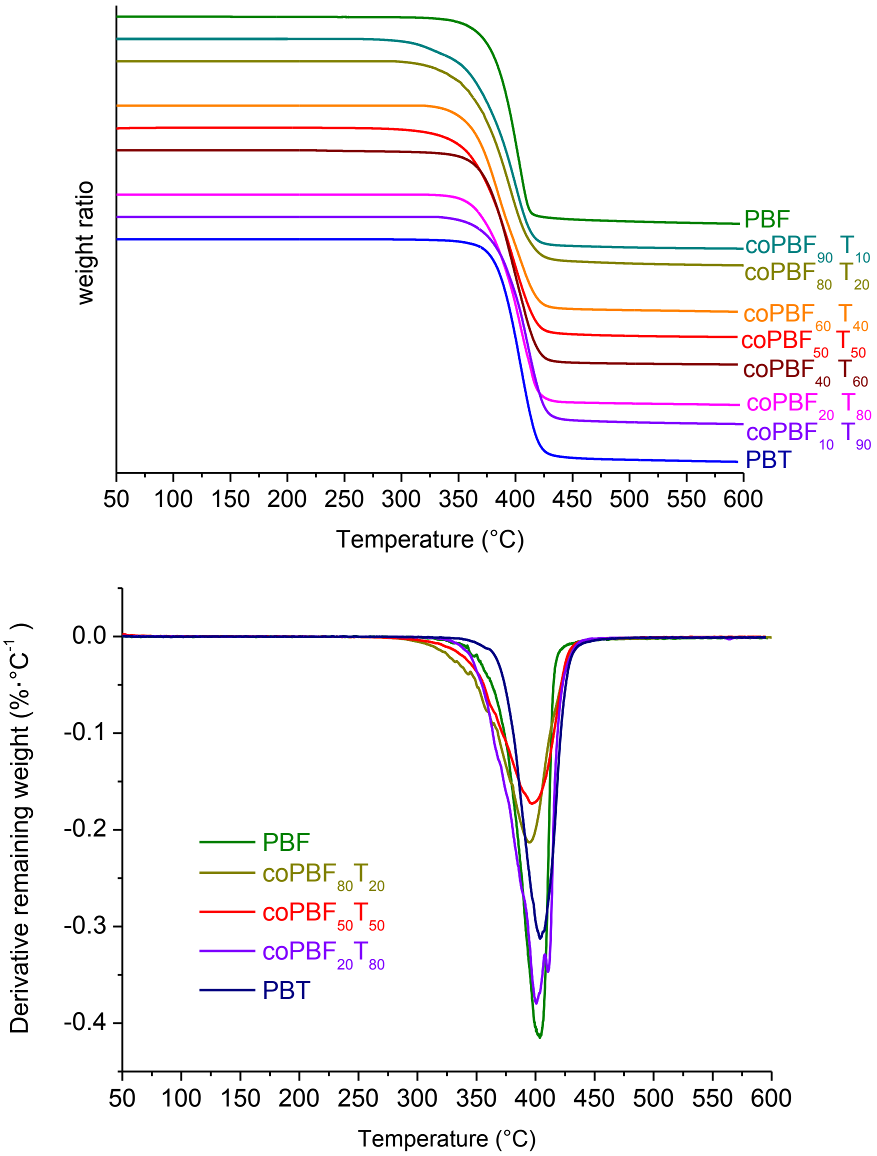


Figure 5.1.4. TGA analysis of *co*PBF$_x$T$_y$. Top: TGA traces registered under inert atmosphere. Bottom: Selected TGA derivative curves showing the main maximum rate degradation peaks.

The DSC traces registered at heating from pristine samples of *co*PBF$_x$T$_y$ without any further treatment are depicted in Figure 5.1.5, and the melting parameters measured on these thermograms are listed in Table 5.1.2.

The trend followed by both T_m and ΔH_m along the *co*PBF$_x$T$_y$ series becomes clearly apparent when these parameters are plotted against copolyester composition as it is shown in Figure 5.1.6a. All copolyesters gave traces displaying melting peaks at temperatures that are situated between or below the T_m of the two parent homopolyesters (PBF: 165 ºC and PBT: 227 ºC).

Exceptionally, the copolyester containing 90% of BF displays a cold crystallization peak in spite that the thermal history is the same for the whole series. A similar behavior was reported by Zhou et al.[26]

The melting enthalpy was also diminished by copolymerization to the point that copolyesters with nearly equilibrated compositions in the two aromatic counterparts, *i.e.* between 40 and 60%, displayed hardly perceivable crystallinities.

Apparently the incorporation of BF units in the PBT chain gives rise to a decreasing in both stability and amount of crystal phase.

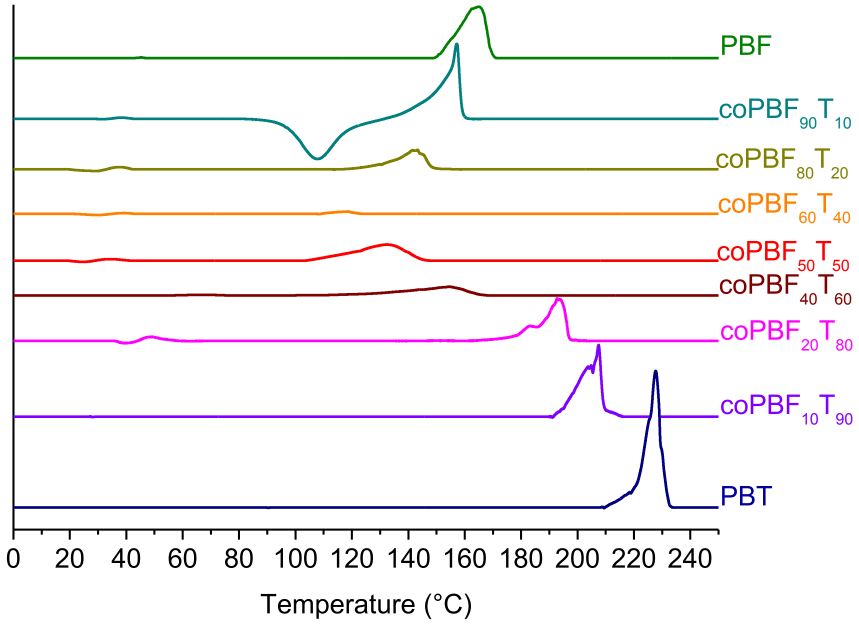


Figure 5.1.5. DSC traces of pristine samples of *co*PBF$_x$T$_y$ registered at heating in the 0-250 ºC interval.

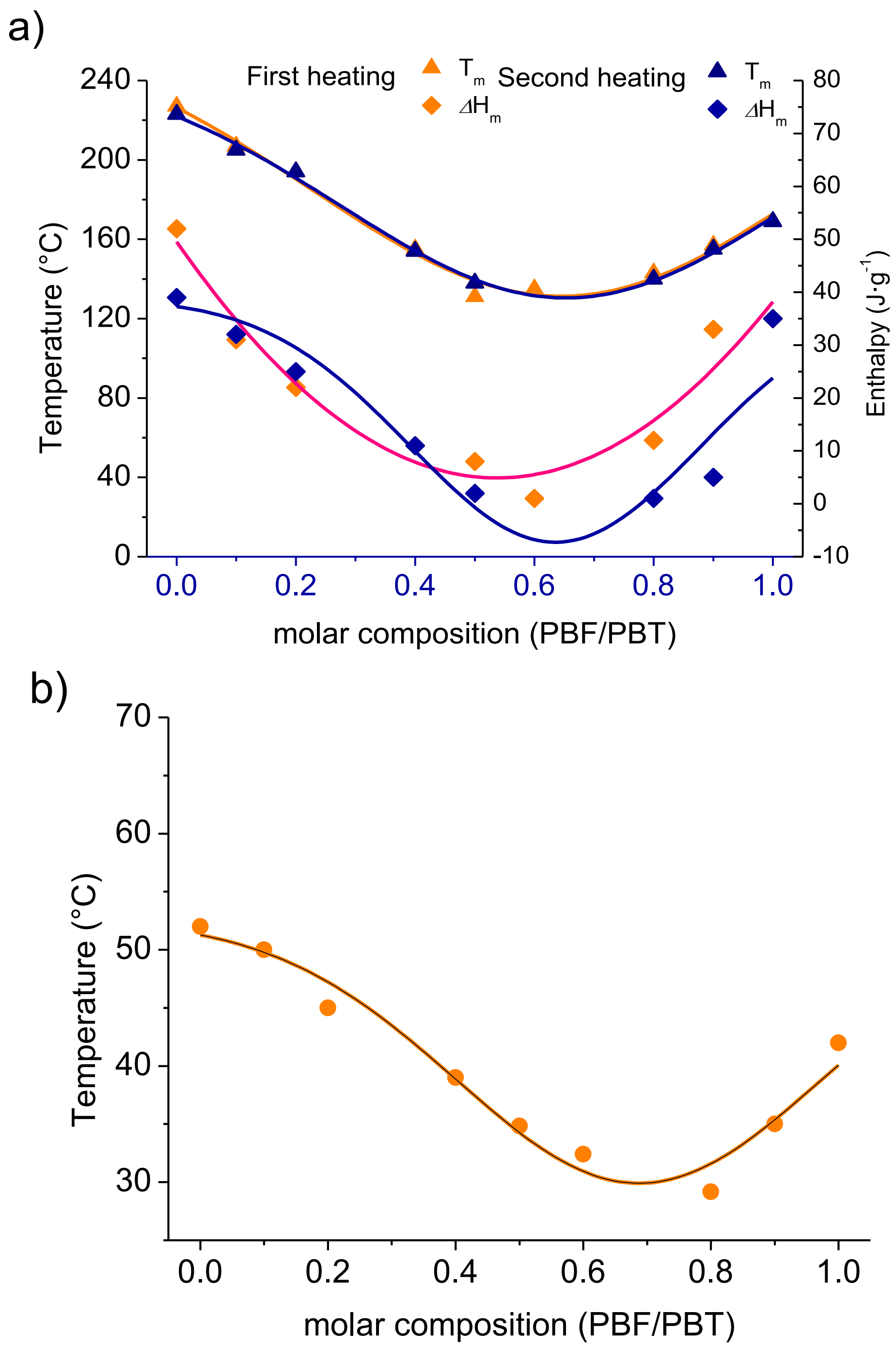


Figure 5.1.6. Variation of T_m (top) and T_g (bottom) in the *co*PBF$_x$T$_y$ copolyesters as a function of the molar composition.

Crystallinity and crystallizability. Polymer crystallizabillity, understood as the ability of a polymer to adopt the crystalline state upon cooling from the melt, is a prime property of the material regarding its suitability to be used as thermoplastic for thermal processing. This property becomes particularly important in the case of PBT given its extensive utilization in injection molding. In fact, the capacity of PBT to develop a considerable degree of crystallinity in a very short cooling time is a distinguishing feature of PBT that makes it the material of choice in a good number of applications. The effect that the total or partial replacement of terephthalate by furanoate units exerts on the crystallizability of PBT is therefore an issue that deserves detailed attention. Accordingly, a preliminary crystallization study of *co*PBF_xT_y copolyesters has been carried out in this work.

Firstly the copolyesters were subjected to X-ray diffraction in order to ascertain their crystallinities and to get an idea of what crystal structure is adopted in each case. The powder WAXS profiles obtained from a representative assortment of polyesters are depicted in Figure 5.1.7.

The profile produced by PBT is the familiar one displaying the well-defined peaks with spacings and intensities characteristic of the monoclinic structure adopted by the α-phase of this polyester when crystallized from the melt under unstrained conditions.[33] As expected, a clearly different profile arose from PBF with three main reflections at approximately 5.0, 3.9 and 3.5 Å indicates that a different crystal structure is adopted in this case. To our knowledge the crystal structure of PBF has not been determined yet.

The scattering produced by the copolyesters was clearly depending on composition with the pattern of PBT remaining clearly perceivable up to 40% contents in BF units but vanishing at higher contents. Conversely no sign revealing the presence of the PBF structure could be detected in the profiles obtained from copolyester enriched in BF units. It seems therefore that the PBF structure is highly sensitive to copolymerization and unable to persist in the presence of small amounts of BT units.

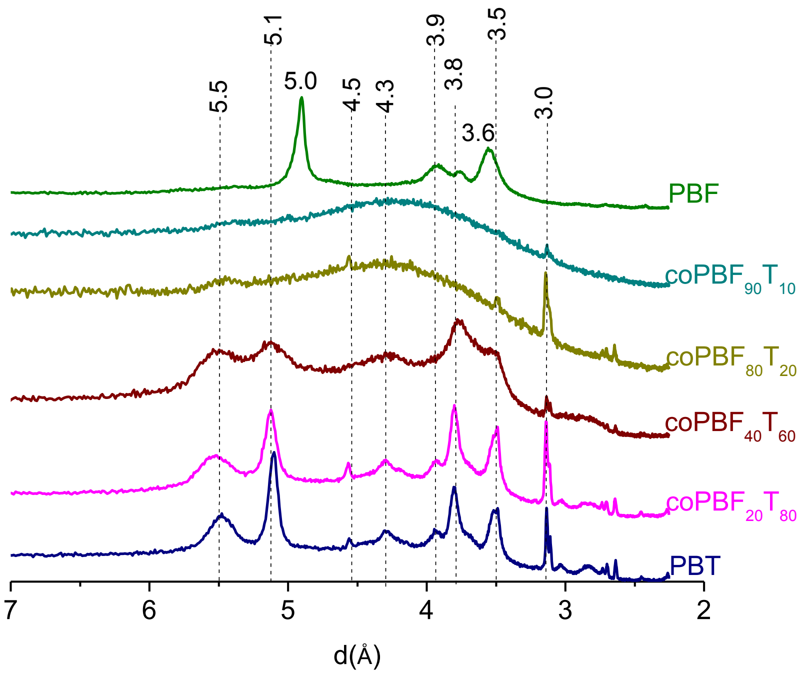


Figure 5.1.7. Powder X-ray diffraction profiles of PBF, PBT and *co*PBF$_x$T$_y$. Main spacings indicated in angstroms.

As it is shown in Table 5.1.2, all *co*PBF$_x$T$_y$ except that containing 60% of BF units, were able to crystallize upon cooling from the melt with a crystallinity degree highly depending on composition. Melting temperatures and enthalpies of the crystallized material are represented against composition in Figure 5.1.6a where they can be compared with values registered for the pristine samples. Whereas differences in T_m for the first and second heating are not high, the enthalpies of the copolyesters decreased considerably after recrystallization. Larger differences were observed for copolyesters containing similar amounts of BF and BT units in which the melting enthalpy of the recrystallized material became very small or even unperceivable. Conversely the two parent homopolyesters PBT and PGT were able to recover almost completely their initial crystallinity after melting and cooling which is indicative that copolymer heterogeneity must be responsible for the decay observed in crystallizability.

The copolyesters *co*PBF$_{10}$T$_{90}$ and *co*PBF$_{20}$T$_{80}$ were selected for the isothermal crystallization kinetics study because they were unique in crystallizing from the melt in an extent large enough as to allow following the evolution of crystallization by DSC.

The study included the homopolyesters PBT and PBF for reference. The cooling and second heating traces of the four polyesters subjected to study are depicted in Figure 5.1.8a showing both the crystallization and melting peaks produced by each of them.

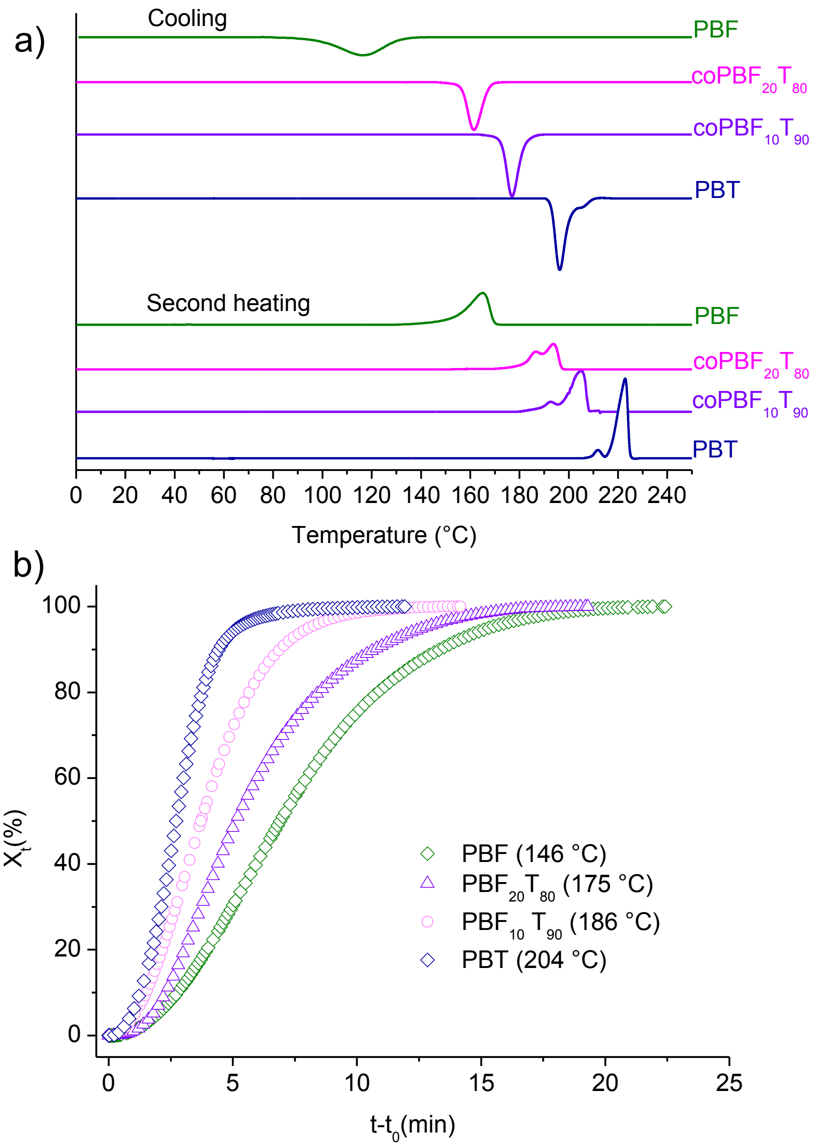


Figure 5.1.8. Cooling and second heating DSC traces (a), and evolution of the relative crystallinity as a function of time in the isothermal crystallization (b) of PBF, PBT and the copolyesters $PBF_{10}T_{90}$ and $PBF_{20}T_{80}$.

Noticeably two melting peaks are seen for PBT and for the two copolyesters whereas PBF was unique in displaying a single peak. As it is usually interpreted in polymer crystallization, the two peaks should arise from two crystal populations differing in size that were generated at two different crystallization stages.[34]

The presence of the secondary peak does not affect the kinetics results since the used data were restricted to short crystallization times when only primary crystallization takes place. The popular Avrami approach was applied here for interpreting isothermal crystallization data.

The increase in relative crystallinity with crystallization time measured by DSC for the four polyesters examined in this work is plotted in Figure 5.1.8b. The double logarithmic plots (see annex, Figure B.1.5) ascertained the validity of the time ranges fixed for this study and they were therefore used for determining the Avrami parameters which are collected in Table 5.1.2.

The polymer morphologies generated upon crystallization were observed by polarizing optical microscopy and a representative selection of them are shown in Figure 5.1.9. Although no well-developed spherulites could be seen at any case, the three-dimensional morphology became much easier recognizable in the crystallized copolymers. According to the values found for the Avrami exponent (n), which are around 2.7-2.8, it can be inferred that isothermal crystallization could be a heterogeneously nucleated spherulitic process.

Unfortunately, the large differences in melting temperatures among homopolyesters and copolyesters prevented to fix a common crystallization temperature for the whole set under study, as it would have been desirable for a more straightforward comparison of crystallizability. A useful approximation is however to crystallize the polymers at the same undercooling degree, *i.e*. at the same $\Delta T = T_m - T_c$.

Thus the four selected polyesters were isothermally crystallized at 19 ºC below their respective melting temperatures and the kinetic parameters obtained from such essays are listed in Table 5.1.2. Valuable conclusions drawn from these results are the following: a) Crystallization half times increased steadily with the amount of furan units present in the polyester indicating that crystallizability is disfavored by the presence of these units. b) PBF crystallized at a considerable lower rate than PBT in spite that crystallization was conducted at 60 ºC lower. c) From a practical point of view, PBF and PBT containing moderate amounts of BF units are able to crystallize from the melt at reasonable crystallization rates.

The crystallizability of a random copolymer composed of crystallizable comonomeric units is usually dictated by composition. The nucleating effect and the relative mobility of the units are the factors determining the crystallinity and the crystallization rate of the copolymer.

The X-ray diffraction data recorded from *co*PBF$_x$T$_y$ (Figure 5.1.7) reveal that the crystal structure of PBF vanished with the presence of small amounts of BT units whereas vestiges of the PBT crystalline scattering remain detectable in the profiles recorded from copolymers containing large amounts of BF units. Since crystallization of *co*PBF$_x$T$_y$ seems to be nucleated by exogenous species, it can be inferred that the straight linear shape of the BT sequences is more favorable to attain the chain packing than the weaving segments made of BF units.

Nevertheless a more detailed study involving the evaluation of the crystallization rate with temperature should be needed to ascertain with higher accuracy the influence of BF units on crystallizability.

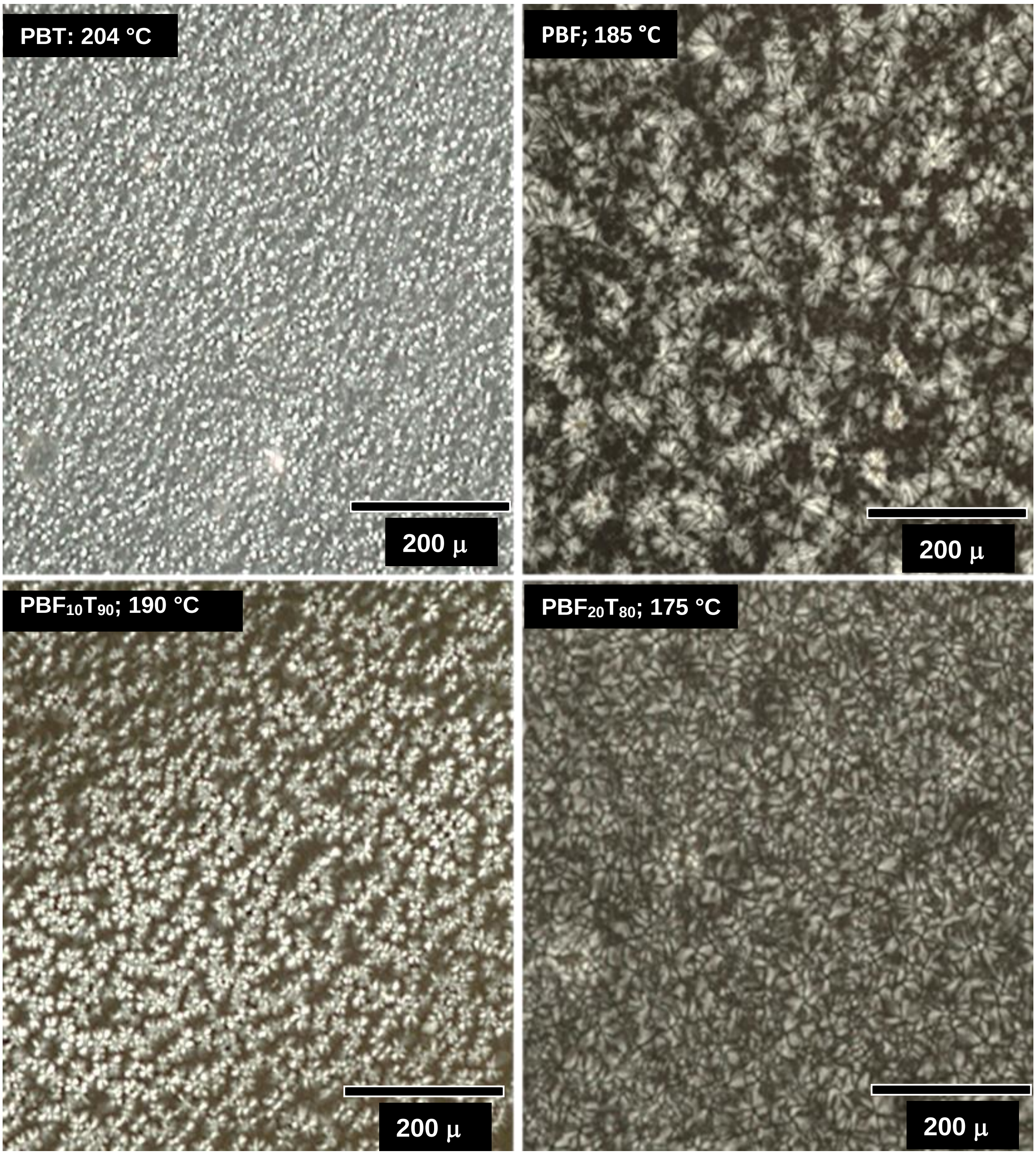


Figure 5.1.9. POM of polyesters isothermally crystallized at the indicated temperatures.

V.1.3 Conclusions

The application of the ROP technique frequently used for the preparation of sustainable aliphatic polyesters has been extended here to bio-based aromatic copolyesters containing 2,5-furandicarboxylate units. Mixtures of cyclic butylene 2,5-furandicarboxylate and butylene terephthalate oligomers were able to react in the melt to produce a series of poly(butylene 2,5-furandicarboxylate-*co*-terephthalate) copolyesters with a random microstructure and weight-average molecular weights above 55,000 g·mol^{-1}. It is remarkable that times required for polymerization of the cyclic oligoesters were considerable shorter than those needed for polycondensation of the diols and diesters mixtures provided that similar molecular weights are reached. The ensuing copolyesters displayed a good thermal stability and were semicrystalline for the almost whole range of compositions. Crystallinity was largely repressed by the presence of furanoate units in spite that the homopyester PBF was highly crystalline. Both T_m and T_g of the copolyesters varied steadily according to the furanoate/terephthalate ratio and the values observed for these temperatures were comparable to those reported for similar copolyesters prepared by melt polycondensation. Copolyesters containing moderate amounts of furanoate units were able to crystallize from the melt by developing a nearly spherulitic texture. It was evidenced however that the replacement of the terephthalate units by the furanoate ones implied a decrease in the crystallizability of PBT. The poly(butylene 2,5-furandicarboxylate) homopolyester is also able to crystallize from the melt but at a much lower rate than PBT, in part due the lower temperature at which it was crystallized.

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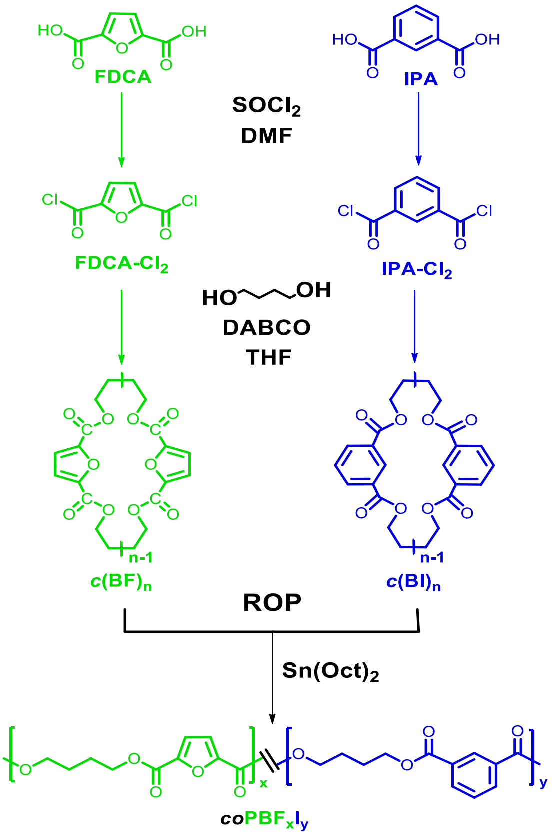
V.2. Poly(butylene isophthalate)s copolyesters

Abstract: Cyclic butylene furanedicarboxylate ($c(\mathrm{BF})_n$) and butylene isophthalate ($c(\mathrm{BI})_n$) oligomers obtained by high dilution condensation (HDC) reaction were polymerized in bulk at 200 ºC with $\mathrm{Sn(Oct)_2}$ catalyst via entropically driven ring opening polymerization (ED-ROP) to give homopolymers and copolymers (*co*PBF$_x$I$_y$) with high weight average molar masses from 61000 to 66000 g·mol^{-1} and dispersities between 1.3 and 1.9. The composition of the copolymers as determined by NMR was practically the same to the feed and they showed an almost random microstructure. The copolymers were thermally stable up to 300 ºC and crystalline for all compositions with T_g decreasing from 41 ºC to 21 ºC linearly with the content of isophthalic units in the copolymer. *co*PBF$_x$I$_y$ copolymers showed that both the melting temperature and the enthalpy decreased as the content of butylene isophthalate units increased just to a composition (30/70 BF/BI) in which the triclinic crystalline phase made exclusively of butylene furanoate units changed to the crystalline phase of PBI. The partial replacement of furanoate by isophthalate units decreased substantially the crystallizability of PBF.



Publication derived form this work:

J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra. Partially renewable poly(butylene 2,5-furandicarboxylate-*co*-isophthalate) copolyesters obtained by entropically-driven ROP. *Polymers* **2018** to be submitted**.**

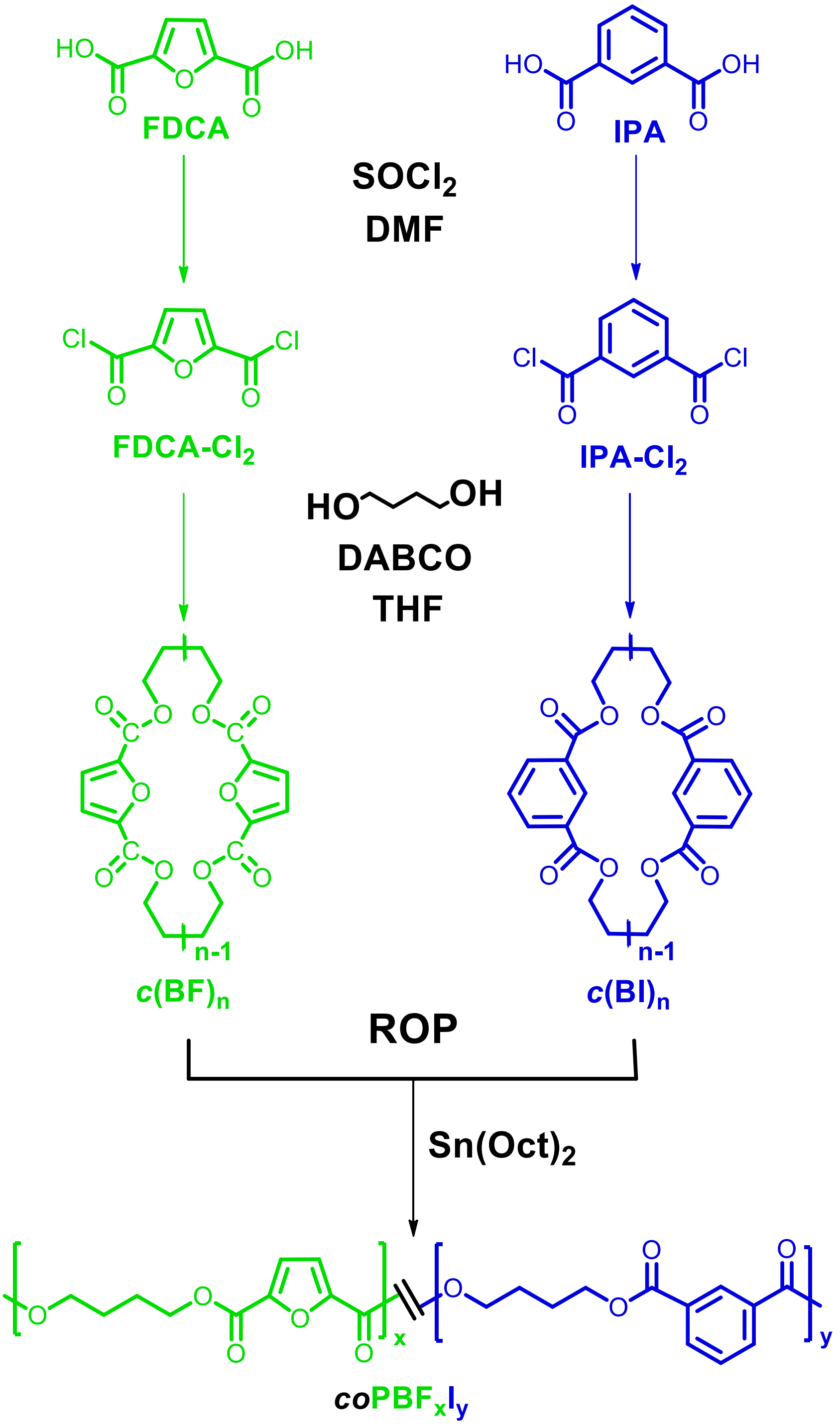
V.2.1 **Introduction**

Due to people's awareness on sustainability, polymers obtained from renewable sources have been developed in the last decade, which would come to replace those obtained from fossil resources[1-5]. One renewable monomer that has attracted more the attention is 2,5-furandicarboxylic acid (FDCA), an aromatic building block obtained from from C5 and C6 sugars or polysaccharides, which can be used to replace the petrochemical terephthalic acid widely used for the preparation of aromatic polyesters such as PET or PBT[6-8]. Although poly(ethylene furanoate) (PEF) has been widely studied because it has similar properties as PET and improved gas barrier properties, which makes it as a serious alternative for applications on soft drink bottles, poly(butylene furanoate) (PBF) has been scarcely studied. It is a semicrystalline polyester with a melting point of 172 ºC and a glass transition temperature of 39 ºC.[9] As well as it happens in PBT, due to the presence of the butylene segment in the repeating unit of PBF, this polymer has a high tendency to crystallize very fast, which can be an inconvenient for some injection moulding processes due to excessive mould shrinkage. In order to overcome these problems one solution is copolymerization. The insertion of either a diol, or a diacid comonomeric unit in small quantities reduces both the melting temperature and enthalpy, reducing its processing costs. This method has been applied to various technical polyesters in order to tune their thermal properties, such as crystallizability, melting or glass transition temperatures[10]. PBF copolymers with enhanced biodegradability have been already prepared by either melt polycondensation[11-14] or entropically driven ROP (ED-ROP) of cyclic oligomers.[15,16] This last method which uses cyclic oligomers to prepare polyesters has some advantage because it does not require any by-product removal during the reaction, is athermal and very high-molecular-weight polymers can be achieved in a matter of minutes, thereby allowing novel processing techniques. It was first developed by Brunelle[17] and recently reviewed by Hogde[18] and Strandman *et al.*[19], and has been used in our group to successfully prepare various PEF and PBF copolymers with enhanced properties.[20,21] In this work we would like to report on the synthesis and characterization of thermal properties and crystallization behaviour of new partially renewable PBF copolymers containing isophthalic units prepared by ED-ROP of cyclic butylene furanoate and butylene isophthalate oligomers.

V.2.2 **Results and discussion**

The synthetic route used for the preparation of $c(\mathrm{BF})_n$ and $c(\mathrm{BI})_n$ cyclic oligomers and their entropically driven-ring opening homo and copolymerization (ED-ROP) is represented in Scheme 1. In a first step the cyclic oligomers were obtained by reaction (HDC) of BD and either FDCA-Cl_2 or IPA-Cl_2. The mixture of cyclic oligomers and linear species were separated by column chromatography and the purity of cyclic oligomers was ascertained by HPLC, NMR and MALDI-TOF mass spectra (Figures B.2.2 and B.2.3). The ^{1}H NMR spectra show the absence of any peaks at around 3.8 ppm due to CH_2OH groups which indicates that only cyclic oligomers are present in the purified fractions. Some signals in both ^{1}H and ^{13}C NMR spectra are split due to the sensitivity of these nuclei to the size of cyclic oligomer. On the other hand MALDI-TOF MS spectra allowed determining the molar mass of the different cyclic species.

Table 5.2.1 shows the composition of the different cycles for the two oligomeric fractions determined by HPLC. A mixture of cyclic oligomers, mainly from dimer to tetramer were obtained for both $c(\mathrm{BF})_n$ and $c(\mathrm{BI})_n$ being the dimer the predominant cycle. Both the flexibility of the butanediol unit and the 1,3- or 2,5-substitution of the phenyl and furanic rings respectively, favor their formation due to kinetic and/or thermodynamic factors and the probable low ring strain of the cycles composed of two repeating units.



Scheme 5.2.1. Synthesis route of poly(butylene 2,5-furandicarboxylate-*co*-isophthalate) (*co*PBF$_x$I$_y$) *via* ROP.

Table 5.2.1. Cyclization reaction results.

	Yield (%)	Composition[a] (2/3/4)	T_m[b] (°C)	$^oT_{5\%}$[b] (°C)	T_d[b] (°C)
***c*(BF)$_n$**	67	61/31/8	147	276	387
***c*(BI)$_n$**	70	75/15/10	149	330	399

[a] Relative content (w/w) of the reaction product in cyclic dimer, trimer and tetramer as measured by HPLC.

[b] Melting and decomposition temperatures measured by DSC and TGA.

The thermal properties of these cycles were evaluated by DSC and TGA (Figure B.2.4 and Table 5.2.1). Both *c*(BF)$_n$ and *c*(BI)$_n$ showed melting peaks at around 150 ºC, and it was observed that they were thermally stable up to 275 and 330 ºC respectively which allowed its thermal polymerization at the temperatures used for the reaction (200 ºC) without any sign of degradation.

Then, these cycles were polymerized via ED-ROP in bulk. First, an equimolar copolymer (*co*PBF$_{50}$I$_{50}$) was chosen to test the effect of the temperature on polymerization results. Three different temperatures above the melting point of the cycles were chosen, 180, 200 and 230 ºC and aliquots of sample were taken to determine the molecular weight of the copolymer obtained at different times of reaction. It was observed that above 200 ºC, after six hours of reaction there was not an improved on the molar mass of the polymer obtained, (Figure 5.2.1a), and then it was chosen as the reaction temperature for all copolyesters synthesis. The evolution of the molar masses of the copolyesters with time of reaction is depicted in Figure 5.2.1b, where a similar tendency is observed for all series, however the maximum molar mass attained was observed to increase slightly with the content in furanic units in the copolymer (Figure 5.2.1c and Table 5.2.2), which can be due to the higher reactivity of the furanic over isophthalic cyclic derivatives or a improved thermal stability of the former. The dispersities of the obtained copolymers oscillated between 1.30 and 1.78, values which are in accordance with those obtained by ED-ROP.[18,19]

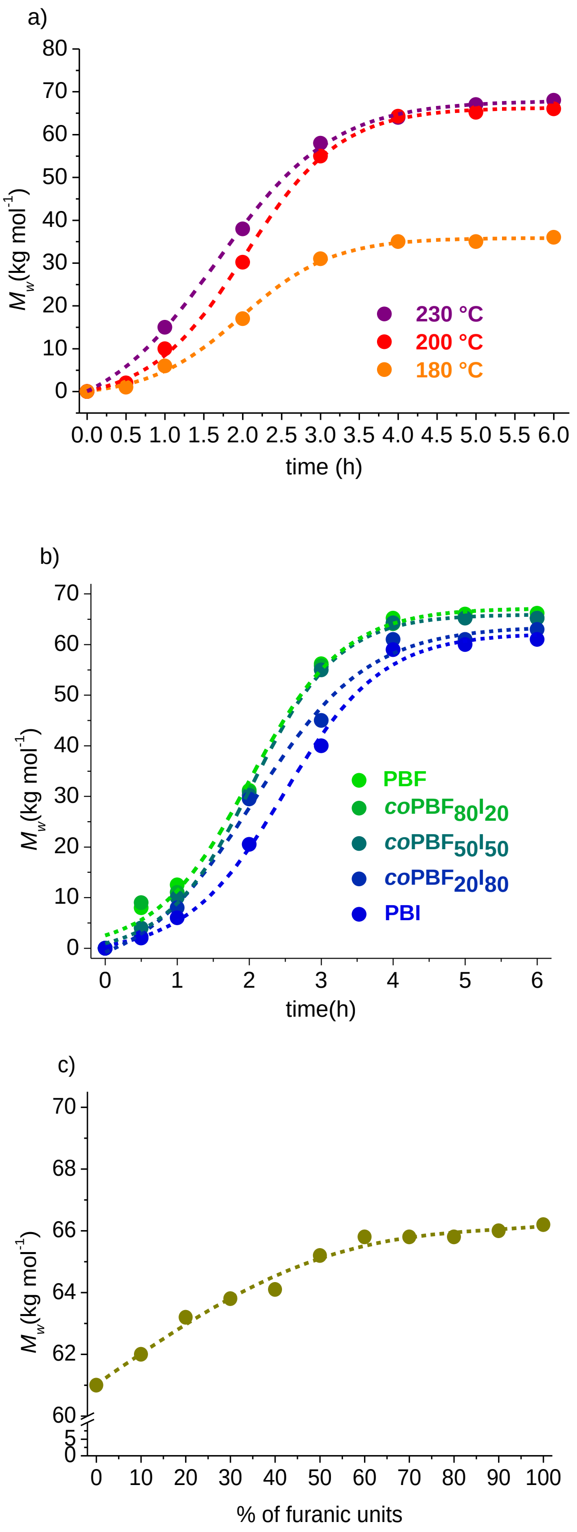


Figure 5.2.1. Evolution of weight average molar mass of a) *co*PBF$_{50}$I$_{50}$ at different temperatures for different times, b) *co*PBF$_x$I$_y$ for different molar compositions for different times at 200 ^{o}C and c) *co*PBF$_x$I$_y$ for different composition at 200 °C for 6 h analyzed by GPC.

The polyesters were obtained with good yields (85-93 %). The chemical structure and composition of *co*PBF$_x$I$_y$ copolymers were determined by NMR. Figure

5.2.2 shows both ^{1}H and ^{13}C NMR spectra of *co*PBF$_{50}$I$_{50}$ with peak assignments as a representative of the series. NMR spectra for all series are depicted in Figure B.2.4 of SI document. Signals due to the furanic proton *a* and isophthalic protons *f'* were chosen for the determination of the copolyester composition. In general, there is a good correlation between the feed and the final copolyester composition determined by ^{1}H-NMR, with slight fluctuations probably due to cyclic's volatilization (Table 5.2.2).

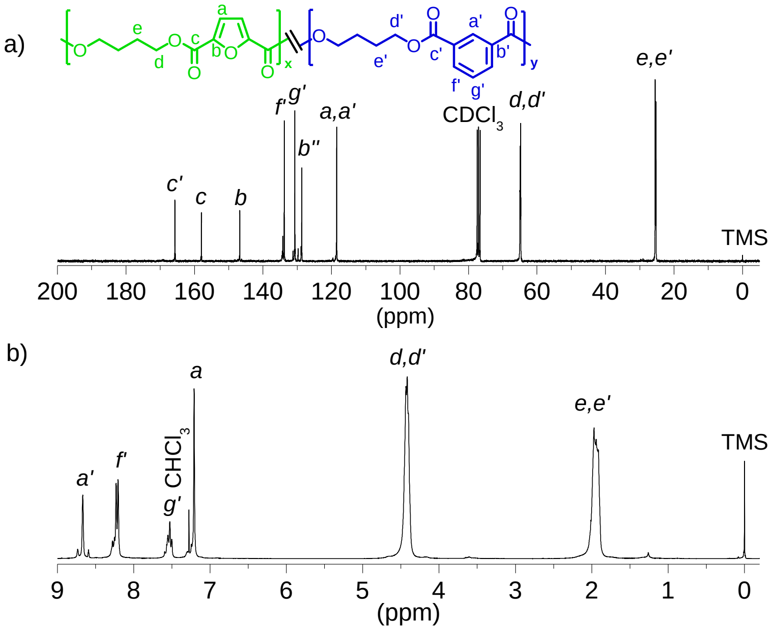


Figure 5.2.2. a) ^{13}C and b) ^{1}H NMR of *co*PBF$_{50}$I$_{50}$ with peak assignments.

On the other hand ^{13}C NMR spectra were used for the determination of the copolymer microstructure. Each carbon signal of butylene segment split into four peaks due to the sensitivity of them to sequence distribution at the level of dyads (Figure 5.2.3). The assignment of different peaks to different dyads was straightforward by comparison with both PBF and PBI homopolymers. By deconvolution of these signals the dyad content (F*B*F, F*B*I+I*B*F, I*B*I) can be obtained and by applying the following expressions the number average sequence length and the degree of randomness could be determined.[24]

$$\bar{\mathrm{n}}_{\mathrm{BF}} = \frac{\mathrm{F}B\mathrm{F} + \frac{1}{2}(\mathrm{F}B\mathrm{I} + \mathrm{I}B\mathrm{F})}{\frac{1}{2}(\mathrm{F}B\mathrm{I} + \mathrm{I}B\mathrm{F})} \quad ; \quad \bar{\mathrm{n}}_{\mathrm{BI}} = \frac{\mathrm{I}B\mathrm{I} + \frac{1}{2}(\mathrm{F}B\mathrm{I} + \mathrm{I}B\mathrm{F})}{\frac{1}{2}(\mathrm{F}B\mathrm{I} + \mathrm{I}B\mathrm{F})} \quad ; \quad \mathrm{R} = \frac{1}{\bar{\mathrm{n}}_{\mathrm{BF}}} + \frac{1}{\bar{\mathrm{n}}_{\mathrm{BI}}}$$

The degree of randomness was close to one with slight deviations for copolymers with close compositions, indicating that all they were mostly random copolymers were extensive transesterification took place (Table 5.2.2).

Table 5.2.2. Results of molecular weight and microstructure analysis for *co*PBF$_x$I$_y$ copolymers obtained *via* ROP.

Copolyester	Yield (%)	x_{BF}/y_{BI}[a] (mol/mol)	Molecular Weight[b]		Dyad content (mol %)[c]			Sequence length[d]		*R* [d]
			M$_w$	*Đ*	FBF	FBI+IBF	IBI	*n*$_{BF}$	*n*$_{BI}$	
PBF	90	100/0	66,200	1.65	-	-	-	-	-	-
*co*PBF$_{90}$I$_{10}$	88	89/11	66,000	1.50	79.7	18.4	1.7	11.30	1.18	0.94
*co*PBF$_{80}$I$_{20}$	85	81/19	65,800	1.45	72.7	14.1	13.2	9.57	1.50	0.94
*co*PBF$_{70}$I$_{30}$	86	70/30	65,800	1.28	43.1	41.7	14.8	3.06	1.71	0.91
*co*PBF$_{60}$I$_{40}$	85	64/36	65,800	1.30	43.3	42.9	14.1	3.02	1.65	0.93
*co*PBF$_{50}$I$_{50}$	86	48/52	65,200	1.45	25.8	36.8	37.5	2.41	3.04	0.80
*co*PBF$_{40}$I$_{60}$	89	40/60	64,100	1.62	22.1	32.5	45.4	2.36	3.79	0.72
*co*PBF$_{30}$I$_{70}$	91	31/69	63,800	1.78	17.9	27.5	55.4	2.24	5.04	0.75
*co*PBF$_{20}$I$_{80}$	88	18/82	63,200	1.60	5.6	24.2	70.2	1.46	6.79	0.83
*co*PBF$_{10}$I$_{90}$	87	10/90	62,000	1.45	1.7	16.2	82.2	1.21	11.17	0.91
PBI	93	0/100	61,000	1.50	-	-	-	-	-	-

[a] Determined by ^{1}H NMR.

[b] Weight-average molar masses in g·mol^{-1} and dispersities determined by GPC.

[c] Determined by deconvolution of the ^{13}C NMR peaks appearing in the 64.6 - 65.2 ppm region.

[d] Number average sequence lengths and degree of randomness (*R*) calculated using the expressions mentioned in the text.

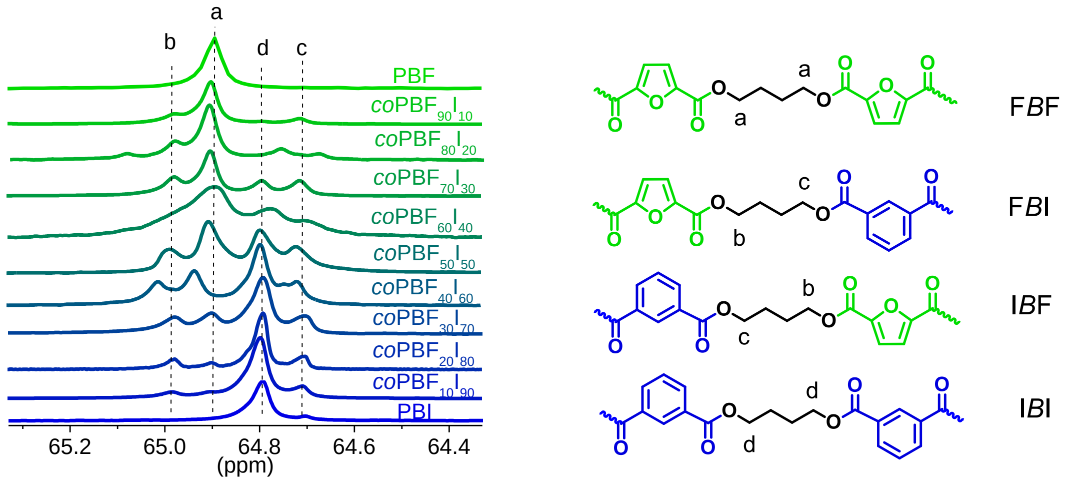


Figure 5.2.3. ^{13}C NMR spectra of *co*PBF$_x$I$_y$ copolyesters in the region of corresponding to to first oxybutylene carbon.

The thermal stability of PBF, PBI and its copolyesters was evaluated by TGA under inert atmosphere. Both, polyesters and copolyesters were observed to be thermally stable up to 300 ºC with onset temperatures above 330 ºC and temperatures of maximum decomposition rate between 396-407 ºC (Figure 5.2.4 and Table 5.2.3), and remaining weights at 600 ºC between 7-11 %. These values allow to conclude that the homopolymers and copolymers have a good thermal stability so as to be able to be processed above their melting temperature without suffering thermal degradation.

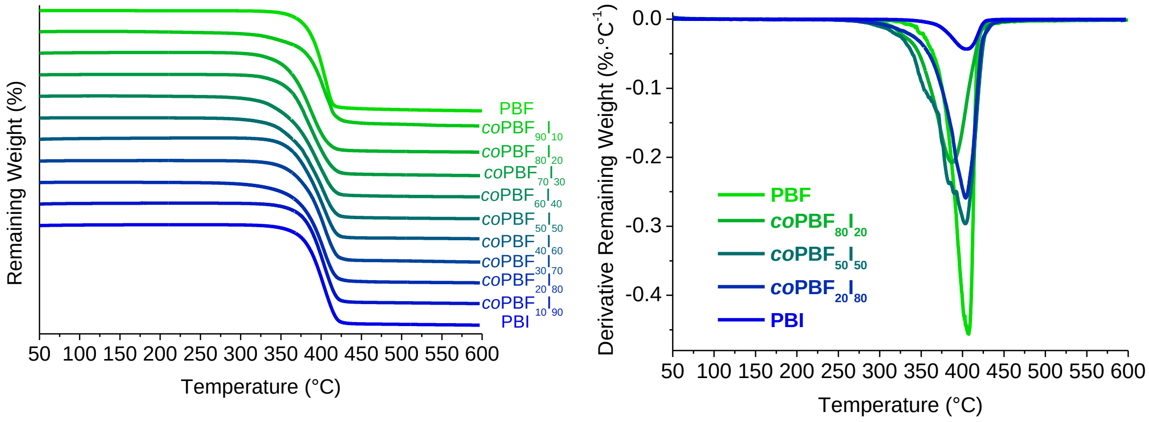


Figure 5.2.4. TGA analysis of *co*PBF$_x$I$_y$

Table 5.2.3. Thermal properties of *co*PBF$_x$I$_y$ copolyesters prepared *via* ED-ROP.

Copolyester	**TGA**			**DSC**					**crystallization kinetics**		
					First heating		Second heating				
	$^{o}T_d{}^a$ (°C)	$^{max}T_d$ (°C)	R_w (%)	T_g (°C)	T_m (°C)	ΔH (J·mol^{-1})	T_m (°C)	ΔH (J·mol^{-1})	n^b	lnK^b	$t_{1/2}$ *(min)*
PBF	364	407	7	41	173	45	173	39	2.2	-4.4	6.9
*co*PBF$_{90}$I$_{10}$	340	404	11	35	164	41	163	35	2.5	-8.6	27.8
*co*PBF$_{80}$I$_{20}$	338	390	9	30	158	29	156	26	-	-	-
*co*PBF$_{70}$I$_{30}$	342	396	7	28	143	21	142	15	-	-	-
*co*PBF$_{60}$I$_{40}$	330	396	7	28	137	12	137	4	-	-	-
*co*PBF$_{50}$I$_{50}$	334	403	7	27	126	10	-	-	-	-	-
*co*PBF$_{40}$I$_{60}$	355	404	8	27	122	3	-	-	-	-	-
*co*PBF$_{30}$I$_{70}$	352	405	7	27	118	1	-	-	-	-	-
*co*PBF$_{20}$I$_{80}$	336	403	8	26	106	2	-	-	-	-	-
*co*PBF$_{10}$I$_{90}$	363	403	8	24	130	5	129	1	-	-	-
PBI	364	404	8	21	142	31	141	1	-	-	-

[a] $^{o}T_d$ obtained at 5% of weight lost.

[b] Avrami parameters obtained from the isothermal crystallizations at 146 ºC.

The thermal properties such as the melting and glass transition temperatures of the polyesters have been evaluated by DSC. The DSC traces obtained at heating from samples coming directly from synthesis are depicted in Figure 5.2.5(a–c) and data taken from these thermograms are collected in Table 5.2.3. Glass transition temperatures taken from melt quenched samples showed a single T_g characteristic of random or miscible copolymers, intermediate between the two homopolymers which increased continuously with the content of furanic units in the copolymer from 21 ºC to 41 ºC. It can be observed from DSC that PBF was a crystalline polymer with a melting temperature of 173 ºC. The insertion of butylene isophthalate units in the polymer restricted the crystallizabiliy reducing gradually both, the melting temperature and enthalpy with increasing amounts isophthalate units to the point that copolymers with contents between 60-80 % of isophthalate units showed low enthalpic melting values in the first heating and remained amorphous in the second heating scan. A similar effect was observed for PBF copolymers containing butylene terephthalate units, however in this case the T_g increased with the content of terephthalic units in the copolymer.[21] PBI was also crystalline, with a melting temperature of 141 ºC and a low melting enthalpy.

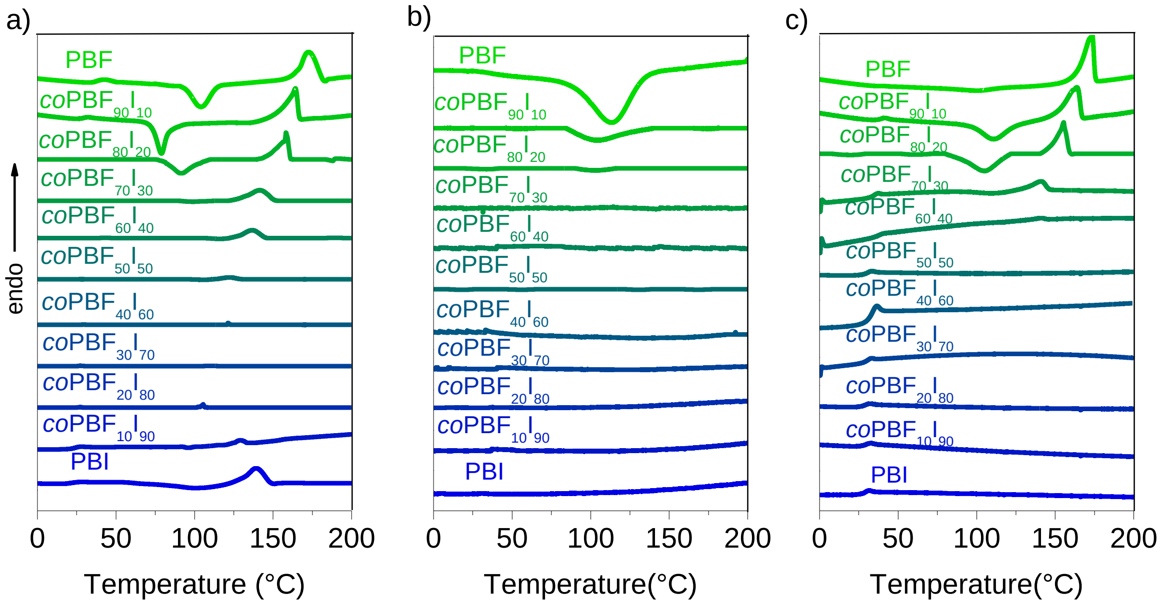


Figure 5.2.5. DSC analysis a) first heating, b) second heating and c) cooling of *co*PBF$_x$I$_y$.

The intensity profiles of the X rays scattered in the reflection mode by powder pristine samples of the representative copolyesters and homopolyesters examined in the present work are compared in Figure 5.2.6, and the measured *d*-spacings are compared in Table 5.2.4. Discrete scatterings were observed for *co*PBF$_x$I$_y$ copolyesters containing isophthalic units up to 50 mol % with spacings at around 4.9, 3.9 and 3.5 Å that increase and broadened slightly with the content of isophthalic units in the copolymer. These copolymers shared the triclinic crystalline structure of PBF, confirming the exclusion of butylene isophthalate units from the crystalline lattice.[9] Over 50 % of isophthalic units the copolymers remained amorphous up to copolyesters with 90 % of these units that showed small reflections at 5.3 and 3.6 Å, characteristics of the crystalline structure of PBI.[25]

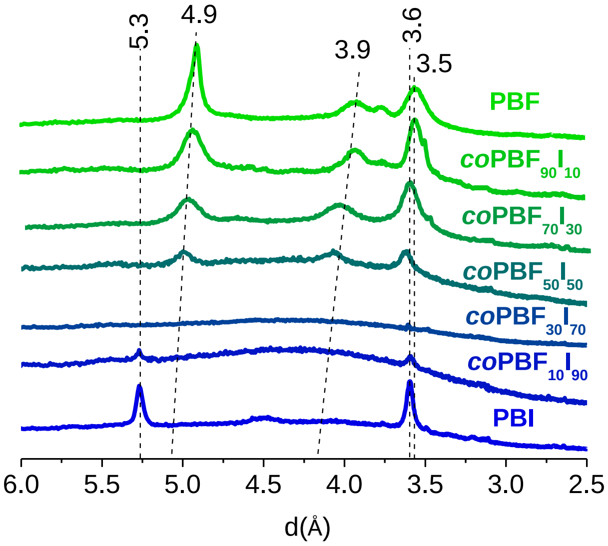


Figure 5.2.6. WAXS diffractograms of *co*PBF$_x$I$_y$.

In order to know more deeply the effect of the copolymerization on the crystallization behavior, an isothermal crystallization study has been carried out on PBF homopolymer and a copolymer containing 10% of isophthalate units. Melt quenched samples were isothermally crystallized for one hour at 146 ºC and enthalpic crystallization data taken from the DSC were registered. It was observed that the relative crystallinity (X_t) increased in a sigmoid trend in both cases (Figure 5.2.7), but it was observed that the crystallization rate decreased substantially in the copolymer *co*PBF$_{90}$I$_{10}$.

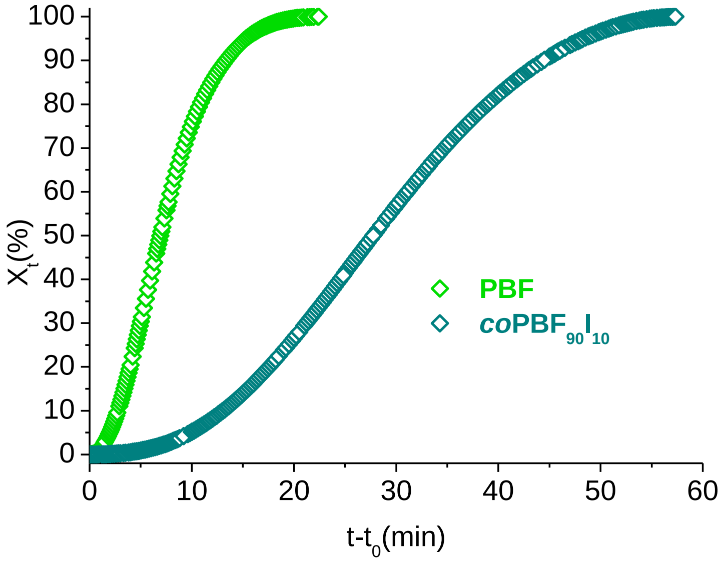


Figure 5.2.7. Evolution of the relative crystallinity as a function of time in the isothermal crystallization of PBF and *co*PBF$_{90}$I$_{10}$ at 146 °C.

The kinetics of crystallization was analyzed by adopting the Avrami equation. Taking the logarithm of both sides of the Avrami equation gives following equation:

$$\log(-\ln(1-X_t)) = \log(k) + n\log(t-t_o)$$

Were X_t is the fraction of crystallized material, *k* is the temperature-dependent rate constant, *t* and t_o is the elapsed and the onset times respectively , and *n* is the Avrami exponent, indicating the type of nucleation and dimension of crystal growth. Both, *n* and log(*k*) were obtained from the slope and the intercept of the linear plot of log(-ln(1-X_t)) against log(*t-to*) (Figure B.2.6). From these results it can be concluded that the crystallization half times increased with the amount of isophthalate units present in the copolyester indicating that crystallizability is restricted by the presence of these units and the increase of the avrami exponent *n* indicates that the crystallization is changing from a plate-like growth to spherulitic growth.

V.2.3 **Conclusions**

Cyclic butylene furanedicarboxylate and butylene isophthalate oligomers were obtained by high dilution condensation reaction. A mixture of cycles mainly from dimer to tetramer was obtained in both cases being the cyclic dimer the predominant specie. The polymerization of these cycles carried out in bulk at 200 ºC with $Sn(Oct)_2$ catalyst via entropically driven ROP gave polymers and copolymers with high weight average molar masses that increased continuously with the content of furanic units in the copolymer from 61000 to 66000 $g \cdot mol^{-1}$. They showed moderate dispersities in accordance with the polymerization reaction used for the synthesis. The copolymer composition determined by NMR was practically the same as the feed and the sequence distribution of the comonomers was almost random, indicating that transesterification reactions took place simultaneously during ROP reaction. The copolymers were thermally stable up to 300 ºC and crystalline for all compositions with T_g decreasing almost linearly with the content of isophthalic units in the copolymer from 41 ºC to 21 ºC. On the other hand *co*PBF_xI_y copolymers showed that both the melting temperature and the enthalpy decreased as the content of butylene isophthalate units increased just to a composition (30/70 BF/BI) in which the triclinic crystalline phase made exclusively of butylene furanoate units changed to the crystalline phase of PBI. Studies made on PBF and *co*$PBF_{90}I_{10}$ revealed that the replacement of furanoate by isophthalate units decreased substantially its crystallizability.

V.2.4 **References**

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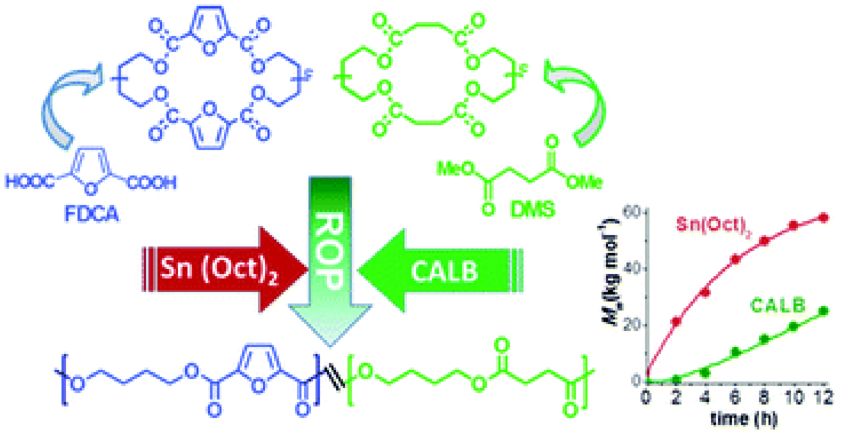
VI.Aliphatic copolyesters containing furanoate units

VI.I Poly(butylene furanoate-*co*-succinate) copolyesters

Abstract: Poly(butylene 2,5-furandicarboxylate-*co*-succinate) copolyesters (*co*PBF$_x$S$_y$), have been synthesized by ring opening polymerization (ROP). Cyclic butylene 2,5-furandicarboxylate and butylene succinate oligomer mixtures to be used as monomers for ROP were prepared by high dilution condensation and enzymatic cyclization reactions, respectively. Two different catalytic systems, tin dioctanoate and supported *Candida antarctica* lipase B (CALB) were used for polymerization. Thus two series of copolyesters covering the whole range of compositions were prepared and their properties comparatively examined. In both cases, random copolyesters with compositions close to those used in their respective feeds were obtained. The influence of composition on reaction kinetics regarding time and temperature was evaluated for the two series. Chemically catalyzed ROP rendered copolyesters with M_w in the ~50,000-65,000 g·mol^{-1} range whereas values between 15,000 and 45,000 g·mol^{-1} were attained when the ROP reaction was assisted by CALB. The thermal behavior of *co*PBF$_x$S$_y$ obtained by ROP was similar to that reported for such copolymers prepared by melt polycondensation. All they start to decompose above 300 ºC and display melting enthalpy and temperatures decreasing with copolymerization and attaining minimum values when comonomer contents approximate to balance. On the contrary, the glass-transition temperature increased almost linearly with the content in butylene furandicarboxylate units covering the whole range of values between those of the two parent homopolyesters. Small deviations in thermal properties observed between the two series could be attributed to their differences in molecular weights. Hydrolytic and enzymatic degradation studies revealed that *co*PBF$_x$S$_y$ became more degradable for increasing contents in succinic units whereas the homopolyester PBF remained practically unaffected when incubated under similar conditions.



Publication derived from this work:

J.C. Morales-Huerta, C.B. Ciulik, A. Martínez de Ilarduya, S. Muñoz-Guerra. Fully bio-based aromatic-aliphatic copolyesters: poly(butylene furandicarboxylate-*co*-succinate)s obtained by ring opening polymerization. *Polym. Chem.,* **2017,** *8*, 748-760. **(RSC Open Access Article).**

VI.1.1 Introduction

2,5-Furandicarboxylic acid (FDCA) is an aromatic diacid that is industrially prepared by catalytic oxidation of 5-methylfurfural, an aldehyde easily obtained from naturally-occurring hexoses. FDCA stands out as a highly promising bio-based monomer able to replace traditional aromatic diacids of fossil-fuel origin in the production of polyesters and other polycondensates.[1-3] It is the aromatic nature of the furanic ring that provides stiffness enough to the molecule as to be able to substitute the phthalate units without deleterious effect on chain mobility. The excellence of FDCA for the preparation of bio-based polyesters and other condensation polymers has been evidenced in a worthy review recently published by Sousa et al.[4] Up to date, several poly(alkylene 2,5-furandicarboxylate)s homopolyesters have been synthesized and it has been shown that their properties compare well with those displayed by their poly(alkylene terephthalate)s analogs. In addition FDCA, either as diacid itself or as its dimethyl ester, has been copolymerized with a number of either aromatic or aliphatic diacids to render furanoate containing copolyesters with satisfactory properties.[5-8]

Poly(butylene succinate) (PBS) is a fully bio-based aliphatic polyester that is reaching amazing popularity because it displays a competent pattern of thermal and mechanical behavior in addition to be fully bio-based and biodegradable.[9-11] Copolymerization has been the approach frequently used to render PBS based materials with higher performance, in particular with improved thermal properties.[12-15] This is by no means an easy challenge provided that the bio-based character has to be retained since renewable compounds with the suitable constitution for the purpose are scarcely available. Recently, several copolyesters of PBS containing monocyclic or bicyclic carbohydrate units with improved thermal properties and displaying biodegradability have been reported.[16-20] Nevertheless, the use of FDCA as comonomer of succinic acid (SA) to produce fully based aromatic-aliphatic copolyesters has been scarcely investigated. To our knowledge the contribution by Wu et al.[6] describing a series of poly(butylene furandicarboxylate-*co*-succinate) copolyesters, the work made by

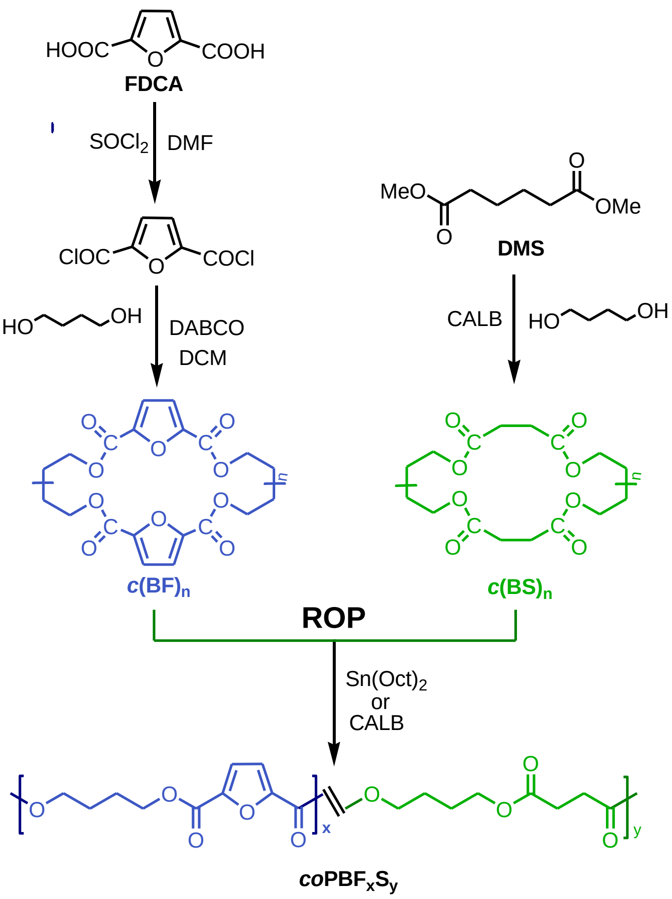
Jacquel et al.[8] bringing into evidence the biodegradability of some of these copolymers, and the recent paper by Lomelí-Rodríguez et al.[21] on poly(propylene furandicarboxylate-*co*-succinate)s copolyesters are the only references dealing with these systems that are available in the accessible literature.

Until very recently the polymerization method invariably applied for the synthesis of both PBF and PBS copolyesters was the conventional melt polycondensation using either the diacid or the dimethyl ester of FDCA and SA.[22-25] The application of the ROP method to the synthesis of PBS was reported for the first time by Japanese researchers using as feed a mixture of cyclic butylene succinate oligomers that were either synthesized by enzymatic cyclization[26-28] or recovered as a subproduct in the preparation of PBS by melt polycondensation.[29] On the other hand, the first papers reporting on the synthesis of PBF homopolyesters by ROP were published at the end of last year,[30,31] and the first work using ROP for the preparation of PBF copolyesters has just brought out; in this work a series of poly(butylene furandicarboxylate-*co*-terephthalate) copolyesters was synthesized and their properties evaluated as a function of the comonomer composition.[32]

Entropically driven ring opening polymerization (ED-ROP) is a well-stablished technique that has been successfully used for the polymerization of cyclic oligoesters.[33-35] Specific advantages of ROP are a high polymerization rate that allows applying relatively mild reaction conditions and the low generation of reaction coproducts with subsequent minimization of undesirable discoloration. In this paper we applied for the first time the ED-ROP methodology to the synthesis of fully bio-based aromatic-aliphatic poly(butylene furandicarboxylate-*co*-succinate) copolyesters (*co*PBF$_x$S$_y$). The synthesis of the cyclic oligomers required for feeding has been accomplished by cyclization condensation and their copolymerization was performed in the bulk using either tin dioctanoate (chemical process) or supported *Candida antarctica* (enzymatic process). The two ROP processes are critically compared and the two respectively produced copolyester series are extensively characterized; in particular their thermal properties are evaluated and collated to each other as well as to those reported for the same polymers obtained by conventional melt polycondensation.

VI.1.2 Results and discussion

The strategy followed in this work to produce the poly(butylene 2,5-furandicarboxylate-*co*-succinate) copolyesters is depicted in Scheme 6.1.1. Firstly cyclic oligomers of both butylene 2,5-furandicarboxylate, *c*(BF)$_n$, and butylene succinate, *c*(BF)$_n$, were synthesized, and secondly, mixtures of the two types of cycles were polymerized through ring opening reaction either chemically or enzymatically catalysed.



Scheme 6.1.1. Synthesis route to poly(butylene furandicarboxylate-*co*-succinate) copolyesters by ROP.

Synthesis of cyclic oligomers: In a recent work we reported for the first time on the synthesis of cyclic (butylene 2,5-furandicarboxylate) oligomers by both high dilution condensation (HDC) and cyclodepolymerization (CD) methods. Both methods were suitable for $c(\mathrm{BF})_n$ synthesis but the former afforded the oligomeric mixture in slightly higher yield and more enriched in the cyclic dimer.[31] In the present work we have made use of the HDC method to produce the $c(\mathrm{BF})_n$ with the results shown in Table 6.1.1. After purification by column chromatography, the ^{1}H NMR analysis (Figure 6.1.1a) was in full agreement with the expected structure and showed no signal arising from linear species. The HPLC chromatogram (Figure 6.1.1b) displayed three peaks corresponding to cyclic dimer, trimer and tetramer in an approximate ratio 8:4:1 although the MALDI-TOF analysis (Figure 6.1.1c) revealed the presence of cyclic species of higher sizes in minor amounts. Nevertheless, this mixture without further fractionation was used for ROP since our previous kinetics study on the polymerization of $c(\mathrm{BF})_n$ showed no relevant differences when cycles of different sizes or their mixtures were used for feeding.[31]

On the other hand, the synthesis of $c(\mathrm{BS})_n$ was enzymatically performed and the obtained results are given in Table 6.1.1. We applied the method reported by Sugihara *et al.*[26] which consists of cyclizing a mixture of BD and DMS dissolved in toluene by the action of CALB. The ^{1}H NMR and MALDI-TOF spectra as well as the HPLC chromatogram of the cyclization reaction product without being subjected to purification are shown in Figure 6.1.2. The mixture is composed almost exclusively of cyclic species with sizes ranging from dimer to nonamer; cyclic dimer, trimer and tetramer are in an approximate 5:4:1 ratio, and their sum amounts more than 90% of the total oligomers present in the mixture. Here again the oligomer mixture without fractionation was used for ROP since kinetics studies carried out by Kondo et al.[36] have shown that polymerization results are not substantially affected by cycle size.

Both *c*(BF)$_n$ and *c*(BS)$_n$ mixtures are white semicrystalline powders with melting temperatures at 147 °C and 105 °C, respectively. They start to decompose by effect of heating at temperatures above 250 °C following a single-step degradation process that display its maximum rate at temperatures between 300 and 400 °C. The TGA traces recorded from these mixtures along with their derivative curves are available in the ESI file (Figure C.1.3).

Table 6.1.1. Cyclization reaction results.

	Method[a]	**Yield (%)**	**Composition**[b] **(2/3/4)**	**T_m**[c] **(°C)**	**$^{o}T_{5\%}$**[c] **(°C)**	**T_d**[c] **(°C)**
***c*(BF)$_n$**	HDC	67	61/31/8	147	276	387
***c*(BS)$_n$**	EC	70	50/40/10	105	266	340

[a] HDC: High dilution cyclization using DABCO/Et$_3$N; EC: Enzymatic cyclization using CALB.
[b] Relative content (w/w) of the reaction product in cyclic dimer, trimer and tetramer as measured by HPLC.
[c] Melting and decomposition temperatures measured by DSC and TGA.

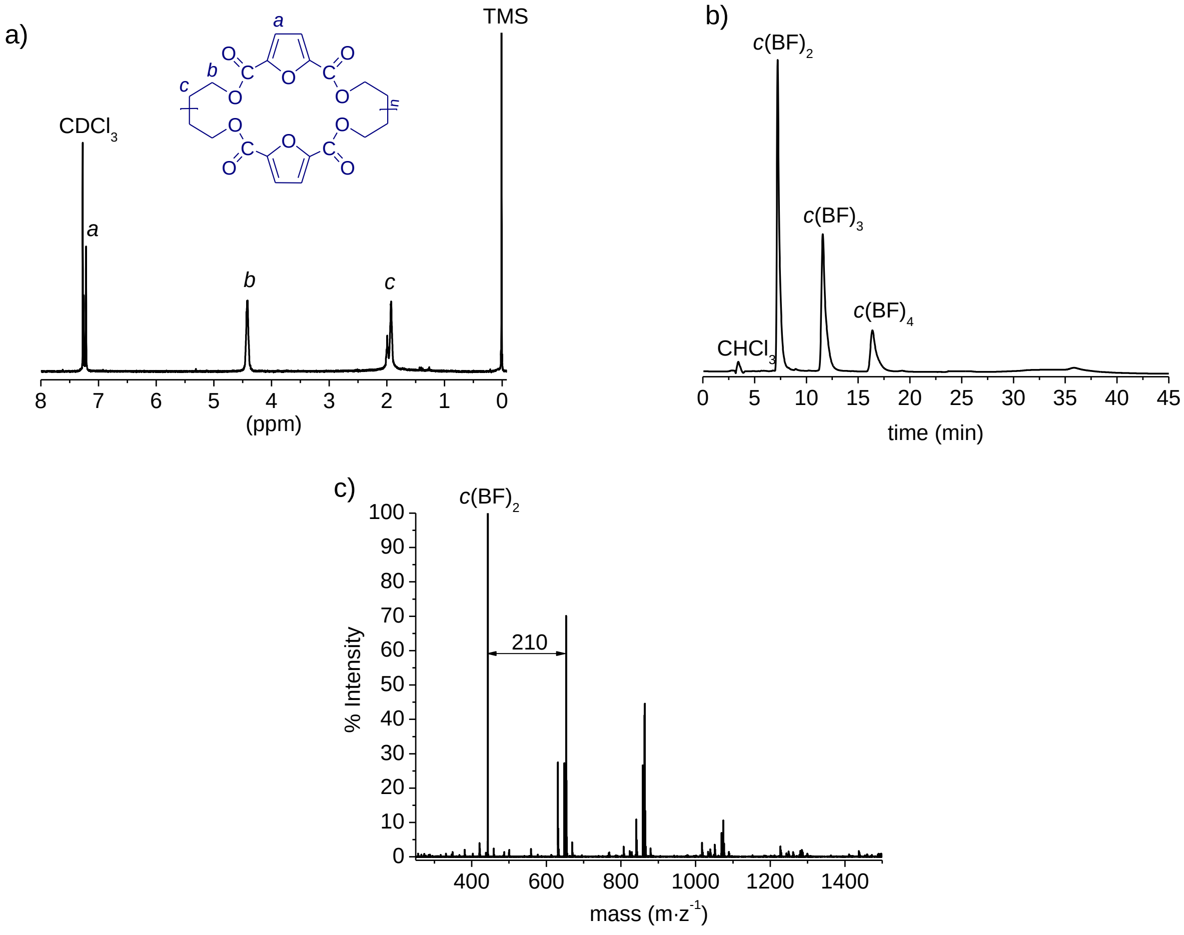


Figure 6.1.1. (a) ^{1}H NMR, (b) HPLC and (c) MALDI-TOF spectra for *c*(BF)$_n$.

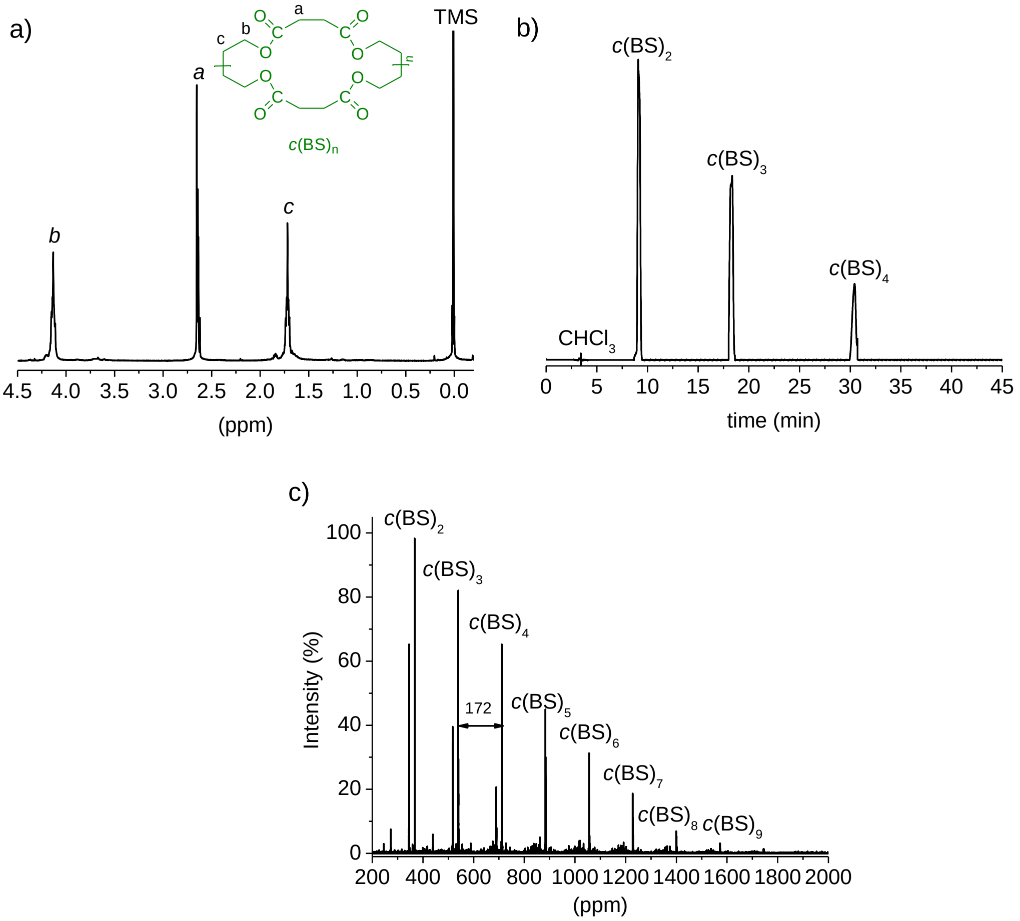


Figure 6.1.2. (a) ^{1}H NMR, (b) HPLC and (c) MALDI-TOF spectra for *c*(BS)$_n$.

Synthesis of *co*PBF$_x$S$_y$ copolyesters

ROP catalysed by tin octanoate: The polymerization of mixtures of *c*(BF)$_n$ and *c*(BS)$_n$ catalysed by tin octanoate was performed at temperatures above melting of the oligomer mixtures. The effect of temperature on polymerization rate was indirectly evaluated by measuring the molecular weight of the polyesters obtained after 12 h of reaction at different temperatures. Three *c*(BF)$_n$/*c*(BS)$_n$ ratios (80/20, 50/50 and 20/80) in addition to the two pristine cyclic oligomer fractions were examined. The results are shown in Figure 6.1.3a where M_w is plotted against six temperatures increasing by 10 ºC from 180 up to 230 ºC. In general a steady increase in molecular weight of the resulting polymer was observed for all compositions as the temperature was raised. It was noticeable however that the M_w of both the copolyester *co*PBF$_{80}$S$_{20}$ and the homopolyester PBF gave up at temperatures above ~200 ºC probably due to the higher thermal sensitivity to degradation of furan-based compounds. Nevertheless, the relevant outcome of this study is that the molecular weight of the resulting polyester increases with the content of the feed in *c*(BF)$_n$ at whichever reaction temperature. This result brings into evidence the higher reactivity of the furan-based cyclic oligomers in chemically catalysed ROP.

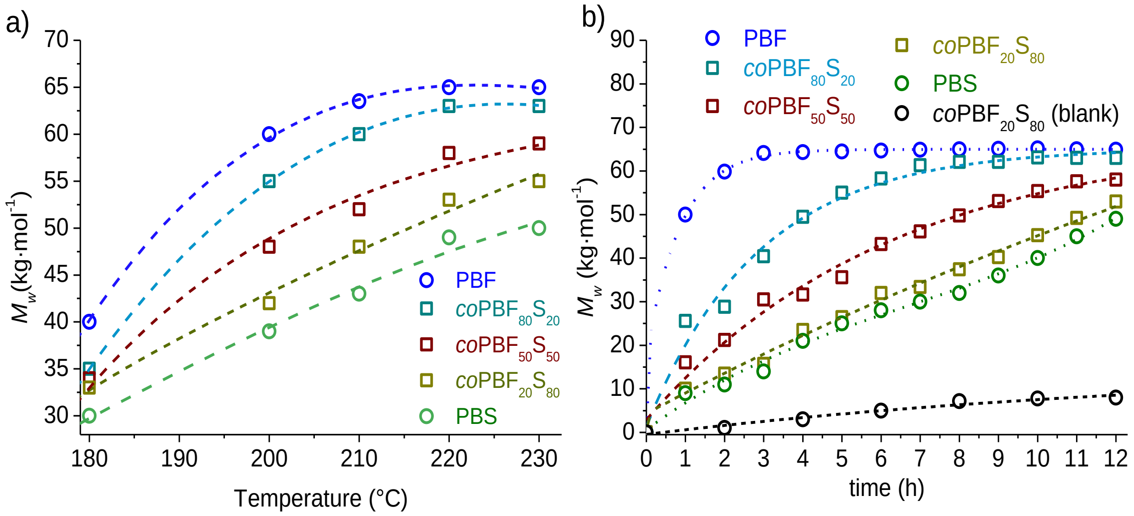


Figure 6.1.3. Effect of temperature and time on Sn(Oct)$_4$ catalyzed ROP of mixtures of *c*(BF)$_n$ and *c*(BS)$_n$ carried out in the melt. a) M_w of *co*PBF$_x$S$_y$ against reaction temperature after 12 h of reaction time. b) Evolution of M_w with reaction time at 220 ºC.

The evolution of the molecular weight along reaction time was then examined for the polymerization of the same oligomer cyclic mixtures carried out at 220 ºC and the obtained results are shown in Figure 6.1.3b. The trends showed by PBF and PBS are remarkably different; the *c*(BF)$_n$ fraction polymerized initially very fast to reach an almost constant molecular weight of about 65,000 g·mol^{-1} after 2-3 h of reaction whereas *c*(BS)$_n$ polymerized following a nearly linear trend to render a PBS with a M_w near 45,000 g·mol^{-1} after 12 h of reaction. The behaviour observed for the copolyesters were intermediate between those displayed by the two homopolymers with the profile being closer to one or the other according to composition.

ROP catalysed by *Candida Antarctica:* The ROP of mixtures of *c*(BF)$_n$ and *c*(BS)$_n$ catalysed by lipase *Candida antarctica* was carried out in the bulk with the fixed CALB dispersed in the molten reaction mass. The kinetics study carried out on this system was similar to that described above for the chemically catalysed ROP, *i.e.* the influence of both temperature and time on the molecular weight of the growing polyester was evaluated for different compositions. However essays conditions had to be adapted to the limitations imposed by the use of the enzyme. The temperature had to be restricted to the 120-150 ºC range because below 120 ºC the mixture was not fully molten and above 150 ºC the enzyme activity was rapidly lost. This prevented the preparation by this method of polyesters with melting temperatures above 150 ºC as it is the case of both PBF and the copolyester *co*$PBF_{90}S_{10.}$ Results obtained after 24 h of reaction at temperatures of 120, 130, 140, 145 and 150 °C, are plotted in Figure 6.1.4a.

The trend followed by molecular weight with increasing reaction temperature was not so predictable as in the case of chemocatalyzed ROP. The profile shape changed significantly with composition and differences among M_w values largely vary with temperature. Notwithstanding it was interestingly noticed that polymer growing catalyzed by *C. antarctica* was more favoured as the content in butylene succinate increased, which is exactly opposite to the behaviour observed in tin catalysed reactions. In fact minimum M_w values were reached at any essayed temperature for the $PBF_{80}S_{20}$, which is the copolyester with the highest content in butylene furandicarboxylate units attainable by this method.

The evolution of the molecular weight of the polyesters with time in the CALB assisted ROP of $c(BF)_n/c(BS)_n$ mixtures at 150 ºC along a period of 24 h is depicted in Figure 6.1.4b. The M_w vs time profiles are of similar shape for the four essayed polyesters with the slope decreasing with the content in BF units. Differences in polymerization rate become more apparent as the reaction progress and the molecular weights reached at the end of the process were lower or higher than those obtained by chemocatalysis depending on composition.

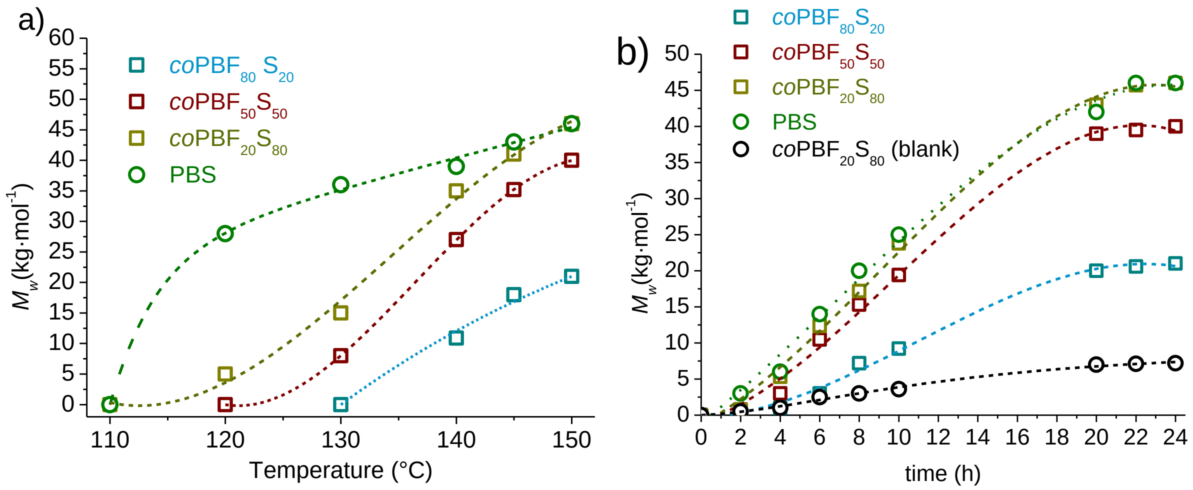


Figure 6.1.4. Effect of temperature and time on CALB assisted ROP of mixtures of *c*(BF)$_n$ and *c*(BS)$_n$ in the melt. a) M_w of PBF$_x$S$_y$ against reaction temperature for a reaction time of 24 h. b) Evolution of M_w with reaction time at 150 ºC.

Table 6.1.2. Yields, compositions, average molecular weights, and microstructure of *co*PBF$_x$S$_y$ copolyesters obtained *via* chemical and enzymatic ROP.[a]

Copolyester	**Yield (%)**	**Composition[b] X_{BF}/Y_{BS} (mol/mol)**	**Molecular weight[c]**			**Dyad content[d] (%-mol)**			**Average sequence length[e]**		**R^e**
			M_w (g·mol^{-1})	**Đ**	**[η] (dL·g^{-1})**	**FBF**	**FBS+SBF**	**SBS**	**n_{BF}**	**n_{BS}**	
PBF	95	100/0	65,000	1.98	0.76	-	-	-	-	-	-
	-	100/0	-	-	-	-	-	-	-	-	-
*co*PBF$_{90}$S$_{10}$	92	94/6	64,000	1.79	0.74	93.2	2.6	4.2	6.58	1.30	0.92
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
*co*PBF$_{80}$S$_{20}$	93	84/16	63,000	1.85	0.74	66.7	28.2	5.1	5.73	1.36	0.91
	65	81/19	21,000	1.30	0.25	67.8	25.2	7.0	6.38	1.56	0.80
*co*PBF$_{60}$S$_{40}$	90	65/35	62,000	1.90	0.71	39.5	48.8	11.7	2.62	1.48	1.06
	70	58/42	23,000	1.30	0.30	35.3	45.1	19.6	2.57	1.87	0.92
*co*PBF$_{50}$S$_{50}$	90	51/49	58,000	1.79	0.62	27.0	48.6	48.7	2.11	2.00	0.97
	91	49/51	40,000	1.60	0.55	15.7	47.6	36.6	1.66	2.53	0.99
*co*PBF$_{40}$S$_{60}$	90	43/57	56,000	1.95	0.65	16.7	52.2	31.1	1.64	2.19	1.07
	92	41/59	43,000	1.70	0.55	13.4	41.3	65.9	1.65	3.19	0.91
*co*PBF$_{20}$S$_{80}$	89	22/78	53,000	1.90	0.54	5.2	31.3	63.5	1.33	5.06	0.95
	91	22/78	46,000	1.50	0.53	3.2	33.7	63.0	1.19	4.73	1.05
*co*PBF$_{10}$S$_{90}$	88	12/88	53,000	1.89	0.60	11.9	29.2	88.1	1.22	6.03	0.98
	91	11/89	47,000	1.50	0.53	1.7	13.6	91.4	1.25	13.45	0.88
PBS	95	0/100	49,000	1.97	0.55	-	-	-	-	-	-
	92	0/100	46,000	1.40	0.51	-	-	-	-	-	-

[a] Copolyesters synthesized using Sn(Oct)$_2$ (top row) and CALB (bottom row).
[b] Copolyester compositions determined from signals observed in the ^{1}H NMR spectra.
[c] *M_w, Đ;* and η determined by GPC and Ubbelohde viscosity, respectively.
[d] Determined by integration of the α-methylene signals in the butylene segments in ^{13}C NMR spectra.
[e] Average lengths of homogeneous BF and BS sequences and ramdoness (*R*) calculated by applying statistical approach.[37]

In order to appraise the possible occurrence of self-polymerization of the *c*(BF)$_n$/*c*(BS)$_n$ by ring opening reaction induced by heating, a series of blank essays, *i.e*, essays conducted under the same reaction conditions but in absence of any catalyst, was carried out with the mixture *c*(BF)$_n$/*c*(BS)$_n$ (20:80). The profiles M_w *vs* either temperature or time that were obtained from these essays under chemically or enzymatically catalyzed conditions are included in Figures 6.1.3b and 6.1.4b for comparison. The highest molecular weight reached in these essays was about 5,000 g·mol^{-1} corresponding to oligomers of about 10 monomeric units. The ^{1}H NMR spectra of the feeding mixture and the reaction product of the ROP carried out either without catalyst or in the presence of CALB are compared in Figure 6.1.5. This comparison reveals that *c*(BF)$_n$ remained unreacted in the blank whereas an appreciable amount of *c*(BS)$_n$ cycles disappeared. Conversely, both *c*(BF)$_n$ and *c*(BS)$_n$ reacted almost completely in the presence of CALB.

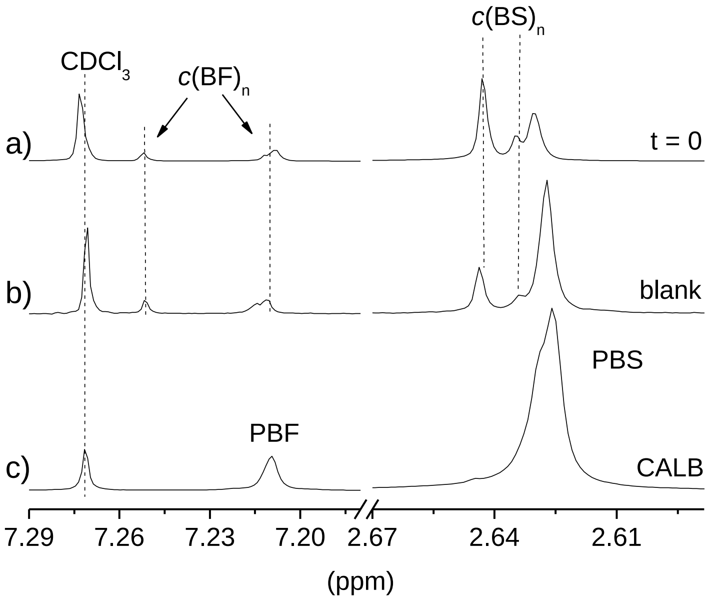


Figure 6.1.5. Enlarged 7.3-7.18 and 2.68-2.60 ppm regions of ^{1}H NMR spectra of the initial *c*(BF)$_n$/*c*(BS)$_n$ (20:80) mixture (a), after reaction at 150 ºC for 24 h in the absence of catalyst (b), and with CALB added (c).

Chemical structure and microstructure of copolyesters: The chemical structure including both composition and microstructure as well as the molecular weight of the homopolyesters and copolyesters obtained by the two ROP methods applied in this work were systematically determined, and results are gathered in Table 6.1.2. These data refer to polyesters synthesized with $Sn(Oct)_2$ as catalyst at 230 ºC for 12 h, and to those synthesized with the concourse of CALB at 150 ºC for 24 h. The chemical constitution of all the polyesters was ascertained by NMR spectroscopy. The ^{1}H NMR spectra of the copolyester $PBF_{50}S_{50}$ prepared by either chemo-ROP or enzym-ROP are shown in Figure 6.1.6 for illustrative purposes. Both spectra are almost undistinguishable with all peaks dully assigned and displaying no signal from other than those expected for the predicted chemical constitution. Both the ^{1}H and ^{13}C NMR spectra of the two whole sets of synthesized polyesters are given in the annex (Figure C.1.1).

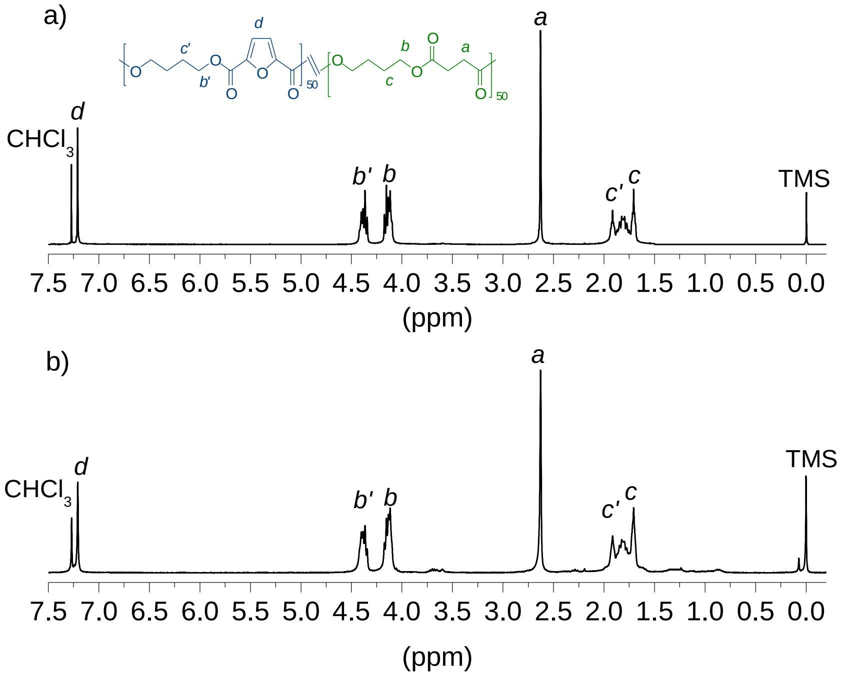


Figure 6.1.6. ^{1}H NMR of *co*$PBF_{50}S_{50}$ obtained by (a) chemically and (b) enzymatically catalyzed ROP.

The molar composition in BF and BS units of the two series of copolyesters was determined by quantification of the signals *b* and *b*' arising from the α-methylene of the butylene furandicarboxylate and butylene succinate units, respectively, and the found values are listed in Table 6.1.2. A comparative inspection of the feed and copolyester compositions reveals that deviations between them are higher when ROP is chemically catalysed, and that in this case, they correspond to BS unit losses. Furthermore, differences become more noticeable as the content in BF increases with the loss in BS becoming around 40% for the *co*PBF$_{90}$S$_{10}$ copolyester. Conversely, the observed deviations were lesser than 5% for the copolyesters synthesized by enzymatically assisted ROP. These results are consistent with the different relative reactivity appreciated for the *c*(BF)$_n$ and *c*(BS)$_n$ species in the two polymerization methods although reasons due to differences in volatility should not be fully neglected provided that much higher temperatures are used in the chemical procedure.

The molecular weights measured by GPC against polystyrene standards were in the 65,000-50,000 and 47,000-20,000 g·mol^{-1} ranges for polyesters obtained by chemical and enzymatic catalysed ROP with dispersities significantly lower in the latter case. Intrinsic viscosities were in agreement with M_w values determined by GPC. The trends observed for molecular weights in the two series are opposite to each other according again to the different relative reactivities displayed by *c*(BF)$_n$ and *c*(BS)$_n$ in each of the two polymerization methods..

The microstructure of the copolyesters was elucidated by ^{13}C NMR analysis taking benefit of the sensitivity of the α-carbon of the butylene segment to the sequence at the dyad level. The four possible dyads FBF, SBS, and FBS/SBF appear within the 60.5-58.5 ppm region (Figure C.1.4) as four well resolved peaks whose areas were integrated for each copolyester composition and the resulting values used in the corresponding equations to calculate the number average sequence length.

The results are listed in Table 6.1.2 for the two copolyester series where it can be seen that the n_{BF} and n_{BS} values vary steadily with composition in opposite directions and both approximate to 2 for the 50/50 composition. The degree of randomness is between 0.9 and 1.1 indicating that an approximate random distribution of BF and BS units is present in all the copolyesters. The conclusion that a *co*PBF$_x$S$_y$ random copolyester is genuinely generated in the ROP of mixtures of *c*(BF)$_n$ and *c*(BS)$_n$ whether it is chemically or enzymatically catalyzed cannot be straightforwardly drawn from such results since randomization by transesterification is very probable to occur at the high temperatures used in these processes. In order to clarify this point, ROP of the *c*(BF)$_n$/*c*(BS)$_n$ (50:50) mixture assisted by CALB was accomplished in solution at 50 ºC, a temperature at which the occurrence of transesterification reactions may be neglected.

The *co*PBF$_{50}$S$_{50}$ copolyester resulting in these conditions was obtained in a 80% yield and had a M_w of 14,000 g·mol^{-1} and a *Đ* of 1.8. Its ^{13}C NMR spectrum was similar to that recorded from the copolyester obtained a high temperature; specifically, no differences can be appreciated when they are compared in the 60.5-58.5 ppm region (Figure 6.1.7, inset). It can be concluded therefore that ROP of *c*(BF)$_n$/*c*(BS) renders random copolyesters whichever are the applied reaction conditions.

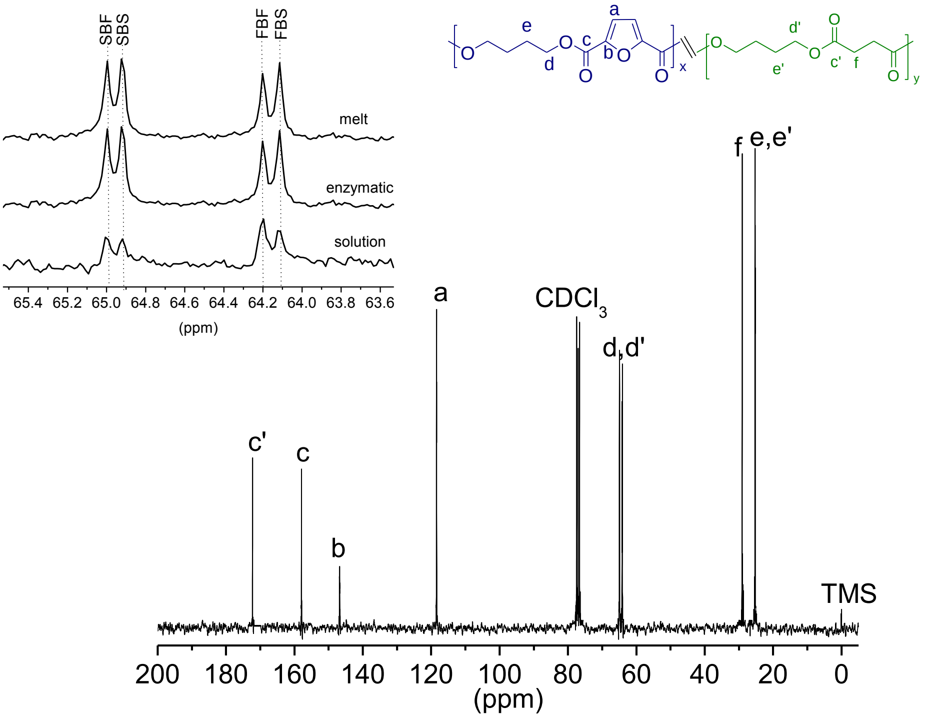


Figure 6.1.7. ^{13}C NMR of *co*PBF$_{50}$S$_{50}$ obtained by ROP at 50 ºC in solution catalyzed by Sn (Oct)$_2$. Inset: Enlarged 60.5-58.5 ppm region compared for different methods of polymerization.

Thermal properties: The thermal properties of the polyesters and copolyesters composing the two series prepared by ROP were comparatively examined by TGA and DSC, and the most relevant parameters resulting from such study are collected in Table 6.1.3. Moreover, data are also compared with those reported by Wu et al., which were obtained from polyesters with similar compositions but prepared by two-step melt polycondensation.[6]

The TGA weight loss-*T* traces of all the polyesters synthesized in this work as well as their derivative curves are available in the annex (Figure C.1.5). In all cases thermal decomposition proceeded through a single step taking place within the 390-400 ºC range and without significant differences between the two series. The onset decomposition temperatures of the copolyesters were between 350 and 340 ºC, and polymers prepared by enzymatic ROP invariably started to decompose at a few degrees below those obtained by ROP catalysed by Sn(Oct)$_2$, which is reasonable due to their lower molecular weight.

The residue left after heating at 600 ºC under a nitrogen flow was significantly smaller in the enzymatically synthesized polyesters. This is a much expected result because the absence of metallic components in these polymers.

The thermal decomposition data obtained for the ROP synthesized *co*PBF$_x$S$_y$ are essentially coincident with those reported for this family of copolyesters obtained by polycondensation with slight differences in magnitudes being explainable by differences in molecular weight or experimental inaccuracy.

Table 6.1.3. Thermal properties of *co*PBF$_x$S$_y$^{a}

Copolyester	TGA^b			DSC^c				
	^oT_d (°C)	$^{max}T_d$ (°C)	W (%)	T_g (°C)	T_m^1 (°C)	ΔH_m^1 (J·g^{-1})	T_m^2 (°C)	ΔH_m^2 (J·g^{-1})
PBF	370	400	7	42	170	40	170	35
	-	-	-	-	-	-	-	-
*co*PBF$_{90}$S$_{10}$	350	395	8	28	166	38	164	30
	-	-	-	-	-	-	-	-
*co*PBF$_{80}$S$_{20}$	350	395	7	23	146	33	146	27
	348	396	5	20	140	15	140	17
*co*PBF$_{60}$S$_{40}$	343	397	6	7	114	13	-	-
	342	397	5	5	126	7	-	-
*co*PBF$_{50}$S$_{50}$	349	400	5	-1	95	11	-	-
	341	399	1	-6	86	4	-	-
*co*PBF$_{40}$S$_{60}$	347	399	6	-13	60	6	-	-
	344	399	2	-20	72	10	-	-
*co*PBF$_{20}$S$_{80}$	343	399	5	-23	90	55	93	32
	338	400	3	-23	93	30	93	51
*co*PBF$_{10}$S$_{90}$	340	401	3	-23	100	71	105	49
	337	400	2	-25	102	55	103	63
PBS	350	399	3	-30	112	106	114	82
	348	398	3	-40	112	60	111	87

^{a}Values in upper and lower rows correspond to polyesters obtained by tin and lipase catalyzed ROP, respectively.

^{b} ^oT_d is the onset degradation temperature for 5% of weight lost and $^{max}T_d$ is temperature at which degradation happens at the maximum rate.

^{c}1 and 2 refer to data registered at first heating and second heating, respectively.

The thermal transitions, *i.e.* glass and melting/crystallization, were examined by DSC. The DSC traces of the two series registered at heating and cooling from the melt are included in the annex (Figure C.1.6) and the thermal parameters there measured are listed in Table 6.1.3. All the pristine copolyesters displayed crystallinity with enthalpy values decreasing as the content in BF and BS units becomes more equilibrate so that only those copolyesters containing more than 40% of one or another unit are able to crystallize from the melt. A representative selection of polarizing optical micrographs showing the crystalline textures displayed by these copolyesters upon crystallization are available in the annex file (Figure C.1.7). The XRD analysis of the copolyesters gave results in agreement with DSC data. The scattering profiles registered from crystalline *co*PBF$_x$S$_y$ and from the two homopolyesters PBF and PBS prepared by chemically catalyzed ROP are compared in Figure 6.1.8. It is clearly seen that the characteristic scattering produced by one or another homopolyester is present in the copolyesters profiles with more or less intensity depending on composition. For BF/BS ratios close to one, the crystallinity becomes so low that not discrete scattering is perceivable on the XRD profiles of the copolyesters. As it is commonly found, the crystal structure of the homopolyesters is fully retained by the copolyesters containing limited amounts of the second comonomer, beyond which they become essentially amorphous.

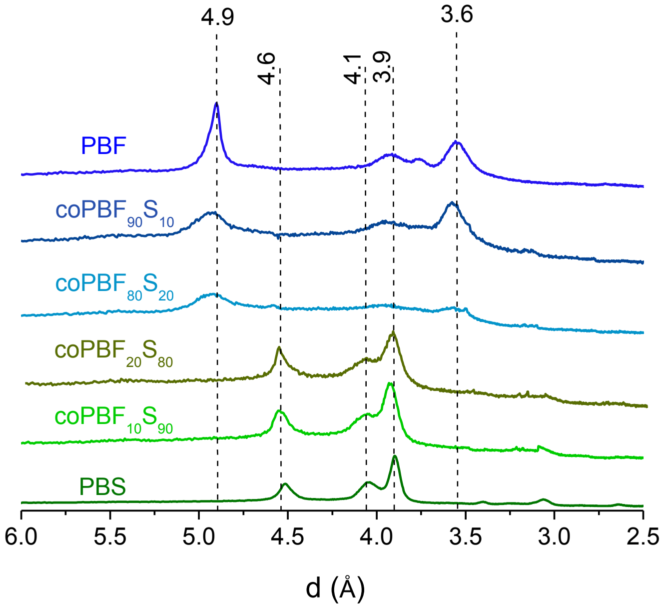


Figure 6.1.8. Powder X-ray diffraction profiles of *co*PBF$_x$S$_y$ synthesized by ROP with Sn(Oct)$_2$.

Melting and glass-transition temperatures of *co*PBF$_x$S$_y$ copolyesters are properties of high relevance regarding their possible applications as thermoplastics. The consequence of incorporating the furanoate units in the PBS is to modify both T_m

and T_g. The variation of T_m with composition for the two series of *co*PBF$_x$S$_y$ copolyesters respectively prepared by the two ROP methods here described is plotted in Figure 6.1.9a. In this plot, it is clearly shown how T_m decreases along the BS-high composition range to invert the trend when the copolyester starts to become enriched in BF units. This behavior is very similar for the two series, and also similar to that described for the same copolyesters prepared by melt polycondensation with the slight deviations observed among them being attributable to differences in molecular weights or of experimental origin. A similar trend is observed for the melting enthalpy which is readily explained by the incompatibility of BF and BS to cocrystallize. Nevertheless it is worthy to notice the presence of some crystallinity in the copolyesters containing approximately similar amounts of the two units, which brings into evidence the ability of BF and BS short sequences for crystallizing. A similar behavior has been recently reported for random copolyesters made of butylene furanoate and butylene terephthalate units.[32]

All the copolyesters display single T_g in agreement with the random monomer distribution determined by NMR. T_g variation with composition is plotted in Figure 6.1.9b for the two series as well as for the series made by melt polycondensation reported by Wu et al.[6] In all cases the T_g of PBS goes up continuously with the content in BF units according to that should be expected for the increase in chain stiffness. These results demonstrate the possibility of tuning the T_g of the copolyesters by adjusting the composition. Again small discrepancies are observed among copolyesters produced by different procedures. Such deviations become more apparent for the copolyesters with intermediate compositions produced by enzyme catalyzed ROP, which are those presenting higher differences in molecular weight.

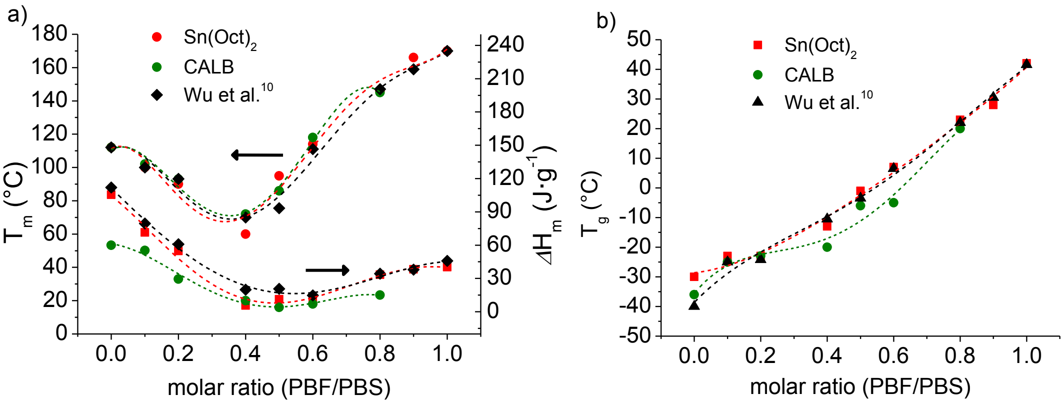


Figure 6.1.9. T_m (a) and T_g (b) of *co*PBF$_x$S$_y$ as a function of composition. Data reported by Wu et al.[6] are also plotted for comparison.

Hydrolytic and enzymatic degradation: It has been reported that PBS is hydrolysable and also biodegradable[17,38,39] whereas PBF is known to be high resistant to hydrolysis and apparently insensitive to biodegradation,[40] in agreement with the behaviour commonly displayed by aromatic polyesters. It is also known that the degradability of aromatic polyesters may be enhanced by inserting at random aliphatic ester units in the polymer chain. In fact the enzymatic degradation of random poly(butylene furanoate-*co*-adipate) copolyesters has been recently demonstrated although a minimum content of 50% of adipate units were required to perceive the degradation effects.[40]

In order to evaluate the degradability of PBF as a function of the incorporation of succinate units, the homopolyesters PBF and PBS and the copolyesters *co*PBF$_{60}$S$_{40}$ and *co*PBF$_{40}$S$_{60}$ were subjected in parallel to degradation essays. Samples were incubated at 37 °C and either pH 2.0 or pH 7.4, in the latter case both in the presence and in the absence of porcine pancreas lipase. The changes taking place in both sample weight and molecular weight along an incubation period of 30 days were recorded and plotted in Figure 6.1.10. According to that has been reported, PBF remained practically unchanged under any essayed conditions whereas PBS was more or less degraded depending on pH and whether the enzyme is present or not and showing a maximum of losses at around 25%. As expected, the results obtained for the copolyesters were depending on composition with degradation being faster as the content in succinate units increased. The degradation rate of the copolyesters was similar at the two essayed pH's whereas a significant increase was observed in the presence of lipase where both sample weight and molecular weight losses arrived to be around 20%. The conclusion that may be drawn from this preliminary study is that the degradability of PBF can be increased and controlled by a proper adjustment of the amount of succinate units that are incorporated by copolymerization.

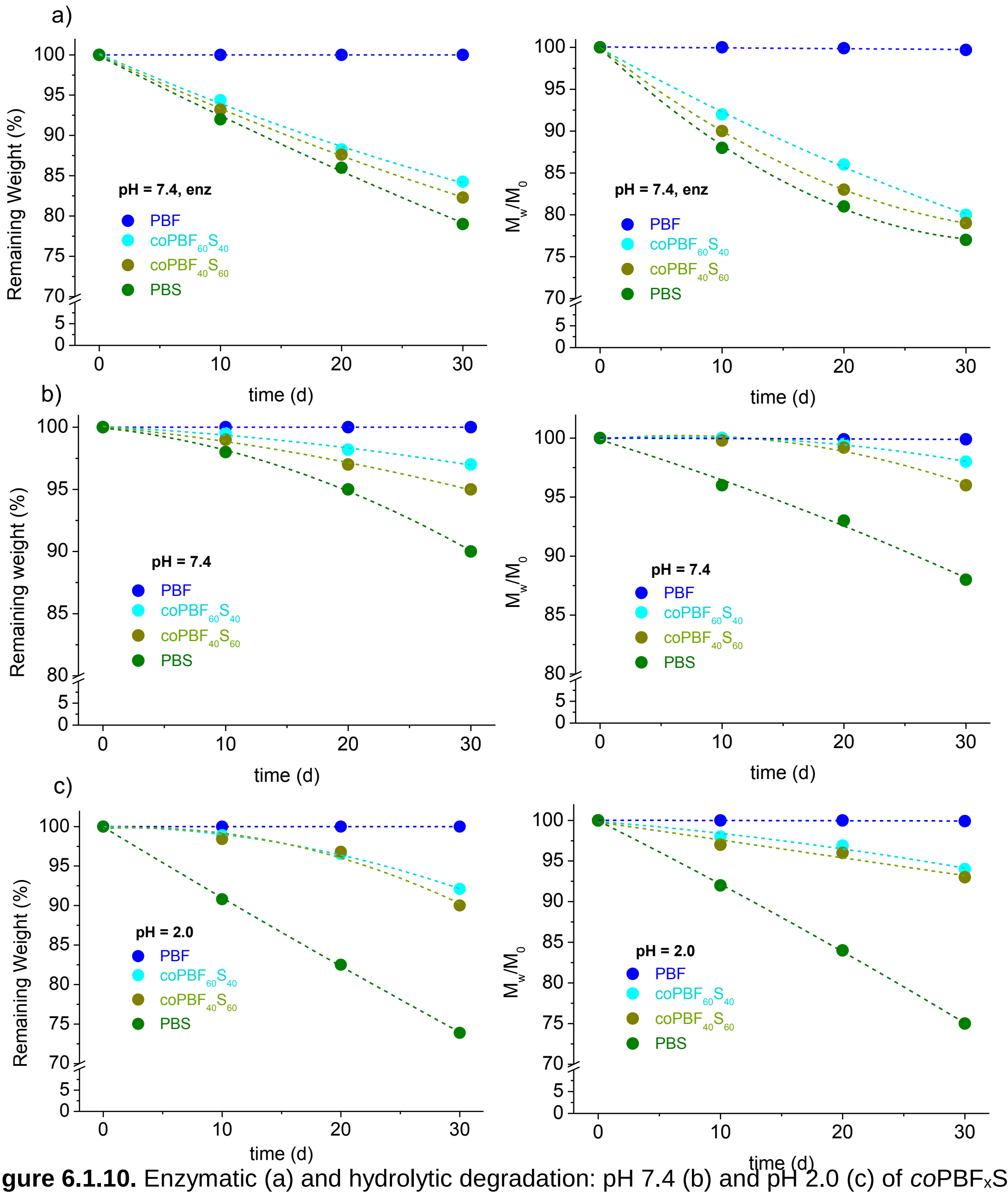


Figure 6.1.10. Enzymatic (a) and hydrolytic degradation: pH 7.4 (b) and pH 2.0 (c) of *co*PBF$_x$S$_y$. Remaining weight (left) and molecular weight (right) *vs* incubation time.

VI.1.3 Conclusions

The results attained in this work demonstrate for the first time that fully bio-based poly(butylene 2,5-furandicarboxylate-*co*-butylene succinate) copolyesters can be successfully synthesized by ROP. Furthermore, the reaction can be either chemically or enzymatically activated by using $Sn(Oct)_2$ or CALB as catalyst, respectively. A series of copolyesters covering the whole range of compositions including the two parent homopolyesters could be prepared by chemically catalyzed ROP whereas only the copolyesters containing up to 80%-mole of butylene furanoate units could be prepared by the enzymatic procedure. Nevertheless, the ROP method has been proven suitable for providing the poly(butylene 2,5-furandicarboxylate-*co*-succinate) copolyesters with high molecular weight under reaction conditions milder than those required for melt polycondensation. However significantly lower molecular weights are obtained when the ROP reaction is catalyzed by lipase. The composition of the copolyesters can be easily controlled by adjusting the composition of the feed and their microstructure is random in all cases. The differences in thermal properties between the two series (chemically and enzymatically catalyzed) are small and reasonable according to their differences in molecular weights. Comparison of our results with those reported by Wu et al,[6] for the same copolyesters produced by melt polycondensation leads to conclude that the ROP method is a promising option for the synthesis of the *co*PBF_xS_y copolyesters whose success will depend largely on the availability of the cyclic oligomers used for polymerization. The preliminary results obtained in this work on biodegradability will contribute to encourage the interest for these copolyesters as fully bio-based materials suitable for short-term applications.

VI.1.4 References

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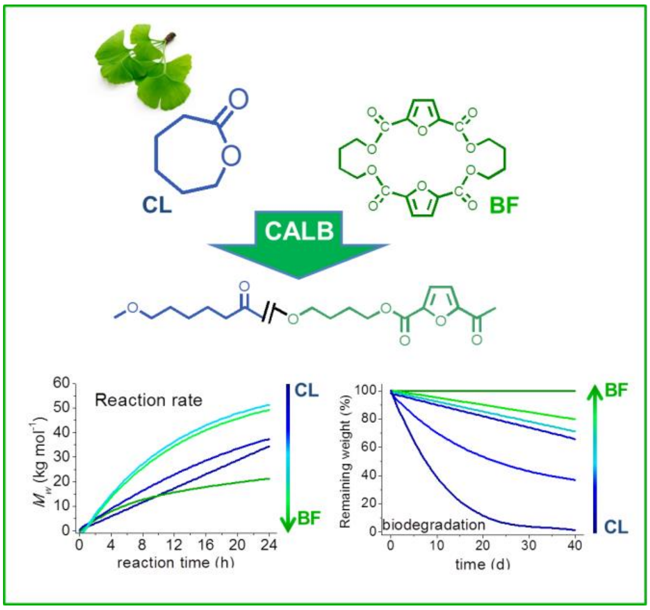
VI.II Poly(ε-caprolactone-*co*-butylene furanoate) copolyesters

Abstract: Cyclic oligo(butylene 2,5-furandicarboxylate) and ε-caprolactone were copolymerized in bulk at 130-150 ºC by enzymatic ring opening polymerization using CALB as catalyst. Copolyesters within a wide range of compositions were thus synthesized with weight-average molecular weights between 20,000 and 50,000, the highest values being obtained for equimolar or nearly equimolar contents in the two components. The copolyesters consisted of a blocky distribution of the ε-oxycaproate (CL) and butylene furanoate (BF) units that could be further randomized by heating treatment. The thermal stability of these copolyesters was comparable to those of the parent homopolyesters (PBF and PCL), and they all showed crystallinity in more or less degree depending on composition. Their melting and glass-transition temperatures were ranging between those of PBF and PCL with values increasing almost linearly with the content in BF units. The ability of these copolyesters for crystallizing from the melt was evaluated by comparative isothermal crystallization and found to be favored by the presence of flexible ε-oxycaproate blocks. These copolyesters are essentially insensitive to hydrolysis in neutral aqueous medium but they became noticeably degraded by lipases in an extend that increased with the content in CL units.



Publication derived from this work:

J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra. Blocky poly(epsilon-caprolactone-*co*-butylene 2,5-furandicarboxylate) copolyesters via enzymatic ring opening polymerization. *J. App. Polym. Sci. Pol. Chem.* **2018**, *56*, 290-299.

VI.2.1 Introduction

ROP (Ring Opening Polymerization) is a well-recognized polymerization method suitable for preparing polymers from cyclic monomers that may be opened by either enthalpical or entropical driving forces.[1,2] Although this procedure has been used for the synthesis of a great diversity of polymers, its application to the preparation of polyesters from lactones is by far the most widely known.[3,4] The milder reaction conditions required, the absence of volatile by-products, and the minimization of undesirable sub-products, are appreciated advantages of ROP over conventional polycondensation. Furthermore lipases seem to work particularly well as catalysts for the polymerization of lactones so that enzymatic Ring Opening Polymerization (*e*-ROP) is becoming a specialty of the method that reaches particular interest when green processing and sustainability are main synthesis concerns.[5-7]

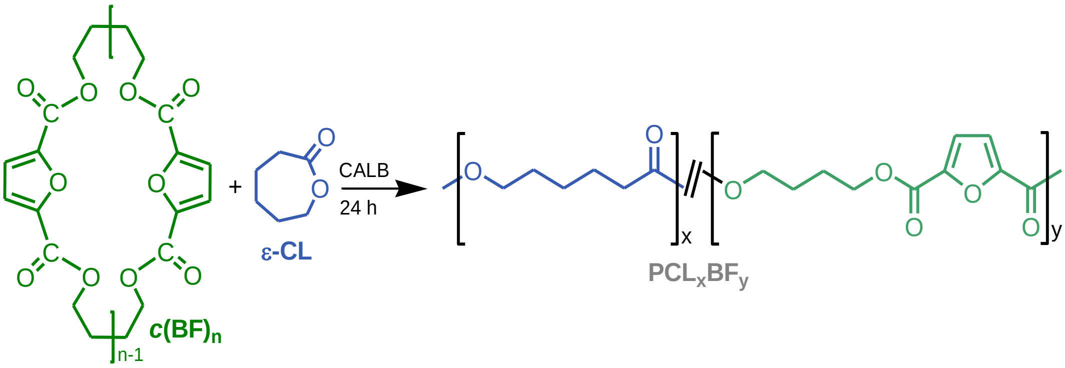
Poly(alkylene furanoate)s, specifically poly(ethylene 2,5-furandicarboxylate) (PEF) and poly(butylene 2,5-furandicarboxylate) (PBF), are aromatic polyesters of renewable origin that are highly fashionable because of their potential for replacing poly(alkylene terephthalate)s (PET and PBT) in their industrial applications.[8,9] The exceptional relevance of 2,5-furandicarboxylic acid (FDCA) as monomer for the synthesis of bio-based polyesters has been splendidly shown by Sousa *et al*. in a recent review.[10] Polyfuranoates are semicrystalline polymers that display high melting and glass-transition temperatures and that have barrier properties even better than poly(terephthalate)s. As it is characteristic of aromatic polyesters, PEF and PBF are highly resistant to hydrolysis and show very low biodegradability.[11,12] PEF and PBF are usually prepared by polycondensation of FDCA or its dimethyl ester (FDCA-Me) with ethylene glycol and 1,4-butanediol, respectively.[8] However the access to cyclic (alkylene 2,5-furandicarboxylate) oligomers ($c(\mathrm{EF})_n$ and $c(\mathrm{BF})_n$) recently afforded by chemical synthesis has opened the ROP route towards the preparation of these polyesters.[13,14] Additionally aromatic copolyesters made of butylene furanoate (BF) and butylene terephthalate (BT),[15] as well as aromatic-aliphatic copolyesters made from BF and butylene succinate (BS)[16] have been prepared by ROP in good yields with pretty high molecular weights. In these copolymerizations cyclic (butylene terephthalate) and (butylene succinate) oligomers were the respective comonomers of $c(BF)_n$, and tin octoate or/and supported lipases (CALB) were the catalysts used therein.

Poly(ε-caprolactone) (PCL) is a semicrystalline polyester of great interest in the biomedical field due to its excellent biocompatibility and exceptional biodegradability.[17,18] This polyester has however severe flaws derived from its low melting (~ 65 ºC) and its very low glass-transition (~-60 ºC) temperatures. PCL is invariably produced by ROP of ε-caprolactone by using either chemical or enzymatic methods. ROP copolymerization of CL with a wide variety of other cyclic monomers has been extensively examined with the purpose of designing PCL copolyesters with improved thermal and mechanical properties.[19-22] In this sense, the PCL copolyesters containing aromatic units and synthesized by ROP, as they are PCL-PHT[23] and PCL-PBT,[24] are particularly noteworthy in the present context. In these cases cyclic (hexamethylene terephthalate) ($c(HT)_n$ and cyclic (butylene terephthalate) ($c(BT)_n$ oligomers were copolymerized with CL at high temperature and in the presence of a tin catalyst to render random copolyesters with properties adjustable by composition.

In this paper we wish to report on copolyesters prepared by *e*-ROP of ε-caprolactone with butylene 2,5-furandicarboxylate. The approach followed in this work is again to design PCL copolyesters with improved properties but using a bio-based aromatic comonomer and applying a greener synthetic route. A series of copolyesters covering the almost full range of compositions are prepared and duly characterized, and their thermal properties and degradability evaluated as well. It should be mentioned that a set of PBF-PCL copolyesters with a similar chemical composition has been recently described by Zheng et al.[25] These copolyesters were prepared by a combination of polycondensation and ROP procedures and they have a microstructure made of soft and hard segments characteristic of thermoplastic elastomers.

VI.2.2 Results and disscusion

Synthesis of PCL$_x$BF$_y$ copolyesters by *e*-ROP: The method of synthesis used in this work for the preparation of copolyesters composed of 6-oxycaproate and butylene 2,5-furandicarboxylate units is based on the enzymatic ring opening polymerization (*e*-ROP) of mixtures of ε-caprolactone (CL) and a fraction of oligo(butylene 2,5-furandicarboxylate) cycles (*c*(BF)$_n$), as it is depicted in Scheme 6.2.1.



Scheme 6.2.1. Enzymatic Ring Opening Polymerization (*e*-ROP) reaction leading to PCL$_x$BF$_y$ copolyesters.

The oligomeric *c*(BF)$_n$ fraction was prepared by cyclocondensation of 1,4-butanediol and dimethyl 2,5-furandicarboxylate according to a procedure recently described by us.[14] It consisted exclusively of cyclic species and was obtained in around 70% yield with a molar composition of approximately 60:30:10 in dimer, trimer and tetramer, respectively. It melts at 147 ºC and starts to decompose slightly above 275 ºC. This oligomeric fraction was used as it is, *i.e.* without separation of their different size components. A comparative kinetics study on the cyclopolymerization of individual *c*(BF)$_n$ species leading to PBF homopolyesters showed although reactivity is higher for smaller cycle sizes, such differences are however not large enough as to warrant further fractionation.[14]

The polymerization reaction was carried out in bulk with both CL and *c*(BF)$_n$ in the molten state and the supported enzyme CALB suspended in the reaction mass. Reaction temperatures were set between 130 ºC, which is the minimum value required for melting the reactants, and 150 ºC, which is the maximum value compatible with enzyme activity. CL:*c*(BF)$_n$ mixtures with molar ratios covering the whole range of compositions were assayed for producing a complete palette of PCL$_x$BF$_y$ copolyesters.

However, copolyesters containing more than 80% of BF units as well as the PBF homopolyester could not be obtained by this procedure because of the too high melting temperature of these BF-enriched polyesters. In such cases the reaction mass became solid as soon as the polymer started to form which prevented further chain growing and attaining therefore acceptable molecular weights. The influence of the comonomer composition and temperature on the progress of the polymerization reaction was examined by following the increase in molecular weight of the resulting copolyester with time for a series of polymerization essays (Figure 6.2.1). As it should be expected, the polymerization reaction progressed exponentially at the earlier stages to follow later an asymptotic trend. First the influence of temperature was evaluated within the 130-150 ºC range for the CL:BF (60:40) mixture. Results are shown in Figure 6.2.1a which indicate that, according to expectations, the reaction rate increased with temperature, and that a M_w about 50,000 g·mol^{-1} was attained after one day of reaction. Secondly the influence of composition of the feed on the reaction progress was studied for an assortment of CL:*c*(BF)$_n$ ratios ranging from 1:0 to 1:4 (reaction was stopped at low conversion for lower ratios) that were made to react at 150 ºC. As it seen in Figure 6.2.1b,

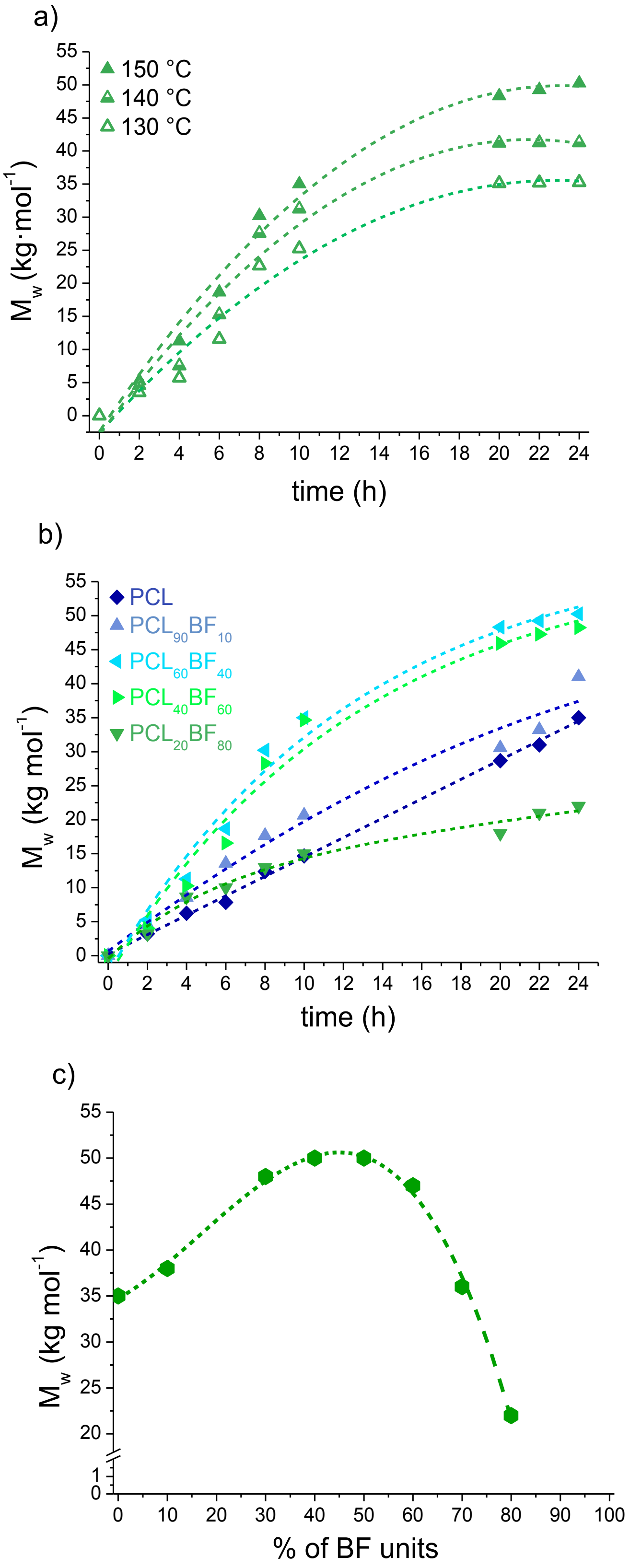


Figure 6.2.1. Evolution of M_w of PCL$_x$BF$_y$ formed in the *e*-ROP of mixtures of CL and *c*(BF)$_n$, a) along reaction time at different temperatures for the CL:BF (60:40) mixture, b) along reaction time at 150 °C for different mixture compositions and c) with the CL:*c*(BF)$_n$ ratio at 150 °C after 24 h of reaction.

Significant differences in reaction rate were observed for different feed compositions with the general trend depicted in Figure 6.1.1c. Apparently, the *e*-ROP reaction of CL was enhanced by the presence of *c*(BF)$_n$ up to compositions of approximately 50 %-mol. Above this value, the copolymerization reaction decreased with increasing contents in *c*(BF)$_n$, which could be probably due to the high viscosity attained by the reaction mass for such compositions. According to the results obtained in these previous essays, PCL and PCL$_x$BF$_y$ copolyesters subjected to study in this work (Table 6.2.1) were prepared by *e*-ROP at 150 ºC and had M_w ranging between 50,000 for PCL$_{50}$BF$_{50}$ and 22,000 for PCL$_{20}$BF$_{80}$, and molar dispersities between 2.1 and 1.2. The PBF homopolyester used for reference had to be prepared by ROP at 250 ºC catalyzed by TBT and had a M_w of 65,000.

Table 6.2.1. Composition, Molecular Weight and Randomness of PCL$_x$BF$_y$ Synthesized by *e*-ROP.

Polyester	Composition[a] [CL]/[BF]		Molecular weight[b]		Microstructure[c]	
	Feed	Copolyester	M_w (g·mol^{-1})	*Đ*	n_{CL}	(*B*)
PCL	100/0	-	35,000	1.80	-	-
PCL$_{90}$BF$_{10}$	90/10	86/14	39,000	2.00	11.2 (6.6)	0.32 (0.50)
PCL$_{70}$BF$_{30}$	70/30	73/27	48,000	1.80	8.4 (3.2)	0.28 (0.36)
PCL$_{60}$BF$_{40}$	60/40	67/33	50,000	1.72	5.6 (5.5)	0.50 (0.55)
PCL$_{50}$BF$_{50}$	50/50	42/58	50,000	1.60	2.9 (1.3)	0.43 (0.66)
PCL$_{40}$BF$_{60}$	40/60	36/64	47,000	1.65	2.8 (n.d.)	0.44 (n.d.)
PCL$_{30}$BF$_{70}$	30/70	33/67	36,000	1.25	2.5 (1.5)	0.50 (0.70)
PCL$_{20}$BF$_{80}$	20/80	18/82	22,000	1.25	2.2 (1.3)	0.51 (0.58)
PBF	0/100	-	65,000	1.97	-	-

[a]Molar composition determined by ^{1}H NMR. [b] Weight-average molecular mass and dispersity determined by GPC. [c] Average sequence lengths of CL units (n_{CL}) and degree of randomness (*B*) determined by ^{13}C NMR. In parenthesis, the values calculated for the copolyesters after heating treatment. n.d.: not determined.

Copolyesters composition and microstructure: The composition and microstructure of the whole series of PCL$_x$BF$_y$ copolyesters obtained by *e*-ROP were determined by ^{1}H and ^{13}C NMR. These spectra are provided in the annex associated to this paper (Figures C.2.2 and C.2.3) while the spectra registered from PCL$_{60}$BF$_{40}$ are presented in Figure 6.2.2 for illustration. The molar composition of copolyesters in CL and BF units was determined by quantification of the ^{1}H NMR signals *d* and *d'* arising from the α-methylene of the ε-oxicaproate and oxybutylene units (Figure 6.2.2), respectively, and the resulting values are given in Table 6.2.1. A reasonable agreement between the CL:*c*(BF)$_n$ ratios found in the copolyesters and those used for their respective feeds was observed although differences became significant as the composition in the twounits tended to equilibrate (about 15% for PCL$_{40}$BF$_{60}$ and PCL$_{50}$BF$_{50}$). Strikingly no apparent correspondence between the unbalancing sense and copolyester composition seems to exist.

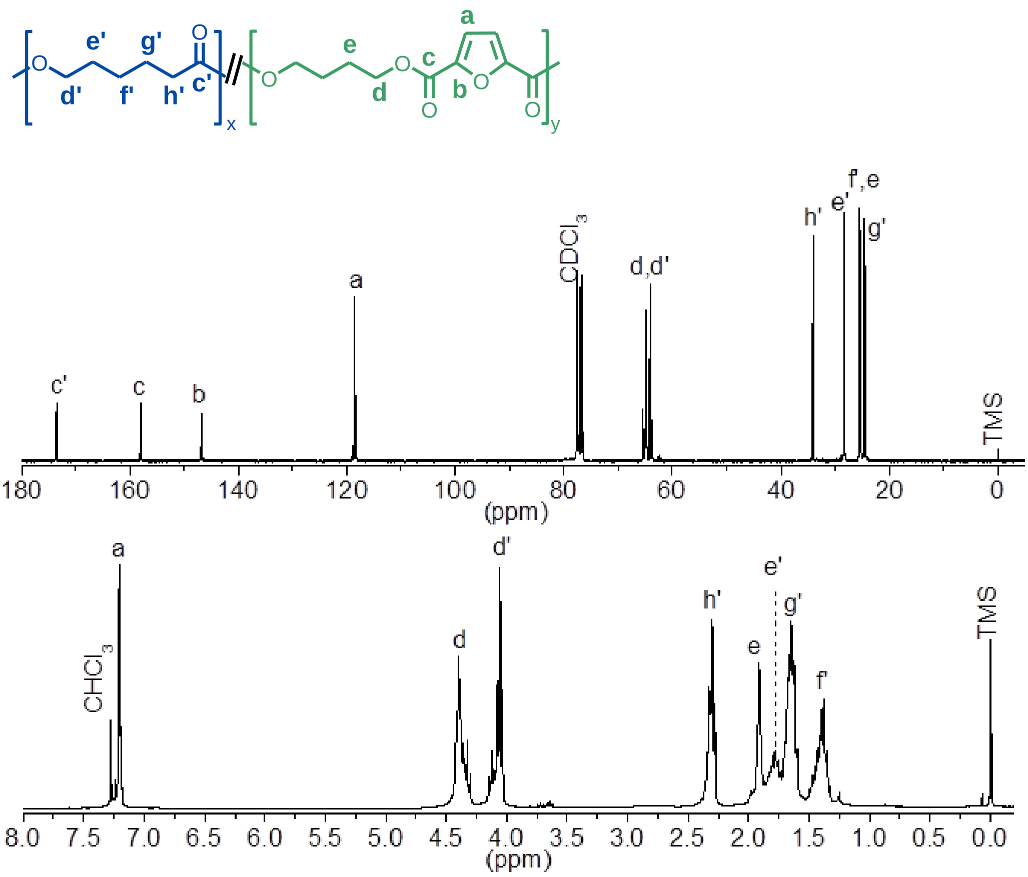


Figure 6.2.2. ^{13}C (top) and ^{1}H (bottom) NMR of PCL$_{60}$F$_{40}$.

The microstructure of the copolyesters was elucidated by NMR analysis on the basis of the ^{13}C NMR 24.5-24.6 ppm signal arising from the β-methylene of the ε-oxicaproate unit. This signal appears split into four peaks corresponding to the CLCLCL, CLBFCL, BFCLBF and BFBFBF triads present in the copolyesters (Figure 6.2.3a). The degree of randomness *B* was determined using the procedure reported by Tessier and Fradet[26] and later applied by us to copolymers made of cyclic oligo(hexamethylene terephthalate) with either CL[23] or *p*-dioxanone,[27] which is based on the relative integration of the peak arising from homogeneous CL sequences. The degree of randomness *B* is defined by equation 1 where x_{CL} and x_{BF} are the molar fractions of CL and BF units, respectively. *a* is a parameter specific for each composition that is calculated by means of equation 2 making use of the value of the triad fraction $F_{(CLCLCL)}$ obtained by integration of the corresponding ^{13}C NMR peak. The *B* values resulting from these calculations are listed in Table 6.2.1. These values are in the 0.28-0.51 range indicating that the microstructure of PCL$_x$BF$_y$ prepared by *e*-ROP is in blocks with average homogeneous CL sequence lengths oscillating between 2 and 12 depending on composition.

$$\boldsymbol{B} = \frac{(1-a)(2X_f + X_c)}{X_c} \qquad (\mathbf{eq\ 1}) \qquad\qquad F(\mathrm{CLCLCL}) = \left(1 - \frac{2X_f(1-a)}{X_c}\right)^2 \qquad (\mathbf{eq\ 2})$$

As it is well known transesterification reactions usually take place in polyesters when they are heated at temperatures above their softening point and an appropriate catalyst is added. With the purpose of increasing the degree of randomness in the blocky PCL$_x$BF$_y$ copolyesters prepared by *e*-ROP, samples were subjected to heating at 200 ºC in the presence of TBT for 24 h. As a consequence of this treatment slight changes in the copolyester compositions and molecular weights, which could be partially attributed to thermal degradation, were observed (for details see Table C.2.1 in the annex). The ^{13}C NMR 24.5-24.6 ppm signal profiles registered from the heated copolyesters are compared with those obtained from the pristine samples in Figure. 6.2.3b. According to which should be expected for transesterification, a relative increasing of intensity of the peaks arising from triads other than CLCLCL became apparent after the heating treatment. The *B* values resulting for the heated copolyesters were found to range from 0.36 to 0.70, and the maximum length of the homogeneous CL sequences present in these copolyesters was now reduced to about six (Tables 6.2.1 and C.2.1).

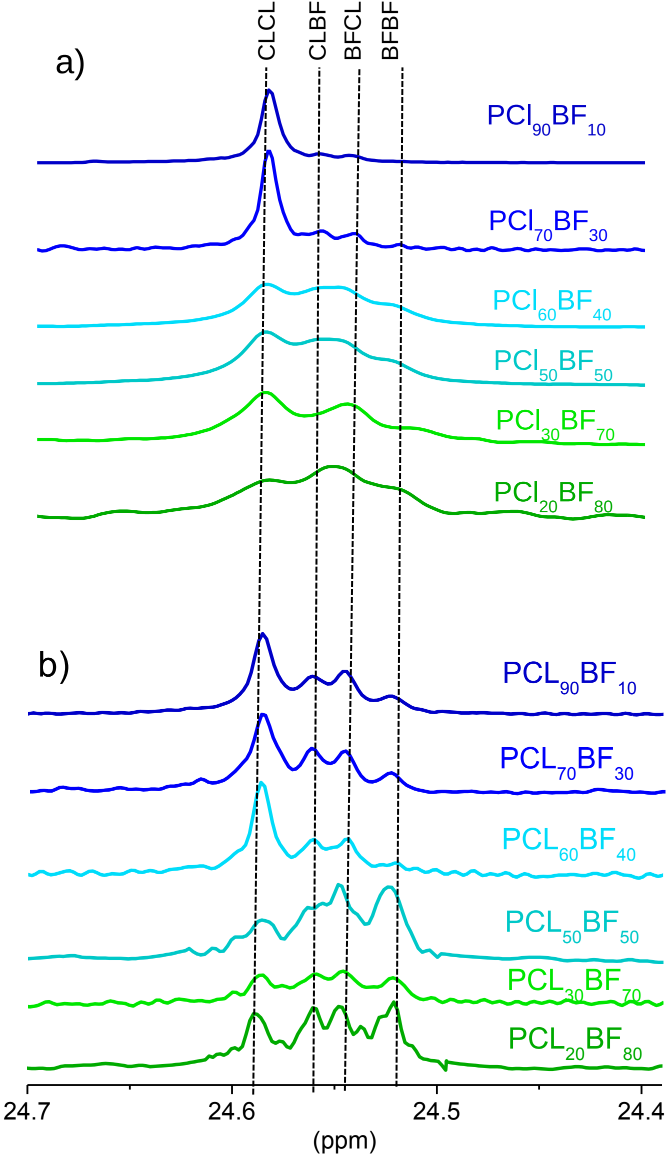


Figure 6.2.3. ^{13}C NMR spectra of the PCL$_x$BF$_y$ copolyesters enlarged in the region 24.4-24.7 ppm. a) Before transesterification and b) after transesterification.

Thermal properties of PCL_xBF_y copolyesters: The thermal behavior of the PCL_xBF_y copolyesters obtained by *e*-ROP was examined by both TGA and DSC, and the most representative decomposition and phase transition parameters were measured by these techniques and listed in Table 6.2.2.

Table 6.2.2. Thermal Properties and Crystallizability of PCL_xBF_y Copolyesters Prepared *via e*-ROP.

Copolyester	TGA[a]			DSC[b]					Crystallization kinetics[c]			
					First heating		Second heating					
	$^{o}T_d$ (°C)	$^{max}T_d$ (°C)	R_w (%)	T_g (°C)	T_m (°C)	ΔH ($J{\cdot}mol^{-1}$)	T_m (°C)	ΔH ($J{\cdot}mol^{-1}$)	T_c (ºC)	n	ln$K$	$t_{1/2}$ (min)
PCL	345	401	10	-60	65	56	64	40	40	2.4	-2.59	2.4
									36	3.2	-1.75	0.4
$PCL_{90}F_{10}$	330	384	11	-37	52	35	51	27	27	2.3	-4.23	4.7
									36	2.4	-4.94	2.4
$PCL_{70}F_{30}$	332	392	7	-13	101	21	100	16	76	2.3	-4.44	5.6
$PCL_{60}F_{40}$	342	390	6	-8	116	26	115	12	-	-	-	-
$PCL_{50}F_{50}$	321	382	11	0	130	13	130	13	-	-	-	-
$PCL_{40}F_{60}$	317	386	8	8	135	12	135	4	-	-	-	-
$PCL_{30}F_{70}$	325	387	9	11	135	17	136	15	136	1.7	-1.65	2.0
$PCL_{20}F_{80}$	323	388	8	19	148	33	152	32	128	2.4	-5.62	9.1
									136	2.4	-6.90	2.5
PBF	346	391	7	42	172	38	170	38	146	2.2	-4.42	10.3
									136	2.5	-5.33	6.7

[a] Thermogravimetric analysis under inert atmosphere. Thermal decomposition temperatures measured at 5% of weight lost ($^{0}T_d$) and at maximum weight loss rate ($^{max}T_d$). R_w:weight remaining after heating at 600 ºC.

[b] DSC analysis for the first heating and for the second heating registered after cooling. The glass transition temperature (T_g) was measured at heating from samples quenched from the melt.

[c] Avrami parameters (n and K) and crystallization half-time ($t_{1/2}$) determined by isothermal crystallization at the indicated temperatures.

The TGA traces recorded for the whole copolyesters series are compared in Figure 6.2.4a and the derivative curves of a representative selection of them are depicted in Figure 6.2.4b. PCL and PBF homopolyesters have a very close behavior when subjected to heating at high temperatures under an inert atmosphere with onset and maximum rate decomposition temperatures differing in less than 3%. The values measured for the copolyesters are between those of the parent homopolyesters with

$^{o}T_d$ and $^{max}T_d$ located within the 315-345 ºC 380-390 ºC ranges approximately. These results bring into evidence the high thermal resistance to heating of the PCL$_x$BF$_y$ copolyesters and ensure their suitability for being processed by thermal methods.

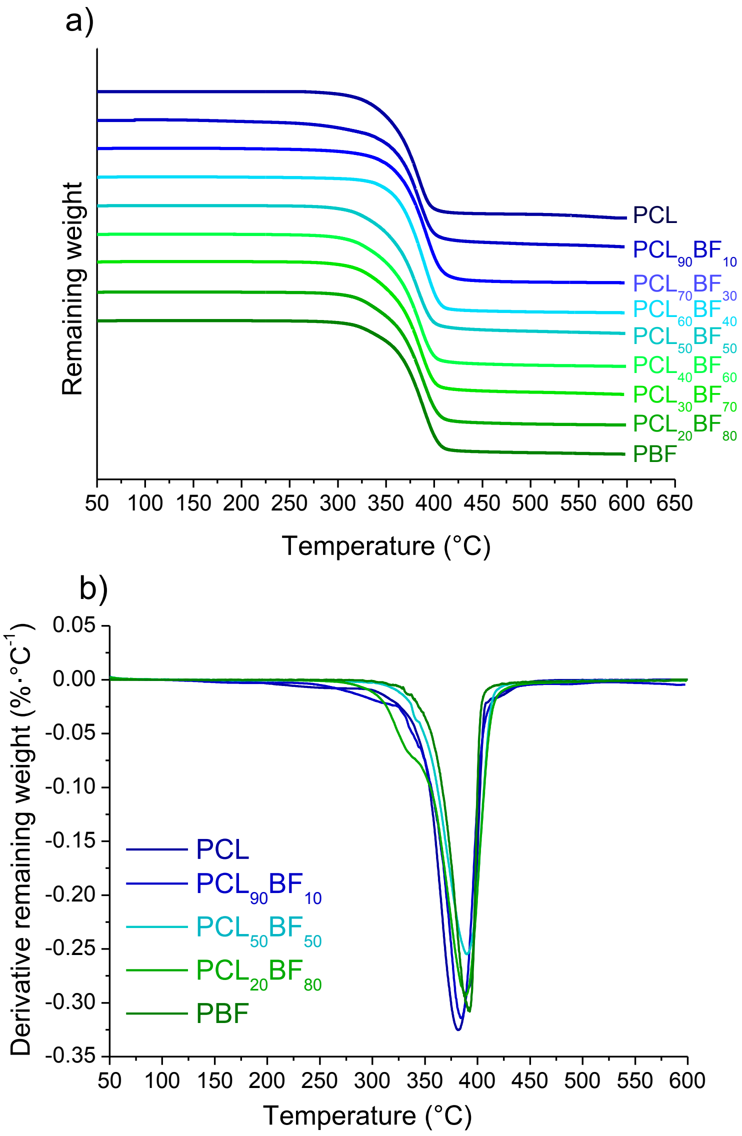


Figure 6.2.4. TGA traces of PCL$_x$BF$_y$ copolyesters recorded under inert atmosphere (a) and the derivative curves of a selection of them (b).

The DSC traces recorded for the PCL$_x$BF$_y$ series as well as for the two parent homopolyesters along the first heating-cooling-second heating cycle are shown in Figure 6.2.5. PCL and PBF are semicrystalline polyesters with T_m at 64-65 ºC and 170-172 ºC, respectively, and both were able to crystallize from the melt by almost reproducing the initial melting temperatures and developing a considerable crystallinity. All the copolyesters showed melting with enthalpy and temperature progressively decreasing from those of PBF as the content in CL increased (Figure 6.2.5a, first heating traces), and this behavior was shared by copolyesters that were crystallized from the melt (Figure 6.2.5b, second heating traces). With the exception of $PCL_{90}BF_{10}$, the melting observed in the copolyesters arises from the crystalline phase made of homogeneous BF sequences. It seems therefore that upon cooling, butylene 2,5-furandicarboxylate segments crystallized firstly preventing the crystallization of the ε-oxycaproate segments that became confined in between the initially formed PBF crystallites. This situation is only avoided for very low contents in BF (10% or less) because the BF sequences are then too short (less than four units) to be able to form stable crystallites. This interpretation is strongly supported by powder X-ray diffraction (XRD) which provided crystalline scattering profiles containing only characteristic PBF peaks[9,28,] for polyesters with less than 90% of CL units (Figure C.2.6 in the annex). Furthermore polarizing optical microscopy (MOP) of films crystallized from the melt showed crystalline morphologies consistent with composition with texture changes taking place when 30% of content in BF units in the copolyester was reached (Figure C.2.7 in the annex). On the other hand the glass-transition temperature of the copolyesters was observed to increase steadily along the whole -60-42 ºC interval limited by the values of PCL and PBF. Apparently the insertion of the rigid BF units in the flexible chain of PCL largely restricts the mobility with the consequence of a very notable increase in T_g. Both T_m and T_g of PCL_xBF_y are plotted against the content in BF units in Figure 6.2.6. The trend observed for T_m is nearly linear for the whole series excluding $PCL_{90}BF_{10}$ which is highly reasonable since this copolyester is the only one containing crystallites made of PCL segments.The plot of T_g against the percentage content in BF units is also roughly linear with a moderate dispersion of values and an average positive slope of about 1 $^oC \cdot (BF\text{-}\%)^{-1}$. This result is particularly remarkable since it indicates that significant improvements in properties as rigidity, hardness and barrier may be achieved for PCL when moderate amounts of BF units are inserted in its chain.

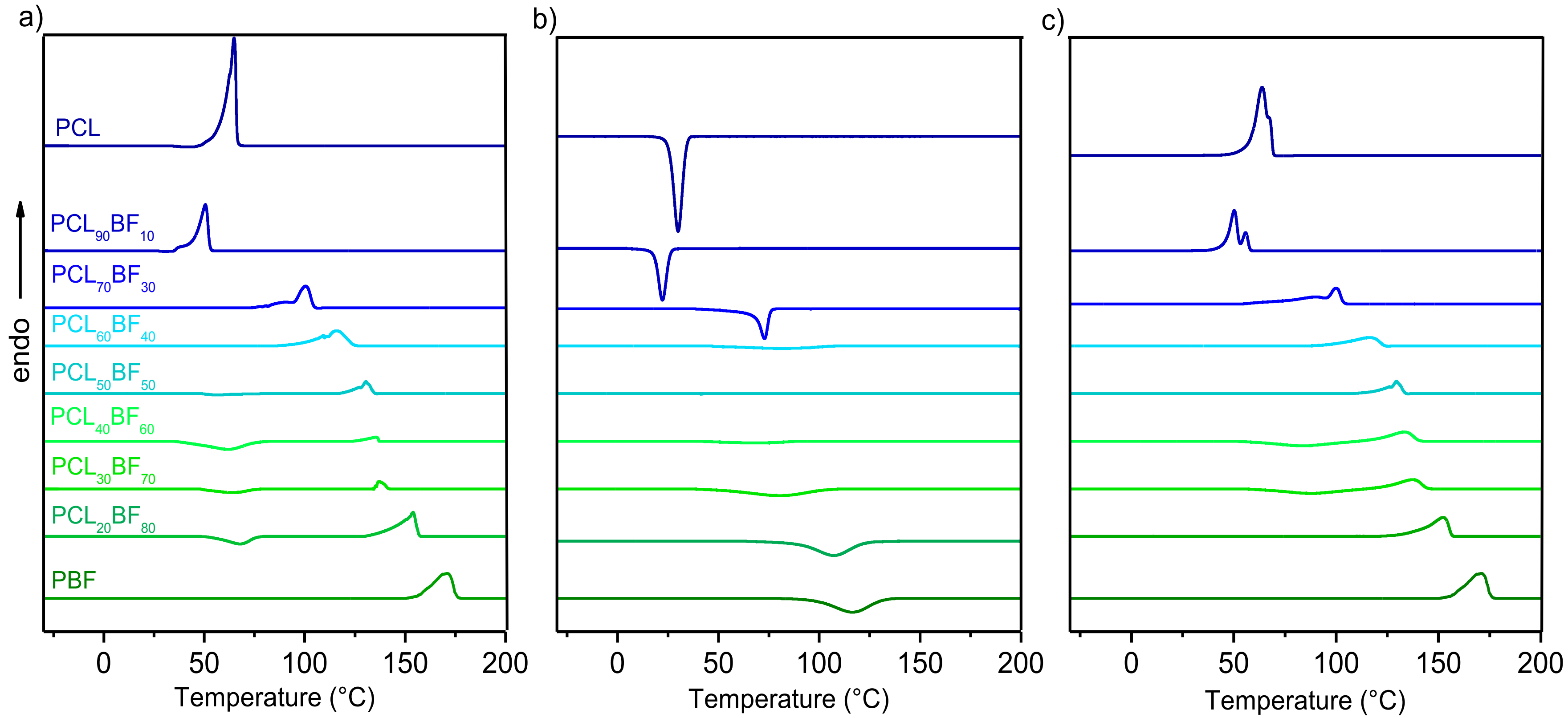


Figure. 6.2.5. DSC traces of PCL_xBF_y. a) First heating, b) cooling and c) second heating.

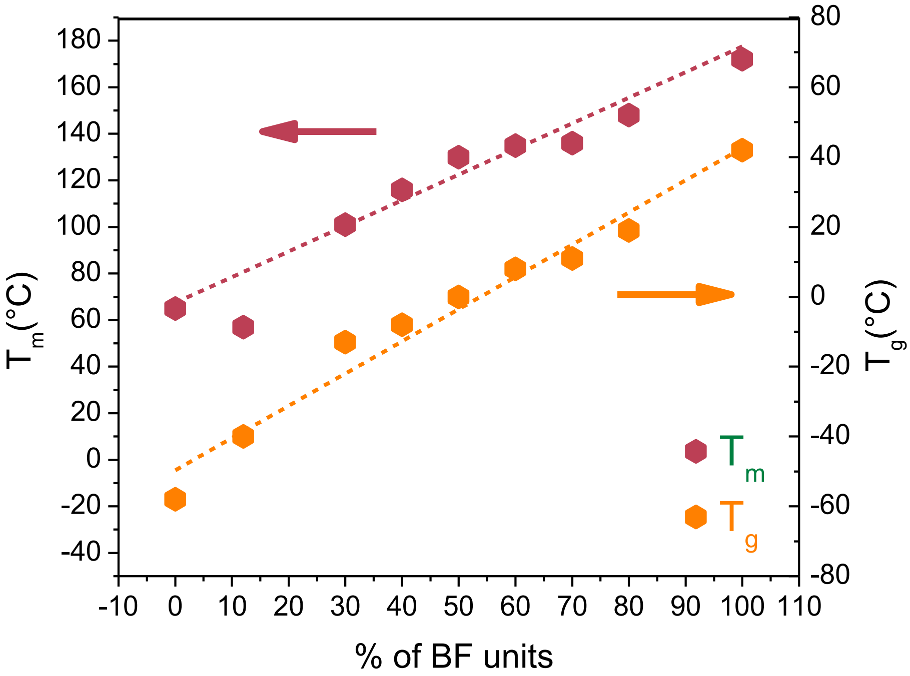


Figure. 6.2.6. Plots of T_m (a) and T_g (b) of PCL$_x$F$_y$ against the content of the polymer in BF-units.

Crystallizability: The ability for crystallizing upon cooling from the melt is a polymer property of high relevance as far as thermal processing is concerned. Both crystallization rate and crystallinity are the most significant parameters for a quantitative evaluation of polymer “crystallizability”. In order to appraise the effect of copolymerization on the crystallizability of the PCL$_x$BF$_y$ system, a kinetics study of the isothermal crystallization of these polyesters has been carried out. Since crystallization temperature of PCL$_x$BF$_y$ varies largely according to composition, the comparative study has to be limited to small groups of polyesters able to crystallize at the same temperature. The plots of relative crystallinity *vs* crystallization time for three different cases are shown in Figure 6.2.7. In Figure. 6.2.7a, the homopolyesters and a selection of copolyesters with different composition are compared at different crystallization temperatures. According to what it is well known, PCL was observed to crystallize much faster than PBF, and in agreement whit this, crystallization rate of copolyesters was found to decrease for increasing contents in BF units. The observed behavior is not irrefutable however since it is obviously affected by differences in crystallization temperatures. In Figure 6.2.7b, the isothermal crystallization curves registered at 136 ºC for PBF and for two copolyesters containing different amounts of CL units are compared. This result certainty demonstrates the enhancing effect that the flexible ε-oxycaproate structure has on the crystallization rate of PBF. Reciprocally, the influence of the BF units on the crystallizability of PCL is evidenced in Figure 6.2.7c where the *X-t* curve of the homopolyester registered at 36 ºC is compared with that of the $PCL_{90}BF_{10}$ copolyester crystallizing at the same temperature. It is apparent therefore that the presence of the relative stiff furanoate units delays the crystallization of PCL.

Isothermal crystallization data were used for carrying out the Avrami kinetics analysis of all the compared polyesters. Double logarithmic plots of crystallinity *vs* time (see Figure. C.2.8) were used for selecting the periods of time suitable for the analysis, and the Avrami parameters resulting for the homopolyesters and the selected copolyesters at different temperatures are listed in Table 6.2.2. Crystallization half times ($t_{1/2}$) oscillated between 0.4 min for the crystallization of PCL at 36 ºC and 10.3 min for PBF crystallized at 146 ºC. As it was already qualitatively deduced form the graphical representations (Figure 6.2.7), $t_{1/2}$ of CL-enriched copolyesters increased with the presence of PBF and the opposite happened when the CL content increased in the BF-enriched copolyesters . It is worthy to note the effect of crystallization temperature on $t_{1/2}$ when comparison is made for the same polyester. In the case of homopolyesters crystallization rate decreased with temperature whereas the contrary effect was observed for copolyesters. It seems therefore that self-nucleation and chain mobility are the factors determining crystal growth for homopolyesters and copolyesters,

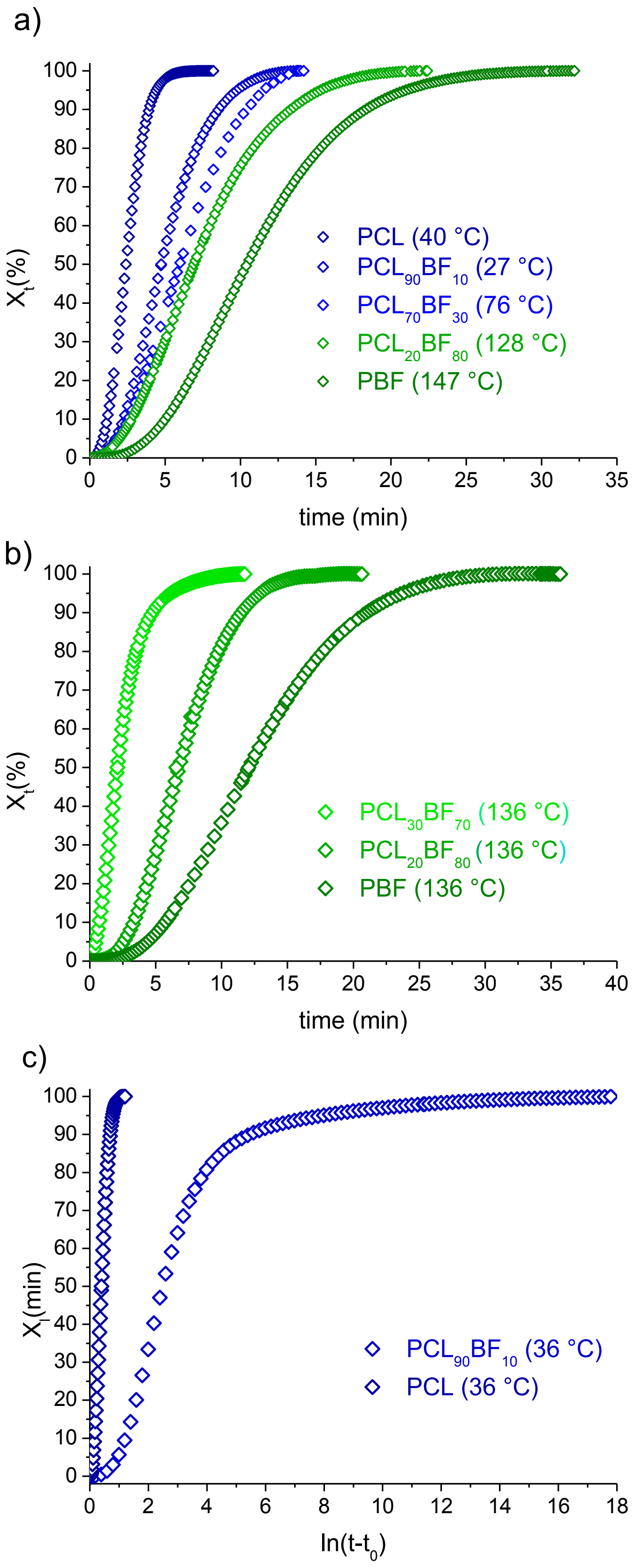


Figure 6.2.7. Crystallinity vs time plots for the isothermal crystallization of PCL_xBF_ycopolyesters. a) A selection of polyesters crystallizing at different temperatures. b) BF-enriched polyesters with different contents in CL units crystallizing at the same temperature. c) PCL and PCL containing BF units crystalizing at the same temperature.

respectively. This result is consistent with the blocky microstructure of the copolyesters since crystallization of the small blocks implies a topological rearrangement of the polymer chains that is favored by temperature, a requirement that is not needed by homopolyesters.

Hydrolytic degradation and biodegradation: The response of PCL to the action of water is well known. At temperatures close to ambient this polyester displays a high resistance to hydrolysis whereas it is rapidly degraded in the presence of lipases. On the contrary, PBF is quite resistant to the aqueous media both with and without enzymes added. The biodegradability of PCL-PBF copolyesters prepared by polycondensation has been explored by following by SEM the morphological changes taking place on the surface of samples incubated in water for four weeks.[25] This study reported that the copolyesters were eroded in an extent that increased with the content in CL units. In the present work a quantitative study of the degradability of PCL_xBF_y copolyesters has been carried out by following the decrease in both weight sample and polymer molecular weight along 40 days of incubation in water at 25 ºC with and without lipases added to the medium. A set of four copolyesters differing significantly in composition in addition to their two parent homopolyesters was selected for this study. Results are shown in Figure 6.2.8 where percentages of the remaining weight and the weight-average molecular weight are plotted against time. In the absence of lipases degradation was very scarce for all the examined polymers with practically no changes for PBF and maximum changes observed for PCL that were however of only about 2% and 4% for sample and molecular polymer losses, respectively (Figures 6.2.8a and 6.2.8a'). Conversely the observed response was much more pronounced when samples were incubated in the presence of porcine pancreas lipases so that ostensible differences were observed depending on composition (Figs. 6.2.8b and 6.2.8b'). In full agreement with expectations, PBF remained unaltered whereas PCL degraded completely. The changes observed for copolyesters were more pronounced for higher contents in CL units with weight losses ranging from 20 and 40 % for $PCL_{30}BF_{70}$ and $PCL_{70}BF_{30}$, respectively. It becomes clear from our study that the hydrodegradability of

PCL_xBF_y copolyesters under mild conditions is practically negligible whereas they become notably hydrolyzed in the presence of lipases. It is worth noting also that PBF may be made biodegradable by introducing in its chain moderate amounts of CL without practical alteration of their hydrolytic resistance.

VI.2.3 Conclusions

The synthesis of cyclic (butylene 2,5-furandicarboxylate) oligomers, $c(BF)_n$, recently reported by us has prompted their use as monomers in Ring Opening Polymerizations leading to PBF homopolyesters and copolyesters. In the present work these cyclic oligomers have been copolymerized in bulk with ε-caprolactone by using CALB as catalyst. It is the first time that this synthesis is reported and that $c(BF)_n$ is copolymerized with a lactone of A-B type. The procedure avoids the use of both organic solvents and organometallic catalysts and leads therefore to polymers greener than those obtained by conventional polycondensation. Our results show that PCL-PBF copolyesters with a wide range of compositions and satisfactory molecular weights could be produced in high yields. Amazingly these copolyesters display a blocky distribution of the comonomers along the polymer chain which is in contrast with the random microstructure found for other PBF copolyesters prepared by this method. The copolyesters are semicrystalline with their T_m*’s* and T_g’s oscillating between those of PCL and PBF. Copolyesters with minor contents in any of the two components are able to crystallize from the melt at a rate that decreases with the presence of stiff furanoate units. Furthermore, it is remarkable the notable increasing attained in the T_g of PCL when moderate amounts of furanoate units are incorporated in the chain for the relevance that this property has on the physical behavior of the polyester. On the other side, the influence of the presence of CL units on the biodegradability of PBF is more than remarkable given the strong reluctance of this polyester to be hydrolyzed under mild conditions. The overall conclusion is that a greener synthetic method has been developed for the preparation of PCL-PBF copolyesters exempt of metallic contaminants, and that these polymers display properties of interest for their potential use in packaging and biomedicine.

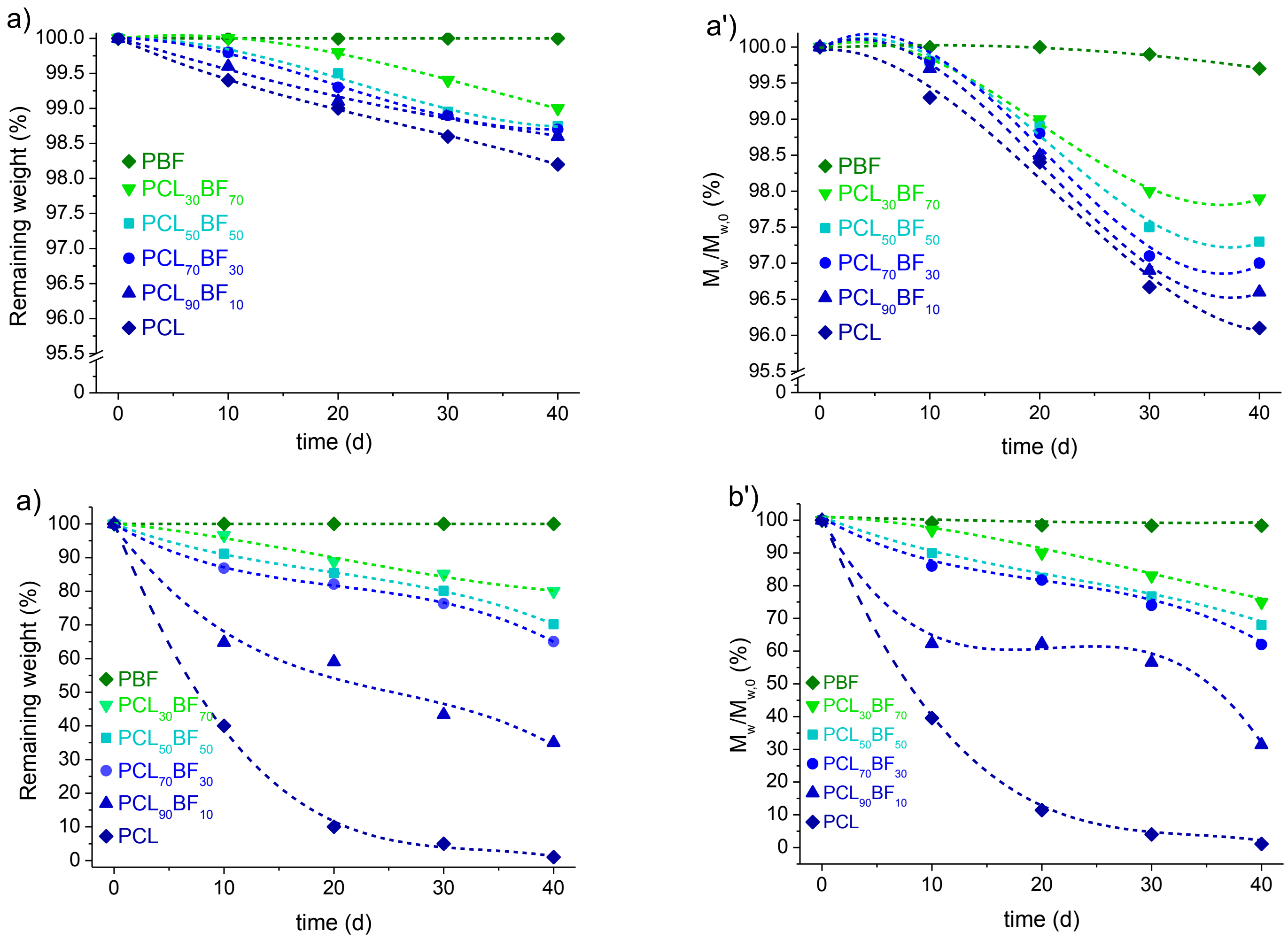


Figure 6.2.8. Degradation of PCL$_x$BF$_y$ upon incubation in aqueous medium at pH 7.4 and 25 ºC followed by the decreasing in both weight and molecular weight with time a,a') In the absence of enzymes. b,b') With lipases added.

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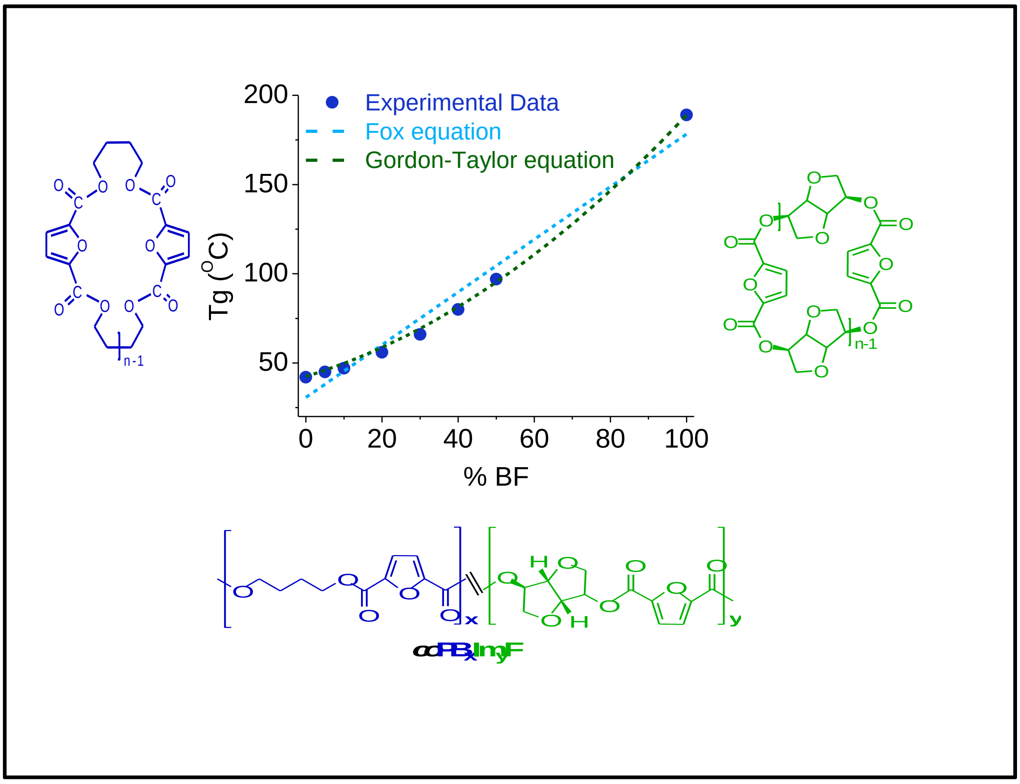
VII Copolyesters containing isomannide units

VII.1 Poly(butylene furanoate) copolyesters

Abstract: Cyclic oligomers of isommanide 2,5-furandicarboxylate were synthesized for the first time using the high dilution condensation method. A mixture of dimer, trimer and tetramer species largely enriched in the former was obtained. These cyclic oligomers were copolymerized with those made of butylene 2,5-furandicarboxylate in bulk at 220 ºC by ring opening polymerization using $Sn(Oct)_2$ as catalyst. A series of random 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 ºC and only those containing less than 10% of isomannide showed some sign of crystallinity. They displayed glass-transition temperatures in the 40-100 ºC that increased steadily with the content in isomannide. At difference with the poly(butylene 2,5-furandicarboxylate) homopolyester that is fully reluctant to hydrolysis, the isomannide containing copolyesters were noticeable degraded by water and much more rapidly when exposed to the presence of lipases.



Publication derived from this work:

J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra. Isomannide-containing poly(butylene 2,5-furandicarboxylate) copolyesters via ring opening polymerization. *Macromolecules* **2018**, to be submitted**.**

VII.1.1 Introduction

In this paper we wish to report on copolyesters of poly(butylene 2,5-furandicarboxylate) (PBF) containing isomannide (Im) prepared by ROP. It is the first time that aromatic polyesters containing isohexides are synthesized by this method and that the thermal properties and biodegradability of PBF are enhanced without detriment of its sustainability.

Ring Opening Polymerization (ROP) of cyclic monomers is a method widely known in polymer chemistry, in particular when the synthesis of polycondensation polymers is pursuit.[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 cyclic lactones required for the application of ROP.[3,4] Nevertheless some representatives polyesters such as polylactic acid or polycaprolactone, are industrially produced by ROP,[5-7] and the expansion of this method, although gradual, is incessant. Both enthalpy and entropy driven ROP processes are known to operate depending on the lactone cycle size.[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.[10-12]Nonetheless a diversity of cyclic oligophthalates as well as their ROP to polyesters have been reported in the scientific literature.[1,2] The synthesis of these cycles using the so-called high-dilution condensation method and the synthesis of poly(alkylene terephthalate)s and poly(alkylene isophthalate)s therefrom 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 has been reported by [21,22] which has opened a new via towards the preparation of furane-based polyesters and copolyesters. Thus random furanoate-terephthalate[23] and furanoate-succinate[24] copolyesters, as well as furanoate copolyesters containing caprolactone[25] have been synthesized by ROP with results comparable to those attained by polycondensation.

Polyfuranoates derived from 2,5-furandicarboxylic acid are polyesters of maximum current interest.[26] Poly(butylene 2,5-furandicarboxylate) (PBF) is an aromatic polyester that is proposed as a potential substitute of poly(butylene terephthalate) (PBT) with improved sustainability. In fact, PBF combines a bio-based character with a set of properties that compares or even surpasses those of PBT.[27-28,30] Considerable efforts have been made however to modify its behavior and a number of PBF copolyesters displaying novel properties may be today found in the literature. [23-25, 26,29-30] One usually applied approach has been to make PBF copolymers with enhanced T_g or/and biodegradability without detriment of its sustainability. This is really challenging since stiff monomers coming from renewable sources are not frequent. Bicyclic dianhydroalditols[31,32] and diacetalized alditols[33] are exceptional examples of diols that could be used for such purpose.

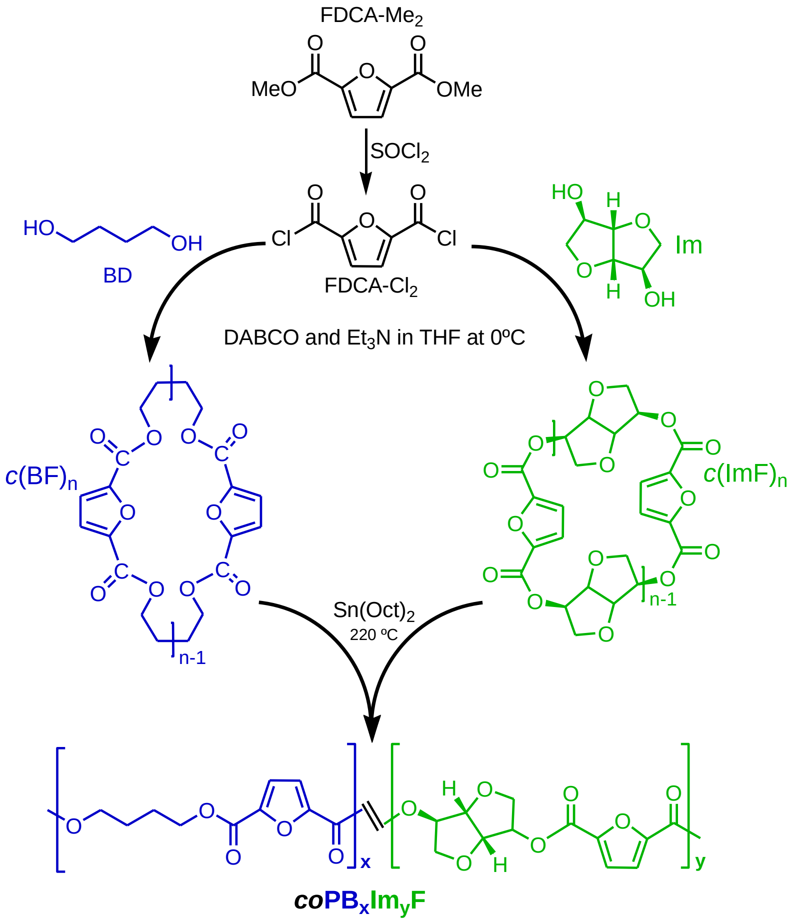
Isomannide (Im) together with isosorbide (Is) and isoidide (Ii) are 1,4:3,6 dianhydroalditols (commonly known as isohexides), a family of bio-based bicyclic diols that have attracted great attention in these last decades as new monomers for polycondensation.[31,32]The high interest for isohexides arises 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 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 less studied because its accessibility is much more difficult. However, the only cyclic oligomers containing isohexides suitable for ROP that have been reported in the literature are those made from aliphatic dicarboxylic acids reported by Kricheldorf et al.[39,40]

In this work, novel cyclic oligo(isomannide 2,5-furandicarboxylate), *c*(ImF)$_n$ have been synthesized for the first time and copolymerized with oligo(butylene 2,5-furandicarboxylate) *c*(BF)$_n$ to obtain a series of poly(butylene-*co*-isomannide 2,5-furandicarboxylate) (*co*PB$_x$Im$_y$F) with Im contents ranging from 0 up to 50 %-mole. The copolyesters 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 copolyesters and conventional polycondensation was the technique invariably applied in these cases.[41,42.]

VII.1.2 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 *co*PB$_x$Im$_y$F is depicted in Scheme 7.1.1.

Cyclic oligomers. *c*(BF)$_n$ were synthesized as described in several works recently reported by us. [22] following the high dilution (HDC) technique assisted by the organic catalyst DABCO. Characterization details of these cyclic oligomers are provided in the annex (Figure D.1.1). The same technique was then applied to the synthesis of cyclic oligo(isomannide 2,5-furandicarboxylate) *c*(ImF)$_{n,}$ which are described in the 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 D.1.2). After removing the linear oligomers by flash chromatography, the eluted sample was analyzed by NMR, Maldi-Tof and HPLC (Figure 7.1.1) which demonstrated that this fraction consisted mainly



Scheme 7.1.1. Synthetic route to poly(butylene-*co*-isomannide 2,5 furandicarboxylate) copolyesters.

of dimer (85%) accompanied by minor amounts of trimer and tetramer (10 and 5%, respectively). The thermal analysis of *c*(ImF)$_n$ by TGA showed that these cycles are resistant to heat up to temperatures around 350 ºC, and the DSC analysis revealed that they are crystalline with melting at 160 ºC (Figure 7.1.2). The most relevant characteristics of these cycles compared with those of *c*(BF)$_n$ are collected in Table 7.1.1.

Table 7.1.1. 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] $^{o}T_d$ (°C)	$^{max}T_d$ (°C)	T_m (°C)
c(BF)$_n$	FDCA-Cl$_2$ + BD	67	62/30/8	240	378	147
c(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 determined by HPLC.
[c] Determined by TGA and DSC. $^{o}T_d$ is the onset temperature determined for a weight loss of 5%, $^{max}T_d$ is the temperature for maximum decomposition rate, and T_m is the melting temperature.

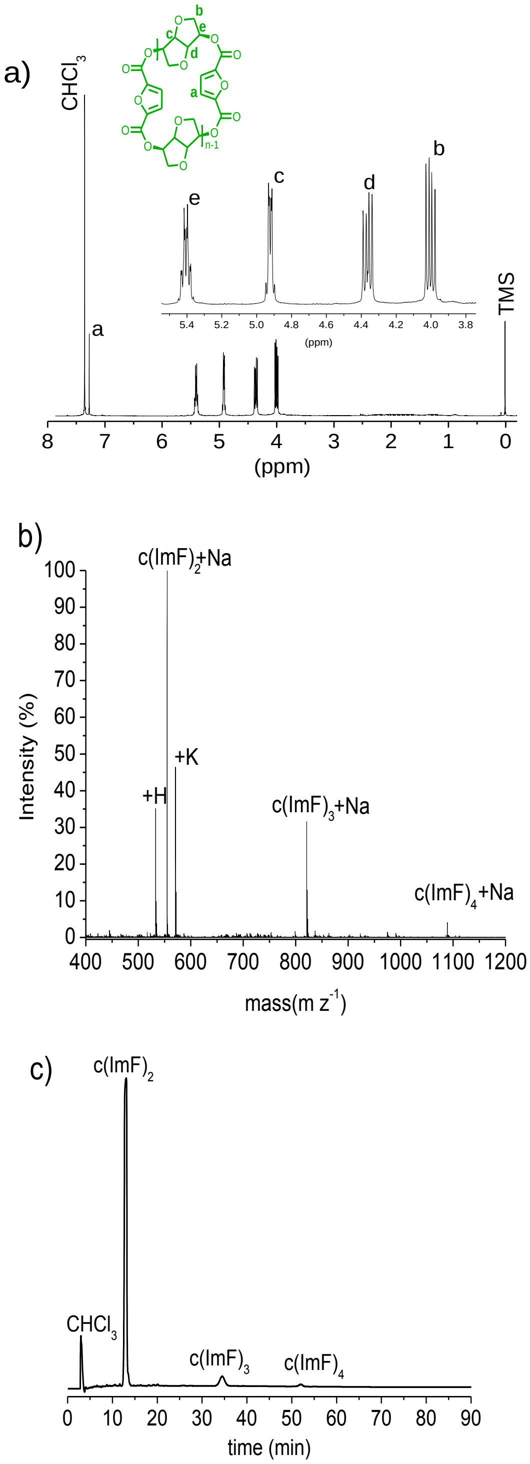


Figure 7.1.1. a) ^{1}H NMR, b) MALDI-ToF, and c) HPLC of *c*(ImF)$_n$ after purification.

It is noteworthy to report that a series of experiments similar to those carried out for the synthesis of *c*(ImF)$_n$ were made using isosorbide (Is), *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 D.1.3). 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 Ii) was comparatively performed by molecular simulations. The results clearly revealed that cyclic oligomers made of Is are much less stable than those made of Im (Figure D.1.4), which is fully consistent with the experimental results reached in the attempts of cyclization carried out with isomannide or isosorbide. Simulation results also indicated a relative high energy for the cyclic oligofuranoates containing isoidide, which leads to expect that cyclization involving this diol will not be easy 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*(BF)$_n$ and *c*(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 copolyesters series *co*PB$_x$Im$_y$F. The homopolyesters PBF and PImF 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*(BF)$_n$ and *c*(ImF)$_n$ with a 60/40

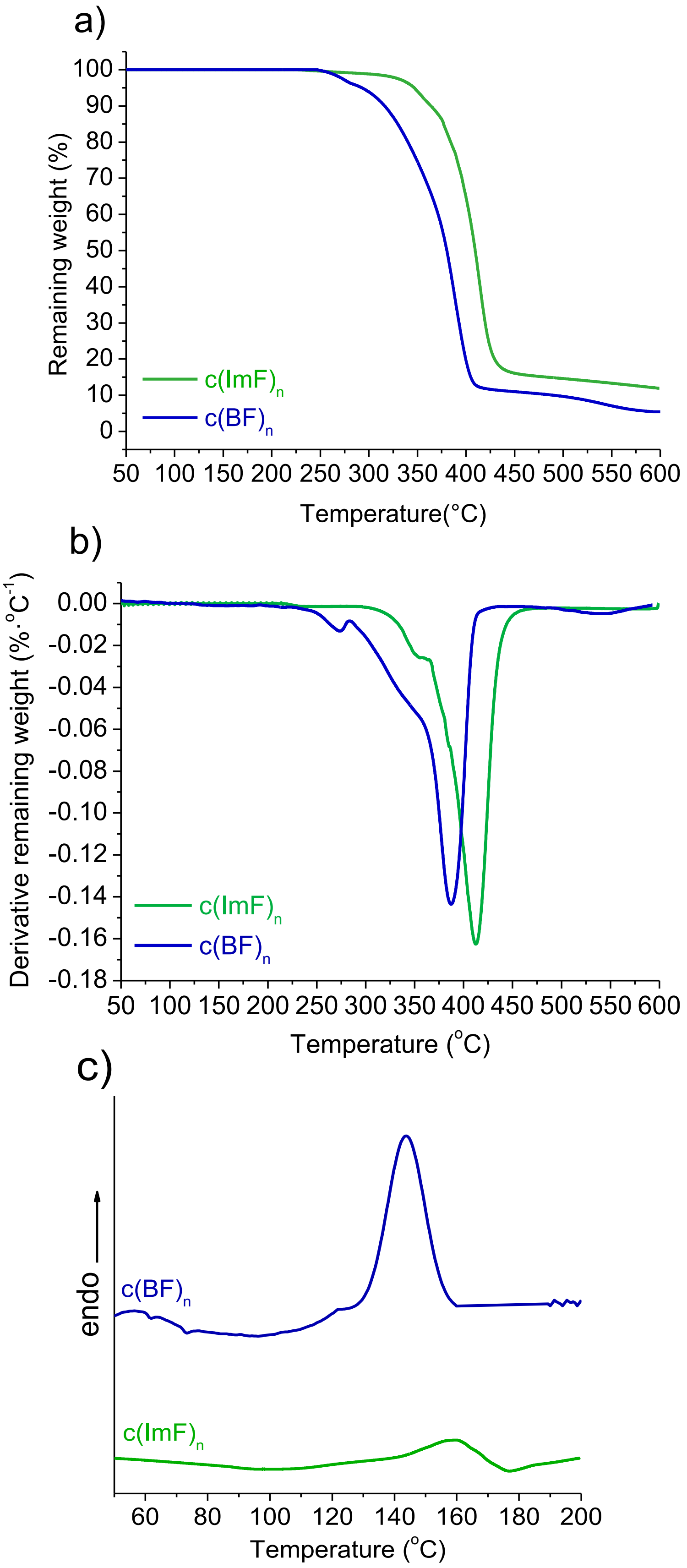


Figure 7.1.2. a) TGA (a and b) and DSC (c) of *c*(BF)$_n$ and *c*(ImF)$_n$.

molar ratio was made to react at 200, 220 and 230 ºC, 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 7.1.3a 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 $c(\mathrm{BF})_n$ 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 $c(\mathrm{BF})_n/c(\mathrm{ImF})_n$ mixtures differing in composition was followed by using the same methodology as before, and results obtained therefrom are shown in Figure 7.1.3b.

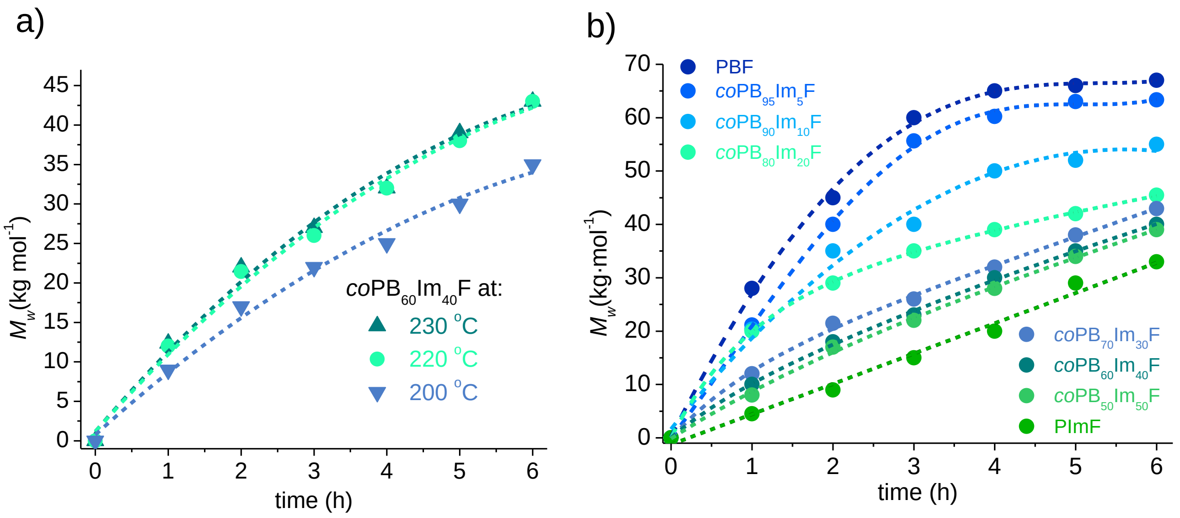


Figure 7.1.3. Plots of the evolution of Mw of the resulting copolyesters coPB$_x$Im$_y$F against reaction time. a) coPB$_{60}$Im$_{40}$F at different temperatures. b) coPB$_x$Im$_y$F with different compositions.

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 $c(\mathrm{ImF})_n$ cycles compared to the $c(\mathrm{BF})_n$ in the ROP of their mixtures. Nevertheless, all the copolyesters could be obtained in yields and with molecular weights high enough as to may validate successfully the suitability of the applied methodology in the synthesis of coPB$_x$Im$_y$F.

Yields, molecular weights and compositions of the whole *co*PB$_x$Im$_y$F series are collected in Table 7.1.2. Yields were above 80% in all cases and losses can be ascribed to the low molecular species that are unrecovered in the precipitation treatment to which the final reaction product is subjected. M_w of copolyesters are roughly in the ~40,000-60,000 g·mol^{-1} range and the homopolyesters PBF and PImF 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. *Đ* 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 ^{13}C and ^{1}H NMR spectroscopy and the spectra recorded from *co*PB$_{60}$Im$_{40}$F with indication of all peak assignments are depicted in Figure 7.1.4. The spectra of the whole series are included in the annex (Figure D.1.5). The quantitative analysis of the ^{1}H NMR spectra based on the integration of group specific

Table 7.1.2. Composition, yield, molecular weight, and microstructure of *co*PB$_x$Im$_y$F.

Polyester	**Yield (%)**	**Composition[a] x(BF/y(ImF) (mole/mole)**		**Molecular weight[b]**		**Microstructure[c]**					
		Feed	**Copol**	M_w **(g·mol^{-1})**	***Đ***	**BB**	**BIm ImB**	**ImIm**	n_{BF}	n_{ImF}	***R***
PBF	95	100	0	65,000	1.8	-		-	-	-	
PB$_{95}$Im$_5$F	93	95/5	96/4	63,000	1.6	91.5	8.5	0	22.4	1.00	1.04
PB$_{90}$Im$_{10}$F	90	90/10	92/8	55,000	1.9	80.4	18	1.6	9.9	1.18	0.95
PB$_{80}$Im$_{20}$F	85	80/20	80/20	45,000	1.9	66.3	28.5	5.2	5.7	1.37	0.91
PB$_{70}$Im$_{30}$F	85	70/30	66/34	43,000	1.4	54.9	35.4	9.7	4.1	1.55	0.89
PB$_{60}$Im$_{40}$F	82	60/40	58/42	40,000	1.8	46.8	33.5	19.7	3.8	2.17	0.76
PB$_{50}$Im$_{50}$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] Molar-% feed and copolymer composition determined by NMR.

[b] Weight-average molecular weight (*M$_w$*) and dispersity (*Đ*) determined by GPC.

[c] % of dyads (BB, BIm. ImB and ImIm) determined by NMR, number average chain lengths (n_{BF} and nI$_{mF}$) and degree of randomness calculated using the approach reported by Randall .[43]

signals provided an accurate estimation of the copolymer composition in BF (butylene furanoate) and ImF (isomannide furanoate) units. As it is seen in Table 7.1.2, 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.

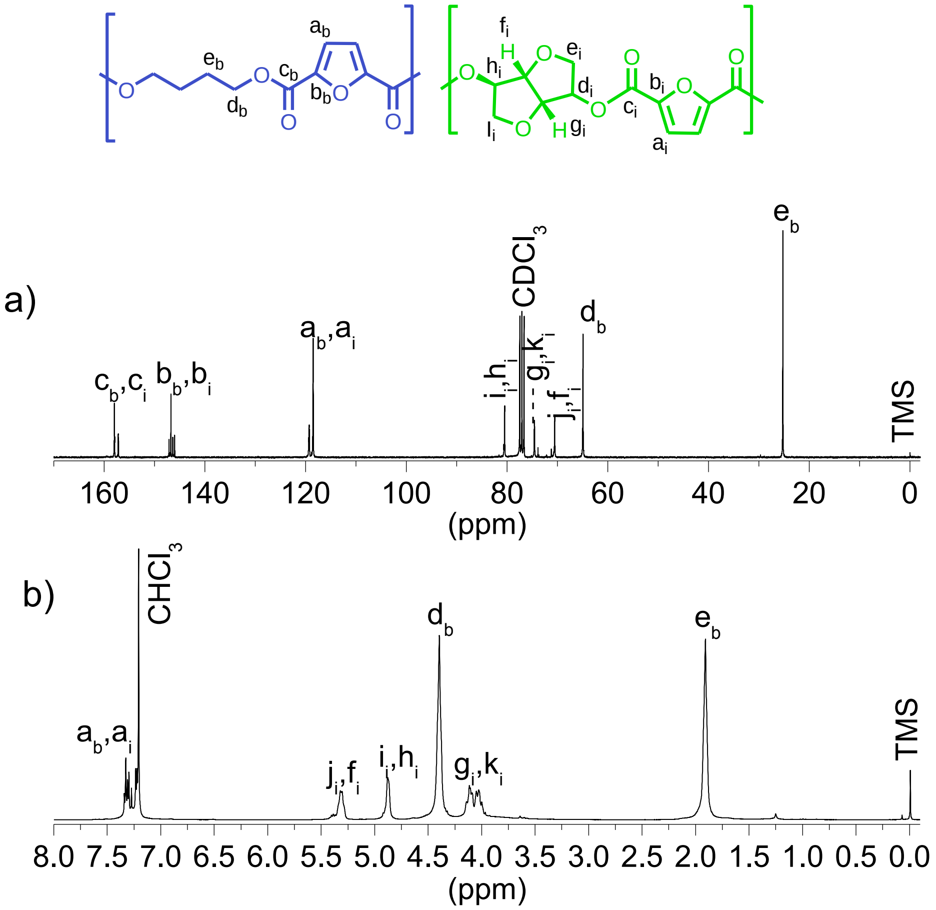


Figure 7.1.4. ^{13}C (top) and ^{1}H (bottom) NMR of *co*PB$_{60}$Im$_{40}$F.

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 carbonyl group of the furanic unit that is sensitive to dyads. In consequence the signal appears split into four peaks (Figure 7.1.5) corresponding to the four feasible dyads BB, ImIm, BIm and ImB. Peak areas were used to calculate, according to the procedure reported by Randall,[43] the number-average sequence lengths (*n*) and the random degree (*R*) for each composition. *n* and *R* values are listed Table 7.1.2 indicating that a nearly statistical distribution of BF and Im is present in the *co*PB$_x$Im$_y$F copolyesters with a random degree that decreases as the content of the copolyester in isomannide increases.

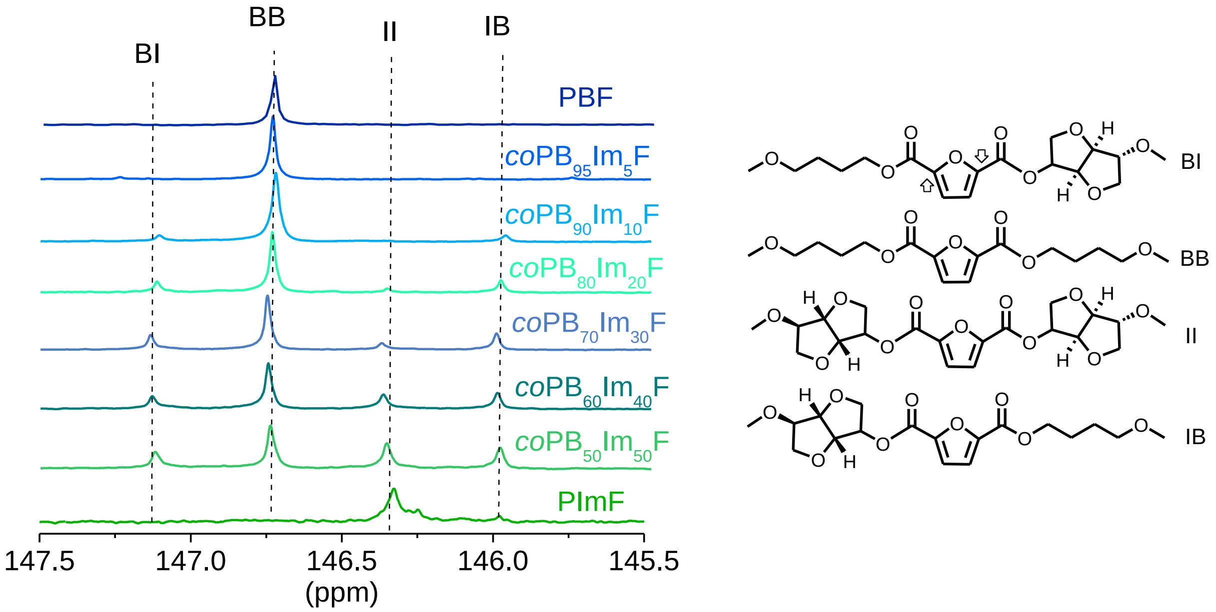


Figure 7.1.5. ^{13}C NMR signals used for microstructure analysis of *co*PB$_x$Im$_y$F with indication of the dyad assignments.

Thermal properties: The thermal properties of the *co*PB$_x$Im$_y$F copolyesters were analyzed by DSC and TGA, and data collected in these analyses are gathered in Table 7.1.3.

Table 7.1.3. Thermal properties of *co*PB$_x$ImF$_y$ copolyesters prepared *via* ROP.

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

[a] Onset temperature measured for 5% of weight loss.

[b] Avrami parameters determined from isothermal crystallization at T_c.

The thermogravimetric traces of the copolyesters recorded under an inert atmosphere over the 50/600 range, are depicted in Figure 7.1.6a and a representative selection of their derivative curves are shown in Figure 7.1.6b. PBF and PImF homopolyesters start to decompose around 360 ºC and 325 ºC, respectively, whereas the *co*PB$_x$Im$_y$F copolyesters do it at intermediate values but without following a recognizable trend. Nevertheless ${}^{o}T_{d,5\%}$ is far above 300 ºC 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, ${}^{max}T_d$ of copolyesters is confined in the ~390-400 ºC, which are values very close to that of PBF but clearly above the 376 ºC 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 ºC oscillated between 5% and 10% of the initial sample weight without showing apparent interrelation with the polyester composition.

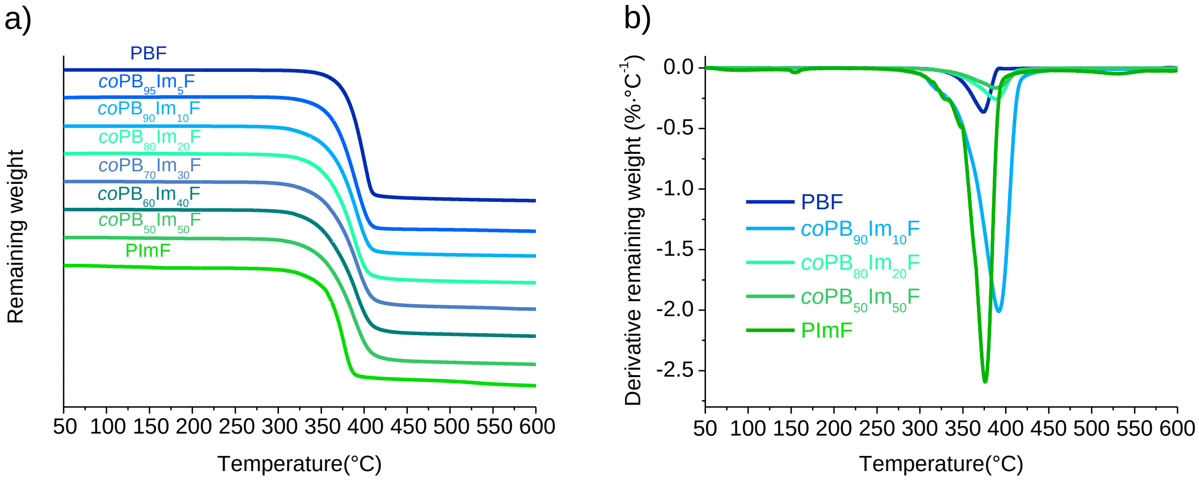


Figure 7.1.6. TGA traces of *co*PB$_x$Im$_y$F (a) and a selection of their derivative curves (b).

The DSC traces of *co*PB$_x$Im$_y$F together with those of PBF and PImF homopolyesters, recording at heating and cooling over the 0-200 ºC range, are depicted in Figure 7.1.7. Only PBF and copolyesters containing as maximum 10% of Im were found to display thermal changes indicative of melting and crystallization. Furthermore, only *co*PB$_{95}$Im$_5$F was able to crystallize clearly from the melt whereas an extremely weak broad crystallization exotherm was hardly seen on the cooling trace of *co*PB$_{90}$Im$_{10}$F. As expected, both melting temperature and enthalpy decreased with the content in isomannide. It can be said therefore that *co*PB$_x$Im$_y$F copolyesters are essentially amorphous polymers as it is also the case for PImF 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 in 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 isohexide are known to be unable to crystallize.[44-46]

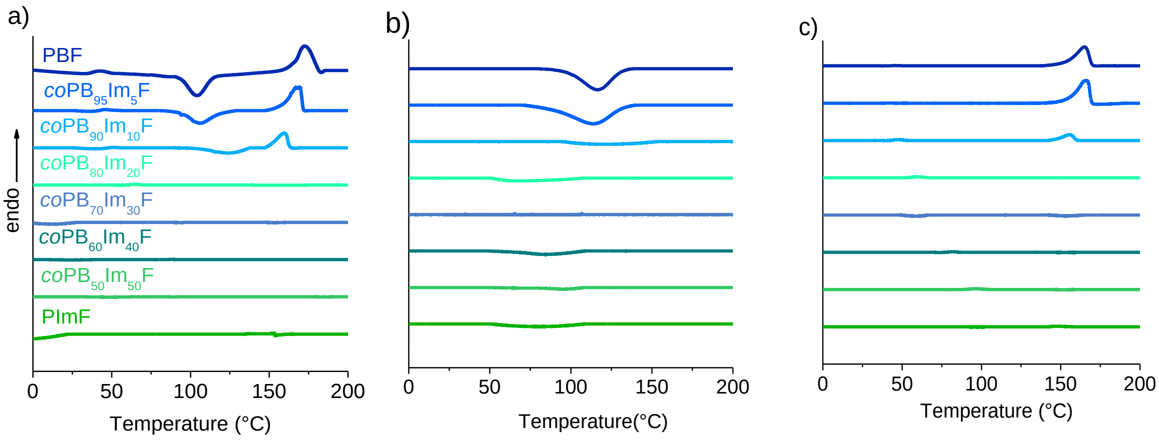


Figure 7.1.7. a) First heating, b) cooling, and c) second heating of *co*PB$_x$Im$_y$F.

The crystallinity of *co*PB$_{95}$Im$_5$F detected by DSC was firmly sustained by XRD analysis (Figure D.1.6). 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 *co*PB$_{90}$Im$_{10}$F 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 observed by POM was also present in the films of these two copolyesters (Figure D.1.7). It can be concluded from these observations therefore that both *co*$PB_{95}Im_5F$ and *co*$PB_{90}Im_{10}F$ 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. It is easily understood by assuming that upon crystallization, the minor comonomer is rejected to the amorphous phase.[47-49] Since the capacity of *co*PB_xIm_yF to crystallize is so severely restricted, the kinetics study addressed to quantify the influence of composition on crystallizability had to be restricted to the PBF/*co*$PB_{95}Im_5F$ pair. The isothermal crystallization of these two polyesters was carried out at 146 ºC and the evolution of crystallinity with time was compared. The typical sigmoidal curves resulting from these assays are plotted in Figure 7.1.8, and the kinetic parameters estimated by application of the Avrami approach to the experimental data are given in Table 7.1.3. As it could anticipated, PBF and *co*$PB_{95}Im_5F$ crystallized through a similar mechanism (their Avrami exponents are comparable) but the crystallization process is highly delayed for the copolyester ($t_{1/2}$ is doubled).

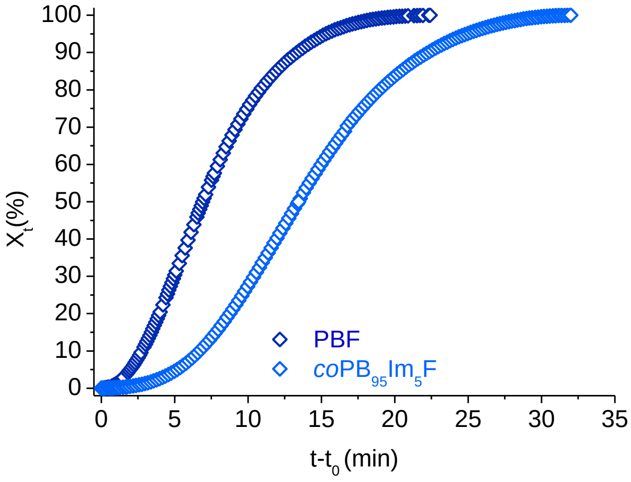


Figure 7.1.8. Relative crystallinity vs time in the isothermal crystallization of PBF and *co*$PB_{95}Im_5F$ at 146 ºC.

The glass-transition temperature of the copolyesters was measured on DSC heating traces registered from samples that were rapidly cooled from the melt. These traces showing the inflections indicative of transitions may be inspected in the annex (Figure D.1.8), and the T_g values estimated from them are listed in Table 7.1.3. It was found that the T_g of PBF appearing at 42 ºC noticeably raised up to 97 ºC as the content of the polymer in Im increased from 0 to 50 %-molar. 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 evidence in the PImF homopolyester itself, which has a T_g of 189 ºC. The variation of T_g with the copolyester composition is plotted in Figure 7.1.9 where the experimentally observed values are compare with those predicted by the Fox and Gordon-Taylor equations.[50,51] A good fit is attained for contents in Im of 20% and higher, as it is largely expected for amorphous polymers. The slight deviations detected for PBF, *co*PB$_{95}$Im$_5$F and *co*PB$_{90}$Im$_{10}$F are most likely due to the crystallinity present in these polyesters.

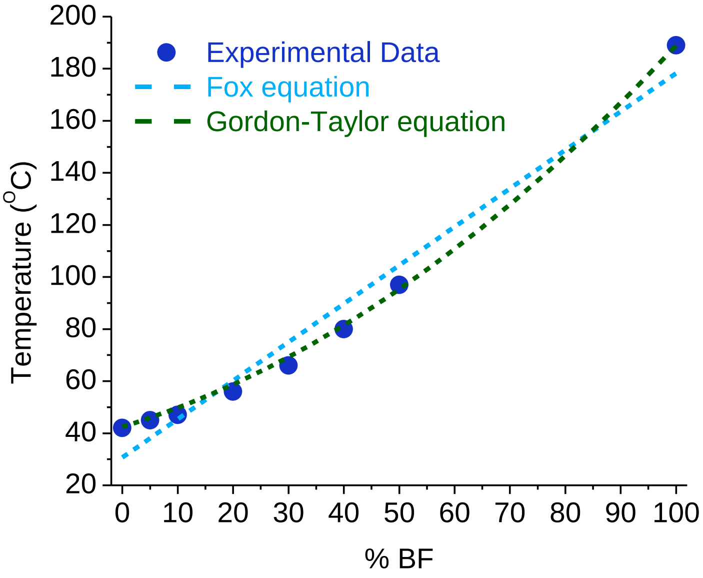


Figure 7.1.9. Variation of T_g with composition in the *co*PB$_x$Im$_y$F series.

Hydrolytic and enzymatic degradation. Both hydrolytic degradation and biodegradation of PBF have been examined by different authors in previous works,[23-25, 52,53] 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 high hydrophobicity and T_g caused by the presence of the aromatic units. On the other hand, the incorporation of isohexides 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 presence of porcine pancreas enzyme was monitored for the *co*PB_xIm_yF copolyesters containing 30 and 40 %-molar of Im as well as for the PBF and PImF homopolyesters and results are plotted in Figure 7.1.10. It is apparent in these plots that copolymerization enhances significantly the degradability of PBF. In fact, an essentially invariable function independent of time is obtained in the incubation of PBF for both sample weight and molecular weight, and either with or without enzyme assistance.

On the contrary, PImF 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 ºC), and brings into evidence the great sensitivity of Im to biodegradation. In agreement with the behavior observed for the two reference homopolyesters, *co*$PB_{70}Im_{30}F$ and *co*$PB_{60}Im_{40}F$ copolyesters showed apparent hydrolytic degradation at a degree that increased with the content in Im and that was significantly enhanced in the presence of lipases.

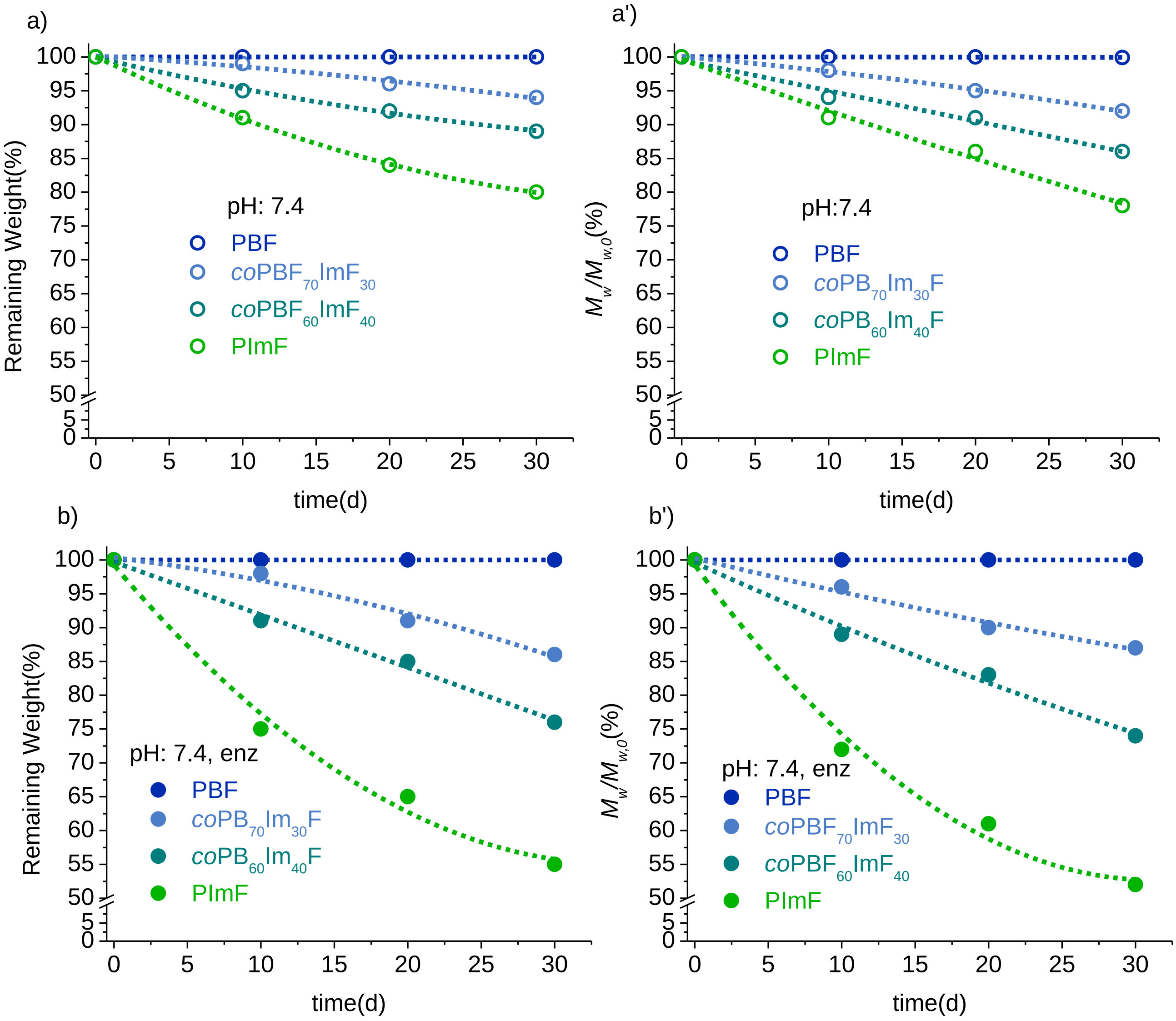


Figure 7.1.10. Hydrolytic (a and a') and enzymatic (b and b') degradation of *co*PB$_x$Im$_y$F upon incubation in water at pH 7.4.

VII.1.3 Conclusions

Furanoate based cyclic oligomers have been demonstrated in several previous reports to be useful monomers for ring opening polymerization and copolymerization. Oligomers of isommanide 2,5 furandicarboxylate were successfully synthesized in this work in high yield for the first time. As it generally happens, a mixture of dimer, trimer and tetramer species, largely enriched in the former, were 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 copolyesters is their high T_g which increases almost monotonically with the content in isomannide to reach a value near to 100 ºC for a 50% of composition. A second merit of these copolyesters is their apparent sensitivity to hydrolytic degradation because the homopolyester entirely made of butylene furanoate is essentially inert to water. Moreover the isomannide containing copolyfuranoates become much more rapidly hydrolyzed when subjected to the action of lipases, a certainly amazing behavior given its 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 represent s a step-forward to the generalization of the ROP technique for the synthesis of furanoate-based polyesters, and b) Polyfuranoates containing isomannide are fully bio-based copolyesters that are distinguished by being amorphous, having high T_g and displaying biodegradability.

VII.1.4 References

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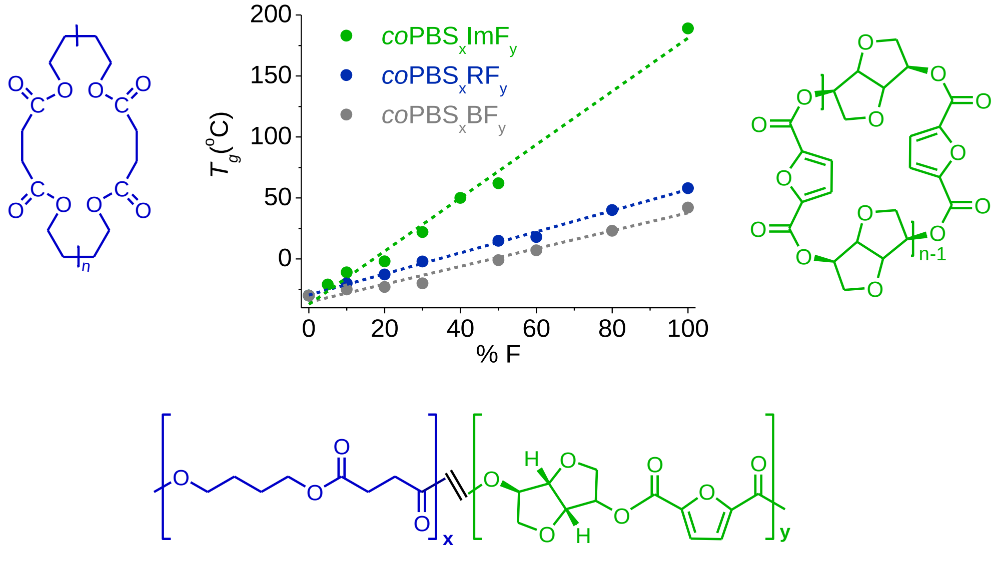
VII.2 Poly(butylene succinate) copolyesters

Abstract: Cyclic oligo(butylene succinate)s and oligo(isomannide 2,5-furandicarboxylate)s were copolymerized by ROP in the bulk at 220 ºC using $Sn(Oct)_2$ as catalyst. A series of random copolyesters containing isomannide furanoate units (ImF) 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 all copolyesters started to decompose above 300 ºC and were semicrystalline for contents in ImF units up to 30 %-mole. T_m slightly decreased with the content in ImF whereas Tg rapidly increased to reach a value of 62 ºC for the copolyester having equimolar composition. The genuine sensitivity to hydrolysis of PBS was enhanced by the incorporation of the ImF units, and degradation happened faster in the presence of lipases. The copolyester containing 40 %-mole of ImF was enzymatically hydrolyzed in about 30% in 30 days whereas the hopolyester PImF degraded near 50% under the same conditions.



***co*PBS$_x$ImF$_y$**

Publication derived from this work:

J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra. Fully bio-based PBS copolyesters with high Tg: ring opening copolymerization of cyclic (butylene succinate) and (isomannide furanoate) oligomers *Macromolecules*, **2018**, to be submitted**.**

VII.2.1 Introduction

Poly(butylene succinate) (PBS) is an aliphatic polyester that is today envisaged with great expectation for its potential as a sustainable material suitable for applications in packaging and biomedicine.[1,2] PBS is industrially produced by melt polycondensation of 1,4-butanediol (BD) and dimethyl succinate (DMS) or succinic acid (SA), although its synthesis by ring opening polymerization is perfectly feasible.[3,4] Both BD and SA are accessible at large scale from sugar fermentation[5,6] which makes PBS to be catalogued as a fully bio-based polymer. PBS is also moderately biodegradable and their main degradation products, BD and SA, are readily metabolized by living organisms.[7,8] PBS is semicrystalline with a T_m around 110 ºC and a T_g near to -30 ºC, which makes its physical behavior comparable to high density polyethylene. Nevertheless, a variety of copolyesters of PBS have been synthesized with the purpose of providing materials with improved properties.[9,10] One of the most applied approaches is the insertion of rigid comonomers with the purpose of rising the T_g.[11-13] The replacement of succinic acid by terephthalic acid is a well illustrative example of such approach.[14,15] However, aliphatic-aromatic copolyesters are not entirely satisfactory because they suffer from a notable reduction in sustainability and biodegradability. Recently other rigid monomers coming from renewable resources have been explored in this regard [16-18] with more or less agreeable results.

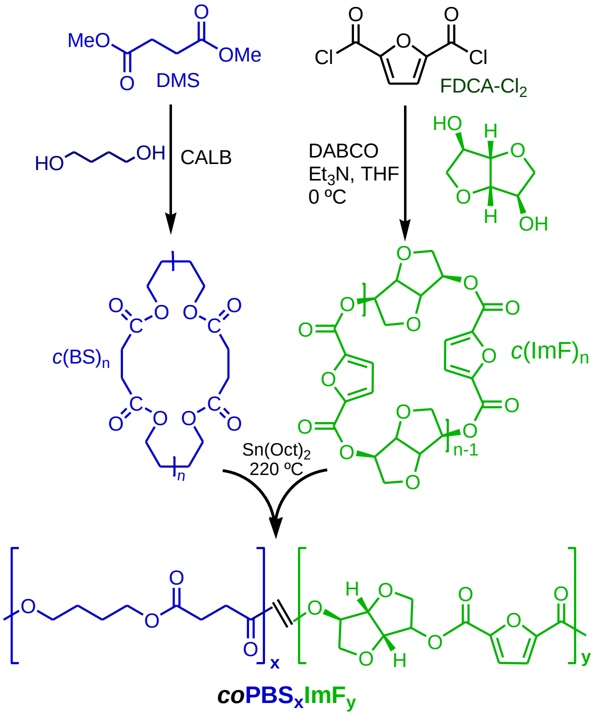
In this paper we wish to report on fully bio-based PBS copolyesters with high T_g and noticeable biodegradability which are obtained by inserting isomannide furanoate (ImF) units in the PBS chain by ROP. The oligo(butylene succinate) cycles $c(BS)_n$, which are well described in the literature, have been used for ROP in several occasions to produce PBS and its copolyesters. They are prepared by the so-called enzymatic cyclization method,[19,20] and their polymerization is performed by using both organometallic catalyst[21,22] and enzymes.[23,24] The comonomers used so far for designing PBS copolyesters by ROP include caprolactone,[25,26] and a variety of cyclic oligoesters such as ethylene succinate,[27] butylene furanoate[28] or di-*O*-2-(hydroxyethyl) resorcinol 2,5-furandicarboxylate[29]. The application of the ROP methodology to the synthesis of PBS copolyesters containing Imf is possible because the cyclic oligo(isomannide 2,5-furandicarboxylate), *c*$(\text{ImF})_n$ are now accessible by synthesis according to the procedure described recently by us.[30] Mixtures of *c*$(\text{BS})_n$ and *c*$(\text{ImF})_n$ are copolymerized to produce a series of random poly(butylene succinate-*co*-isomannide 2,5-furandicarboxylate) (*co*PBS_xImF_y) copolyesters with ImF contents ranging from 0 up to 50 %-mole. The copolyesters are fully characterized and their thermal properties and degradability are evaluated as a function of the comonomeric composition.

Isomannide (Im) is one the three bicyclic diols known as isohexides (1,4:3,6 dianhydroalditols) that have attracted great attention in these last decades as renewable monomers appropriate 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 stiffness of their bicyclic structure. A wide number of polycondensates containing isosorbide (Is), which is the isohexide derived from D-glucose, have been described, and even some of them have achieved industrial realization.[33-35] Isomannide has certain chemical advantages on Is due to its more symmetrical structure but it has been much less studied because it is not easily accessible. The only cyclic oligomers containing isohexides that have been reported in the literature are those made from aliphatic dicarboxylic acids reported by Kricheldorf et al.[36,37] Nonetheless, we reported in a previous paper on copolyesters of poly(butylene furanoate) containing Im that could be successfully synthesized by ROP from mixtures of *c*(BF)n and c(ImF). It should be remarked that ROP is an efficient well-known method for polymer synthesis in spite that its industrial application is scarce, a situation that is mainly determined by difficulty met in the access to the necessary lactones.[38,39] Nevertheless, the exceptional advantages offered by ROP (milder reaction conditions, absence of subproducts, minimization of side-reactions, etc.), places it on the focus of plenty of research, and its expansion, although gradual, is incessant.[40,41] Both enthalpy and entropy driven ROP processes are known to operate depending on the lactone size.[42-44]

VII.2.2 **Results and discussion**

The strategy followed to synthesize the copolyesters *co*PBS$_x$ImF$_y$ is depicted in Scheme 7.2.1.

Synthesis of copolyesters. Mixtures of *c*(BS)$_n$ and *c*(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 *co*PBS$_x$ImF$_y$ copolyesters series. The homopolyesters PBS and PImF to be used as references in characterization and properties evaluation 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*(BS)$_n$ and *c*(ImF)$_n$



Scheme 7.2.1. Synthetic route to poly(butylene succinate-*co*-isomannide 2,5 furandicarboxylate) copolyesters.

with a 60/40 molar ratio was made to react at 200, 220 and 230 ºC, 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 7.2.1a to show the enhancing effect of temperature on conversion upon raising it from 200 to 220 ºC whereas not significant change seems to happen at further increasing. According to these results and since the $c(BS)_n$ cycles started to decompose around 260 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 $c(BS)_n/c(ImF)_n$ mixtures differing in composition was followed by using the same methodology as before, and results obtained therefrom are shown in Figure 7.2.1b.

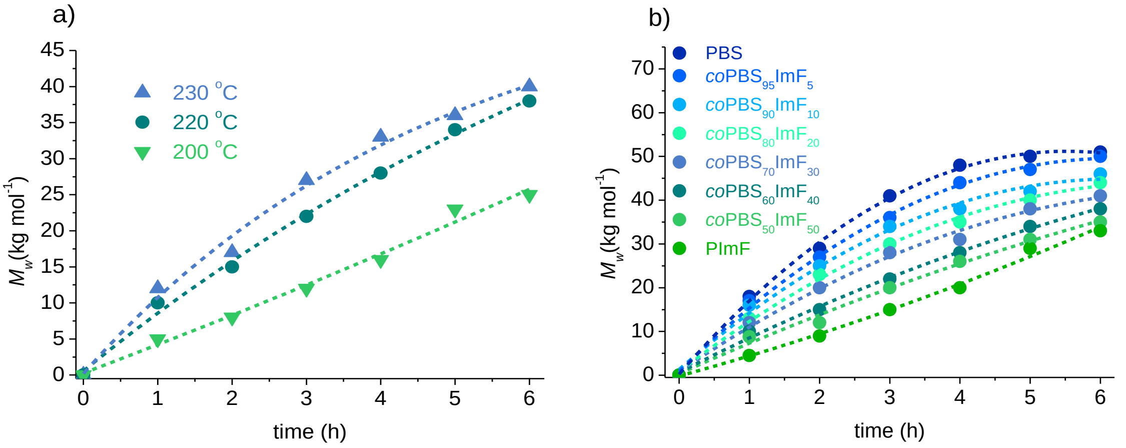


Figure 7.2.1. Plots of the evolution of M_w of the resulting copolyesters *co*PBS$_x$ImF$_y$ against reaction time. a) *co*PBS$_{60}$ImF$_{40}$ at different temperatures. b) *co*PBS$_x$ImF$_y$ with different compositions.

The M_w *vs* time plots showed that the M_w of the copolyesters decreased steadily with the content in ImF bringing out the less reactivity of the $c(ImF)_n$ cycles compared to the $c(BS)_n$ 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 for the synthesis of *co*PBS$_x$ImF$_y$.

Yields, molecular weights and compositions of the whole *co*PBS$_x$ImF$_y$ series are collected in Table 7.2.2. Yields were above 80% in all cases and losses can be ascribed to the low molecular species that were unrecovered in the precipitation treatment applied to the final reaction product. M_w of copolyesters are roughly in the ~30,000-50,000 g·mol^{-1} range with values monotonically descending as the content in ImF units increases. The homopolyesters PBS and PImF were obtained with 65,000 g·mol^{-1} and 28,000 g·mol^{-1} respectively, which is in full agreement with the trend observed for the whole copolyesters series. *Đ* values are between 1.5 and 2.0 which is a range of molar-mass 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.

Table 7.2.2. Composition, yield, molecular weight, and microstructure of *co*PB$_x$ImF$_y$.

Polyester	**Yield (%)**	**Composition^a x(BS/y(ImF) (mole/mole)**		**Molecular weight^b**		**Microstructure^c**		
		Feed	**Copol**	**M_w (g·mol^{-1})**	**Đ**	**n_{BS}**	**n_{IF}**	***R***
PBF	95	100	0	65,000	1.8	-	-	
PBS$_{95}$ImF$_5$	91	95/5	97/3	50,000	1.5	1.65	1.66	1.20
PBS$_{90}$ImF$_{10}$	86	90/10	91/9	46,000	1.6	1.87	4.62	0.78
PBS$_{80}$ImF$_{20}$	83	80/20	84/16	43,000	1.6	2.15	4.34	0.92
PBS$_{70}$ImF$_{30}$	81	70/30	78/22	41,000	1.8	1.15	3.51	1.15
PBS$_{60}$ImF$_{40}$	81	60/40	72/28	37,000	1.9	1.65	3.51	0.89
PBS$_{50}$ImF$_{50}$	80	50/50	53/47	33,000	2.0	1.25	4.29	1.03
PImF	80	0	100	28,000	1.9	-	-	-

[a] Molar-% feed and copolymer composition determined by NMR.

[b] Weight-average molecular weight (M_w) and dispersity (*Đ*) determined by GPC.

[c] % of dyads n_{BF} and n_{IF} determined by NMR, number average chain lengths (n_{BF} and $n\text{I}_{mF}$) and degree of randomness calculated using the approach reported by Devaux .[46]

The constitution of the polymers was ascertained by ^{13}C and ^{1}H NMR spectroscopy and the spectra recorded from *co*PBS$_{60}$ImF$_{40}$ with indication of all peak assignments are depicted in Figure 7.2.2. The spectra of the whole series are included in

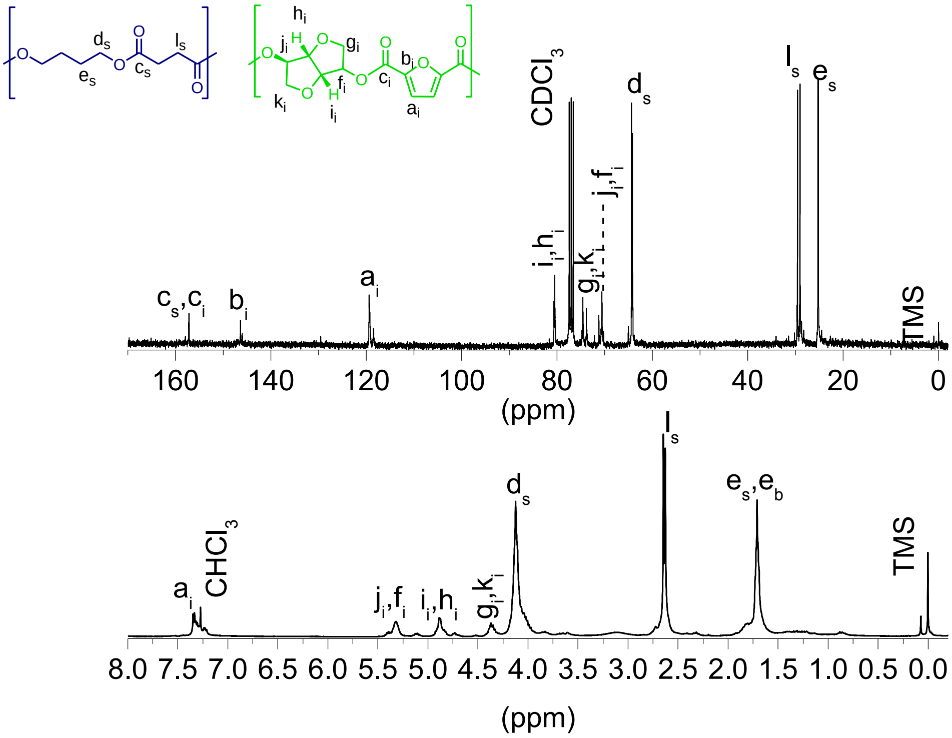


Figure 7.2.2. ^{13}C (top) and ^{1}H (bottom) NMR of *co*PBS$_{60}$ImF$_{40}$.

the annex (Figure D.2.1). The quantitative analysis of the ^{1}H NMR spectra based on the integration of specific signals provided an accurate estimation of the copolymer composition in BS and ImF units. As it is seen in Table 7.2.2, differences in ImF contents between the feed and its generated copolyester may arrive to be up to 12%. These deviations, although not exaggerated, are significantly larger than those found for other related copolyesters obtained by ROP.[28-30] Since ImF is invariably the unit that is defectively incorporated in the copolyester, it should be inferred that is the lower relative reactivity of *c*(ImF)$_n$ that motivates such differences.

Microstructure of copolyesters. The number average sequence lengths (*n*) and the degree of randomness (*B*) were determined by ^{13}C NMR, applying the statistical method used by Devaux[46] and assuming that [S] = [B] and [F] = [I] and [BF] = [IS]. The following expressions were used for the calculation of *n* and *B*:

$$n_{BS} = \frac{[BS]}{[BF]} + 1 \qquad n_{BF} = \frac{[BF]}{[BS]} + 1 \qquad n_{IS} = \frac{[IS]}{[IF]} + 1 \qquad n_{IF} = \frac{[IF]}{[IS]} + 1 \quad B = \frac{1}{n_{BS}} + \frac{1}{n_{IF}}$$

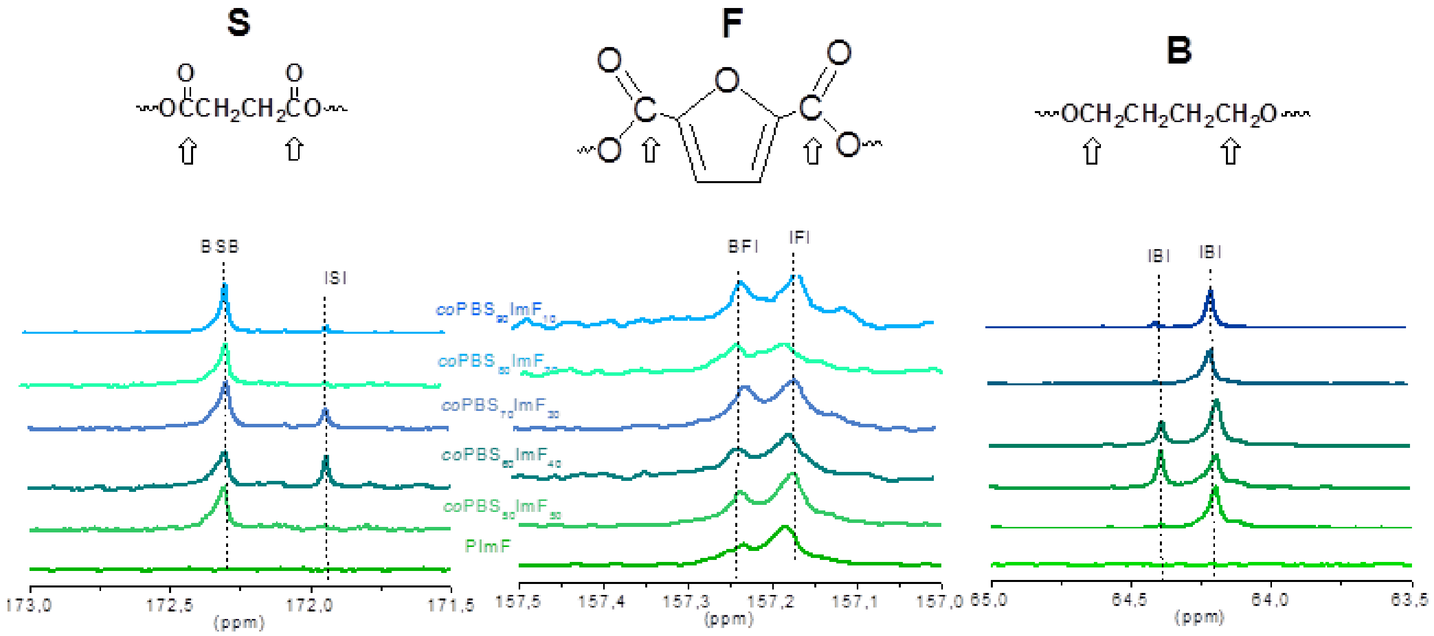


Figure 7.2.3. ^{13}C NMR signals used for microstructure analysis of *co*PBS$_x$ImF$_y$ with indication of the dyad assignments.

Table 7.2.3. Thermal properties of *co*PBS$_x$ImF$_y$ copolyesters prepared *via* ROP.

Copolyester	**TGA**			**DSC**					**Crystallization kinetics**^{b}			
					First heating		Second heating					
	$^oT_d{}^a$ (°C)	$^{max}T_d$ (°C)	R_w (%)	T_g (°C)	T_m (°C)	ΔH_m (J·mol^{-1})	T_m (°C)	ΔHm (J·mol^{-1})	T_c (°C)	n	lnK	$t_{1/2}$ (min)
PBS	345	401	3	-30	112	79	111	72	75	2.49	-2.52	2.37
PBS$_{95}$ImF$_5$	330	388	7	-21	103	47	102	48	75	2.57	-3.73	4.18
PBS$_{90}$ImF$_{10}$	325	395	5	-11	95	44	92	45	75	2.58	-7.59	17.09
PBS$_{80}$ImF$_{20}$	314	383	7	-5	95	15	95	15	-	-	-	-
PBS$_{70}$ImF$_{30}$	313	383	8	15	94	13	-	-	-	-	-	-
PBS$_{60}$ImF$_{40}$	314	378	9	50	-	-	-	-	-	-	-	-
PBS$_{50}$ImF$_{50}$	334	390	9	62	-	-	-	-	-	-	-	-
PImF	325	376	9	189	-	-	-	-	-	-	-	-

[a] Onset temperature measured for 5% of weight loss.

[b] Avrami parameters determined from isothermal crystallization at T_c.

The dyads were calculated from the signals of the ^{13}C NMR spectra and assuming similar relaxation times for the same carbon in the different dyads. In addition, it was assumed that in the triads the substitution on the left of a central unit does not affect the substitution on the right. The spectra of the *co*PBS$_x$ImF$_y$ series is shown in Figure 7.2.3. By deconvolution of the signals, the content of the different dyads could be obtained and consequently n_{BS}, n_{IF} and B can be calculated applying the equations aforementioned. The values of the serie are given in Table 7.2.2 revealing that the microstructure is essentially random.

Thermal properties: The thermal properties of the *co*PBS$_x$ImF$_y$ copolyesters were analyzed by DSC and TGA, and data collected in these analyses are gathered in Table 7.2.3. The thermogravimetric traces of the copolyesters recorded under an inert atmosphere over the 50-600 ºC range are depicted in Figure 7.2.4a, and a representative selection of their derivative curves are shown in Figure 7.2.4b. PBS and PImF homopolyesters started to decompose around 325 ºC and 345 ºC, respectively, whereas the *co*PBS$_x$ImF$_y$ copolyesters did it in the ~310-335 range without showing any systematic trend. The same was found to happen with $^{max}T_d$ which appears confined in the ~390-380 ºC range. In both cases differences are too small as to deserve a specific discussion, and the valuable conclusion that can be drawn from these data is that *co*PBS$_x$ImF$_y$ copolyesters have a resistance to heat that allows their thermal processing at temperatures similar to those used for PBS. 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 ImF units. Residual weights after heating at 600 ºC oscillated between 5% and 9% of the initial sample weight without showing apparent interrelation with the polyester composition.

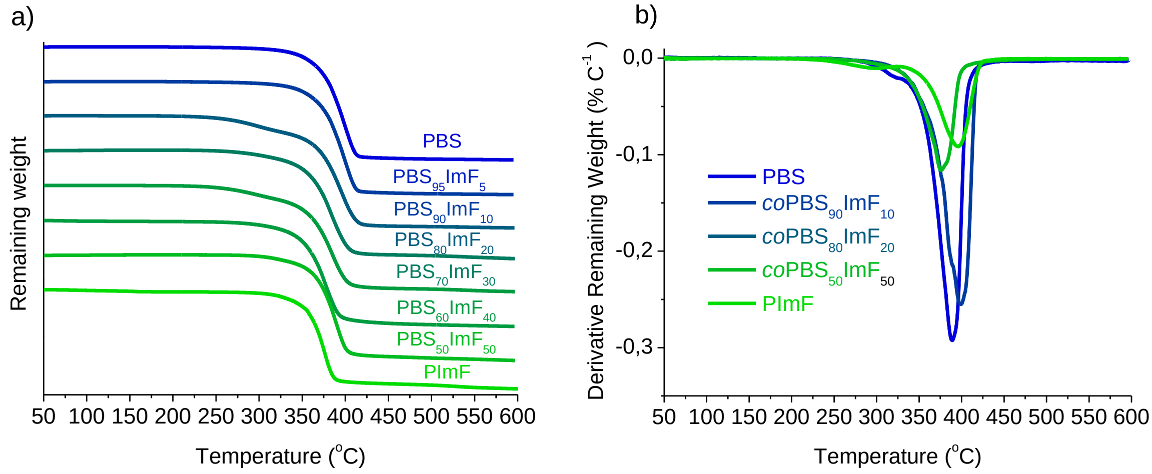


Figure 7.2.4. TGA traces of *co*PBS$_x$ImF$_y$ (a) and a selection of their derivative curves (b).

The DSC traces of *co*PBS$_x$ImF$_y$ together with those of PBS and PImF homopolyesters, recording at heating and cooling over the 20-180 ºC range, are depicted in Figure 7.2.5.

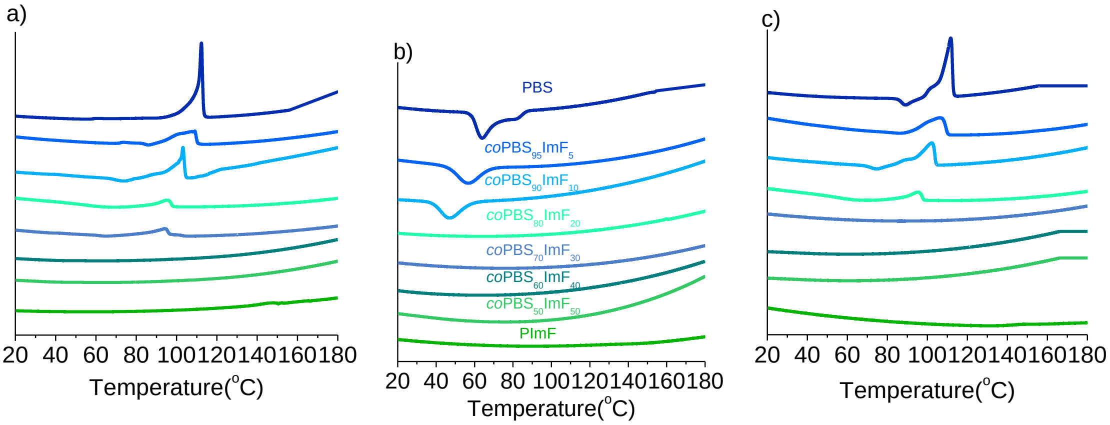


Figure 7.2.5. a) First heating, b) cooling, and c) second heating of *co*PBS$_x$ImF$_y$

As expected, both melting temperature and enthalpy decreased with the content in ImF so that *co*PBS$_x$ImF$_y$ become amorphous as the content in such units reached 40%. PImF homopolyester is also amorphous, a feature that had been earlier reported by Okada et al.[47] These results bring into evidence the notable repressing effect that the insertion of ImF units in the PBS chain exerts on the genuine crystallinity of this polyester. The occurrence of such effect is by no means surprising since most of aromatic homopolyesters containing isohexides are known to be unable to crystallize[48-

[50] It should be noted however that all semicrystalline *co*PBS$_x$ImF$_y$ but the one containing 40% of Imf, were able to crystallize upon cooling from the melt with a more than satisfactory reproducibility of both T_m and ΔH_m. This is an interesting result that adds value to the potential of these copolyesters for being processed by thermal methods.

The crystallinity present in *co*PBS$_x$ImF$_y$ was firmly sustained by XRD analysis (Figure D.2.2). The powder diffraction patterns recorded from the copolyesters showing melting by DSC displayed discrete scattering that was coincident in both spacing and intensity to that of PBS. Additionally, the characteristic grainy texture displayed by PBS films when observed by POM was also present in the films of these copolyesters (Figure D.2.3). It can be therefore definitely concluded from these observations that *co*PBS$_x$ImF$_y$ with contents in ImF up to 30% are semicrystalline and that these copolyesters crystallize sharing the crystal structure of PBS.[51,52] Crystallization of copolyesters containing small amounts of one of the comonomers in the crystal lattice of the homopolymer made of the major comonomer is a well-known common fact. The phenomenon is easily understood by assuming that upon crystallization, the comonomeric unit present in minor amount becomes selectively rejected to the amorphous phase.[53,54]

Given the high relevance that crystallization from the melt has on the potential utilization of PBS and its copolyesters in applications based on heat processing, a kinetics study has been addressed to quantify the influence of composition on the crystallizability of semicrystalline *co*PBS$_x$ImF$_y$. The isothermal crystallization of molten *co*PBS$_{95}$ImF$_5$ and *co*PBS$_{90}$ImF$_{10}$ was carried out at 75 ºC, and the evolution of crystallinity observed for them along crystallization time was compared with that observed for PBS. The typical sigmoidal curves resulting from these assays are plotted in Figure 7.2.6, and the kinetic parameters estimated by application of the Avrami approach to the experimental data are given in Table 7.2.3. As it could anticipated, PBS and the copolyesters crystallized through a similar mechanism (their Avrami exponents are comparable) but the crystallization process is largely delayed in the copolyesters with $t_{1/2}$ taking up to near eight times value for that containing 10 %-mole of ImF units.

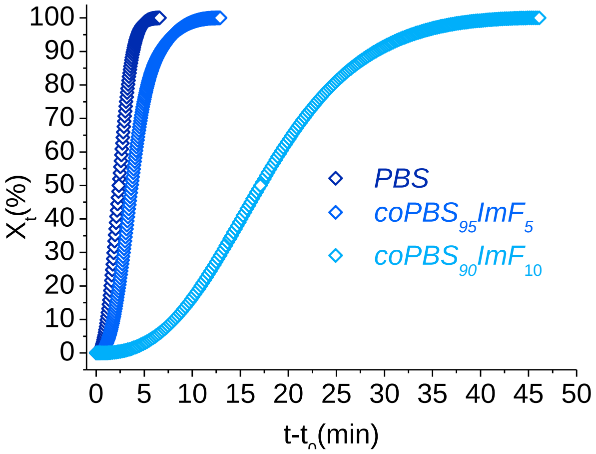


Figure 7.2.6. Relative crystallinity *vs* time in the isothermal crystallization of PBS and *co*PBS_xImF_y copolyesters at 75 ºC.

The glass transition in *co*PBS_xImF_y copolyesters. The glass-transition temperature of the copolyesters was measured on DSC heating traces registered from samples that were rapidly cooled from the melt. These traces showing the inflections indicative of transitions are shown in Figure 7.2.7 and the T_g values estimated from them are listed in Table 7.2.3. It was found that the T_g of PBS appearing at -30 ºC raised up to 60 ºC as the content of the polymer in ImF increased from 0 to 50 %-mole. The high stiffness of Im and its capacity to enhance T_g becomes clearly evidenced in the PImF homopolyester, which has a T_g of 189 ºC. The variation of T_g with the copolyester composition is plotted in Figure 7.2.8a where the experimentally observed values are compared with those predicted by the Fox and Taylor equations.[55,56] A good fit is attained with the slight detected deviations being most likely due to the crystallinity still present in the polyesters with lower content in ImF units.

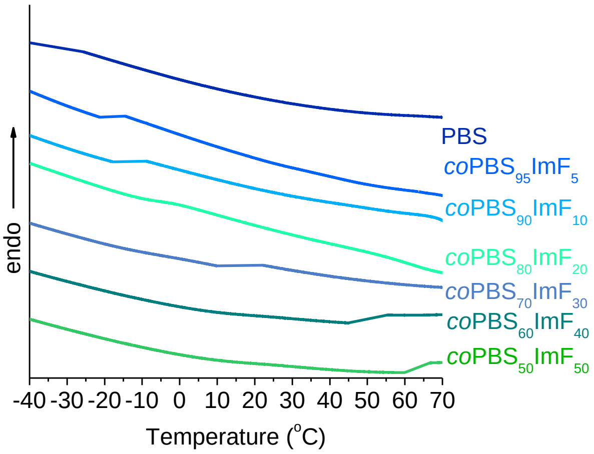


Figure 7.2.7. Traces of T_g of *co*PBS$_x$ImF$_y$.

The enhancing effect on T_g attained by incorporating isomannide furanoate in PBS is certainly outstanding with a raise of near 2 ºC for every 1% increment of ImF units. Obviously the stiffness of the bicyclic isomannide and the furanic structures are summed up to produce a polyester chain with a highly impeded mobility. To our knowledge such an effect is the highest attained so far on PBS by copolymerization. The PBS-PBT copolyester, in which 50% of the succinic acid was replaced by terephthalic acid, displayed a T_g of only ~15 ºC, [15,57,58] and the PBS-PBF, in which the diacid comonomer is 2,5-furandicarboxylic has a T_g of -1 ºC.[13,28] On the other hand the replacement of 1,4-butanediol by bicyclic acetalized hexitols led to higher increases in T_g[59-60] In fact the bicyclic D-glucitol was able to cause an increase in the T_g of PBS near to that observed in *co*PBS$_x$ImF$_y$, with a value of 54 ºC for a 50 %-mole of butylene replaced by the sugar unit.[61,62] The effect played by isosorbide cannot be properly compared because available data on copolyesters containing this isohexide are limited to contents below 30 %-mole.T_g around -10 to -15 ºC have been the maximum values reported for these isosorbide-containing PBS copolyesters.[61-62] A graphical representation of the variation of T_g with composition for those most relevant related systems is shown in Figure 7.2.8b.

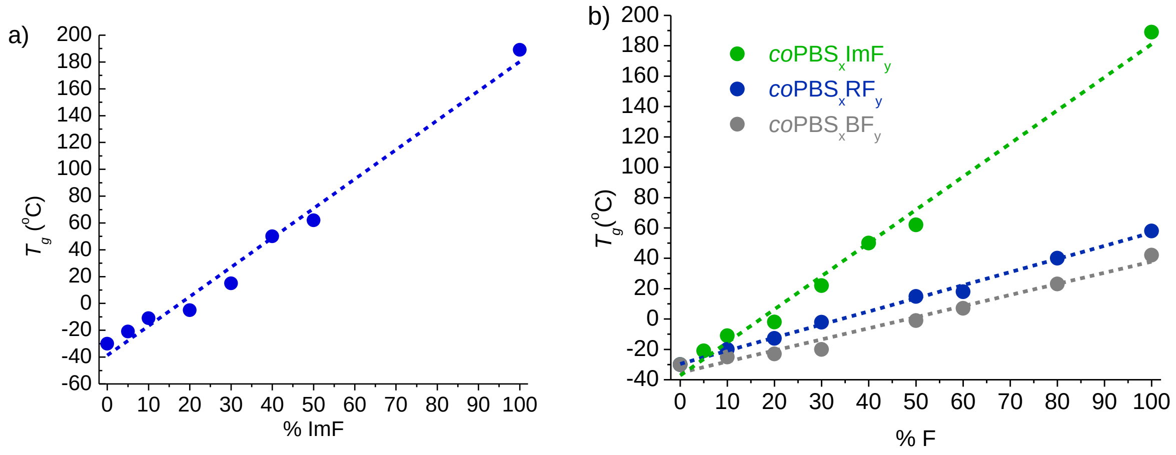


Figure 7.2.8. a) Variation of T_g with composition in the *co*PBS$_x$ImF$_y$ series. b) T_g *vs* composition compared for some selected PBS copolyesters. *co*PBS$_x$RF$_y$ and coPBS$_x$BF$_y$ data taken from Morales-Huerta et al. [28,29]

Hydrolytic and enzymatic degradation. The degradation of PBS by the action of water is a well-studied issue.[,2,9,11,28] This polyester is known to be slowly hydrolyzed under physiological conditions and its degradation is significantly speeded up by lipases.[16-18,63,64] The effect played by the incorporation of ImF units in PBS has been examined in this work for two different compositions. Both the decrease in sample weight and molecular weight happening along 30 days of incubation at 7.4 with and without porcine pancreas lipases added was monitored for the *co*PBS$_x$ImF$_y$ copolyesters containing 30 and 40 %-molar of ImF, as well as for the PBS and PImF homopolyesters, and results are plotted in Figure 7.2.9. It is apparent in these plots that copolymerization enhances slightly the degradability of PBS, and that PImF appears to be most 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 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 ºC), and it brings out the great sensitivity of the ImF units to biodegradation. In agreement with the behavior observed for the two reference homopolyesters, *co*PBS$_{70}$ImF$_{30}$ and *co*PBS$_{60}$ImF$_{40}$ copolyesters showed increasing hydrolytic degradation with increasing content in ImF units, an effect that was significantly enhanced when incubation was performed in the presence of lipases.

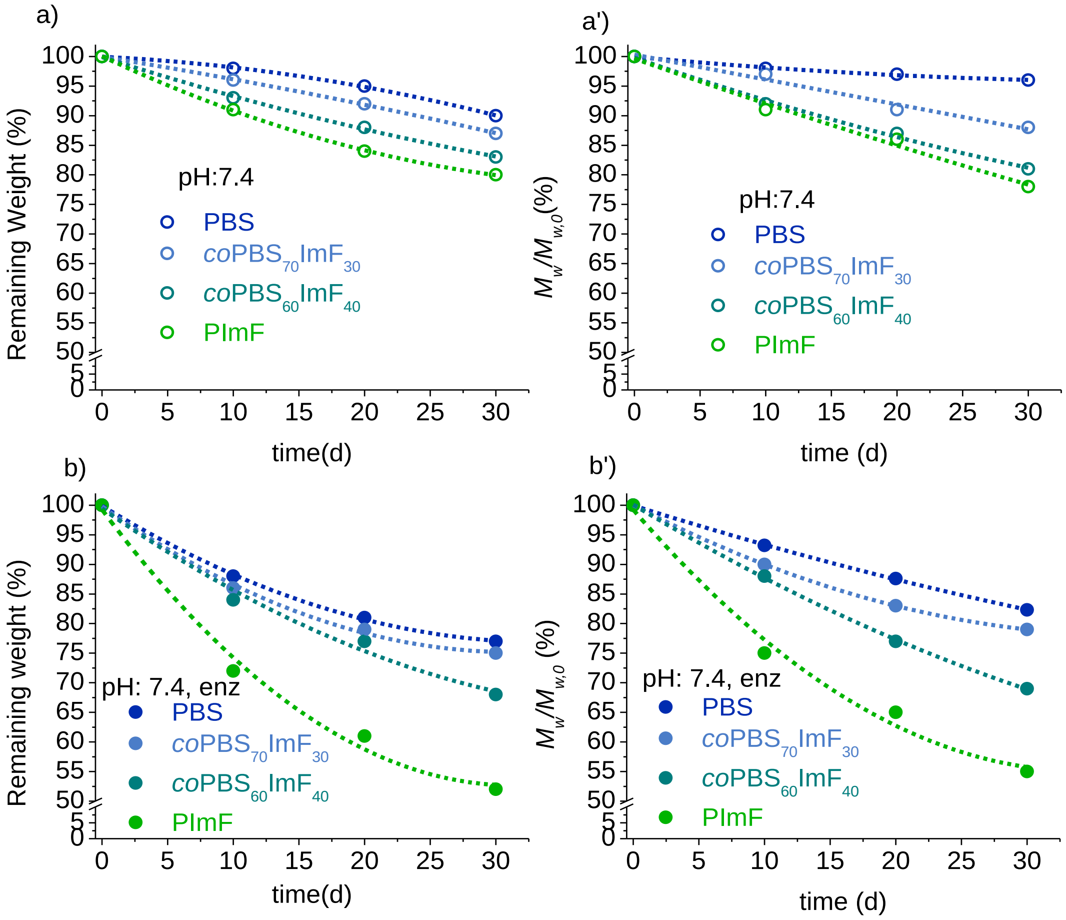


Figure 7.2.9. Hydrolytic (a and a') and enzymatic (b and b') degradation of *co*PBS$_x$ImF$_y$ upon incubation in water at pH 7.4.

VII.2.3 Conclusions

Copolymerization is the approach mostly used with PBS to modify its properties, in particular its $T_{g.}$ Random copolyesters with satisfactory molecular weights and controlled compositions were obtained by ROP of mixtures of oligo(butylene succinate) and oligo(isomannide furanoate) cycles. The application of this methodology has been possible because the isomannide furanoate cycles have become recently accessible by synthesis. It is noteworthy that PBS copolyesters containing isomannide furanoate units are able to retain the good thermal stability of PBS and that they are able to crystallize for contents up to 30 %-mole in such units. It is also outstanding that the degradability of PBS is enhanced by the presence of the isomannide furanoate units which is contrary to what happens when alkylene aromatic units are incorporated in this polyester. However the most outstanding feature of PBS copolyesters containing isomannide furanoate units is doubtlessly their high T_g that arrives to be 62 ºC for an composition equimolar in comonomers. It is apparent that of the rigid structures of bicyclic isomannide and furan are efficiently combined to induce a high T_g in the flexible chain of PBS. To our knowledge the approach applied in this work is that giving place to the maximum increasing of T_g in PBS by copolymerization. The conclusion that can be stated with general application is that isomannide furanoate is an extremely efficient building block for the design of bio-based copolyesters with enhanced T_g. This effect is even more appreciated provided that biodegradability is also slightly increased and crystallizability is preserved for moderate contents of such units.

VII.2.4 References

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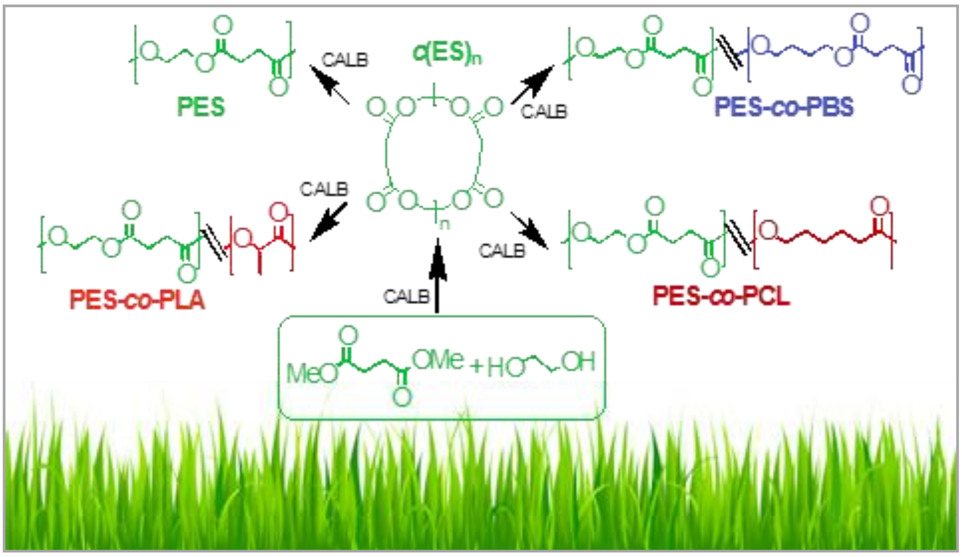
VIII Polyesters of alkylene succinate with resorcinol 2,5-furandicarboxylate by ring opening polymerization

VIII.1 Poly(ethylene succinate) by ROP

Abstract: High-molecular-weight poly(ethylene succinate) (PES) was prepared by enzymatic ring opening polymerization (*e*-ROP) of cyclic oligo(ethylene succinate)s (*c*(ES)$_n$). The oligomeric fraction, consisting essentially of a mixture of trimer and tetramer, was synthesized by lipase-catalyzed condensation of dimethyl succinate and ethylene glycol in highly dilute solution. *e*-ROP of *c*(ES)$_n$ conducted at 125 ºC for 24 h afforded PES with a molecular weight above 60,000 g·mol^{-1}. The methodology was then applied to the preparation of PES copolyesters containing butylene succinate, ε-hydroxycaproate or L-lactate units in an approximately unity ratio. The copolyesters had molecular weights similar to the homopolyester and all they displayed a random microstructure. This strategy allows preparing efficiently PES and its copolyesters with high molecular weights and absent of metallic contaminants, and constitutes a green alternative to the procedures currently in use.



Publication derived from this work:

J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra. A green strategy for the synthesis of poly(ethylene succinate) and its copolyesters via enzymatic ring opening polymerization. *Eur. Polym. J.*, **2017**, 97, 514-519.

VIII.1.1 Introduction

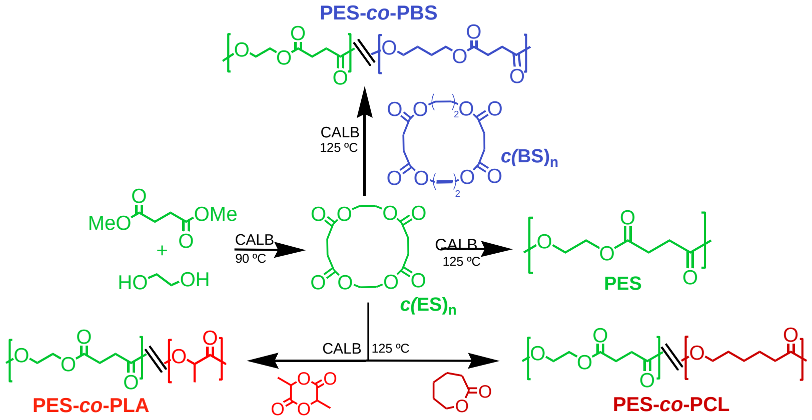
Sustainable polymers coming from renewable feedstocks and able to be biodegraded at convenient periods of time constitute nowadays a distinguished group of materials with high industrial potential and great interest in the biomedical field.[1,2] Among them, aliphatic polyesters consisting of rather short repeating units and including both AA-BB and A-B types, are by far the most studied and commercially used.[3,4] The good accessibility to bio-based chemical blocks suitable for building these polyesters, their particular susceptibility to biodegradation, and their favorable basic properties, are the main reasons for the outstanding position that they have reached.

Ring opening polymerization (ROP) of strained lactones is the method of choice for the synthesis of poly(hydroxyalkanoate)s whereas poly(alkylene alkanedioate)s are preferably produced by polycondensation of alkanediols with dicarboxylic acids or their esters, mostly in the molten state.[5,6] The ROP method offers advantages over the polycondensation one so that makes it particularly suitable for polymer synthesis under certain conditions. The low viscosity of lactones and the no generation of volatiles in ROP are much appreciated features when polymerization has to be performed *in situ* such as it is the case of both nanocomposite manufacture and reactive injection molding. Furthermore, polyester formation by ROP usually takes place at high rates than polycondensation with a minimum formation of subproducts. Cleaner polymers may be therefore obtained by ROP using relatively mild reaction condition.[7,8] An additional noteworthy merit of ROP is that it is efficiently catalyzed by enzymes making feasible the preparation of fully metal-free polymers.[9-11]

In 2004, the US Department of Energy declared bio-based succinic acid (SA) as a high-potential chemical platform for the synthesis of compounds able to replace those currently in use but coming from fossil resources.[12] This is one of the reasons explaining why poly(alkylene succinate)s, more specifically poly(butylene succinate) (PBS), are ahead of sustainable polyesters of AA-BB type.[13] The industrial synthesis of

PBS is usually performed by polycondensation of SA (or its dimethyl ester) with 1,4-butanediol (BDO) in the presence of tin or titanium organometallic catalysts. In 2006 Matsamura[14,15] et al. reported the synthesis of PBS by *e*-ROP of cyclic di(butylene succinate) which is highly relevant since the monomer may be profited from the byproduct downstream of the industrial production of PBS by polycondensation.[16] Poly(ethylene succinate) (PES) is the other polysuccinate that is commercially accessible although it has not attained yet production at the ton-scale. PES is more biodegradable than PBS, melts slightly above 100 ºC and displays favorable mechanical properties.[17-19] This polyester is currently under extensive investigation addressed to the development of copolyesters with properties able to give response to the present-day biomaterial demands.[20-23] The synthesis of PES is carried out by reaction of succinic acid either with ethylene glycol or ethylene oxide. These methods lead to polyesters of moderate molecular weights and both of them require the concourse of organometallic catalysts.

In this letter we wish to communicate on a new strategy for the synthesis of PES that combines *e*-ROP of cyclic oligo(ethylene succinate)s, *c*$(ES)_n$, with enzymatic polymerization to render polymers with high molecular weight and absent of metallic impurities. The procedure is readily extensible to the preparation of random copolyesters by copolymerization of *c*$(ES)_n$ with other cyclic esters either commercially available or straightforwardly accessible by synthesis. The proposed strategy is depicted in Scheme 8.1.1.



Scheme 8.1.1. Route to PES and PES copolyesters by *e*-ROP.

VIII.1.2 Results and discussion

The cyclic oligomers of ethylene succinate *c*(ES)$_n$ were synthesized by applying the method recently reported by us for the preparation of the cyclic oligomers of butylene succinate *c*(BS)$_n$.[20] The cyclization reaction of DMS with EG was performed in toluene at 96 ºC for a period of two days in the presence of an equal weight amount of supported lipase from *Candida antarctica* (CALB). After removal of the enzyme by filtration and solvent evaporation, the crude residue was subjected to flash chromatography to eliminate the acyclic species and to render the purified *c*(ES)$_n$ mixture in approximately 70% yield. Spectroscopic and chromatographic results obtained in the characterization of the cyclic mixture are shown in Figure 8.1.1, and a detail account of the corresponding numerical data is provided in the Supporting Information file. The NMR spectra (Figure 8.1.1a) were in full agreement with the constitution of *c*(ES)$_n$ mixture and did not show any signal indicative of the presence of linear oligomers. The MALDI-TOF spectrum (Figure 8.1.1b) contained the *m/z* signal sequence arising from the molar mass of 144 expected for the ethylene succinate repeating unit whereas no signals corresponding to open fragments were detected.

Two peaks were only seen in the HPLC chromatogram (Figure 8.1.1c) which according to MALDI-TOF results could be reasonably attributed to the trimer and tetramer species. A comparison of these results with those reported for *c*(BS)$_n$ is given in Table 8.1.1.

The two fractions are obtained in similar yields but the *c*(ES)$_n$ appears to be more homogenous with trimer and tetramer species being clearly predominant in this fraction. The fact that the *c*(BS)$_n$ fraction is composed of smaller cycle sizes (dimer and trimer) is fully reasonable by taking into account the longer length of the butylene unit.

Thermal properties of the two fractions are not very different. Both fractions melt around 100 ºC and display the same thermal decomposition pattern although *c*(BS)$_n$ starts to decompose almost 50 ºC higher than *c*(ES)$_n$. The TGA traces of *c*(ES)$_n$ show two weight falls at around 250 ºC and 400 ºC which are made to correspond to decomposition of the cyclic mixture and the polymer formed *in situ* upon heating, respectively. Comparison of GPC and NMR analysis of *c*(ES)$_n$ before and after being heated at 200 ºC gave support to this interpretation (Figure E.1.1).

Table 8.1.1. Alkylene Succinate Cyclic Oligomers *c*(ES)$_n$ and *c*(BS)$_n$.

Cyclic oligomers	Precursors	Yield[a] (%)	Composition[b] (<u>n</u>: 2/3/4/≥5)	Thermal Properties[c] T_m (°C)	$T_{d,5\%}$(°C)	T_{max}(°C)
c(ES)$_n$	DMS + EG	70	0/~45/~55/<10	100	200	300/400
c(BS)$_n$	DMS + BD	70	~50/~40/~10/<10	105	266	340/400

[a] Yields for the oligomeric mixture after removing the linear species by flash chromatography.
[b] Mixture composition determined by HPLC.
[c] Melting and decomposition temperatures determined by DSC and TGA, respectively.

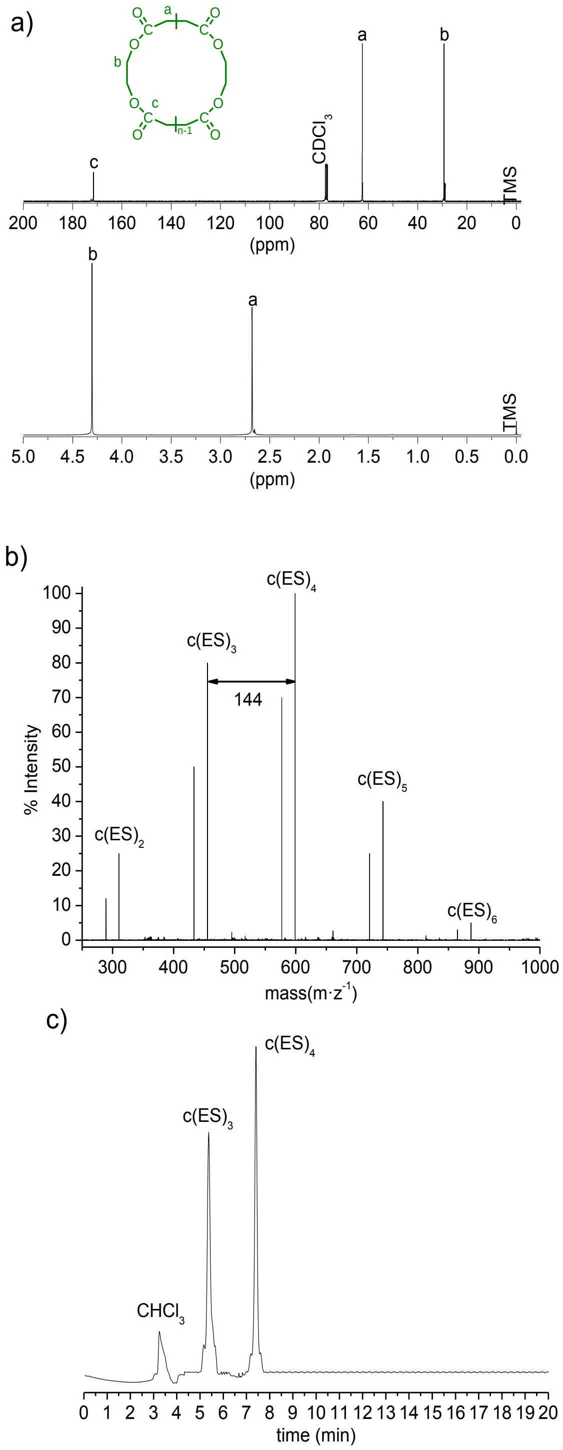


Figure 8.1.1. Characterization of cyclic ethylene succinate oligomers *c*(ES)$_n$. a) ^{13}C (top) and ^{1}H (bottom) NMR; b) MALDI-TOF; c) HPLC. The peak eluted at short time corresponded to chloroform used for dissolving the sample.

The enzymatic ROP of *c*(ES)$_n$ was performed in the bulk at 125 ºC with 40% of CALB added to the molten cycles mixture. The evolution of the polymerization reaction was followed by GPC analysis of aliquots which revealed a continuous increasing of the average molecular weight with time. Data recorded from these measurements are plotted in Figure 8.1.2 which shows an exponential chain growing at the earlier stages that becomes asymptotic after one day of reaction to finally achieve a M_w about 65,000 g·mol^{-1} with a *Đ* of 1.7 was attained. For comparison, *c*(ES)$_n$ was also polymerized under the same conditions but replacing the enzyme by 1% of tin dioctanoate. The M_w-t profile resulting in this case was also asymptotic but the attained M_w was around 50,000 g·mol^{-1}. A parallel reaction assay performed in the absence of catalyst revealed that ROP of *c*(ES)$_n$ in the absence of catalyst, *i.e.* exclusively induced by heating, progressed linearly with a final M_w about 10,000 g·mol^{-1}.

Table 8.1.2. PBE copolyesters prepared by enzymatic ROP.

Copolyester[a]	**GPC**			**TGA**			**DSC**		
	Yield (%)	M_w	Đ	$^{o}T_d{}^{c}$ (°C)	$^{max}T_d$ (°C)	R_w (%)	T_g (°C)	T_m (°C)	ΔH (J·mol^{-1})
PES	90	65,000	1.7	310	385	7	-12	100	55
*co*PES$_{52}$BS$_{48}$	85	60,000	1.9	300	400	5	-28	49	20
*co*PES$_{49}$CL$_{51}$	80	60,000	1.8	295	401	4	-31	40	18
*co*PES$_{50}$LA$_{50}$	85	61,000	1.9	330	387	5	-17	61	21

[a] Composition of copolyesters measured by ^{1}H NMR.
[b] Molecular weight measured by GPC.
[c] T_d obtained at 5% of weight lost.

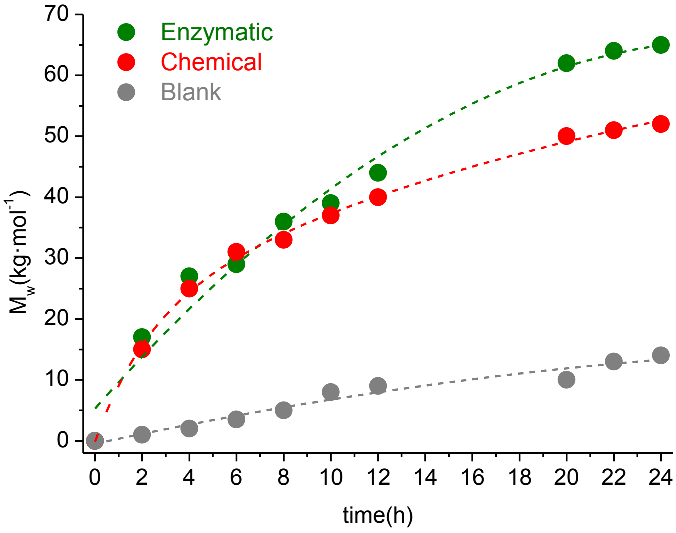


Figure 8.1.2. Evolution of the molecular weight (M_w) of PES generated in the ROP of *c*(ES)$_n$ at 125 °C using CALB, Sn(Oct)$_2$ and in the absence of catalyst.

The exceptional attention that nowadays is receiving the development of aliphatic copolyesters containing alkylene succinate units has encouraged us to explore the feasibility for preparing such copolyesters from the *c*(ES)$_n$ fraction by *e*-ROP. With such purpose polymerization experiments of equimolar mixtures of *c*(ES)$_n$ and other selected lactones were carried out for 24 h under the same reaction conditions that were used for the synthesis of PES homopolyesters. *c*(BS)$_n$ synthesized by enzymatic cyclocondensation and showing the features indicated in Table 8.1.1 (graphical data are provided in Figure E.1.2), and commercial L-lactide (LA) and caprolactone (CL), were the cyclic comonomers of choice.

Results obtained in the copolymerization experiments are compared in Table 8.1.2 and the ^{1}H NMR spectra of PES and the three copolyesters are shown in Figure 8.1.4. The examination of these spectra allowed ascertaining the chemical constitution expected for the polymers and determining the compositions of the copolyesters which turn out to be very close to those used in their respective feeds. Furthermore, the analysis of the signals multiplicity appearing in the ^{13}C NMR spectra (Figure E.1.3) strongly suggested that the comonomeric units are randomly distributed in the polymer chain for the all three prepared copolyesters.

Finally GPC measurements revealed that their molecular weights and dispersities were similar to that obtained for the PES homopolyester. A rapid estimation of the more substantial thermal properties of *co*PES$_{52}$BS$_{48}$ by TGA and DSC (Figure E.1.4 and E.1.5) brought into evidence the good coincidence of the thermal degradation and reversible transition temperatures with those previously reported for similar copolyesters prepared by chemical methods.[21,22] Although the values measured for *co*PES$_{49}$CL$_{51}$ and *co*PES$_{50}$LA$_{50}$ could not be compared in the same way because these copolyesters are not described in the accessible literature, the observed behaviour is in line what should be expected from both the constitution of the comonomers and copolyester composition.

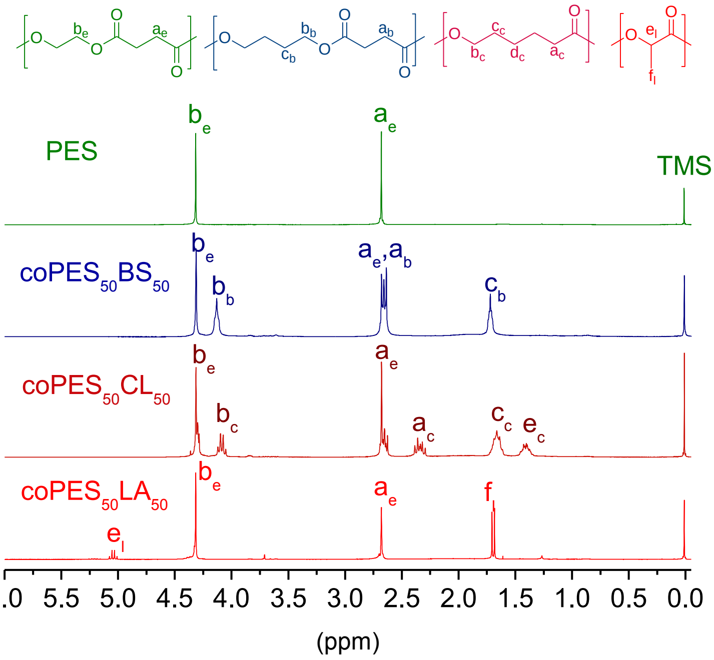


Figure 8.1.3.· ^{1}H NMR of PES, *co*PES$_{50}$BS$_{50}$, *co*PES$_{50}$CL$_{50}$ and *co*PES$_{50}$LA$_{50}$.

VIII.1.3 Conclusions

In conclusion, ring opening polymerization catalysed by lipase has been demonstrated to be a convenient tool for the preparation of PES homopolyester and aliphatic copolyesters containing ethylene succinate units. The oligo(ethylene succinate)s cycles *c*(ES)$_n$ required for *e*-ROP could be efficiently prepared by enzymatic cyclization of potentially bio-based ethylene glycol and dimethyl succinate. Since organometallic compounds are avoided through the whole process, free-metal polymers were therefore afforded. The polymerization reaction of *c*(ES)$_n$ took place faster in the presence of lipase than when catalysed by organometallic compounds. Noteworthy the polymers resulting by *e*-ROP had molecular weights high enough as to make unnecessary the application of additional treatments (post polycondensation or use of extenders) for increasing chain lengths. Cyclic esters including both AA-BB and A-B types and covering a range of ring structures with different strain were used as comonomers of for *c*(ES)$_n$ in the *e*-ROP. Since high molecular weights copolyesters with the expected compositions and a random microstructure were obtained, it seems that relative reactivities in *e*-ROP of the tested cycle pairs are no far from unit. The results obtained in this piece of work demonstrate the suitability of *e*-ROP as a green alternative for the synthesis of poly(ethylene succinate) homo- and copolyesters intended for biomedical applications.

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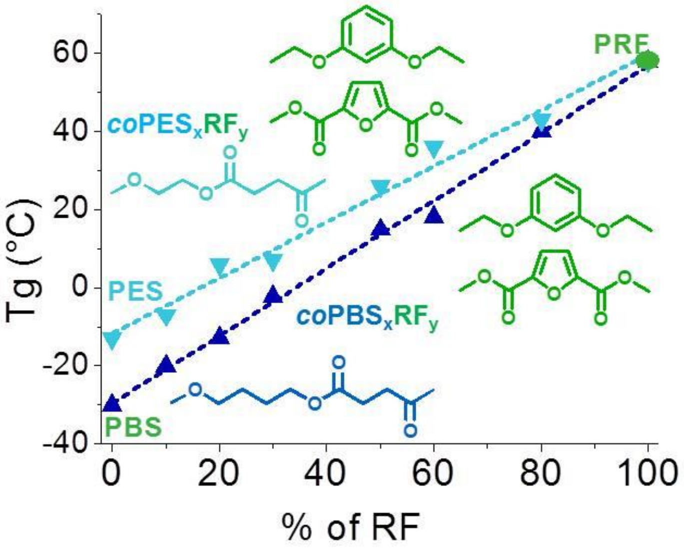
VIII.2 Poly(alkylene succinate-*co*-furanoate) copolyesters containing resorcinol.

Abstract: Two series of aliphatic-aromatic copolyesters derived from succinic and 2,5-furandicarboxylic acids, and resorcinol bis(hydroxyethyl)ether as diol substituent of either 1,4-butanediol or ethylene glycol, respectively, were obtained by ROP performed in the bulk and catalyzed by $Sn(Oct)_2$. Cyclic oligomers of resorcinol-based furandicarboxylate were successfully synthesized by high dilution condensation, and then copolymerized with cyclic oligomers of either ethylene or butylene succinate. The synthesized resorcinol furanoate-containing copolyesters had M_w oscillating between 50,000 and 30,000 g·mol^{-1} depending on composition, and all they displayed a nearly random microstructure. They showed an excellent thermal stability with onset decomposition temperatures near 300 ºC. They are amorphous (hay uno que es semicristalino) with T_g increasing monotonically with the content in resorcinol in both series with values ranging from -30 or -13 ºC for butylene and ethylene-based copolyesters, respectively, up to around 45 ºC. The resorcinol furanoate-containing copolyesters showed appreciable hydrolytic degradation when incubated for a few weeks in water under physiological conditions, a behavior that was notably enhanced in the presence of lipases.



Publication derived from this work:

J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra. Fully bio-based PBS copolyesters with high Tg: ring opening copolymerization of cyclic (butylene succinate) and (isomannide furanoate) oligomers *Polymers,* **2017**, *9*, 701.

VIII.2.1. Introduction

Poly(alkylene succinate)s is a family of aliphatic polyesters that are distinguished by their easy accessibility from natural-occurring compounds and their noticeable biodegradability[1,2]. In fact, the US Department of Energy declared bio-based succinic acid as a high-potential chemical platform for compounds so far obtained from fossil feedstock, which is indeed the case of poly(succinate)s.[3] Also most of alkanediols, and in particular 1,2-ethanediol and 1,4-butanediol, are compounds accessible from renewable resources.[4-6] Poly(alkylene succinate)s are highly crystalline polyesters with thermal and mechanical properties largely depending on the length of the alkylene moiety.[7,8] Poly(butylene succinate) (PBS) and poly(ethylene succinate) (PES), with melting temperatures of 115 and 100 ºC respectively, are by far the most known members of the family, the former being currently produced at industrial scale, and both of them showing excellent potential for packaging and biomedical applications.[9] Nonetheless, due to the high flexibility inherent to the aliphatic polyester chain, the glass transition temperatures of poly(alkylene succinate)s are too low with values around -12 and -30 ºC for PES and PBS, respectively. Copolymerization including benzenedicarboxylic acids as comonomers, has proven to be a highly effective method to increase the T_g of the aliphatic polyesters.[10] This is not however a fully satisfactory approach since the sustainability of the parent aliphatic copolyester becomes largely reduced, and its biodegradability is almost lost when significant amounts of aromatic moieties are introduced in the polymer chain.[11] Copolymerization using bio-based 2,5-furandicarboxylic acid has represented a noteworthy step forward in this regards. Poly(butylene succinate-*co*-furandicarboxylate) copolyesters, abbreviated as *co*(PBS_xBF_y), with T_g within the ±30 ºC range depending on composition, and retaining appreciable biodegradability have been described by different authors.[12-14] Also Bikiaris et al. have recently reported on poly(ethylene succinate-*co*-furandicarboxylate)s, abbreviated as *co*(PES_xEF_y), that display T_g increasing monotonically up to near 80 ºC and that are able to show perceptible biodegradability even for high contents in furanoate units.[15]

In the present work, copolyesters of PES and PBS containing both 2,5-furandicarboxylate (F) and 1,3-benzenedioxyethylene (R) units, which derive from the 2,5-furandicarboxilic acid (FDCA) and resorcinol, respectively, are reported. FDCA is a well-known bio-based compound that is currently receiving enormous attention as a possible substitute of terephthalic and isophthalic acids in the industrial synthesis of aromatic polyesters.[16-18] Resorcinol (1,3-dihydroxybenzene) is a diphenol currently produced at industrial scale by alkaline fusion of *m*-benzene disulfonic acid but that may be also obtained from glucose by fermentation either via inositol[19,20] or via triacetic acid lactone.[21] This compound is extensively used in medicine as external antiseptic[22], and it is also consumed in big amounts in the industrial manufacture of formaldehyde resins.[23]

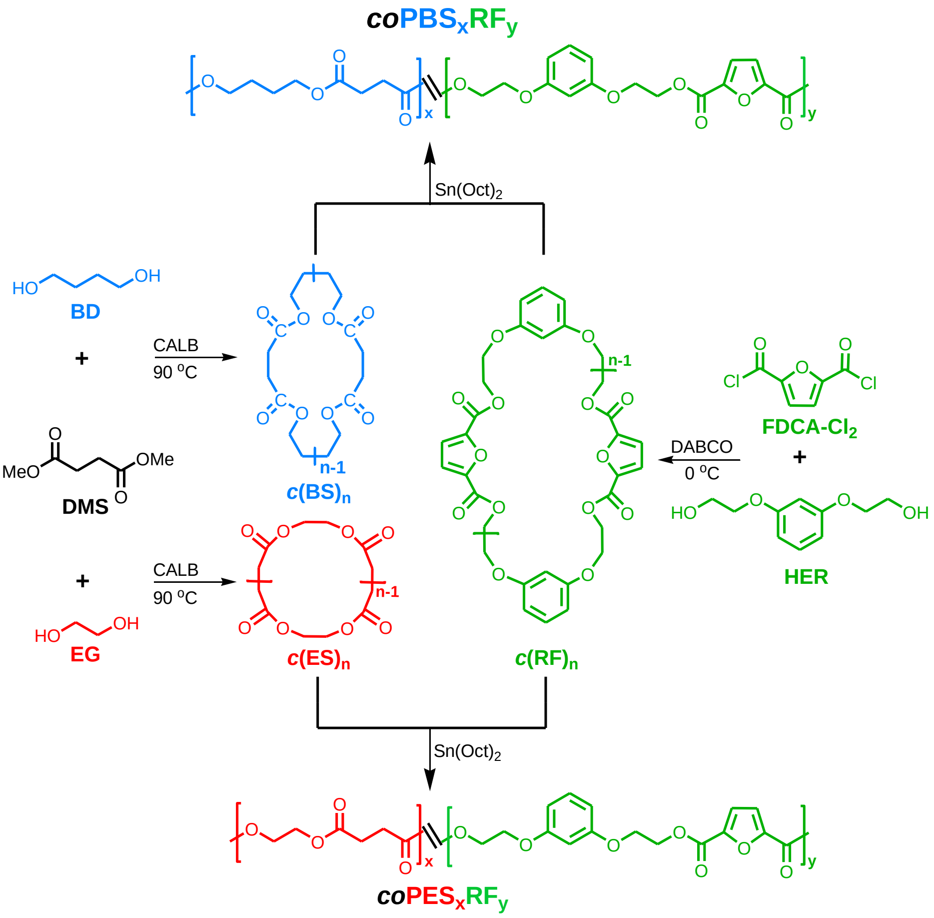
The synthesis of linear polyesters using a resorcinol-based monomer was firstly reported by Vijayakumar et al.[24] and later by Gioia et al.[25] These authors eterified resorcinol with ethylene carbonate to resorcinol bis(2-hydroxyethyl)ether (HER). This primary aliphatic diol allowed avoiding the polymerization restraints derived from the low reactivity of the aromatic hydroxyl groups. HER was made to react with both aromatic and aliphatic dicarboxylic acids, both saturated and unsaturated, to obtain an assortment of potentially sustainable amorphous polyesters. Resorcinol-containing polymers with M_w up to near 55,000 g·mol^{-1} were reported by Goia et al.[25] Additionally several patents covering diverse aromatic copolyesters of resorcinol displaying high barrier properties have been also reported.[26-27] The ability of resorcinol to repress gas permeability in polymers is in line with the general behavior that is characteristic of 1,3-disubstituted aromatic compounds.

The aim of the present paper was to obtain PES and PBS copolyesters with enhanced T_g but without losing the potential sustainability of the parent homopolyesters. The hypothesis applied to the work was that the substitution of the alkylene unit by resorcinol-derived diethylene unit in poly(alkylene succinate-*co*-furanoate) copolyesters may further increase the stiffness of the chain in a similar manner as aromatic diacids do. In order to favor the sustainability of the synthesis, the copolyesters have been prepared by entropically driven ring-opening copolymerization in bulk following the methodology previously used by us for the synthesis of *co*(PBS_xBF_y) copolyesters [14]. By this method solvents are avoided and generation of byproducts is minimized. Cyclic (1,3-benzenedioxyethylene 2,5-furandicarboxylate) oligomers required for ROP have been prepared for the first time and characterized following the same methodology reported by us for the synthesis of butylene furanoate oligomers. By this means two series of succinate-furanoate copolyesters made from mixtures of either 1,4-butanediol or ethylene glycol and HER have been obtained for a wide range of compositions. The thermal behavior and biodegradability of the two series was comparatively evaluated between them and also taking as reference the poly(alkylene succinate-*co*-furanoate) series previously reported.[14,15]

VIII.2.2. Results and discussion

The synthetic route followed in this work for the preparation of *co*PBS_xRF_y and *co*PES_xRF_y copolyesters by ROP including the synthesis of the cyclic oligomers and their polymerization is depicted in Scheme 8.2.1.

Synthesis of cyclic oligomers: The cyclic oligomers *c*$(BS)_n$ and *c*$(ES)_n$ were first synthesized by enzimatic cyclocondensation of dimethyl succinate (DMS) with either 1,4-butanediol or ethylene glycol, respectively, applying the general procedure previously described by us.[29] A summary of relevant features of these cyclic oligomers



Scheme 8.2.1. Route of synthesis leading to PBS and PES copolyesters containing furane and resorcinol units.

fractions is given in Table 7.2.1. It is worthy to notice that both fractions are heterogeneous in cycle sizes and that no dimer is detected in the *c*(ES)$_n$ fraction.

Table 8.2.1. Cyclic Oligomers Fractions used for ROP.

Fraction	Precursors	Yield (%)[a]	Composition mol-% [b]	Thermal Properties		
				T_m (°C)[c]	$^{o}T_{d,5\%}$ (°C)[d]	$^{max}T_d$ (°C)[d]
c(BS)$_n$	DMS+BD	70	50/40/10	105	266	340/400
c(ES)$_n$	DMS+EG	70	0/45/55	100	200	300/400
c(RF)$_n$	FDCA-Cl$_2$+ HER	60	28/57/15	158/166/185	263	415

[a] Yields for the oligomeric after the removal of the linear species (flashed).
[b] Mixtures of dimer/trimer/tetramer species measured by HPLC (%wt).
[c] Determined by DSC at 10 °C·min^{-1}.
[d] Decomposition temperatures (onset and maximum rate) determined by TGA

The *c*(RF)$_n$ fraction has been synthesized for the first time in this work from FDCA-Cl$_2$ and HER in 60% yield after removing the linear oligomers by flash chromatography. The ^{1}H and ^{13}C NMR spectra of this purified oligomeric fraction were fully consistent with the expected cyclic chemical structure without showing signs of linear species (Figure 8.2.1). The composition of the *c*(RF)$_n$ fraction was determined by HPLC chromatography and MALDI-TOF spectroscopy, and results obtained therefrom are shown in Figure 8.2.2. Three peaks were observed in the HPLC chromatograms which correspond to dimer, trimer and tetramer species in an approximate molar ratio of 2/4/1, as it was ascertained in the MALDI-TOF spectra. According to these results, the content of this fraction in species of size higher than tetramer may be considered almost negligible.

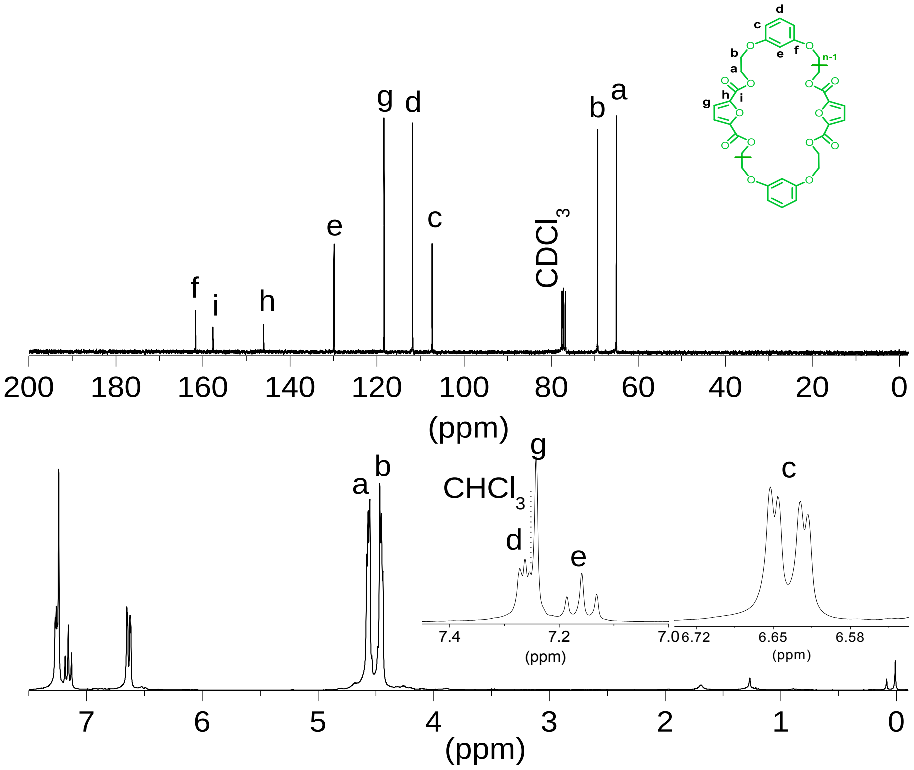


Figure 8.2.1. ^{13}C and ^{1}H NMR spectra of *c*(RF)$_n$.

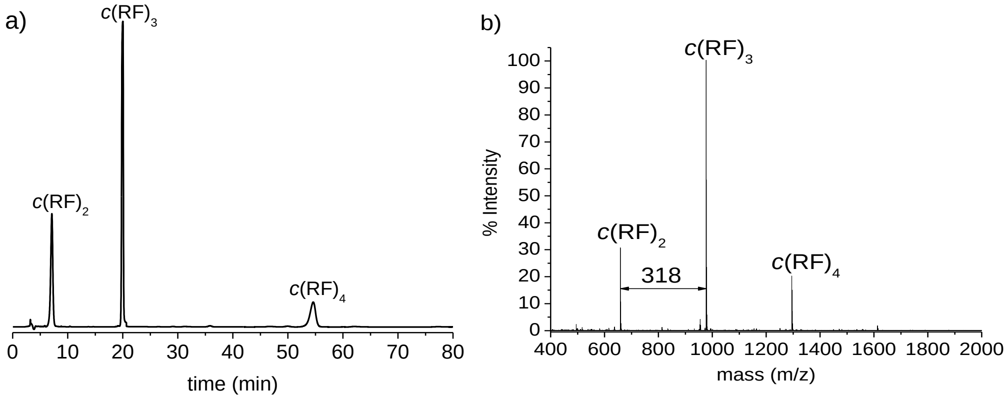


Figure 8.2.2. HPLC (a) and MALDI-TOF (b) of *c*$(RF)_n$

As it is seen in Table 8.2.1, thermal properties of *c*$(RF)_n$ differ significantly from those of *c*$(BS)_n$ and *c*$(ES)_n$. These resorcinol-containing cycles not only melt at higher temperature but also display much greater resistance to decomposition by heating. Furthermore, as it is shown in Figure 8.2.3, the TGA trace of *c*$(RF)_n$ only shows one single weight loss step at difference with the two well separate falls that are observed for alkylene succinate cycles. This is a very reasonable result since the weight losses displayed by *c*$(BS)_n$ and *c*$(ES)_n$ at temperatures in the 300-350 ºC range are reported to be due to partial volatilization of the sample, a fact that is not expected to happen in the case of *c*$(RF)_n$.

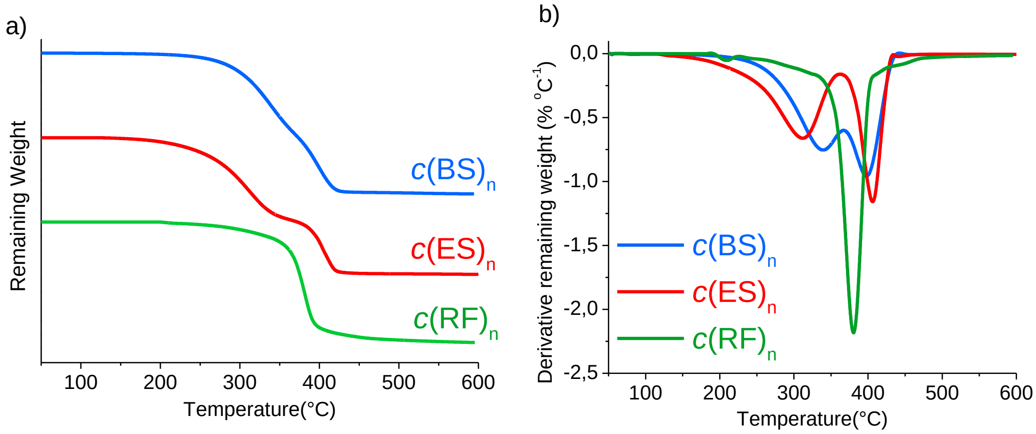


Figure 8.2.3. Compared TGA analysis of cyclic oligomers. a) TGA traces, b) Derivative curves showing temperatures at which degradation takes place at maximum rate.

Synthesis of copolyesters: The synthesis of the copolyesters was performed by ED-ROP in bulk using Sn(Oct)$_2$ as catalyst. Two copolyesters series, *i.e*. *co*PBS$_x$RF$_y$ and *co*PES$_x$RF$_y$, were prepared from mixtures of either *c*(BS)$_n$ or *c*(ES)$_n$ and *c*(RF)$_n$ at molar ratios ranging between 10 and 90%, in addition to the homopolyesters PBS, PES and PRF. Reaction temperatures above 190 ºC were used to insure melting of the cycles. Preliminary assays indicated that reaction noticeably speeded when temperature was raised from 190 to 200 ºC but not significant change in rate was observed when temperature was further increased, a behavior that was shared by the two series (Figure 8.2.4).

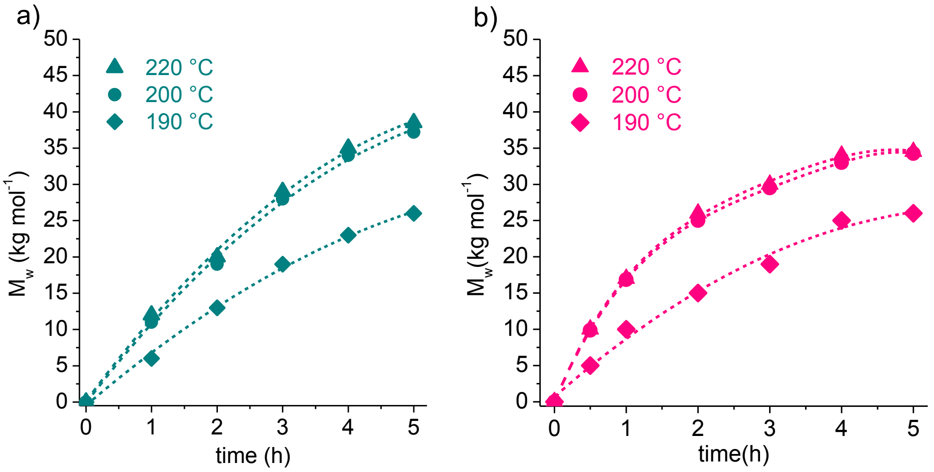


Figure 8.2.4. Evolution of M_w along reaction time in the ROP of equimolar mixtures of *c*(RF)$_n$ and either *c*(BS)$_n$ (a) or *c*(ES)$_n$ (b) for three different temperatures.

According to these results, this was the temperature of choice applied for the synthesis of the whole collection of copolyesters. The evolution of the molecular weight of the forming polymer as a function of reaction time for several selected compositions is represented in Figure 8.2.5 for the two series. An asymptotic trend was followed in all cases showing a notable decay in reaction rate after five hours with attained weight-average molecular weight values between 40,000 and 50,000 g·mol^{-1}. Interestingly, ROP proceeded faster as the content of the feed in *c*(RF)$_n$ diminished, which may be interpreted as due to the higher relative reactivity of the alkylene succinate cycles. An assay of polymerization in absence of catalyst showed not significant increase in molecular weight indicating that ROP was unable to proceed by exclusive action of heating.

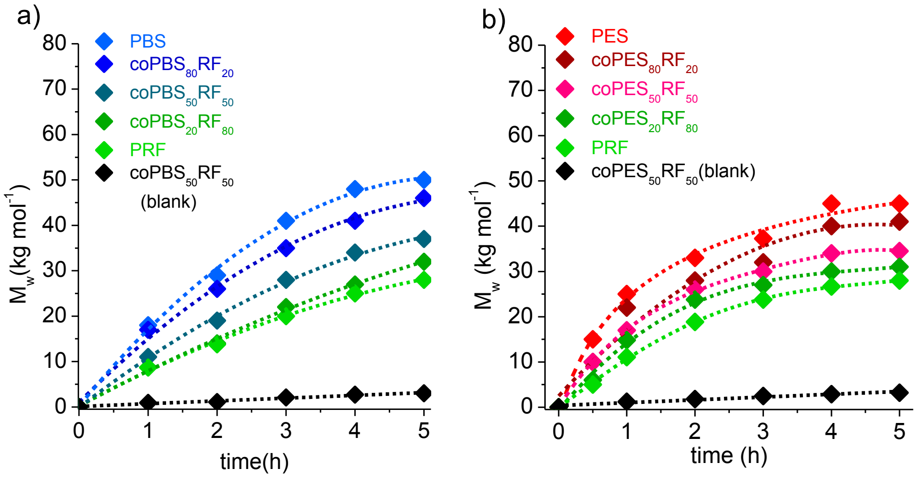


Figure 8.2.5. Evolution of M_w along reaction time in the ROP of mixtures of *c*(RF)$_n$ and either *c*(BS)$_n$ (a) or *c*(ES)$_n$ (b) for different feed compositions.

The NMR analysis of the copolyesters ascertained the chemical constitution expected for them. ^{1}H NMR spectra of *co*PBS$_{50}$RF$_{50}$ and *co*PES$_{50}$RF$_{50}$ are shown in Figure 8.2.6 as representative examples and the whole collection for the two series are accessible in the annex (Figures E.2.1 and E.2.2). The comonomer content in the copolyesters determined from the information provided by ^{1}H NMR spectra revealed a good correlation with the composition used in the feed with deviations being always below 5%. The values obtained for every case are detailed in Table 8.2.2.

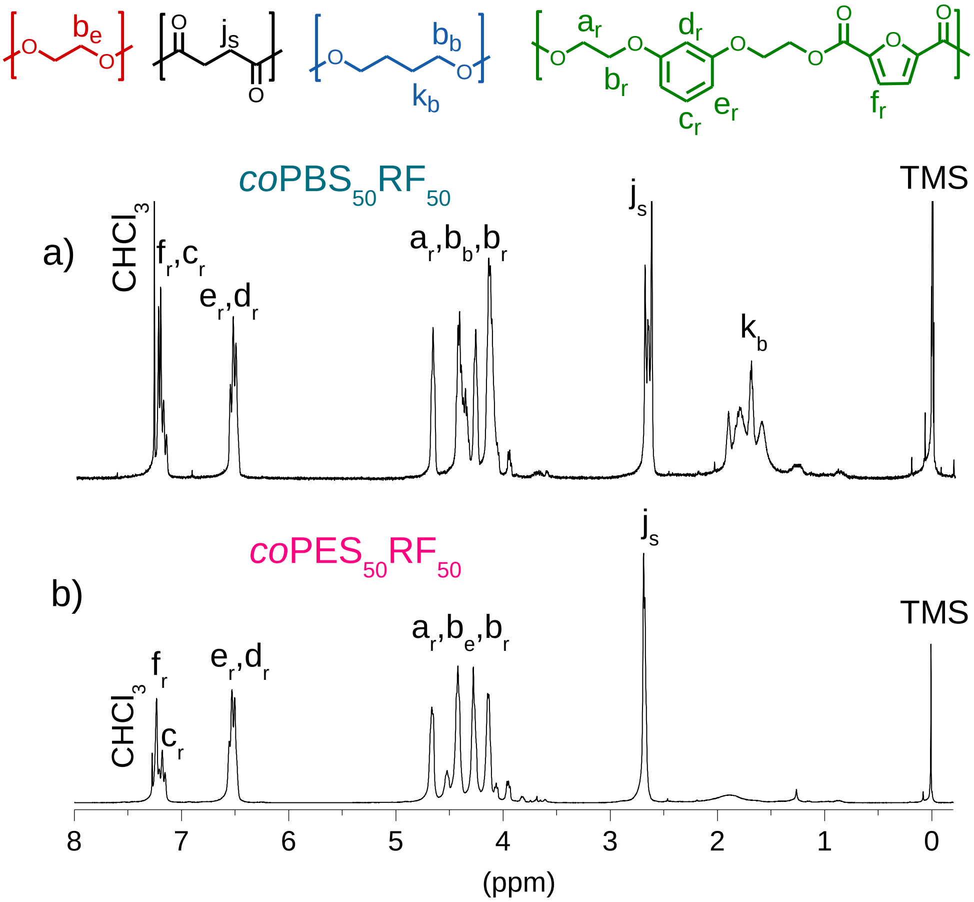


Figure 8.2.6. ^{1}H NMR spectra of resorcinol-containing copolyesters.

Microstructure of the copolyesters: The number average sequence lengths (*n*) present in the copolyesters as well as their degrees of randomness (*B*) were determined by NMR. For this analysis we have applied the statistical model described by Devaux et al. [30] for polycondensates with four components. The following relation of contents are assumed for the *co*PBS$_{x}$RF$_{y}$ and *co*PES$_{x}$RF$_{y}$ copolyesters:

[S] = [B] or [S] = [E], and [F] = [R] and [BF] = [RS] or [EF] = [RS], for the two series.

The number average sequence lengths (*n*) and the degree of randomness (*B*) were calculated using the following expressions:

Table 8.2.2. Resorcinol-containing Copolyesters Obtained by ROP.

Copolyester	**Yield (%)**	**GPC**[a]		**Composition**[b] **x(BS or ES)/y(RF)**		**Chain Microstructure**[c]				
		M_w (g·mol^{-1})	Đ	Feed	Copolyester	$n_{(B/E)S}$	$n_{(B/E)F}$	n_{RS}	n_{RF}	B
PBS	90	50,000	1.9	100/-	100/-	-	-	-	-	-
*co*PBS$_{90}$RF$_{10}$	96	48,000	2.0	90/10	86/14	17.3	1.1	2.8	1.5	0.72
*co*PBS$_{80}$RF$_{20}$	95	46,000	1.8	80/20	78/22	7.2	1.2	3.8	1.4	0.89
*co*PBS$_{70}$RF$_{30}$	90	42,500	1.6	70/30	64/36	4.2	1.3	2.8	1.6	0.90
*co*PBS$_{50}$RF$_{50}$	80	37,200	2.0	50/50	49/51	2.3	1.9	2.1	1.9	0.96
*co*PBS$_{40}$RF$_{60}$	80	36,000	1.7	40/60	37/63	1.8	2.2	1.7	2.5	0.96
*co*PBS$_{20}$RF$_{80}$	85	32,200	1.8	20/80	21/79	1.5	3.2	1.3	3.9	0.92
PES	90	45,000	1.7	100/-	100/-	-	-	-	-	-
*co*PES$_{90}$RF$_{10}$	95	42,500	1.9	90/10	86/14	4.6	1.3	7.3	1.2	1.07
*co*PES$_{80}$RF$_{20}$	92	41,000	1.8	80/20	77/23	3.3	1.4	4.9	1.3	1.17
*co*PES$_{70}$RF$_{30}$	80	39,200	1.5	70/30	76/24	3.0	1.5	4.2	1.3	1.08
*co*PES$_{50}$RF$_{50}$	85	34,500	1.4	50/50	49/51	1.5	3.2	2.3	1.8	1.23
*co*PES$_{40}$RF$_{60}$	90	34,000	1.6	40/60	36/64	1.7	2.5	1.6	2.7	0.98
*co*PES$_{20}$RF$_{80}$	91	31,000	1.8	20/80	19/81	1.3	4.1	1.2	5.6	0.95
PRF	80	28,000	1.9	-/100	-/100	-	-	-	-	-

[a] Molecular weight and dispersity measured by GPC.

[b] Composition of the feed and the copolyester.

[c] Number-average sequence length of the different sequences present in the copolyesters (see text) and randomness determined by ^{13}C NMR spectra using the equations reported by Devaux [30].

$$n_{BS} = \frac{[BS]}{[BF]} + 1 \qquad n_{BF} = \frac{[BF]}{[BS]} + 1 \qquad n_{RS} = \frac{[RS]}{[RF]} + 1 \qquad n_{RF} = \frac{[RF]}{[RS]} + 1$$

$$B = \frac{1}{n_{BS}} + \frac{1}{n_{RF}}$$

$$n_{ES} = \frac{[ES]}{[EF]} + 1 \qquad n_{EF} = \frac{[EF]}{[ES]} + 1 \qquad n_{RS} = \frac{[RS]}{[RF]} + 1 \qquad n_{RF} = \frac{[RF]}{[RS]} + 1$$

$$B = \frac{1}{n_{ES}} + \frac{1}{n_{RF}}$$

where the dyads fractions were calculated from the integrals of the ^{13}C NMR spectra, and assuming similar relaxation times for the same carbons in the different dyads. It was additionally assumed that in all triads the substitution on the left of a central unit does not influence the substitution on the right. The ^{13}C NMR spectra of the *co*PBS$_x$RF$_y$ series are shown in Figure 8.2.7 where it is seen that some of the signals split into four peaks due to the sensitivity of these carbons to sequence distribution at the level of triads. By deconvolution of these signals the content of the different dyads could be easily obtained and then n_{BS} and n_{RF}, and the degree of randomness B calculated by applying the equations described above. A similar approach was used for the analysis of the *co*PES$_x$RF$_y$ series whose ^{13}C NMR spectra are shown in Figure E.2.3 of the annex. B an n values for the two series are given in Table 8.2.2 revealing that the microstructure of the two series of copolyesters is essentially at random.

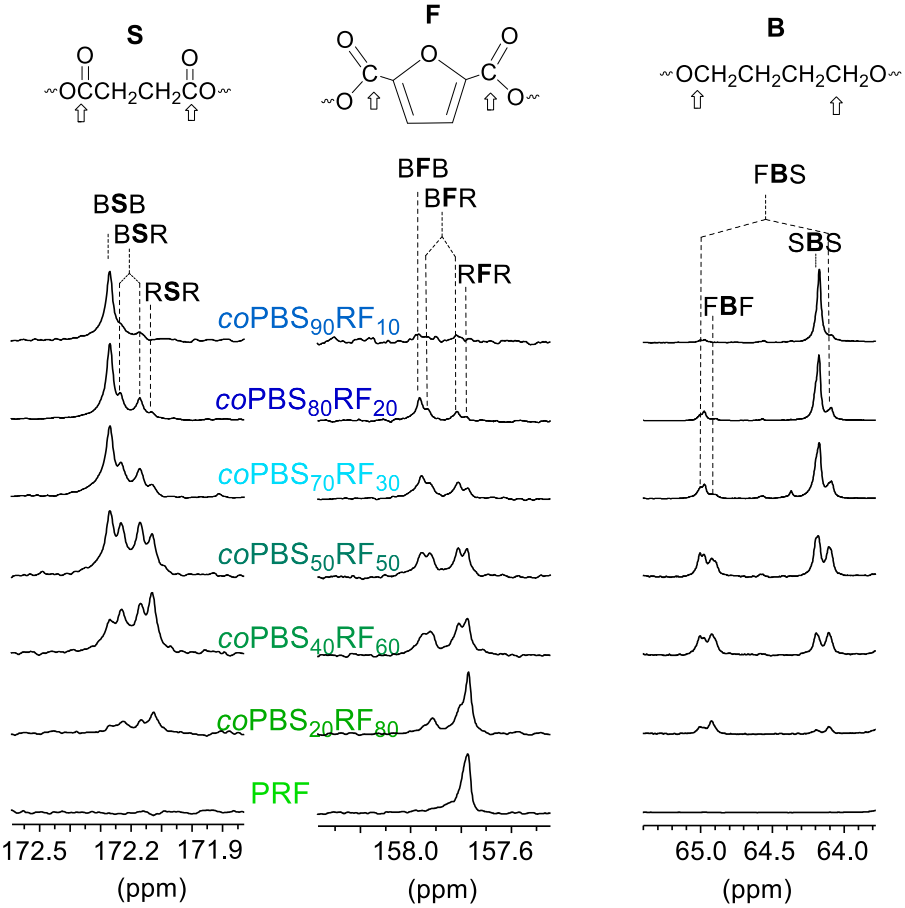


Figure 8.2.7. Carbonyls and aromatic carbons regions of the ^{13}C NMR spectra of *co*PBS$_x$RF$_y$ copolyesters used for calculation of their microstructure.

Thermal properties: The thermal properties of the *co*PBS$_x$RF$_y$ and *co*PES$_x$RF$_y$ copolyesters were evaluated by TGA and DSC, and the most relevant parameters provided by these analyses are collected in Table 8.2.3.

The TGA traces of all copolyesters recorded under a nitrogen atmosphere, as well as their derivative curves, are shown in Figure 8.2.8. The main conclusion drawn from TGA results is that succinate-furanoate copolyesters containing resorcinol are well stable to non-oxidative heating. In fact, the onset temperature is always above 320 ºC and maximum decomposition rate temperatures are not far from 400 ºC. Slight differences observed between the two series should be related to the intrinsically lower thermal stability of PES as compared to PBS. As it is well illustrated by the derivative curves shown in Figure 8.2.8a' and 8.2.8b', the decomposition process takes place essentially in a single stage although a smooth shoulder leans out some *co*PES$_x$RF$_y$ peaks indicating a greater complexity in the thermal decomposition of this series.

Table 8.2.3. Thermal Properties of Resorcinol Furanoate-containing Copolyesters.

Copolyester	**TGA**^{a}			**DSC**^{b}		
	$^{o}T_d$ (°C)	$^{max}T_d$ (°C)	R_w (%)	T_g (°C)	T_m (°C)	ΔH (J·mol^{-1})
PBS	350	399	3	-30	114	82
*co*PBS$_{90}$RF$_{10}$	336	391	8	-20	100	74
*co*PBS$_{80}$RF$_{20}$	344	398	6	-13	-	-
*co*PBS$_{70}$RF$_{30}$	326	391	9	-2	-	-
*co*PBS$_{50}$RF$_{50}$	336	399	10	15	-	-
*co*PBS$_{40}$RF$_{60}$	331	391	11	18		
*co*PBS$_{20}$RF$_{80}$	345	400	9	40	-	-
PES	310	385	7	-13	100	55
*co*PES$_{90}$RF$_{10}$	323	389	7	-7	-	-
*co*PES$_{80}$RF$_{20}$	335	386	9	6	-	-
*co*PES$_{70}$RF$_{30}$	325	374	9	8	-	-
*co*PES$_{50}$RF$_{50}$	342	390	9	26	-	-
*co*PES$_{40}$RF$_{60}$	340	396	5	36	-	-
*co*PES$_{20}$RF$_{80}$	347	411	11	43	-	-
PRF	321	401	10	58	-	-

[a] Thermal decomposition temperatures ($^{o}T_d$ and $^{max}T_d$) and remaining weight (R_w) determined by TGA.

[b] Glass-transition temperature and melting temperature and enthalpy determined by DSC at heating.

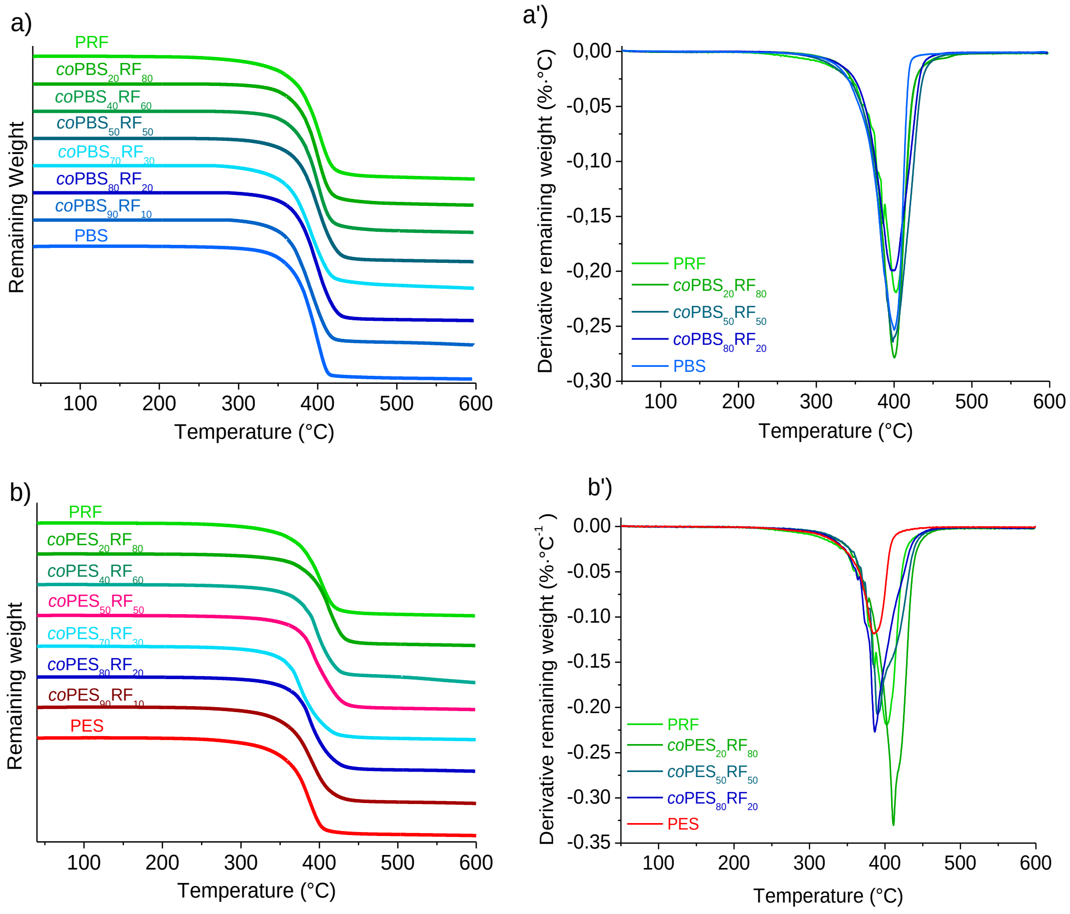


Figure 8.2.8. TGA traces of *co*PBS$_x$RF$_y$ and *co*PES$_x$RF$_y$ series (a and b) and their derivative curves (a' and b').

The DSC traces of the *co*PBS$_x$RF$_y$ and *co*PES$_x$RF$_y$ copolyesters did not show any heat exchange indicative of melting except for *co*PBS$_{90}$RF$_{10}$ that displayed an endothermal peak at 100 ºC with an associate enthalpy of 74 J·mol^{-1}. This behaviour contrasts with that of both PBS and PES homopolyesters which are highly crystalline, but is in agreement with the amorphous character of PRF. It is apparent that the insertion of the RF units in the polyalkylene succinate chain in amounts above 14%-

mole, totally inhibits the crystallinity of the polyester. This is not unexpected at all given the large differences in both nature and size between the ES or BS units and the RF units.

The evaluation of the glass-transition temperature in these copolyesters has deserved particular attention since tuning this parameter by adjusting the content in RF units constitutes one of the main aims of this work. T_g was measured by DSC from samples that were previously heated at 200 ºC to erase their previous history. The thermograms of all the members of the two copolyesters series are comparatively depicted in Figure 8.2.9 where T_g is denoted as a clear positive inflection of the trace recorded at heating, and their numerical values are given in Table 8.2.3.

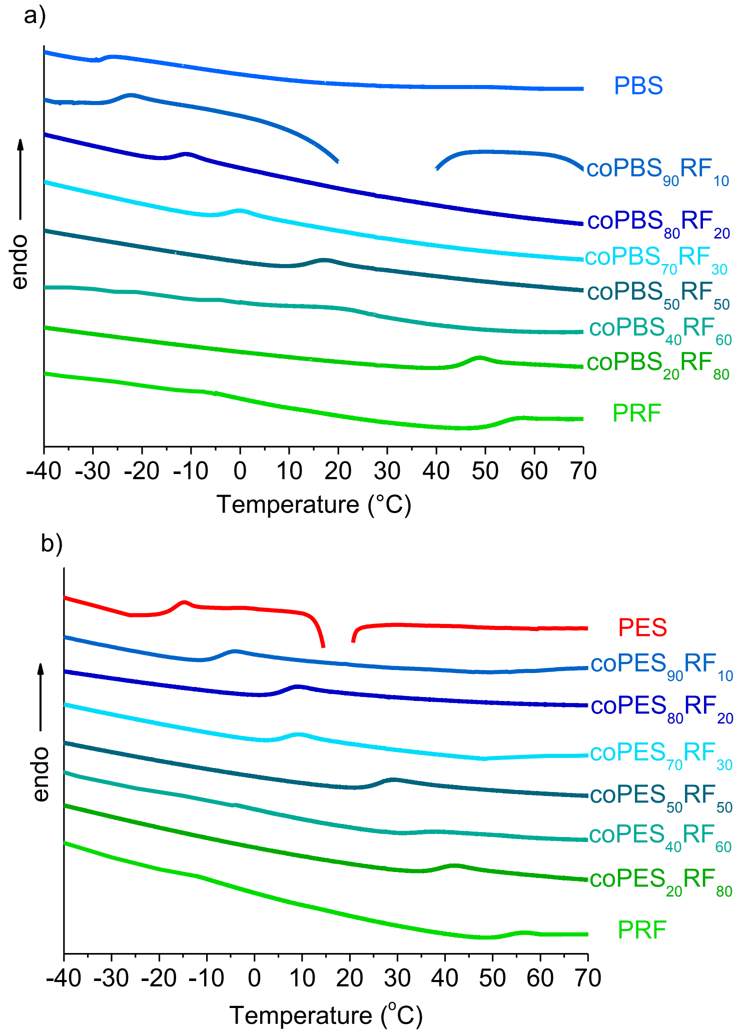


Figure 8.2.9. DSC traces showing the T_g of the two series of resorcinol-containing copolyesters.

The conclusions that may be drawn from these data, are the following: a) In both series, T_g varies with composition monotonically between the values of the two respective parent homopolyesters largely according to what is predicted by the Fox equation [32] (slight deviations observed may be explained at least in part by differences in molecular weight). b) Incorporation of the RF units entails an increasing of the T_g with a slope noticeably higher for the *co*PBS$_x$RF$_y$ series in consistence with the lower T_g of PBS compared to PES. c) Differences in T_g between the two series diminish as the content in RF increases to finally converge in 58 ºC which is the T_g of the PRF homopolyester.

Random copolyesters of PBS and PES containing furanoate units, *co*PBS$_x$BF$_y$ and *co*PES$_x$EF$_y$ respectively, have been described previously and the effect of copolymerization on T_g has been evaluated for both families [14,15]. In these cases the relatively flexible succinate unit was replaced by the stiffer cyclic furanoate unit while the content in the alkanediol unit (butylene or ethylene) remained constant. As a logical consequence T_g increased steadily with the content in furanoate units with a similar slope in the two series. The *co*PBS$_x$RF$_y$ and *co*PES$_x$RF$_y$ copolyesters studied in this work may be envisaged as deriving from *co*PBS$_x$BF$_y$ and *co*PES$_x$EF$_y$ where either the butylene (B) or the ethylene (E) units are replaced by the 1,3-benzenediethoxyethylene (R) units. It is of interest therefore to compare the influence that composition has on T_g in both types of copolyesters. The T_g of the two series pairs is plotted against composition in Figure 8.2.10 to show the enhancing effect that is exerted by the insertion of aromatic units in the all four cases. Comparison between the two ethylene-based series, *i.e.* *co*PES$_x$EF$_y$ and *co*PES$_x$RF$_y$, shows similar T_g values in the two series for similar compositions in furanoate units except for very high contents in these units. Conversely, T_g in the *co*PBS$_x$RF$_y$ series is invariably higher than in the *co*PBS$_x$BF$_y$ series with differences becoming larger as copolyesters contain higher amounts of furanoate units. These results reflect the relative stiffness of the diol units that are involved in each case, being the 1,3-benzenediethoxyethylene units are intermediate between the stiffness of ethylene and butylene units.

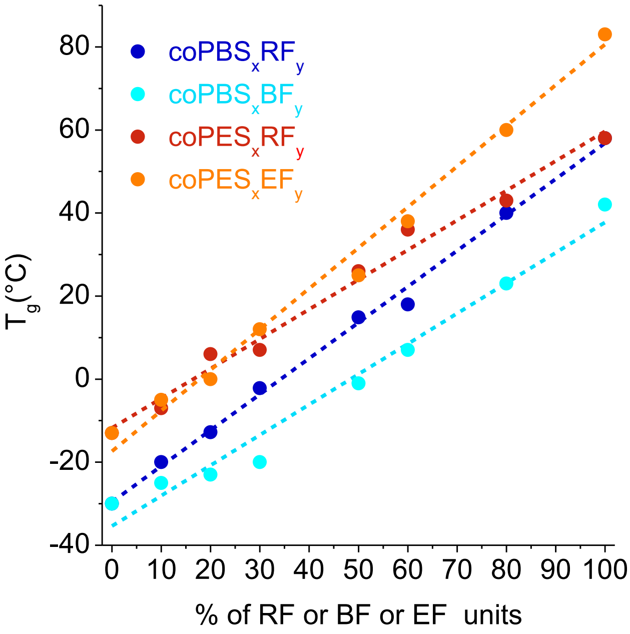


Figure 8.2.10. T_g of furanoate-succinate copolyesters as a function of composition. Data reported by Morales-Huerta et al. [14] for *co*PBS$_x$BF$_y$ and Terzoupolou et al. [15] for *co*PES$_x$EF$_y$ are taken for comparison.

Biodegradability: The biodegradability of the resorcinol-containing copolyesters was evaluated by following the evolution of sample weight and molecular weight with time in samples with selected compositions that were incubated in aqueous buffer at pH 7.4 and 37 ºC with or without lipases added. Sample weight loss data collected for copolyesters containing 30, 50 and 60%-mole for the two series are plotted in Figure 8.2.11. No weight change was observed for PRF under any assayed conditions whereas PBS and PES lost approximately 10 and 20% of weight, respectively, when incubated in absence of lipases for 30 days. These amounts became approximately 20-30% greater when lipases were added to the incubation medium revealing the notable susceptibility of these poly(alkylene succinate)s to biodegradation, a fact that is widely known in the related literature [33]. The results obtained for *co*PBS_xRF_y and *co*PES_xRF_y copolyesters were fully consistent with those obtained for their parent homopolyesters. In both series significant weight losses were observed upon incubation with values steadily increasing with time and being significantly higher when lipases were added to the medium. A similar behavior was displayed by these copolyesters when degradation was followed by measuring the molecular weight by GPC. The M_w-t plots, which are accessible in the annex (Figure E.2.4), revealed decays in molecular weight that were more noticeable in the samples subjected to the enzymes action.

A reference of the biodegradation results obtained here for *co*PBS_xRF_y and *co*PES_xRF_y to those reported for the *co*PBS_xBF_y and *co*PES_xBF_y series is opportune. Comparison had to be however restricted to those particular compositions for which biodegradation data are provided by the different works, which actually are limited to the *co*$PBS_{40}RF_{60}$/*co*$PBS_{40}BF_{60}$ and *co*$PES_{50}RF_{50}$/*co*$PES_{50}EF_{50}$ pairs. Biodegradability of these four copolyesters taken as the sample weight loss observed upon incubation with enzymes is compared in the graphic bar depicted in Figure 8,2,12. In this plot it is clearly shown that the sensitivity of copolyesters made from BD to enzymatic degradation is scarcely dependent on the substitution of this alkanediol by HER. On the contrary, comparison of $PES_{50}RF_{50}$ with $PES_{50}EF_{50}$ reveal that the weight lost in the former was about five times than in the latter, which is indicative that *co*PES_xRF_y copolyesters are much more sensitive to biodegradation than their *co*PES_xEF_y analogs containing similar amounts of furanoate units. The rather striking different behavior displayed by butylene and ethylene based copolyesters could be explained taken into account the relative differences in both T_g and crystallinity between the two series of copolyesters under comparison.

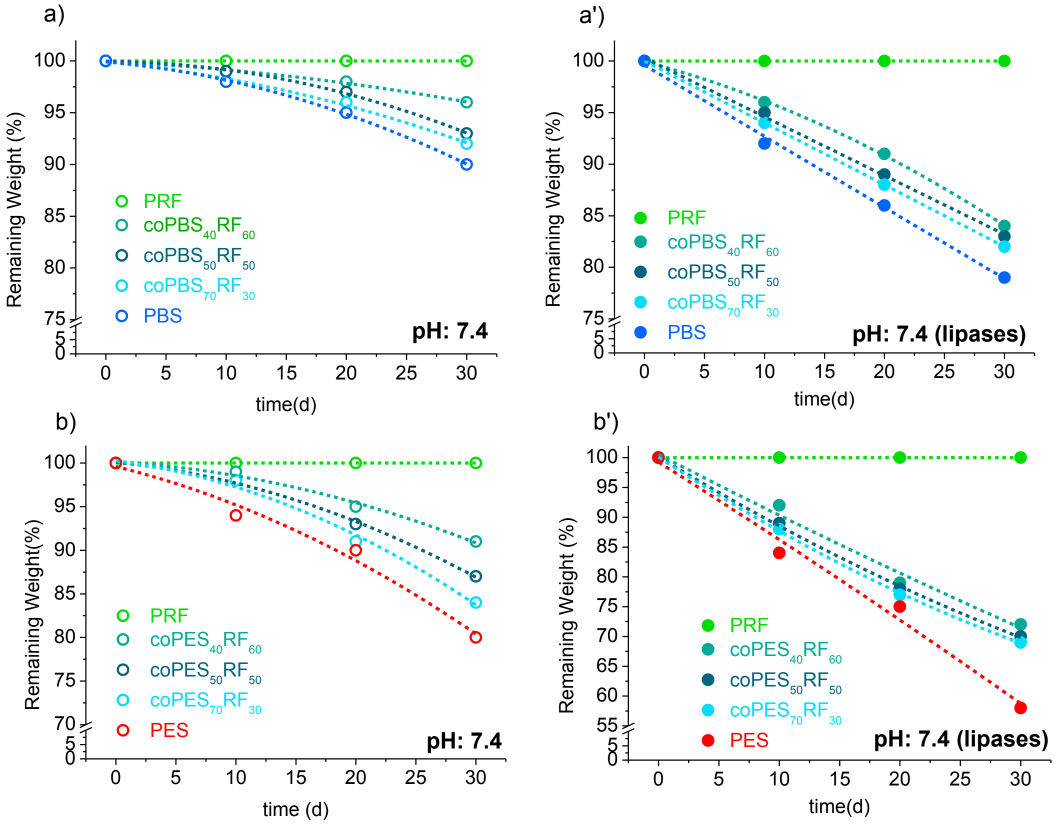


Figure 8.2.11. Weight loss of resorcinol-containing copolyesters as a function of incubation time in aqueous buffer at pH 4 and 37 ºC (a and b) and under the same conditions but with lipases added to the incubation medium (a' and b').

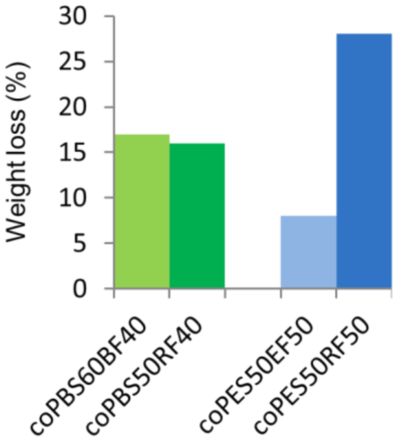


Figure 8.2.12. Compared biodegradability for butylene and ethylene-based copolyesters differing in the content in resorcinol-derived units. Data reported by Morales-Huerta et al. [14] for *co*PBS$_{60}$BF$_{40}$ and Terzoupolou et al. [15] for *co*PES$_{50}$EF$_{50}$ are taken for comparison.

VIII.2.3. Conclusions

Bis(2-hydroxyethyl) resorcinol, an aromatic diol of bio-based origin, has been used to replace either 1,4-butanediol or ethylene glycol in the synthesis of random copolyesters made of 2,5-furandicarboxylic and succinic acids. These copolyesters are distinguished by being fully sustainable and containing high amounts of aromatic units. The copolyesters are amorphous and display a more than good thermal stability with onset temperatures not far from 300 ºC. The incorporation of the aromatic units causes an increasing in the T_g that is more noticeable in the case of the butylene containing copolyesters. The substitution of the alkanediol by resorcinol does not repress the biodegradability of the copolyesters but contrarily it is even enhanced in the case of 1,4-butanediol.

The ring opening polymerization (ROP) method has been proven to be an excellent tool for the preparation of these copolyesters. Cyclic oligomers of resorcinol diethylen furanoate could be readily prepared by means of the high dilution condensation method and copolymerization with oligo(alkylene succinate) cycles proceeded in short time and rendered good yields. The resulting copolyesters had satisfactory molecular weights and their compositions are very similar to those of the feeds used for their synthesis. The copolymerization approach described in this paper is of interest for modulating the T_g of poly(alkylene succinate)s without detriment of the polyester sustainability.

VIII.2.4 References

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IX Conclusions

1) Cyclic alkylene 2,5-furandicarboxylate oligoesters were successfully prepared from 2,5-furandicarboxylic acid dichloride and either ethylene glycol or 1,4-butanediol by applying both high dilution condensation and cyclodepolymerization techniques. After purification, mixtures of cyclic oligomers enriched in dimer, trimer and tetramer species were attained in high yields. Poly(ethylene 2,5-furandicarboxylate) and poly(butylene 2,5-furandicarboxylate) polyesters were successfully obtained by Ring Opening Polymerization (ROP) in the bulk of their respective cyclic oligo(ethylene 2,5,-furandicarboxylate)s and oligo(butylene 2,5-furandicarboxylate)s. Weight-average molecular weights in the 50,000-70,000 g·mol^{-1} range were attained regardless mixture composition and size of the oligomers contained therein

2) Poly(butylene 2,5-furandicarboxylate-*co*-terephthalate) copolyesters were successfully prepared by ROP in the bulk of mixtures of cyclic butylene 2,5-furandicarboxylate and butylene terephthalate oligoesters for a wide range of compositions. The copolyesters were random and displayed molecular weights higher than those obtained by melt polycondensation. The furanoate-terephthalate copolyesters prepared by ROP were practically undistinguishable in structure and properties from those obtained by polycondensation by other authors.

3) Poly(butylene 2,5-furandicarboxylate-*co*-isophthalate)s were obtained by ROP of cyclic butylene 2,5-furandicarboxylate and butylene isophthalate oligoester mixtures using the same technique as for terephthalate copolyesters. The copolyesters were obtained in good yields and high molecular weights, and with a random microstructure. Most of these copolyesters were amorphous so that only those with compositions close to the parent homopolyesters displayed crystallinity.

4) Poly(butylene 2,5-furandicarboxylate-*co*-succinate) were successfully synthesized by ROP in the bulk of mixtures of cyclic butylene 2,5-furandicarboxylate and butylene succinate oligoesters for a wide range of compositions using both organometallic and enzymatic catalysis. Random copolyesters in high yields were obtained in both cases but lower molecular weights were achieved when enzymes were used Thermal properties were similar in both cases and comparable with those reported for similar copolyesters obtained by polycondensation.

5) Cyclic (butylene 2,5.furandicarboxylate) oligoesters were enzymatically copolymerized with ε-caprolactone to produce novel poly(butylene furanoate-*co*-caprolactone) copolyesters avoiding the use of organic solvents and organometallic catalysts. The copolyesters displayed a blocky microstructure contrary to the expected random distribution. A slight increase in randomization could be achieved by transesterification of the copolyesters assisted with organometallic catalysis. The copolyesters were well heat resistant, displayed high glass-transition temperatures, were able to crystallize for minor contents in any of the two comonomers, and their biodegradability increased with the content in caprolactone

6) Cyclic (ethylene succinate) oligoesters were synthesized for the first time by enzymatic condensation with results similar to that reported by us and others authors for the synthesis of cyclic oligo(butylene succinate)s but without presence of cyclic dimer. The enzymatic copolymerization of these cycles with different lactones constitutes a very suitable technique for the sustainable preparation of a variety of aliphatic copolyesters. The whole process constitutes an original strategy for the production of poly(ethylene succinate) copolyesters exempt of metallic contaminants. The procedure is envisaged as very adequate for the synthesis of fully bio-based aliphatic copolyesters for applications in biomedicine.

7) Cyclic oligofuranoates made of bio-based cyclic diols (bis (2-hydroxyethyl) benzene derived from resorcinol and 1,4:3;6, dianhidro mannitol (isomannide) derived from mucic acid) were synthesized for the first time by the high dilution condensation technique. Both types of cyclic oligoesters were obtained in good yields as heterogeneous mixtures of species of different sizes with dimer, trimer and tetramer being the main constituents.

8) Copolymerization of resorcinol derived cyclic oligofuranoates with cyclic (butylene succinate)s or cyclic(ethylene succinate) to the preparation of a series of random aliphatic-aromatic terpoly esters derived from poly(butylene succinate) and poly(ethylene succinate) that distinguished by being potentially fully bio.based. These copolyesters are thermally stable, have high glass transition temperatures and show a notable biodegradability.

9) Cyclic oligoesters made of isomannide furanoate were successfully copolymerized with cyclic oligo(butylene furanoate) to produce random poly(butylene-*co*-isomannide furanoate) copolyesters with a wide range of compositions. The incorporation of the isomannide units in PBF decreased its crystallinity but increased its glass-transition temperature and biodegradability. These effects on structure and thermal properties were more noticeable as the content of the copolyesters in isomannide increased.

10) Cyclic oligoesters made of isomannide furanoate were successfully copolymerized in bulk with cyclic oligo(butylene succinate)s to produce random poly(isomannide furanoate-*co* butylene succinate) copolyesters with a wide range of compositions. The incorporation of the isomannide furanoate units in PBS decreased its crystallinity but increased its biodegradability. The glass-transition temperature increased rapidly with the content in isomannide furanoate units making this approach the most effective known so far for rising this temperature, All these effects on structure and thermal properties were more noticeable as the content of the copolyesters in isomannide increased.

11) A general conclusion of this Thesis regarding synthesis is that ROP in the bulk of cyclic oligofuranoates has been demonstrated to be an effective technique for the preparation of furanoate-based homopolyesters and random or nearly-random copolyesters with yields and molecular weights comparable to those obtained by conventional polycondensation. Since both oligomer formation and cyclopolymerization can be realized with the concourse of enzymes, the ROP approach for polyfuranoate's synthesis constitutes an excellent strategy towards the preparation of these polymers with a high degree of sustainability. This methodology is potentially applicable to a unlimited number of polyesters and copolyesters, and it is only restricted by the accessibility of the cyclic monomers required for performing ROP.

12) A second general conclusion refers to the novel furanoate-based copolyesters synthesized in this Thesis. The results here obtained has well demonstrated that fundamental properties of poly(butylene furanoate) may be conveniently modified by the incorporation of adequate comonomeric units. As expected crystallinity and crystallizability are invariably depressed by copolymerization but the thermal stability remains essentially unaffected. Glass-transition temperature and biodegradability can be tuned over a significant wide interval by proper selection of the comonomer and composition adjustment. The application of enzymatic process leads to materials absent of metallic contaminants, a merit that is every time more appreciated for both food packaging and biomaterial applications.

Annex

Annex A

Support information of Chapter IV:

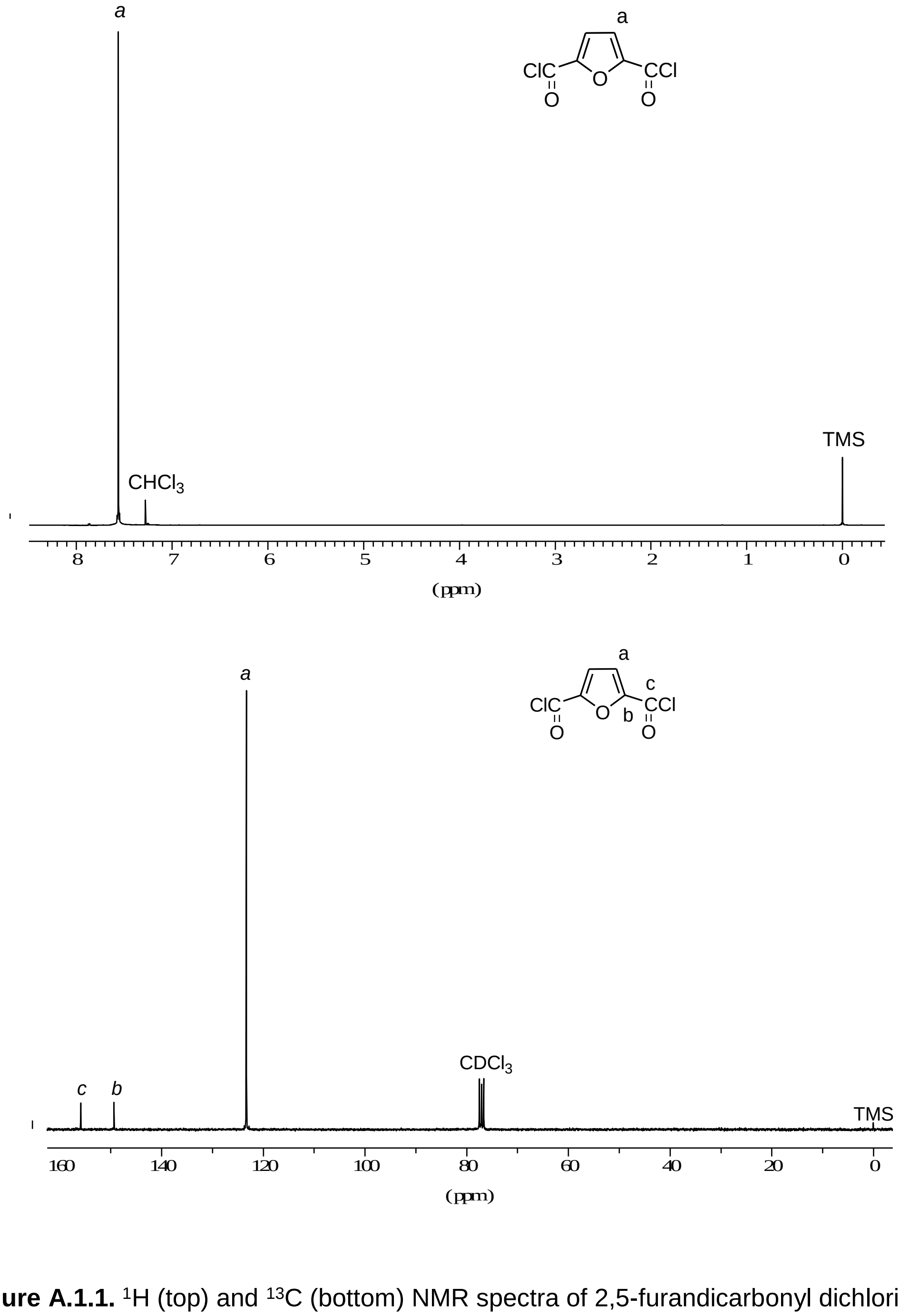


Figure A.1.1. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2,5-furandicarbonyl dichloride in $CDCl_3$.

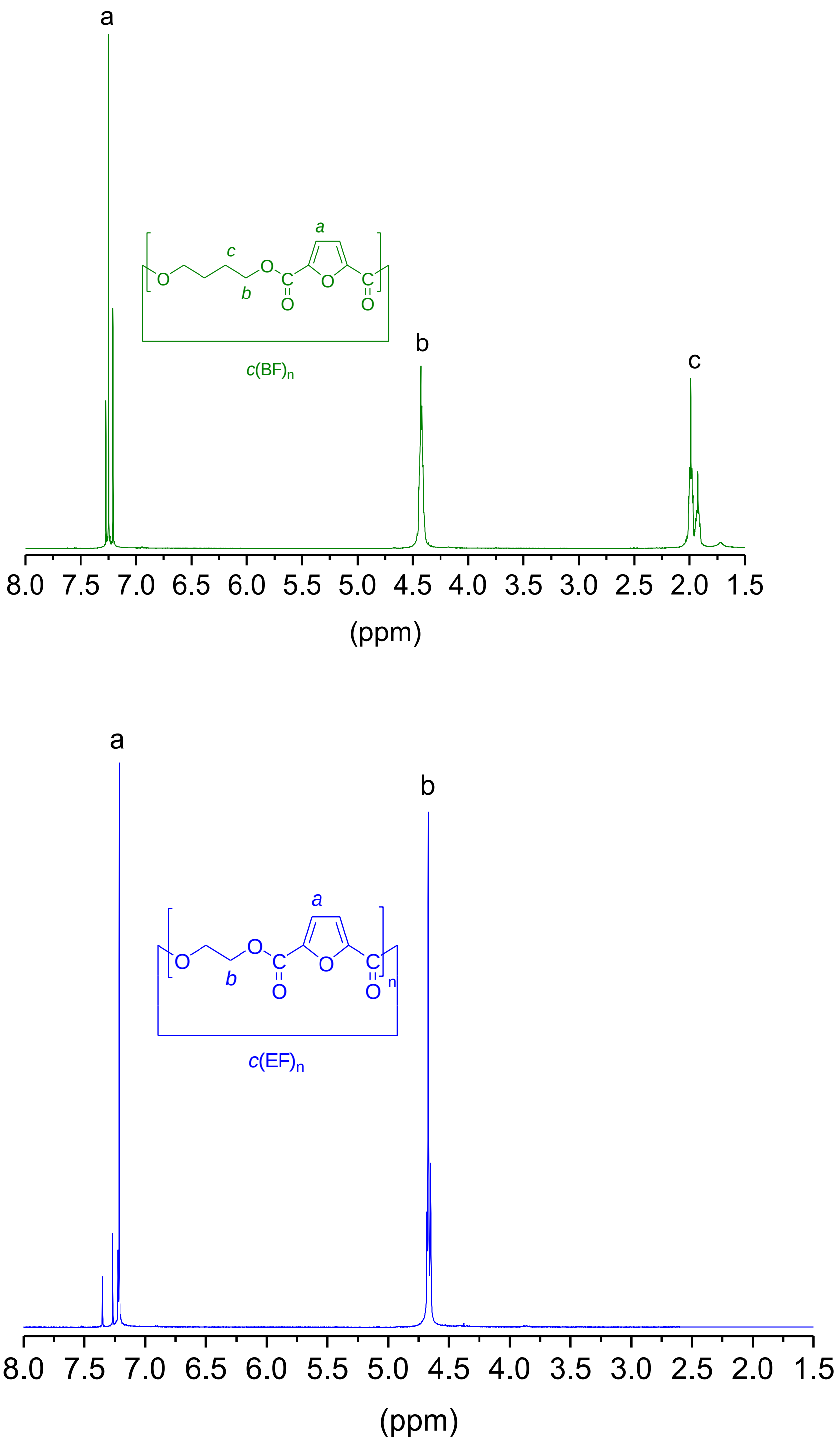


Figure A.1.2. ^{1}H NMR of *c*(BF)$_n$ and *c*(EF)$_n$ synthesized *via* CD.

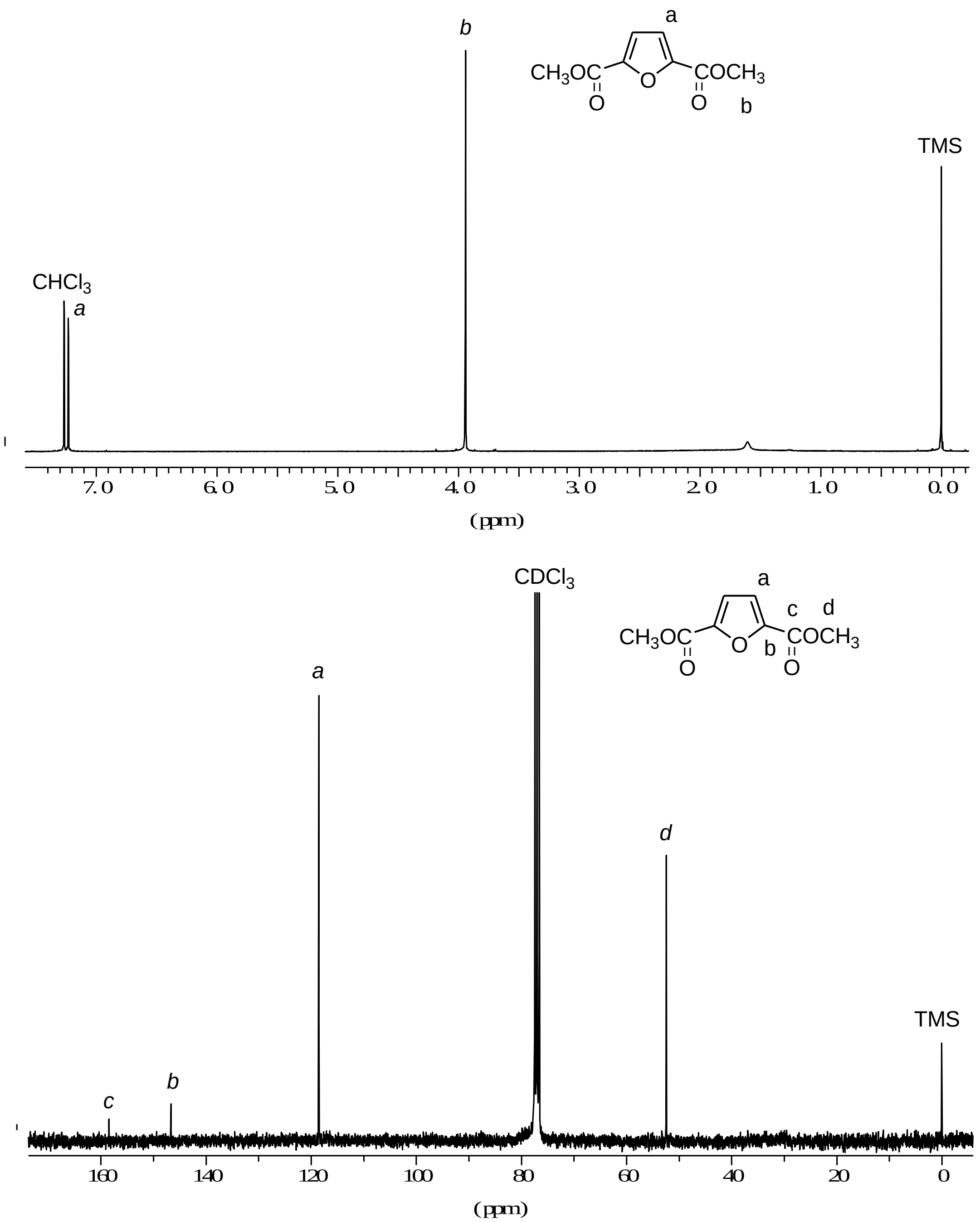


Figure A.1.3. ^{1}H (top) and ^{13}C (bottom) NMR spectra of dimethyl 2,5-furandicarboxylate in $CDCl_3$.

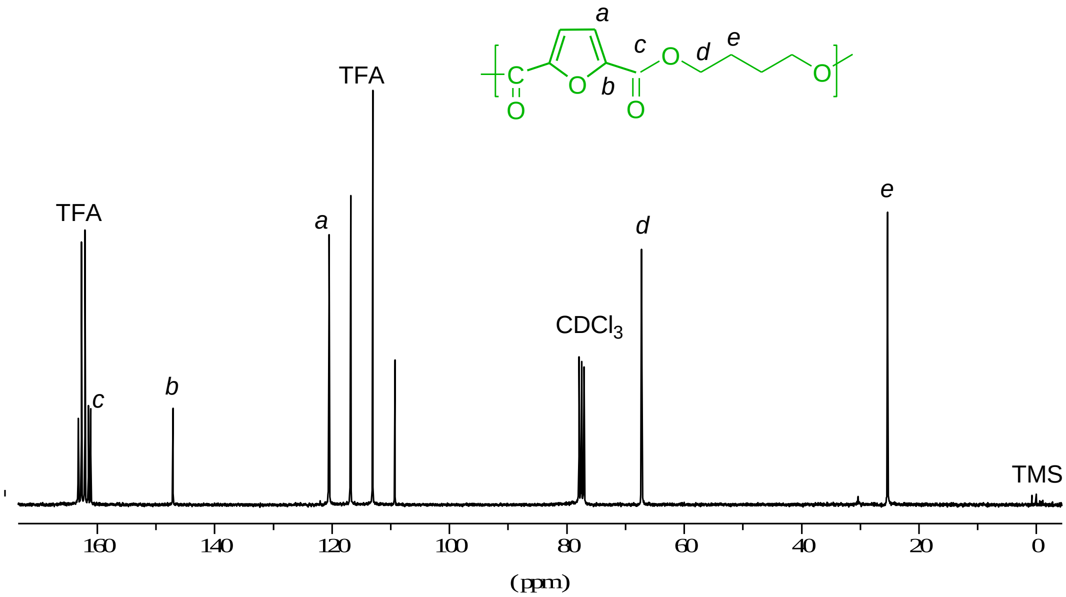


Figure A.1.4a. ^{1}H (top) and ^{13}C (bottom) NMR spectra of PBF obtained by melt polycondensation in $CDCl_3$/TFA.

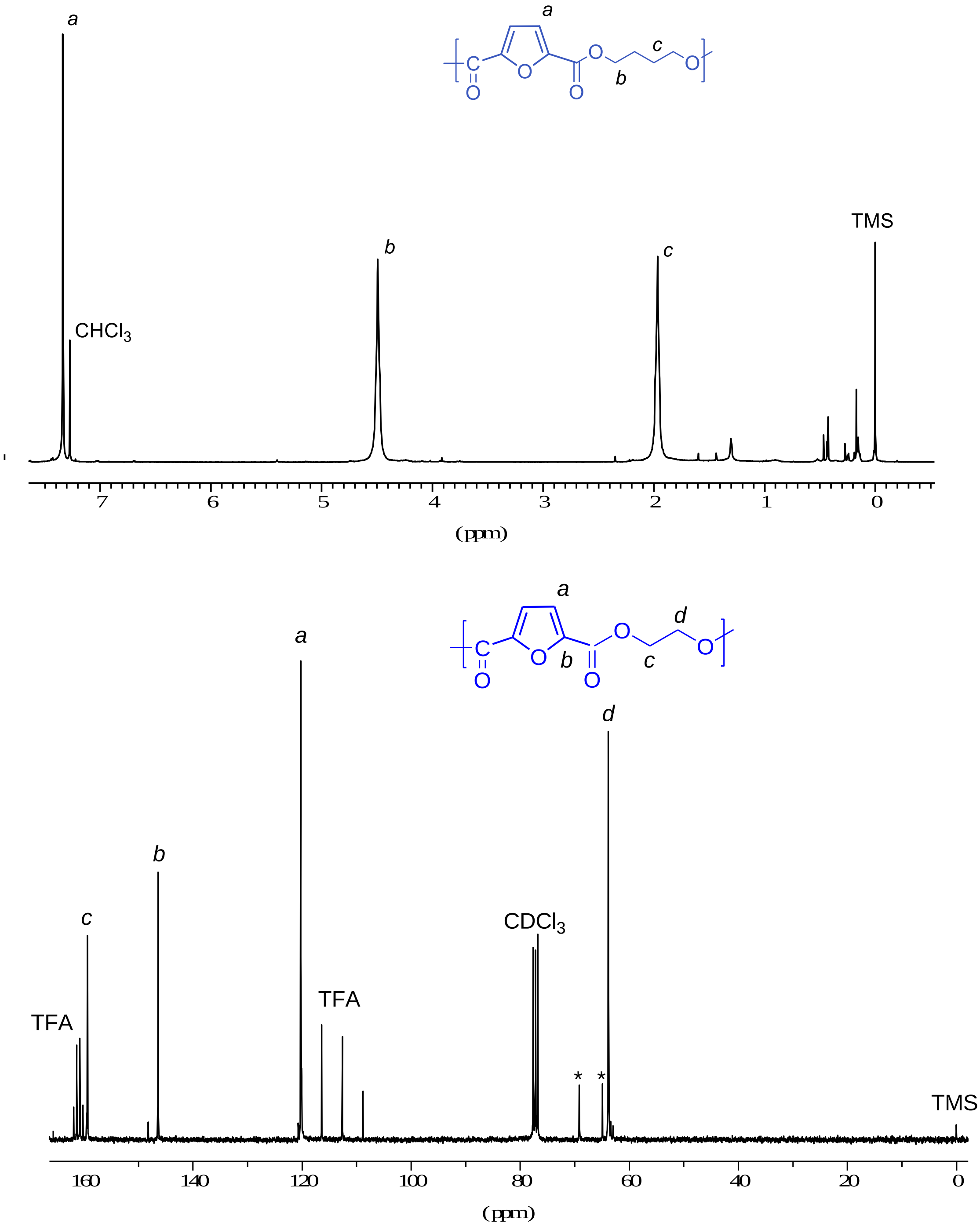


Figure A.1.4b. ^{1}H (top) and ^{13}C (bottom) NMR spectra of PEF obtained by melt polycondensation in $CDCl_3$/TFA.

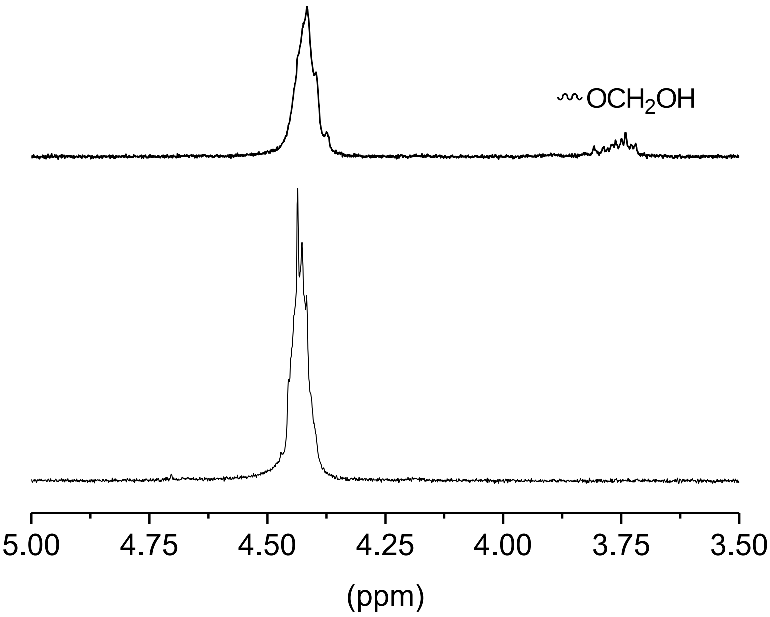


Figure A.1.5. Enlarged ^{1}H NMR spectra of BF oligomers before (top) and after purification (bottom) showing the 3.5-5.0 ppm region where hydroxyl ends of linear species appear.

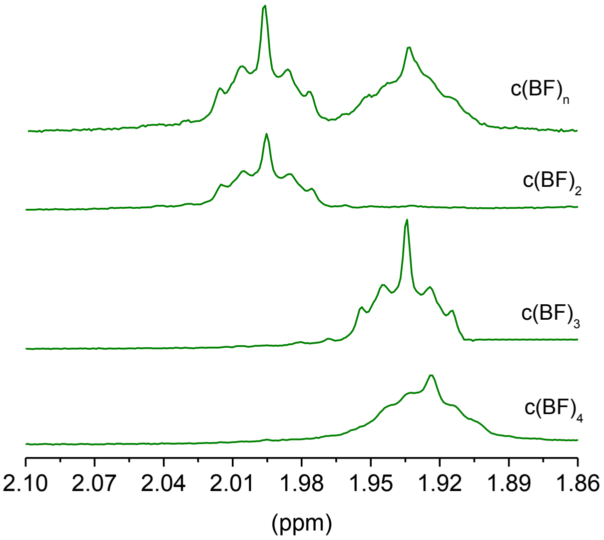


Figure A.1.6. Enlarged ^{1}H NMR spectra (2.10–1.86 ppm region) of *c*$(BF)_n$ and *c*$(BF)_2$, *c*$(BF)_3$ and *c*$(BF)_4$ after fractionation by column chromatography.

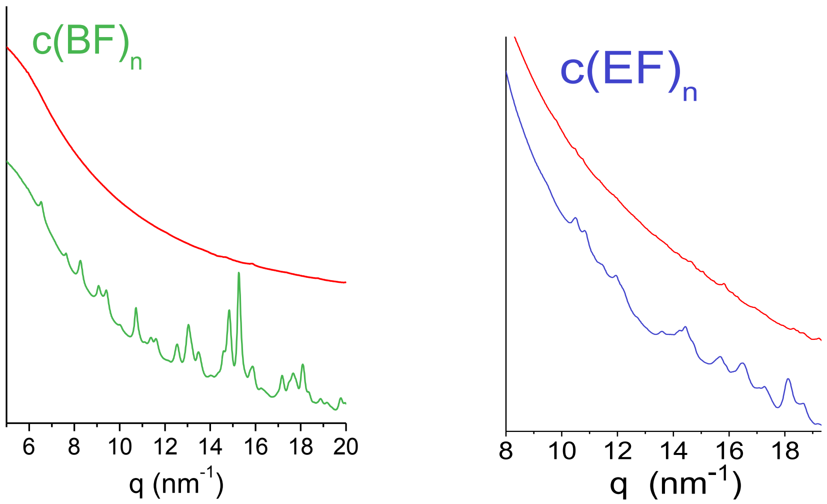


Figure A.1.7. XRD profiles registered from *c*(BF)$_n$ and *c*(EF)$_n$ at room temperature and after heating (red traces).

Table A.1. Properties of PBF and PEF obtained by polycondensation and used for cyclodepolymerization.

Polymer	M_w (g·mol^{-1})	*Đ*	T_m^b (°C)	T_m (°C)	T_g (°C)	T_d (°C)	T_{onset}	*Rw (%)*
PBF	34,000	3.6	112	168	39	400	428	8
PEF	38,000	1.8	112	214	77	320	350	9

Annex B.

B.1. Support Information of Subchapter V.1

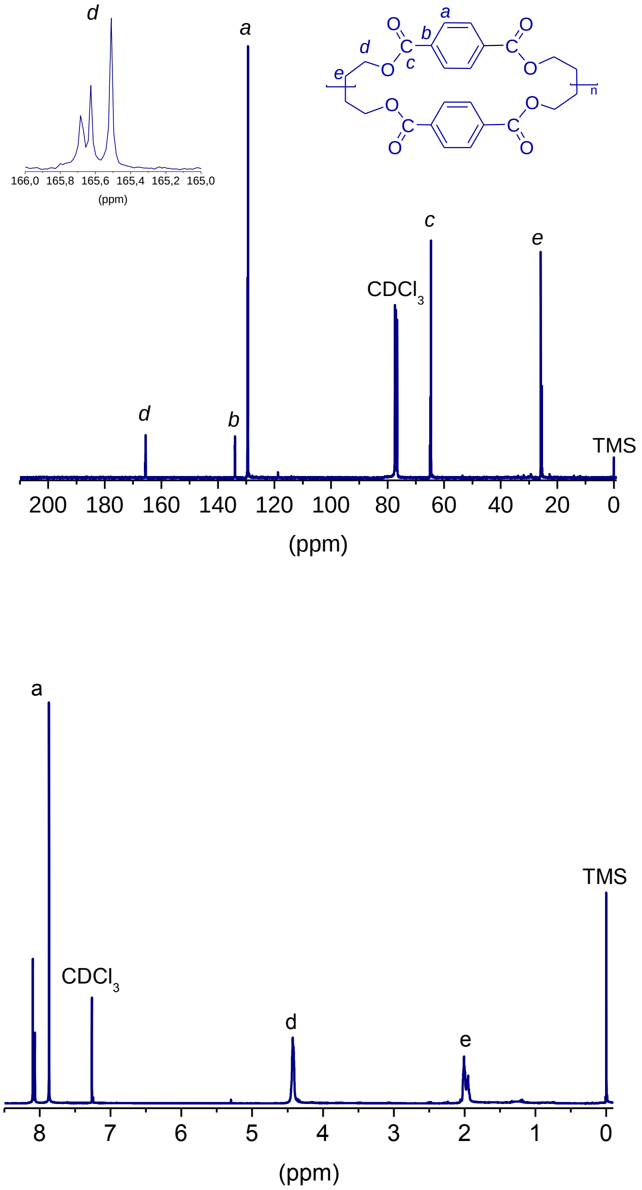


Figure B.1.1. ^{13}C (top) and ^{1}H (bottom) NMR of *c*(BT)$_n$.

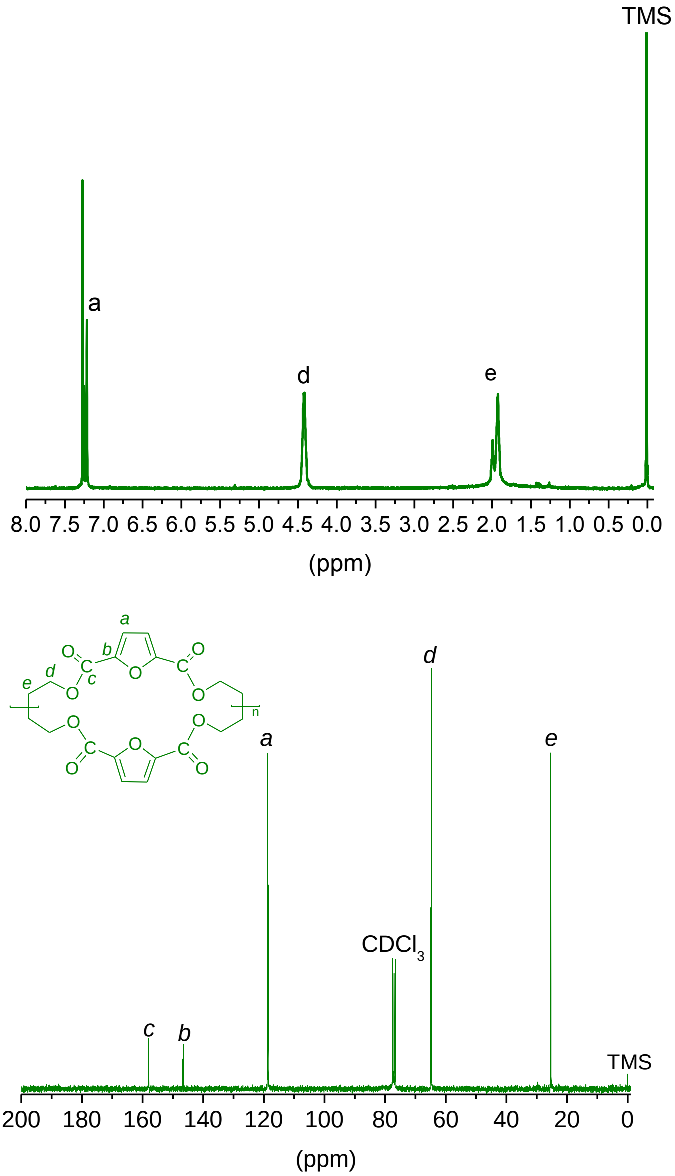
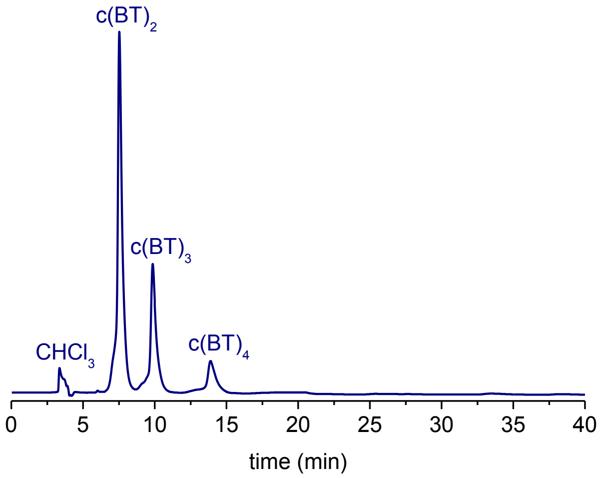


Figure B.1.2.^{13}C (top) and ^{1}H (bottom) NMR of *c*(BF)$_n$.



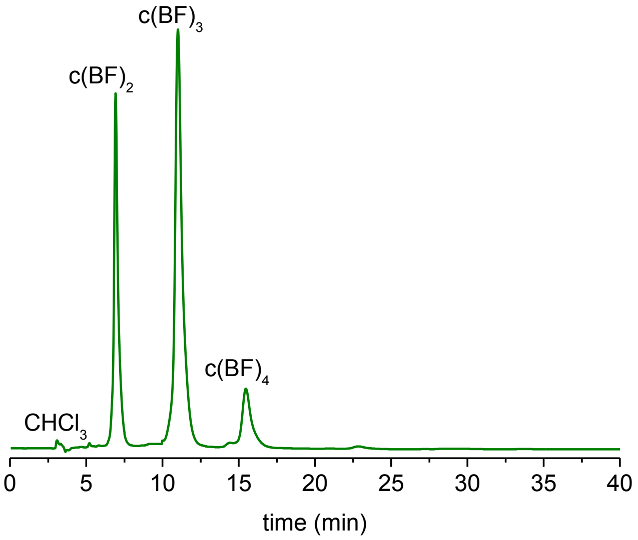


Figure B.1.3. HPLC of *c*(BT)$_n$ (top) and *c*(BF)$_n$ (bottom).

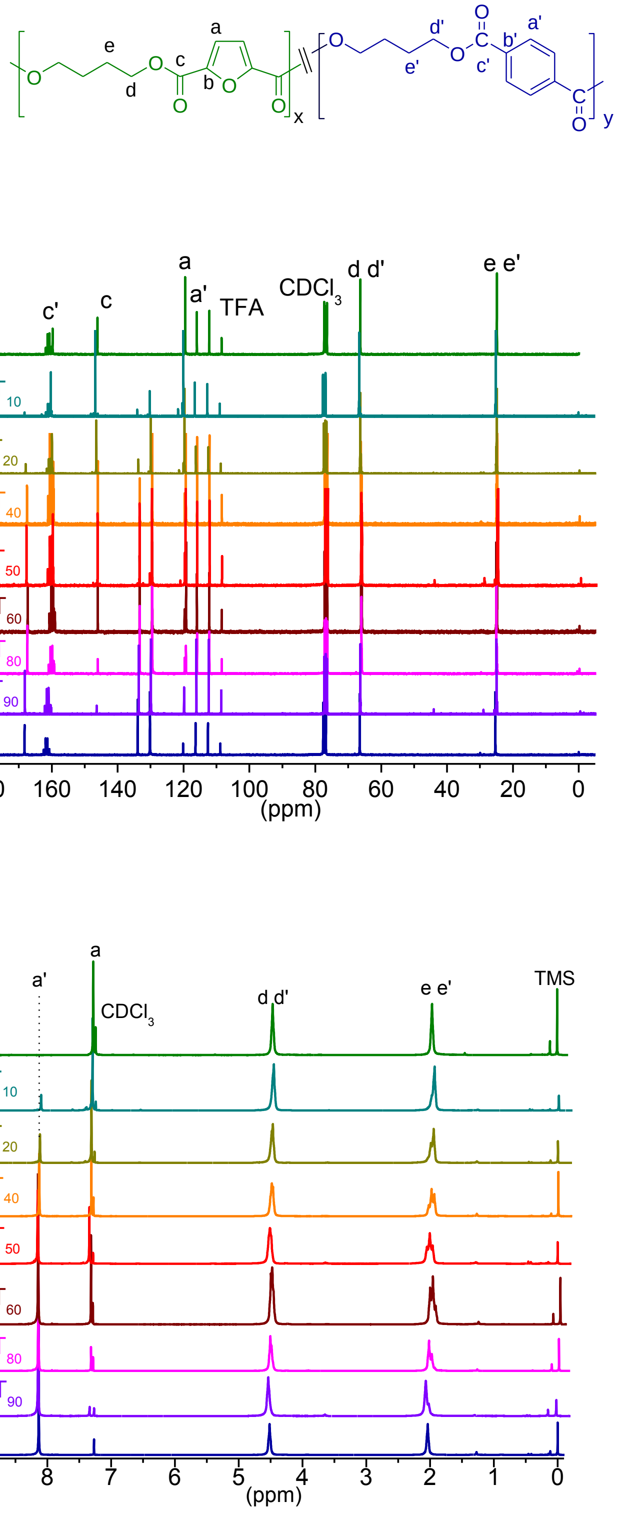


Figure B.1.4. ^{13}C (top) and ^{13}H (bottom) NMR spectra of *co*PBF$_x$T$_y$.

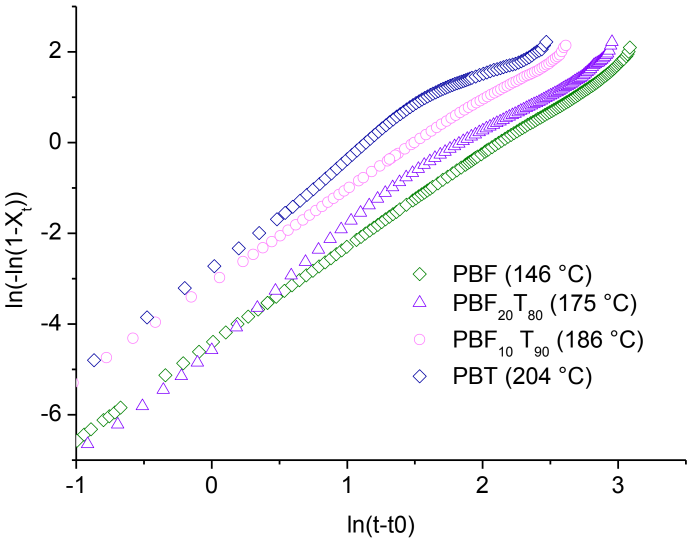


Figure B.1.5. Double logarithmic plots of crystallinity versus time for the isothermal crystallization of PBT, PBF, *co*PBF$_{10}$T$_{90}$ and *co*PBF$_{20}$T$_{80}$.

B.2 Support information to subchapter V.2

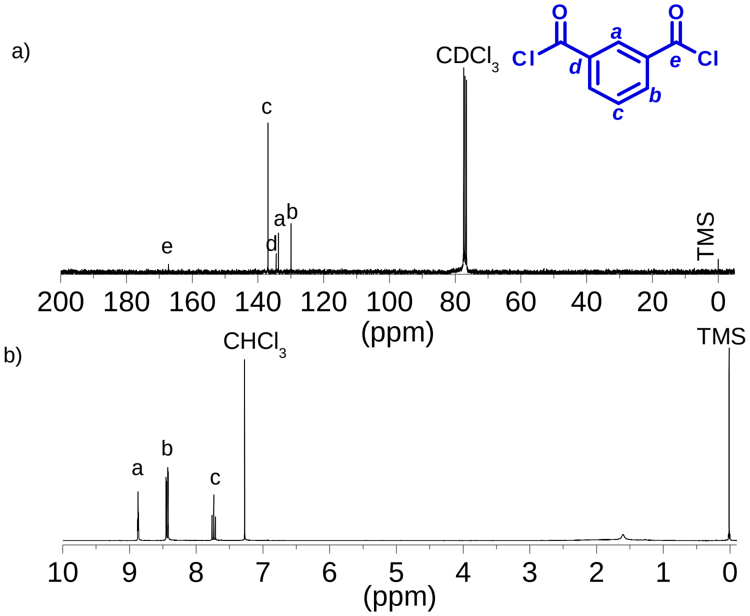


Figure B.2.1. a) ^{13}C NMR, b) ^{1}H NMR spectra of isophthaloyl chloride

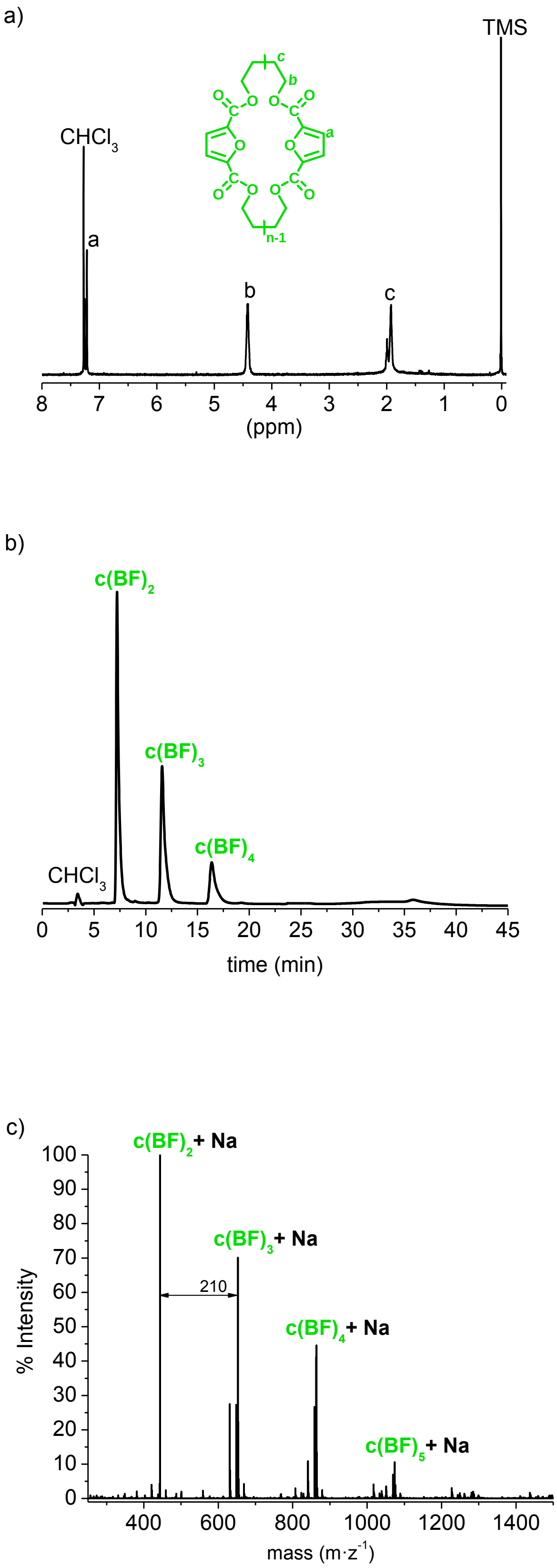


Figure B.2.2. a) ^{1}H NMR, b) HPLC and c) MALDI-ToF of *c*(BF)$_n$.

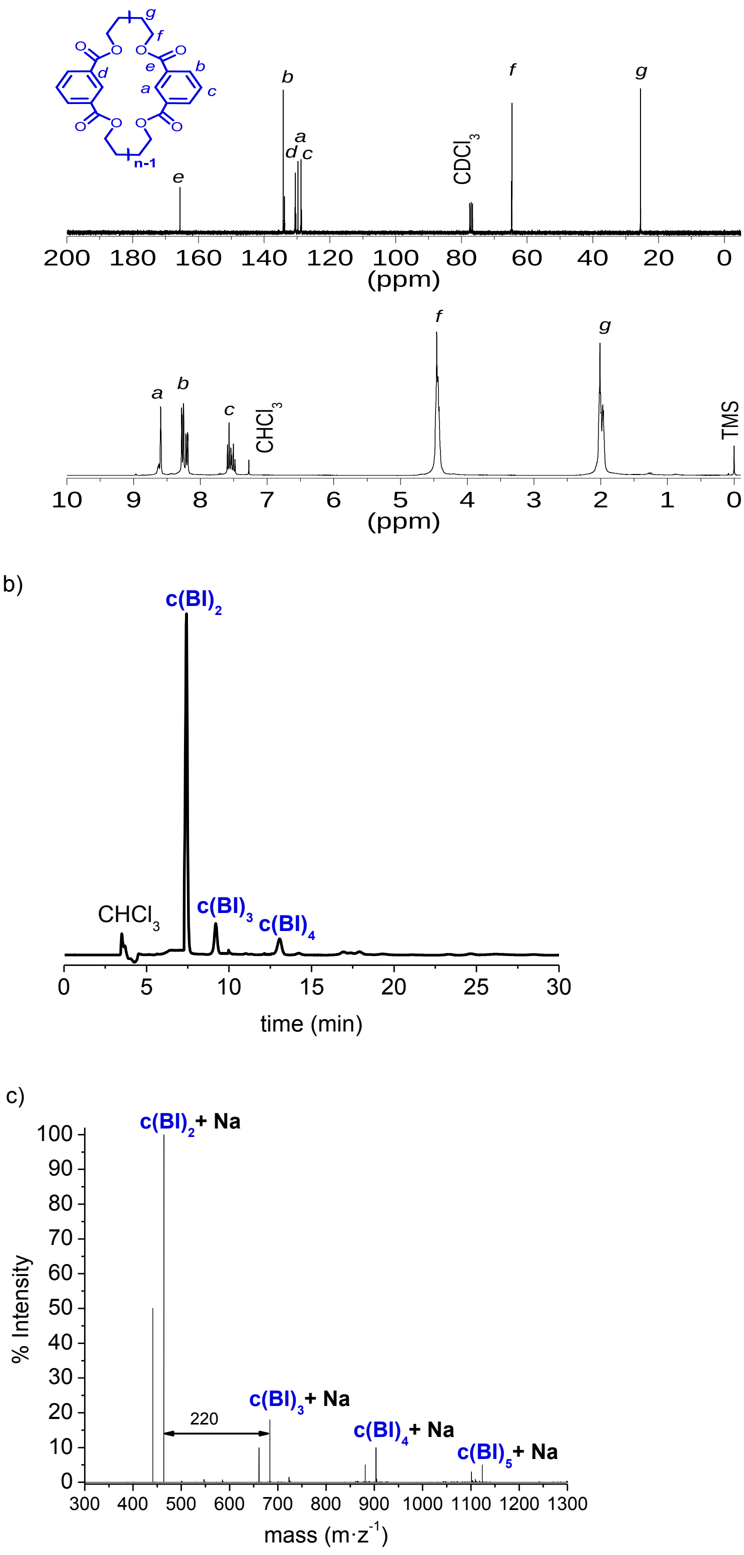


Figure B.2.3. a) NMR, b) HPLC and c) MALDI-ToF of *c*(BI)ₙ.

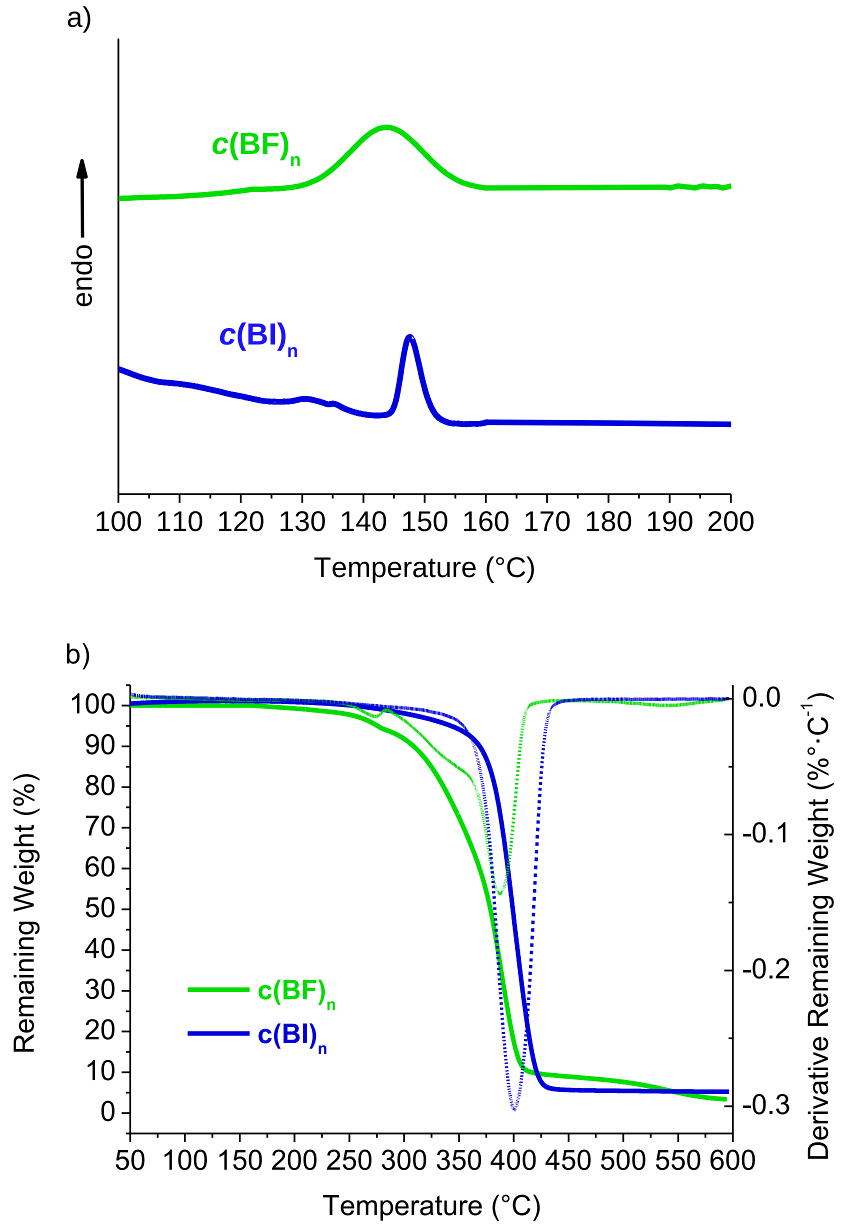


Figure B.2.4. a) DSC and b) TGA analysis of *c*(BF)$_n$ and *c*(BI)$_n$.

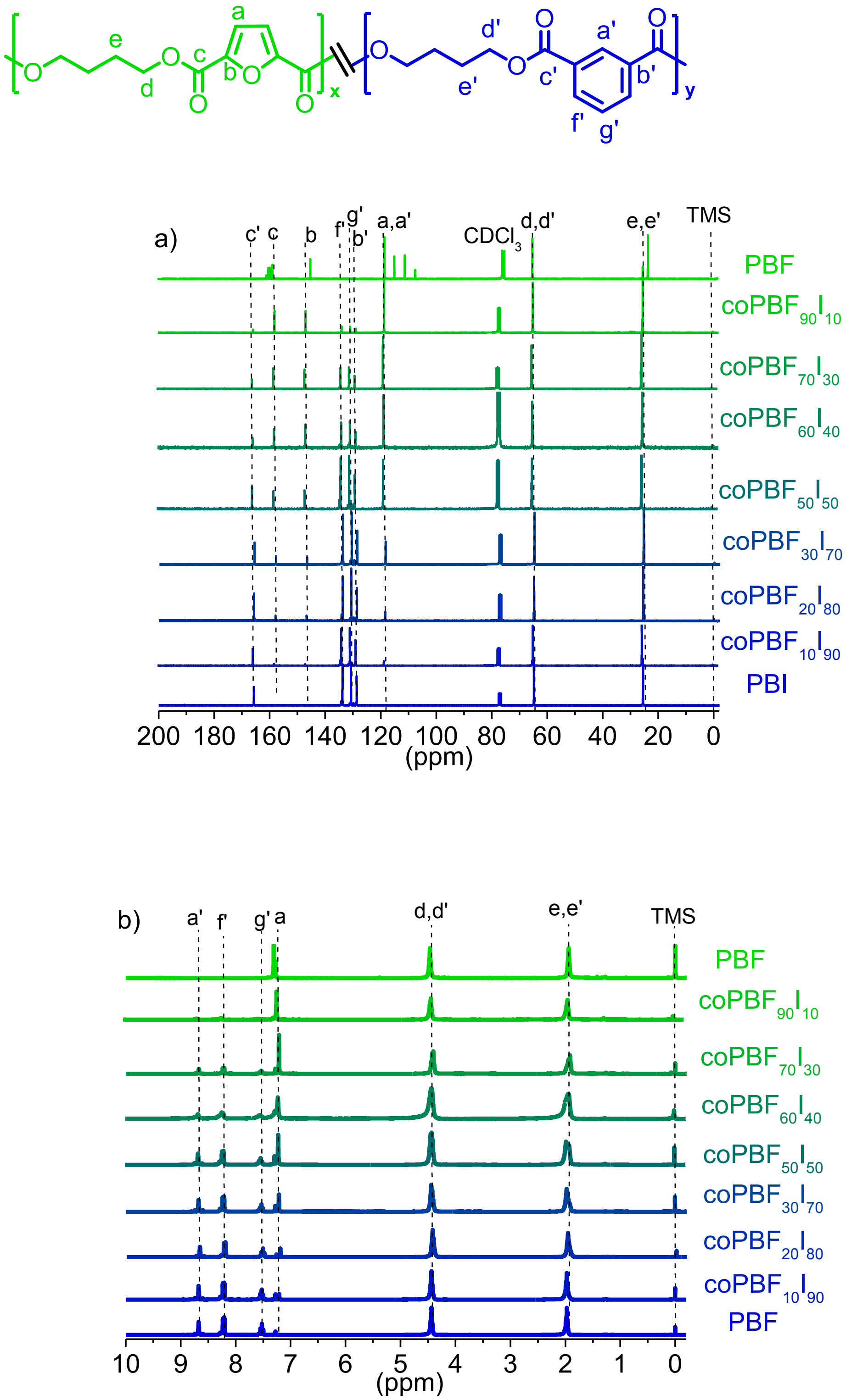


Figure B.2.5. a) ^{13}C and b) ^{1}H NMR of *co*PBF$_x$I$_y$

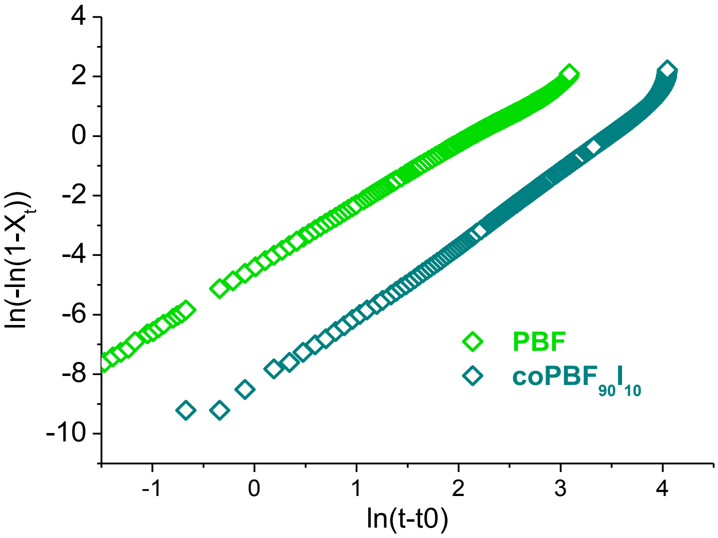


Figure B.2.6. Double logarithmic plot of crystallization of *co*PBF$_{90}$I$_{10}$ compared with PBF.

Annex C:

C.1 Support Information of subchapter VI.1

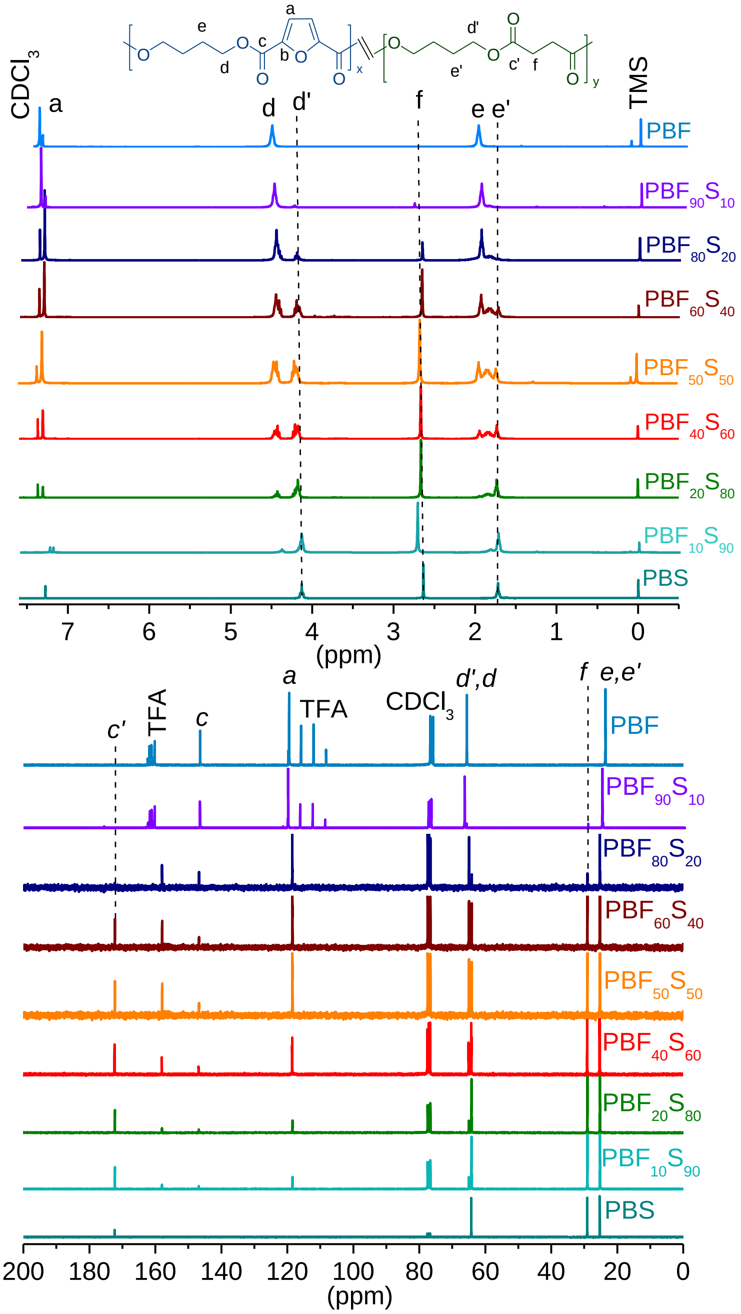


Figure C.1.1. ^{1}H (top) and ^{13}C NMR(bottom) spectra of the *co*PBF$_x$S$_y$ using Sn(Oct)$_2$ as catalyst.

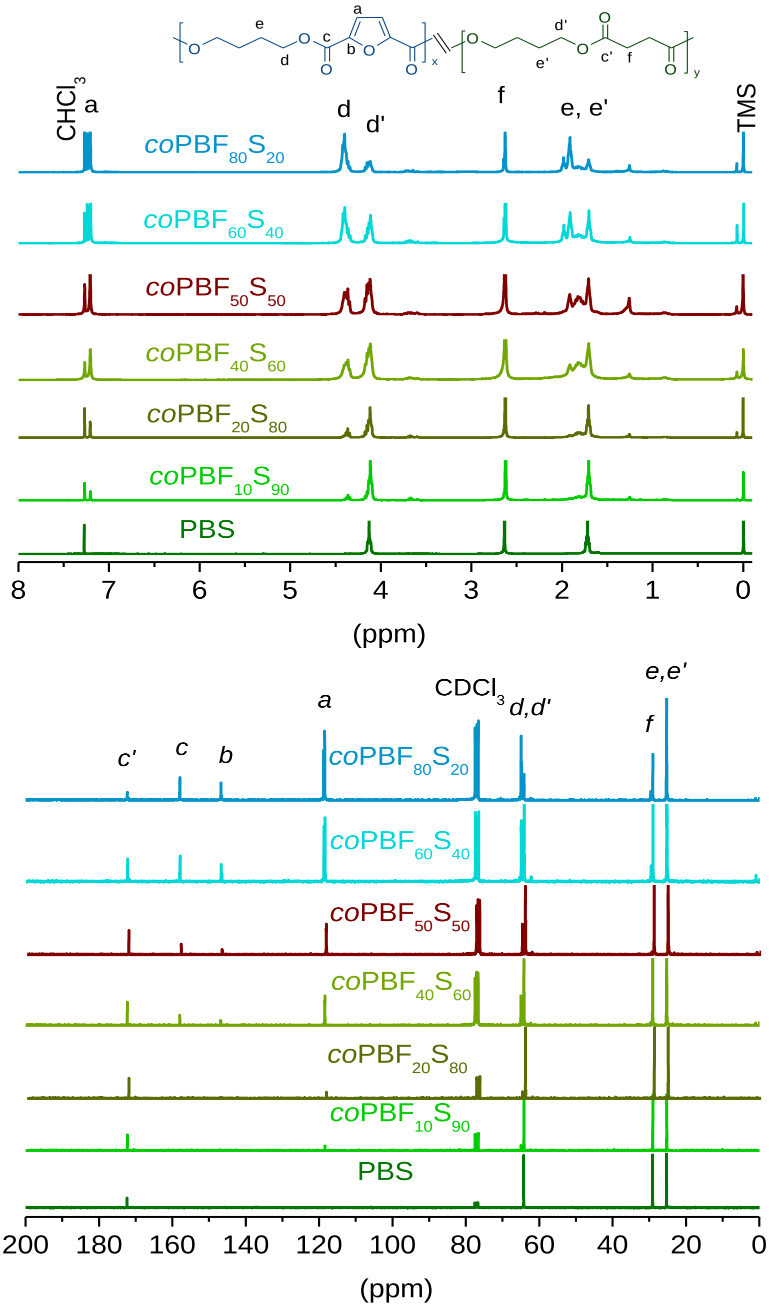


Figure C.1.2. ^{1}H (top) and ^{13}C NMR(bottom) spectra of the *co*PBF$_x$S$_y$ using CALB as catalyst.

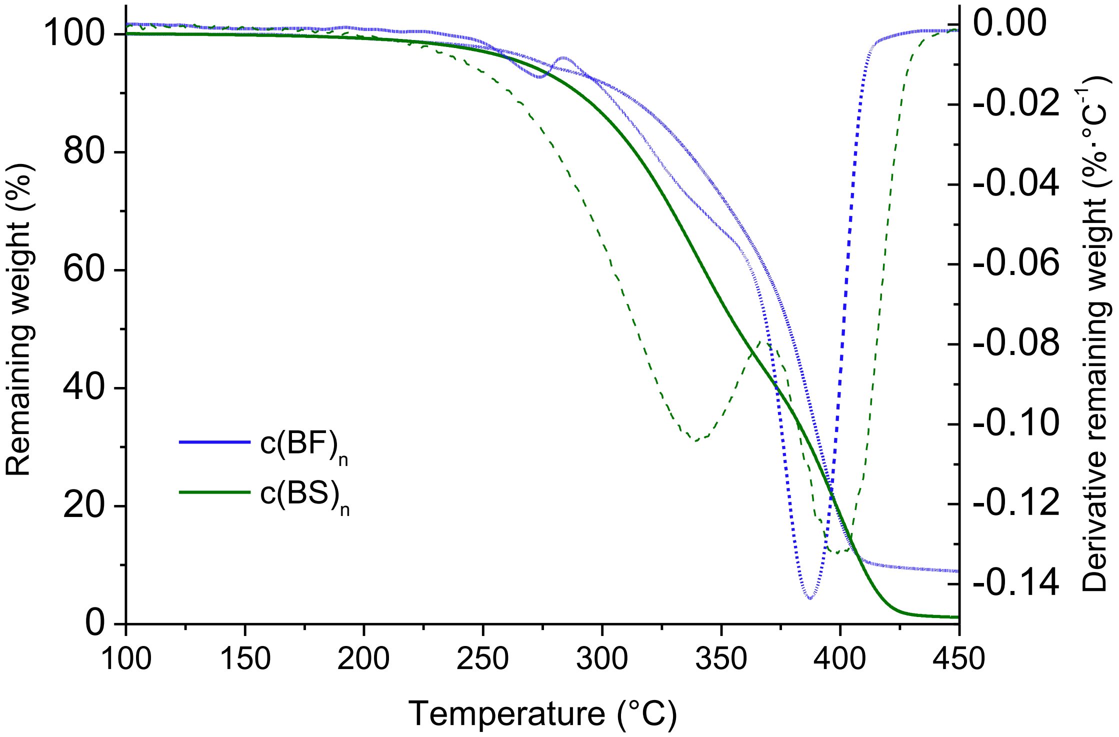


Figure C.1.3. TGA analysis of *c*(BF)n and *c*(BS)n.

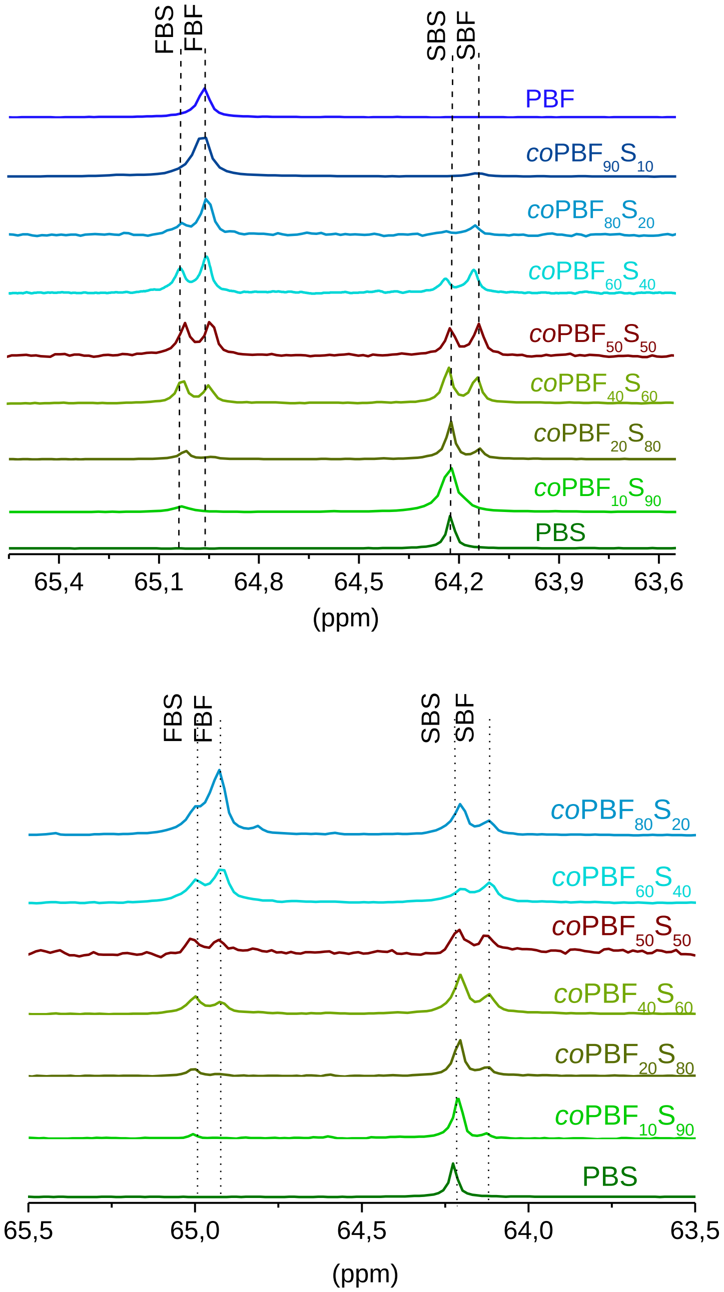


Figure C.1.4. ^{13}C NMR enlarged in the region 65.5-63.5 of *co*PBF$_x$S$_y$ using Sn(Oct)$_2$ (top) and CALB (bottom) as catalyst.

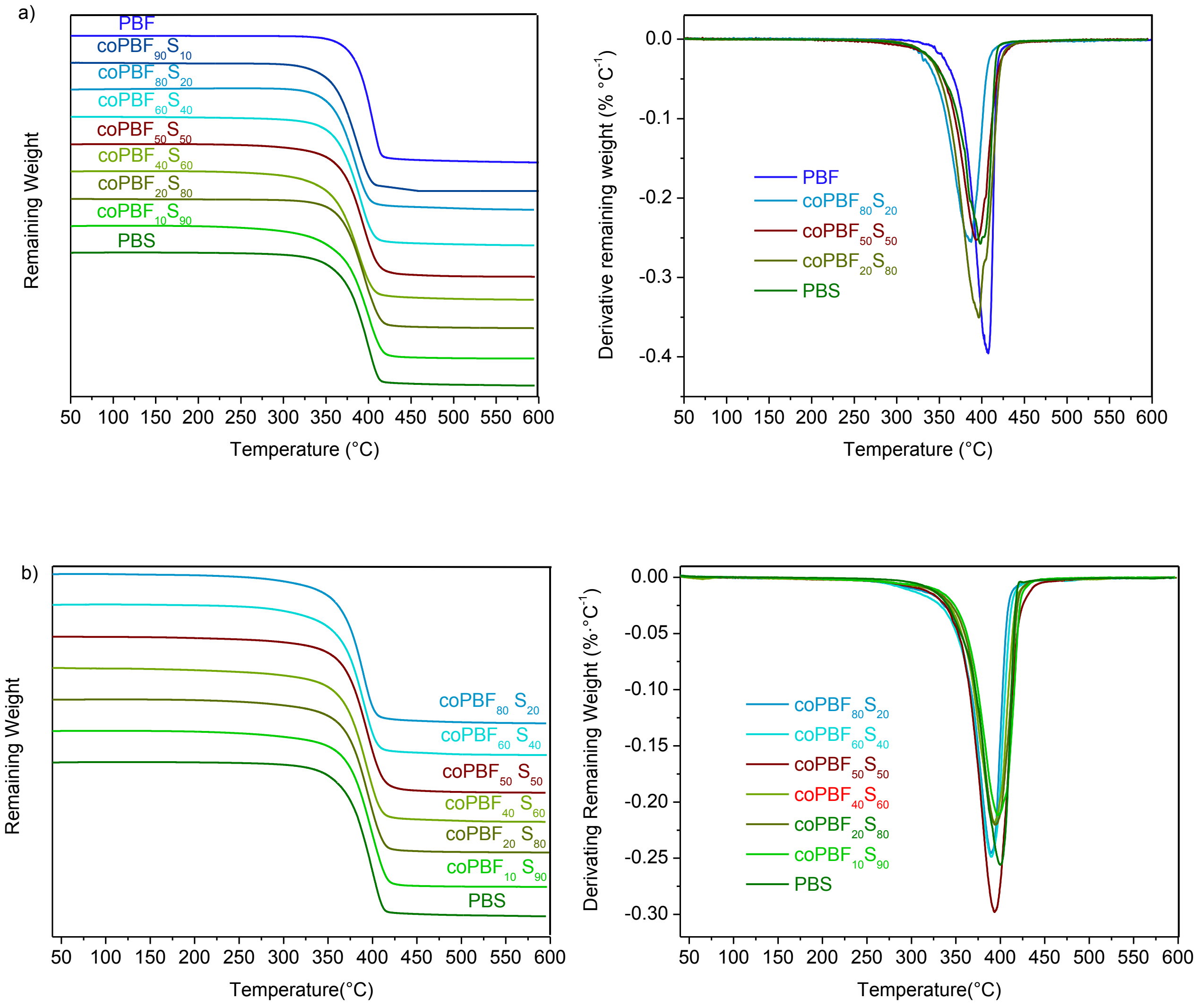


Figure C.1.5. TGA analysis of *co*PBF$_x$ S$_y$: a) using Sn(Oct)$_2$ and b) using CALB as catalysts.

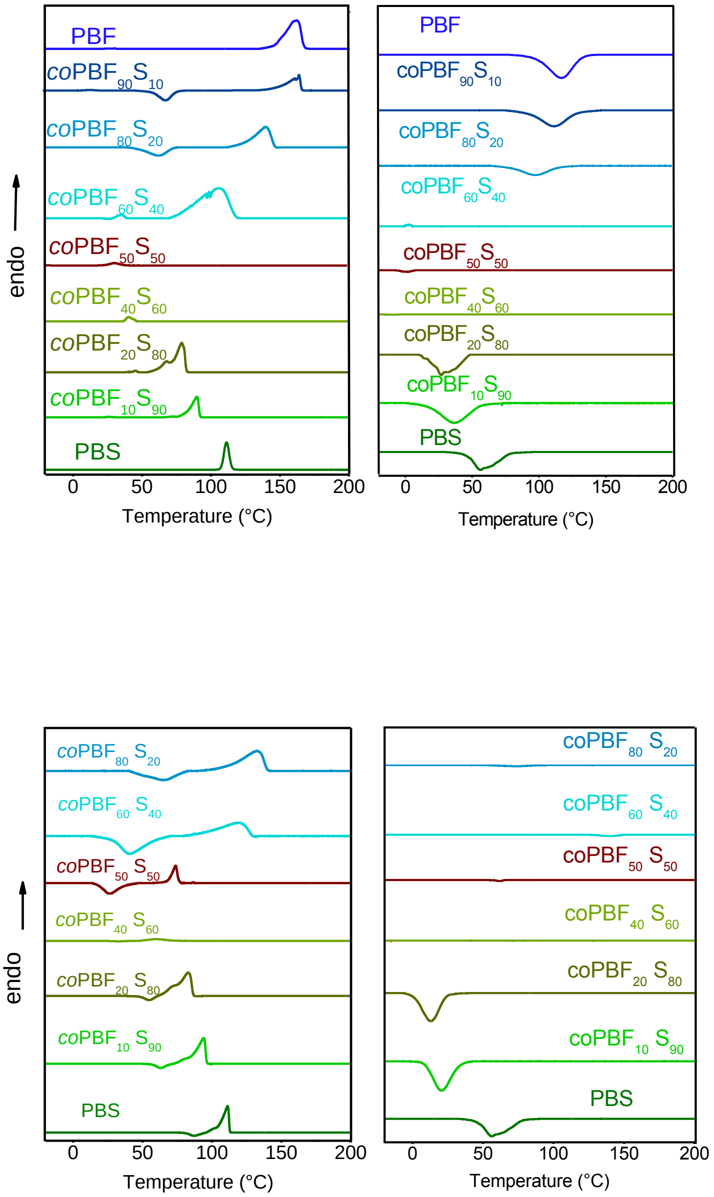


Figure C.1.6. DSC analysis of *co*PBF$_x$ S$_y$, left (first heating) and rigth (cooling from the melt) a) using Sn(Oct)$_2$ and b) CALB as catalysts.

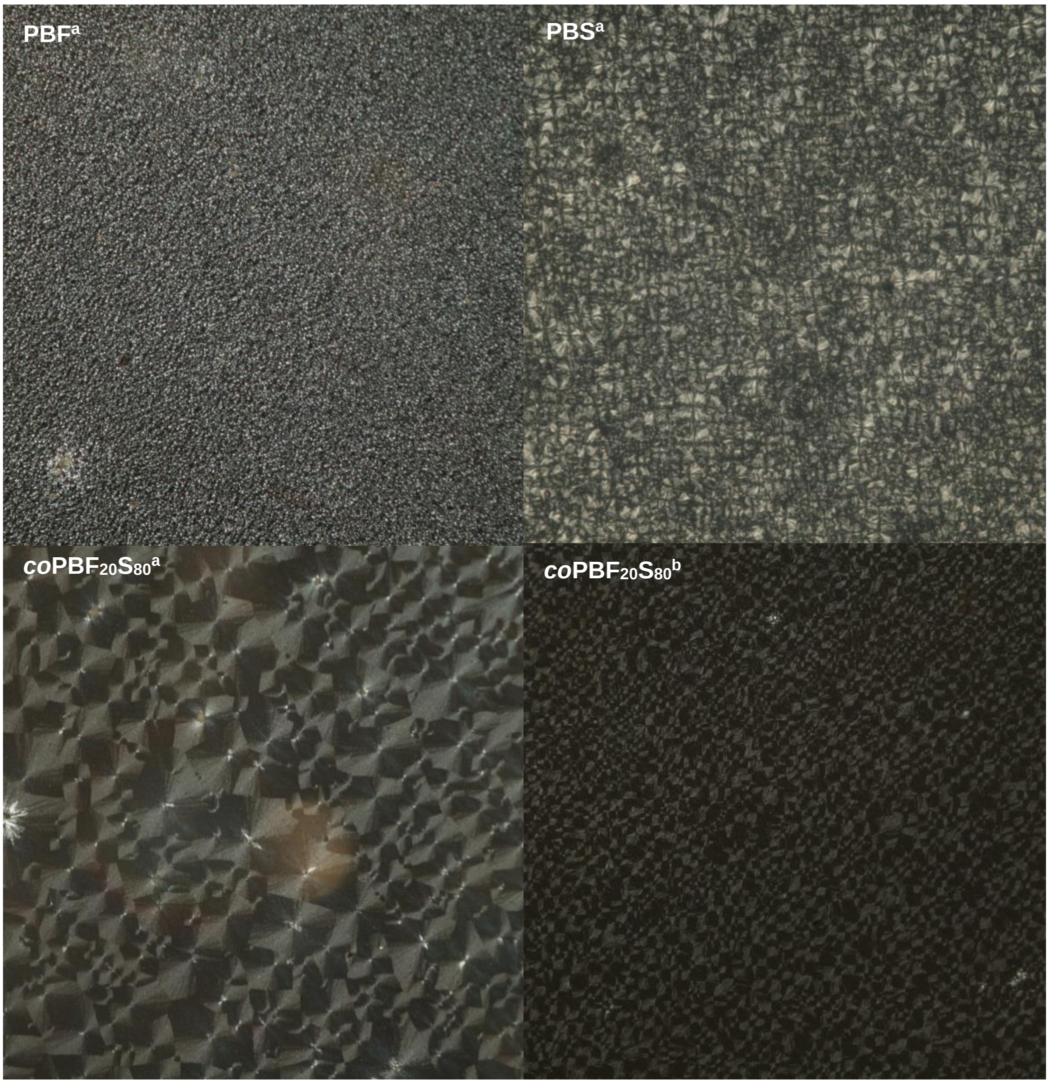


Figure C.1.7. POM of polyesters crystallized. a) Sn(Oct)$_2$ b) CALB used as catalyst.

C2. Support information of subchapter VI.2

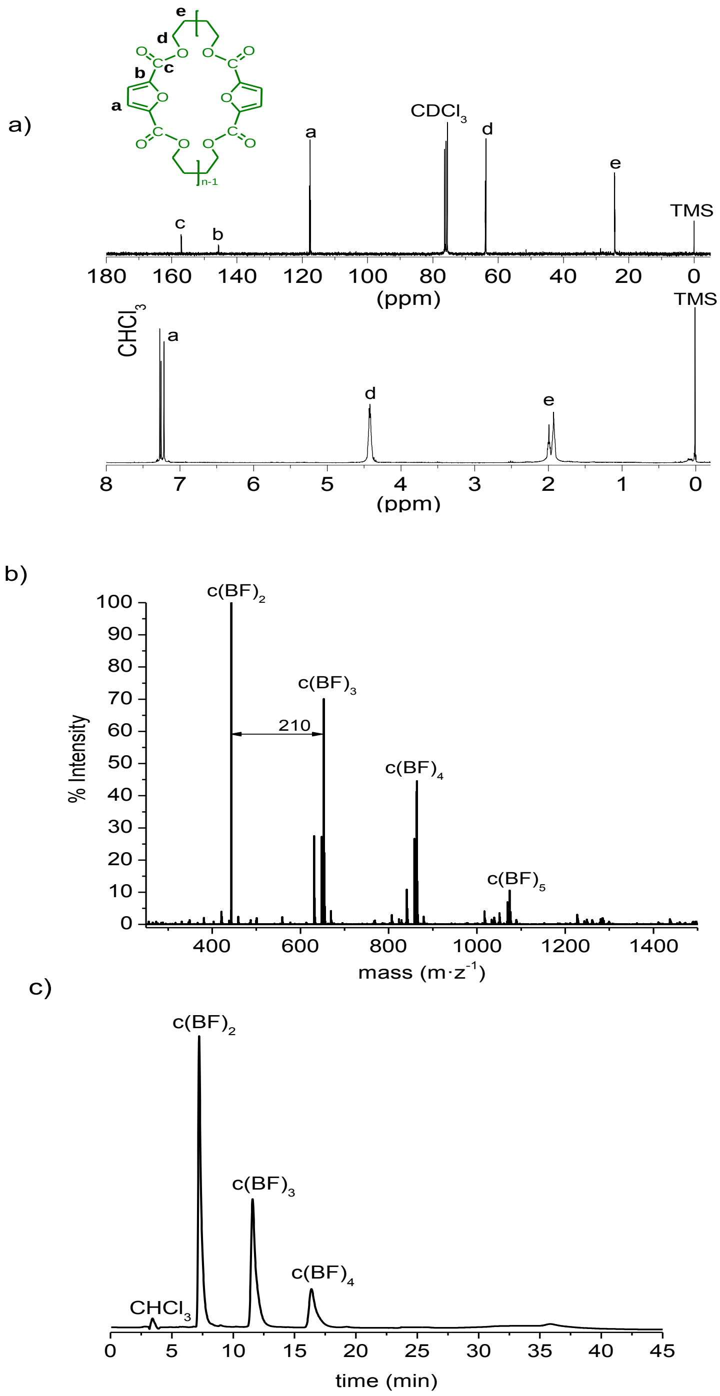


Figure C.2.1. a) ^{13}C (top), ^{1}H NMR (bottom) , b) HPLC and c) MALDI-TOF spectra for *c*(BF)$_n$.

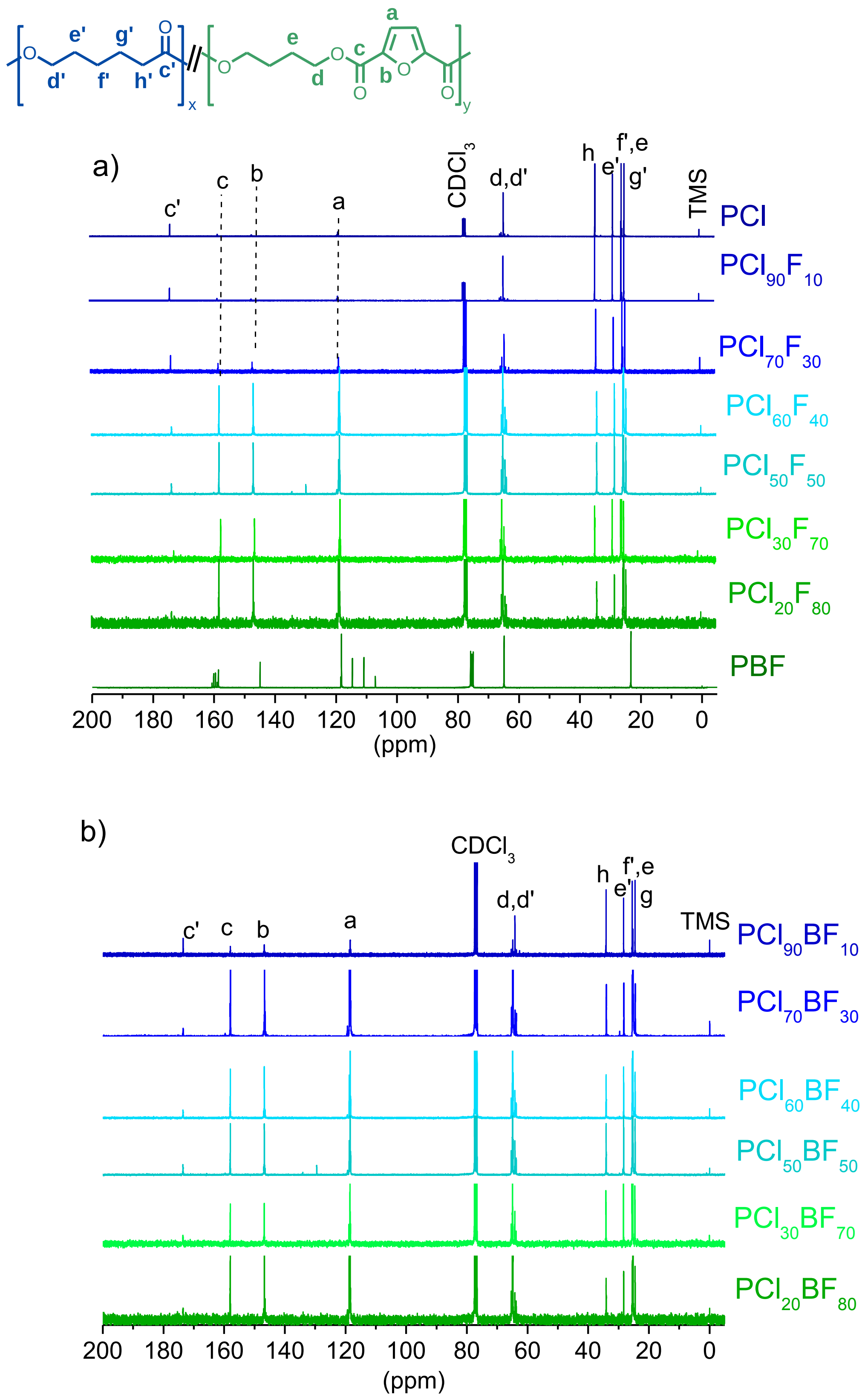


Figure C.2.2. ^{13}C NMR of PBF, PCL and PCL$_x$BF$_y$ copolyesters a) before and b) after transesterification.

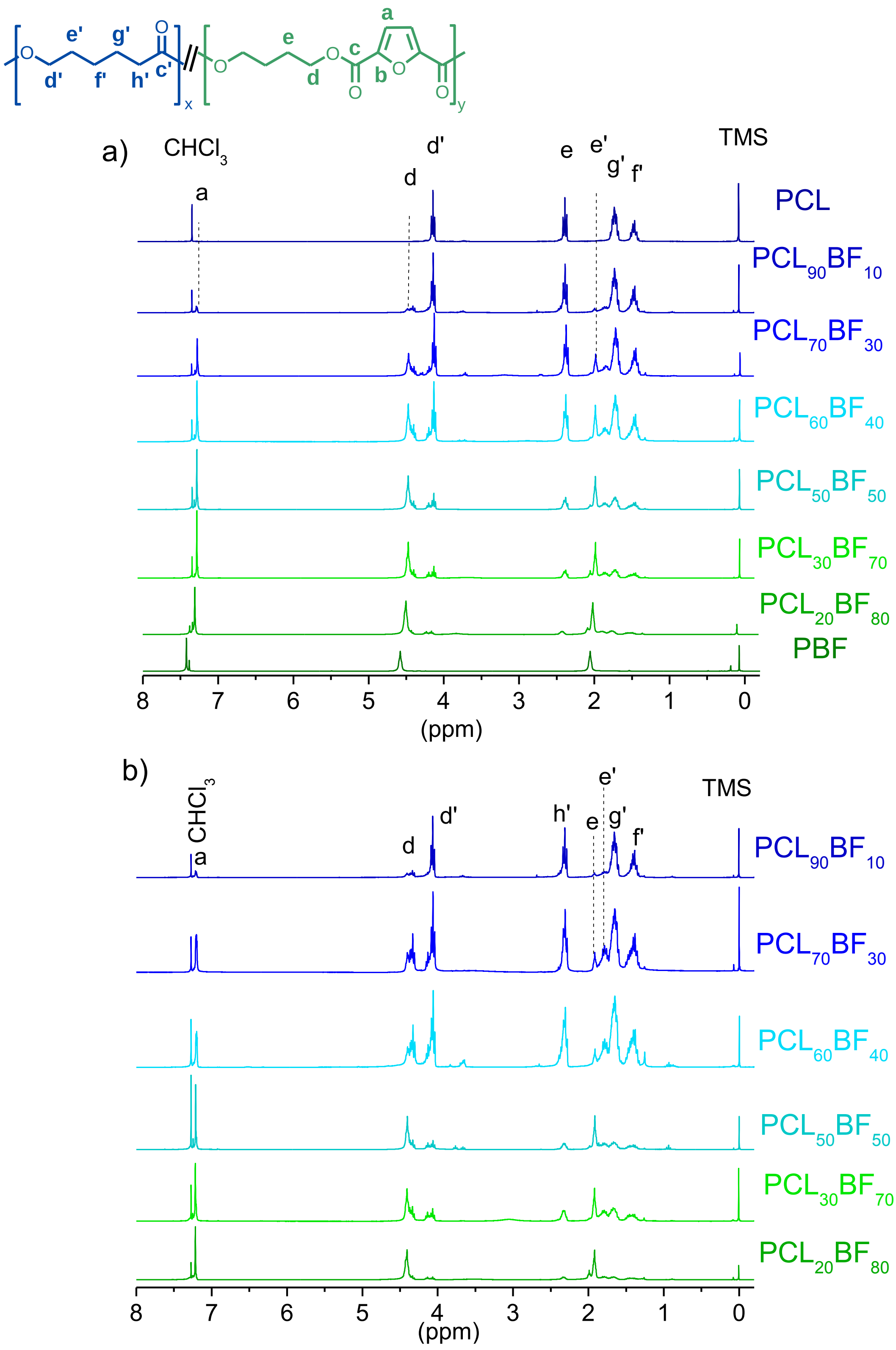


Figure C.2.3. ^{1}H NMR of PBF, PCL and PCL$_x$BF$_y$ copolyesters a) before and b) after transesterification.

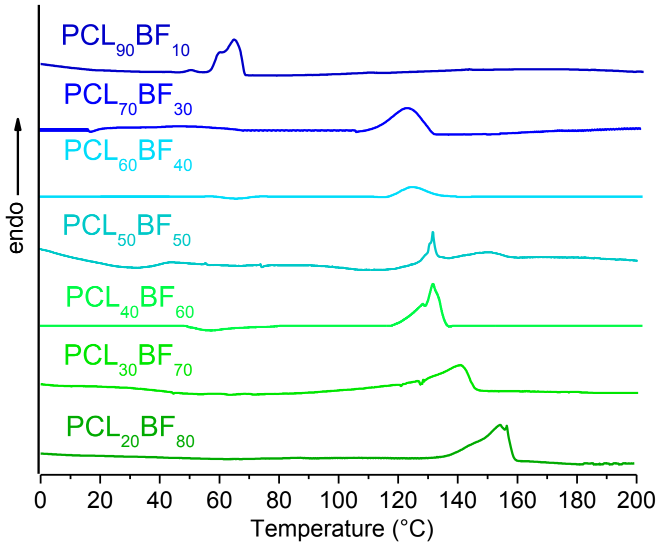


Figure C.2.4. a) DSC traces of analysis of PCL_xBF_y copolyesters after transesterification.

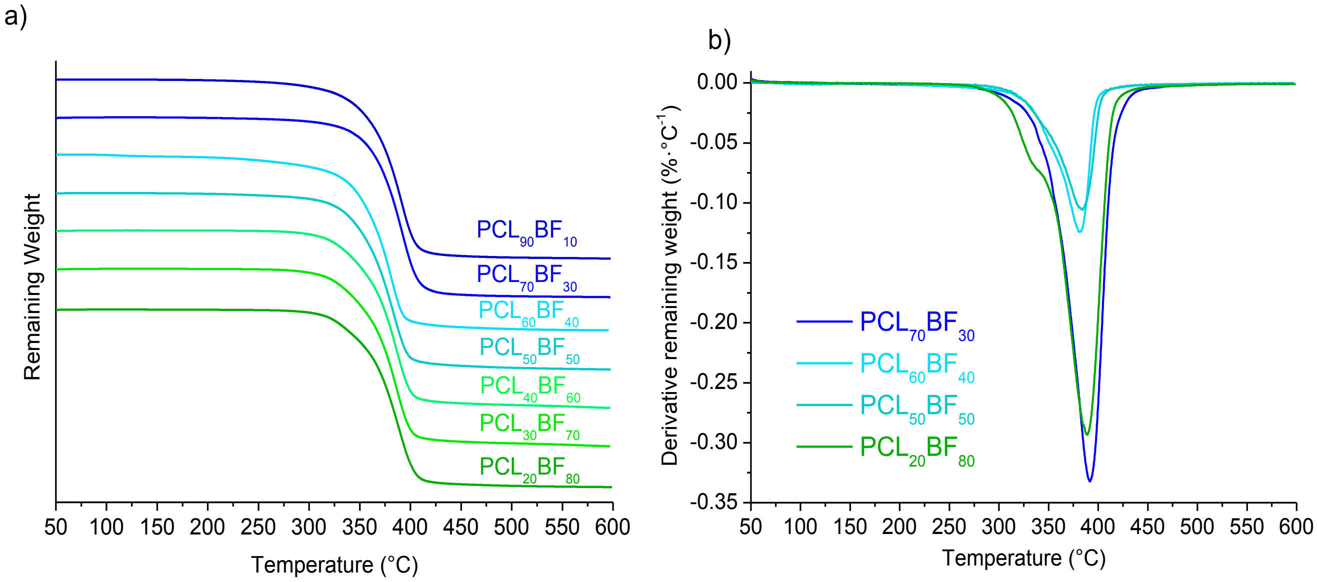


Figure C.2.5. TGA traces of PCL_xBF_y after transesterification a) and TGA derivative curves of a representative selection of them.

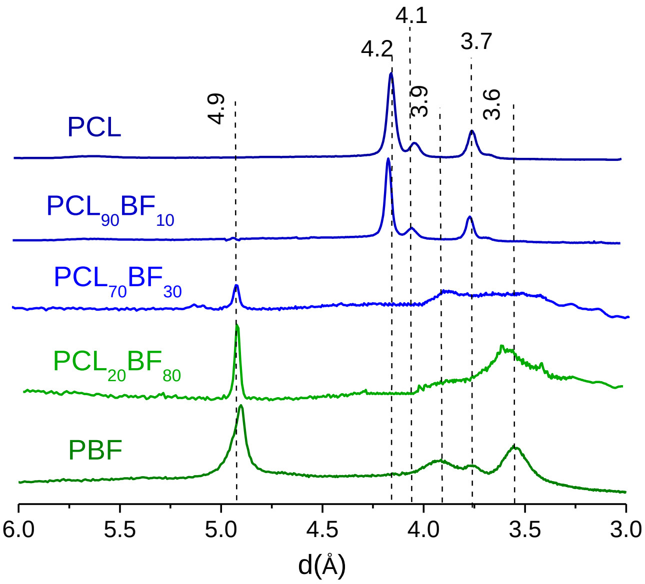


Figure C.2.6. Powder XRD profiles of PCL_xBF_y copolyesters as prepared..

Figure C.2.7.. POM micrographs recorded from films of the indicated polyesters at different temperatures.

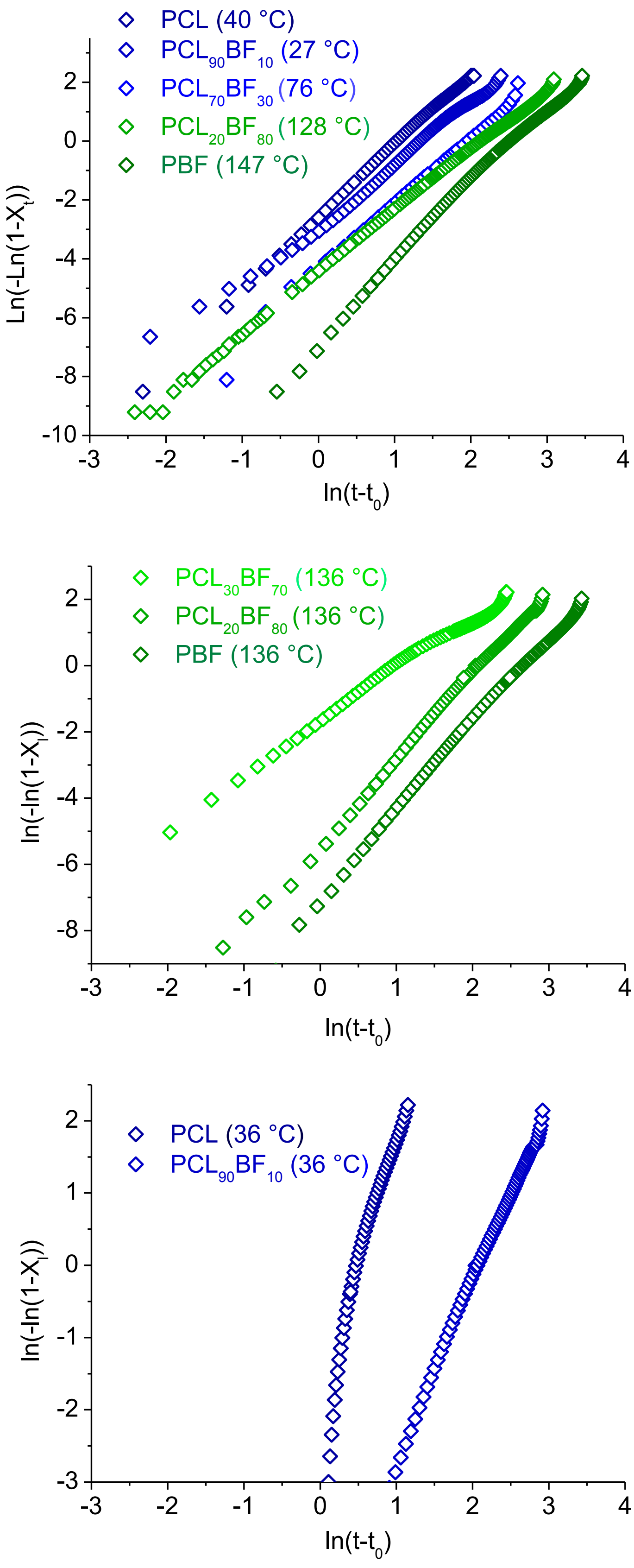


Figure C.2.8. Double logarithmic plots for the isothermal crystallization of PCL_xBF_y.

Table C.2.1. Compositions, yield, molecular weight, average sequence lengths and randomness of PCL$_x$BF$_y$ (top: before, bottom: after transesterification).

Feed composition PCL/PBF	Yield (%)	Composition[a]		Molecular weight[b]		a[c]	Number average length[d]		Degree of randomness (*B*)[e]
		x_{CL}	x_{BF}	M_w (g·mol^{-1})	Đ		n_{CL}	n_{BF}	
100	95	-	-	35,000	1.80	-	-	-	-
90/10	65	86.2	13.8	39,000	2.00	0.72	3.57	11.15	0.32
		86.8	13.2	37,000	2.10	0.50	2.00	6.57	0.50
70/30	80	72.9	27.1	48,000	1.80	0.84	6.25	8.40	0.28
		72.2	27.8	42,000	1.73	0.60	2.50	3.24	0.56
60/40	90	66.8	33.2	50,000	1.72	0.82	5.55	5.59	0.50
		70.7	29.3	45,256	1.85	0.45	1.81	2.19	0.55
50/50	90	41.5	58.5	50,000	1.60	0.88	8.33	2.95	0.43
		37.9	62.1	44,000	1.70	0.77	4.34	1.33	0.66
40/60	89	36.2	63.8	47,000	1.65	0.90	10	2.83	0.44
	-.	-	-	-.	-	-	-.	-.	-
30/70	91	33.1	66.9	36,000	1.25	0.90	10	2.47	0.50
		42.2	57.9	32,000	1.20	0.76	4.16	1.51	0.70
20/80	90	18.0	82.0	22,000	1.25	0.95	20	2.19	0.51
		17.8	82.2	18,000	1.40	0.92	12.5	1.35	0.59
0/100	95	-	-	65,000	1.97	-	-	-	-

[a] Composition of the copolymer obtained from ^{1}H NMR. [b] Determined by GPC. [c] Auxiliary variable for the calculation of number average length and degree of randomness. [d] Number average length calculated by integration of signal due to CL that appears at 24.6 ppm in ^{13}C NMR split into four peaks and using equations proposed by Tessier and Fradet [e] Degree of randomness determined by integration of signal due to CL that appears at 24.6 ppm split into four peaks and using equations proposed by Tessier and Fradet in ^{13}C NMR.

Annex D:

D.1. Support information of Chapter VII.1

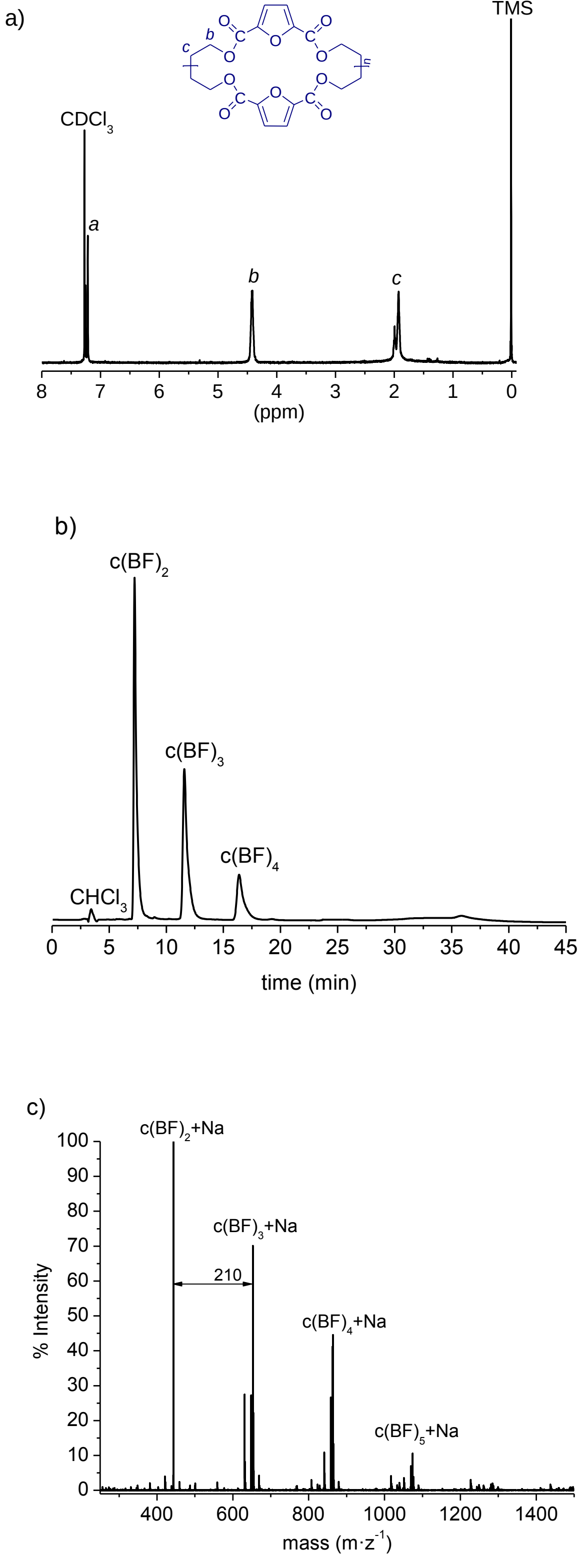


Figure D.1.1. a) ^{1}H NMR, b) HPLC and c) MALDI TOF of c(BF)$_n$.

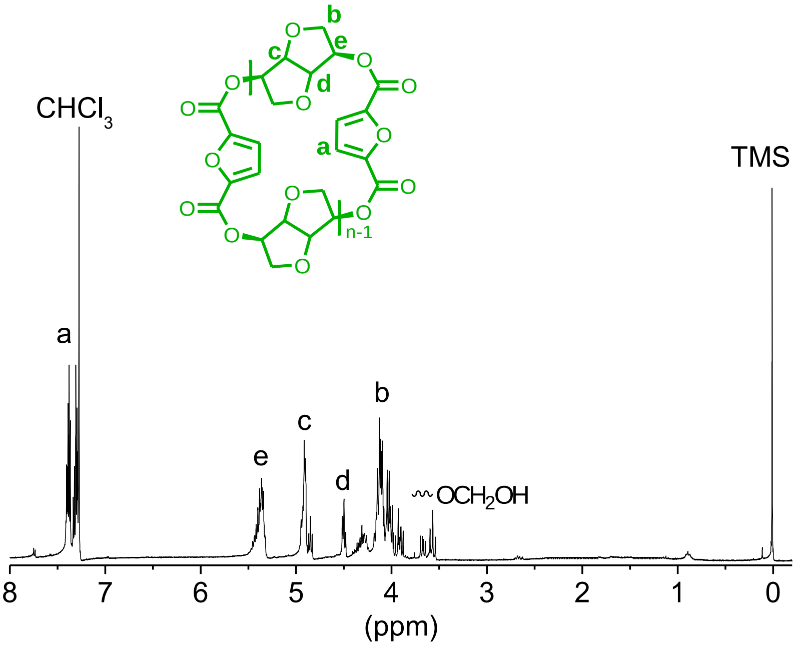


Figure D.1.2. ^{1}H NMR of crude c(ImF)$_n$.

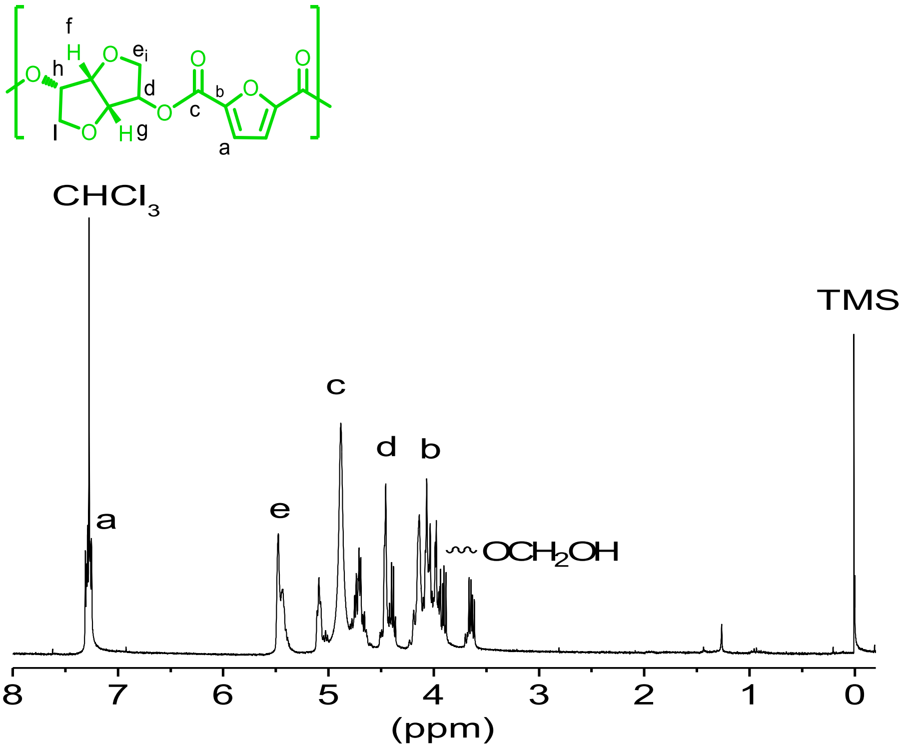


Figure D.1.3. ^{1}H NMR of linear oligomers of PIsF.

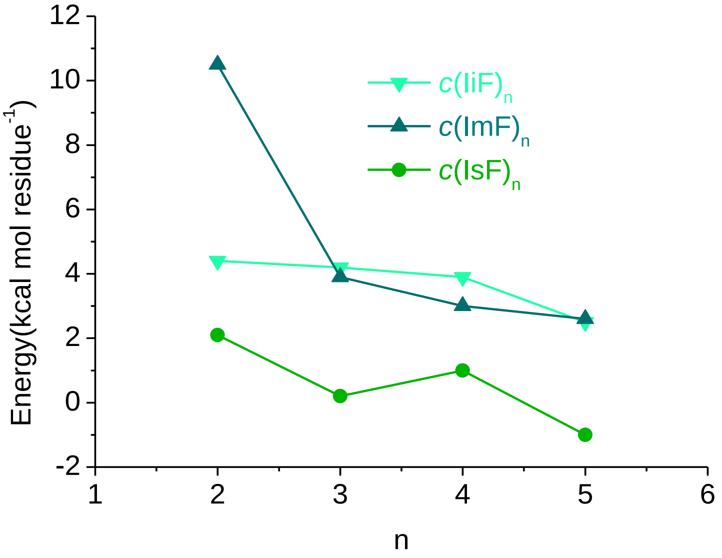


Figure D.1.4. Relative energy (kcal/mol residue) of cyclic oligo(isohexide furanoate) determined by energy minimization with application of the GROMACS forcefield and taken as reference the corresponding linear species.

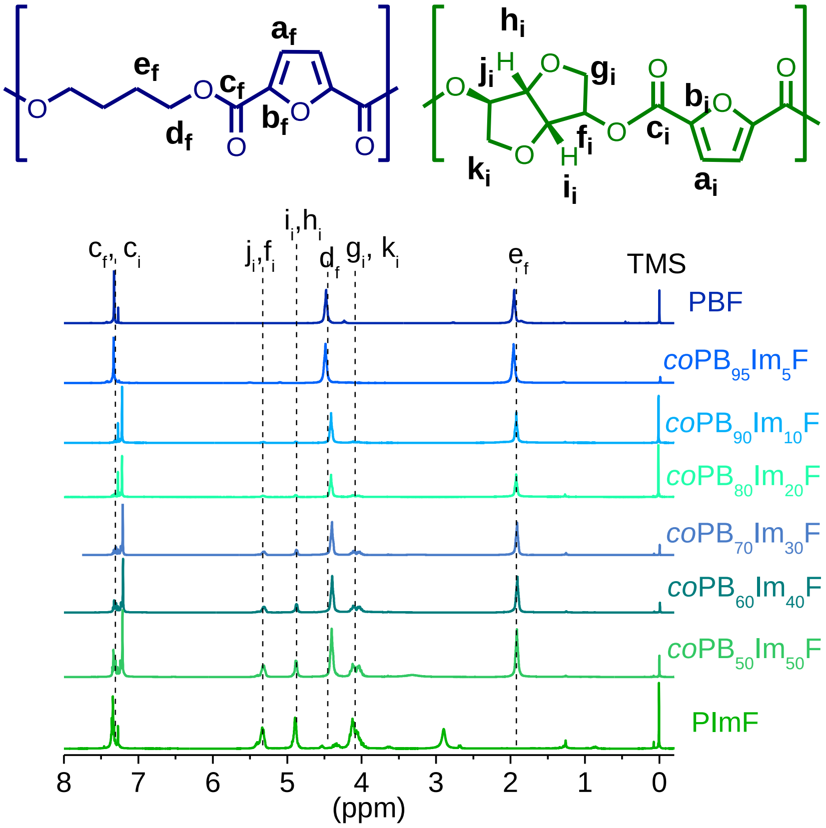


Figure D.1.5. ^{1}H NMR spectra of the whole series of coPB$_x$Im$_y$F copolyesters with indication of signal assignments.

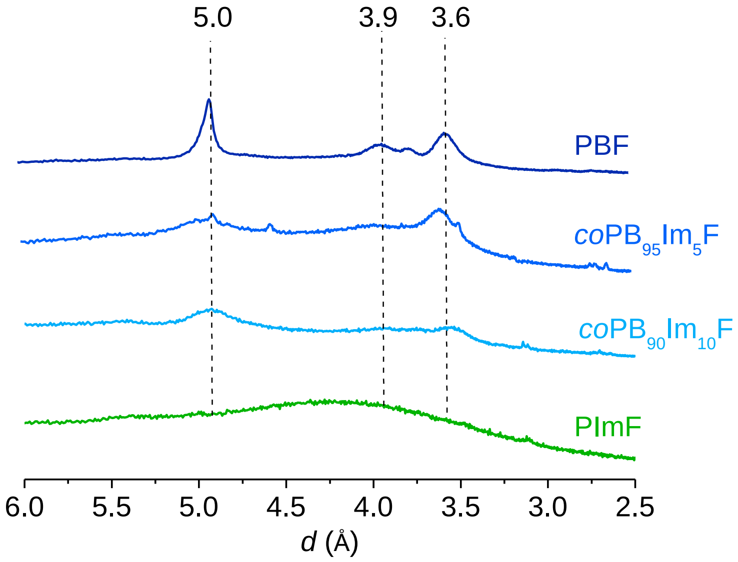


Figure D.1.6. Powder XRD profiles recorded from semicrystalline coPB$_x$Im$_y$F and the PBF and PImF homopolyesters. Spacings indicated in Å.

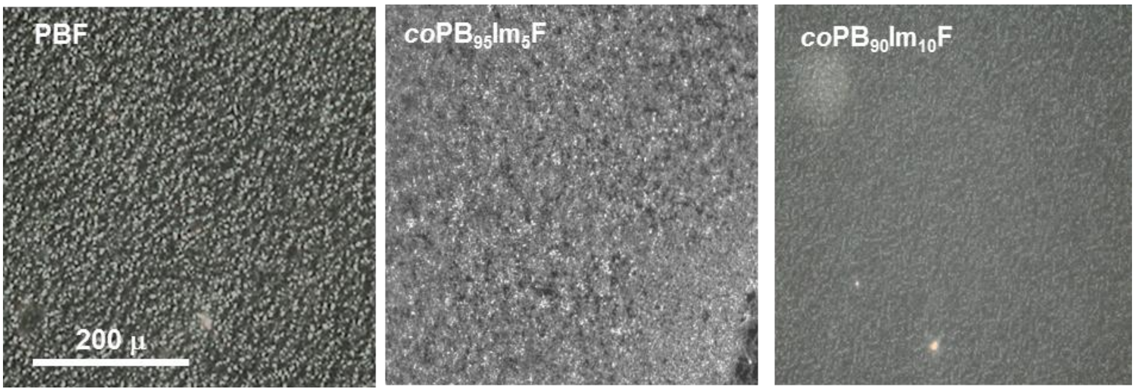


Figure D.1.7. Polarizing optical micrographs of thin films of PBF and semicrystalline *co*PB$_x$Im$_y$F.

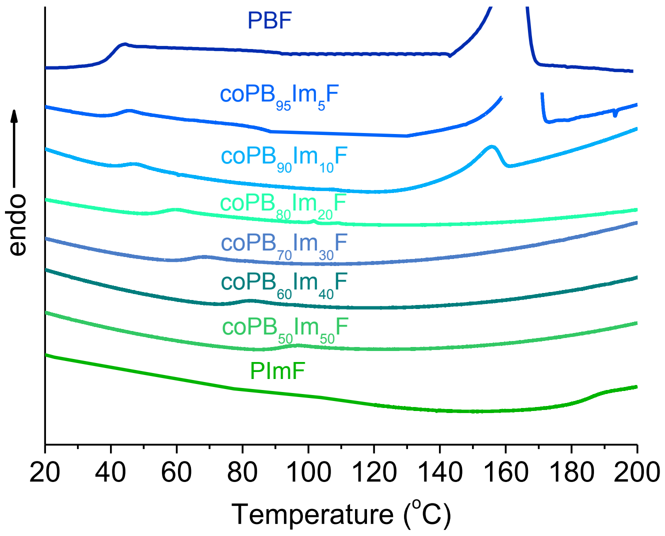


Figure D.1.8. DSC traces of PBF, PImF and *co*PB$_x$Im$_y$F copolyesters showing the inflections due to glass-transitions.

D.2. Support information of the subchapter VII.2

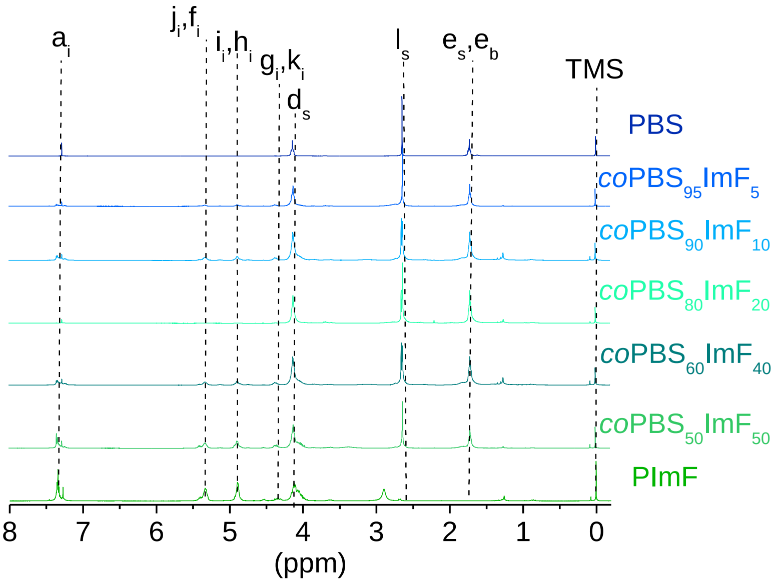


Figure D.2.1. ^{1}H NMR spectra of the whole series of coPBS$_x$ImF$_y$ copolyesters with indication of signal assignments.

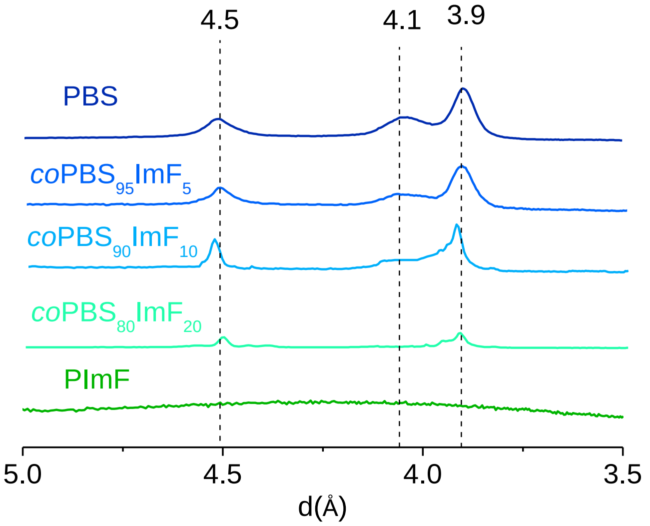


Figure D.2.2. Powder XRD profiles recorded from semicrystalline coPBS$_x$ImF$_y$ and the PBS and PImF homopolyesters. Spacings indicated in Å.

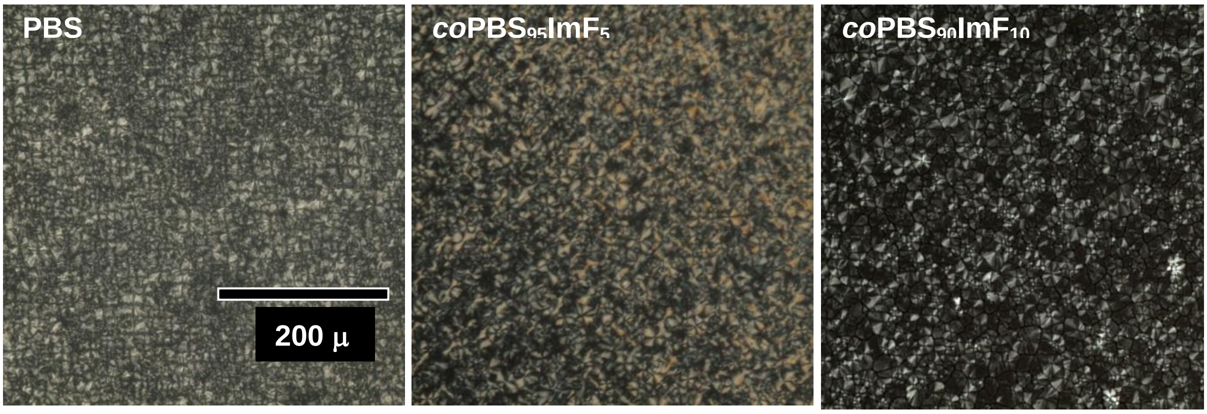


Figure D.2.3. Polarizing optical micrographs of thin films of PBS and semicrystalline *co*PBS$_x$ImF$_y$.

Annex E.

E.1 Support information of the subchapter VIII.1

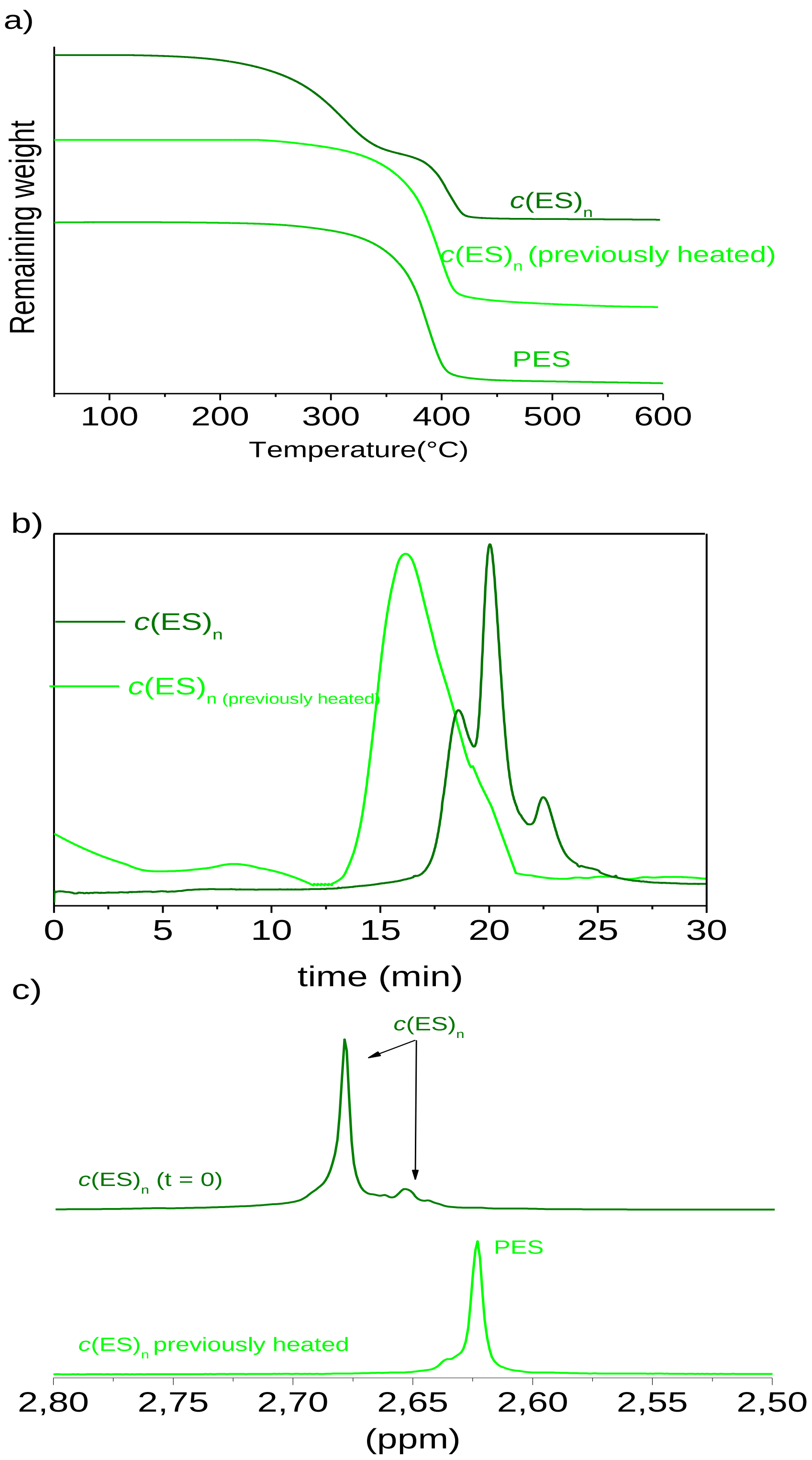


Figure E.1.1. a) TGA, b) GPC and c) ^{1}H NMR of *c*(ES)$_n$ before and after being heated up to 350 ºC. Data for PES are included for comparison.

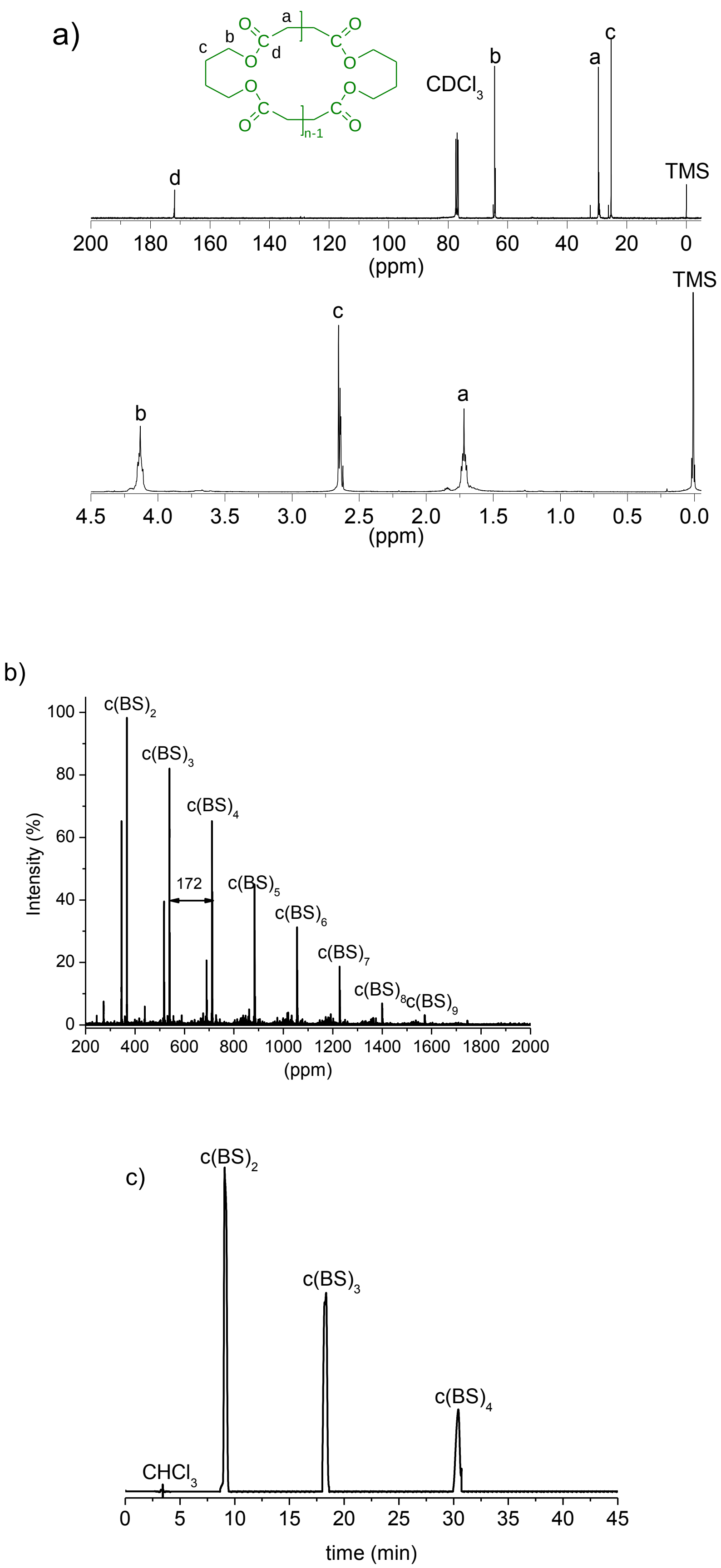


Figure E.1.2. Characterization of cyclic butylene succinate oligomers *c*(BS)$_n$. a) ^{13}C (top) and ^{1}H (bottom) NMR; b) MALDI-TOF; c) HPLC. The peak eluted at short time corresponded to chloroform used for dissolving the sample.

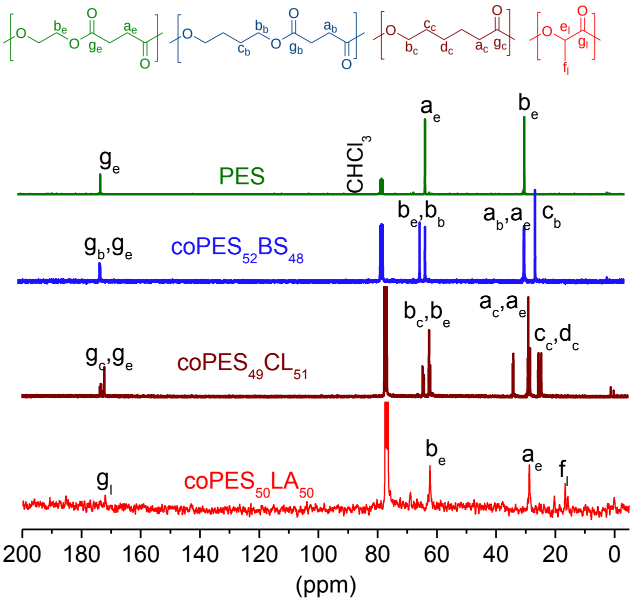


Figure E.1.3. ^{13}C NMR of PES and copolymers.

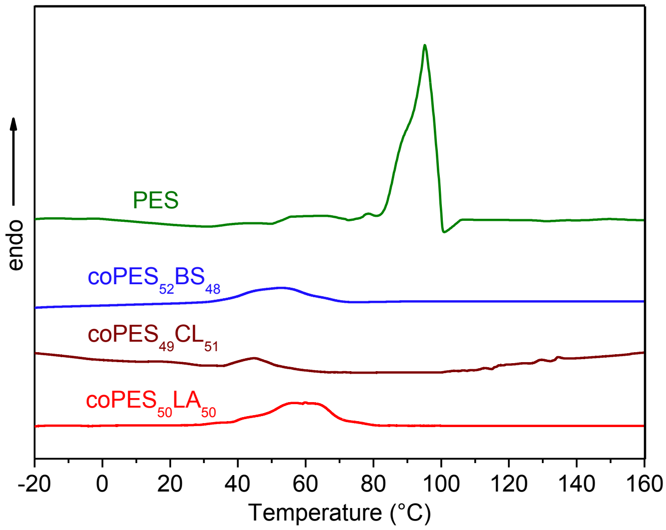


Figure E.1.4. DSC of PES and copolymers.

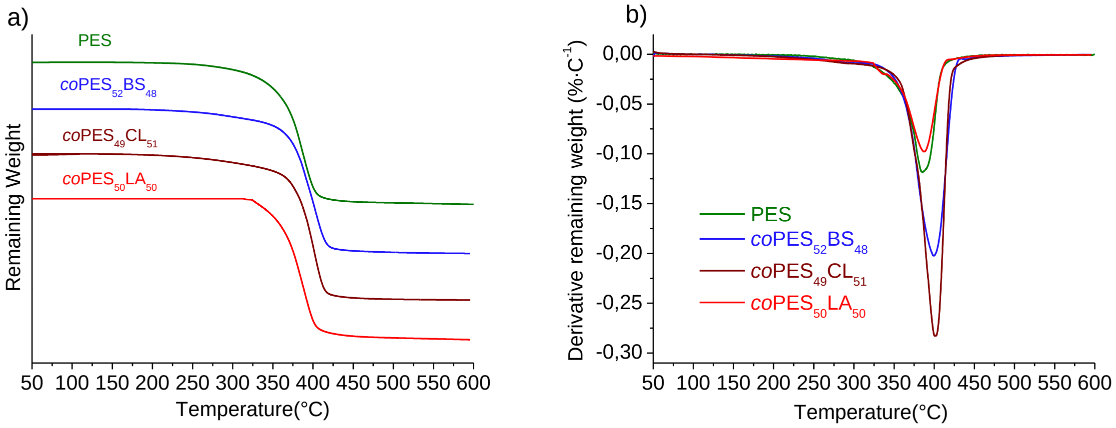


Figure E.1.5. a) TGA and b) derivative TGA of PES and copolymers.

E.2. Support information of the subchapter VIII.2

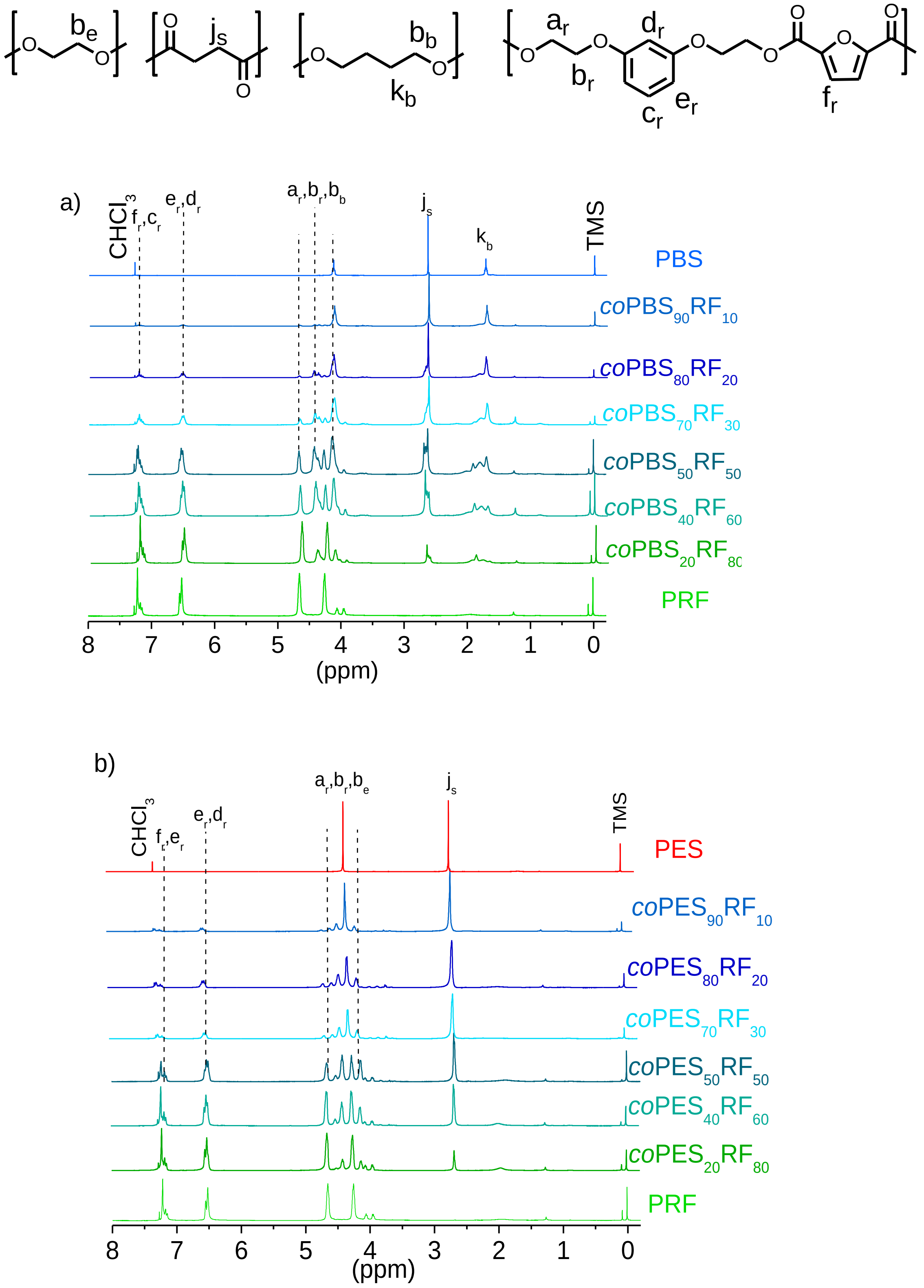


Figure E.2.1. ^{1}H NMR of *co*PBS$_x$RF$_y$ and *co*PES$_x$RF$_y$.

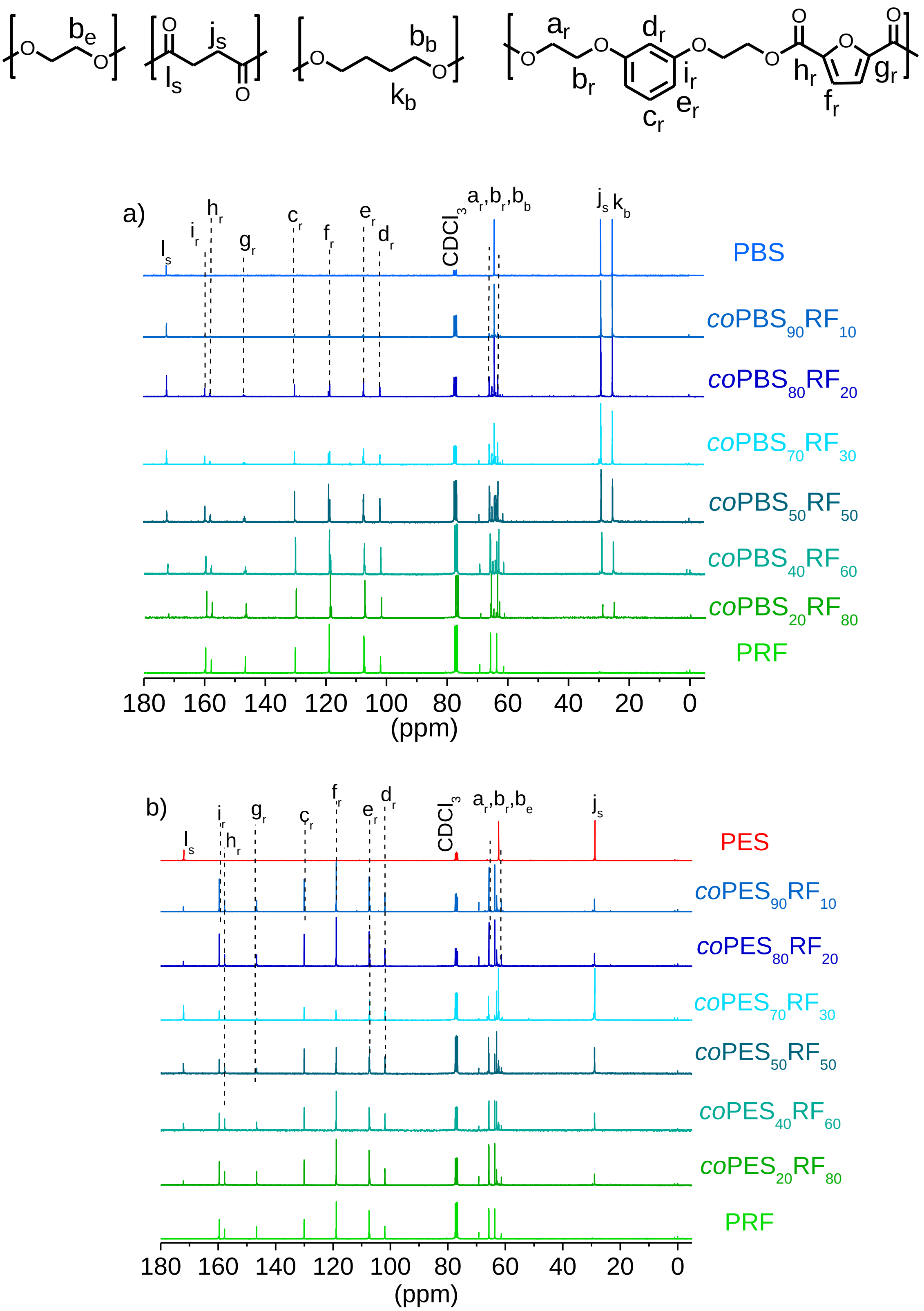


Figure E.2.2. ^{13}C NMR of *co*PBS$_x$RF$_y$ and *co*PES$_x$RF$_y$.

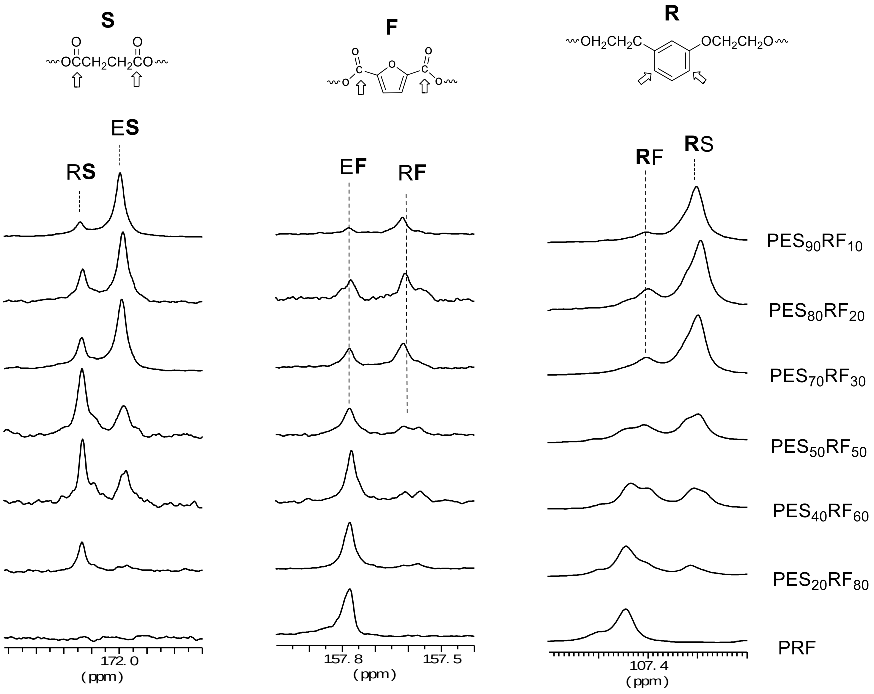


Figure E.2.3. ^{13}C NMR spectra of *co*PES$_x$RF$_y$ copolyesters in the regions of the carbonyls and aromatic carbons.

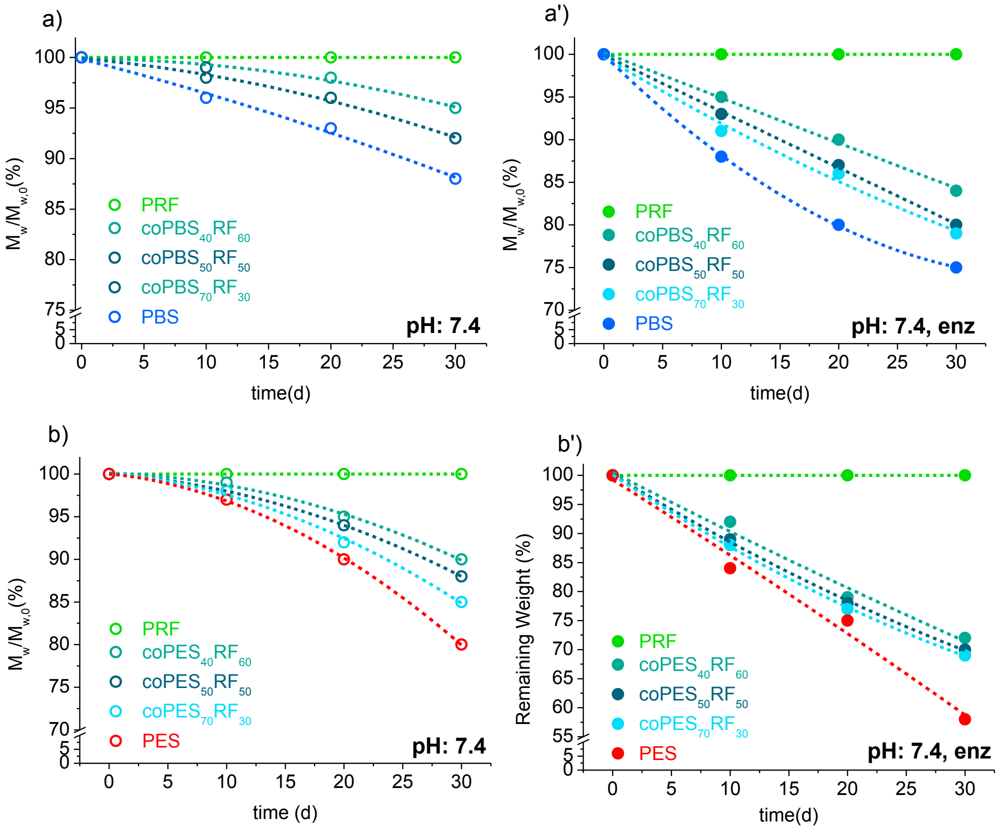


Figure E.2.4. Molecular weight reduction of resorcinol-containing copolyesters as a function of incubation time in aqueous buffer at pH 4 and 37 ºC (a and b) and under the same conditions but with lipases added to the incubation medium (a' and b').

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About the Author

Juan Carlos Morales Huerta was born on June 27, 1984 in Puebla, Mexico. In 2006, he obtained his bachelor degree in Chemical Engineering by the Universidad Popular Autónoma del Estado de Puebla (UPAEP). After work in the polymeric industry for two years, he decided to continue his studies focusing on biopolymers. In 2011, he obtained the master degree in Engineering in the National Autonomous University of Mexico (UNAM) working in the project BABETHANOL for the production of bioethanol from lignocellulosic materials. Afterwards, he continued working in this project for two years. In 2014, he decided to begin his Ph. D. research work in the program of Polymers and Biopolymers in the Tecnical University of Catalonia (UPC) under the supervision of Prof. Dr. Sebastián Muñoz Guerra and Dr. Antxon Martínez de Ilarduya. The results generated in his research on polyesters containing cyclic carbohydrate-based units obtained by Ring Opening Polymerization are presented in this Thesis.

Publications

i. J.C. Morales-Huerta, A. Martínez de Ilarduya, Muñoz-Guerra S., Poly(alkylene 2,5-furandicarboxylate)s (PEF and PBF) by ring opening polymerization. *Polymer* **2016**, 87, 148-158.

ii. J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra. Sustainable aromatic copolyesters via ring opening polymerization: poly(butylene 2,5-furandicarboxylate-*co*-terephthalate) *ACS Sustainable Chem. Eng.* **2016**, 4, 4965-4973. **(ACS Editor's Choice: September 2016)**.

iii. J.C. Morales-Huerta, C.B. Ciulik, A. Martínez de Ilarduya, S. Muñoz-Guerra. Fully bio-based aromatic-aliphatic copolyesters: poly(butylene furandicarboxylate-*co*-succinate)s obtained by ring opening polymerization. *Polym. Chem.* **2017**, 8, 748-760.

iv. J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra. A green strategy for the synthesis of poly(ethylene succinate) and its copolyesters via enzymatic ring opening polymerization. *Eur. Polym. J.* **2017**, 97, 514-519.

v. J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra. Blocky poly(epsilon-caprolactone-*co*-butylene 2,5-furandicarboxylate) copolyesters via enzymatic ring opening polymerization. *J. App. Polym. Sci. Polym. Chem.* **2018**, 56, 290-299.

vi. J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra. Polyesters of alkylene succinate copolymerized with resorcinol-2,5-furandicarboxylate by ring opening polymerization. *Polymers* **2017**, 9, 701.

vii. J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra. Poly(butylene 2,5-furandicarboxylate-*co*-isophthalate). *Polymers* **2018** to be submitted**.**

viii. J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra. Isomannide-containing poly(butylene 2,5-furandicarboxylate) copolyesters via ring opening polymerization. *Macromolecules* **2018**, to be submitted**.**

ix. J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra. Fully bio-based PBS copolyesters with high Tg: ring opening copolymerization of cyclic (butylene succinate) and (isomannide furanoate) oligomers *ACS. Sustainable. Chem. Eng* 2018, to be submitted**.**

Communications:

a) J. C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra. Macrocyclic Oligoesters of 2,5-furan dicarboxylic acid for Ring Opening Polymerization. **1st French-Spanish Joint Congress for Young Researchers in Polymers**. **2015**, Spain, Oral Communication.

b) J.C. Morales-Huerta, C.B. Ciulik, A. Martínez de Ilarduya, S. Muñoz-Guerra. Poly(butylene 2,5-furan dicarboxylate-*co*-butylene succinate) *via* Ring Opening Polymerization. **Avances en materiales poliméricos: XIV Reunión del grupo especializado de polímeros (GEP) de la RSEQ y RSEF, 2016,** Spain. Oral Communication.

c) J.C. Morales-Huerta, C.B. Ciulik, A. Martínez de Ilarduya, S. Muñoz-Guerra. Bio-based Aromatic Polyesters and Copolyesters by Ring Opening Polymerization. **Avances en materiales poliméricos: XIV Reunión del grupo especializado de polímeros (GEP) de la RSEQ y RSEF**, **2016**, Spain. Poster.

d) J.C. Morales-Huerta, C.B. Ciulik, A. Martínez de Ilarduya, S. Muñoz-Guerra. Furan-based copolyesters by ring opening polymerization. **XXXVI Reunion BIENAL de la Real Sociedad Española de Química (RSEQ), 2017,** Spain. Oral Communication.