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Cyclic derivatives of D-glucose and tartaric acid as building blocks for renewable polyesters

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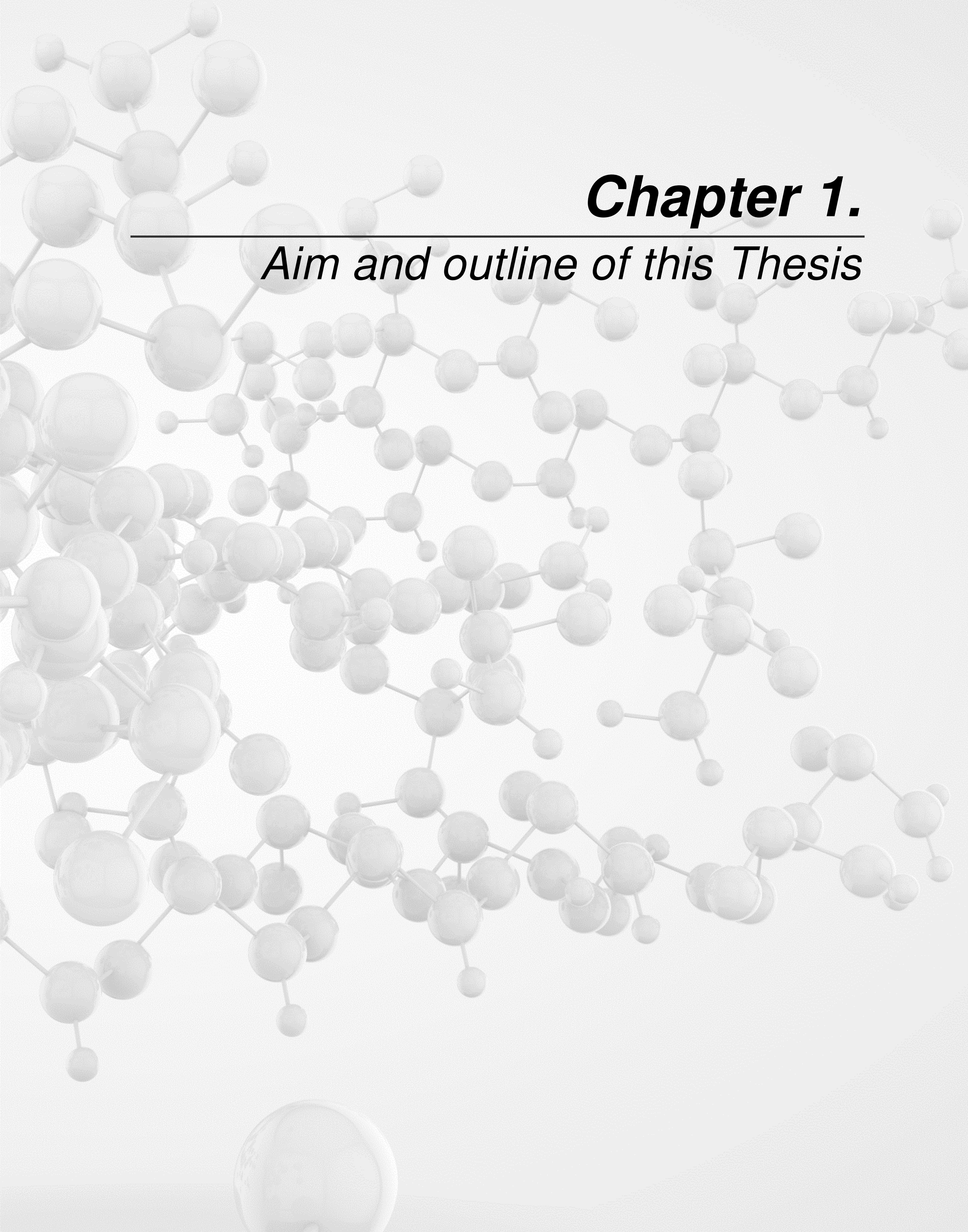
Glossary

MeOH	Methanol
M_n	Number-average molecular weight
M_w	Weight-average molecular weight
n.d.	Not determined
NMR	Nuclear magnetic resonance
PBS	Poly(butylene succinate)
PBSeb	Poly(butylene sebacate)
PCL	Poly(ε-caprolactone)
PET	Poly(ethylene terephthalate)
PHA	Polyhydroxyalkanoate
PHB	Polyhydroxybutyrate
PLA	Poly(lactic acid)
PMMA	Poly(methyl methacrylate)
POM	Polarizing optical microscopy
σ	Tensile strength
SEM	Scanning electron microscopy
SI	Supporting information
T_c	Crystallization temperature
T_d	Temperature for maximum decomposition rate (in TGA)
TFA	Trifluoroacetic acid
T_g	Glass transition temperature
TGA	Termogravimetric analysis
T_m	Melting temperature
TMS	Tetramethylsilane
ν	Wavenumber (cm^{-1})
W	Remaining final weight (in TGA)
WAXS	Wide angle X-ray scattering
XRD	X-Ray diffraction
ΔH_c	Crystallization enthalpy
ΔH_m	Melting enthalpy

Chapter 1.

Aim and outline of this Thesis



Aim and outline of this Thesis

Polymers play a prominent role as extraordinarily versatile and diversified structural and multifunctional macromolecular materials. Without polymers, modern life would be impossible because polymers assure the high quality of life with the development of modern technologies.

The growing environmental awareness over limited fossil fuel reserves (and consequently the increase of oil prices) has stimulated the search for novel polymeric materials and production processes drawn from renewable feedstocks. In addition, from the widespread use of synthetic polymeric materials has emerged another major concern; indeed, despite the increasing popularity of plastic recycling, disposal of these undegradable materials has led to serious environmental pollution. From this point of view, the continuous depletion of landfill space available for discarded plastic wastes leads to the need for biodegradable polymeric materials to be used as substitutes for non-degradable conventional plastics. Such biocompatible and biodegradable polymers are thus currently emerging as valuable alternatives to conventional synthetic (petroleum-based) polymers and might be produced from raw materials. Although this renewed interest in polymers from renewable resources has gained wings recently, this whole idea is not new. Indeed, the advent of bio-based polymeric materials is entangled with the birth of macromolecular science and technology in the 19th century with the synthesis of some very well-known materials such as celluloid, vulcanized natural rubber or even nylon-6,6.

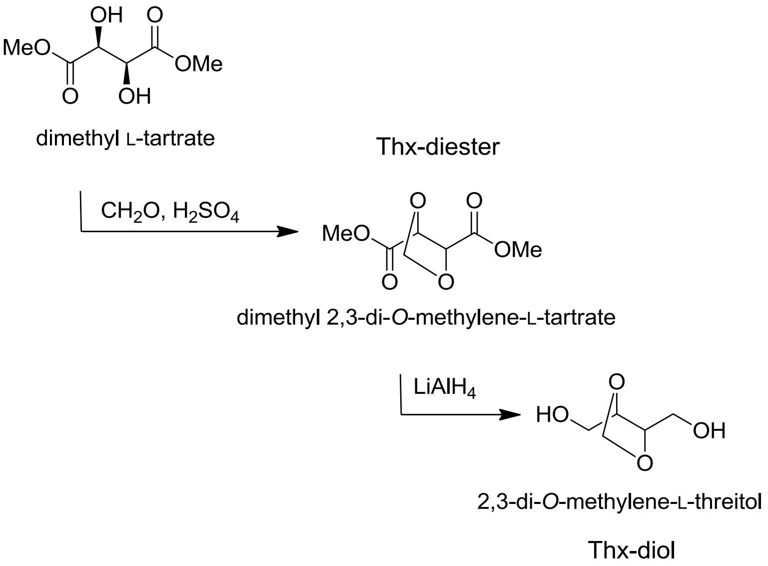
At the beginning of the 21st Century, we are experiencing a renaissance of renewable polymers and a major thrust towards the development of bio-based macromolecular materials. Actually, the production of bio-plastics (partially or totally bio-based, biodegradable or both) is already a growing niche market that has increased from less than 300 000 metric tons in 2009 to surpass 1.0 million metric tons in 2011 and with a forecast of 5.8 million metric tons for 2016. Fermentation of glucose, obtained from lignocelluloses and starch, can be used to produce a great variety of bio-based monomers. For example, bioethanol is readily converted into ethylene, propylene, and also butadiene that can be used to synthesize bio-based polyolefins and butadiene rubber. Also available are diols, polyols, diacids, hydroxyalkanoic acids, aminoalkanoic acids, and diamines that can be used in melt polycondensation reactions to produce bio-based polyesters, polyamides, polycarbonates, as well as thermoset resins such as unsaturated polyesters and air-drying finishes. Starting from glucose, it is possible to obtain sorbitol, isosorbide (Is), and also a large variety of furans, most of which are not natural products. Furan derivatives offer attractive opportunities for preparing bio-based thermoset and thermoplastic resins from furfuryl alcohol, furfuryl aldehyde, hydroxymethyl furfuryl aldehyde, and 2,5-furandicarboxylic acid (FDCA). Side-products of biofuel production, such as glycerol, are also attractive bioresources for producing bio-based monomers such as acrylic acids, epichlorohydrine, 1,3-propanediol, and acrolein.

The synthesis of polyesters and copolyesters made from monomers obtained by chemical modification of naturally-occurring compounds may lead to renewable polyesters with improved properties regarding to those displayed by the traditional ones. Carbohydrates are suitable resources to provide bio-based building block monomers useful for polycondensation. For example FDCA appears to be an excellent replacement for terephthalic acid in the production of aromatic polyesters. Another example is the incorporation of rigid diols such as isosorbide in polyesters was shown to increase glass transition temperature (T_g), allowing new high-temperature applications for such polymers. Isosorbide, isoidide and isomannide belong to 1,4:3,6-dianhydrohexitols, a family of stereoisometric bicyclic secondary diols. A major drawback for isohexides as polymer building blocks is the relatively poor reactivity of the secondary hydroxyl groups used for the polymerization reaction, which often results in low molecular weights and undesirable colored polymers. Cyclic acetalized alditols and aldaric acids prepared from C4, C5 and C6 sugars are being currently explored as an attractive option for the preparation of bio-based polyesters with enhanced T_g. These bulky and stiff monomers tend to restrict the chain mobility by reducing the free volume and increasing the T_g which is necessary in applications related with hot-filling packaging. Also, it is important to mention that these monomers have primary hydroxyl groups that confer major reactivity comparing to isosorbide.

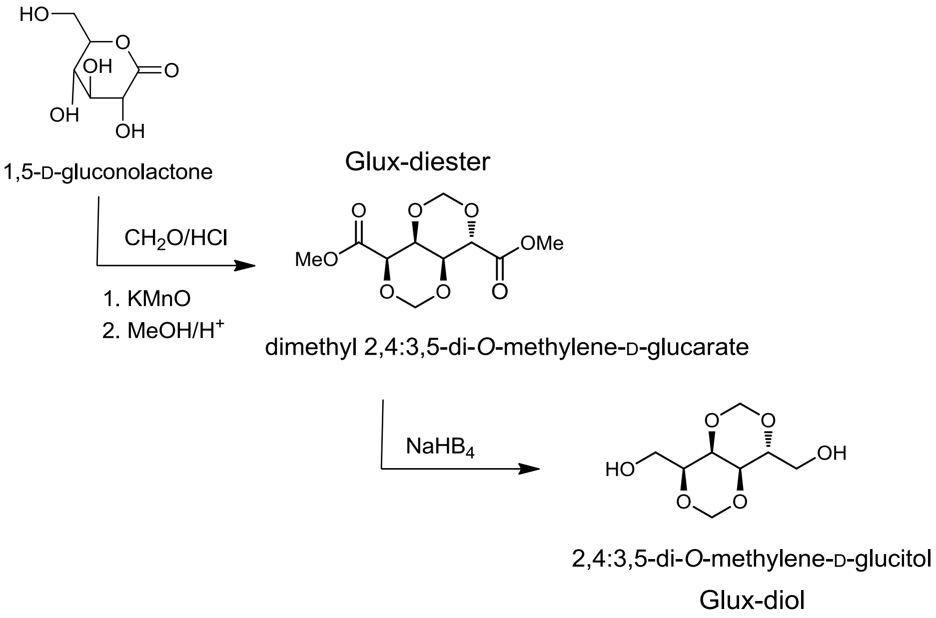
An alditol is an aldose derivative which has the carbonyl group reduced to hydroxyl group. The protection of the secondary hydroxyl groups, leaving the two primary hydroxyl groups free for reaction, allows the use of alditols as monomers for the synthesis of linear polyesters by reaction with dicarboxylic acids. On the other hand, an aldaric acid is an aldose derivative which has both the primary hydroxyl and the carbonyl groups oxidized to carboxylic groups. The protection of all the secondary hydroxyl groups makes the aldaric acid suitable as monomers to obtain linear polyesters by reaction with diols. In this work, the secondary hydroxyl groups of are protected as methylene acetals, leading to carbohydrate-based compounds with a monocyclic or bicyclic structure.

The aim of this Thesis was to prepare renewable polyesters with better thermal properties and with enhanced hydro- and biodegradability. The strategy followed was the insertion in the polyester chain of monocyclic and fused bicyclic building blocks monomers derivatives of tartaric acid and D-glucose by polycondensation. The final objective is to deeper insight the structure-properties relationship of theses polymers and to explore their potential as new materials.

A brief description of the preparation of the four cyclic carbohydrate monomers used in Thesis is depicted in Scheme 1 and 2 and detailed in Chapter 3-6.



Scheme 1. Synthesis of 2,3-*O*-methylene-L-threitol (Thx-diol) and dimethyl 2,3-*O*-methylene-L-tartrate (Thx-diester) from commercially available dimethyl L-tartrate.

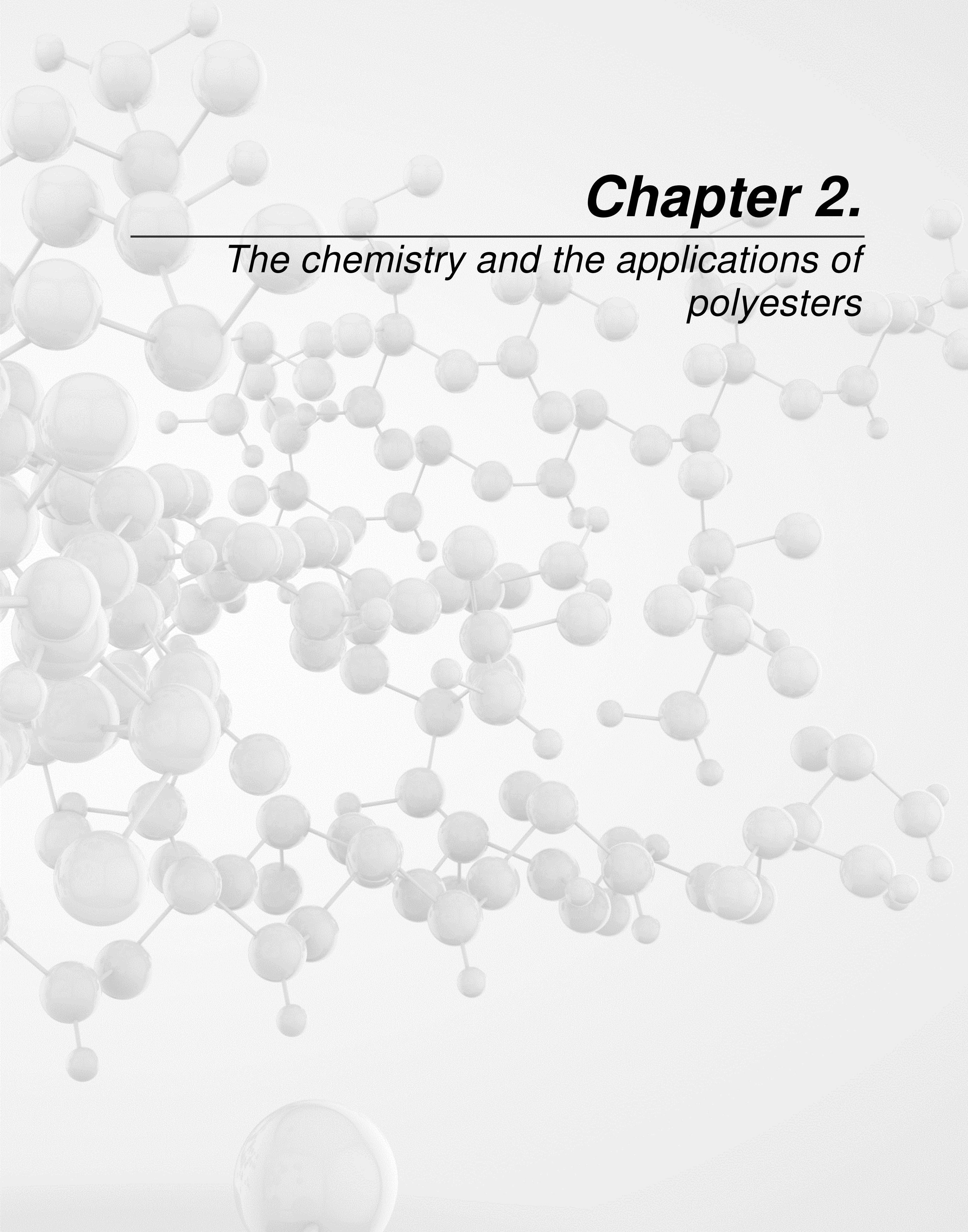


Scheme 2. Synthesis of 2,4:3,5-di-*O*-methylene-D-glucitol (Glux-diol) and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester) from commercially available D-glucolactone.

The monocyclic pair of monomers used in this Thesis are 2,3-*O*-methylene L-threitol (Thx-diol) and dimethyl 2,3-*O*-methylene L-threarate (Thx-diester). Their structure consists in a C4-segment backbone forming part of 1,3-dioxolane ring and bearing the two hydroxyl or methoxycarbonyl functions at the end positions. In turn, the other pair of monomers used in this Thesis, is formed by 2,4:3,5-di-*O*-methylene-D-glucitol (Glux-diol) and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester), wich have a bicyclic asymmetric structure consisting of a C6-segment backbone forming part of the two fused 1,3-dioxane rings and bearing the two hydroxyl or methoxycarbonyl functions at the end positions.

Chapter 2.

The chemistry and the applications of polyesters



2.1. Introduction

Historical background

Natural polyesters have been known since ancient times. Shellac, a natural polyester secreted by the lac insect, was used by the ancient Egyptians for embalming mummies.

Polyesters were initially developed for coating applications and are commonly known as 'alkyd resins'. The term 'alkyd' was coined by combining the first part of the word 'alcohol' and the last part of the word 'acid'. Alkyd resin was first marketed by the General Electric Co. of the USA, with the trade name of Glyptal®, which has become an alternative name to alkyd resin[1]. Glyptals were essentially produced by extended condensation reactions involving glycerol, phthalic anhydride and the fatty acids of various oils such as linseed oil, soya bean oil, dehydrated castor oil and tung oil. These resins, readily soluble in aromatic or aliphatic hydrocarbons, are still widely used in coatings, varnishes, and paints.

Earlier reports of this type of polyester include those from Berzelius (1847),[2] who reported a resin from tartaric acid and glycerol, Berthelot (1853),[3] who obtained a resin from glycerol and camphoric acid (*cis*-1,2,2-trimethyl-1,3-cyclopentane-dicarboxylic acid), and Van Bemmelen (1856),[4] who made glycerides of succinic acid and citric acid.

In 1930 the synthesis of polyesters knew a new era named as "the modern history of polyesters" when Carothers proved the macromolecular theory of Staudinger by carrying out experimental studies on reactions between aliphatic dibasic acids and diols. At that point was established the relationships between degree of polymerization, conversion, functionality, and gel point, that is, the base relationships of step-growth polymerization.**[5-7]** The polyesters made by Carothers and his team were not suitable for commercial applications because they had low melting points and were sensitive to hydrolysis. Carothers turned to other classes of polymer, including, polyamides, which he had previously briefly explored with Hill without any success. This work led to nylon fibers, first with Coffman, to nylon 9, then with Peterson, to nylon 5,10, and then, early in 1935, with Berchet, to nylon 6,6.**[8]**

To increase the polyester melting point and to approach the thermo-mechanical properties obtained with nylons, it was necessary to stiffen the polyester chain by using rigid aromatic monomers instead of flexible aliphatic ones. This was realized in the early 1940s in the laboratories of the Calico Printers Association in the United Kingdom when Whinfield in collaboration with Dickson synthesized high-melting-point fiber-forming polyesters from terephthalic acid and aliphatic diols.[9,10]

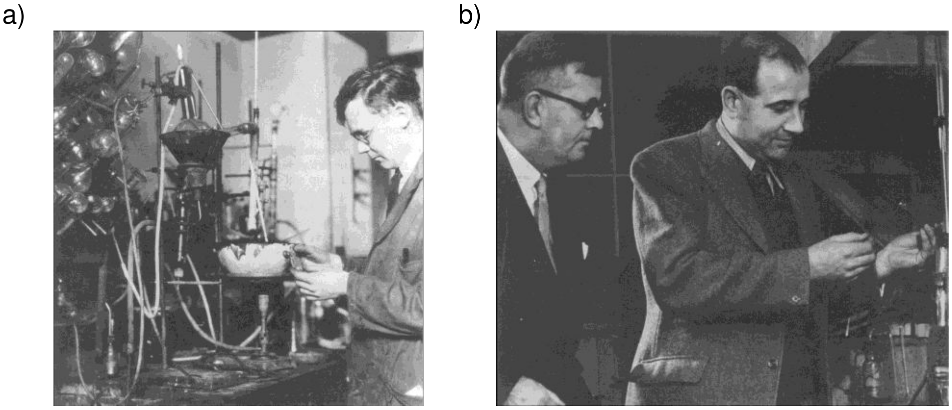


Figure 1. a) Wallace H. Carothers; b) J. R. Whinfield (left) and J. T. Dickson (right) reenact the discovery of fibre-forming poly(ethylene terephthalate).

After the second World War the patent rights on these aliphatic-aromatic polyesters were shared between I.C.I. and DuPont, and several members of this family became-and are still today-major commercial polymers. Poly(ethylene terephthalate) (PET) is now one of the most produced polymers, mainly for textile and packaging applications. Poly(butylene terephthalate) (PBT) finds uses as solid-state molding resin. Poly(trimethylene terephthalate) (PTT), though described in Whinfield's original patent, is a newcomer in the commercial polyester family and has found its first applications in the textile industry.

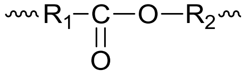
At the end of the 1930s, a new type of thermosetting resin was developed, based on unsaturated polyesters.[11] Unsaturated polyesters are synthesized by reacting mixtures of saturated and unsaturated dibasic acids or anhydrides with aliphatic 1,2-diols. After commercial production of maleic anhydride by catalytic oxidation of benzene began in 1933, maleic anhydride and fumaric acid rapidly became the most important sources of unsaturated monomers in polyesters. The thermosetting resin is obtained by dissolving this linear polyester in an unsaturated monomer, such as styrene, capable of undergoing free-radical copolymerization with the unsaturations in polyester chains. The liquid resin is transformed into a rigid, insoluble, and infusible crosslinked polymer network after radical polymerization in the presence of heat or catalysts. Unsaturated polyester (UP) resins found their first applications in combination with glass fibers for protective radar domes during World War II,[12] but the technology was widely commercially available only in the mid-1950s. UPs are now one of the most important matrix resins for glass-fiber-reinforced composite materials.

Between the late 1950s and the 1960s it was commercialized for the first time aliphatic polyesters with low molecular weight for the synthesis of polyurethane foams and elastomers. In the 1970s DuPont produced the polyesterether block copolymers under the trade name *Hytrel* that displayed characteristics of thermoplastic elastomers.[13] During this period and later in the 1980s, much attention was also focused on high-performance wholly aromatic polyesters. So in the mid-1970s it was commercialized the amorphous poly(bisphenol-A isophthalate-terephthalate) by Union Carbide's Ardel.[14] In spite of relatively high cost, liquid crystalline thermotropic polyesters, such as poly(6-hydroxy-2-naphthoic acid-*co*-4-hydroxybenzoic acid) (Ticona's Vectra), described at the end of the 1970s, now find a number of applications in high-technology markets.[15]

In the 1990s the interest for environmental issues began to gain ground, recycling technology emerging as an effective answer to environmental problems associated to plastic handling. The versatility of the ester linkage, able to undergo hydrolysis, alcoholysis, and acidolysis in some conditions, makes polyesters the preferred polymers for recyclable and/or biodegradable polymers. This has resulted in a renewed interest in aliphatic polyesters, such as poly(lactones), poly(lactides), or copolyesters containing aliphatic moieties. PET production is also strongly driven by the demand of recyclable polymers.

Polyesters

Polyesters are polymeric materials containing ester groups in the polymeric main chain of macromolecules and not the ester groups in the side chains of the macromolecules, as in the case of poly(vinyl acetate) (or) poly(methyl methacrylate), etc. They can be obtained by a wide range of reactions, the most important being polyesterifications between dibasic acids and diols or their derivatives.



$$\sim R_1-\underset{\underset{O}{\|}}{C}-O-R_2\sim$$

Scheme 1. General formula of polyesters.

The polyester family is extremely large and, depending on the nature of R1 and R2 (Scheme 1), exhibits an enormous variety of structures, architectures, properties, and, therefore, applications.

Aliphatic polyesters comprise (a) linear low-molar-mass hydroxy-terminated macromonomers used in the synthesis of polyurethanes, (b) biodegradable and bioabsorbable thermoplastic linear polyesters such as polylactides and polylactones and (c) hyperbranched polyesters applied as crosslinkers in coatings or as rheology modifiers in thermoplastics.

Aliphatic–aromatic polyesters such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are processed into economically important fibers, films, and engineering thermoplastics. Aromatic copolyesters exhibit superior mechanical properties and heat resistance and they have found a number of applications as high-performance thermoplastics.

Unsaturated polyesters and alkyd resins (glyptal resins) are thermosetting resins widely used in the coating and composite industries. The polyester family comprises not only thermoplastic polymers and thermosetting resins but also rubberlike polymers: thermoplastic polyester elastomers (ester TPEs)-copolyesters of terephthalic acid, 1,4-butanediol, and dihydroxy aliphatic polyethers-associate the mechanical properties of rubber with the processing characteristics of thermoplastics. Many other ester-containing polymers could be added to the polyester family, such as polyesteramides, obtained by reaction between diacids, diols and diamines; polyestercarbonates, prepared by reaction of ester-containing monomers; or block copolyesters, prepared by reactions of polyester macromonomers.

2.2. Green monomers

The environmental contamination from discarded polymeric products at the end of their useful life drove the “green” movement and encouraged the chemical industry towards sustainable development.[16-20] The multiple concerns of economy, environmental and social responsibility lead to a humanitarian concept aimed at the improvement in quality of life and welfare of humanity without sacrificing the needs of future generations. There was a growing urgency to seek the renewable sources and convert them to useful products including chemicals, energy sources and materials for replacing the enormous demand for fossil fuels.[21] Agricultural feed stocks as natural, renewable and sustainable resources have potential for use as biopolymers, bioenergy sources and bio-chemicals.[22-25]

The replacement of petroleum-based monomers by the equivalents coming from renewable sources turned into one of the paramount challenges in current polymer research. The biomass components, namely carbohydrates, lignin, oils and proteins, can be subjected to a set of transformations to yield renewable chemical building blocks for the preparation of sustainable polymers.[26-28] In general, biomass-derived monomers can be divided according to their natural molecular biomass origins as: (a) oxygen-rich monomers namely carboxylic acids, polyols, dianhydroalditols, and furans, (b) hydrocarbon-rich monomers including vegetable oils, fatty acids, terpenes, terpenoids and resin acids, (c) hydrocarbon monomers such as bio-ethene, bio-propene, bio-isoprene and bio-butene, and (d) non-hydrocarbon monomers namely carbon dioxide and carbon monoxide.

Among the abundance of building blocks sources for polyester synthesis, carbohydrates, lignin, and vegetable oils are the most interesting ones.

2.2.1. Bio-based routes for some conventional monomers

There are many monomers used in the production of most important polyesters that are accessible from renewable feedstock. Some of them are currently produced at ton levels and many other are still in an incipient state of development.

Succinic Acid

Bio-based Succinic acid (SA) can be produced by microbial fermentation using different microorganisms. Bacteria such as *Actinobacillus succinogenes*, *Anaerobiospirillum succiniciproducens*, and *Mannheimia succiniciproducens* are commonly used for industrial SA production.[29-33] The used feedstock for microbial SA production is formed by corn starch, corn steep liquor, whey, cane molasses, glycerol, lignocelluloses, cereals and straw hydrolysates. The production costs were significant so the actual purpose is to develop low cost processes for the production of pure SA. Chemical companies as DSM from Netherland and the starch derivative French producer Roquette have built a demonstration plant in France for production of several hundred tons of SA from starch, using an innovative enzyme-based fermentation technology.[34] Also BASF and the Dutch company Purac are jointly pursuing SA production.[26] The fermentative production of SA is particularly advantageous from an environmental standpoint, since it uses CO_2 to convert the substrates into the product. Although the fermentation process brings important benefits to the environment, the optimization of the process is still required, namely in what concerns the isolation and purifcation of the product from the fermentation broth.

Adipic acid

The bio-based route to obtain adipic acid (AA) is still in its nascent state. Companies as Verdezyne and Rennovia are developing bio-based pathways to produce AA. So the process carried out by Verdezyne uses genetically modified enzymes to ferment glucose to AA. On the other hand, Rennovia uses air oxidation to convert glucose to glucaric acid, followed by hydrodeoxygenation converting glucaric acid into adipic acid (HIS Chemical Process Economics Program, 2012).[35]

Sebacic Acid

The castor oil is the main feedstock to prepare bio-based sebacic acid (SebA). The treatment of castor oil with strong bases as NaOH or KOH at high temperatures in the presence of catalysts produces sebacic acid and 2-octanol preferentially. Different research groups have worked to optimize the synthesis of SA which is used as co-monomer in many syntheses of polymers. The alkali pyrolysis of castor oil in the presence of white mineral oil (mixture of alkanes from 15-40 carbons and cyclic paraffins) was investigated by Vasishtha *et al.*[36] With the optimization of the operating parameters, the alkali pyrolysis at ~280 ºC in the presence of catalyst obtained 2-octanol and sebacic acid, both in ~ 70% yield. A US patent describes the use of heat transfer fluids such as an aromatic oil, glycol oil or petroleum oil as a diluent to allow for mechanical agitation of the reaction mixture in the castor oil alkali cleavage to sebacic acid and 2-octanol.[37] Another US patent discloses a process for the synthesis of sebacic acid and 2-octanol at high temperature accomplished by using a chemically inert thinning agent, which changes the fluidity of the solution, thus allowing for improved yield and efficiency of the reaction.[38] Azcan *et al.* reported the effect of microwave irradiation on the alkali cleavage of castor oil considering different parameters, such as NaOH/oil ratio, reaction temperature, and reaction time.[39] This process allowed obtaining SebA and 2-octanol with high purity since the side reactions were prevented.

Terephthalic acid

Bio-based terephthalic acid (TA) has been reported as potentially being produced from p-xylene generated by depolymerization of lignin.[40] Another route to bio-based TA uses the limonene oil present in citric fruits as raw material.[41,42] Recently, the production of TA from limonene has been patented.[43] The procedure involves hydrogenation of limonene to p-cymene using zeolites and subsequent oxidation of this compound with an overall yield close to 85%. The current world production of limonene is around 30 000 tons per year,[44] well below what is needed to meet the current production of poly(terephthalate)s (only PET production of bottles amounted to 13 Mtons in 2009).[45] Although considerable progress is being attained in this synthesis,[42] the cost of the implied technology and the difficult accessibility to limonene lead to a presumption that a substantial replacement of petrochemical TA by the bio-based one will be not feasible in the short term.

Ethylene glycol

Microbial ethanol for application as a biofuel is produced at the multimillion ton scale from starch and from sugar. Bioethanol can be readily dehydrated to ethylene using different catalysts as phosphoric acid, sulfuric acid, actvated alumina, metal oxides and zeolites.[46] Bio-based ethylene glycol can be produced via the conventional route of direct oxidation of bio-based ethylene to ethylene oxide followed by thermal hydrolysis.[47] The beverage company Coca-Cola Co. introduced in 2009 the PlantBottle as the first recyclable PET bottle using up to 30% bio-based ethylene glycol as a bio-based monomer for the PET production. Since the Coca-Cola Company introduced PlantBottle Technology to the market as the first-ever recyclable PET plastic bottle made partially from plants, more than 18 billion PlantBottle packages have been distributed in 28 countries resulting in more than 400,000 barrels of oil saved. At the end of 2013 it was announced the collaboration between this innovative plant and the car company Ford to develop new products produced from renewable materials. Ford Fusion Energi uses PlantBottle Technology for seat cushions, seat backs, head restraints, door panel inserts and headliners.

1,3-Propanediol

The industrial production of bio-based 1,3-propanediol has been developed and commercialized by the joint venture DuPont Tate & Lyle LLC, with an annual capacity of 45 000 tons. In nature, the process has two steps: first yeast ferment glucose to glycerol which it converts to 1,3-propanediol through fermentation with microbes. In the patented industrial bioprocess, glucose derived from corn is metabolized by genetically engineered microorganism E. coli which is able to convert glucose into 1,3-propanediol in a single step.[48]

1,4-butanediol

Genomatica Inc., a USA company has developed a sucrose-based process for the manufacture of 1,4-butanediol by an engineered microorganism.[26] Also, 1,4-butanediol can be produced by catalytic hydrogenation of bio-based succinic acid involving three steps: first SA is obtained by fermentation of corn-derived glucose which is purified by electrodialysis and finaly it is reduced to 1,4-butanediol in presence of catalyst.[49] However, most 1,4-butanediol is still produced nowadays from petrochemical feedstock.

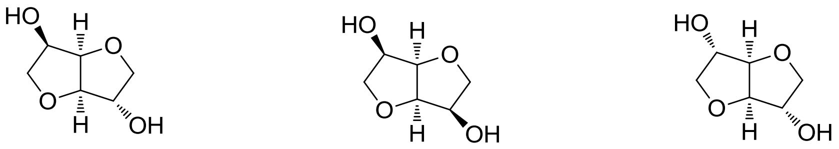
1,10-Decanediol

Castor oil is the natural resorce to obtain sebacic acid that can be then converted into 1,10-decanediol by hydrogenation.[50]

2.2.2. Carbohydrate-based monomers as building blocks for polyesters

Isohexides based polyesters

1,4:3,6-Dianhydrohexitols (DAHs) carbohydrates are among the most extensively studied sugar-based monomers with different polycondensation systems. The three members of this family of isomers named isosorbide, isomannide and isoidide respectively, have deserved particular consideration as monomers for polyester synthesis, as a result of the attractive features of the ensuing polyesters such as rigidity, chirality, non-toxicity and renewable nature. Isosorbide (1,4:3,6-dianhydrosorbitol)[51] is a rigid bicyclic diol that is derived from sorbitol and can ultimately be obtained from glucose-based polysaccharides such as starch and cellulose. In isosorbide the hydroxyl groups on C2 and C5 are in situated in the *exo* and *endo* positions, respectively; in symmetrical isomannide the hydroxyl groups are located in *endo-endo* and in isoidide there are in *exo-exo* respectively (Scheme 2).



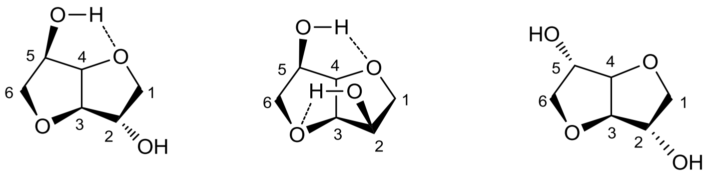
Isosorbide
1,4:3,6-dianhydrosorbitol
D-*gluco*

Isomannide
1,4:3,6-dianhydromannitol
D-*manno*

Isoidide
1,4:3,6-dianhydroiditol
L-*ido*

Scheme 2. 1,4:3,6-Dianhydrohexitols (DAHs) or isohexide isomers.

The main disadvantage of these monomers is the low reactivity of the secondary and relatively hindered hydroxyl groups that leads generally to polyesters with low molecular weights. The reactivity also depends on the existence of intramolecular hydrogen bonds (Scheme 3). Isomannide is less studied because of its lower reactivity and isoidide as not forms hydrogen bonds should be the most attractive isomer of this family. Unfortunately, it can be produced from L-idose which rarely exists in nature and can not be extracted from vegetal biomass; so in present this monomer is an expensive one.



Isosorbide

Isomannide

Isoidide

Scheme 3. Molecular structures of isosorbide, isomannide and isoidide.

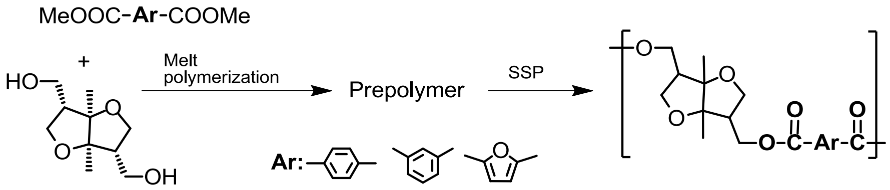
In the case of isosorbide the different steric position of the hydroxyl group regarding to the bicyclic frame (*endo* and *exo* positions) is an additional reason for its low reactivity in polycondensation reactions.[51] Still, isosorbide and its isomers can be used directly to prepare polyesters with high glass transition temperature and/or with special optical properties. DAHs have been widely (co)polymerized with several diacids including, e.g. suberic acid,[52] 1,4-cyclohexane dicarboxylic acid,[53] 1,4-cyclohexane dicarboxylic acid and succinic acid,[54] itaconic acid and succinic acid,[55] succinic acid and adipic acid,[56] among many others.[51] Important recent additions to the field of aliphatic polyesters from DAHs include the work of Wu et al.[57] on the melt polymerization of a series of rigid bio-based polyesters solely based on renewable isohexide building blocks for performance polymers, in which the diacid, isoiodide dicarboxylic acid, and the diol, isoidide dimethanol, were prepared by a multistep process from isomannide. Goerz and Ritter[55] prepared fully bio-based unsaturated oligoesters from isosorbide, itaconic acid and succinic acid which showed a shape memory effect after cross-linking with dimethyl itaconate.

As an alternative to DAHs monomers, very recently it was investigated the use of sugar derived alditol and aldaric cyclic monomers. For example, Lavilla *et al*. reported the synthesis and characterization of several aliphatic polyesters with high solubility and wettability made from dimethyl 2,3:4,5-di-*O*-methylene-galactarate, a bicyclic monomer obtained by internal acetalization of galactaric acid.[58,59] In another study, Lavilla *et al*. prepared a series of random copolyesters from 1,4-butanediol, bicyclic 2,4:3,5-di-*O*-methylene-D-mannitol (Manx) and dimethyl succinate by a two-step melt polycondensation process whose properties are comparable to the copolyesters prepared from isosorbide.[60] The bio-based PBS copolyesters containing Manx units had high T_g and they were biodegradable.

Since some time ago the different scientists have investigated the preparation of aromatic polyesters and copolyesters trying to replace aliphatic linear diols by the isohexides. They reported a deficient incorporation of isosorbide in PET[61] or PBT[62,63] copolyesters when they prepared the polymers by the classical two-step melt polycondensation process. The common explanation of different authors was the poor reactivity of isohexides. Charbonneau *et al*.[64] reported 16 examples of synthesis of aromatic copolyesters varying in content in isosorbide units with an average rate of incorporation of this monomer of only 48%.

Several strategies have been applied to overcome the reduced reactivity inherent in isohexides. A new catalytic system based on the combination of antimony oxide with a second metal salt has been recently shown to increase the efficiency of the transesterification step of isosorbide in the synthesis of PET derived copolyesters, producing materials with lower discoloration.[65] Also a trivalent bismuth catalyst has been claimed for preparing the same copolyesters at reduced polycondensation temperatures with lower raw material losses.[66]

Hayes *et al*.[67] prepared bis(2-hydroxyethyl)-isosorbide by reaction of isosorbide with ethylene oxide or ethylene carbonate, and reported its complete incorporation into high molecular weight polymers, including aromatic polyesters. Following the same idea, isoidide has been conveniently modified by converting the secondary hydroxyl groups into primary ones through methylene extension. The 2,5-dimethanol isoidide derivative was used for the synthesis of a series of aromatic polyesters including poly(terephthalate)s, poly(isophthalate)s and poly(2,5-furandicarboxylate)s (Scheme 4) via melt and solid state polycondensation (SSP).[68] Aromatic terpolyesters containing isosorbide display thermal properties highly dependent on composition in cyclic units.



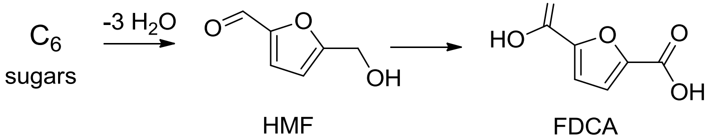
Scheme 4. Synthesis of aromatic polyesters from 2,5-dimethanol isoidide.

Quintana *et al.* prepared a series of random poly(ethylene terephthalate) (PET) terpolyesters containing variable amounts of 1,4-cyclohexanedimethanol (CHDM) and isosorbide.[61] The glass-transition temperature of these copolyesters increased and the crystallization rate decreased with the total content on cyclic diol but these effects were more pronounced when isosorbide was the replacing comonomer. On the other hand, the use of the furanic monomer 5,5′ isopropylidene bis(ethyl 2-furoate) together with isosorbide allowed the synthesis of new amorphous PET terpolyesters with T_g between 104 and 127 °C according to the terephthalate/furoate and ethylene glycol/isosorbide ratios with good thermal stability and enhanced solubility in common solvents.[69]

Chatti *et al.*[70] synthesized a new class of biodegradable copolyesters from isosorbide, succinic and isophthalic acid, whose glass transition temperatures (90-160 ºC) can rival those of most commercial amorphous engineered plastics.

Furan-based polyesters

FDCA (2,5-furandicarboxylic acid) can be used as a substitute of terephthalic acid and isophthalic acid in the synthesis of polyesters. This dicarboxylic acid results from the catalytic oxidation of 5-hydroxymethylfurfural (HMF), which is obtained from the acid catalysed-dehydration of C6-sugars (mainly fructose).[71] The conversion of HMF into FDCA comprises two steps: conversion of HMF to a dialdehyde derivative, followed by the oxidation of the two aldehyde groups to carboxylic acid groups (Scheme 5).[72]



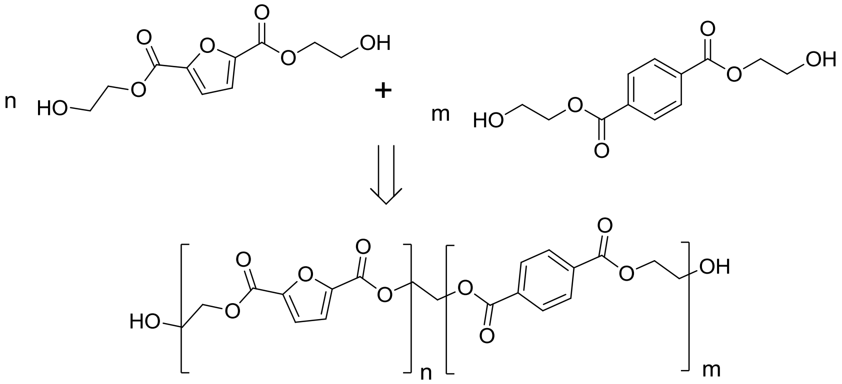
Scheme 5. Conversion of C6-sugars into FDCA.

As it was mentioned before FDCA, furan derivative obtained from different carbohydrate sources, has recently gained particular attention as a suitable monomer for replacing terephthalic acid for step-growth polymerization. After the ground-breaking work of Moore and Kelly about the synthesis of a number of linear polyesters from FDCA or the corresponding dichloride,[73] some groups have devoted considerable attention to furan polyesters in the last couple of years.[74-81]

For example, Gandini *et al.*[76] have demonstrated that FDCA can be used in polycondensation reactions to produce poly(ethylene 2,5-furanoate) (PEF) and other FDCA based (co)polyesters. In the case of PEF, the similarity with PET in terms of thermal properties (e.g. glass transition, melting and the onset of thermal decomposition temperatures around 80, 215 and 300 ºC, respectively) was unambiguously demonstrated.[76a]

The field of FDCA can be extended to a more vast number of polyesters besides PEF, such as the ones prepared by using FDCA and three isomers of 1,4:3,6-dianhydrohexitol, PDO or hydroquinone.[76c] Moreover, the polycondensation using different linear diols (C2-C8)[77] or the random copolymerizations of FDCA with different amounts of ethylene glycol and butanediol[78a] have also been reported.

Notwithstanding the enormous potential of the polyesters based on FDCA, recently renewed interest in terephthalic acid (TPA) obtained by the sugar-based p-xylene route to prepare 100% renewable TPA.[26,82] Thus, Sousa *et al.*[83] reported the partial substitution of renewable PET with copolymers of TPA and FDCA derivatives (Scheme 6). These PET-ran-PEF copolyesters showed average molecular weights, thermal and mechanical properties comparable to petrochemical derived materials.

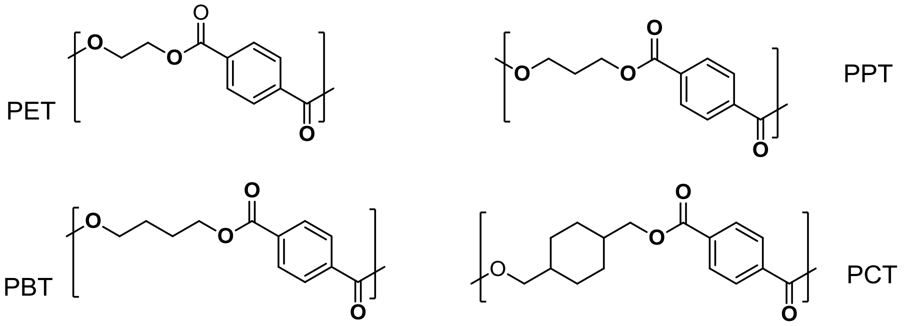


Scheme 6. Polytransesterification reaction of bis(2-hydroxyethyl) terephthalate and bis(hydroxyethyl)-2,5-furandicarboxylate to obtain PET-ran-PEF copolyesters.[83]

2.3. Aromatic polyesters

By far the most extended aromatic polyesters are poly(alkylene terepthalate)s, specifically poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), along with several other homologues of increasing importance such as poly(trimethylene terephthalate) (PPT) and poly(cyclohexylenedimethylene terephthalate) (PCT) but that are positioned at a long distance behind the former two.[84]

PET accounts for 8% of the global polymer production[85] with an extensive use in food packaging as well as in the textile field where it has reached a consumption level close to that of cotton.[86] Due to its low crystallization rate in the unoriented state but its capacity for crystallizing rapidly under stress, transparent semicrystalline films exhibiting excellent thermal and mechanical properties can be produced from PET by biaxial stretching under blowing.[87] PBT follows PET in terms of volume production and technical importance. PBT crystallizes very fast with an excellent dimensional retention and without needing nucleating agents. These exceptional properties make PBT the thermoplastic of choice for processing and rapid production cycles. The chemical structure of the most representative poly(alkylene terephthalate)s is depicted in Scheme 6.



Scheme 6. Chemical formula of top poly(alkylene terephthalate)s.

In terms of volume and economic importance, thermoplastic polyesters are dominated by PET, which has experienced a tremendous development in fibers and molding resins due to a strong demand for textile applications and in food packaging and bottle markets for glass replacement.

Formation of PET consists of two main reactions namely: esterification and polycondensation. The esterification reaction is conducted in excess of MEG. The first step produces a prepolymer which contains bis(hydroxyethyl terephthalate) (BHET) (or) diethylene glycol terephthalate and short chain oligomers and by-products namely water (or) methanol depending upon the raw material used namely PTA (purified terephthalic acid) or DMT (dimethyl terephthalate) respectively. In order to accelerate the rate of polycondensation, a catalyst such as antimony acetate, antimony trioxide, germanium dioxide or titanium can normally be used.

PBT thermoplastic polyester is prepared by polycondensation of 1,4-butanediol (BDO) with PTA (or) DMT. As it was mentioned before PBT differs only slightly from PET in chemical composition but more substantially in its properties such as higher crystallization rate and lower melting point. PBT fibers are manufactured by Zimmer and Ticona in the name of Celanex®.
PBT is used for textile applications due to its strechability and improved dyeability. PBT fibers are used as a tooth brush, carpet yarn and sports wear and hosiery. It is also used for swim wear since it has high tenacity, stability and good resistance to chlorine. PBT is preferable used for the production of engineering plastics due to its combination of dimensional stability, tensile strength, increased flexibility and fast crystallization rate. PBT resins are used in drapery hardware, heavy duty zippers, hair dryers, pocket calculators, iron and toasting housing and food processor blades.

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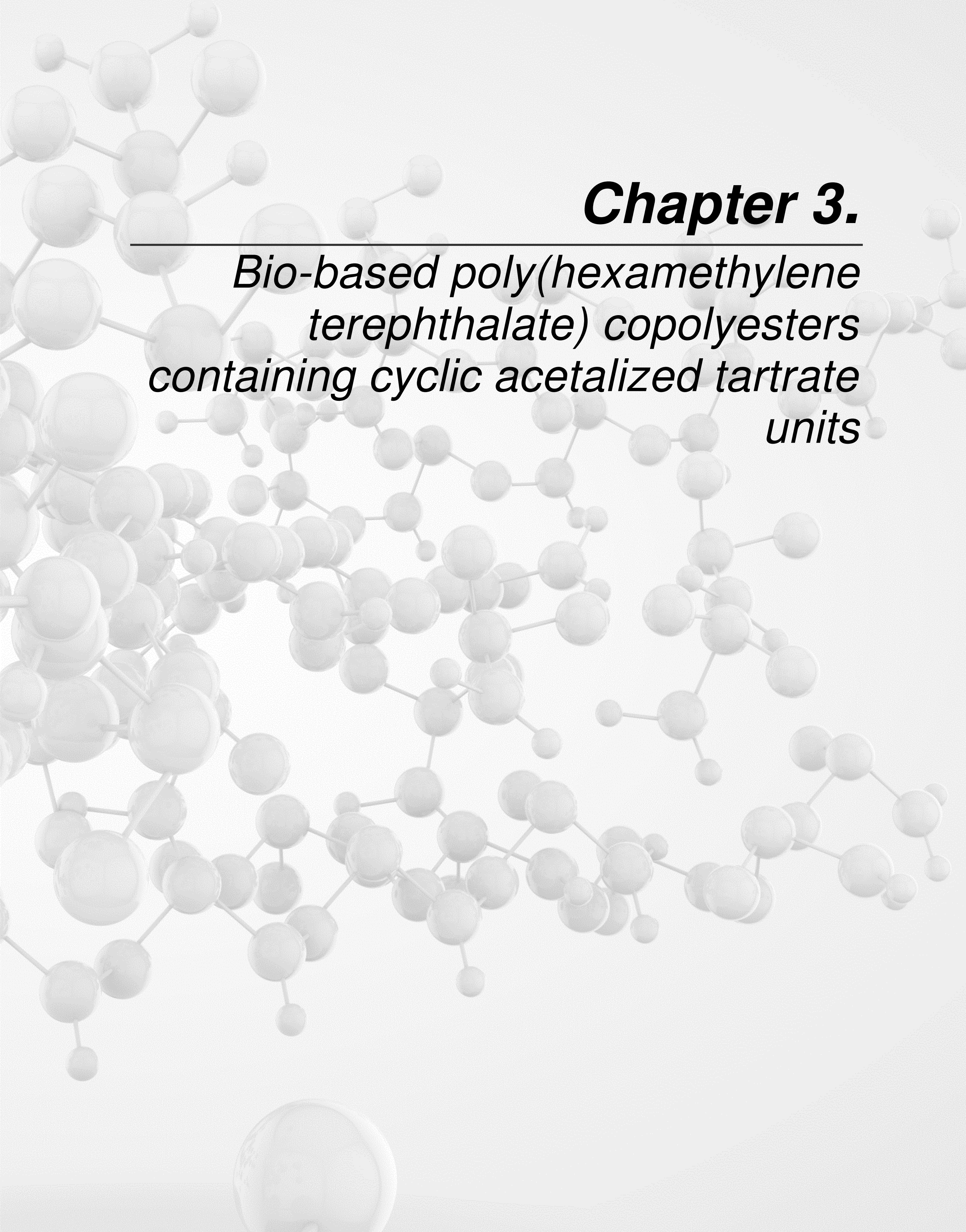
Chapter 3.

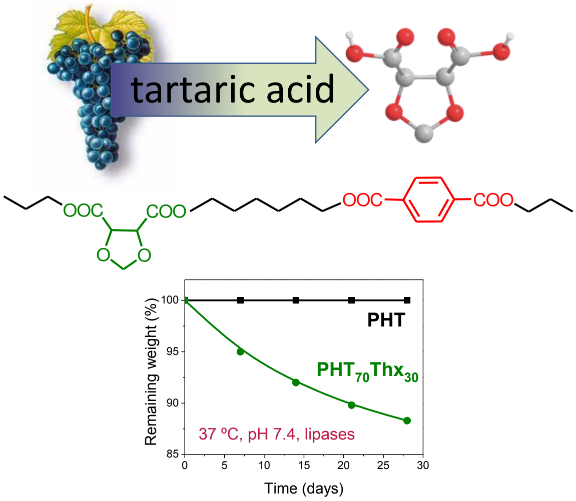
Bio-based poly(hexamethylene terephthalate) copolyesters containing cyclic acetalized tartrate units



Biobased poly(hexamethylene terephthalate) copolyesters containing cyclic acetalized tartrate units

Abstract

A cyclic acetal of dimethyl L-tartrate (dimethyl 2,3-di-*O*-methylene L-threarate, (Thx) was used as comonomer of dimethyl terephthalate (DMT) in the polycondensation with 1,6-hexanediol (HD) in the melt. Random copolyesters PHT$_x$Thx$_y$ with contents in tartrate units up to 50% were obtained with satisfactory molecular weights (M_w between 20,000 and 50,000) and dispersities slightly above 2, and without apparent discoloration. The copolyesters started to decompose above 300 ºC. The T_g of the copolyesters oscillated between +9 and -9 ºC with values steadily decreasing with increasing contents in Thx units. All the copolyesters as well as the homopolyester entirely made of tartrate units were semicrystalline with T_m falling from ~145 ºC for PHT to ~70 ºC for PHThx with intermediate values decreasing as the content in Thx increased. Copolyesters containing up to 30% of tartrate units were able to crystallize from the melt at crystallization rates that were delayed by the presence of tartrate units. The PHT$_{70}$Thx$_{30}$ copolyester displayed significant hydrodegradability when incubated in aqueous buffer and also certain biodegradability when subjected to the action of porcine pancreas lipases.



Publication derived from this work:

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3.1. Introduction

The modification of aromatic polyesters addressed to make them more sustainable is currently an issue of maximum interest.[1,2] The mostly applied approach is replacing the traditionally used monomers of petrochemical origin by bio-based monomers. The challenge is to carry out the replacement without significant detriment of the original basic behavior of the polyesters or even with some improvement of certain selected properties. Carbohydrate-based compounds have received great consideration as suitable sustainable comonomers for aromatic polyesters,[3-6] particularly cyclic derivatives such as some alditol dianhydrides[7,8] and 2,5-furandicarboxylic acid.[9,10] The advantages afforded by these cyclic compounds when used as monomers is that, thanks to their molecular rigidity, they are able to preserve or even increase the glass transition temperature of the polyesters in which they are inserted.[11,12] We have recently published on bio-based aromatic polyesters in which either the diol or the diacid has been partially replaced by bicyclic diacetals of alditols or aldaric acids, respectively. Depending on which monomer was replaced and the extent of replacement attained, the crystallinity of the copolyesters varied in one sense or another but in general the T_g was retained near the original values or even increased for certain cases.[13]

In this paper we wish to report on the synthesis, characterization and properties of a set copolyesters obtained by polycondensation of 1,6-hexanediol (HD) with mixtures of dimethyl terephtalate (DMT) and the monocyclic methylene acetal of dimethyl L-tartrate (Thx). Our purpose is to evaluate the capacity of acetal tartrates to replace the terephthalate units in PHT with especial attention paid to the viability of the polycondensation, and also to show the effect that such replacement exerts on thermal properties and the chemical and biological hidrodegradability of the parent aromatic homopolyester poly(hexamethylene terephthalate) (PHT).

The reference polyester in this study is poly(hexamethylene terephthalate). PHT is a semicrystalline aromatic polyester that although has not achieved commercial realization, deserves interest because its relatively low melting temperature (~140 ºC) compared to PET and PBT (~270 and ~220 ºC, respectively) and will require less severe processing conditions. However PHT is not biodegradable and extremely reluctant to chemical hydrolysis. Presently, HD is produced via petrochemistry but it may be also obtained from sorbitol by hydrogenolysis under pressure in water.[14] On the other hand, L-threaric acid, widely known as tartaric acid, is a low-cost by-product of the wine industry.[15] The reaction of L-tartaric acid with carbonyl compounds is a simple reaction that generates 2,3-di-*O*-alkylene cyclic acetals in good yields.[16] The combination of HD with Thx as a comonomeric pair for polycondensation with terephthalic acid constitutes an interesting approach to the synthesis of partially sustainable PHT copolyesters. At difference with other 1,3-dioxolane acetals made from higher carbonylic compounds, the methylene acetal is a structure quite resistant to both temperature and chemical hydrolysis, and due to its relative small size, it is easily crystallizable. Dhamaniya and Jacob[17,18] have recently reported on aliphatic polyesters obtained from the cyclic 2,3-*O*-isopropylene acetal of both dimethyl L-tartrate and L-threitol; these polyesters are mostly amorphous due to the presence of the isopropylene side group but they distinguish in being easily convertible into interesting hydroxyl-free bearing polyesters by hydrolysis of the acetal group.

3.2. Experimental section

3.2.1. Materials and methods

Materials

Dimethyl terephthalate (DMT) (99%), 1,6-hexanediol (HD) (99%) and dibutyl tin oxide (DBTO, 98%) were purchased from Sigma-Aldrich. The solvents used for purification and characterization, such as chloroform, diethyl ether, dichloracetic acid (DCA), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), were of high purity grade and used as received.

Methods

Viscosities were measured in dichloroacetic acid at 25.0 ºC, using an Ubbelohde microviscometer at concentrations ranging from 5 to 10 mg mL^{-1}.

Molecular weight determinations were performed by GPC using HFIP containing 0.05 M sodium trifluoroacetate-hexafluoroisopropanol (NaTFA-HFIP) as mobile phase in a Waters equipment provided with RI and UV detectors. 100 µL of 0.1% (w/v) sample solution were injected and chromatographed with a flow of 0.5 mL min^{-1} in a linear HR5E Water Styragel column (7.8x300 mm) packed with cross-linked polystyrene and protected with a pre-column. Average molecular weights and their distributions were calculated against PMMA standards.

Infrared spectra were recorded with a PerkinElmer FTIR Frontier equipped with an ATR diamond accessory. Eight scans with a resolution of 2 cm^{-1} were collected and signal averaged for each sample.

^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer at 25 ºC operating at 300.1 and 75.5 MHz, respectively. The polyesters were dissolved in deuterated chloroform ($CDCl_3$) and spectra were internally referenced to tetramethylsilane. About 10 and 50 mg of sample in 1 mL solvent were used for ^1H and ^{13}C, respectively. Sixty-four scans were recorded for ^1H, and between 5,000 and 15,000 scans were taken for ^{13}C with 32 and 64 K data points and relaxation delays of 1 and 2 s, respectively. 2D ^1H-^1H homonuclear (COSY) and ^{13}C-^1H heteronuclear shift correlation (HETCOR) spectra were recorded by means of the *cosy* and *hxco*, respectively, pulse sequences implemented in the Bruker NMR instrument package.

TGA measurements were performed under a nitrogen flow of 20 mL min^{-1} at a heating rate of 10 ºC min^{-1} and within a temperature range of 30 to 600 ºC, using a Perkin-Elmer TGA6 thermobalance. Sample weights of about 10 mg were used in these experiments.

The thermal behavior of the polymers was examined by differential scanning calorimetry (DSC) using a PerkinElmer Pyris 1 apparatus. Thermograms were obtained from 4-6 mg samples under a nitrogen flow of 20 mL min^{-1}. Indium and zinc were used as standards for temperature and enthalpy calibrations. Melting temperatures (T_m) were taken as the maximum of the endothermic peak appearing on heating traces recorded at 10 ºC min^{-1}, and glass transition temperature (T_g) was taken as the inflection point seen on heating traces recorded at 20 ºC min^{-1} from samples quenched from the melt.

X-ray diffraction profiles were recorded on the PANalytical X'Pert PRO MPD θ/θ diffractometer using the Cu-K$_\alpha$ radiation of wavelength 0.1542 nm from powdered samples coming directly from synthesis.

Scanning electron microscopy (SEM) images were taken with a field emission JEOL JSM-7001F instrument (JEOL, Japan). The samples were covert with Pt/Pd with a thickness about 1 nm using a Cressington Sputter Coater 208 HR equipment.

3.2.2. Synthesis of monomers

Dimethyl 2,3-O-methylene-L-tartrate. This acetalized tartrate (Thx) was synthesized following the procedure described by Rodríguez-Galán *et al.*[19] To a mixture of dimethyl L-tartrate (40 g) and paraformaldehyde (40 g) heated at 60 ºC under stirring, 98% sulfuric acid (40 mL) was added dropwise and stirred until complete dissolution. The reaction solution was then repeatedly extracted with chloroform, the organic phase successively washed with 25% aqueous ammonia solution and water, and dried over anhydrous sodium sulfate. The solution was evaporated to dryness and distilled under vacuum (0.1 bar, 100 ºC) to obtain Thx as an oily colorless product (16 g, 50% yield).

3.2.3. Synthesis of polyesters

Homopolyesters (PHT and PHThx) as well as PHT$_x$Thx$_y$ copolyesters were synthesized by two-stage polymerization process (transesterification and polycondensation) carried out in the bulk from 1,6 hexanediol and DMT or Thx or their mixtures with a variety of selected compositions covering the 10-50% range in the tartrate comonomer. A 20% molar excess of diol to diester was used in all cases to compensate the loss in volatiles and DBTO in a 0.44% molar ratio was the catalyst of choice. Reactions were performed in a three-necked, cylindrical flask equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum distillation outlet. The apparatus was vented with nitrogen several times at room temperature to remove the air and to avoid oxidation during the polymerization. The transesterification stage was carried out under a low nitrogen flow for a period of 3 h at 160 ºC and polycondensation was left to proceed for 5 h at 160 ºC under a 0.03-0.06 mbar vacuum. The highly viscous reaction mixture was then cooled to room temperature, and the atmospheric pressure was recovered with nitrogen to prevent degradation. The resulting solid mass was dissolved in chloroform and precipitated in an excess of methanol to remove unreacted monomers and oligomers. The precipitate polymer was collected by filtration, extensively washed with methanol and diethyl ether, and finally dried under vacuum.

PHT. IR υ (cm^{-1}): 1700 (C=O aromatic st). ^1H NMR ($CDCl_3$, 300 MHz), δ (ppm): 1.54-1.63 (m, $OCH_2CH_2\mathbf{CH_2}$), 1.82 (q, $OCH_2\mathbf{CH_2}CH_2$), 4.36 (t, $O\mathbf{CH_2}CH_2CH_2$), 8.08 (s, *Ar*H). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75.5 MHz): δ (ppm) 165.8 (C=O), 134.0-129.0 (*Ar*C), 65.20 ($O\mathbf{CH_2}CH_2CH_2$), 28.50 ($OCH_2\mathbf{CH_2}CH_2$), 25.67 ($OCH_2CH_2\mathbf{CH_2}$).

PHT_xThx_y. IR υ (cm^{-1}): 1700 (C=O aromatic st), 1740 (C=O aliphatic st), 1198 (C-O acetal st), 1067, 912 (C-O acetal st). ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) 1.56-1.40 (m, $OCH_2CH_2\mathbf{CH_2}$), 1.82-1.67 (2m, $OCH_2\mathbf{CH_2}CH_2$), 4.38-4.19 (2q, $O\mathbf{CH_2}CH_2CH_2$), 4.73 (s, CH), 5.25 (s, OCH_2O), 8.09 (s, *Ar*H). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75.5 MHz): δ (ppm) 169.19 (C=O), 165.73 (C=O), 134.0-129.0 (*Ar*C), 97.41 (OCH_2O), 76.80 (CH), 65.79-65.14 ($O\mathbf{CH_2}CH_2CH_2$), 28.50-28.28 ($OCH_2\mathbf{CH_2}CH_2$), 25.67-25.28 ($OCH_2CH_2\mathbf{CH_2}$).

PHThx. IR υ (cm^{-1}): 1740 (C=O aliphatic st), 1198 (C-O acetal st), 1067, 912 (C-O acetal st). ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) 5.24 (s, OCH_2O), 4.72 (s, CH), 4.20 (t, $O\mathbf{CH_2}CH_2CH_2$), 1.70 (m, $OCH_2\mathbf{CH_2}CH_2$), 1.40 (m, $OCH_2CH_2\mathbf{CH_2}$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75.5 MHz): δ (ppm) 169.0 (C=O), 97.38 (OCH_2O), 76.77 (CH), 65.70 ($O\mathbf{CH_2}CH_2CH_2$), 28.26 ($OCH_2\mathbf{CH_2}CH_2$), 25.26 ($OCH_2CH_2\mathbf{CH_2}$).

3.2.4. Hydrolytic and enzymatic degradation assays

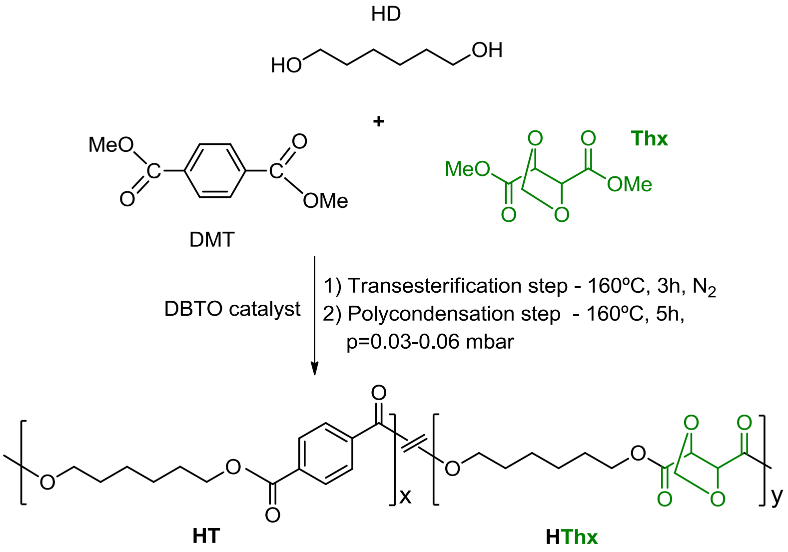
For both hydrolytic and enzymatic degradation studies, films of polyesters and copolyesters with a thickness of about 200 µm were prepared by casting from a chloroform solution (62 mg mL^{-1}). The films were cut into 10 mm diameter disks and dried under vacuum to constant weight, which finally remained between 20 to 30 mg. The disks were individually immersed in vials containing 10 mL of either sodium phosphate buffer pH 5.0 or citric acid buffer pH 2.0 (hydrolytic degradation), or sodium phosphate buffer pH 7.4 containing 10 mg of porcine pancreas lipases (enzymatic degradation) and left incubating at 37 ºC for one or two months. The buffered enzyme solution was replaced every 72 h to maintain the enzyme activity. The disks were withdrawn from the incubation medium at scheduled incubation periods, washed thoroughly with distilled water, and dried to constant weight.

3.3. Results and discution

3.3.1. Polyesters synthesis and microstructure of PHT$_x$Thx$_y$ copolyesters

Synthesis

The synthesis of PHT and PHThx homopolyesters, as well as of the PHT$_x$Thx$_y$ copolyesters, was carried out following essentially the methodology used for the settled industrial production of aromatic polyesters. As depicted in Scheme 1, the molten mixture of monomers with the added catalyst was made to react in two successive stages at increasing vacuum to favor initially the formation of oligomers with subsequent releasing of methanol and to attain the removal of exceeding diols, respectively. The reaction temperature was fixed at 160 ºC as a compromise between a satisfactory reaction rate and a minimum thermal decomposition of the tartrate containing compounds. Furthermore, such temperature was high enough to keep the forming polymer in the molten state throughout the whole process. DBTO was the catalyst of choice since previous works have shown its superior activity over the most commonly used tetrabutyl titanate (TBT) in polycondensation reactions involving sugar-based monomers.[20] Polymerization evolved with a continuous increase in viscosity of the reaction mixture which became so high as to impede the stirring. At this point the reaction was finished and the polymer conveniently recovered and purified. In this way PHT, PHThx and a set of PHT$_x$Thx$_y$ copolyesters in which the terephthalate unit has been replaced by the tartrate unit in a range of 10 up to 50 % were prepared in yields around 90%.



Scheme 1. Reaction scheme for the preparation of PHT$_x$Thx$_y$ copolyesters.

As is it shown in Table 1, the resulting homopolyesters and copolyesters presented satisfactory molecular weights with values steadily decreasing with the content in Thx. The intrinsic viscosities measured in DCA oscillated between 0.5 and 1.3 dL·g^{-1} and the GPC analysis afforded M_w values comprised in the 23,000-50,000 g·mol^{-1} range with dispersities between 2.0 and 2.3.

Table 1. Yields, compositions and molecular weights of PHT, PHThx and PHT$_x$Thx$_y$ copolyesters.

Polyester	Yield (%)	Composition [T]/[Thx]		Molecular weight			
		Feed^a	Polymer^b	$[\eta]^c$	$M_n{}^d$	$M_w{}^d$	$Đ^d$
PHT	92	100/0	100/0	1.33	21,900	50,300	2.3
PHT$_{90}$Thx$_{10}$	91	90/10	91/9	0.86	18,600	41,000	2.2
PHT$_{80}$Thx$_{20}$	90	80/20	82/18	0.76	17,200	35,700	2.1
PHT$_{70}$Thx$_{30}$	90	70/30	72/28	0.73	16,800	34,300	2.0
PHT$_{60}$Thx$_{40}$	88	60/40	61/39	0.72	16,000	34,000	2.1
PHT$_{50}$Thx$_{50}$	88	50/50	51/49	0.54	10,500	23,200	2.2
PHThx	86	0/100	0/100	0.53	10,500	23,100	2.2

[a] Molar ratio in the initial feed. [b] Molar ratio in the copolyester determined by ^{1}H NMR.
[c] Intrinsic viscosity (dL·g^{-1}) measured in DCA at 25 °C.
[d] Number- and weight-average (M_n, M_w) molecular weights and dispersities ($Đ$) determined by GPC.

The incorporation of the Thx units in the polyesters was well evidenced by infrared spectroscopy as a partial or total replacement of the carbonyl 1700 cm^{-1} band of terephthalate by the 1740 cm^{-1} one characteristic of the tartrate unit. In addition new bands arising from the stretching of the dioxolane ring appeared in the 1200-900 cm^{-1} range displaying an intensity that increased with the content of the polyester in Thx units. The evolution of the FTIR spectra with composition is illustrated in the Electronic Supplementary Material (ESM) file linked to this paper.

The chemical constitution of the polyesters was ascertained by NMR spectroscopy; a detailed description of the NMR data recorded from homopolyesters and copolyesters are given in Experimental Section, and the ^{1}H and ^{13}C spectra of PHT$_{70}$Thx$_{30}$ are shown in Figure 1 for illustration. The assignment of peaks was done with the help of 2D NMR spectra (*cosy* and *hetcor*) that are provided in the ESM document. The compositions of PHT$_x$Thx$_y$ copolyesters in T and Thx units could be accurately determined by integration of the signals observed at 5.2 ppm (singlet, 2H of the methylene in the acetal group) and 4.4 ppm (m, 4H of first methylene of HD from T unit).

The area ratios for these signals afforded the copolyester compositions given in Table 1, where they are compared with those used in their respective copolymerization feeds. This comparison reveals that invariably, the content of tartrate units in the copolyesters is slightly lower than in their corresponding feeds, which can be attributed to slight losses of the highly volatile dimethyl tartrate compared to dimethyl terephthalate.

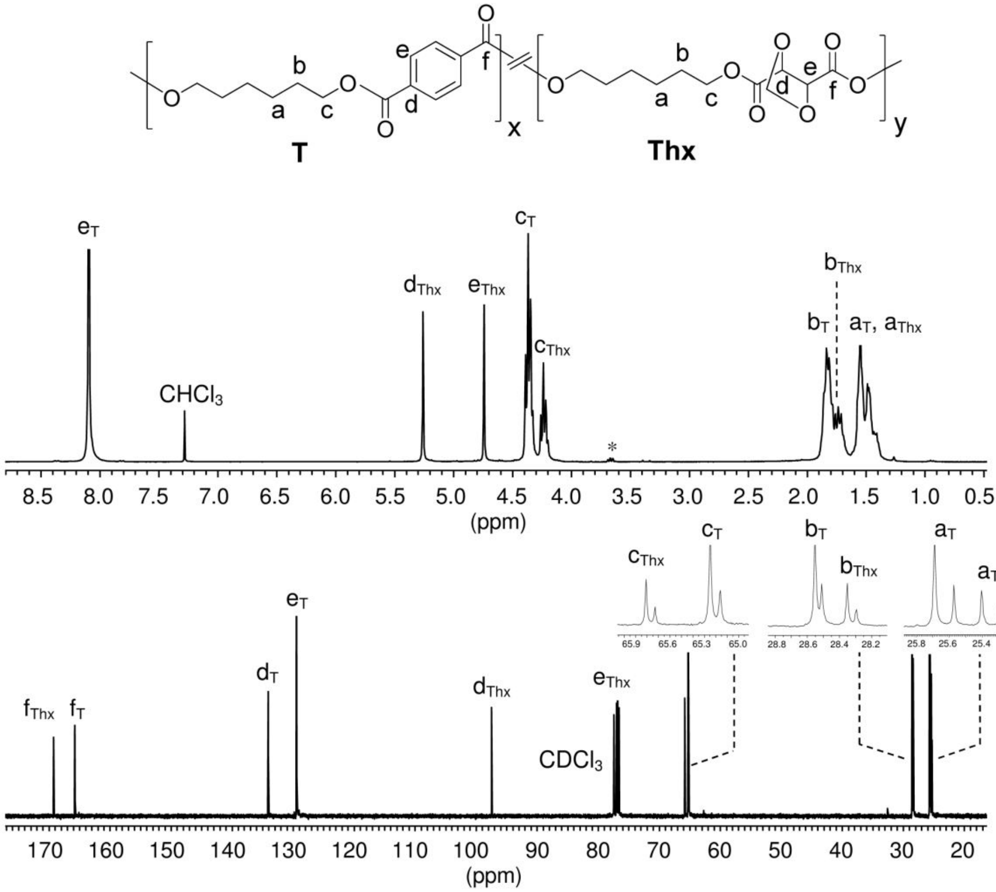


Figure 1. ^{1}H (top) and ^{13}C (bottom) NMR spectra of PHT$_{70}$Thx$_{30}$ (*CH_2OH end groups).

On the other hand, the detailed ^{13}C NMR analysis afforded the determination of the copolyesters microstructure as it has been done in previous woks for several related copolyesters.[21] All signals due to hexamethylene carbons were split into four peaks due to the different chemical environment provided by the four possible dyads T-T, T-Thx/Thx-T and Thx-Thx occurring along the copolyester chain (Figure 2a). The assignment of these peaks to the dyads (Figure 2b) was possible by comparison with the ^{13}C NMR spectra produced by the homopolyesters.

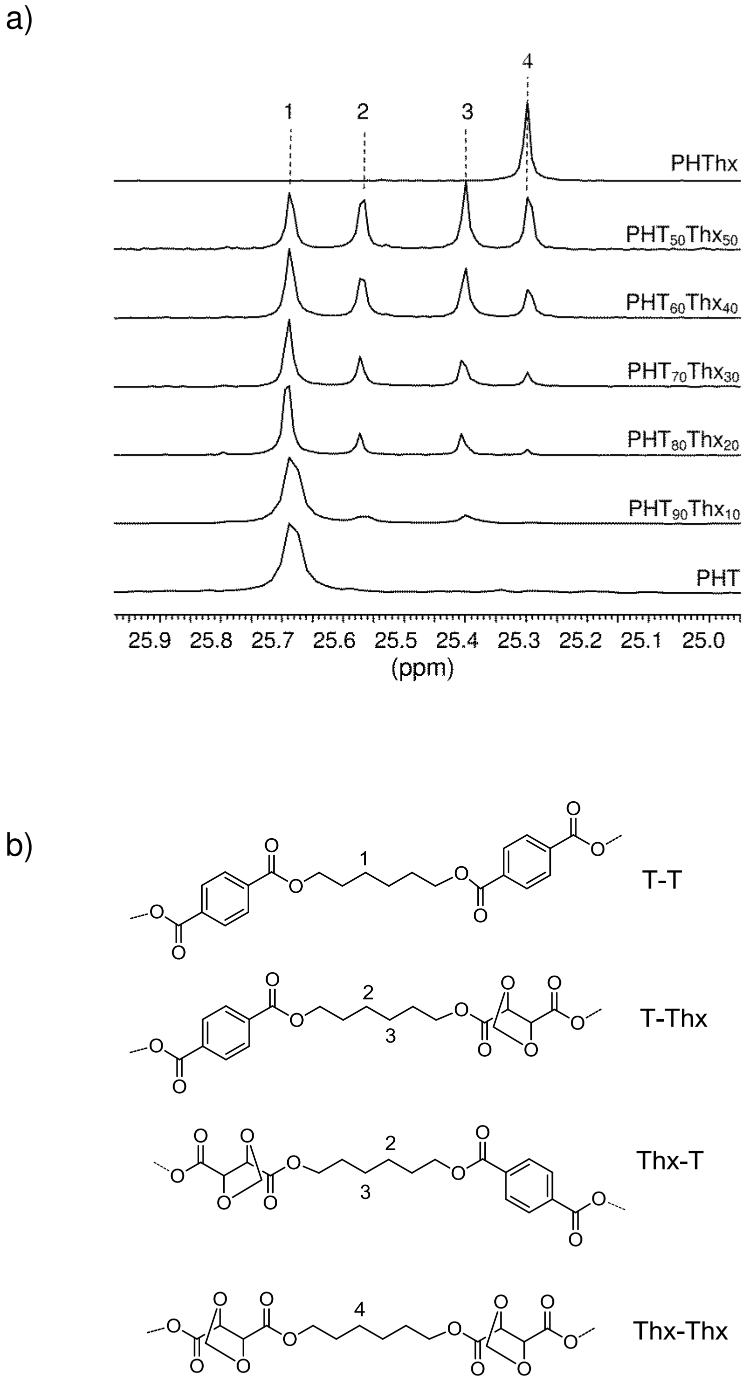


Figure 2. (a) The four possible dyads present in PHT$_x$Thx$_y$ copolyesters. (b) ^{13}C NMR spectra in the region of the inner HD methylenes for PHT$_x$Thx$_y$ copolyesters and homopolyesters.

The content of the copolyesters in the four possible dyads was determined by quantification of the areas of these peaks previously resolved by lorentzian deconvolution of the signals using the WinNMR software. The number average sequence lengths and the degree of randomness of these copolyesters could be established by using the expressions given below.[22] The results of this microstructural analysis are presented in Table 2; the degree of randomness are near to 1 for all compositions with values of sequence lengths very close to those calculated for theoretical random copolymers. It is concluded therefore that the distribution of the T and Thx comonomers in PHT$_x$Thx$_y$ copolyesters is essentially statistical.

$$n_{HT} = (N_{T\text{-}T} + \tfrac{1}{2}(N_{T\text{-}Thx} + N_{Thx\text{-}T})) / \tfrac{1}{2}(N_{T\text{-}Thx} + N_{Thx\text{-}T})$$

$$n_{HThx} = (N_{Thx\text{-}Thx} + \tfrac{1}{2}(N_{T\text{-}Thx} + N_{Thx\text{-}T})) / \tfrac{1}{2}(N_{T\text{-}Thx} + N_{Thx\text{-}T})$$

$$R = (1/n_{HT}) + (1/n_{HThx})$$

Table 2. Composition and microstructure of the PHT$_x$Thx$_y$ copolyesters.

Copolyester	Composition[a] (%)		Dyad content[b] (%)			Sequence Lenght[b]		R
	X_T	X_{Thx}	$N_{T\text{-}T}$	$N_{T\text{-}Thx/Thx\text{-}T}$	$N_{Thx\text{-}Thx}$	n_{HT}	n_{HThx}	
PHT$_{90}$Thx$_{10}$	91	9	81.2 (82.8)	17.6 (16.4)	1.2 (0.8)	10.2 (11.1)	1.1 (1.1)	0.98 (1.00)
PHT$_{80}$Thx$_{20}$	82	18	67.5 (67.2)	29.0 (29.5)	3.5 (3.2)	5.6 (5.5)	1.2 (1.2)	0.98 (1.00)
PHT$_{70}$Thx$_{30}$	72	28	51.2 (51.8)	40.2 (40.3)	8.6 (7.8)	3.5 (3.6)	1.4 (1.4)	0.98 (1.00)
PHT$_{60}$Thx$_{40}$	61	39	38.2 (37.2)	47.1 (47.6)	14.7 (15.2)	2.6 (2.5)	1.6 (1.6)	1.00 (1.00)
PHT$_{50}$Thx$_{50}$	51	49	26.6 (26.0)	49.8 (49.9)	24.6 (24.0)	2.0 (2.0)	1.9 (1.9)	0.99 (1.00)

[a]Calculated from the ^{1}H NMR spectra. [b]Dyad molar fractions (*N*) experimentally determined by ^{13}C NMR and number-average sequences lengths (*n*) estimated by the equations given in the text.

Theoretical values (in parentheses) were calculated on the basis of a statistical dyad distribution using the copolyesters composition data given in this Table.

3.3.2. Thermal properties

The thermal behavior of PHT$_x$Thx$_y$ copolyesters has been comparatively studied by TGA and DSC taking as reference their parent homopolyesters, PHT and PHThx, (Table 3). First, the thermal stability was evaluated by TGA under an inert atmosphere. The weight loss versus temperature plots registered for the polyesters and their corresponding derivative curves are shown in Figures 3a and 3b, respectively. The temperatures at the decomposition onset and for maximum rate, together with the weight remaining after heating at 600 ºC, are listed in Table 3. All the polyesters started to decompose above 300 ºC with the maximum rate taking place in the proximities of 400 ºC to leave less than 10% of the initial mass after heating at 600 ºC.

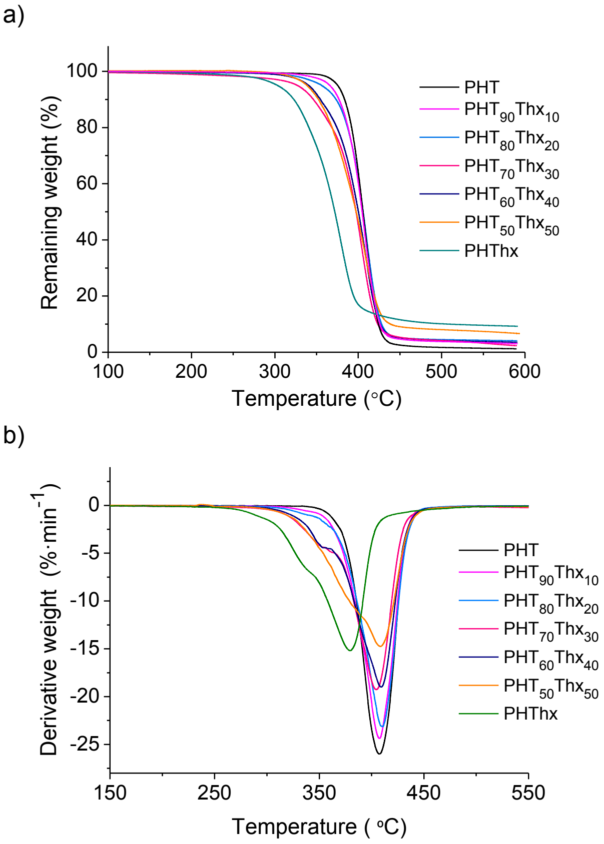


Figure 3. a) TGA traces of PHT$_x$Thx$_y$ copolyesters and PHT, PHThx homopolyesters registered under an inert atmosphere. b) Derivative curves of the whole series of polyesters with labels on those showing two decomposition steps.

Table 3. Thermal properties of PHT, PHThx and the $\mathrm{PHT_xThx_y}$ copolyesters.

Polyester	TGA			DSC									
					First heating[e]		Cooling[e]		Second heating[e]		Annealing[f]		T_{e}[g] (°C)
	T_{d}[a] (°C)	T_{d}[b] (°C)	RW[c] (%)	T_{g}[d] (°C)	T_{m} (°C)	ΔH_{m} (J·g^{-1})	T_{c} (°C)	ΔH_{c} (J·g^{-1})	T_{m} (°C)	ΔH_{m} (J·g^{-1})	T_{m} (°C)	ΔH_{m} (J·g^{-1})	
PHT	375	407	2.1	16	144	35	111	-28	139	29	151	46	152.6
$\mathrm{PHT_{90}Thx_{10}}$	366	408	3.0	9	133	34	95	-31	136	31	150	49	151.7
$\mathrm{PHT_{80}Thx_{20}}$	356	410	4.1	3	124	29	80	-27	124	27	128	37	133.7
$\mathrm{PHT_{70}Thx_{30}}$	344	411	4.2	-1	107	25	51	-23	107	23	114	32	133.3
$\mathrm{PHT_{60}Thx_{40}}$	340	410	3.5	-4	91	15	-	-	90	17	93	14	-
$\mathrm{PHT_{50}Thx_{50}}$	338	409	6.7	-9	68	16	-	-	-	-	68	20	-
PHThx	303	378	9.2	-20	73	30	-	-	-	-	72	33	-

TGA: [a]Temperature at which a 5% weight loss was observed in the traces recorded at 10 °C min^{-1}; [b]Temperature of maximum degradation rate. [c]Remaining weight after heating at 600ºC.

DSC: [d]Glass-transition temperature taken as the inflection point of the heating traces of melt-quenched samples recorded at 20 °C min^{-1}; [e]Melting (T_{m}) and crystallization (T_{c}) temperatures and their respective enthalpies (ΔH_{m}, ΔH_{c}) measured at heating/cooling rates of 10 °C min^{-1}; [f]Melting temperature and enthalpy after annealing at ~20 ºC below the melting temperature.

[g]Equilibrium melting temperatures of polyesters obtained by Hoffman-Weeks plot.

Although a common pattern of behavior is followed by all them, some differences associated to composition are noticeable: a) The onset decomposition temperature steadily decreases with the increasing content in tartrate units setting a difference of about 75 ºC between the two parent homopolyesters; b) The decomposition profile becomes more complex for high contents in Thx units due to the appearance of a shoulder at ~350 ºC corresponding to a second decomposition step that becomes more apparent for the PHThx homopolyester. The conclusion from the TGA analysis is that the thermal stability of PHT decreases with the insertion of Thx units although it remains at fully acceptable levels for usual handling and processing.

The DSC heating scans recorded for PHT$_x$Thx$_y$ samples coming directly from synthesis are shown in Figure 4 (left). All the polyesters display endothermic peaks characteristic of melting at temperatures decreasing from 144 ºC to 68 ºC along with apparent weakening and broadening as the content in Thx increased. The observed trend is indicative of the gradual loss of crystallite perfection and crystallinity caused by the presence of two different repeating units distributed at random along the polymer chain. In fact, a much better defined melting peak is displayed by the homopolyesters, particularly by PHThx demonstrating the crystallization ability of the Thx unit. Accordingly a minimum T_m should be expected at the surrounding of the 50% composition with values increasing as the composition moves towards any of the two parent homopolyesters.

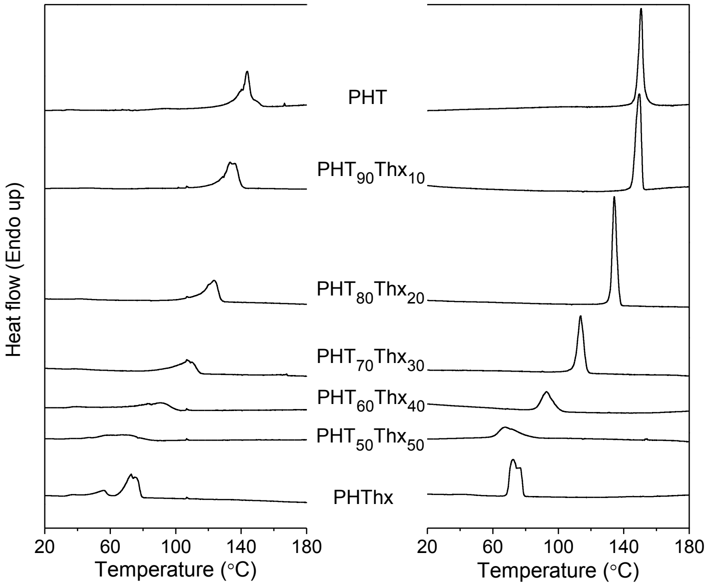


Figure 4. DSC traces of PHTxThxy copolyesters and PHT, PHThx homopolyesters. Original samples (left), and after annealing (right).

In order to see whether the amount and size of polyester crystallites are improved by thermal treatment, the polyesters were subjected to annealing. The efficiency of such treatment depends both on the inherent capability of chains to form large crystallites and on the wise selection of conditions. The annealing treatment was carried out at temperatures around 20ºC below melting temperatures for a period of time of 12 hours. As it is seen on the right part of Figure 4, the annealed copolyesters display much stronger and sharper peaks than untreated ones indicating that they are able to form homogeneous populations of crystals despite containing high amounts of Thx units (~30%).

The DSC measurements of samples quenched from the melt brought out the occurrence of a unique T_g for all PHT_xThx_y copolyesters in full agreement with their statistical microstructure. The T_g values decreased steadily with the increasing content in Thx tending to the -20 ºC displayed by the PHThx homopolyester. The observed trend is in accordance with expectations; the replacement of the highly rigid phenylene ring by the relatively more flexible 1,3-dioxolane cycle reduces the stiffness of the polymer chain and increases its mobility with the consequent decreasing in T_g.

3.3.3. Structure and isothermal crystallization

The X-ray diffraction analysis of copolyesters is in full agreement with the results afforded by DSC. The powder WAXS profiles recorded from PHT_xThx_y copolyesters and the two parent homopolyesters PHT and PHThx are depicted in Figure 5, and a list of the Bragg spacings measured on such profiles with qualitative indication of the observed intensities and crystallinities is provided in the ESM file. The presence of sharp scattering corroborated the semicrystalline nature of all polyesters regardless their composition. This is an outstanding result since copolyesters containing sugar-based cyclic units usually display crystallinity only for a restricted range of compositions. Furthermore, copolyesters of PHT containing isopropylene acetal tartrate units were reported to be amorphous for all compositions.[17,18] The exceptional ability of the cyclic methylene acetal structure to crystallize when inserted in a polymer chain had been observed previously for aliphatic polyamides.[19,23] Both the C_2 symmetry and the relatively small size of the unsubstituted dioxolane ring are surely the features favoring such behavior. Furthermore, a comparative study of aromatic copolyesters of PBT containing bicyclic sugar units replacing either the diacid or the diol showed that the crystallinity of the copolyesters was better preserved when the terephthalate unit was the replaced unit.[24]

A qualitative comparison of the spacings and intensities of the peaks observed in the profiles depicted in Figure 5 allows to conjecturing about the crystal structure adopted by the copolyesters. It should be noted that PHT is known to display a complex crystallization behavior involving at least three allomorphs (α, β and γ) that are generated together or more or less separately, depending on what crystallization conditions are applied;[25-27] such complexity makes difficult to identify the crystal structure of this polyester on the only basis of powdered diffraction patterns.

In spite of the different resolution displayed in each case, it is unquestionable that PHT and PHThx produced very dissimilar scattering profiles varying in both peak spacings and intensities, which is indicative that the two homopolyesters adopt different crystal structures, as it could be reasonably anticipated from their compositions. The copolyesters containing between 30 and 50% of Thx produced very similar profiles with almost identical spacings and intensities indicating that the same crystalline structure must be shared by all of them.

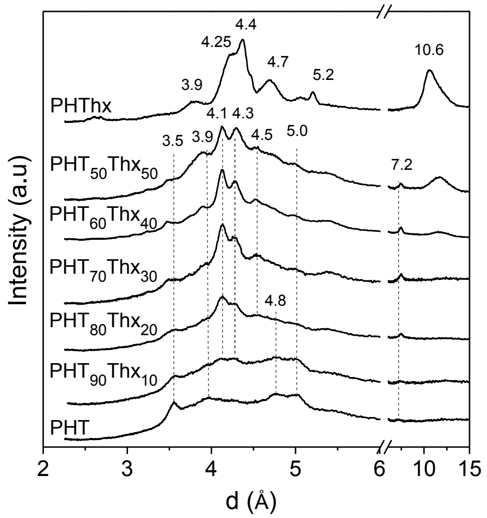


Figure 5. WAXS profiles of PHT_xThx_y copolyesters and their parent homopolyesters recorded from powder samples without any previous thermal treatment.

On the other hand, the scattering produced by $PHT_{90}T_{10}$ is almost coincident to that of PHT but due to the poor resolution displayed in these two cases, their comparison with the other profiles is not straightforward. Nevertheless some minor differences in spacing and relative intensities between the two groups are detected (see details in ESM). This is a behavior differing clearly from that exhibited by other sugar-based PHT systems previously studied by us, in which the shape of diffraction pattern of PHT was strictly maintained for the whole set of copolyesters.[13] In those cases, the sugar-based units were unable to cocrystalize and in consequence segregated from the crystal lattice to the amorphous phase. The results obtained for PHT_xThx_y copolyesters with high contents in Thx suggest that the two diacidic comonomers may be crystallized together in a new structure dissimilar to that of PHT. Obviously further research is needed to draw more definite conclusions in this regard.

Although the DSC analysis of pristine samples showed that all the copolyesters are semicrystalline, only those containing up to 30% of Thx were able to crystallize upon cooling from the melt. The crystallized polymers showed melting temperatures and enthalpies very close to those displayed by the original samples indicating that a similar degree of crystallinity has been reached (Table 3). To evaluate quantitatively the effect of composition on crystallizability, a comparative isothermal crystallizationstudy of the copolyesters containing 10, 20 and 30 % of Thx in addition to PHT, was carried out by DSC. Powder samples were previously melted under exactly the same conditions and left to crystallize at the selected temperatures. The Avrami treatment of crystallization data making use of the popular equation,

$$X_t = e^{-kt^n}$$

(where X_t is the crystalline volume fraction formed a time t, and k and n are the well-known Avrami constants) afforded the kinetics parameters listed in Table 4, and the relative crystallinity *vs* crystallization time plots as well as the double logarithmic plots from which such data were extracted, are available in the ESM file linked to this article.

Table 4. Isothermal crystallization data of PHT and PHT$_x$Thx$_y$ copolymers.

Polyester	T_c (ºC)[a]	ΔT (ºC)[b]	t_0 (min)[c]	$t_{1/2}$ (min)[d]	n[e]	-Lnk[f]	T_m(ºC)[g]
PHT	115	29	0.16	0.83	2.11	0.40	141.2
	120	24	0.40	1.70	2.54	5.19	142.7
PHT$_{90}$Thx$_{10}$	110	23	0.24	1.78	1.83	1.19	133.0
	115	18	0.39	3.31	2.24	2.63	135.1
	120	13	0.49	12.33	2.56	6.60	137.5
PHT$_{80}$Thx$_{20}$	100	24	0.57	3.98	2.07	2.82	124.2
	105	19	0.69	9.20	2.22	5.05	125.1
	110	14	1.57	13.41	2.25	5.87	127.1
PHT$_{70}$Thx$_{30}$	80	27	0.30	3.80	1.74	2.53	104.6
	85	22	0.59	7.03	2.28	4.63	107.4
	90	17	0.91	13.50	2.33	6.30	110.0

[a] Crystallization temperature. [b] $\Delta T = T_m - T_c$. [c] Onset crystallization time. [d] Crystallization half-time $t_{1/2}$. [e] Avrami exponent n. [f] Kinetic rate constant k (min^{-1}). [g] Melting temperature after crystallization.

A comparison of the values listed in Table 4 leads to the overall conclusion that lower temperatures and longer periods of time are required for the crystallization of polyesters with higher contents in Thx units. The Avrami exponent was within the 1.7-2.5 interval with values for each polyester steadily increasing with crystallization temperature. Such values around to 2 are lower than usually found for other related polyesters[13a,20,28] containing cyclic sugar units and they suggest that crystallization happened in this case following a stronger two-dimensional growing trend.

Unfortunately the isothermal crystallization of the copolyesters could not be studied at the same T_c due to the large differences in crystallization rates displayed by them and to the short range of temperatures at which the crystallization process is measurable by DSC. Actually only $PHT_{90}Thx_{10}$ and $PHT_{80}Thx_{20}$ could be compared at the same T_c of 110 ºC ascertaining the dependence of crystallizability on composition. The isothermal crystallization plots of these two copolyesters are compared in Figure 6 illustrating vividly the rate delay in the crystallization of $PHT_{80}Thx_{20}$ consequent to its higher content in Thx units. The equilibrium melting temperature of the isothermally crystallized polyesters could be estimated by application of the Hoffman-Weeks graphical method (see ESM file) and the resulting values are given in Table 3 to compare with other T_m values obtained out of thermodynamic equilibrium conditions.

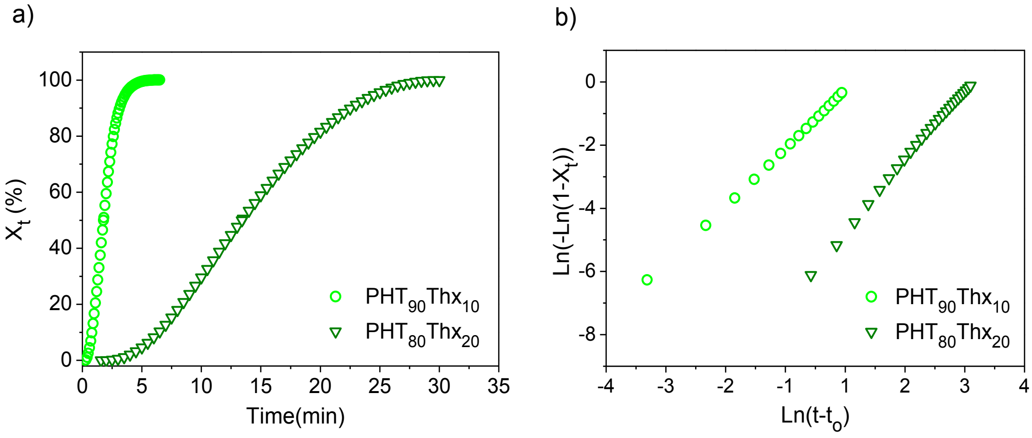


Figure 6. Compared isothermal crystallization conducted at 110 ºC of $PHT_{90}Thx_{10}$ and $PHT_{80}Thx_{20}$ copolyesters. a) Relative crystallinity *vs* crystallization time. b) Double logarithmic Avrami plot.

3.3.4. Hydrolytic and enzymatic degradability

To evaluate the influence of the tartrate units on the hydrodegradability and biodegradability of PHT derived copolyesters, a comparative hydrolytic study of $PHT_{70}Thx_{30}$ copolyester and the PHT homopolyester was carried out both in absence and presence of enzymes.

Hydrolytic degradation experiments were performed in aqueous buffer, under mild as well as aggressive conditions (37 ºC, pH 5.0 and 80 ºC, pH 2, respectively). The change in sample weight taking place in these experiments along an incubation period of 8 weeks is plotted against time in Figure 7a. As it was expected not weight loss was observed for PHT under whichever condition used; the extreme reluctance of this polyester to hydrolysis is a well known fact severally reported by us in recent related papers.[13a,21a,28] On the contrary, $PHT_{70}Thx_{30}$ showed an appreciable weight loss with a degradation rate depending on pH and temperature; the noteworthy result is the significant degradation (around 15% of weight loss) that the copolyester is able to undergo when it is incubated under soft conditions, which strongly contrasts with the hydrolytic inertness displayed by PHT.

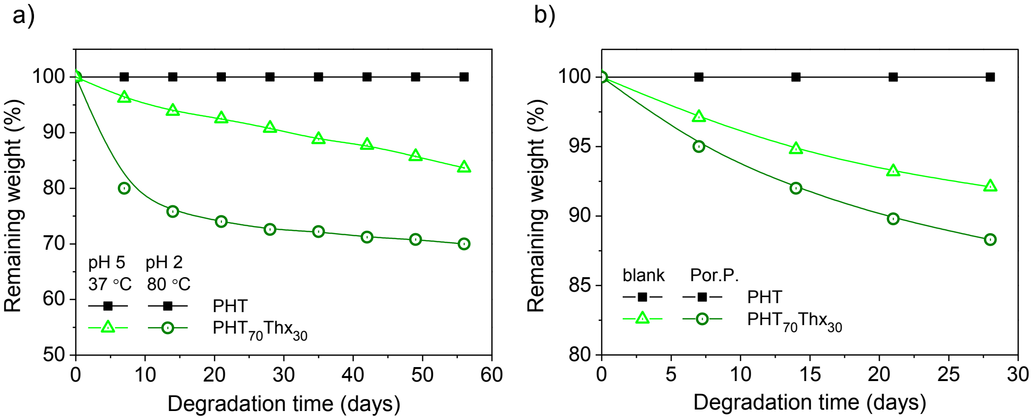


Figure 7. Remaining weight *vs* incubation time for PHT and $PHT_{70}Thx_{30}$ subjected to hydrolytic degradation under the indicated conditions. a) In the absence of enzymes; b) with added porcine pancreas lipases.

The presence of enzymes still enhanced the degradability of $PHT_{70}Thx_{30}$ as it is illustrated in Figure 7b, where the sample weights remaining after incubation for several weeks under physiological conditions, in the absence and presence of porcine pancreas, are compared. Although the effect is moderate, the degradation of the copolyester was clearly enhanced when enzymes were added to the incubation medium. On the contrary, no effect was perceived on PHT whose initial weight remained essentially unchanged along the whole incubation period.

The analysis by SEM of samples of copolyesters before and after incubation afforded valuable insight into the mechanism operating in the degradation process. A selection of pictures is presented in Figure 8 to illustrate the morphological alterations that take place in the $PHT_{70}Thx_{30}$ film upon degradation under different conditions. Apparently, the original film has a spherulitic texture composed of spherulites of diameter close to 0.5 mm with significant amounts amorphous material deposited on their surfaces. The interspherulitic material is very scarce and large empty spaces are frequent between spherulites (Figure 8a). The degradation process under mild conditions with or without enzymes evolves in a similar manner with spherulites becoming cracked but retaining their initial morphology (Figure 8b). On the contrary, degradation at pH 2 at 80 ºC appears to proceed essentially by an eroding mechanism with superficial deterioration of the spherulite shape and releasing of non-soluble material that remains deposited on the surroundings (Figure 8c); after longer incubation time, spherulites disappeared and only dispersed minute particles of material are observed in the pictures (Figure 8d). Complementary SEM micrographs showing the morphological changes accompanying the hydrolytic degradation of the PHT$_{70}$Thx$_{30}$ copolyester are provided in the ESM file.

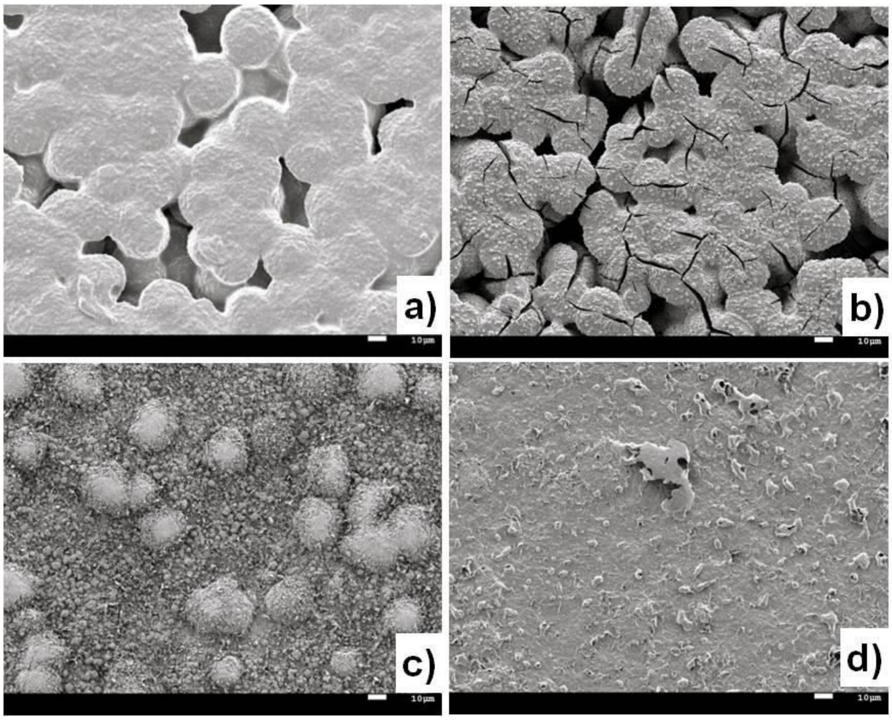
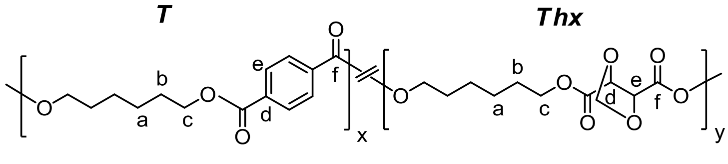


Figure 8. SEM micrographs of PHT$_{70}$Thx$_{30}$ copolyester subjected to hydrolytic degradation. a) Initial sample; b) After incubation for two weeks at pH 7.4, 30 ºC with lipases added; c,d) After incubation at pH 2, 80 ºC for two and eight weeks, respectively.

The ^{1}H NMR analysis of incubated PHT$_{70}$Thx$_{30}$ clearly showed that the tartrate units are very prone to undergo hydrolytic degradation and it must be therefore the reason for the enhanced degradability displayed by these copolyesters. The ^{1}H NMR spectrum of the residue left by the sample after one week of incubation at pH 2, 80 ºC, showed that more than 70% of the tartrate units were missing in the polymer (Figure 9a).



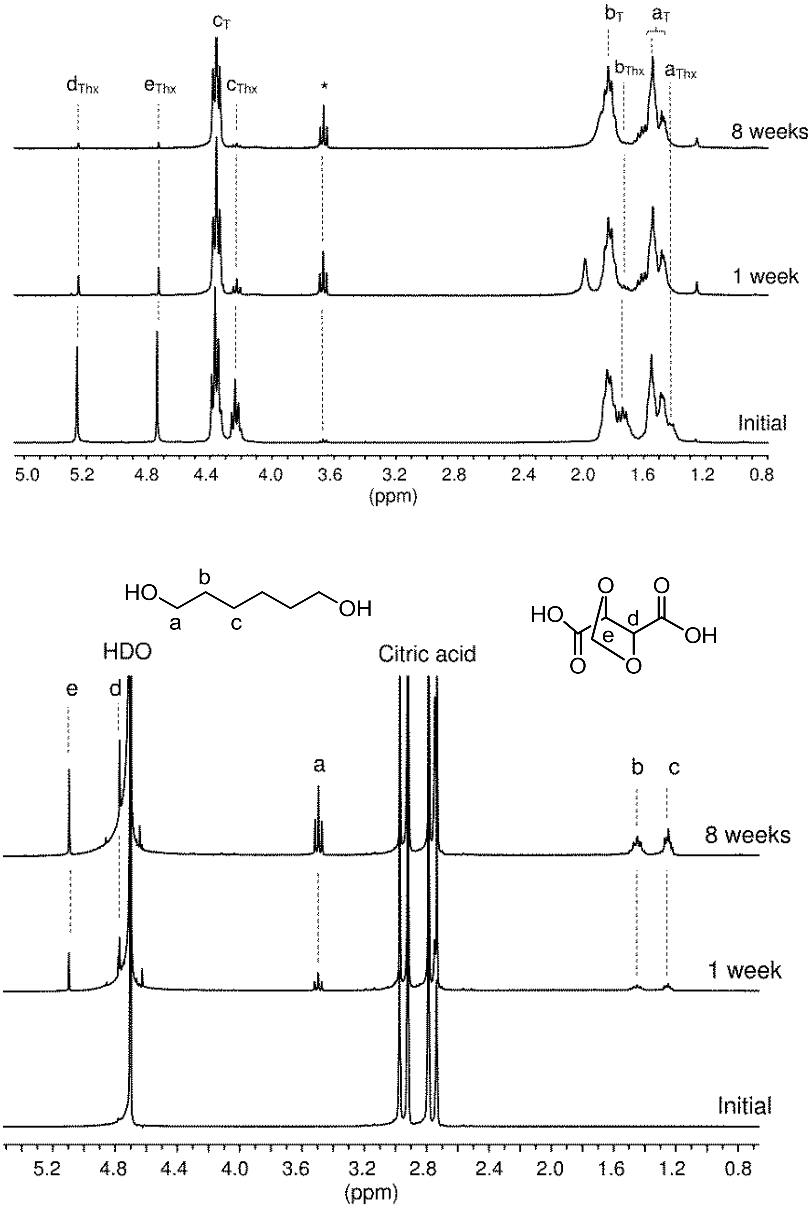


Figure 9. ^{1}H NMR spectra of $PHT_{70}Thx_{30}$ and degraded samples incubated at pH 2, 80ºC; a) Degraded residue. (*) CH_2OH end groups. b) Degradation products released to the aqueous medium.

This amount increased to more than 95% after eight weeks of incubation. Furthermore, the spectrum contains a triplet at 3.65 ppm whose intensity significantly increases with time. This signal is attributable to the α-methylene of hydroxyl ending chains and their occurrence indicative of the decreasing in molecular weight resulting from the hydrolysis of the tartrate ester bonds. The ^{1}H NMR spectrum of the products released to the incubation medium revealed the presence of only hexanediol and acetalized tartaric acid (Figure 9b). Presumably, oligomeric species generated in the hydrolysis were non-water soluble and remained deposited in the residue.

3.4. Conclusions

3.5. References

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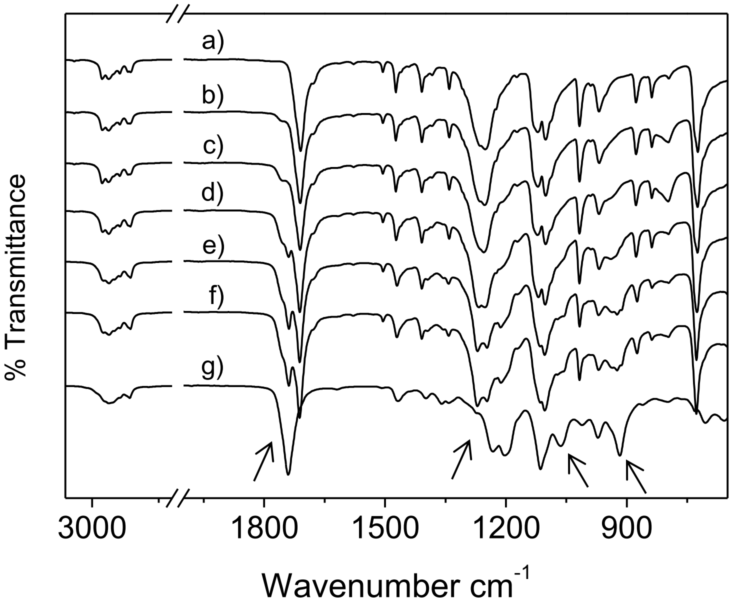
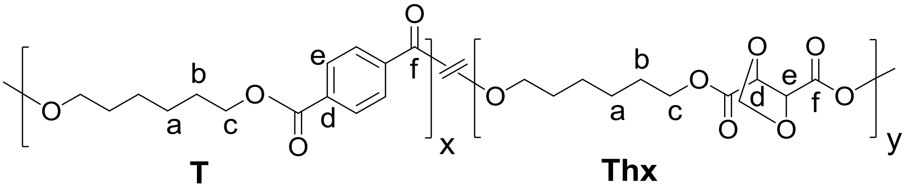
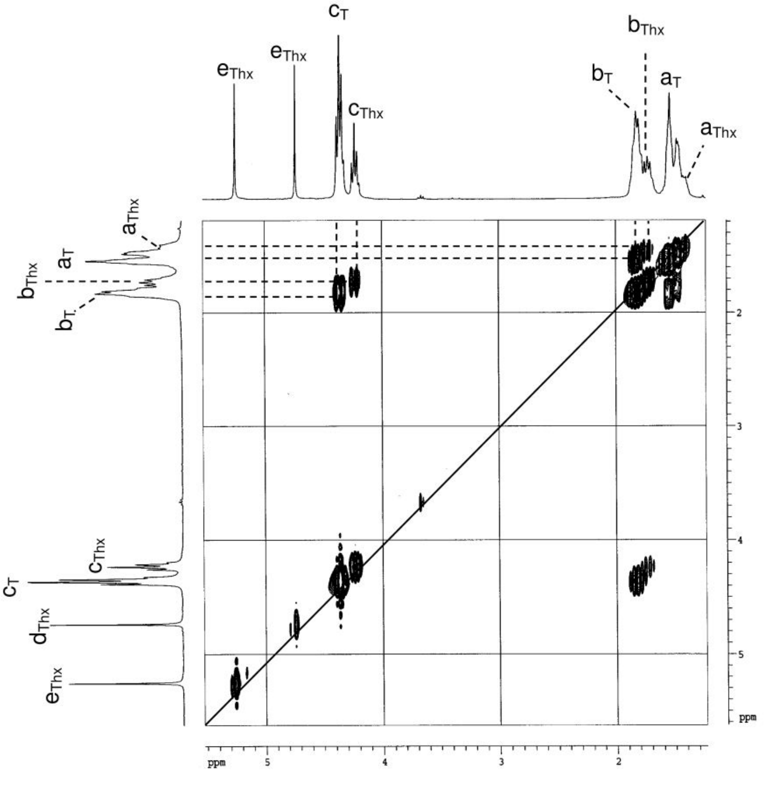
Supporting information

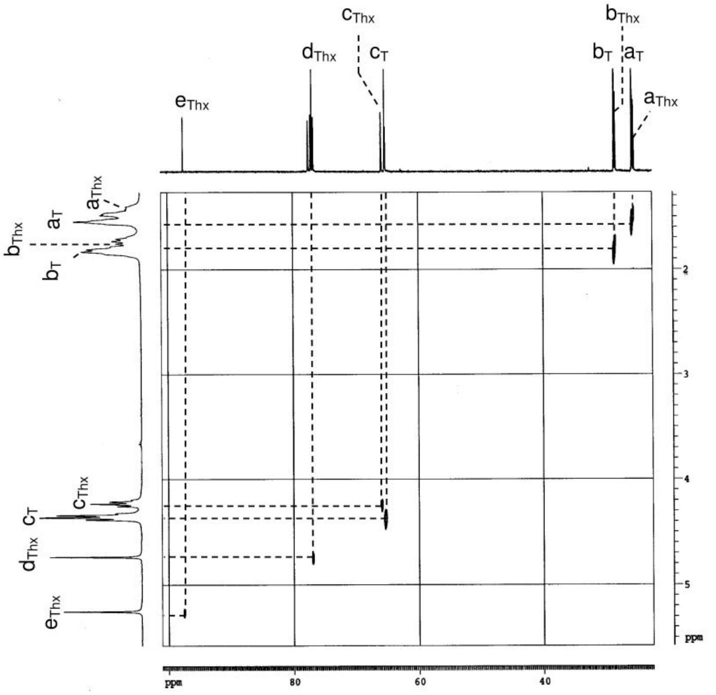


SI-Figure 1. Compared FT-IR spectra for a) PHT, b) $PHT_{90}Thx_{10}$, c) $PHT_{80}Thx_{20}$, d) $PHT_{70}Thx_{30}$, e) $PHT_{60}Thx_{40}$, f) $PHT_{50}Thx_{50}$ and g) PHThx. In shadows, absorptions due to tartrate units increasing with their contents in the copolyester.





SI-Figure 2. ^{1}H-^{1}H COSY NMR spectrum of PHT$_{70}$Thx$_{30}$.

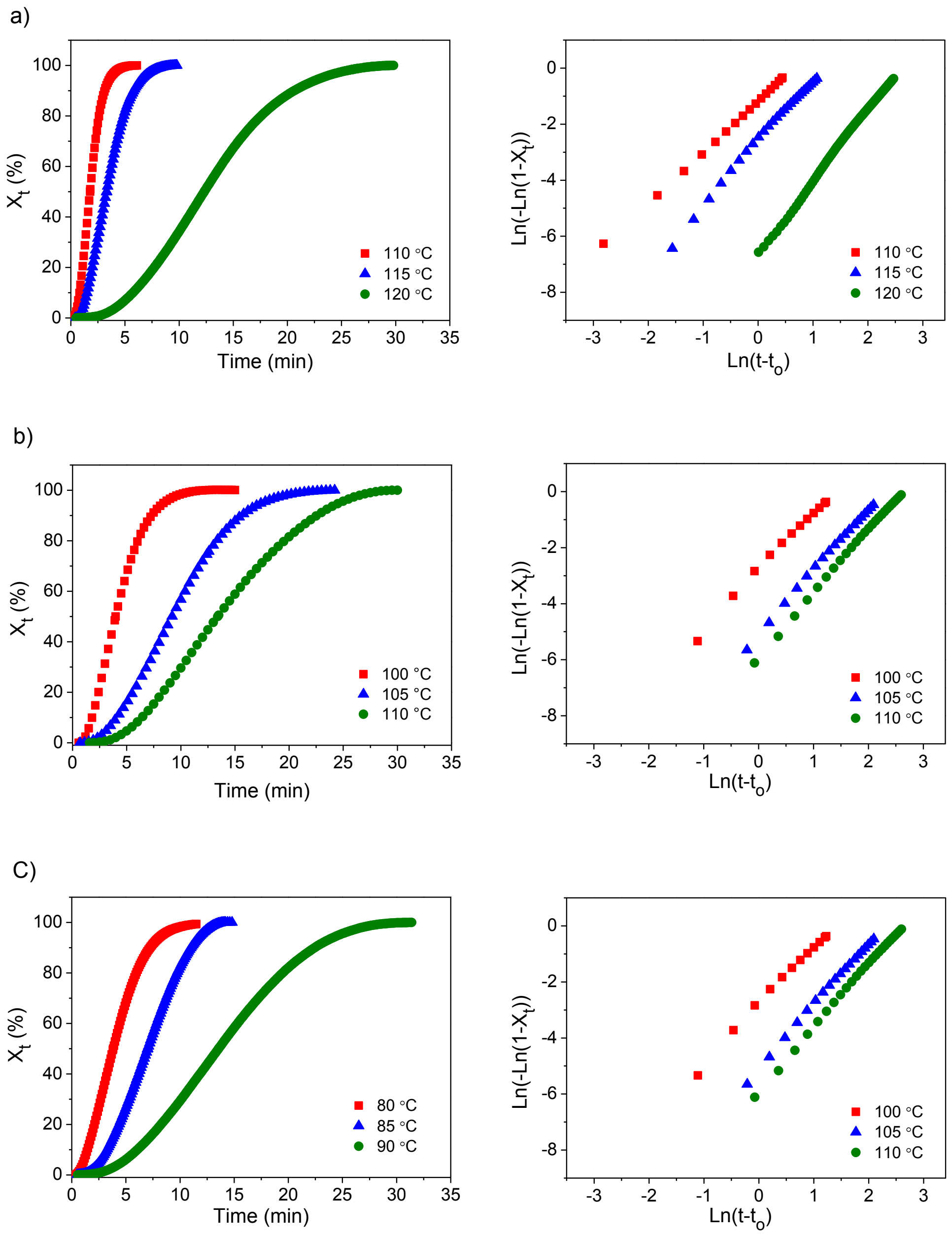


SI-Figure 3. ^{1}H-^{13}C HETCOR NMR spectrum of PHT$_{70}$Thx$_{30}$.

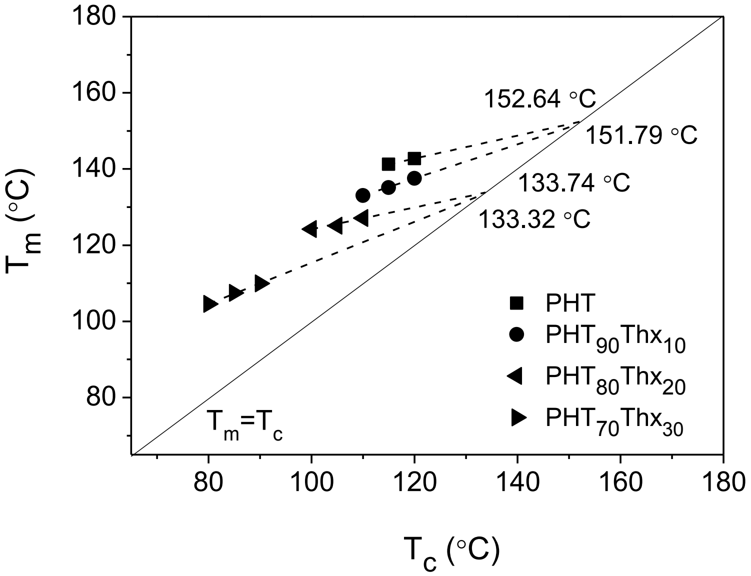
SI-Table 1. Solubility of PHT$_x$Thx$_y$

Polymer	H_2O, EtOH, Et_2O	DMSO	DMF	THF, NMP	$CHCl_3$	HFIP, TFA, DCA
PHT	-	-	-	-	+	+
PHT$_{90}$Thx$_{10}$	-	-	-	-	+	+
PHT$_{80}$Thx$_{20}$	-	-	-	-	+	+
PHT$_{70}$Thx$_{30}$	-	-	-	+	+	+
PHT$_{60}$Thx$_{40}$	-	-	-	+	+	+
PHT$_{50}$Thx$_{50}$	-	-	±	+	+	+
PHThx	-	+	+	+	+	+

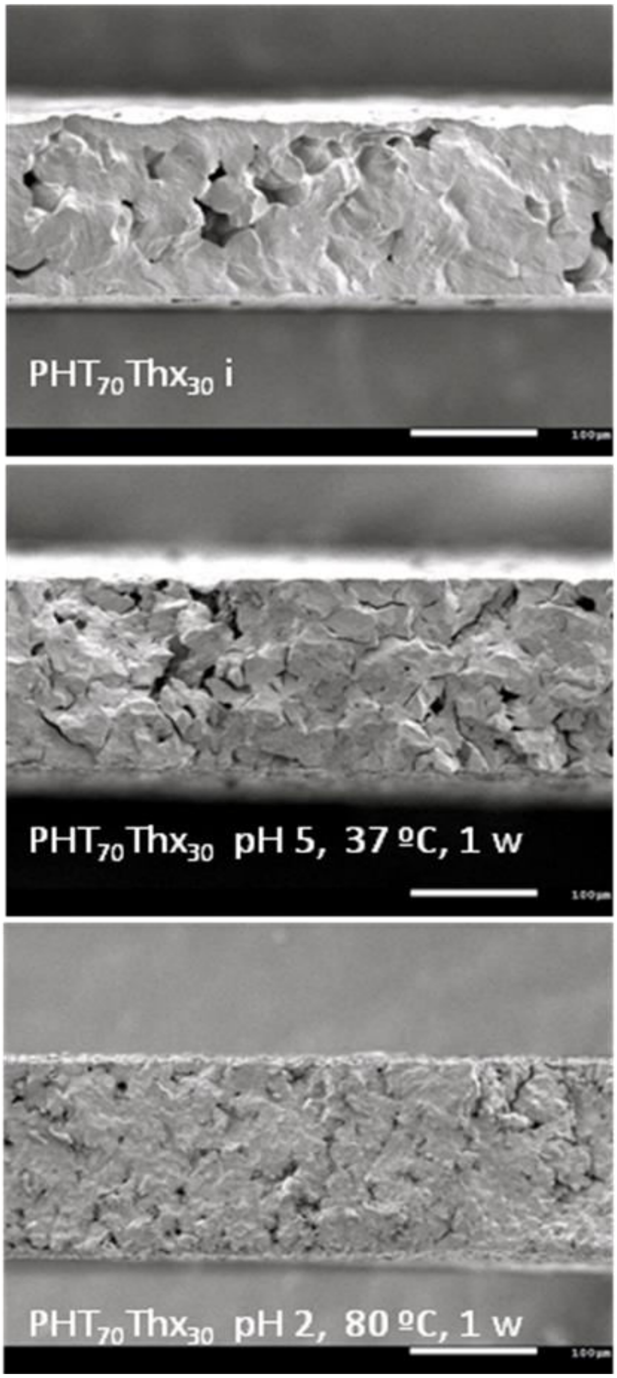
(+) Soluble at room temperature; (±) partial; (-) insoluble; THF (tetrahydrofuran); DMSO (dimethyl sulfoxide); DMF (*N,N′*-dimethylformamide); NMP (1-methyl-2-pyrolidone; THF (tetrahydrofuran); TFA (trifluoroacetic acid); DCA (dichloroacetic acid), HFIP (hexafluoroisopropanol).



SI-Figure 4. Compared isothermal crystallization of PHT_xThx_y copolyesters: Left: Relative crystallinity vs crystallization time. Right: Double logarithmic Avrami plot. a) $PHT_{90}Thx_{10}$; b) $PHT_{80}Thx_{20}$; c) $PHT_{70}Thx_{30}$.



SI-Figure 5. Hoffman-Weeks plot for isothermally crystallized PHT, $PHT_{90}Thx_{10}$ and $PHT_{80}Thx_{20}$ and $PHT_{70}Thx_{30}$ polyesters.



SI-Figure 6. Edge-on SEM micrographs of $PHT_{70}Thx_{30}$ before and after degradation under the indicated conditions

SI-Table. 1. Powder X-ray diffraction data of polyesters.

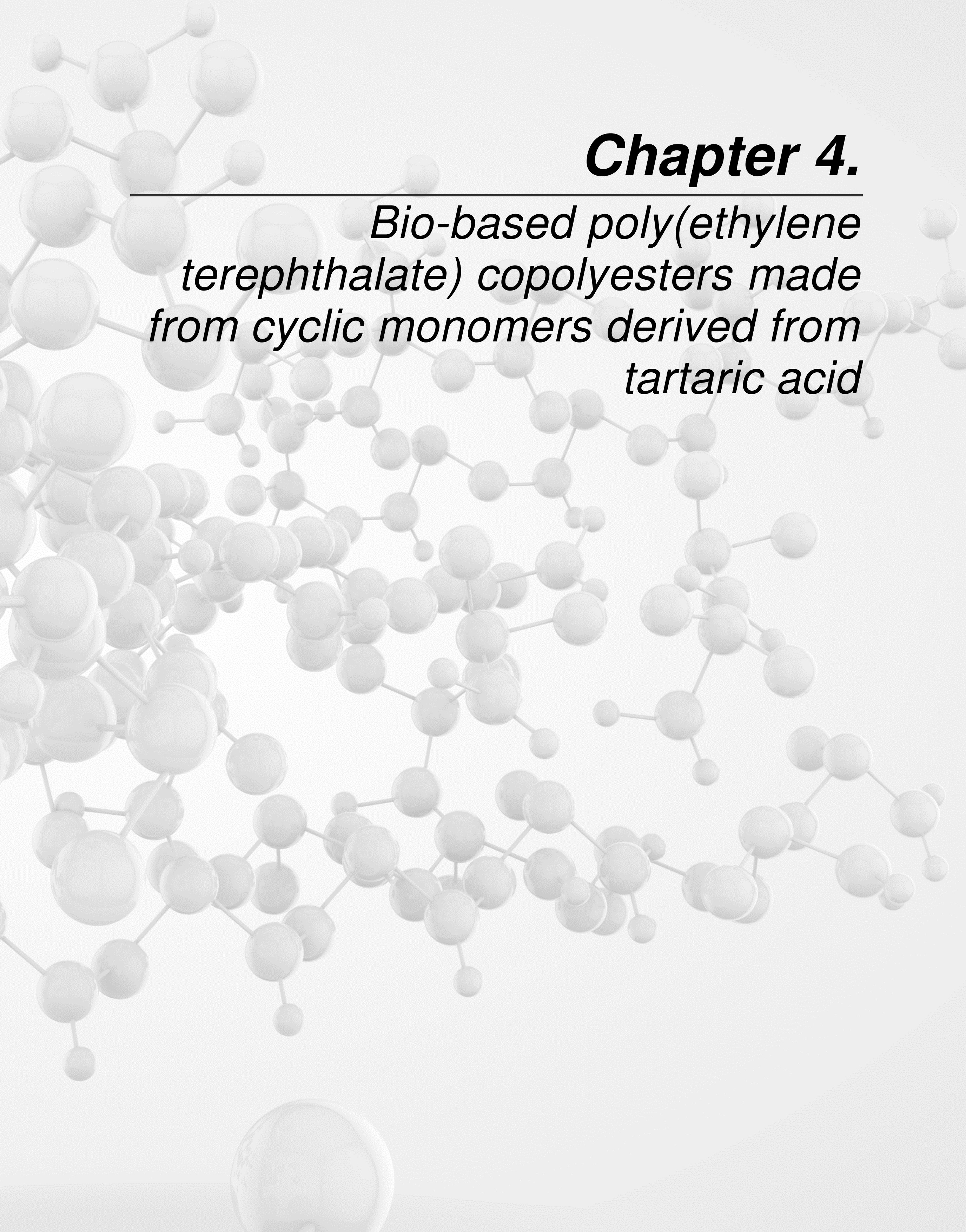
Polyester	d_{hkl} [a] (Å)															X_c [b]
PHT			7.2w	5.4w		5.0m		4.8m			4.25w	4.10w	3.95m	3.55s		0.42
$PHT_{90}Thx_{10}$			7.2w	5.4w		5.0m		4.8m			4.30w	4.10w	3.95w	3.55m		0.40
$PHT_{80}Thx_{20}$			7.4w	5.4w		5.0w		4.8w	4.55w		4.30m	4.15m	3.95w	3.50m		0.38
$PHT_{70}Thx_{30}$			7.5w	5.4w		5.0w		4.8w	4.55w		4.30m	4.15s	3.95w	3.50m		0.34
$PHT_{60}Thx_{40}$	11.6		7.5w	5.4w		5.0w		4.8w	4.55w		4.30m	4.15s	3.90m	3.50w	3.25w	0.20
$PHT_{50}Thx_{50}$	11.7		7.5w	5.4w		5.0w		4.8w	4.55w		4.30s	4.15s	3.90m	3.50w	3.25w	0.19
PHThx		10.6			5.20	5.0w	4.7		4.50m	4.40s		4.25s	3.85m			0.39

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

[b] Crystallinity index calculated as the quotient between crystalline area and total area. Crystalline and amorphous areas in the X-ray diffraction pattern were quantified using PeakFit v4.12 software.

Chapter 4.

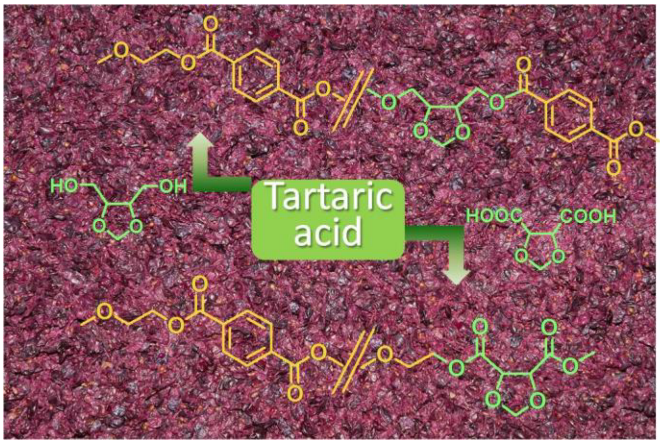
Bio-based poly(ethylene terephthalate) copolyesters made from cyclic monomers derived from tartaric acid



Bio-based poly(ethylene terephthalate) copolyesters made from cyclic monomers derived from tartaric acid

Abstract

Two cyclic acetal compounds, 2,3-*O*-methylene L-threitol and dimethyl 2,3-*O*-methylene L-threarate, both coming from naturally-occurring tartaric acid, were used as comonomers to replace ethylene glycol and dimethyl terephthalate respectively, in the preparation of PET-based copolyesters by polycondensation in the melt. Synthesis results, structure and thermal properties of the two afforded copolyester series were evaluated and compared regarding composition and type of comonomer used in each case. All the copolyesters had a random microstructure and molecular weights in the 25,000-35,000 g·mol^{-1} range. Their thermal properties varied logically with composition along each series but they significantly changed according to which acetal comonomer was used. PET copolyesters made from acetalized L-threitol displayed thermal stability and T_g comparable to PET, whereas these two properties were depressed in the copolyesters containing threarate units. Both types of copolyesters were able to crystallize for contents in tartaric acid derived units up to around 30% by adopting the crystal structure of PET. Crystallization rates and melting temperatures decreased with copolymerization in the two series but this effect was more noticeable in copolyesters made from threitol.



Publication derived from this work:

C. Japu, A. Martínez de Ilarduya, A. Alla and S. Muñoz-Guerra, “Bio-based poly(ethylene terephthalate) copolyesters made from cyclic monomers derived from tartaric acid”, *Polymer,* 2014, **55**, 2294.

4.1. Introduction

The interest in carbohydrate derivatives as monomers for polycondensation to bio-based polymers has grown greatly in these last years.[1] Carbohydrates are very well positioned feedstock because they are yearly renewable and easily available, they occur in a wide variety of structures, and are fully biodegradable. Carbohydrates are however multifunctional compounds that need certain chemical protection in order to avoid branching or cross-linking reactions. Although some linear polymers have been synthesized using carbohydrate-based monomers bearing more than two reactive functions,[2,3] most of the synthesis reported to date have been carried out with derivatives in which the secondary hydroxyl groups were protected by either etherification or esterification.[4,5]

Protection of alditols and aldaric acids by internal cyclization is a very convenient method when stiffness of the resulting polymer is prioritary. Internally anhydridized alditols (isohexides)[6] as well as diacetalized alditols and aldaric acids are bicyclic compounds that have been extensively explored as suitable monomers for replacing alkanediols and dicarboxylic acids in both aliphatic and aromatic polyesters.[7] The resulting polymers have a bio-based grade depending on composition, and they are distinguished by displaying high T_g, good thermal stability and satisfactory mechanical behavior.[8] The outstanding capacity of these bicyclic monomers to enhance T_g is manifested not only on flexible aliphatic polyester but also on the highly rigid poly(ethylene terephthalate) (PET) and poly(butylene terephthalate (PBT) aromatic polyesters. Moreover some susceptibility to biodegradation is displayed by all these copolyesters according to their content in carbohydrate units and their configuration.[8c] Although monocyclic monomers are also rigid, they are expected to be less effective in providing chain stiffness due to their less bulkiness, a difference that will become more apparent when they are used to replace the terephthalate units in aromatic polyesters. An exceptional situation is however observed for 2,5-furandicarboxylic acid (FDCA), which is a monocyclic structure but of aromatic nature. In fact this compound is able to replace terephthalic acid in PET and PBT without significant alteration of T_g.[9,10]

This paper describes the synthesis, chemical characterization and thermal properties of bio-based PET copolyesters containing 1,3-dioxolane units derived from tartaric acid. Two series, namely PE_xThx_yT and PET_xThx_y, corresponding respectively to which monomer, ethylene glycol (EG) or dimethyl terephthalate (DMT) is replaced, are studied. The bio-based monomers used in these copolymerizations are 2,3-*O*-methylene-L-threitol (Thx-diol) and dimethyl 2,3-*O*-methylene-L-tartrate (Thx-diester), two monocyclic acetal compounds obtained from L-tartaric acid (Scheme I). Thx monomers are attractive because of their good accessibility and also because the 1,3-dioxolane cyclic structure is well stable to both temperature and hydrolysis.

Scheme 1. Chemical formulae of tartaric acid derived monomers.

Tartaric acid (TA) is the common name of L-(+)-threaric acid, a low-cost naturally-occurring compound present in many fruits, and that is also formed in the grape juice fermentation, becoming a surplus byproduct of the wine industry. The chemistry of TA is well settled, and a wide diversity of derivatives is today available through relatively simple synthetic routes. Acyclic monomers derived from TA have been extensively used in the synthesis of both aliphatic and aromatic polycondensates such as polyamides,[11] poly(ester amide)s,[12] polyurethanes[13] and polycarbonates.[14] On the contrary the account of cyclic TA compounds used in polycondensation is much more limited. A couple of polytartaramides made from 2,3-*O*-methylene tartaric acid[15] and a family of copolyesters made from either threitol or threaric acid with the secondary hydroxyl groups protected as isopropylene acetal are the only known examples of aliphatic polycondensates containing TA units.[16] In addition the effect that the insertion of acetalized tartrate and threitol units exerts on the properties of aromatic polyesters has been examined recently in poly(hexamethylene terephthalate) and poly(butylene terephthalate copolyesters), respectively.[17] It was found that these copolyesters displayed lower or higher T_g than the parent homopolyester in accordance with which unit, diacid or diol, was replaced by copolymerization. Both series were more hydrodegradable than the homopolyesters and the copolyesters containing tartrate units showed certain biodegradability when subjected to the action of lipases. No study has been carried out yet to appraise the differences in properties that will arise when either the diol or the diacid units are replaced by acetalized threitylene or tartrate units in the same aromatic polyester.

In the present work, PET copolyesters resulting from replacing either EG or DMT by monocyclic Thx units are examined throughout a detailed comparative study that emphasizes the modification produced in thermal properties by copolymerization. PET is the most important polyester produced today with a set of properties that makes it the thermoplastic of choice for a wide diversity of applications. Nevertheless some properties of PET, specifically thermal properties, need to be improved in order to satisfy new demanding applications. The melting temperature (T_m) and glass-transition temperature (T_g) of PET are around 250 ºC and 80 ºC, respectively. A higher T_g will make PET more suitable for applications such as hot-filling bottles and high-barrier films, and a moderately lower T_m would render an easier and cheaper processing of this polyester.[18,19] Furthermore a greater susceptibility to hydrolysis and biodegradation would add merits to the use of PET in temporal applications and would facilitate its chemical recycling.

4.2. Experimental section

4.2.1. Materials and methods

Materials

Ethylene glycol (EG) (99%), dimethyl terephthalate (DMT) (99%), dibutyl tin oxide (DBTO, 98%), dimethyl L-tartrate and paraformaldehyde were purchased from Sigma-Aldrich. *Irganox 1010* and *Irgafos 126* antioxidants were generous gifts from BASF. Sodium trifluoroacetate (98%) used to stabilize 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was also purchased from Sigma-Aldrich. The solvents used for purification and characterization, such as chloroform, trifluoroacetic acid (TFA), methanol, diethyl ether, dichloracetic acid (DCA) and HFIP, were high purity grade and used as received.

Methods

Intrinsic viscosities were measured in DCA using an Ubbelohde microviscometer thermostated at 25 ± 0.1 ºC with polymer concentrations ranging from 0.3 to 1 $g\cdot dL^{-1}$. Molecular weights were determined by GPC using a Waters equipment provided with a RI detector. HFIP containing sodium trifluoroacetate (6.8 $g\cdot L^{-1}$) was the mobile phase. 100 μL of 0.1% (w/v) sample solution were injected and chromatographed with a flow of 0.5 $mL\cdot min^{-1}$. A PL HFIP gel 300 x 7.5 mm column protected with a pre-column was used at 35 ºC. Molar mass averages and their distributions were calculated against PMMA standards.

^{1}H and ^{13}C NMR spectra were recorded at 25 ºC using a Bruker AMX-300 spectrometer operating at 300.1 and 75.5 MHz, respectively. Samples were prepared by dissolving the polymer in either trifluoroacetic acid or a mixture of deuterated chloroform:trifluoroacetic acid (9:1). The spectra were internally referenced with tetramethylsilane. For ^{1}H and ^{13}C analyses ~10 and ~50 mg of sample in 1 mL of solvent were respectively used. Sixty-four scans were recorded for ^{1}H, and between 5,000 and 15,000 scans were taken for ^{13}C with 32 and 64 K data points and relaxation delays of 1 and 2 s, respectively. ^{13}C-^{1}H heteronuclear shift correlation (HETCOR) two-dimensional spectra were recorded by means of the *hxco* pulse sequence implemented in the Bruker NMR instrument package.

Thermogravimetric analysis was carried out in a nitrogen atmosphere with a Perkin-Elmer TGA 6 thermobalance. Polymer samples with an approximate mass of 10 mg were degraded between 30 to 600 ºC at a heating rate of 10 $ºC\cdot min^{-1}$.

The thermal behavior of the polymers was examined by differential scanning calorimetry (DSC) using a Perkin-Elmer Pyris 1 apparatus. Thermograms were obtained from 4-6 mg samples under a nitrogen flow of 20 mL·min^{-1}. Indium and zinc were used as standards for temperature and enthalpy calibrations. The melting temperature (T_m) was taken as the maximum of the endothermic peak appearing on heating traces recorded at 10 ºC·min^{-1}, and the glass transition temperature (T_g) was taken as the inflection point seen on heating traces recorded at 20 ºC·min^{-1} from samples quenched from the melt.

Wide angle X-ray diffraction (WAXD) profiles were recorded on the PANalytical X'Pert PRO MPD θ/θ diffractometer using the Cu-Kα radiation of wavelength 0.1542 nm from powder samples coming directly from synthesis or after annealing treatment.

4.2.2. Synthesis of monomers

Dimethyl 2,3-O-methylene-L-tartrate (Thx-diester) was synthesized following the procedure described by Marin *et al.*[13] To a mixture of commercial dimethyl L-tartrate (40 g) and paraformaldehyde (40 g) heated at 60 ºC, 98% sulfuric acid (40 mL) was added dropwise under stirring, and the agitation continued until complete dissolution. The reaction solution was then repeatedly extracted with chloroform and the organic phase successively washed with 25% aqueous ammonia solution and water, and finally dried over anhydrous sodium sulfate. The solution was evaporated to dryness and the residue distilled under vacuum (0.1 bar, 100 ºC) to obtain dimethyl 2,3-*O*-methylene-L-tartrate as an oily colorless product (16 g, 50% yield).

2,3-O-methylene-L-threitol (Thx-diol) was obtained from the dimethyl ester according to the following procedure: To an ice cooled dispersion of $LiAlH_4$ (11 g, 0.3 mol) in dried diethyl ether (200 mL) a solution of dimethyl 2,3-*O*-methylene-L-tartrate (25 g, 0.13 mol) in dried diethyl ether (130 mL) was added dropwise under vigorous stirring in an inert atmosphere, and the mixture left under agitation overnight at room temperature. The flask was reintroduced in the ice bath and water (10 mL), 15% NaOH solution (10 mL) and water (60 mL) were successively added dropwise. The mixture was left under stirring for one hour at room temperature, filtered and extensively washed with warm acetone. The filtrates were pooled, concentrated, and the residue distilled under vacuum (0.1 bar, 105°C). The 2,3-*O*-methylene-L-threitol was collected as a yellowish oil (9.5 g, 53% yield).

4.2.3. Synthesis of polyesters and copolyesters

Homopolyesters (PET, PThxT, PEThx) as well as PE_xThx_yT and PET_xThx_y copolyesters were synthesized through a two-stage polymerization process carried out in the bulk. The reaction was performed in a three-necked, cylindrical-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum distillation outlet. PET homopolyester was obtained from ethylene glycol and dimethyl terephthalate and PThxT and PEThx homopolyesters from mixtures of 2,3-*O*-methylene-L-threitol, and dimethyl terephthalate, and ethylene glycol and dimethyl 2,3-*O*-methylene-L-tartrate, respectively. PE_xThx_yT copolyesters were obtained from dimethyl terephthalate and mixtures composed of ethylene glycol and 2,3-*O*-methylene-L-threitol, and PET_xThx_y copolyesters from ethylene glycol and mixtures of dimethyl terephthalate and 2,3-*O*-methylene-L-tartrate. In the abbreviated name of these copolyesters *x* and *y* subscripts indicate the mol percentage (mol-%) of the comonomers (ethylene glycol or dimethyl terephthalate and Thx-diol or Thx-diester) that entered in the copolyester upon polycondensation.

The copolyesters were synthesized by using a molar ratio of 1.5/1 and 2.2/1 of diols to dimethyl esters for PE_xThx_yT and PET_xThx_y respectively. The excess of diols respect to diesters was used to ensure the complete transesterification of all methyl ester groups which is known to favor the further growth of the polymer chain. This is a common practice that is applied at both laboratory and industrial scale. 0.5% DBTO respect to DMT (mol/mol) was used as catalyst. Antioxidants *Irganox 1010* (0.1% w/w) and *Irgafos 126* (0.3% w/w) were added to the mixture at the beginning of the polymerization reaction to minimize degradation of the thermally-sensitive sugar-derived monomers. The apparatus was vented with nitrogen several times at room temperature to avoid oxidation by air during polymerization. The transesterification reaction was carried out under a low nitrogen flow at slightly over atmospheric pressure whereas polycondensation was conducted under a 0.03-0.06 mbar vacuum. Temperatures were increased from 160-180 ºC at the first stage up to 230-260 ºC in the second one with specific values precisely fixed according to composition. The excess of diols was removed along the second stage of the polycondensation reaction where high temperature and low vacuum were applied. Then, the reaction mixture was cooled to room temperature and the atmospheric pressure recovered with nitrogen to prevent degradation. The reaction mass was dissolved in chloroform or in a mixture of chloroform and trifluoroacetic acid (9:1) and precipitated in an excess of methanol in order to remove unreacted monomers and formed oligomers. Finally, the polymer was recovered by filtration, extensively washed with methanol, and dried under vacuum.

PET. A 2.2/1 molar ratio of EG to DMT. Transesterification reactions at 190 ºC for 2 h, and at 240 ºC for 0.5 h under low nitrogen flow. Polycondensation reactions at 260 ºC for 2 h under a 0.03-0.06 mbar vacuum.

^{1}H NMR (TFA-d_1, 300 MHz), δ (ppm: 8.17 (s, *Ar*H), 4.86 (s, OCH_2). $^{13}C\{^1H\}$-NMR (TFA-d_1, 75.5 MHz), δ (ppm: 170.8 (C=O), 135.64-132.14 (*Ar*C), 66.25 (OCH_2).

PE_xThx_yT. A 1.5/1 molar ratio of the mixture of EG and Thx-diol to DMT. Transesterification: 185 ºC, 3 h under a low nitrogen flow. Polycondensation: 255 ºC, 1 h (for *y*=8 mol-%), 250 ºC, 2 h (for *y* between 15 and 23 mol%), 230 ºC, 4 h (for *y*=38 mol-%) and 200ºC, 5.5 h (for *y* = 57 mol-%) under a 0.03-0.06 mbar vacuum.

^{1}H NMR ($CDCl_3$/TFA, 300 MHz), δ (ppm): 8.14 (s, *Ar*H), 5.27 (OCH_2O), 4.72 (s, OCH_2), 4.75-4.55 (m, O**CH₂**CH), 4.49 (m, CH). $^{13}C\{^1H\}$-NMR ($CDCl_3$/TFA, 75.5 MHz), δ (ppm): 167.24-166.92 (C=O), 135.58-130.1 (*Ar*C), 95.51 (OCH_2O), 75.7 (CH), 64.72 (O**CH₂**CH), 63.8 (OCH_2).

***PET$_x$Thx$_y$*.** A 2.2/1 molar ratio of EG to the mixture of DMT and Thx-diester. Transesterification: 170-185 ºC, 3-4.5h under a low nitrogen flow. Polycondensation: 240 ºC, 3.5 h (for *y* = 7 and 11 mol-%), 230 ºC, 4h (for *y*=15 mol-%), 200 ºC, 6h (for *y*=20 and 30 mol-%) under a 0.03-0.06 mbar vacuum.

^{1}H NMR (TFA-d_1, 300 MHz), δ (ppm): 8.26 (s, *Ar*H), 5.36 (s, OCH_2O), 5.16 (s, CH), 5.0-4.65 (m, OCH_2). $^{13}C\{^1H\}$-NMR (TFA-d_1, 75.5 MHz), δ (ppm): 173.76-170.87 (C=O), 135.71-132.14 (*Ar*C), 99.64 (OCH_2O), 78.76 (CH), 66.84-65.90 (OCH_2).

PThxT and PEThx. Firstly the mixture was heated at 180 ºC for 0.5 h for melting and then the temperature was lowered to 160ºC and maintained at this value for 3 h under low nitrogen flow. Polycondensation reactions were conducted under a 0.03-0.06 mbar vacuum in two successive periods, 1h at 200 ºC and 2h at 235 ºC.

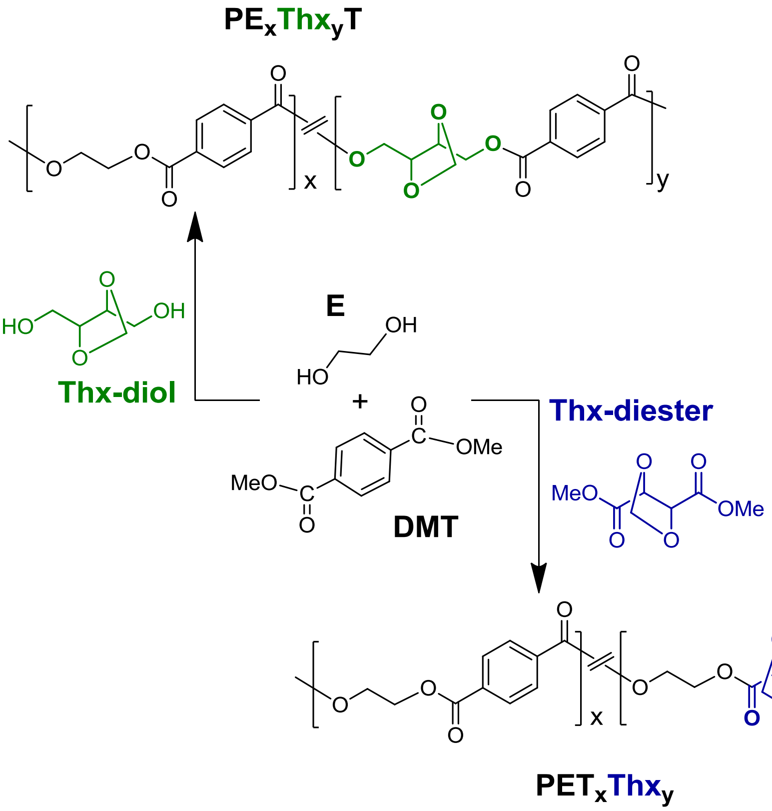
***PThxT*:** ^{1}H NMR ($CDCl_3$/TFA, 300 MHz), δ (ppm): 8.14 (*Ar*H), 5.29 (s, OCH_2O), 4.90-4.40 (m, O**CH₂**CH, CH). $^{13}C\{^1H\}$-NMR ($CDCl_3$/TFA, 75.5 MHz), δ (ppm): 170 (C=O), 135.59-132.55 (*Ar*C), 97.76 (OCH_2O), 78.06 (CH), 67.23 (O**CH₂**CH).

PEThx: ^{1}H NMR (TFA-d_1, 300 MHz), δ (ppm): 5.19 (OCH_2O), 4.88 (s, CH), 4.55-4.50 (dd, OCH_2). $^{13}C\{^1H\}$-NMR (TFA-d_1, 75.5 MHz), δ (ppm): 173.17 (C=O), 99.90 (OCH_2O), 78.78 (CH), 66.41 (OCH_2).

4.3. Results and discussion

4.3.1. Polyesters synthesis

Two series of PET copolyesters have been synthesized using as comonomers 2,3-*O*-methylene acetals derived from TA (Scheme I). The difference between the two series lies in which unit, diol or diacid, was substituted in PET by the tartaric acid-based unit. In the synthesis of the PE$_x$Thx$_y$T series, EG monomer was replaced by Thx-diol so poly(ethylene-*co*-threitylene terephthalate) copolyesters with contents in Thx units from 8 to 60% were prepared. The PET$_x$Thx$_y$ series was obtained from EG and mixtures of DMT and Thx-diester; these copolyesters are poly(ethylene terephthalate-*co*-threarate)s with Thx contents between 7 and 30%. The two respective homopolyesters made of exclusively Thx-diol or Thx-diester monomers, *i.e*. PEThx and PThxT, were also synthesized. These syntheses were performed in the melt, *i.e*. in the total absence of solvents, in a manner similar to that followed in the industry for producing PET using DMT. Since carbohydrate derived compounds are particularly sensitive to heat, reaction conditions regarding time and temperature, were carefully adjusted according to composition in order to optimize conversion and minimize thermal degradation. Polymerization evolved with a continuous increase in viscosity so the advance of the reaction could be followed by measuring the torque. It was considered that the reaction was over when stirring was no longer feasible. Synthesis results obtained for the two series are compared in Table 1. All copolyesters were prepared in yields around 80-90 % after purification, and yields and molecular weights were observed to decrease with increasing contents in Thx units. It is also noteworthy that both intrinsic viscosities and molecular weighs are lower for the PET$_x$Thx$_y$ series which must be attributed to the higher sensitivity to temperature of the threarate units compared to the threitylene ones.



Scheme 1. Reaction scheme for the preparation of PE$_x$Thx$_y$T and PET$_x$Thx$_y$ copolyesters.

The solubility of the copolyesters in organic solvents increases with the content in Thx units so that they start to be soluble in $CHCl_3$ as soon as the composition in such units reaches 20%. (Table S1 in the SM file). The chemical constitution and composition of the resulting copolyesters were ascertained by NMR (Figures 1 and 2). The correct assignment of the signals arising from the sugar units was supported by 2D NMR HETCOR spectrum (Figures S1 and S2 in the SM file). Compositions of PE_xThx_yT were determined by quantification of the aromatic proton signals (4H) emerging at 8.14 ppm and the signals arising from the two repeating units (*c_{Thx}*, *a_T*, *a_{Thx}* and *b_{Thx}*) present in the copolyesters, which appear between 5.40-4.40 ppm (Figure 1). On the other hand, compositions of PET_xThx_y copolyesters could be accurately determined by integration of the signals observed at 8.26 ppm (4H of the terephthalate unit) and 5.27 ppm (2H of the methylene in the acetal group of the threarate unit) (Figure 2).

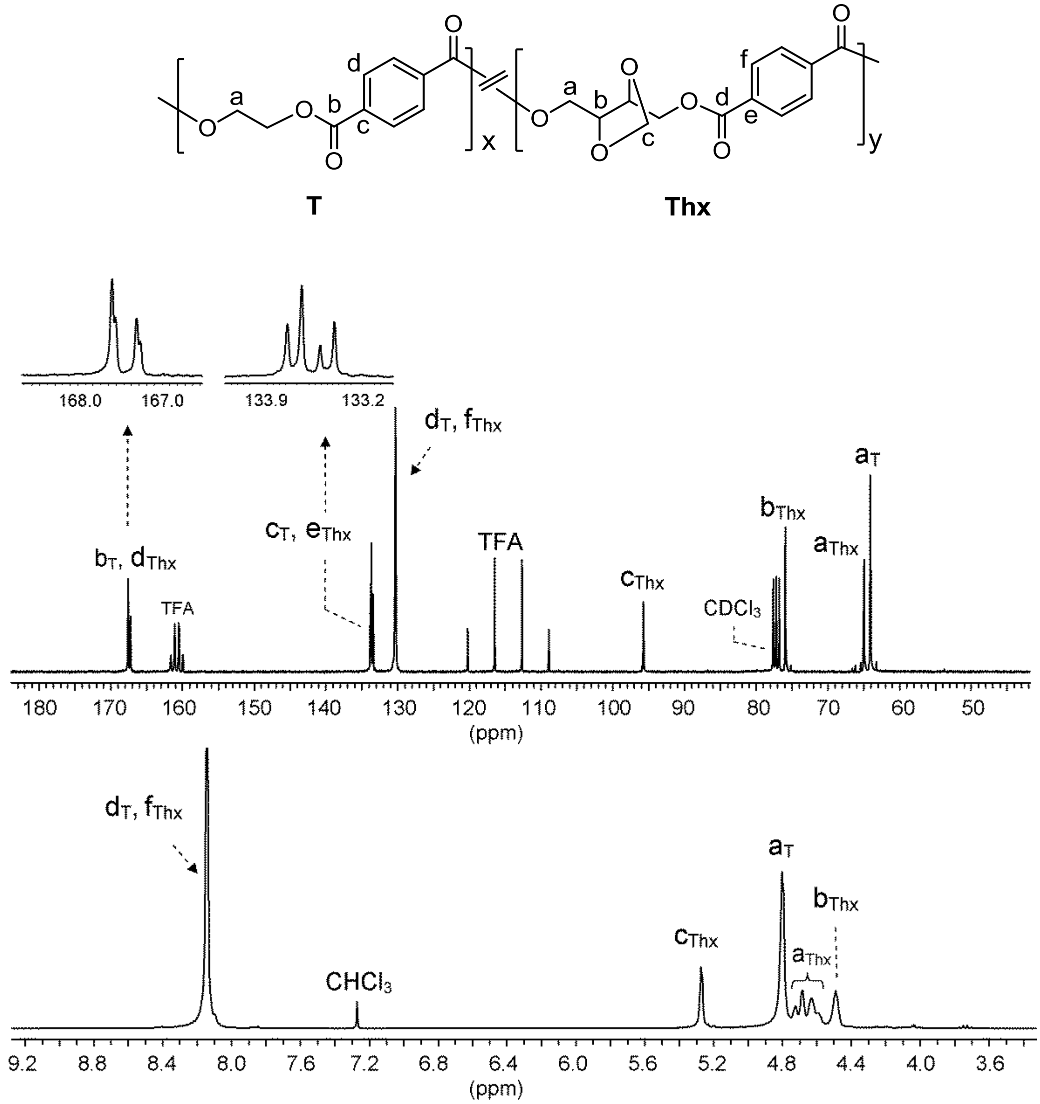


Figure 1. ^1H (top) and ^{13}C (bottom) NMR spectra of $PE_{68}Thx_{32}T$ copolyesters.

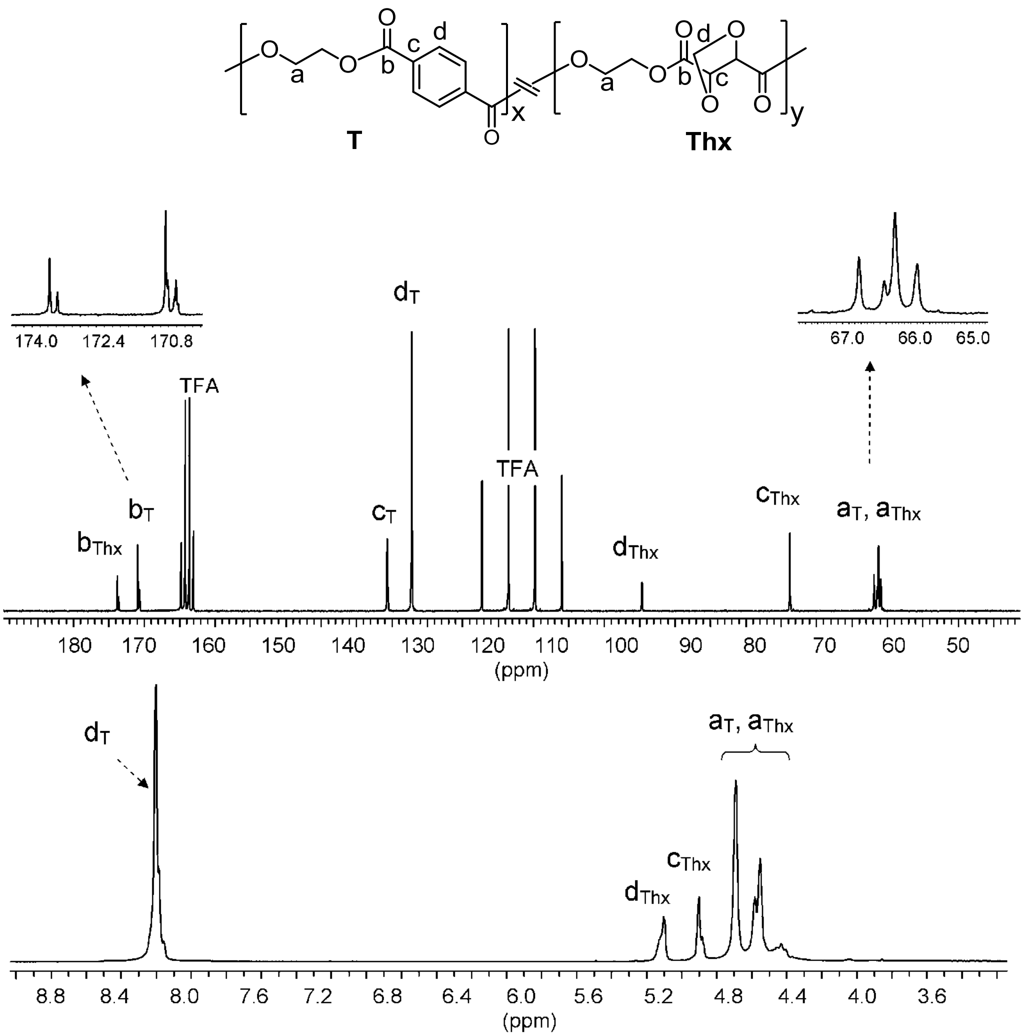


Figure 2. ^{1}H (top) and ^{13}C (bottom) NMR spectra of PET$_{70}$Thx$_{30}$copolyesters.

The correspondence between copolyester and feed compositions deserves attention. In PE$_x$Thx$_y$T, the amount of Thx incorporated into the polymer was found to be higher than expected, which is attributed to the comparatively higher volatility of EG. In the case of PET$_x$Thx$_y$ copolyesters, the polymer compositions appeared to be close to those of their respective feeds, which makes sense given the comparable low volatility of DMT and Thx-diester compounds. This behavior was similar to that previously observed by us in the synthesis of PET copolyesters containing bicyclic acetalized units derived from glucose and mannose,[20,21] and also attributed there to volatilization effects.

Table 1. Molar composition and molecular weight of PE$_x$Thx$_y$T and PET$_x$Thx$_y$.

Copolyester	Yield (%)	Molar composition								Molecular weight				
		Feed				Copolyester^a								
		Diol		Diacid		Diol		Diacid						
		[E]	[Thx]	[T]	[Thx]	[E]	[Thx]	[T]	[Thx]	$[\eta]^b$	$M_v{}^c$	$M_n{}^d$	$M_w{}^d$	$Đ^d$
PET	90	100	0	100	0	100	0	100	0	0.68	18,500	12,800	32,100	2.5
PE$_{92}$Thx$_{8}$T	90	95	5	100	0	92	8	100	-	0.62	15,300	12,600	30,200	2.4
PE$_{85}$Thx$_{15}$T	92	90	10	100	0	89	11	100	-	0.70	19,800	14,700	33,800	2.3
PE$_{83}$Thx$_{17}$T	88	85	15	100	0	78	22	100	-	0.71	20,400	14,800	34,000	2.3
PE$_{77}$Thx$_{23}$T	85	80	20	100	0	74	26	100	-	0.68	18,600	14,000	32,300	2.3
PE$_{62}$Thx$_{38}$T	82	70	30	100	0	62	38	100	-	0.65	16,900	13,100	31,500	2.4
PE$_{43}$Thx$_{57}$T	80	50	50	100	0	43	57	100	-	0.60	14,200	11,500	28,700	2.5
PThxT	83	0	100	100	0	0	100	100	-	n.d.	n.d.	3,800	8,800	2.3
PET$_{93}$Thx$_{7}$	90	100	0	95	5	100	-	93	7	0.63	15,800	14,000	30,500	2.2
PET$_{89}$Thx$_{11}$	90	100	0	90	10	100	-	89	11	0.51	10,100	11,200	25,800	2.3
PET$_{85}$Thx$_{15}$	85	100	0	85	15	100	-	85	15	0.60	14,200	13,200	29,000	2.2
PET$_{80}$Thx$_{20}$	80	100	0	80	20	100	-	80	20	0.50	9,600	10,400	25,000	2.4
PET$_{70}$Thx$_{30}$	80	100	0	70	30	100	-	70	30	0.53	10,900	11,300	26,000	2.3
PEThx	30	100	0	0	100	100	-	0	100	0.42	6,600	6,200	15,000	2.4

[a] Molar composition determined by integration of ^{1}H NMR spectra.

[b] Intrinsic viscosity in dL·g^{-1} measured in dichloroacetic acid at 25 ºC.

[c] Viscosimetric molecular weight in g·mol^{-1} determined using the Mark-Houwink parameters K= 6.7 ×10^{-3} and a =0.47, reported for PET.

*Data from literature.[21b]

4.3.2. Microstructure of PE$_x$Thx$_y$T and PET$_x$Thx$_y$ copolyesters

The microstructure of all copolyesters in the two series could be determined by ^{13}C NMR spectroscopy. As it is depicted in Figure 3, the ^{13}C NMR spectra of PThxT, PET and PE$_x$Thx$_y$T copolyesters show the non-protonated aromatic carbon signals (c_T and e_{Thx}) with enough resolution to elucidate the microstructure as far as distribution of ethylene and threitylene units along the copolyester chain is concerned. The non-protonated aromatic carbons are sensitive to sequence distributions at the level of dyads, and this signal appears split into four peaks spread within 133.9-133.2 ppm interval. By integration of the peaks included in this signal, E-E, E-Thx/Thx-E and Thx-Thx dyad contents were calculated. Based on these values, the number-average lengths (*n*) of ethylene terephthalate (ET) and threitylene terephthalate (ThxT) homogeneous sequences, as well as the degree of randomness *R,* were estimated for each copolyester by using the following equations:

$$n_{ET} = (N_{EE} + ½\,(N_{EThx} + N_{ThxE}))\;/\;½(N_{EThx} + N_{ThxE})$$

$$n_{ThxT} = (N_{ThxThx} + ½\,(N_{EThx} + N_{ThxE}))\;/\;½(N_{EThx} + N_{ThxE})$$

$$R = (1/\tilde{n}_{ET}) + (1/\,\tilde{n}_{ThxT})$$

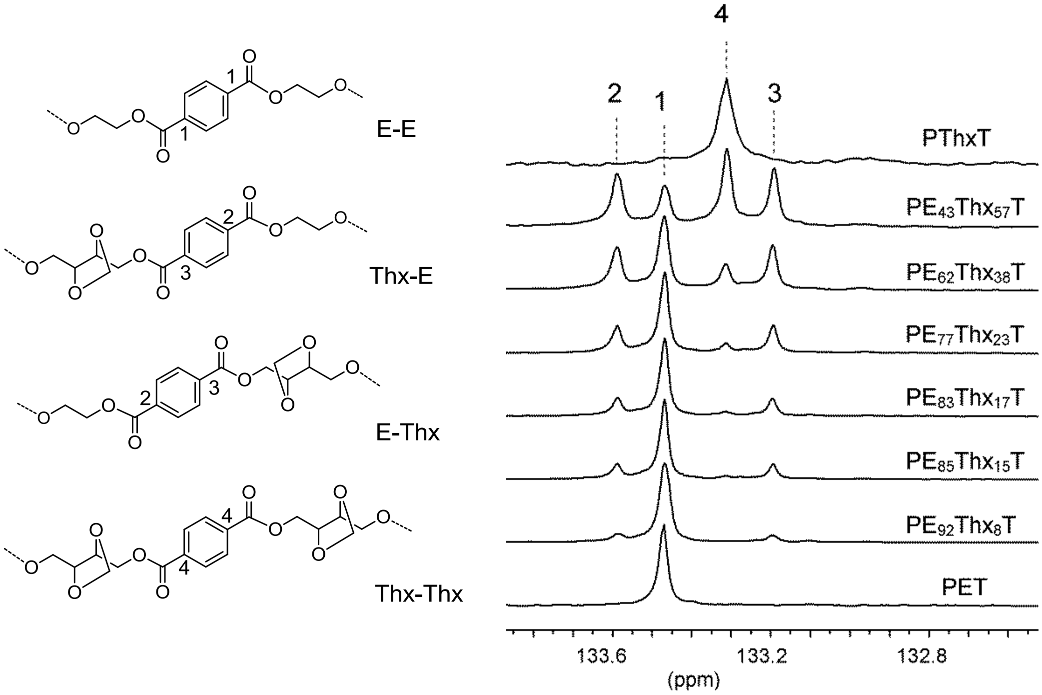


Figure 3. The four possible dyads present in PE$_x$Thx$_y$T copolyesters (left).^{13}C NMR spectra of the non-protonated aromatic carbons for the indicated polyesters with assignments of the peaks to dyads (right).

The same methodology was applied to the determination of the microstructure of PET_xThx_y. In this case the signals corresponding to methylene carbons of EG split into four peaks due to the different chemical environments provided by the four possible dyads T-T, T-Thx/Thx-T and Thx-Thx occurring along the copolyester chain (Figure 4a). The assignment of these peaks to the dyads (Figure. 4b) was possible by comparison with the ^{13}C NMR spectra produced by the homopolyesters. The equations used in this case for calculating the sequence lengths and randomness were the following:

$$n_{ET} = (N_{T\text{-}T} + ½\,(N_{T\text{-}Thx} + N_{Thx\text{-}T}))\ /\ ½\,(N_{T\text{-}Thx} + N_{Thx\text{-}T})$$

$$n_{EThx} = (N_{Thx\text{-}Thx} + ½\,(N_{T\text{-}Thx} + N_{Thx\text{-}T}))\ /\ ½\,(N_{T\text{-}Thx} + N_{Thx\text{-}T})$$

$$R = (1/\tilde{n}_{ET}) + (1/\tilde{n}_{EThx}).$$

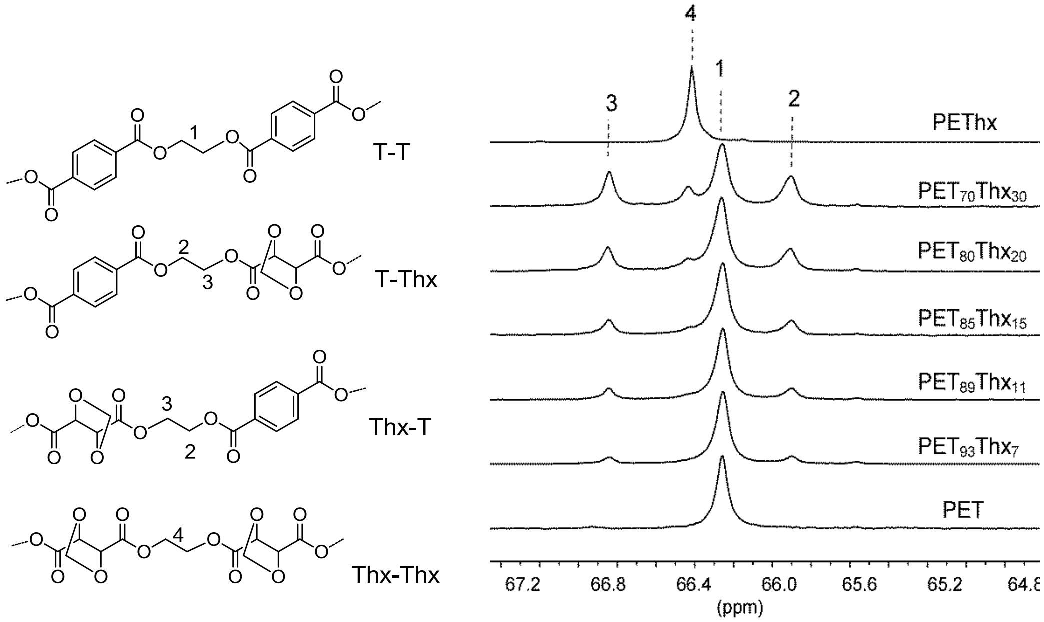


Figure 4. (a) The four possible dyads present in PET_xThx_y copolyesters. (b) ^{13}C NMR spectra of the EG carbons for the indicated polyesters with assignments of the peaks to different carbons.

Results from all these calculations are summarized in Table 2 which show that the sequence distribution in both PE_xThx_yT and PET_xThx_y series is essentially random for the whole range of compositions with values of R being very close to unit.

Table 2. Composition and microstructure of PE$_x$Thx$_y$T and PET$_x$Thx$_y$ copolyesters.

Copolyesters	Composition[a]		Dyad content (mol-%)[b]			Sequence lenghts[b]		R[c]
	X_E	X_{Thx}	E-E	E-Thx/Thx-E	Thx-Thx	$\tilde{n}_{ET}$	$\tilde{n}_{ThxT}$	
PE$_{92}$Thx$_8$T	92	8	82.5	17.5	0.0	10.4	1.0	1.10 (1.0)
PE$_{85}$Thx$_{15}$T	85	15	71.3	26.1	2.6	6.5	1.2	0.99 (1.0)
PE$_{83}$Thx$_{17}$T	83	17	67.5	29.1	3.4	5.6	1.2	0.99 (1.0)
PE$_{77}$Thx$_{23}$T	77	23	57.2	36.8	6.0	4.1	1.3	1.00 (1.0)
PE$_{62}$Thx$_{38}$T	62	38	38.5	47.6	13.9	2.6	1.6	1.00 (1.0)
PE$_{43}$Thx$_{57}$T	43	57	18.4	48.5	33.1	1.7	2.4	0.99 (1.0)

	X_T	X_{Thx}	T-T	T-Thx/Thx-T	Thx-Thx	$\tilde{n}_{ET}$	$\tilde{n}_{EThx}$	R
PET$_{93}$Thx$_7$	93	7	85.4	14.6	0.0	12.7	1.0	1.08 (1.0)
PET$_{89}$Thx$_{11}$	89	11	78.4	20.2	1.4	8.8	1.1	1.02 (1.0)
PET$_{85}$Thx$_{15}$	85	15	71.3	26.2	2.5	6.4	1.2	0.99 (1.0)
PET$_{80}$Thx$_{20}$	80	20	63.0	32.6	4.4	4.9	1.3	0.99 (1.0)
PHT$_{70}$Thx$_{30}$	70	30	48.8	42.7	8.5	3.3	1.4	1.01 (1.0)

[a] Calculated from the ^{1}H NMR spectra.

[b] Number-average sequence lengths obtained by means of the equations mentioned in the text and using the ^{13}C NMR data.

[c] Theoretical values of R (in parentheses) corresponding to a fully random copolyester.

4.3.3. Thermal properties

The thermal behaviour of PE$_x$Thx$_y$T and PET$_x$Thx$_y$ copolyesters has been comparatively studied by TGA and DSC; the thermal parameters resulting from these analyses are given in Table 3, where the corresponding data for the parent homopolyesters PET, PThxT and PEThx are also included for comparison. The TGA traces of the two series of copolyesters and their derivative curves are comparatively depicted in Figure 5. PE$_x$Thx$_y$T copolyesters start to lose weight above 400 ºC and the decomposition process happens in a single stage with a maximum rate at ~440 ºC following a profile practically undistinguishable from that of PET. It is highly remarkable that the thermal stability of PET remains practically unaltered when ethylene units are partially or even totally replaced by threitylene units. It can be stated therefore that as far as heat resistance is concerned, the behavior of PE$_x$Thx$_y$T is really satisfactory. On the other hand the TGA results obtained from the PET$_x$Thx$_y$ series are much less exciting. In these copolyesters, decomposition starts at lower temperatures than in PET and proceeds along several steps. In fact the onset temperature falls down considerably when the terephthalate units are replaced by threarate units showing a decrease of near 40 ºC for a 30% of replacement. The two or three poorly resolved peaks that are observed in the 385-400 ºC region of the TGA derivative curves of PET_xThx_y must correspond to decomposition of those sequences containing Thx units whereas the prominent peak at ~440 ºC is attributed to the decomposition of ET homogeneous sequences. The homopolyester PEThx is much less stable than PET; it starts to decompose at around 320 ºC and the maximum decomposition rate occurs at 350 ºC. It should be remarked that although the thermal stability of PET_xThx_y is clearly inferior to that of PET, decomposition of these copolyesters still happens at temperatures of 150-200 ºC above melting (Table 3) which ensures their comfortable handling at both using and processing.

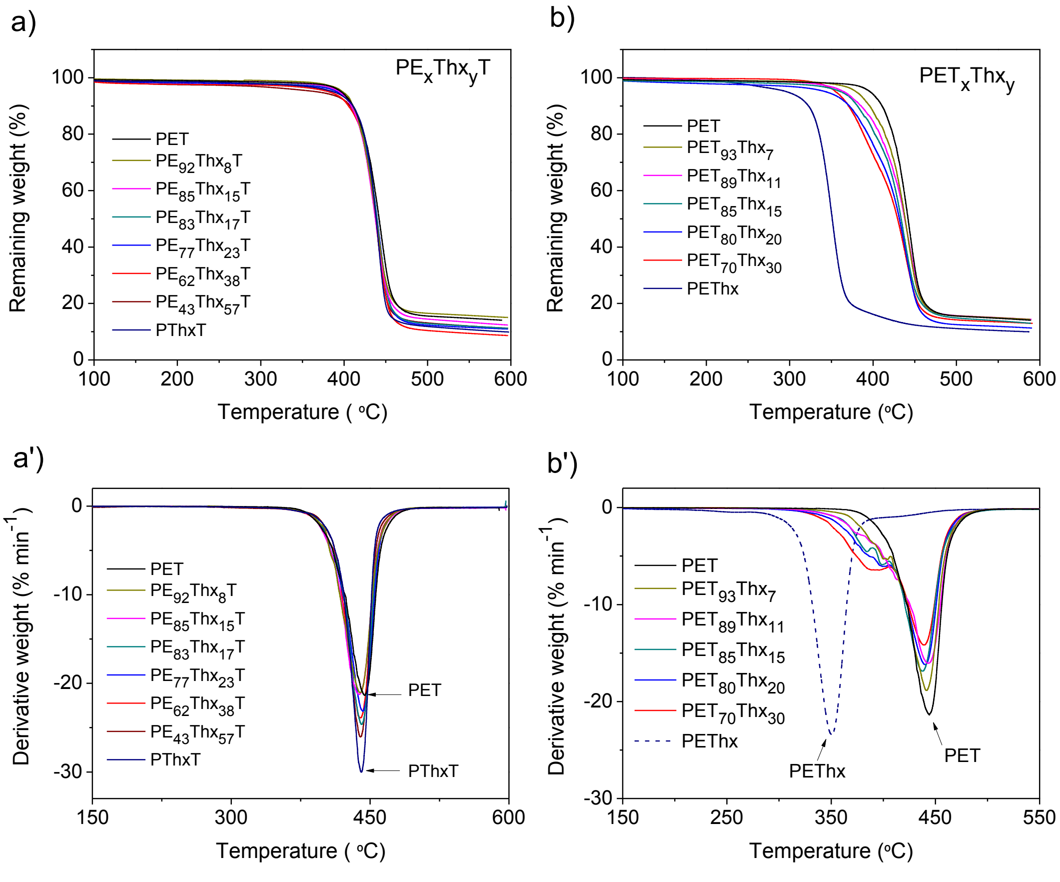


Figure 5. TGA traces of PE_xThx_yT (a) and PET_xThx_y (b) copolyesters and their respective derivative curves (a' and b').

Table 3. Thermal properties of PET, PThxT, PEThx, and PE_xThx_yT, PET_xThx_ycopolyesters.

Polyester	TGA			DSC								
				First Heating[e]					Cooling[e]		Second Heating[e]	
	T_d[a] (°C)	T_{ds}[b] (°C)	RW[c] (%)	T_g[d] (°C)	T_{cc} (°C)	ΔH_{cc} ($J\cdot g^{-1}$)	T_m (°C)	ΔH_m ($J\cdot g^{-1}$)	T_c (°C)	ΔH_c ($J\cdot g^{-1}$)	T_m (°C)	ΔH_m ($J\cdot g^{-1}$)
PET	411	445	15	81	122	-15	250	44	200	-33	249	29
PE_xThx_yT												
$PE_{92}Thx_8T$	410	439	15	82	128	-8	235	30	163	-27	230	27
$PE_{85}Thx_{15}T$	409	438	12	87	145	-21	218	22	-	-	-	-
$PE_{83}Thx_{17}T$	410	440	11	85	149	-19	206	19	-	-	-	-
$PE_{77}Thx_{23}T$	408	442	11	84	-	-	190	11	-	-	-	-
$PE_{62}Thx_{38}T$	405	440	9	83	-	-	-	-	-	-	-	-
$PE_{43}Thx_{57}T$	407	439	10	84	-	-	-	-	-	-	-	-
PThxT[f]	410	441	11	83	-	-	-	-	-	-	-	-
PET_xThx_y												
$PET_{93}Thx_7$	396	441	15	75	120	-15	238	34	184	-30	229	26
$PET_{89}Thx_{11}$	386	443	15	72	118	-16	232	30	163	-30	224	20
$PET_{85}Thx_{15}$	381	385-400/**438**	14	69	119	-15	222	32	156	-26	218	28
$PET_{80}Thx_{20}$	371	385-400/**440**	12	63	120	-19	207	19	-	-	198	6
$PET_{70}Thx_{30}$	370	385-400/**439**	13	59	-	-	178	9	-	-	-	-
PEThx	322	350	10	7	-	-	-	-	-	-	-	-

[a] Temperature at which a 10 % weight loss was observed in the TGA traces recorded at 10 °C min^{-1}. [b] Temperature of maximum degradation rate. [c] Remaining weight at 600ºC. [d] Glass-transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 °C min^{-1}. [e] Melting (T_m) and crystallization (T_c) temperatures and their respective enthalpies ΔH_m and ΔH_c, measured by DSC at heating/cooling rates of 10 °C min^{-1}; T_{cc}, ΔH_{cc}: cold crystallization. temperature and enthalpy. [f] Data taken from literature.[17b]

DSC traces of PE_xThx_yT and PET_xThx_y copolyesters, as well as PET, PThxT and PEThx homopolyesters, registered at heating from samples coming directly from synthesis, *i.e.* without any further heating treatment, are depicted in Figure 6. Whereas PET is a semicrystalline polymer melting at 250 ºC, both PThxT and PEThx homopolyesters are amorphous. On the contrary, endothermic peaks characteristic of melting are observed for some PE_xThx_yT and PET_xThx_y copolyesters indicating the presence of crystallinity in both series. As it is shown in Table 3, melting temperatures and enthalpies steadily decrease with the content in Thx in both series but the decay is more pronounced when the diol unit is the replaced one. In any case it can be roughly said that these copolyesters become amorphous when their content in Thx units reaches around 30%. It is observed that all the semicrystalline copolyesters display cold crystallization in a similar manner as it is well known to occur in PET, and that it happens at much lower temperatures and with sharper definition in the PET_xThx_y series than in the PE_xThx_yT one. Such differences must be associated to the different flexibility of the polymer chain in each series, an issue that will be dealt below in relation to the glass transition exhibited by the copolyesters.

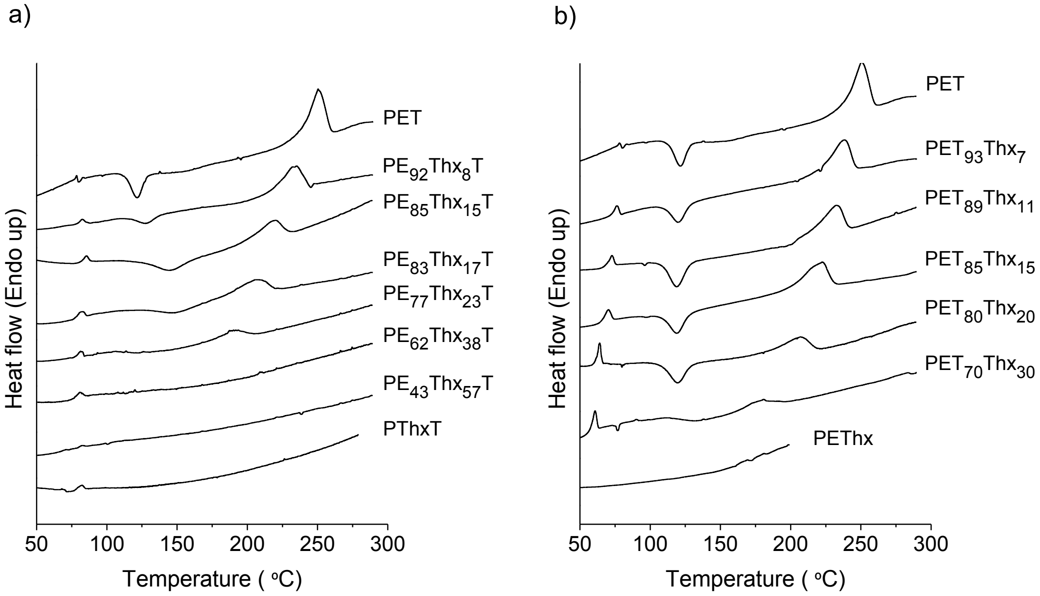


Figure 6. DSC heating traces of PE_xThx_yT (a) and PET_xThx_y (b) copolyesters coming directly from synthesis.

The T_g of polyesters and copolyesters were clearly perceived on the heating DSC traces of samples quenched from the melt (Figure 7), and the values measured from these experiments are listed in Table 3. In the PET_xThx_y series, where the terephthalate unit was replaced by the threarate units, T_g decreases noticeably with the content in Thx units to the extent that its value goes down to 7 ºC for a 100% of replacement, *i.e.* for the PEThx homopolyester. Conversely, replacing the ethylene unit by the threitylene unit has an opposite effect. In fact, the homopolyester PThxT has a T_g of 83 ºC which is slightly higher than the T_g of PET (~80 ºC). Such difference is very likely underestimated since the molecular weight of the poly(2,3-*O*-methylene-threitylene terephthalate) is about an a half of that of PET. Accordingly to the values observed for the parent homopolyesters, PE$_x$Thx$_y$T copolyesters were found to display T_g values within the 82-87 ºC range, *i.e.* the T_g of PET is maintained upon copolymerization whichever was the copolyester composition.

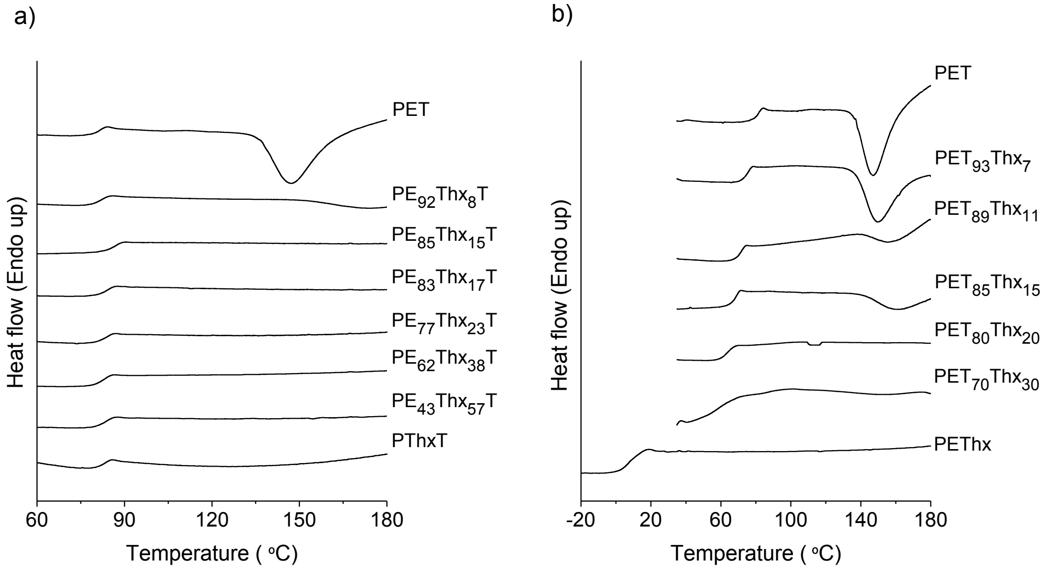


Figure 7. DSC traces of PE$_x$Thx$_y$T (a) and PET$_x$Thx$_y$ (b) copolyesters recorded at heating from quenched samples for T_g observation.

The effect of the incorporation of Thx on the thermal properties of PET, specifically on T_m and T_g, is an issue of maximum significance for the prospective of the PET copolyesters since these parameters are which mainly determine the suitability of these materials in most of their current applications. The changes taking place in T_g and T_m in the PET copolyesters containing Thx units, either as diol or diacid, are represented in Figure 8 as a function of the composition.

For both series, T_m decreases almost linearly with a slope of around 2.5 ºC per %-Thx indicating that the effect of substitution on crystal size and perfection must be approximately the same for the two series. On the other hand, the evolution of T_g with composition exhibits a different tendency depending on which type of unit is replaced. In both cases the measured T_g values are not far from those predicted by the Fox equation with larger divergences probably due to the fluctuations displayed by molecular weights (Figure S3). The correlation between observed

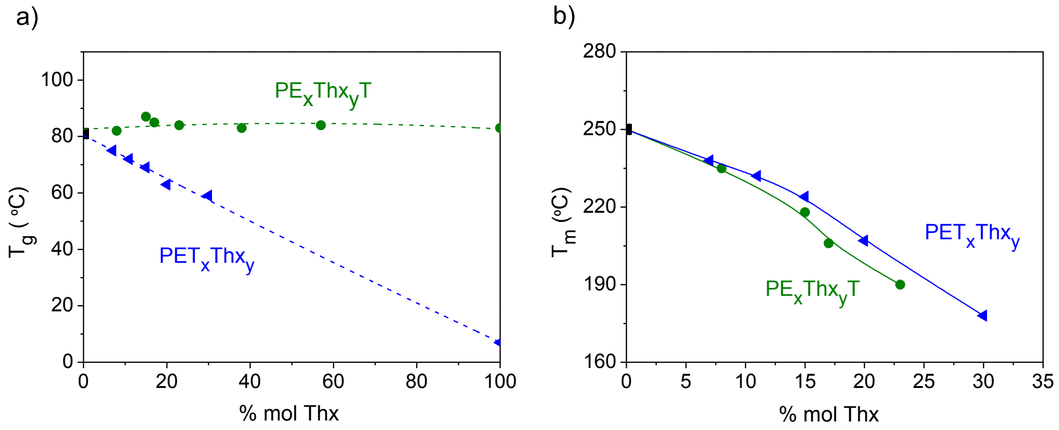


Figure 8. (a) Glass-transition temperature *vs*. composition plot for PE_xThx_yT and PET_xThx_y copolyesters. (b) Melting temperature *vs*. composition plot for PE_xThx_yT and PET_xThx_y copolyesters.

and predicted values is however better than in other series of aromatic copolyesters containing Thx units.[17] The opposite trend observed for the T_g in PE_xThx_yT and PET_xThx_y series may be rationalized taking into account the relative flexibility of the units that are replaced. When the aromatic phenylene cycle is substituted by the 2,3-dioxolane ring, the flexibility of the polymer chain increases, the free volume increases as well, and therefore T_g decreases. It should be remarked that substitution of the aromatic unit in polyesters usually leads to a decay in T_g when they are replaced by non-aromatic units.[22] To our best knowledge, only the incorporation of the fused bicyclic 2,4:3,5-dioxane-glucarate units have proven to be able to increase the T_g of PET and PBT upon substitution of the terephthalate units.[20,23] On the other hand, the replacement of the two-carbon ethylene unit by the four-carbon cyclic Thx unit provides a rather stiffer chain and therefore a polymer with slightly enhanced T_g. There are several examples in which the replacement of the ethylene unit in PET results in polyesters with enhanced or sustained T_g.[19-21,24] The behavior observed in PET_xThx_y is therefore an additional example showing such characteristics. The merits of Thx making it a more valuable option rely on its bio-based origin and also on the relatively ease of its synthesis.

4.3.3. Structure and isothermal crystallization

As mentioned above both PE_xThx_yT and PET_xThx_y copolyesters display crystallinity for contents in Thx units below 30 %-mole. The melting enthalpy of these copolyesters progressively decreased with the Thx content clearly revealing that crystallinity is depressed by the presence of such units. The WAXS profiles obtained from annealed samples of some representative semicrystalline copolyesters, namely $PE_{92}Thx_8T$, $PE_{85}Thx_{15}T$, $PET_{93}Thx_7$ and $PET_{85}Thx_{15}$ as well as from PET, are shown in Figure 9 with indication of the Bragg spacings associated to the diffraction peaks that are detected. At a simple glance it becomes evident that the PET profile is shared by all the copolymers with an almost exactly reproduction of peak positions and intensities. It is concluded therefore that both PE_xThx_yT and PET_xThx_y crystallize in the well-known triclinic structure of PET.[25] This is not at all the first time that aromatic copolyesters are found to adopt the crystal lattice of the parent homopolymer, a fact that is accepted to be feasible provided that Thx units are segregated to the amorphous phase.[17,23] Above a certain Thx content (around 30% in the present case), the crystallizing homogeneous ET sequences are so short that the crystallite does not reach the minimum thickness required to be stable and crystallinity is no longer observed. The similar effect exerted on crystallinity by the Thx units regardless they are diol or diacid is fully consistent with this interpretation; it is the composition and the microstructure of the copolyester but not the constitution of the unit that restrains the crystallization phenomenon.

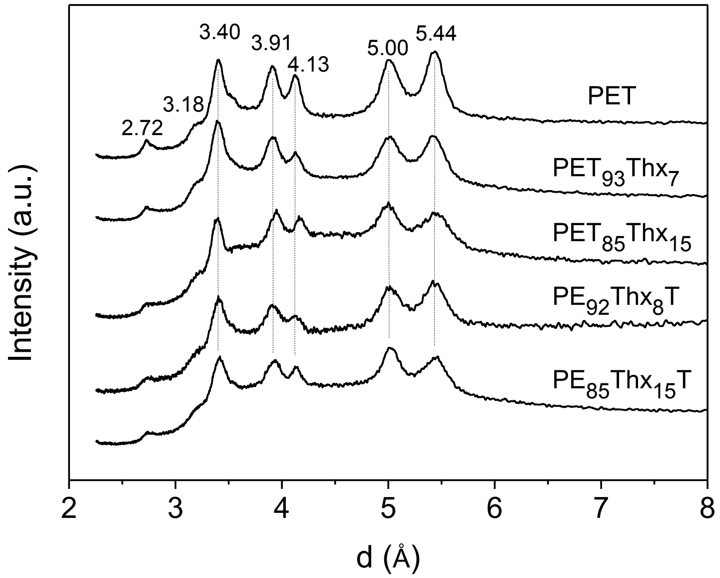


Figure 9. a) Powder WAXS profiles of some PE_xGlux_yT and PET_xGlux_y copolyesters, and PET recorded from annealed powder samples.

Crystallization from the melt is a property that has particular significance in aromatic polyesters. PBT is distinguished by its capacity for crystallizing very fast with achievement of high crystallinity. This is an unanimously appreciated property of PBT that makes it to be the thermoplastic of choice for injection processing with fastness and good dimensional stability. Conversely, crystallizability of PET deserves different appreciations depending on application. Although crystallized or microcrystallized PET is the form in general desired for most of its applications, crystallization needs to be avoided when PET is used in the manufacture of thick transparent plates.[26] Polarizing optical micrographs taken from thin films of PET, $PE_{92}Thx_8T$ and

PET$_{93}$Thx$_{7}$ polyesters crystallized at 205-210 ºC revealed the presence of imperfect spherulites of small size in the three cases (Figure S4). Interestingly it cannot be discarded from these pictures that the material crystallized without achieving a complete three-dimensional order as it is known to occur in aromatic polyesters under restricted mobility conditions. To appraise in more detail the effect of the insertion of Thx units on the crystallizability of PET, the crystallization rates of the three polyesters were compared at the same crystallization temperature. Powder samples were previously melted and then left to crystallize at 205 ºC and 210 ºC. The relative crystallinity *vs.* crystallization time plots obtained from these experiments are compared in Figure 10.

The conclusions drawn from the plots are the following: a) In all cases crystallization rate decreases with temperature as it should be expected for a crystallization process governed by nucleation. b) The crystallization rate of PET decreases with the incorporation of Thx units whatever they are diol or diacid. c) The depressing effect on crystallization rate is noticeably higher when the diol is the replaced unit. It is logical that the random occurrence of Thx units along the polyester chain makes more difficult to achieve the adequate arrangement of the chains for crystal packing. In the PE$_{x}$Thx$_{y}$T series the crystallization delay will increase because of the more restricted mobility of the polyester chain (higher T_g). The basic application of the Avrami approach to the crystallization data afforded the kinetics parameters for each polyester, which corroborated our conclusions (Table S3) in spite of the limitations of the study. The double logarithmic plots used for kinetics calculations as well as the Hoffman-Weeks plots (T_m *vs.* T_c) built for providing the equilibrium melting temperatures are available in the Figure S5 of the SM file.

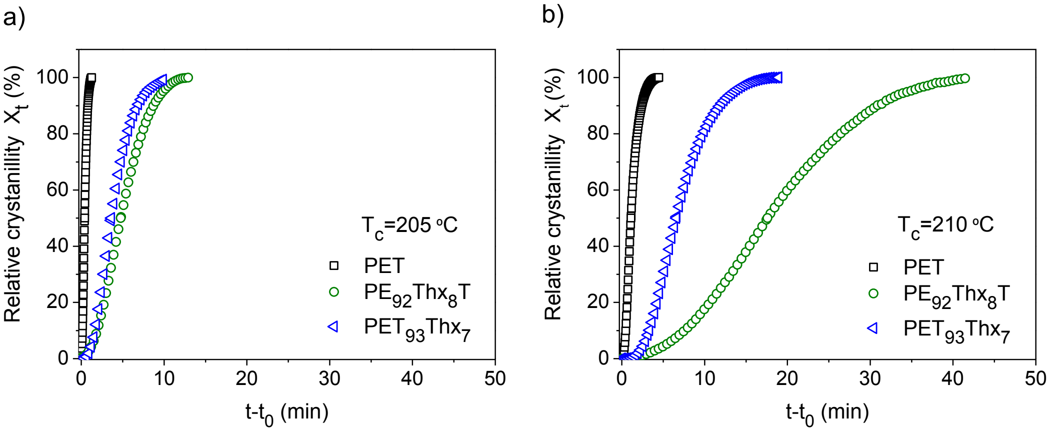


Figure 10. Isothermal crystallization of PE$_{92}$Thx$_{8}$T and PET$_{93}$Thx$_{7}$ copolyesters, and PET homopolyester. Relative crystallinity *vs.* time plot at 205 ºC (a) and 210 ºC (b).

4.4. Conclusions

Naturally-occurring tartaric acid stands out as a unique platform for providing difunctional monomers suitable for polycondensation without excessive chemical manipulations. In this work it has been proven that the two cyclic compounds containing the 1,3-dioxolane structure, 2,3-di-*O*-methylene-L-threitol (Thx-diol) and 2,3-di-*O*-methylene-L-threarate (Thx-diester) may be successfully used for the synthesis of partially sustainable PET copolyesters through a methodology similar to that usually applied at industrial scale.

The partially replacing of either ethylene glycol by Thx-diol or dimethyl terephthalate by Thx-diester in melt polycondensation afforded two series of random copolyesters of PET with bio-based contents up to 60 and 30%, respectively, and weight-average molecular weights in the 25,000-35,000 range. The respective homopolyesters consisting entirely of Thx units could be also prepared but with noticeably lower molecular weights. Copolyesters containing Thx-diester units are significantly less stable to heat than PET, whereas those made of Thx-diol have a stability comparable or even slightly higher than that of PET.

The replacement of terephthalate by threarate units entails a decrease in the T_g of PET. On the contrary, terephthalate copolyesters containing threitylene units have the same or even slightly higher T_g than PET. These results are in full agreement with what should be expected from the changes introduced in the stiffness of the polyester chain by copolymerization. Melting temperature, crystallinity and crystallization rate of PET are properties that decrease with the insertion of Thx units but the depressing effect is much more pronounced when the diol unit is the replaced one. Nevertheless crystallinity is retained in the copolyesters up to contents in Thx units around 30%, and all the semicrystalline polyesters share the triclinic crystal structure of PET.

This work proves the suitability of tartaric acid as source of monomers, both diol and diacid, for preparing bio-based PET copolyesters. Results are particularly exciting with regards to the use of diol compound (Thx-diol) because in this case thermal stability and T_g are enhanced whereas crystallizability is depressed, a behavior that is in full accord with what is required to PET for some specific applications.

4.5. References

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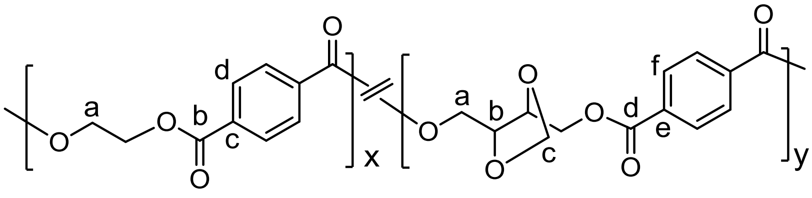
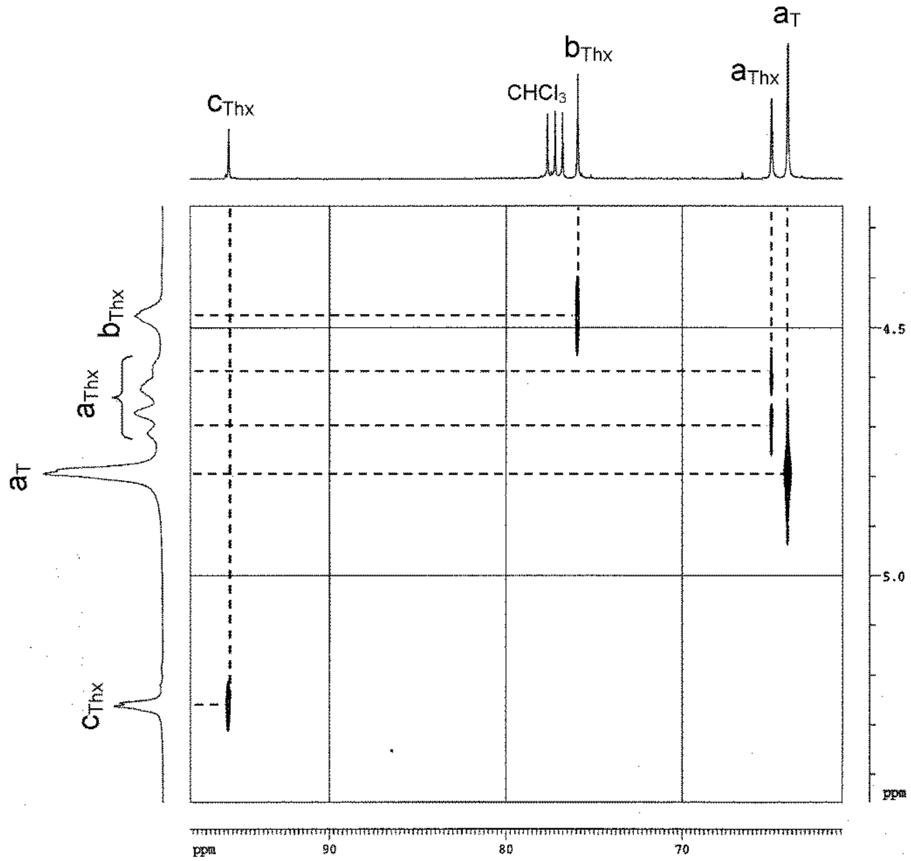
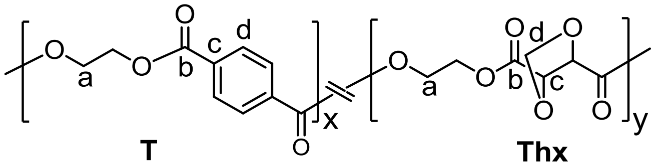
Supporting information

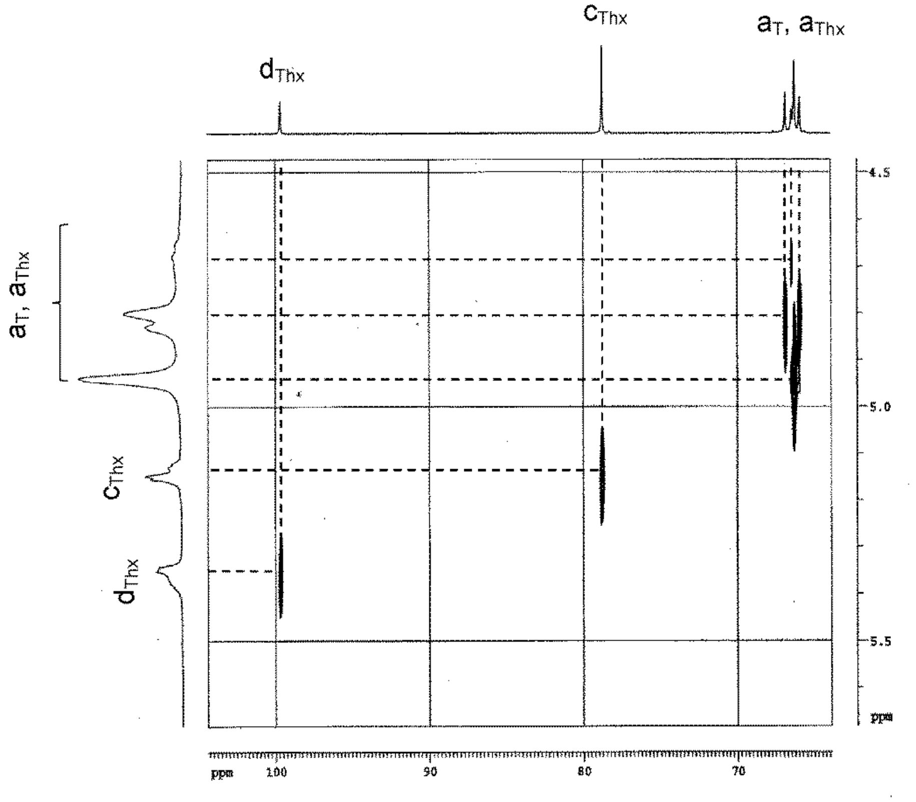


T **Thx**

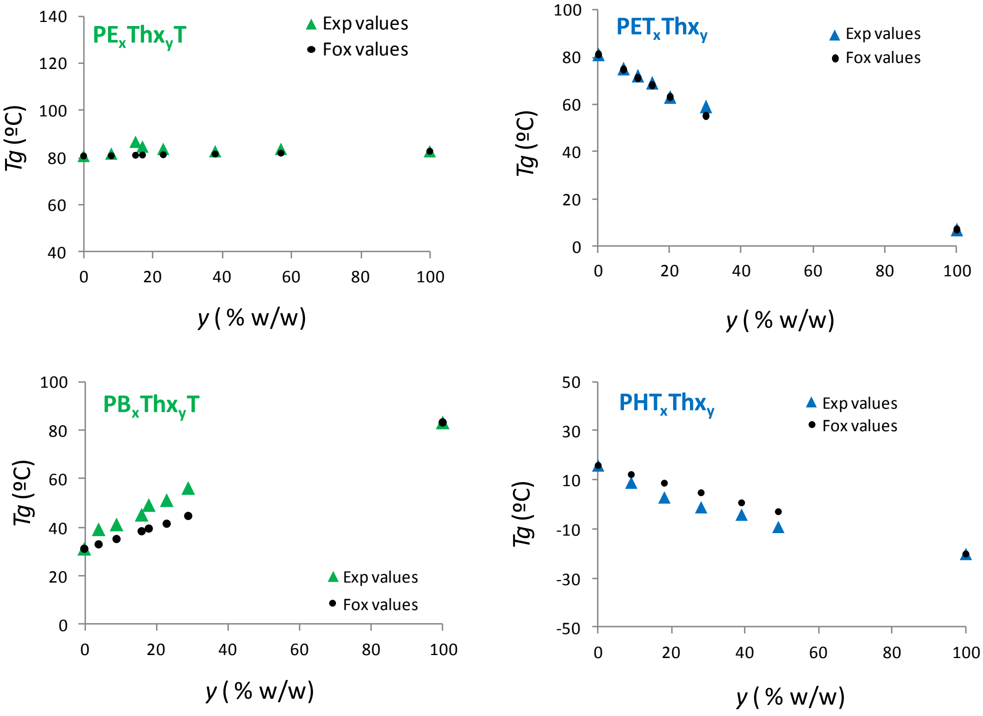


SI-Figure 1.^{13}C-^{1}H HETCOR NMR spectrum of PE$_{62}$Thx$_{38}$T.

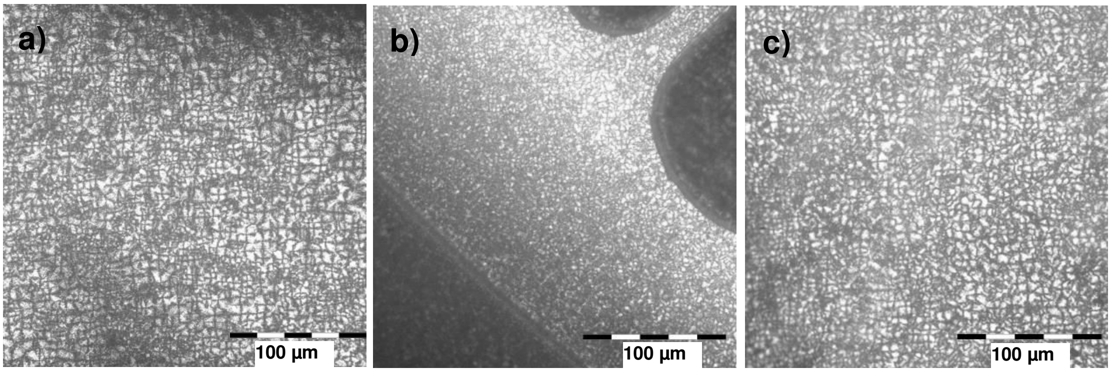




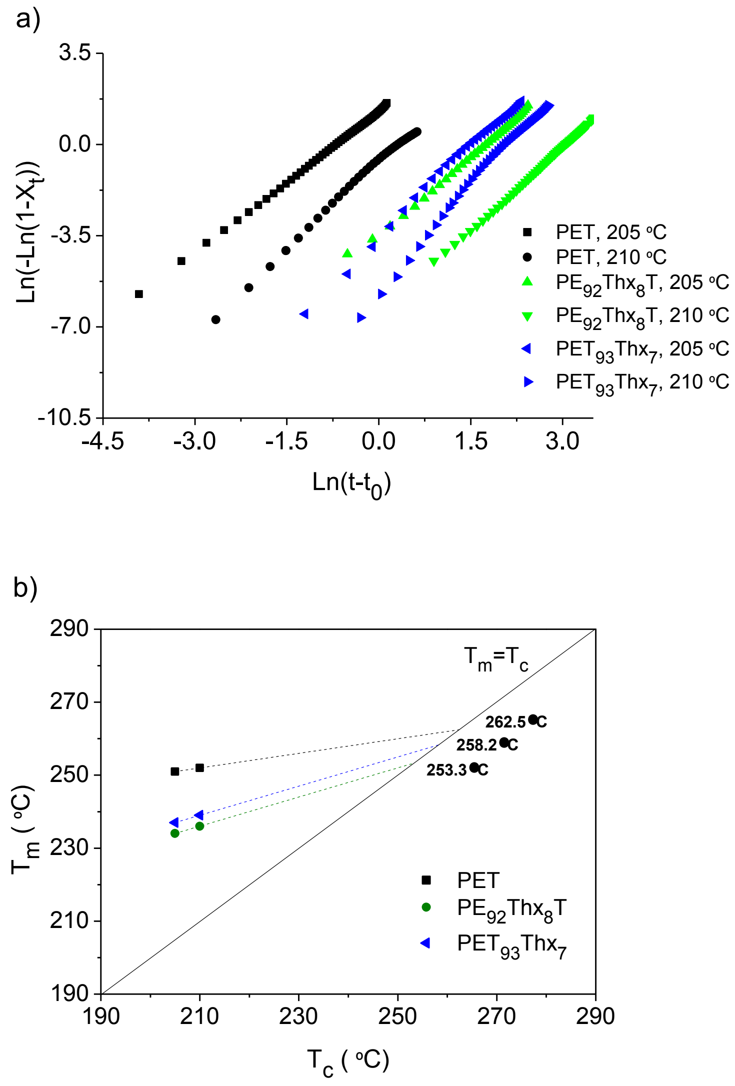
SI-Figure 2. ^{13}C-^{1}H HETCOR NMR spectrum of PET$_{70}$Thx$_{30}$.



SI-Figure 3. T_g values of different series of aromatic copolyesters containing Thx units. Experimental values and values predicted by the Fox equation for the seame Thx copolymer contents are compared at each case. PE$_x$Thx$_y$T and PET$_x$Thx$_y$: PET-based copolyester series studied in this work. PB$_x$Thx$_y$T: PBT-based copolyester series.[17b] PHT$_x$Thx$_y$: PHT-based copolyester series.[17a]



SI-Figure 4. Polarizing optical micrographs of samples isothermally crystallized at the indicated temperatures: (a) PET at 205 ºC; (b) PE$_{92}$Thx$_8$T at 210 ºC; (c) PET$_{93}$Thx$_7$ at 210 ºC. The scale bar corresponds to 100 µm.



SI-Figure 5. Isothermal crystallization of PE$_{92}$Thx$_8$T and PET$_{93}$Thx$_7$ copolyesters and PET homopolyester at 205 ºC and 210 ºC. a) Double logarithmic Avrami plot and (b) Hoffman-Weeks plot.

SI-Table 1. Solubility of homopolyesters and copolyesters.

Polyester	H_2O, EtOH, Et_2O	DMSO	THF	NMP	DMF	$CHCl_3$	HFIP, TFA, DCA
PET	-	-	-	-	-	-	+
$PE_{92}Thx_8T$	-	-	-	-	-	-	+
$PE_{85}Thx_{15}T$	-	-	-	-	-	-	+
$PE_{83}Thx_{17}T$	-	-	-	-	-	-	+
$PE_{77}Thx_{23}T$	-	-	-	-	-	±	+
$PE_{62}Thx_{38}T$	-	-	-	±	-	+	+
$PE_{43}Thx_{57}T$	-	-	-	+	-	+	+
PThxT	-	-	±	+	-	+	+
$PET_{93}Thx_7$	-	-	-	-	-	-	+
$PET_{89}Thx_{11}$	-	-	-	-	-	-	+
$PET_{85}Thx_{15}$	-	-	-	-	-	-	+
$PET_{80}Thx_{20}$	-	-	-	-	-	±	+
$PET_{70}Thx_{30}$	-	-	-	±	±	+	+
PEThx	-	+	±	+	+	+	+

(+) Soluble at room temperature; (±) partial; (-) insoluble; THF (tetrahydrofuran); DMSO (dimethylsulfoxide); DMF (*N,N´*-dimethylformamide); NMP (1-methyl-2-pyrrolidone; TFA (trifluoroacetic acid); DCA (dichloroacetic acid), HFIP (hexafluoroisopropanol).

SI-Table 2. Powder X-ray diffraction data of PET and their copolyesters.

Polyester	d_{hkl}[a] (Å)						
PET	5.44 s	5.00 s	4.13 s	3.91 s	3.40 s	3.18 m	2.72 m
$PE_{92}Thx_8T$	5.44s	5.00s	4.13 s	3.91s	3.40s	3.18m	2.72m
$PE_{85}Thx_{15}T$	5.44s	5.00s	4.13s	3.91s	3.40s	3.18w	2.72m
$PET_{93}Thx_7$	5.44s	5.00s	4.13s	3.91s	4.40s	3.18w	2.72m
$PET_{85}Thx_{15}$	5.43 s	5.00 s	4.16s	3.94 s	3.40 s	3.18 w	2.72 m

[a] Bragg spacings measured in powder diffraction patterns obtained from annealed samples. Intensities visually estimated as follows: m, medium; s, strong; w, weak.

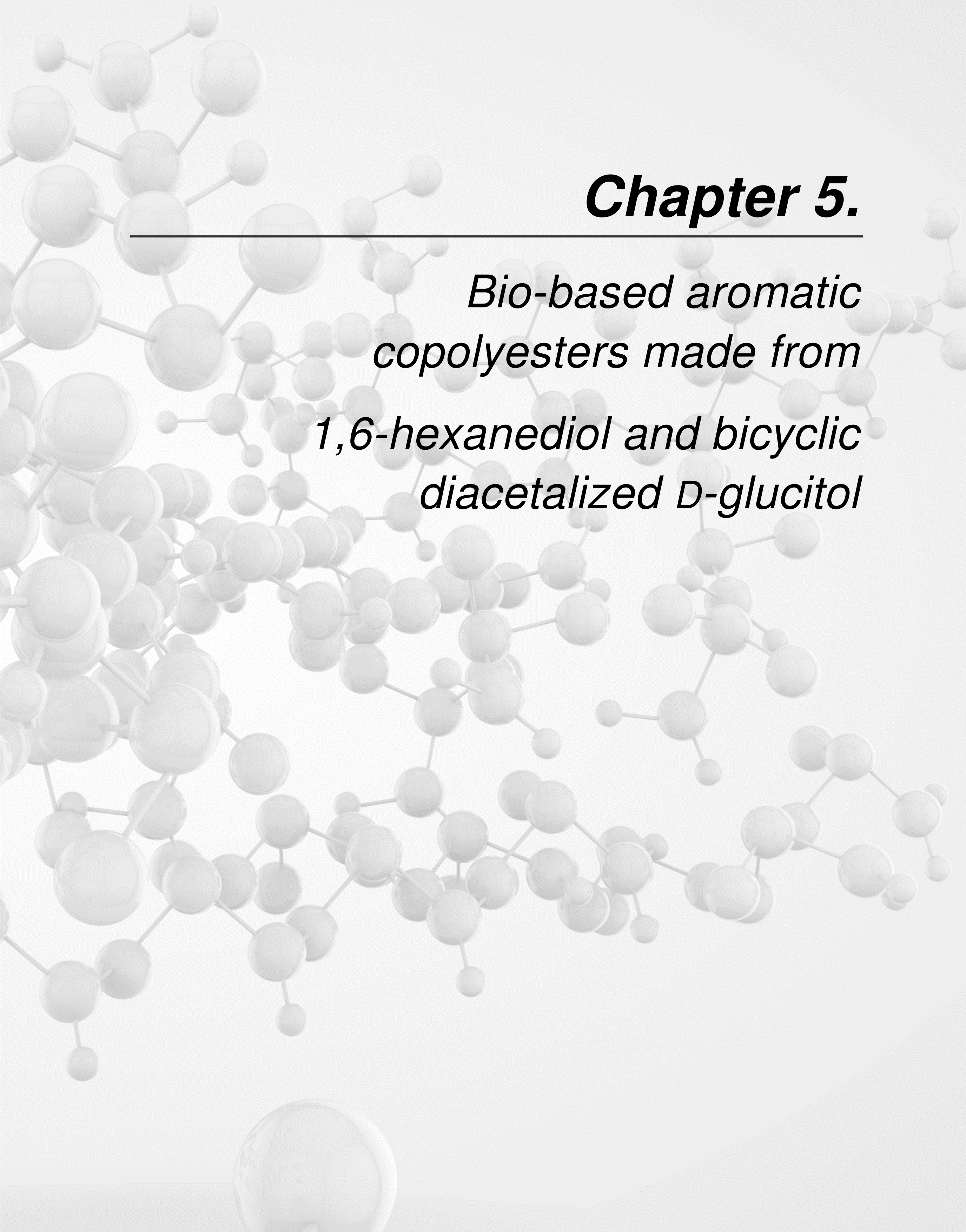
SI-Table 3. Isothermal crystallization data of PET and their copolyesters.

Polyester	T_c (ºC)[a]	ΔT (ºC)[b]	t_0 (min)[c]	$t_{1/2}$ (min)[d]	n[e]	-Lnk[e]	T_m[f] (ºC)	ΔH_m[f] ($J \cdot g^{-1}$)
PET	205	45	0.10	0.46	2.1	-1.1	251	43
	210	40	0.28	1.39	2.2	0.6	252	37
$PE_{92}Thx_8T$	205	30	3.00	7.77	2.0	3.5	234	35
	210	35	4.04	21.63	2.2	6.6	236	24
$PET_{93}Thx_7$	205	33	1.20	4.84	2.5	3.6	237	36
	210	28	2.16	8.76	2.9	5.9	239	41

[a] Crystallization temperature; [b] $\Delta T = T_m - T_c$; [c] Onset crystallization time. [d] Crystallization half-time. [e] Avrami exponent (n) and kinetics rate constant (k); [f] Melting temperature and enthalpy.

Chapter 5.

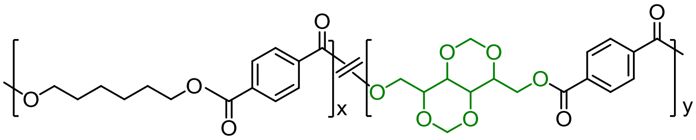
Bio-based aromatic copolyesters made from 1,6-hexanediol and bicyclic diacetalized D-glucitol

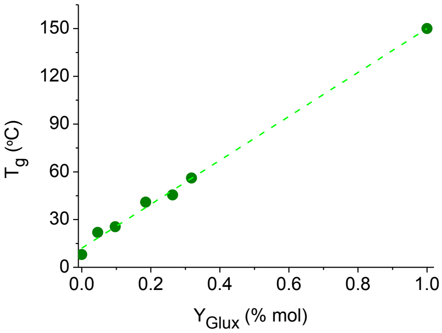


Bio-based aromatic copolyesters made from 1,6-hexanediol and bicyclic diacetalized D-glucitol

Abstract

The diacetalized diol 2,4:3,5-di-O-methylene-D-glucitol (Glux), a bicyclic compound derived from D-glucose, was used as comonomer of 1,6-hexanediol in the polycondensation in the melt with dimethyl terephthalate to produce a set of aromatic copolyesters (PH$_x$Glux$_y$T) with contents in Glux ranging from 5 to 32%-mole. These sustainable copolyesters had molecular weights within the 12,000-45,000 g·mol^{-1} range, and polydispersities between 2.0 and 2.5. All they had a random microstructure and displayed slight optical activity. PH$_x$Glux$_y$T showed a good thermal stability and were semicrystalline with both crystallinity degree and crystallization rate decreasing as the content in Glux increased. Conversely, Tg increased with the incorporation of Glux going up from 8 ºC in PHT to near 60 ºC in the copolyester containing 32%-mole of Glux. Compared to PHT, PH$_x$Glux$_y$T copolyesters showed not only an enhanced susceptibility to hydrolysis but also an appreciable biodegradability in the presence of lipases.





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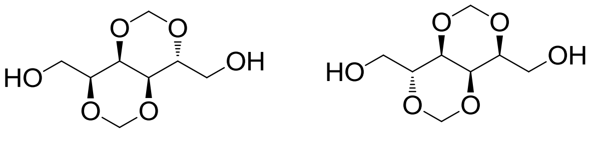
5.1. Introduction

The modification of aromatic polyesters addressed to make them more sustainable and even biodegradable, is a challenging aim that is being pursuit with great interest in these last years.[1,2] Aromatic polyesters like PET or PBT are widely acknowledged as prime thermoplastic materials with excellent thermal, mechanical and optical properties among others. Nevertheless, the possibility of creating copolymers of these polyesters by replacing partially either the diol or the diacid, or even both, by other bio-based monomers is extremely appealing provide that the basic properties of the original polymers are not significantly impoverished. Carbohydrate-based compounds have been extensively explored in the last two decades as suitable comonomers for aromatic polyesters and a fair number of examples have been reported in the literature,[3-5] and many of them have been covered by patents.[6-8] Among the different tested compounds, cyclic carbohydrate-based monomers, such as isosorbide[9] and 2,5-furandicarboxylic acid,[10] have achieved a privileged position because, in addition to their natural origin, they are able to preserve or even increase the glass transition temperature of the polyesters in which they are inserted.[11,12] The use of cyclic acetals of sugar derivatives constitutes a relatively new approach to the synthesis of sustainable polycondensates made of stiff chains. Some years ago we described a series of polyamides made of 2,3-*O*-methylene-L-tartaric acid[13] which were found to show somewhat liquid-crystal behaviour.[14] Much more recently we have reported on the use of bicyclic diacetalized dimethyl galactarate for the synthesis of aliphatic copolyesters.[15,16] This pioneering work demonstrated that bicyclic acetalized sugar derivatives are very suitable to prepare copolyesters by polycondensation in the melt since they are both thermally and chemically stable and able to react at a similar rate as other acyclic conventional monomers.

Following our previous incursions in this subject, we investigate now the use of 2,4:3,5-di-*O*-methylene-D-glucitol, abbreviated Glux, as monomer for the synthesis of aromatic polyesters. This compound is a bicyclic diacetalized diol (Scheme 1) that may be readily prepared from commercially available 1,5-D-gluconolactone.[17]



Scheme 1. Pair-view of the chemical structure of Gludioxol rotated 180º around the view axis.

Glux is thermally stable and greatly resistant to hydrolysis in both basic and acid medium. Since it lacks of any symmetry element and the two hydroxyl groups display similar reactivity, it will enter in the polymer chain with two different orientations producing *aregic* and therefore non-stereoregular polyesters. In this work, a set of copolyesters of poly(hexamethylene terephthalate) (PHT) in which the 1,6-hexamethylenediol has been replaced by Glux has been prepared and characterized, and their basic properties comparatively evaluated. PHT is a semicrystalline aromatic polyester that although has not achieved commercial realization deserves interest because its relatively low melting temperature (~140 ºC) compared to PET and PBT (~270 and ~220 ºC, respectively) will require less severe processing conditions. However PHT is not biodegradable and its potential utilization in applications demanding good compliance above room temperature is seriously weighed down because its glass-transition temperature is rather low (~8 ºC) compared to PET and PBT (~78 and ~40 ºC, respectively). As it will be shown in this paper, the insertion of Glux in the PHT chain confers to the polyester sustainability and a certain biodegradability in addition to increase notably its T_g; these effects merit the utilization of this bicyclic sugar-derived compound as monomer for the preparation of aromatic polyesters with improved properties.

5.2. Experimental section

5.2.1. Materials and methods

Materials

Dimethyl terephthalate (DMT) (99%) and 1,6-hexanediol (HD) (99%) were purchased from Sigma-Aldrich Co. and were used without further purification. Tetrabutyl titanate (TBT) (Merck-Schuchard) was reagent grade and it was used as received. The solvents used for the purification and characterization, such as chloroform, diethyl ether, dichloracetic (DCA), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), were of high purity grade and used as received.

Methods

Viscosities were measured in dichloroacetic acid at 25.0 ºC, using an Ubbelohde microviscometer at concentrations ranging from 5 to 10 mg·mL^{-1}. Molecular weight analysis was performed by GPC using as mobile phase HFIP containing 0.05 M sodium trifluoroacetate-hexafluoroisopropanol (NaTFA-HFIP) in a Waters equipment provided with RI and UV detectors. 100 µL of 0.1 % (w/v) sample solution were injected and chromatographed with a flow of 0.5 mL·min^{-1} in a linear HR5E Water Styragel column (7.8 mm×300 mm) packed with cross-linked polystyrene and protected with a pre-column. Molar mass averages and distributions were calculated against PMMA standards.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer at 25 ºC operating at 300.1 and 75.5 MHz, respectively. The polyesters were dissolved in deuterated trifluoroacetic acid (TFA-d_1), and spectra were internally referenced to tetramethylsilane. About

10 and 50 mg of sample in 1 mL solvent were used for ^{1}H and ^{13}C, respectively. Sixty-four scans were recorded for ^{1}H, and between 5,000 and 15,000 scans for ^{13}C NMR, with 32 and 64 K data points and relaxation delays of 1 and 2 s, respectively.

Infrared spectra were recorded with a Fourier Transform IR 4100 Jasco spectrometer, equipped with a Specac Golden Gate Heated Diamond ATR Top Plate, in the 4000-550 cm^{-1} range with 32 scans for every sample. The specific optical rotation was measured in a Perkin Elmer 341 polarimeter in chloroform solution (c = 6 to 9 g·L^{-1}) at 20 ºC using sodium D line radiation of wavelength 589.3 nm.

TGA measurements were performed under nitrogen flows of 20 mL·min^{-1} at a heating rate of 10 ºC·min^{-1} and within a temperature range of 30 to 60 ºC, using a Perkin-Elmer TGA6 thermo-balance. Sample weights of about 5-10 mg were used in these experiments.

The thermal behavior of the polymers was examined by differential scanning calorimetry (DSC), using a Perkin Elmer Pyris 1 apparatus. Thermograms were obtained from 4-6 mg sample at heating and cooling rates under a nitrogen flow of 20 mL·min^{-1}. Indium and zinc were used as standards for temperature and enthalpy calibrations. Melting temperature (T_m) was taken as the maximum of the endothermic peak appearing on heating traces recorded at 10 ºC·min^{-1}, and glass transition temperature (T_g) was taken as the inflection point seen on heating traces recorded at 20 ºC·min^{-1} from samples quenched from the melt.

Powder X-ray diffraction patterns were recorded on an INEL CPS-120 diffractometer with Debye-Scherrer configuration using the Cu-K$_\alpha$ radiation of wavelength 0.1542 nm from powdered samples coming directly from synthesis. Scanning electron microscopy (SEM) images were taken with a field-emission JEOL JSM-7001F instrument (JEOL, Japan).

5.2.2. Synthesis of monomers

2,4:3,5-Di-*O*-methylidene-D-glucitol (Glux) was prepared by acetalization of 1,5-D-gluconolactone with paraformaldehyde, followed by esterification with methanol and subsequent reduction as described elsewere.[17]

*2,4:3,5-Di-O-methylene-*D*-gluconic acid.* A mixture of 30 g (0.168 mol) of 1,5-D-gluconolactone, 30 g of paraformaldehyde, and 42 mL of concentrated hydrochloric acid were refluxed at 110 ºC for 1 h. The product precipitated from the solution on cooling with a yield of 80%.

*Methyl 2,4:3,5-Di-O-methylene-*D*-gluconate.* A mixture of 30 g (0.136 mol) of 2,4:3,5-di-*O*-methylene-D-gluconic acid, 250 mL of methanol and 0.75 mL of concentrated sulphuric acid was refluxed until complete dissolution. The product precipitated from the solution on cooling and additional crops were obtained on concentrating the mother liquors. Yield: 70%.

*2,4:3,5-Di-O-methylene-*D*-glucitol (Glux)*. To a suspension of methyl 2,4:3,5-di-*O*-methylene-Dgluconate (20 g, 0.085 mol) in dry tetrahydrofuran (100 mL), a suspension of $LiAlH_4$ (97%, 6.8 g, 0.179 mol) in dry tetrahydrofuran (150 mL) was added at 0 ºC under nitrogen atmosphere. The mixture was then refluxed for 24 h and cooled to 0 ºC. Water (25 mL), aqueous solution of NaOH (15% w/v, 25 mL), and water (75 mL) were sequentially and slowly added, and the mixture was then filtered and concentrated to an oily residue (about 20 mL) from which the title compound crystallized as a white solid. Yield: 60%. ^{1}H NMR (DMSO, 300 MHz): δ (ppm) 5.01-4.71 (dd, 2H, O-CH_2-O, *m*), 4.91-4.76 (dd, 2H, O-CH_2-O, *l*), 3.78 (m, 1H, CH, *h*), 3.70 (m, 3H, OCH_2, *k*, and CH, *i*), 3.64 (m, 1H, CH, *j*), 3.60 (m, 1H, CH, *g*), and 3.48 (m, 2H, CH_2, *f*). ^{13}C NMR (DMSO, 75.5 MHz): δ (ppm) 91.83 (O-CH_2-O, *m*), 87.34 (O-CH_2-O, *l*), 78.06 (CH, *g*), 76.05 (CH, *i*), 70.33 (CH, *j*), 66.65 (CH, *h*), 59.49 (OCH_2, *f*), 58.26 (OCH_2, *k*).

5.2.3. Synthesis of polyesters and copolyesters

The reaction was performed in a three-necked, cylindrical flask equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum distillation outlet. A 2.2/1 molar ratio of the diols 1,6 hexanediol (HD) and 2,4:3,5-di-*O*-methylene-D-glucitol (Glux) to dimethylene terephthalate (DMT) and tetrabutyl titanate (TBT) as catalyst (0.6% mmol per mol of DMT) were used. The apparatus was vented with nitrogen several times at room temperature to remove the air and avoid oxidation during the polymerization. Transesterification reactions were carried out under a low nitrogen flow for a period of 3 h at 190 ºC. Polycondensation reactions were left to proceed for 5 h at 200-240 ºC under a 0.03-0.06 mbar vacuum. Then, the reaction mixture was cooled to room temperature, and the atmospheric pressure was recovered with nitrogen to prevent degradation. The obtained polymers were dissolved in chloroform and precipitated in excess of methanol to remove unreacted monomers and remaining oligomers. Finally, the polymer was collected by filtration, extensively washed with methanol and diethyl ether, and dried under vacuum.

PH_xGlux_yT. IR: υ (cm^{-1}) 1052 and 1188 (asymmetric stretching of C-O-C linkage of bicyclic dioxolane rings, 1730, 1350 and 1100 cm^{-1} (stretching of ester group). (IR spectra of the whole set of polyesters are provided in the Electronic Supplementary Information (ESI) file linked to this paper.

^{1}H NMR (TFA-*d*$_1$, 300 MHz): δ (ppm) 8.23 (s, ArH), 5.1-5.5 (2dd, OCH_2O), 5.20-4.85 (m, 2CH_2, 1CH), 4.46-4.65 (m, 1CH, O*CH₂*CH_2), 4,31 (m, CH), 4.1 (m, CH), 2.0 (m, OCH_2*CH₂*), 1.70 (m, OCH_2CH_2*CH₂*). ^{13}C{^{1}H}-NMR (TFA-*d*$_1$, 75.5 MHz): δ (ppm) 170.5 (C=O), 135-137 (ArC), 131.9 (ArC), 95.0 (OCH_2O), 89.91 (OCH_2O), 78.4 (CH), 76.4 (CH), 73.1 (CH), 70.6 (CH), 69.5 (O*CH₂*CH_2), 67.0 (CH_2), 63.3 (CH_2), 30.1 (OCH_2*CH₂*), 27.4 (OCH_2CH_2*CH₂*).

PGluxT. ^{1}H NMR (TFA-*d*$_1$, 300 MHz): δ (ppm) 8.23 (s, 4H, ArH), 5.15-5.50 (2dd, 4H, OCH_2O), 5.20-4.85 (m, 5H, $2CH_2$, 1CH), 4,50 (m, 1H, CH), 4,31 (m, 1H, CH), 4.10 (m, 1H, CH). $^{13}C\{^1H\}$-NMR (TFA-d_1, 75.5 MHz): δ (ppm) 170.5 (C=O), 135-137 (ArC), 131.91 (ArC), 95.0 (OCH_2O), 89.9 (OCH_2O), 78.4 (CH), 76.4 (CH), 73.1 (CH), 70.6 (CH), 67.0 (CH_2), 63.3 (CH_2).

5.2.4. Hydrolytic and enzymatic degradation assays

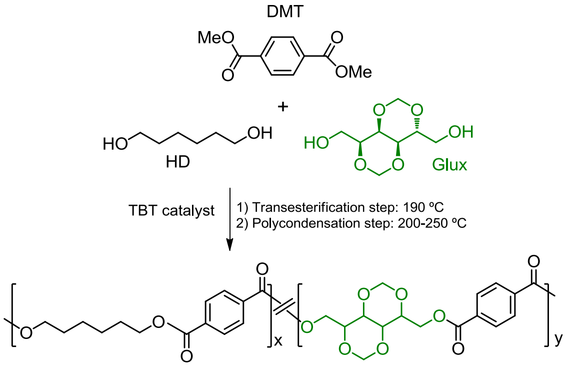
For both hydrolytic and enzymatic degradation studies, films of polyesters and copolyesters with a thickness of about 200 µm were prepared by casting from chloroform solution (0.062 g·mL^{-1}). The films were cut into 10 mm diameter disks and dried under vacuum to constant weight, which finally remained between 20 to 30 mg. Disks were individually immersed at 37 ºC in vials containing 10 mL of either sodium phosphate buffer pH 7.4 or citric acid buffer pH 2.0 (hydrolytic degradation), or sodium phosphate buffer pH 7.4 containing 10 mg of lipase from porcine pancreas or from *Pseudomonas fluorescens* (enzymatic degradation). The buffered enzyme solution was replaced every 72 h to maintain the enzyme activity. At the end of the scheduled incubation periods, the disks were withdrawn from the incubation medium, washed thoroughly with distilled water and dried to constant weight, and then subjected to weighting.

5.3. Results and discussion

5.3.1. Polyesters synthesis and microstructure of PH_xGlux_yT copolyesters

Synthesis

The synthesis followed in this work for the preparation of the PH_xGlux_yT copolyesters was the two-step melt polycondensation of dimethylene terephthalate (DMT) with mixtures of 1,6 hexanediol (HD) and 2,4:3,5-di-*O*-methylene-D-glucitol (Glux) in the presence of tetrabutyl titanate as catalyst (Scheme 2). Copolyesters with HD to Glux molar ratio varying from 95/5 to 70/30 were prepared using feed molar ratio of DMT to the total of diols of 1:2,2 in order to ensure that the growing chains were hydroxyl ended at any polymerization stage.



Scheme 2. Reaction scheme for the preparation of PH_xGlux_yT copolyesters.

In the first step, transesterification of DMT leading to H_xGlux_yT oligomers was accomplished at 190 ºC under atmospheric pressure with formation of methanol, which was removed by distillation. Polycondensation of the oligomers leading to PH_xGlux_yT copolyesters, took place in the second step at 200-250 ºC under vacuum with releasing of the excess of diols. The two homopolyesters, PHT and PGluxT, used in the present study for comparison purposes, were prepared following the same procedure. Since Glux is sensitive to high temperature, it was necessary to adjust the reaction conditions according to composition to minimize thermal degradation. Thus the temperature for the second step was lowered from 250 ºC to 200 ºC when contents in Glux above 20%-mole were used. Nevertheless, as it is shown in Table 1, both yields and molecular weights of the resulting polycondensates remarkably decreased with increasing contents of Glux in the feed whereas polydispersity was found to increase.

Table 1. Synthesis data of PHT, PGluxT and PH_xGlux_yT copolyesters.

Polyester	Yield %	Composition [HD]/[Glux]		Molecular Weights				$[\alpha]_D$[e] (º)
		Feed[a]	Polymer[b]	$[\eta]$[c]	M_n[d]	M_w[d]	$Đ$[d]	
PHT	88	100/0	100/0	0.83	17,700	46,000	2.3	-
$PH_{95}Glux_5T$	80	95/5	95.4/4.6	0.86	18,000	47,500	2.2	1.1
$PH_{90}Glux_{10}T$	76	90/10	90.3/9.7	0.68	14,800	31,400	2.1	1.4
$PH_{81}Glux_{19}T$	68	80/20	81.5/18.5	0.65	13,900	33,000	2.2	6.5
$PH_{74}Glux_{26}T$	60	70/30	73.9/26.1	0.34	6,050	16,000	2.5	7.2
$PH_{68}Glux_{32}T$	57	60/40	68.2/31.8	0.29	5,100	12,400	2.5	9.5
PGluxT	30	0/100	0/100	nd.	3,000	10,100	3.3	n.d.

[a] Molar ratio in the initial feed. The excess of diols to DMT was in all cases made with HD.
[b] Molar ratio in the copolyester determined by ^{1}H NMR.
[c] Intrinsic viscosity (dL·g^{-1}) measured in dichloroacetic acid at 25 °C; not determined for PGluxT because its insolubility in DCA.
[d] Number and weight-averaged molecular weights and polydispersity ($Đ$) determined by GPC.
[e] Specific optical rotations of PH_xGlux_yT copolyesters.

Infrared spectra of copolyesters displayed the bands characteristic of the dioxolane structure with their absorbances increasing with the content of the Glux units (spectra in ESI). Both the ^{1}H and ^{13}C NMR analysis ascertained the constitution of the copolyesters. An example illustrating this analysis is provided in Figure 1 which shows the spectra of $PH_{68}Glx_{32}T$ copolyester with indication of the assignments for all the signals.

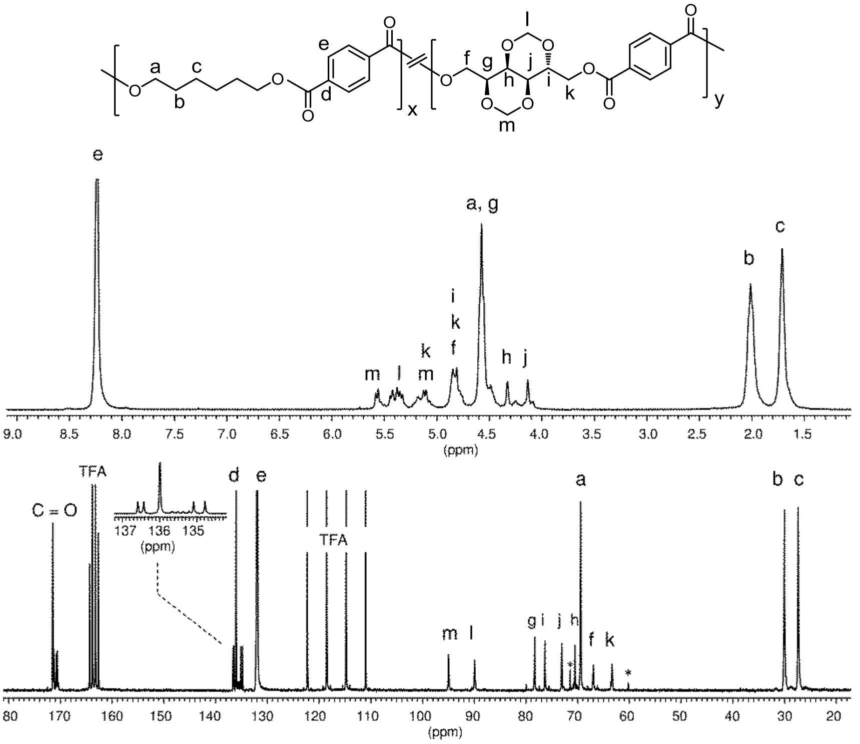


Figure 1. ^1H- (top) and ^{13}C- (bottom) NMR spectra of $PH_{68}Glx_{32}T$ copolyester recorded in TFA-d_1. (*) Signals arising from end groups.

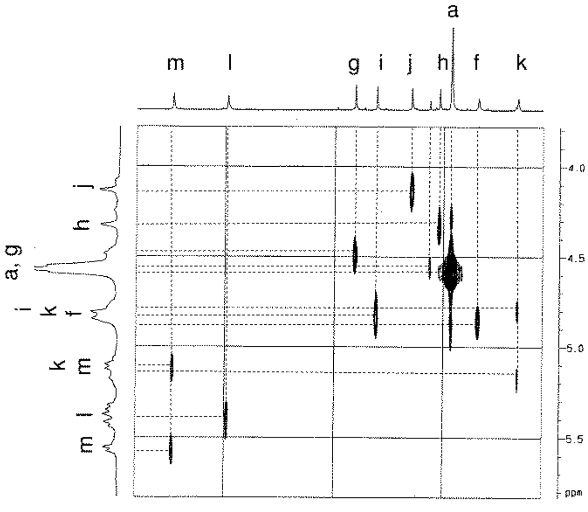


Figure 2. ^1H-^{13}C Heteronuclear Shift Correlation spectrum (HETCOR) of $PH_{68}Glux_{32}T$ recorded in TFA; amplified region containing the signals corresponding to Glux.

The assignment of the signals arising from the sugar unit was supported by the HETCOR spectrum shown in Figure 2. Quantification of the proton signals arising from the second methylene of HD (*b* signal at 2.0 ppm) and the methylene of the acetal Glux (*m* signal at 5.6 ppm) units afforded their compositions, which appeared to be pretty close to those of their respective feeds provided that almost all the excess of HD was removed along the polycondensation reaction (Table 1).

Microstructure

As it is depicted in Figure 3, the ^{13}C NMR spectra of PGluxT and PH$_x$Glux$_y$T copolyesters show the non-protonated aromatic carbon signal (*d* peak) with resolution enough as to make possible the elucidation of the copolyester microstructure as far as distribution of HD and Glux units along the copolyester chain is concerned. As a consequence of the occurrence of different dyad types and also of the two orientations for the Glux unit, this signal appears split into multiple peaks that spread within the 134-137 ppm interval. Nevertheless, three groups of peaks may be discerned in such spectra which are arising from the four types of diol-dyads (GTG, HTH, GTG and HTG) present in the copolyester chain.

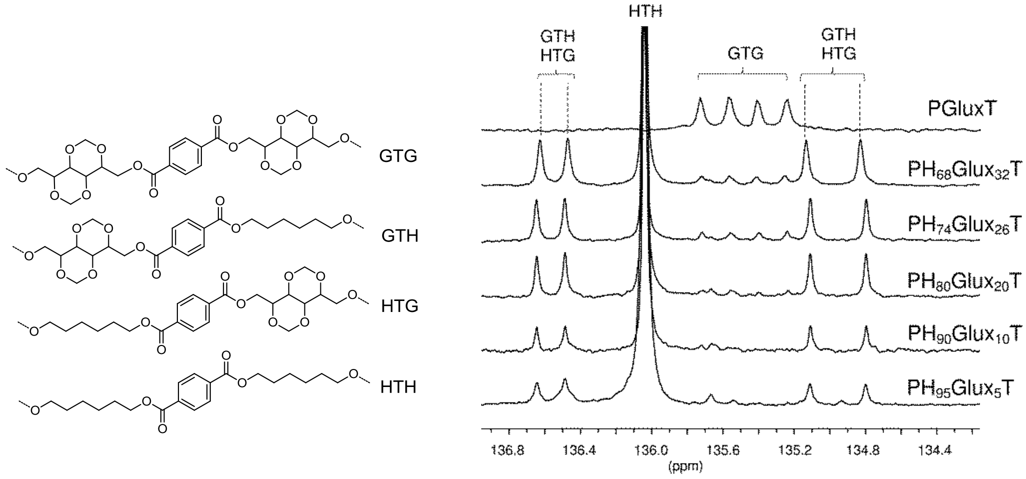


Figure 3. The four possible dyads of HD and Glux (left). ^{13}C NMR spectra of the nonprotonated aromatic carbons for the indicated polyesters with assignments of the peaks to dyads (right).

The molar fractions *N* of the different dyads in the copolyesters were determined by integration of their corresponding peaks or groups of peaks. On the base of such data, the number average sequence lengths *n* of the hexanodiol-terephthalate (HT) and glucitol-terephthalate (GT) homogeneous sequences, as well as the degree of randomness *R*, were estimated for each copolyester by using the following equations.[18,19]

$$n_{HT} = (N_{HTH} + ½\ (N_{HTG}+N_{HTG}))/½\ (N_{HTG}+N_{HTG})$$
$$n_{GT} = (N_{GTG} + ½\ (N_{HTG}+N_{HTG}))/½\ (N_{HTG}+N_{HTG})$$
$$R = (1/n_{HT}) + (1/n_{GT})$$

Results from these calculations (Table 2) showed that the sequence distribution in PH_xGlux_yT copolyesters is essentially at random for the all range of compositions with values of R being very close to unity. The R values resulting from this NMR analysis were in good agreement with those statistically calculated for ideal copolymers with the same composition and a fully random microstructure.

Table 2. Microstructure of copolyesters $PH_xGlux_yT^a$.

Copolyester	Dyad content			Length		R
	N_{HTH}	$N_{GTH/HTG}$	N_{GTG}	n_{HT}	n_{GT}	
$PH_{95}Glux_5T$	87.9 (90.9)	12.1 (8.7)	0 (0.2)	15.5 (21.7)	1.0 (1.0)	1.06 (1)
$PH_{90}Glux_{10}T$	84.0 (81.5)	16.0 (17.5)	0 (0.9)	11.5 (10.3)	1.0 (1.1)	1.08 (1)
$PH_{80}Glux_{20}T$	67.9 (66.4)	27.2 (30.1)	4.9 (3.4)	6.0 (5.4)	1.4 (1.2)	0.90 (1)
$PH_{74}Glux_{26}T$	50.3 (54.3)	39.8 (37.8)	9.9 (6.9)	3.5 (3.8)	1.5 (1.4)	0.95 (1)
$PH_{68}Glux_{32}T$	49.5 (46.5)	40.0 (43.3)	10.5 (10.1)	3.4 (3.1)	1.5 (1.4)	0.94 (1)

[a] Dyad molar fractions (N) experimentally determined by ^{13}C NMR for the copolyester compositions given in Table 1, and number-average sequences lengths (n) estimated by the equations given in the text. In parenthesis values calculated on the basis of an ideal random distribution for the given copolyester compositions.

The orientation effect associated to Glux is well illustrated in the spectra of PGluxT homopolyester observed in Figure 3 where the signal arising from GTG dyad split into four peaks of similar intensities. Obviously, such multiplicity arises from the three different arrangements that are feasible for the GTG dyad according to the relative orientation adopted by the two neighbouring Glux units. The same effect is observed for the GTG dyad signal in copolyesters. It can be concluded therefore that Glux units are placed along the polymer chain without any directional preference. Such *aregic* character of the Glux containing polyester and copolyesters is in principle indicative of a lack of *regioselectivity* in the incorporation of the diol in the growing chain. However the occurrence of extensive polymer transesterification during polycondensation would lead also to a randomization of the Glux unit orientations. In the absence of more detailed studies, the *aregicity* observed for Glux containing polyester and copolyesters should be thought that is due to the combined action of both effects operating simultaneously.

5.3.2. Thermal properties

The effect produced by the incorporation of the Glux units in the chain of PHT on the thermal behaviour of the resulting copolyesters is an issue of prime importance for the valuation of these polymers as potential thermoplastic materials. The basic thermal properties were evaluated by TGA and DSC and the fundamental parameters coming out from these measurements are listed in Table 3.

The TGA traces of the PH_xGlux_yT copolyesters and the parent homopolyesters PHT and PGluxT registered under an inert nitrogen atmosphere are depicted in Figure 4. This comparative plot reveals that although the incorporation of Glux diminishes the thermal stability of PHT, the decay is not significant in the copolyesters. In fact, the decomposition of all the copolyesters started to be perceivable above 360 ºC and found to happen in a single step with the maximum degradation rate taking place around 400 ºC. On the contrary, the PGluxT homopolyester showed a notable reduction in the thermal stability so it started to degrade about 80 ºC below than PHT. Furthermore, it decomposed through a complex process implying at least three differentiated steps. The relatively low thermal stability of copolyesters containing Glux may be due to the presence of the tertiary carbon in β-position to the ester group which will favour the occurrence of α β-elimination process with the subsequent splitting of the main chain.

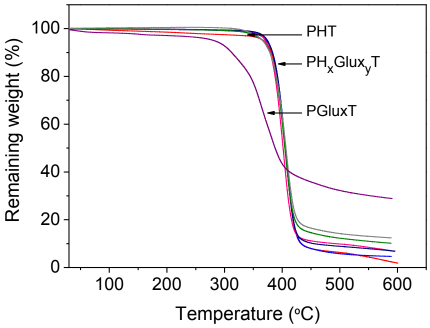


Figure 4. TGA traces of homopolyesters PHT and PGluxT and PH_xGlux_yT copolyesters.

The DSC heating scans recorded from PH_xGlux_yT samples coming directly from synthesis are shown in Figure 5 (left). All they display endothermic peaks characteristic of melting at temperatures decreasing steadily from 144 ºC to 84 ºC and become broader with increasing contents in Glux. Not only the main peak but also the other minor ones moved to lower temperatures as the Glux content in the copolyesters increased.

Table 3. Thermal properties of PHT, PGluxT and PH$_x$Glux$_y$T copolyesters.

Polyester	TGA			DSC								
					First Heating[e]		Cooling[e]		Second Heating[e]		Annealing[f]	
	T_d[a] (°C)	T_d[b] (°C)	RW[c] (%)	T_g[d] (°C)	T_m (°C)	ΔH_m ($J \cdot g^{-1}$)	T_c (°C)	ΔH_c ($J \cdot g^{-1}$)	T_m (°C)	ΔH_m ($J \cdot g^{-1}$)	T_m (°C)	ΔH_m ($J \cdot g^{-1}$)
PHT	360	406	2.1	8	144	34	117	-30	138	31	151	46
PH$_{95}$Glux$_5$T	373	410	4.6	20	136	29	100	-27	137	27	148	44
PH$_{90}$Glux$_{10}$T	371	403	6.7	25	133	31	97	-30	133	30	135	40
PH$_{80}$Glux$_{20}$T	375	408	6.8	41	118	22	-	-	-	-	118	28
PH$_{74}$Glux$_{26}$T	366	404	10	46	119	12	-	-	-	-	116	25
PH$_{68}$Glux$_{32}$T	367	407	12	56	84	9	-	-	-	-	87	9
PGluxT	281	364	29	150	-	-	-	-	-	-	-	-

[a] Temperature at which a 10 % of weight loss was observed in the TGA traces recorded at 10 °C min^{-1}.

[b] Temperature of maximum degradation rate.

[c] Remaining weight at 600ºC.

[d] Glass-transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 °C min^{-1}.

[e] Melting (T_m) and crystallization (T_c) temperatures and their respective enthalpies (ΔH_m, ΔH_c) measured by DSC at heating/cooling rates of 10 °C min^{-1}.

[f] Annealing treatment applied for 12 h at chosen temperatures.

According to which is widely accepted for the melting behaviour of polyesters, such multiple melting should be interpreted as arising from the occurrence of disperse crystallite sizes that generate in a defective crystallization process.

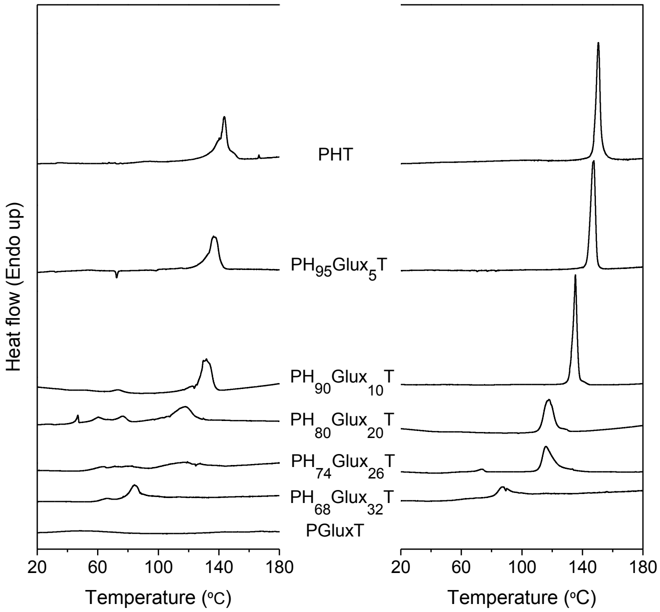


Figure 5. DSC traces of PHT, PH_xGlux_yT and PGluxT. Initial samples (left) and annealed samples (right).

This phenomenum is expected to be enhanced in the PH_xGlux_yT copolyesters due to the presence of the asymmetrical Glux units. In fact, when initial samples of the copolyesters containing minor amounts of Glux were subjected to annealing sharper peaks with larger melting enthalpies indicative of a better crystallized material were generated (Figure 5, right). The effect of the annealing treatment on copolyesters with higher contents in Glux did not afforded similar satisfactory results since the maximum size achievable by the crystallite is largely limited by composition. Changes in T_m and ΔH_m of PHT and PH_xGlux_yT copolyesters induced by annealing are given in Table 3 and the evolution of T_m with composition is plotted in Figure 6.

The T_g of the polyesters and copolyesters were clearly detected in the heating DSC traces of samples previously quenched from the melt (see ESI). In contrast with it happens with the melting temperature, the glass transition temperature of the copolyesters increased with the content in Glux. As it could be reasonably anticipated, the replacement of the highly flexible hexamethylene segment of PHT by the relatively rigid bicyclic dioxolane structure appears to increase the stiffness of the polyester chain and restricts therefore its mobility. In fact, the homopolyester PGluxT displayed a T_g about 140 ºC higher than PHT. Accordingly, the T_g of

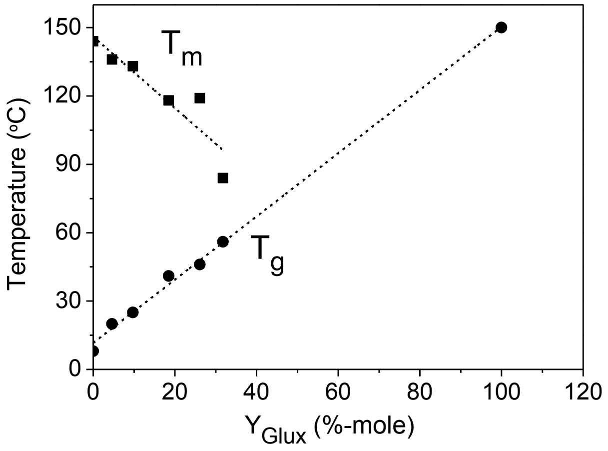


Figure 6. Evolution of T_m and T_g of PH_xGlux_yT with the content in Glux units.

copolyesters increased almost linearly with the content in Glux units with a slope close to 1.5 ºC·%-mole^{-1} (Figure 6).Such a remarkable positive effect of the incorporation of Glux on T_g makes this compound comparable to isosorbide[11,12] as a bio-based comonomer suitable for the preparation of polycondensates with high glass transition temperatures.

5.3.3. Structure and isothermal crystallization

Although DSC showed that all the copolyesters are semicrystalline, only those containing 5 and 10 % of Glux were able to crystallize upon cooling from the melt. It appears therefore that the insertion of the Glux unit in the PHT chain depresses the crystallizability of the polyester, *i.e.* both crystallinity and crystallization rate are significantly diminished. In order to evaluate more precisely the influence of the presence of Glux on the cristallizability of PH_xGlux_yT copolyesters, a comparative isothermal crystallization study on PHT, $PH_{95}Glux_5T$ and $PH_{90}Glux_{10}T$ was carried out by DSC. Respective samples were previously melted under exactly the same conditions and then each one left to crystallize at three different temperatures. The amount of relative crystallinity generated with time is plotted in Figure 7 for PHT and the two copolyesters crystallized at 120 ºC. The plots reveal that longer crystallization times were needed to attain the same level of crystallinity when the content of Glux in the copolyester was increased.

The classical Avrami approach was applied to evaluate the kinetics parameters for the two copolyesters, which are afforded in Table 4 together with those obtained for the PHT homopolyester. A comparison of these kinetics data reveals that both the onset and half-crystallization times largely increased in the copolyesters respect to PHT whereas no significant changes are observed for the Avrami exponent *n* indicating that a similar crystallization mechanism must operate in the three cases. Furthermore, comparison of kinetics data for the same copolyester crystallized at different temperatures evidenced the delaying effect of temperature on crystallization rate, as it could be expected for a nucleation controlled process (ESI).

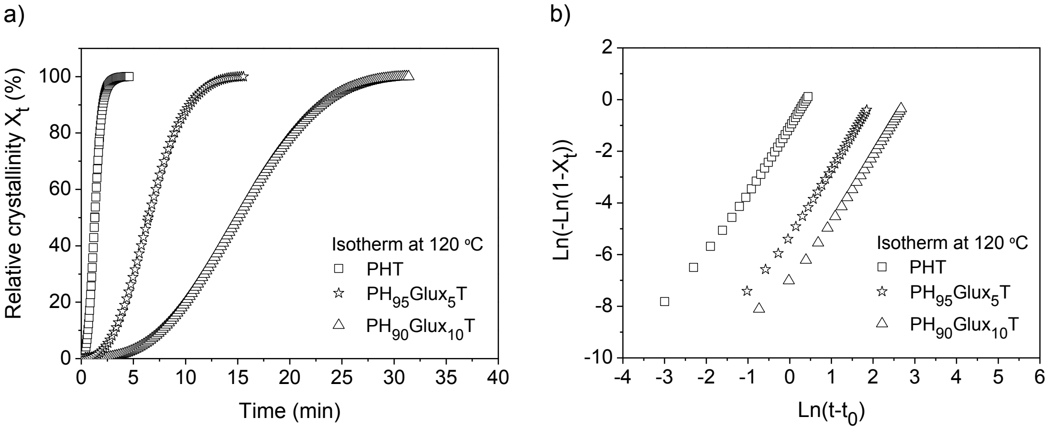


Figure 7. Isothermal crystallization at 120 ºC of PHT, $PH_{95}Glux_5T$ and $PH_{90}Glux_{10}T$. Evolution of the relative crystallinity with time (a). Avrami plots (b).

Table 4. Isothermal crystallization data of PHT and PH_xGlux_yT copolyesters.

Polyester	T_c(ºC)	ΔT(ºC)	t_0(min)	$t_{1/2}$(min)	n	-Lnk
PHT	115	29	0.16	0.83	2.11	0.40
	120	24	0.40	1.70	2.54	5.19
$PH_{95}Glux_5T$	110	26	0.20	1.81	2.40	2.02
	115	21	0.41	3.64	2.43	3.58
	120	16	1.04	6.44	2.54	5.19
$PH_{90}Glux_{10}T$	110	23	0.51	1.89	2.71	2.12
	115	18	0.97	4.94	2.73	4.65
	120	13	2.40	15.21	2.82	8.02

[a] Crystallization temperature; [b]$\Delta T = T_m - T_c$; [c]Onset crystallization time; [d]Crystallization half-time; [e]Avrami exponent (n) and kinetics rate constant (k)

The preliminary X-ray diffraction analysis of copolyesters is in full agreement with the results afforded by DSC. The powder WAXS profiles recorded from PHT and PH_xGlux_yT copolyesters are depicted in Figure 8. The presence of sharp scattering in such profiles corroborated the semicrystalline nature of all the copolyesters and the similitude in spacings and intensities of the peaks with those appearing in the PHT profile, indicated that they must adopt the same crystal structure than the homopolyester, which is known to consist mainly of the triclinic β-form.[20-22] It was seen also that the number and intensity of diffraction peaks decreased with the content in Glux revealing a decay in crystallinity according to what was observed by DSC. Given the lack of symmetry of the *gluco* configuration, it is hardly probable that the Glux units are able to crystallize, and even less to share the lattice with the hexanodiol units. As it has been accounted for other closely related systems previously studied by us,[23] the crystal phase of these copolyesters is interpreted to be composed of homogeneous sequences of HT units with the GT units being rejected to the amorphous phase. This may satisfactorily explain both the occurrence of the PHT crystal structure in the copolyesters and the gradual decay of crystallinity with composition.

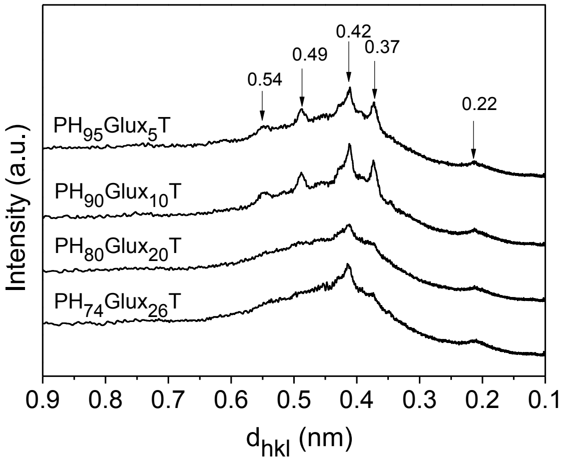


Figure 8. WAXS profiles of annealed PH_xGlux_yT copolyesters.

5.3.4. Hydrolytic and enzymatic degradability

Another relevant modification in the behaviour of PHT that should be expected from the insertion of Glux units in the polyester chain is the enhancement of its hidrodegradability, both with and without the concourse of enzymes. In fact, several recent works have reported that the high resistance to hydrolysis characteristic of conventional aromatic polyesters is lowered when either the diol or the diacid counterparts are replaced by alditols or aldaric acids.[4] To assess the influence of Glux in this regard, the hydrolytic and enzymatic degradation of $PH_{80}Glux_{20}T$ and $PH_{68}Glux_{32}T$ copolyesters was evaluated under different conditions and compared to that undergone by PHT.

Changes in sample weight taking place upon degradation of PHT and the copolyesters as a function of incubation time are plotted in Figure 9. As it was predictable, PHT appeared to be almost unaffected by both neutral and acidic aqueous solutions (pH 7.4 and 2.0) even after five months of incubation, and such behaviour was barely altered by the presence of lipases. Conversely, both $PH_{80}Glux_{20}T$ and $PH_{68}Glux_{32}T$ showed a slight but significant weight loss indicative of the occurrence of a sluggish degradation process (Figure 9a).

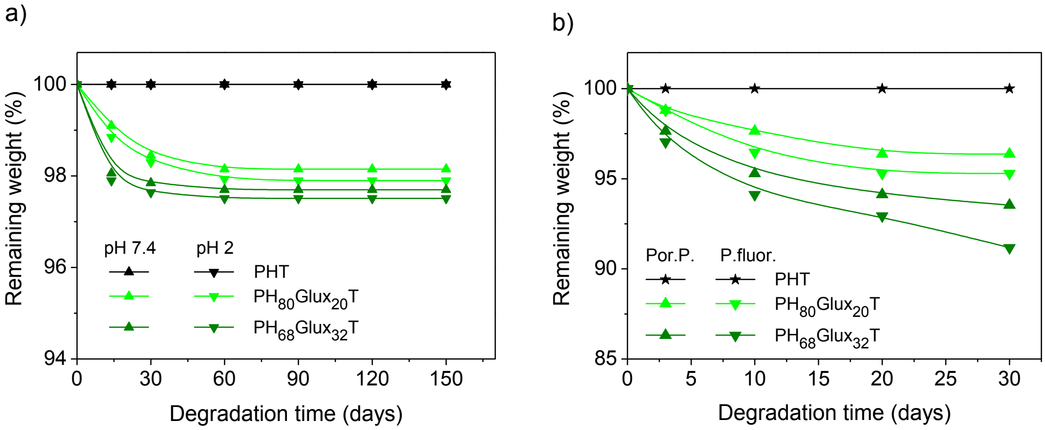


Figure 9. Remaining weight *vs* incubation time for PHT, $PH_{80}Glux_{20}T$ and $PH_{68}Glux_{32}T$ subjected to hydrolytic (a) and enzymatic degradation with lipases porcine pancreas (por.p.) and *Pseudomonas fluorescens* (*P. fluor.*) (b).

Although differences between the two copolyesters are small, it is meaningful that degradation happened faster for that one containing higher amount of Glux, according to what should be expected. The degradability of the copolyesters remarkably increased in the presence of enzymes (Figure 9b). Porcine pancreas and *P. fluorescens* lipases in buffer pH 7.4 were tested at a temperature of 37 ºC, the later showing higher hydrolytic activity. The maximum degradation rate was observed for $PH_{68}Glux_{32}T$ which lost near 10% of its original weight after 30 days of incubation. The degradability of $PH_{80}Glux_{20}T$ was enhanced in a similar extension by lipases although the final weight loss was kept below 5% as correspond to its lower content in Glux.

A SEM analysis of the incubated samples afforded complementary evidences on the alteration taking place in the material upon degradation. The micrographs showed in Figure 10 compare the surface of the initial disk of $PH_{68}Glux_{32}T$ with those incubated in neutral and acidic aqueous buffer without lipases and in the presence of *P. fluorescens*. The smooth surface of the original sample remained essentially unchanged after incubation under neutral conditions. On the contrary, some erosion, which was evidenced by an increase in roughness and the appearance of small holes, started to be perceivable after incubation at pH 2.0 for several months. These alterations became much more apparent after incubation for one month in the presence of lipase with plenty of holes uniformly spread over the whole disk, which unmistakably proved the biodegradability of the copolyester.

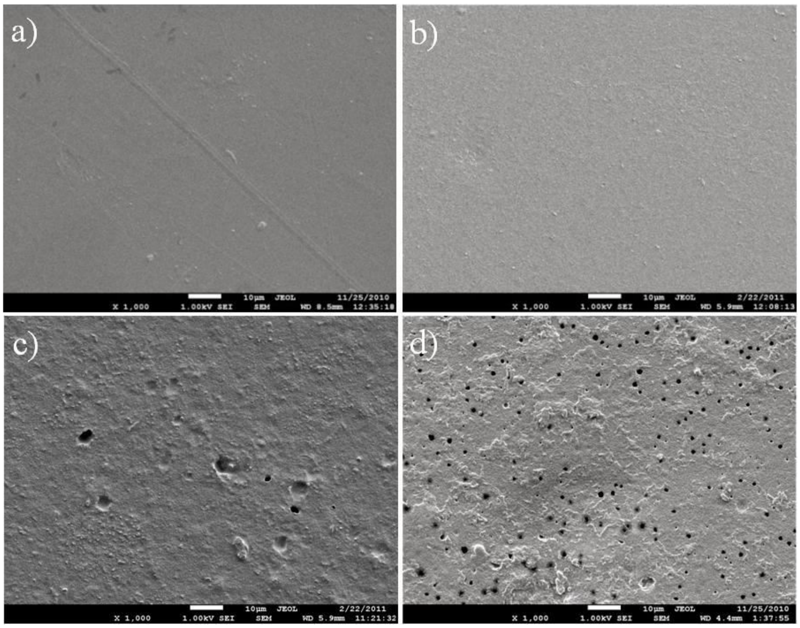


Figure 10. SEM micrographs of $PH_{68}Glux_{32}T$ disk surface. Initial sample (a) and after incubation for five months in aqueous buffer at pH 7.4 (b), pH 2.0 (c) and for one month in a physiological solution containing *P. fluorescens* lipase (d). The scale bar indicates 10 µm in all pictures.

5.4. Conclusions

The bicyclic compound 2,4:3,5-di-*O*-methylene-D-glucitol (Glux) has been successfullyused as comonomer of 1,6-hexanediol for the synthesis of poly(terephthalate)s copolyesters by polycondensation in the melt. The novel copolyesters have molecular weights within a satisfactorily range of values and a random microstructure regardless their composition. In spite of the asymmetrical structure of Glux, all the copolyesters are semicrystalline although their crystallinity diminishes as their content in Glux increases. Copolyester melting temperatures span from 80 to 150 ºC, and those with lower contents in Glux are able to crystallize from the melt; since they are well stable to heat up to temperatures above 350 ºC, these partially bio-based copolyesters are suitable to be used as thermoplastic materials. An outstanding feature of these novel copolyesters is their relatively high T_g, which ranges between 20 and 60 ºC with values increasing with the content in Glux. Another merit is their susceptibility to biodegradation at low rates; this moderate biodegradability is of interest for the potential use of these aromatic polyesters in applications where the self-destruction of the material is scheduled to happen after long times of use.

5.5. References

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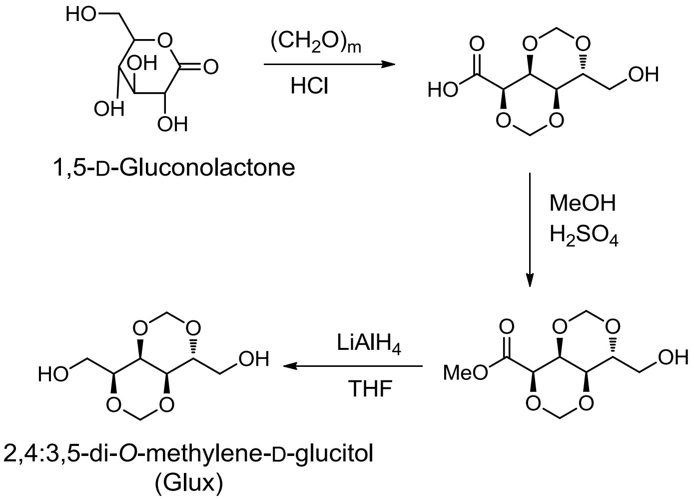
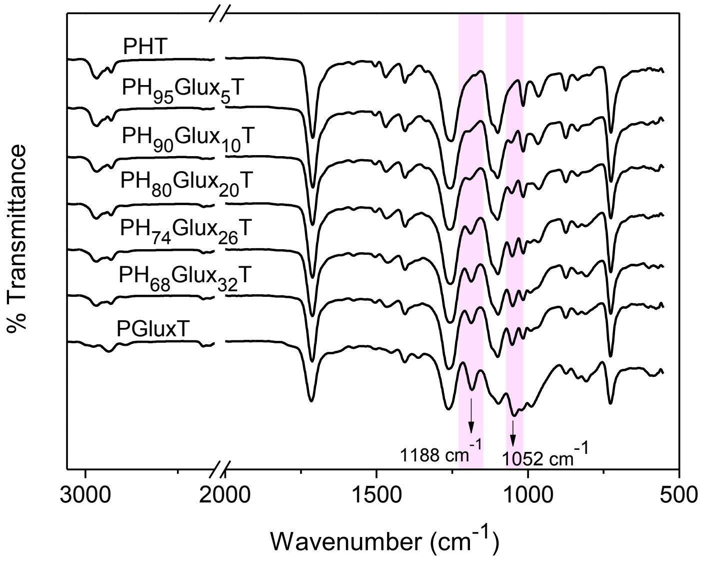
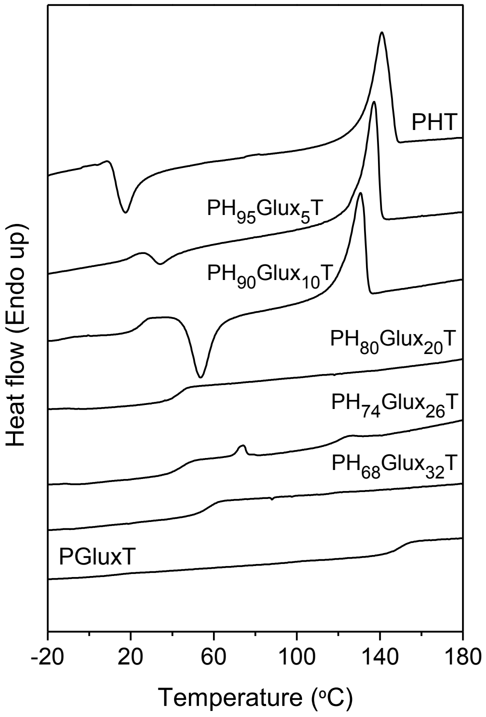
Supporting information



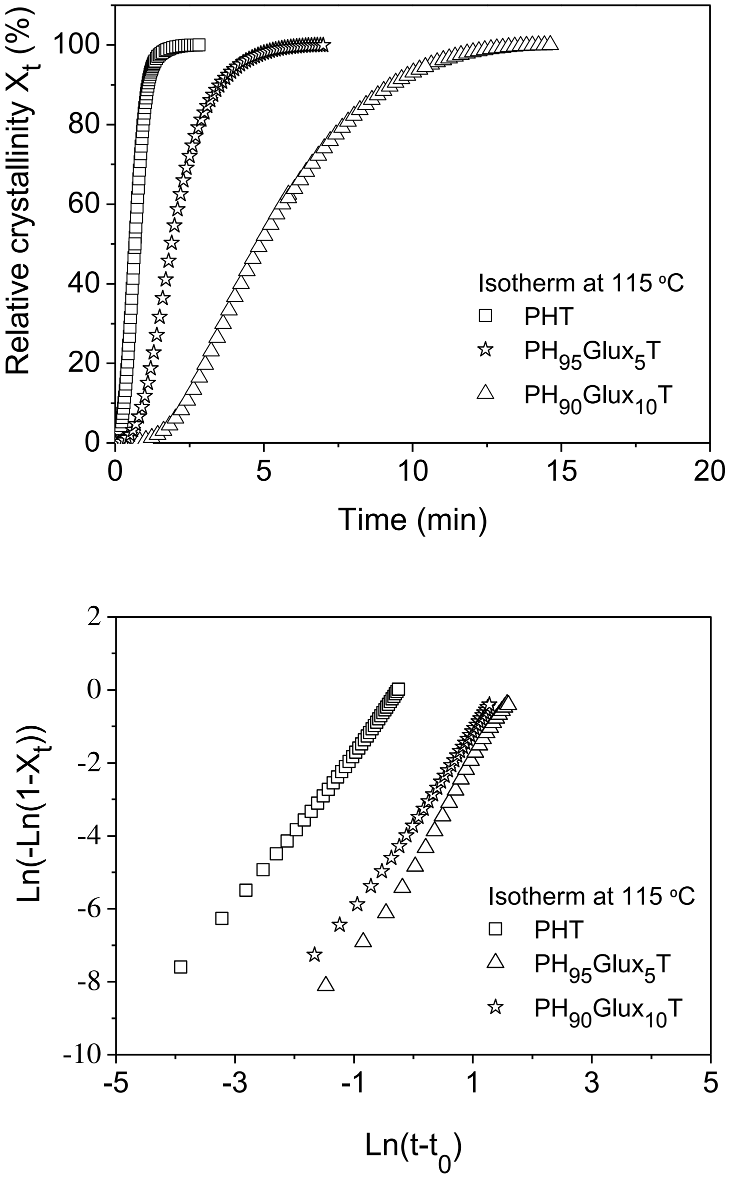
SI-Scheme 1. Synthetic route to Glux from 1,5-D-gluconolactone.



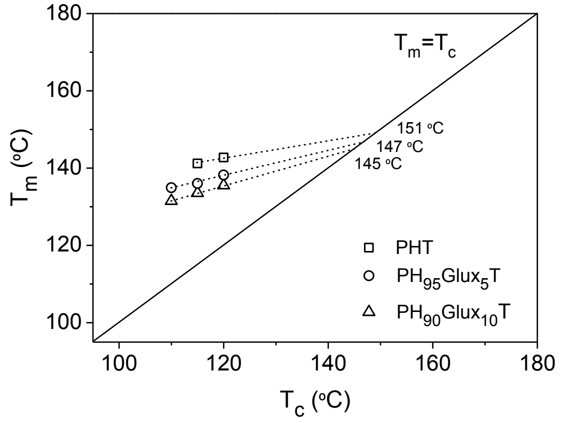
SI-Figure 1. FTIR spectra of the indicated polyesters.



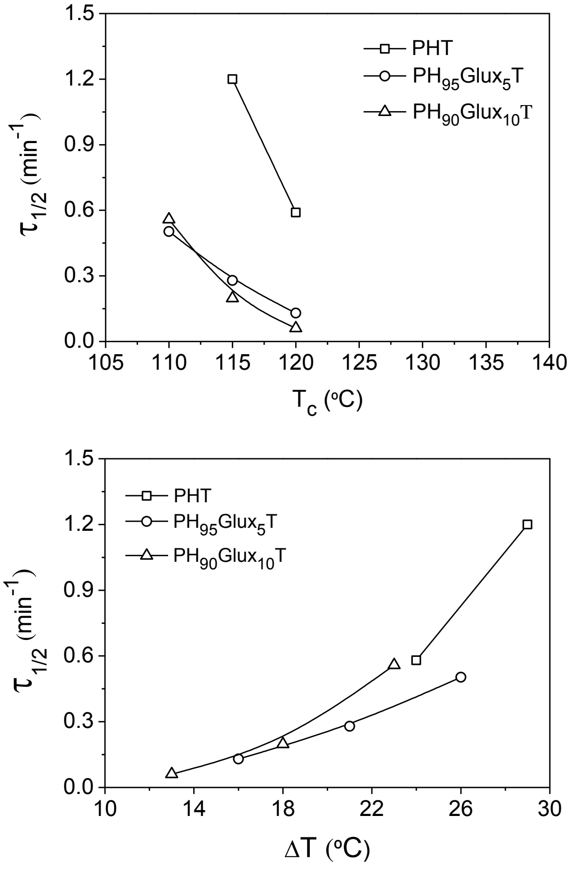
SI-Figure 2. DSC traces of polyesters and copolyesters registered at heating from quenched samples .



SI-Figure 3. Isothermal crystallization at 115 ºC of PHT, PH$_{95}$Glux$_5$T and PH$_{90}$Glux$_{10}$T. Relative crystallinity *vs* crystallization time (top) and Avrami plots (bottom).



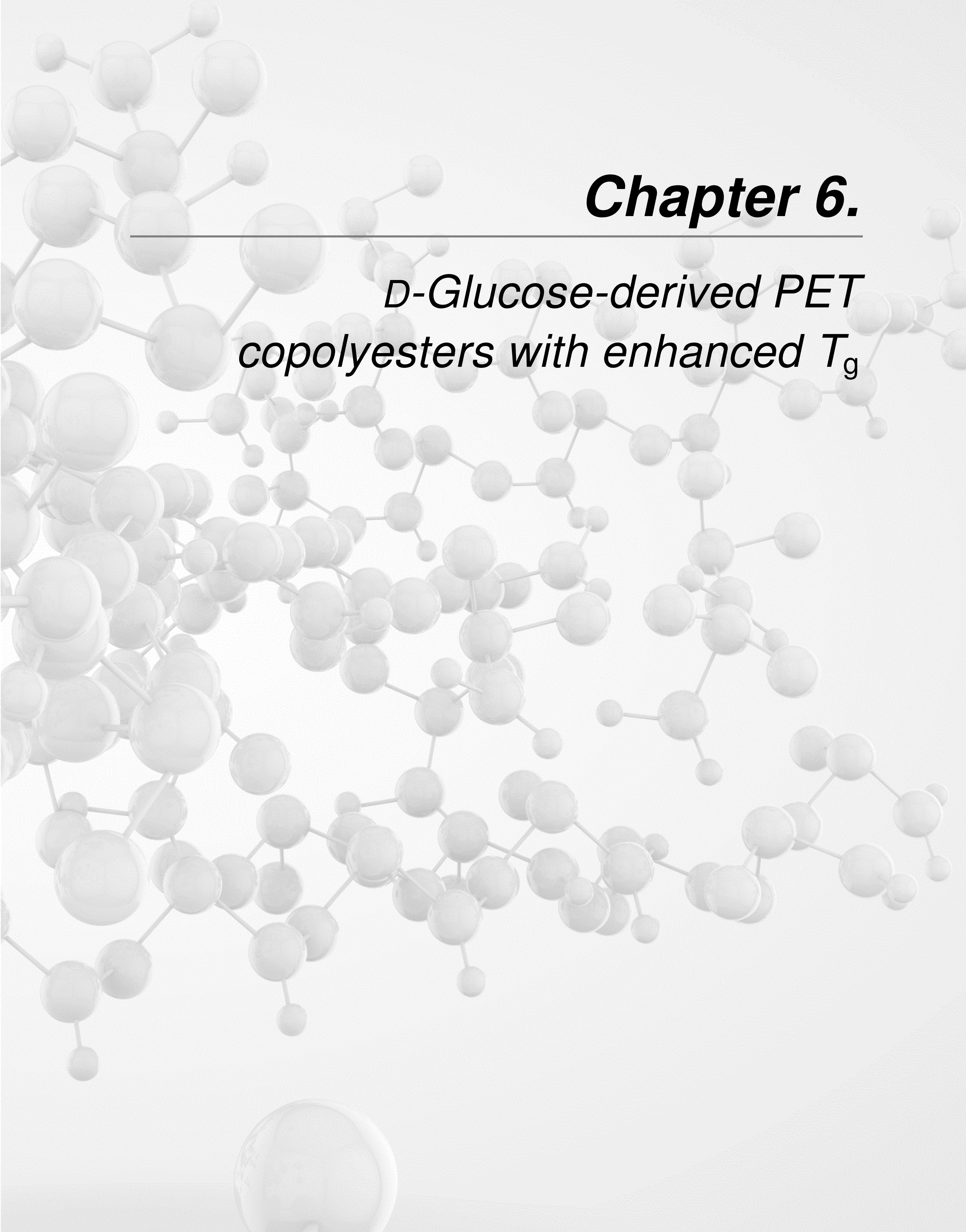
SI-Figure 4. Hoffman-Weeks plots for isothermally crystallized PHT, $PH_{95}Glux_5T$ and $PH_{90}Glux_{10}T$ polyesters.



SI-Figure 5. Inverse of crystallization half-time *vs* crystallization temperature (top) and $\Delta T=(T_m-T_c)$ for the indicated polyesters.

Chapter 6.

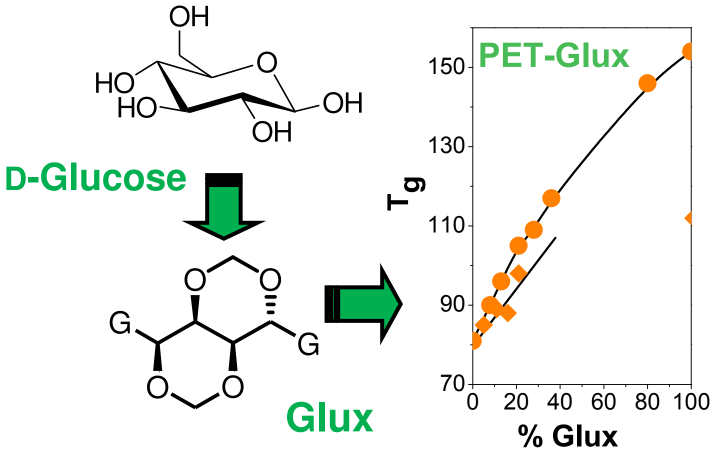
D-Glucose-derived PET copolyesters with enhanced T_g



D-Glucose-derived PET copolyesters with enhanced *T*$_g$

Abstract

2,4:3,5-di-*O*-methylene-D-glucitol (Glux-diol) and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester) have been copolymerized with ethylene glycol and dimethyl terephthalate by polycondensation in the bulk to produce PET copolyesters as well as their respective homopolyesters. These sugar-based bicyclic monomers were synthesized from 1,5-D-gluconolactone, a commercially accessible compound derived from D-glucose. The PET copolyesters with either the diol or the diacid counterpart partially replaced by Glux had molecular weights in the 20,000-40,000 range and a random microstructure, and they were stable well above 300 ºC. The PET copolyesters containing more than 10-15% of sugar-based units were amorphous while those others displaying crystallinity were observed to crystallize from the melt at much lower rates than PET. The glass transition temperature of PET dramatically increased with the incorporation of Glux whichever unit, diol or diacid, was replaced but the enhancing effect was stronger in the former case. A preliminary evaluation of the mechanical behaviour of these copolyesters indicated that the genuine properties of PET were not substantially impoverished by the insertion of Glux. Compared to PET, the copolyesters exhibited higher hydrolysis rate and an appreciable susceptibility towards biodegradation. The homopolyesters made of these sugar-based monomers could not be obtained with high enough molecular weights as to be comparatively evaluated with copolyesters.



Publication derived from this work:

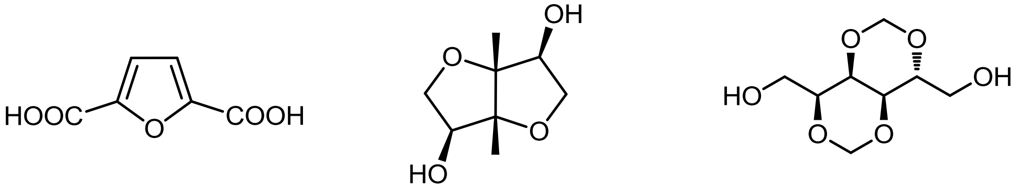
C. Japu, A. Alla, A. Martínez de Ilarduya, M. G. García-Martín, J. A. Galbis and S. Muñoz-Guerra, "D-Glucose-derived PET copolyesters with enhanced *T*$_g$", *Polym.Chem.,* 2013, **4**, 3524.

6.1. Introduction

Polymers from renewable resources are achieving huge interest nowadays mainly due to environmental and accessibility reasons.[1-3] The use of carbohydrate derivatives as monomers for polycondensation is a well-known approach for the synthesis of bio-based polymers that is taking notable relevance in recent times.[4-6] Carbohydrates are fully sustainable, easily accessible, and widely diverse in occurrence. However most of these compounds need to be chemically handled in order to make them suitable for polycondensation.[7,8] In these last decades a good number of polycondensates have been prepared using monomers coming from common monosaccharides that have been conveniently modified.[9-12]

In addition to confer sustainability and biodegradability, sugar-derived monomers may be also able to improve certain properties of traditional polycondensates. It is the case of the enhancing effect that some cyclic sugar-based diols exert on the glass transition temperature of polyesters.[13-15] Increasing the T_g of polyesters and of poly(ethylene terephthalate) in particular, is currently an open front in the injection-moulding applications of these materials. PET with higher T_g will display greater dimensional stability in thermal processing and better barrier properties in packaging. This will contribute to expand the use of PET into highly stringent applications nowadays demanded for special beverages containers and packaging. Streamline hot-filling bottle processes requiring materials with a T_g well above the filling temperature are a good example of the new applications intended today for new PET derivatives.[16]

Copolymerization has been and continues being the most appealing approach addressed to modify the properties of aromatic polyesters.[17,18] When open-chain sugar-derived monomers are introduced in aromatic polyesters, the effect on T_g is not significant or even negative.[19] On the contrary, cyclic monomers, which are bulky and stiff tend to restrict the chain mobility and are able to render polyesters with enhanced T_g. Three types of cyclic sugar-derived monomers, which are represented in Scheme 1, have been explored to date in this regard: a) Furan derivatives coming from both C5 and C6 sugars, and in particular 2,5-dicarboxylic acid (FDCA), which has a large potential for the replacement of terephthalic acid in PET and PBT.[20,21] b) The family of stereoisomeric bicyclic secondary diols based on 1,4:3,6-dianhydrohexitols.[22,23] Isosorbide is the most outstanding isohexide, it is commercially available and has been extensively explored in the preparation of polyesters, polycarbonates and polyurethanes.[24-28] Other isohexides receiving attention for their potential as polycondensation monomers are isoidide and isomannide.[29,30] A major drawback for the expansion of isohexides as polymer building blocks is the relatively poor reactivity of the secondary hydroxyl groups used for the polymerization reaction, which often results in low molecular weights and severely discoloured polymers. Some alternative solutions based on the conversion of these groups in carboxylate, amino or hydroxyethylene groups have been proposed to overcome the problem.[31-33] c) Acetalized alditols and aldaric acids which are prepared from C4, C5 and C6 sugars are being currently explored as a third option for the preparation of bio-based polyesters with enhanced T_g. Monocyclic an bicyclic, either independent or fused, diols and diacids derived from L-tartaric acid, D-galactose and D-mannose have been reported for the preparation of aliphatic[34,35] and aromatic polyesters including some polyterephthalates.[36,37] These monomers were found to be efficient in increasing the T_g of aliphatic polyesters and also of aromatic ones as far as they were used for replacing the diol unit.



2,4-furandicarboxylic acid (FDCA)

1,4:3,6-dianhydro-D-sorbitol (Isosorbide, Is)

2,4:3,5-methylene-D-glucitol (Gludioxol, Glux)

Scheme 1. Chemical structures of sugar-based bicyclic monomers.

In this work we report on the use of bicyclic acetalized D-glucitol and dimethyl D-glucarate in the preparation of PET copolyesters by polycondensation in the bulk. These two compounds share a bicyclic asymmetric structure consisting of a C6-segment backbone forming part of the two fused 1,3-dioxane rings and bearing the two hydroxyl or methoxycarbonyl functions at the end positions. The diol compound was already explored in the synthesis of poly(hexamethylene terephthalate) copolyesters;[36a] in that case, copolymerization resulted in copolyesters displaying higher T_g than their parent homopolyester as well as an enhanced degradability.

In the present case we investigate the use of both the acetalized glucitol and the acetalized glucarate in the synthesis of PET copolyesters by replacing either the diol or the diacid counterpart, respectively. The polycondensation reaction in the melt using sugar derivatives is always difficult due to the high sensitivity to heat exhibited by these compounds and its application to the preparation of PET copolyesters is particularly challenging because higher polymerization temperatures are required in this case to attain satisfactory conversions. The efforts dedicated to explore this approach with PET are more than justified given the enormous industrial importance of this polyester in the thermoplastic field; PET accounts for 8% of the global polymer production.[38]

6.2. Experimental section

6.2.1. Materials and methods

Materials

Dimethyl terephthalate (DMT) (99%), ethylene glycol (EG) (99%) and dibutyl tin oxide (DBTO, 98%) were purchased from Sigma-Aldrich. The solvents used for purification and characterization, such as chloroform, diethyl ether, methanol, dichloracetic acid (DCA), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), were of high purity grade and used as received. Antioxidants Irganox 1010 and Irgafos 126 were generously gifted by BASF.

Methods

Viscosities were measured in DCA at 25.0 ºC, using an Ubbelohde microviscometer at concentrations ranging from 0.3 to 1 $g \cdot dL^{-1}$.

Molecular weight determinations were performed by GPC using HFIP containing sodium trifluoroacetate (0.05 $mol \cdot L^{-1}$) as mobile phase in a Waters equipment provided with an RI detector. 100 µL of 0.1% (w/v) sample solution were injected and chromatographed with a flow of 0.5 mL min^{-1} in a linear HR5E Water Styragel column (7.8 x 300 mm) packed with cross-linked polystyrene and protected with a pre-column. Average molecular weights and their distributions were calculated against PMMA standards.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer at 25 ºC operating at 300.1 and 75.5 MHz, respectively. The polyesters samples were dissolved in deuterated chloroform:trifluoroacetic acid (9:1), and spectra were internally referenced to tetramethylsilane. About 10 and 50 mg of sample in 1 mL of solvent were used for ^{1}H and ^{13}C, respectively. Sixty-four scans were recorded for ^{1}H, and between 5,000 and 15,000 scans were taken for ^{13}C with 32 and 64 K data points and relaxation delays of 1 and 2 s, respectively. 2D ^{1}H-^{1}H homonuclear (COSY) and ^{13}C-^{1}H heteronuclear shift correlation (HETCOR) spectra were recorded by means of the *cosy* and *hxco*, respectively, pulse sequences implemented in the Bruker NMR instrument package.

TGA measurements were performed on a Perkin-Elmer TGA 6 thermobalance under a nitrogen flow of 20 $mL \cdot min^{-1}$ at a heating rate of 10 ºC min^{-1} and within a temperature range of 30 to 600 ºC. Sample weights of about 10 mg were used in these experiments.

The thermal behavior of the polymers was examined by differential scanning calorimetry (DSC) using a Perkin-Elmer Pyris 1 apparatus. Thermograms were obtained from 4-6 mg samples under a nitrogen flow of 20 mL min^{-1}. Indium and zinc were used as standards for temperature and enthalpy calibrations. The melting temperature (T_m) was taken as the maximum of the endothermic peak appearing on heating traces recorded at 10 ºC min^{-1}, and the glass transition temperature (T_g) was taken as the inflection point seen on heating traces recorded at 20 ºC min^{-1} from samples quenched from the melt.

X-ray diffraction profiles were recorded on the PANalytical X'Pert PRO MPD θ/θ diffractometer using the Cu-Kα radiation of wavelength 0.1542 nm from powdered samples coming directly from synthesis.

Scanning electron microscopy (SEM) images were taken with a field emission JEOL JSM-7001F instrument (JEOL, Japan). The samples were coated with Pt/Pd with a thickness about 1 nm using a Cressington Sputter Coater 208 HR equipment.

Films for mechanical testing measurements were prepared with a thickness of ~150 µm by casting from a 100 g L^{-1} solution in either chloroform or a mixture of chloroform:hexafluoroisopropanol (5:1); the films were then cut into strips with a width of 5 mm while the distance between testing marks was 10 mm. The Young's modulus, tensile strength and elongation at break were measured at a stretching rate of 30 mm min^{-1} on a Zwick 2.5/TN1S testing machine coupled with a compressor Dalbe DR 150, at 23 ºC.

6.2.2. Synthesis of monomers

*2,4:3,5-Di-O-methylene-*D*-glucitol* (Glux-diol) prepared by acetalization of 1,5-D-gluconolactone with paraformaldehyde, followed by esterification with methanol and subsequent reduction as described in detail elsewere.[36a]

*Dimethyl 2,4:3,5-di-O-methylene-*D*-glucarate* (Glux-diester) was prepared following the procedure described by Hilbert et al.[39] A stirred solution of 2,4:3,5-di-*O*-methylene-D-gluconic acid (8.8 g, 0.04 mol) in water (40 mL) containing potassium hydroxide (4.8 g, 0.08 mol) was cooled to 0 ºC by addition of cracked ice, and potassium permanganate (6.64 g, 0.04 mol) was added over half an hour. Stirring of the mixture was continued for one hour further keeping the temperature at 0 ºC. The manganese dioxide was removed by filtration through diatomaceous earth and the filtrate neutralized with sulphuric acid to pH 8.0. The colourless filtrate was evaporated to dryness and the resulting semisolid residue was refluxed with methanol (240 mL) containing sulphuric acid (4.3 mL) for six hours. The stability of the acetal structure under these conditions was ascertained by NMR. The reaction mixture was then allowed to reach room temperature, the potassium sulphate filtered off, and the filtrate neutralized by the addition of barium carbonate. The barium salts were then removed by filtration through diatomaceous earth, and the filtrate concentrated to half of the original volume to afford a solid on standing in the cold. The solid was filtered, dried, and recrystallized from methanol to give the title compound (2.0 g, 21% yield, m.p. 157-158 ºC; Lit.[39] m.p. 157-157.5 ºC). The purity of this compound was ascertained by NMR analysis (^{1}H and ^{13}C spectra are provided in the Electronic Supporting Information (ESI) file associated to this paper).

6.2.3. Synthesis of polyesters

All the polyesters studied in this work were prepared by polymerization in the bulk through a two-stage process consisting of transesterification followed by polycondensation. PET, poly(gludioxol terephthalate) (PGluxT), and poly(ethylene gludioxalate) (PEGlux) were obtained by reaction of the corresponding two-component mixtures of 2,4:3,5-di-*O*-methylene-D-glucitol and dimethyl terephthalate or ethylene glycol and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate.

PE_xGlux_yT copolyesters were obtained from mixtures of ethylene glycol, 2,4:3,5-di-*O*-methylene-D-glucitol and dimethyl terephthalate with the selected composition. In the abbreviated name of these copolyesters *x* and *y* subscripts indicate the mol percentages (%-mol) of ethylene and 2,4:3,5-di-*O*-methylene-D-glucitylene units, respectively. In turn PET_xGlux_y copolyesters were obtained from mixtures of ethylene glycol, dimethyl terephthalate and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate with the selected composition. In this case *x* and *y* subscripts refer to mol percentages of terephthalate and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate units, respectively. An excess of diol respect to the dimethyl ester was used, in these polymerizations, and dibutyl tin oxide (DBTO) was added as catalyst (0.5% mol respect to DMT). In order to minimize degradation of the thermally-sensitive sugar-derived monomers small amounts of antioxidants *Irganox 1010* (0.1 % w/w) and *Irgafos 126* (0.3 % w/w) were added to the mixture at the starting of the polymerization reaction.

The polymerization reaction was performed in a three-necked, cylindrical-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum outlet. The apparatus was vented with nitrogen several times at room temperature in order to remove the air and avoid oxidation during the polymerization. Transesterification reactions were carried out under atmospheric pressure assisted with a low nitrogen flow at temperatures between 160 and 190 ºC. Polycondensation reactions were left to proceed at temperatures higher than those used for transesterification and under a 0.03-0.06 mbar vacuum. When polymerization was finished, the reaction mixture was cooled to room temperature, and the atmospheric pressure was recovered with nitrogen to prevent degradation. The collected solid mass was dissolved in chloroform or in a mixture of chloroform:trifluoroacetic acid (9:1) and precipitated in an excess of methanol in order to remove unreacted monomers and formed oligomers. Finally, the polymer was separated by filtration, extensively washed with methanol, and dried under vacuum. The detailed conditions used for the synthesis of homopolyesters and copolyesters are following.

PET homopolyester. EG to DMT molar ratio: 2.2/1 Transesterification: 190 ºC, 2 h and 240 ºC, 0.5 h. Polycondensation: 260 ºC, 2 h. ^{1}H NMR (TFA-d_1, 300 MHz), δ (ppm): 8.17 (s, *Ar*H), 4.86 (s, OCH_2). ^{13}C{^{1}H}-NMR (TFA-d_1, 75.5 MHz), δ (ppm): 170.8 (C=O), 135.64-132.14 (*Ar*C), 66.25 (OCH_2).

PE$_x$Glux$_y$T copolyesters. EG and Glux-diol mixture to DMT molar ratio: 1.5/1. Transesterification: 185 ºC, 2.5 h. Polycondensation: 255 ºC, 1 h (for y between 8 and 28 %-mol) or 240 ºC, 2 h (for y between 36 and 80 %-mol). ^{1}H NMR (TFA-*d*$_1$, 300 MHz), δ (ppm): 8.25 (s, *Ar*H), 5.6-5.05 (m, OCH_2O), 5.05-4.90 (m, OCH_2, CH), 4.47 (t, CH), 4.3 (s, CH), 4.1 (s, CH). ^{13}C{^{1}H}-NMR (TFA-*d*$_1$, 75.5 MHz), δ (ppm): 171-172 (C=O), 135.95-132.14 (*Ar*C), 95 (OCH_2O), 89.9 (OCH_2O), 78.3 (CH), 76.4 (CH), 73.1 (CH), 70.6 (CH), 67.1 (OCH_2), 66.3 (OCH_2), 63.3 (OCH_2).

PGluxT homopolyester. 2,4:3,5-di-*O*-methylene-D-glucitol to dimethyl terephthalate molar ratio: 1.5/1. Transesterification: 180 ºC, 0.5 h and 160 ºC, 2.5 h. Polycondensation: 200 ºC, 1 h and 235 ºC, 2 h. ^{1}H NMR (TFA-*d*1, 300 MHz): δ (ppm): 8.23 (s, ArH), 5.1-5.5 (2dd, OCH_2O), 5.2-4.9 (m, CH_2, CH), 4,5 (m, CH), 4,3 (m, CH), 4.1 (m, CH).^{13}C{^{1}H}-NMR (TFA-d$_1$, 75.5 MHz), δ (ppm): 170.5 (C=O), 135.0-131.9 (*Ar*C), 95.0 (OCH_2O), 89.9 (OCH_2O), 78.4 (CH), 76.4 (CH), 73.1 (CH), 70.6 (CH), 67.0 (CH_2), 63.3 (CH_2).

PET$_x$Glux$_y$. Ethylene glycol to dimethyl terephthalate and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate diesters mixture: 2.2/1. Transesterification: 185 ºC, 2 h and 240 ºC, 0.5 h. Polycondensation: 245-250 ºC, 2-3 h. ^{1}H NMR (TFA-*d*$_1$, 300 MHz), δ (ppm): 8.2 (s, *Ar*H), 5.5-4.7 (m, OCH_2O, OCH_2, CH), 4.4 (s, CH), 4.3 (s, CH). ^{13}C{^{1}H}-NMR (TFA-*d*$_1$, 75.5 MHz), δ (ppm): 172.0-170.5 (C=O), 135.9-132.1 (*Ar*C), 94.4 (OCH_2O), 92.4 (OCH_2O), 78.3 (CH), 77.1(CH), 72.7 (CH), 71.2 (CH), 67.2-66.5 (OCH_2).

PEGlux. Ethylene glycol to dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate molar ratio: 2.2/1 Transesterification: 165 ºC, 5 h. Polycondensation: 170 ºC, 7 h. ^{1}H NMR (TFA-*d*$_1$, 300 MHz), δ (ppm): 5.5–5.0 (m, OCH_2O), 5.3-5.2 (m, OCH_2O), 5,1-4.6 (m, CH-CO), 4.5-4.8 (m, CH_2), 4.3-4.6 (m, CHO).^{13}C{^{1}H}-NMR (TFA-*d*$_1$, 75.5 MHz), δ (ppm): 170.5 (C=O), 94.4 (OCH_2O), 92.5 (OCH_2O), 78.3 (**C**HOCO), 77.1 (**C**HOCO), 72.7 (CHO), 71.2 (CHO), 66.5-65.6 (CH_2).

6.2.4. Hydrolytic and enzymatic degradation assays

For both hydrolytic and enzymatic degradation studies, films of polyesters and copolyesters with a thickness of about 200 μm were prepared by casting from chloroform solution (~80 mg mL^{-1}). The films were cut into 10 mm diameter disks and dried under vacuum to constant weight, which finally remained between 20 and 30 mg. The disks were individually immersed in vials containing 10 mL of either sodium citric acid buffer pH 2.0 (hydrolytic degradation), or sodium phosphate buffer pH 7.4 containing 10 mg of porcine pancreas lipases (enzymatic degradation), and left incubating at 37 ºC for one month. The buffered enzyme solution was replaced every 72 h to maintain the enzyme activity. After scheduled periods of time, the disks were withdrawn from the incubation medium, washed thoroughly with distilled water, and dried to constant weight.

6.3. Results and discussion

6.3.1. Polyesters synthesis and microstructure of PE$_x$Glux$_y$T copolyesters

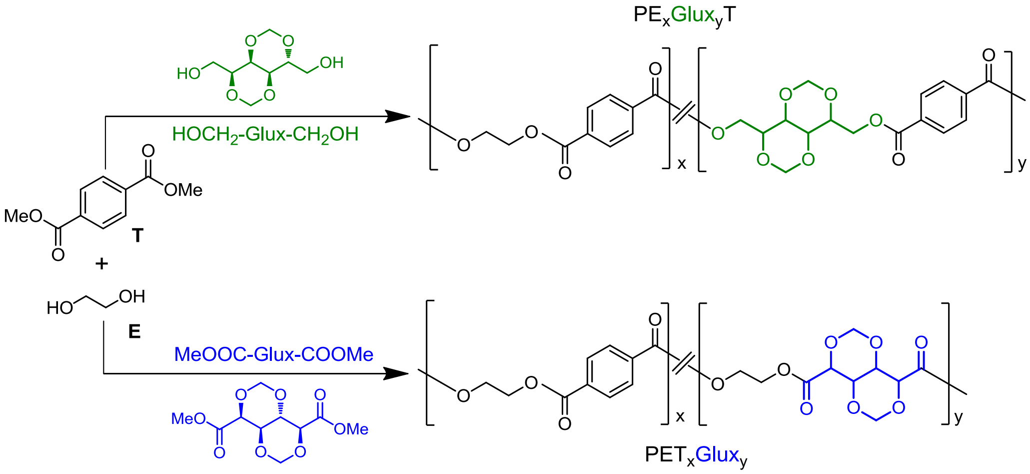
Synthesis

The synthesis of Glux monomers was carried out following traditional procedures reported in the old literature. The oxidation of the 2,4:3,5-di-*O*-methylene-D-gluconic acid could have been also accomplished using chromium or ruthenium based oxidant agents but the isolation of the very polar 2,4:3,5-di-*O*-methylene-D-glucaric acid was expected to be then very difficult, according to our experience in the oxidation of other closely related compounds using such reagents. The isolation of the diacetalized glucaric acid from the high amounts of salts that are generated in the reaction was the main reason for the low yield attained in the synthesis of this compound. It should be noted that the methylene acetal group is very stable under acidic conditions; in fact no alteration of the acetal structure occurred along the synthesis, as it was ascertained by NMR spectroscopy. Nevertheless, a more efficient synthetic methodology should be searched if a scaling-up of these monomers were considered.

The synthesis of polyesters studied in this work was performed in the bulk by following the procedure usually applied in the industry for the high-scale production of aromatic polyesters. Two copolyester series, PE$_x$Glux$_y$T and PET$_x$Glux$_y$, each one with varying compositions in Glux units, as well as their respective parent homopolyesters, PET, PGluxT and PEGlux, were prepared. The reactions involved in these syntheses are formulated in Scheme 2. The mixture of monomers with a diol-to-diester ratio between 1.5 and 2.2 and with the catalyst added was made to react in two successive stages. Using an excess of diol for the preparation of polyesters by polycondensation in the melt is a common practice at both laboratory and industrial scales which is addressed to ensure the total removal of the methyl ester groups as well as to compensate uncontrolled loses of volatiles. In the first reaction stage, short hydroxyl-ended oligoesters are generated by transesterification of the dimethyl esters with the diols with releasing of methanol. In the second stage, the polycondensation reaction among oligoesters is forced to proceed at higher temperature and applying high vacuum to remove the exceeding diol.

Due to the marked sensitivity of carbohydrate derived compounds to thermo- oxidative degradation, special care was taken in order to minimize decomposition reactions. A fine adjustment of reaction conditions including temperature, time, vacuum and catalyst was undertaken. The applied temperatures were minimized and combined with reaction time lengths and vacuum for attaining maximum conversions. In this regard, DBTO was the catalyst of choice since its superior activity over the commonly used tetrabutyl titanate (TBT) in polycondensations involving sugar-based monomers has been verified in several previous works.[35-37] As a rule, lower temperatures and longer reaction times were used in the synthesis of copolyesters with higher contents in Glux units. Furthermore, addition of antioxidants in small amounts was found to be beneficial in preventing discoloration of the final product. These precautions have improved substantially the quality of the resulting polyesters in general. In this regard, the case of PGluxT is remarkable; this homopolyester was hardly prepared by using former conditions[36a] while now it could be obtained as a white powder with a thermal stability comparable to that of PET.

Polymerization evolved with a continuous increase in viscosity of the reaction mass to the point that flowing became unfeasible, which was taken as the end of the polycondensation process. The resulting polymers were purified by dissolving the reaction product in a mixture of chloroform with TFA and precipitating them with methanol. Data concerning yield, composition and molecular weights of polyesters and copolyesters are afforded in Table 1.



Scheme 2. Polymerization reactions leading to PE$_x$Glux$_y$T and PET$_x$Glux$_y$ copolyesters.

Copolyesters were obtained in yields between 80 and 90 % whereas values about 30% were attained in the synthesis of the homopolyesters made from Glux. For copolyesters, intrinsic viscosities varied between 0.42 and 0.84 dL g^{-1} and weight-average molecular weight between 23,000 and 40,000 g·mol^{-1} with dispersity degrees confined within the 2.2-2.5 range. It is worthy to note that molecular weights of the polyterephthalate series were found to be significantly higher than those of the polyglucarate one, which is a consequence of the low thermal stability of the Glux-diester compared to that of the Glux-diol. The weak thermal stability

Table 1.Composition and molecular weight of PE_xGlux_yT and PET_xGlux_y.

Copolyester	Yield (%)	Composition								Molecular weight			
		Feed				Copolyester[a]							
		Diol		Diacid		Diol		Diacid					
		[E]	[Glux]	[T]	[Glux]	[E]	[Glux]	[T]	[Glux]	$[\eta]^b$	M_n^c	M_w^c	D^c
PET	90	100	0	100	0	100	0	100	0	0.68	12,800	32,100	2.5
PE_xGlux_yT													
$PE_{92}Glux_8T$	90	95	5	100	0	92	8	-	-	0.70	14,000	33,000	2.4
$PE_{87}Glux_{13}T$	90	90	10	100	0	87	13	-	-	0.84	16,300	40,100	2.5
$PE_{79}Glux_{21}T$	90	85	15	100	0	79	21	-	-	0.78	15,200	38,000	2.5
$PE_{72}Glux_{28}T$	90	80	20	100	0	72	28	-	-	0.72	14,500	35,000	2.4
$PE_{64}Glux_{36}T$	88	70	30	100	0	64	36	-	-	0.65	12,200	29,000	2.4
$PE_{20}Glux_{80}T$	85	30	70	100	0	20	80	-	-	0.42	9,500	23,000	2.4
PGluxT	30	0	100	100	0	0	100	-	-	0.32	5,500	12,800	2.3
PET_xGlux_y													
$PET_{95}Glux_5$	85	100	0	95	5	-	-	95	5	0.52	11,800	26,000	2.2
$PET_{89}Glux_9$	85	100	0	90	10	-	-	89	11	0.50	10,900	25,100	2.3
$PET_{84}Glux_{16}$	85	100	0	85	15	-	-	84	16	0.60	13,600	30,000	2.2
$PET_{79}Glux_{21}$	80	100	0	80	20	-	-	79	21	0.57	12,900	28,500	2.2
PEGlux	30	100	0	0	100	-	-	0	100	0.27	3,800	9,000	2.4

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

[b] Intrinsic viscosity in $dL{\cdot}g^{-1}$ measured in DCA at 25 ºC.

[c] Number and weight average molecular weights in $g{\cdot}mol^{-1}$, and dispersities measured by GPC in HFIP against PMMA standards.

of Glux monomers is mostly evidenced when they are used unmixed with other comonomers, as it is the case of the synthesis of homopolyesters PGluxT and PEGlux. In such cases, the polycondensation proceeded with more difficulty and the polymers were obtained in poorer yields and with much lower molecular weights.

The chemical constitution of homopolyesters and copolyesters, as well as the composition of the latter, were ascertained by ^{1}H NMR. Representative spectra of each copolyester series with assignments of all the signals arising from their chemical structures are provided in the ESI file together with the 2D NMR COSY and HETCOR spectra used to support the signal assignment.

The composition of the PE_xGlux_yT and PET_xGlux_y copolyesters was determined by integration of the aromatic proton signals (4H) emerging at 8.20-8.25 ppm for the two cases, and the signals appearing between 5.6 and 4.0 ppm that correspond to the two repeating units present in each copolyester series. The percentage of sugar units present in the copolyester was estimated by applying simple proportion calculations (see details in the ESI document). The content of Glux units in PET_xGlux_y copolyesters was essentially the same as that of their respective feeds whereas in the case of PE_xGlux_yT the amount of Glux incorporated to the polymer was found to be significantly larger than expected; the excess attained up to more than 30% in some cases (Table 1). This observation is by no means new in polycondensation of diol mixtures, and it is attributed either to the relatively higher volatility or to the lower reactivity of the diol that is defectively incorporated in the copolyester. Thus similar losses of EG were reported in the copolymerization of mixtures of this glycol and Manx (a bicyclic acetalized diol derived from D-mannose) with DMT.[37c] On the contrary PBT copolyesters prepared from mixtures of 1,4-butanediol and different cyclic acetalized diols derived from D-galactose[37b] or D-mannose[37a] were found to retain the composition of the feeds from which they were generated. In this regard, PET copolyesters made from isosorbide (the bicyclic dianhydride diol derived from sorbitol) are exceptional in that it is the sugar based monomer which is taken up in lesser amounts than expected.[15] Such an opposite behavior is attributed to the lower reactivity of the secondary hydroxyl groups of isosorbide compared to the primary hydroxyl groups present in the diacetalized alditol monomers.

Microstructure

The microstructure of PE_xGlux_yT copolyesters was determined by ^{13}C NMR spectroscopy taking profit from the sensitiveness of the substituted aromatic carbons to sequence distributions at the dyad level. The signals due to these carbons appear split giving a total of nine peaks since four types of dyads (EE, EGlux/GluxE and GluxGlux) are possible, and the Glux unit lacks *C*2 symmetry. The EE dyad will produce one peak whereas four peaks of equal intensity would arise from both EGlux and GluxE dyads due to the two possible orientations that the Glux unit may adopt when incorporated in the chain. By the same reason four additional peaks will be also produced by the GluxGlux dyad. The 135-136 ppm region containing the resonance signals produced by such carbons is shown in Figure 1; the peaks arising from E-E, E-Glux/Glux-E and Glux-Glux dyads appear well resolved as to be quantified by integration with reliability.

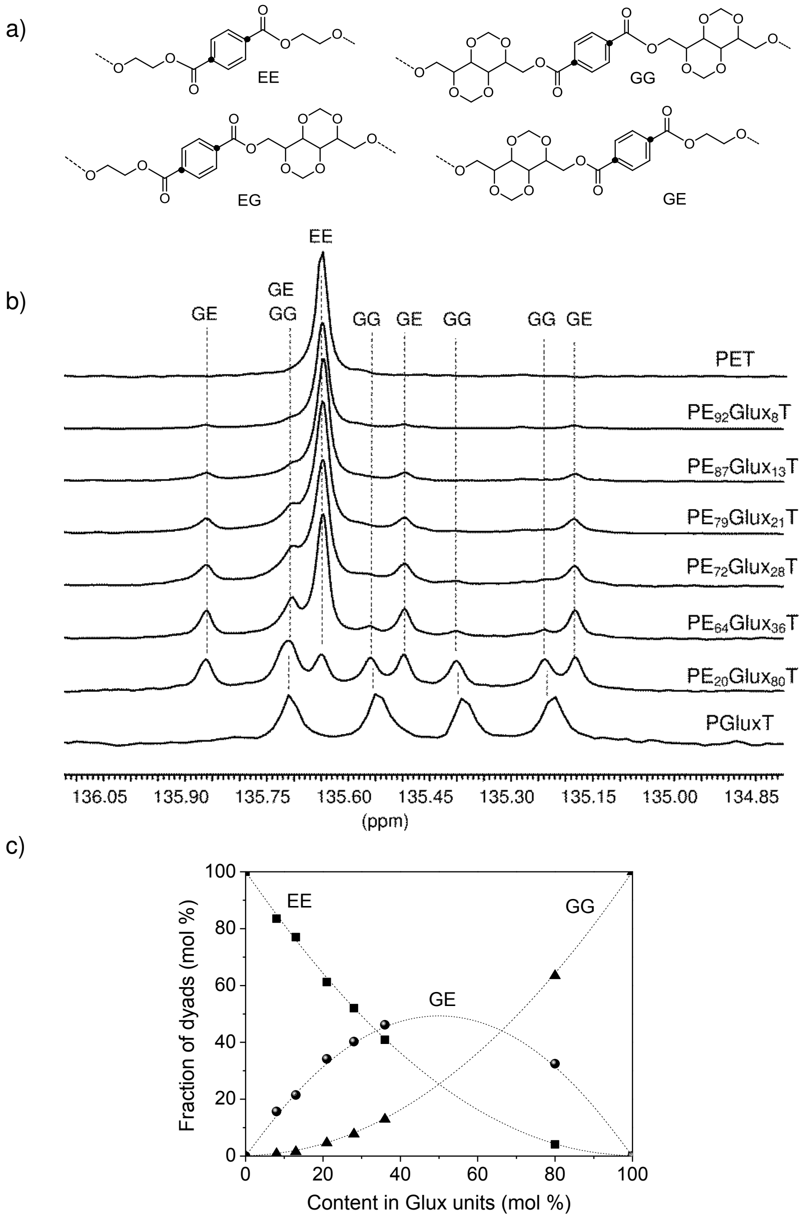


Figure 1. a) The four possible dyads occurring in PE$_x$Glux$_y$T copolyesters. b) The non-protonated aromatic carbon region in the ^{13}C NMR spectra of copolyesters and PET and PGluxT homopolyesters, c) Plot of dyad

contents *vs* copolyester compositions. Dashed lines represent the theoretically calculated contents for random copolyesters.

The number-average sequence lengths *n* of the ethylene glycol-terephthalate (ET) and gludioxol-terephthalate (GluxT) homogeneous sequences, as well as the degree of randomness *R,* were estimated for each PE_xGlux_yT copolyester by using the following equations:

$$n_{ET} = (N_{EE}+ ½ (N_{EGlux}+N_{GluxE})) / ½ (N_{EGlux}+N_{GluxE})$$

$$n_{GluxT} = (N_{GluxGlux}+ ½ (N_{EGlux}+N_{GluxE})) / ½ (N_{EGlux}+N_{GluxE})$$

$$R = (1/n_{ET}) + (1/n_{GluxT}).$$

Results from these calculations are summarized in Table 2 indicating that the sequence distribution in PE_xGlux_yT copolyesters is essentially random for the whole range of compositions with values of *R* being very close to unity. The plots of calculated dyad contents *vs* copolyester compositions are depicted in Figure 1 and compared to the function that would result for ideal random copolyesters with the same compositions.

Table 2. Composition and microstructure of the PE_xGlux_yT copolyesters.

Copolyestes	Composition[a]		Dyad content (%)[b]			Sequence lenghts		*R*
	X_E	X_{Glux}	EE	GE	GG	N_E	N_{Glux}	
$PE_{92}Glux_8T$	92	8	83.47 (84.64)	15.69 (14.72)	0.84 (0.64)	11.64 (12.5)	1.11 (1.1)	0.99 (1.00)
$PE_{87}Glux_{13}T$	87	13	77.00 (75.69)	21.5 (22.62)	1.5 (1.69)	8.16 (7.69)	1.14 (1.15)	0.99 (1.00)
$PE_{79}Glux_{21}T$	79	21	61.19 (62.41)	34.20 (33.18)	4.61 (4.41)	4.58 (4.76)	1.26 (1.26)	1.01 (1.00)
$PE_{72}Glux_{28}T$	72	28	52.00 (51.84)	40.25 (40.32)	7.75 (7.84)	3.58 (3.57)	1.38 (1.39)	1.00 (1.00)
$PE_{64}Glux_{36}T$	64	36	40.88 (40.96)	46.16 (46.08)	12.96 (12.96)	2.77 (2.78)	1.56 (1.56)	1.00 (1.00)
$PE_{20}Glux_{80}T$	20	80	4.10 (4.00)	32.50 (32.00)	63.40 (64.00)	1.25 (1.25)	4.90 (5.00)	1.00 (1.00)

[a] Calculated from the ^1H NMR spectra.

[b] Experimental values were obtained by means of the equations mentioned in the text and using the ^{13}C NMR data. Theoretical values (in parentheses) were calculated on the basis of a statistical distribution using the copolyester composition data given in this Table.

Unfortunately the microstructure for PET_xGlux_y copolyesters could not be determined by this method because the signals of the oxymethylene carbons arising from the different types of sequences appeared overlapped in the ^{13}C-NMR spectra. Several solvents were tried in order to improve the resolution of these signals but without success.

6.3.2. Thermal properties

The thermal behavior of PE_xGlux_yT and PET_xGlux_y copolyesters and PGluxT and PEGlux homopolyesters has been comparatively examined by TGA and DSC taking PET as a reference. The thermal parameters resulting from this study are given in Table 3.

The TGA traces for the two copolyester series registered under an inert atmosphere are depicted in Figure 2. Thermal decomposition of the PE_xGlux_yT copolyesters started to be detectable about 350 ºC with onset temperatures (measured for 10% of weight loss) being near to 400 ºC. A close inspection of data revealed that although the thermal stability of these copolyesters decreased slightly with the content in Glux units, it remained near to that of PET. Decomposition was found to take place in a single stage following a profile identical to PET and leaving a residue of around 15% of the initial weight.

PET_xGlux_y copolyesters exhibited a more complex behaviour encompassing a remarkable lower stability. Decomposition in this case was found to proceed along two stages although the amount of residue left was similar than for PE_xGlux_yT. It is clear that Glux-dicarboxylate units had a much stronger depressing effect on thermal stability than Glux-dioxy units with onset decomposition temperature of PET falling about 90 ºC for a 20% of content in Glux. Nevertheless, these copolyesters remained essentially unaltered upon heating at 300 ºC, and therefore they are still suitable for being comfortably processed by thermal methods. As in the case of the PE_xGlux_yT series, the homopolyester PEGlux distinguished from the PET_xGlux_y copolyesters and also from PGluxT homopolyester by exhibiting an exceptional lower thermal stability. Nevertheless, in addition to the compositional effect, the lower molecular weight of the homopolyesters must be an additional factor negatively affecting their resistance to heat.

The incorporation of Glux in the chain of PET, either as dioxy or as dicarboxylate units, altered significantly the thermal transitions of the polyester. The bicyclic Glux structure is stiff, bulk and asymmetric, which does means that it will produce upon insertion severe distortions in the regularity and flexibility of the polymer chain.

Table 3.Thermal properties of PE_xGlux_yT and PET_xGlux_y.

Polyester	TGA			DSC								
				T_g[d] (°C)	First Heating[e]				Cooling[e]		Second Heating[e]	
	T_d[a] (°C)	T_{ds}[b] (°C)	RW[c] (%)		T_{cc} (°C)	ΔH_{cc} ($J \cdot g^{-1}$)	T_m (°C)	ΔH_m ($J \cdot g^{-1}$)	T_c (°C)	ΔH_c ($J \cdot g^{-1}$)	T_m (°C)	ΔH_m ($J \cdot g^{-1}$)
PET	411	444	14	81	122	15	250	44	200	33	249	31
PE_xGlux_y												
$PE_{92}Glux_8T$	406	438	16	90	150	22	233	29	-	-	232	18
$PE_{87}Glux_{13}T$	406	435	16	96	160	9	218	21	-	-	-	-
$PE_{79}Glux_{21}T$	403	432	15	105	-	-	-	-	-	-	-	-
$PE_{72}Glux_{28}T$	396	430	12	109	-	-	-	-	-	-	-	-
$PE_{64}Glux_{36}T$	396	429	10	117	-	-	-	-	-	-	-	-
$PE_{20}Glux_{80}T$	386	422	8	146	-	-	-	-	-	-	-	-
PGluxT	377	420	15	154	-	-	(~272)	(~15)	-	-	-	-
PET_xGlux_y												
$PET_{95}Glux_5$	393	438	16	85	134	17	237	30	168	19	231	21
$PET_{89}Glux_{11}$	361	350/**434**	16	89	148	23	226	27	162	22	226	23
$PET_{84}Glux_{16}$	347	353/**435**	15	88	-	-	-	-	-	-	-	-
$PET_{79}Glux_{20}$	323	322/**430**	16	98	-	-	-	-	-	-	-	-
PEGlux	262	303	17	112	-	-	-	-	-	-	-	-

TGA: [a]Temperature at which 10% weight loss was observed in the TGA traces recorded at 10 °C min^{-1}; [b]Temperature for maximum degradation rate; [c]Remaining weight at 600ºC.

DSC: [d]Glass-transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 °C min^{-1}.

[e]Cold-crystallization (T_{cc}), melting (T_m) and crystallization (T_c) temperatures and their respective enthalpies (ΔH_{cc}, ΔH_m, ΔH_c) measured by DSC at heating/cooling rates of 10 °C min^{-1}. In parenthesis, imprecise values measured for PGluxT.

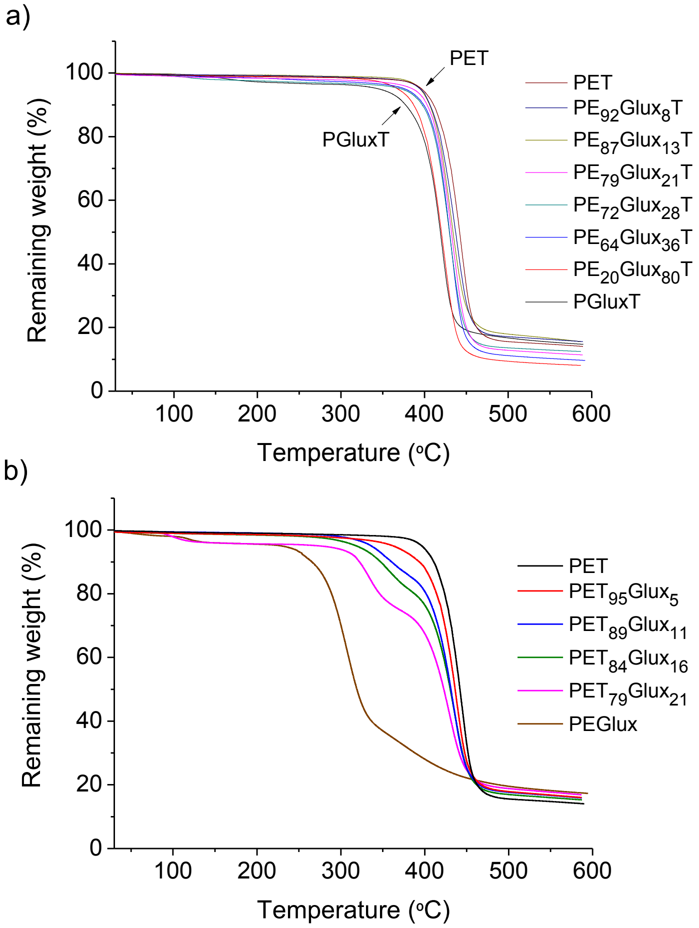


Figure 2. TGA traces of PE$_x$Glux$_y$T (a) and PET$_x$Glux$_y$ (b) copolyesters registered under inert atmosphere.

The DSC traces of the two copolyester series and their corresponding parent homopolyesters are depicted in Figure 3, and the melting and glass transition data measured on them are collected in Table 3. Whereas PET is semicrystalline with a melting temperature of around 250 ºC, most of copolyesters appeared to be amorphous. In fact, endothermic peaks characteristic of melting were only observed for copolyesters containing up to ~10-15% of Glux units, and in such cases melting occurred at temperatures notably lower than in PET and involved much smaller associated enthalpies. These results clearly bring out the strong depressing effect exerted by the Glux units on crystallinity. The homopolyesters made from Glux, PGluxT and PEGlux appeared to be also essentially amorphous although weak signs of melting at temperatures near to 270 ºC could be appreciated in the DSC trace of the former. According to the molecular features of Glux, both chain packing and crystallization rate appeared to be hampered by copolymerization; this issue will be dealt below in more detail.

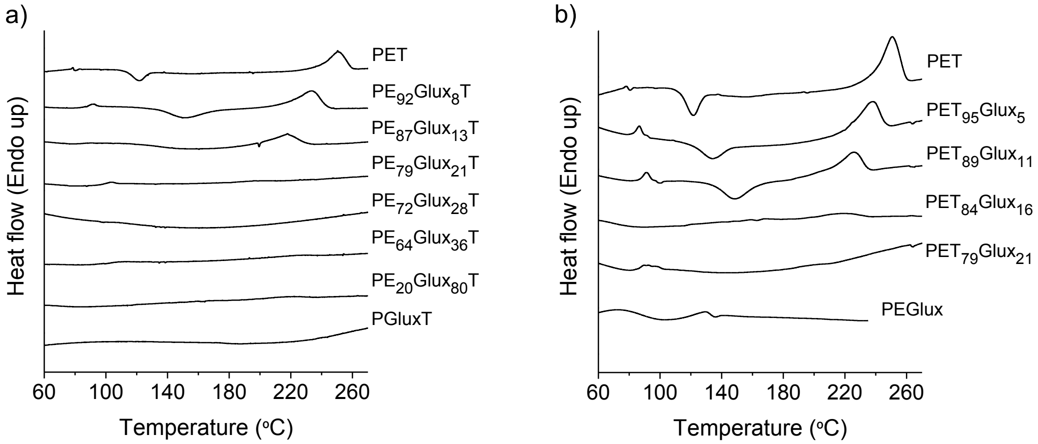


Figure 3. DSC heating traces of PE_xGlux_yT (a) and PET_xGlux_y (b) copolyesters.

The T_g of the polyesters and copolyesters could be clearly detected in the heating DSC traces of samples previously quenched from the melt (Figure 4).

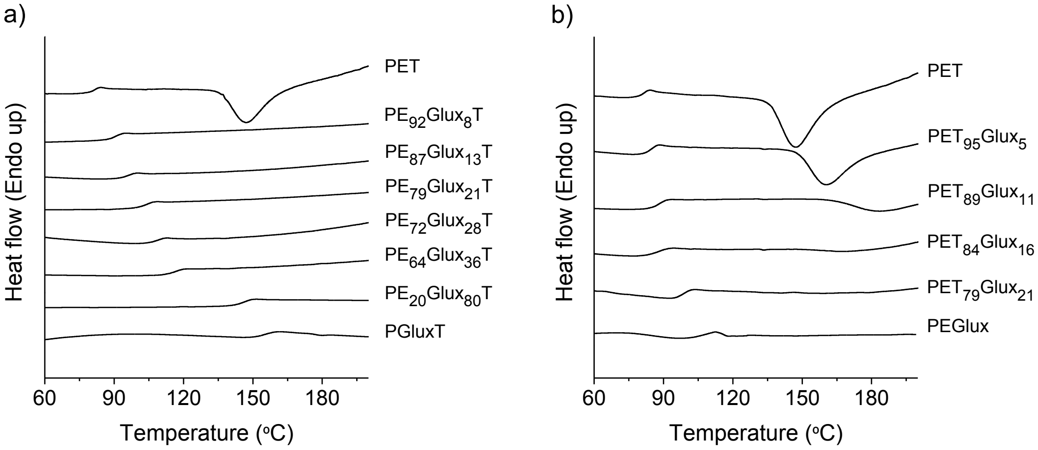


Figure. 4. DSC traces of PE_xGlux_yT (a) and PET_xGlux_y (b) copolyesters recorded at heating from quenched samples for T_g observation.

Contrary to what happened for melting, the glass transition temperature increased with the content in Glux units, either as they are dioxy or dicarboxylate units. It does make much sense since the Glux structure will confer stiffness and viscosity to the polymer chain and will reduce therefore the free volume. The variation of T_g of PE_xGlux_yT and PET_xGlux_y copolyesters as a function of composition is plotted in Figure 5; an almost linear with a slope near to 1 $^{\circ}C \cdot \%$-mol^{-1} trend was observed for the former case whereas a rather erratic variation was found for the latter. The T_g enhancing effect was stronger in PE_xGlux_yT copolyesters because in such case it is the relatively flexible ethylene segment which is replaced by the Glux unit. In this series the T_g attained a value of 154 ºC for the homopolyester, which is almost the double of the value of the PET's T_g. In the PET_xGlux_y series, the increase in T_g was rather less noticeable because it is the stiff aromatic ring that is replaced in this case. This is however a very remarkable result since the substitution of the aromatic ring in polyesters by non-aromatic units usually leads to a decrease in T_g. In fact, all previous copolyesters studied by us, in which the terephthalate unit was replaced by monocyclic or bicyclic sugar derived units, showed a decrease in T_g upon copolymerization.[32,33] As far as we know, this is the first example of sugar-derived copolyesters in which T_g increased after decreasing the content in aromatic units.

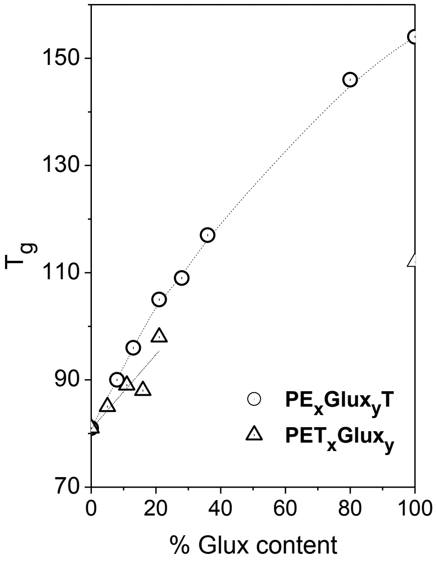


Figure 5. T_g values as a function of the content in Glux units.

6.3.3. Isothermal crystallization, structure and and stress-strain behaviour

DSC showed that PE_xGlux_yT and PET_xGlux_y copolyesters with low content in sugar units were semicrystalline but only those containing Glux dicarboxylate units were able to crystallize upon cooling from the melt (see Table 3). It is fully consistent with the depressing effect that the insertion of these units has on the crystallizability of the polyester. In order to assess the influence of the content in Glux on crystallizability, a comparative isothermal crystallization study of the crystallizable PET_xGlux_y copolyesters ($PET_{89}Glux_{11}$and $PET_{95}Glux_5$) and PET, has been carried out at the same crystallization temperature. The evolution of the relative crystallinity, X_c, versus crystallization time and their respective Avrami (Ln[-ln((100-X_c)/100)] versus Ln(t-t_0) plots are depicted in Figure 6 and experimental data are gathered in Table 4, where the observed onset and half-crystallization times, as well as the corresponding calculated Avrami parameters, are given for each case. Avrami exponent *n* oscillated in the 1.9-2.1 range indicating that a similar crystallization mechanism, probably consisting of a heterogeneous nucleation with preferentially bidimensional crystal growth, must operate in the three cases. What is really relevant of this study is that half-crystallization time increased enormously for relatively small amounts of Glux incorporated in the polyester (more than ten times for 10% of Glux). These results provided quantitative prove on the suppressing effect that the Glux units have on the crystallization rate, and will explain in part the lack of crystallinity observed in most of the Glux containing copolyesters.

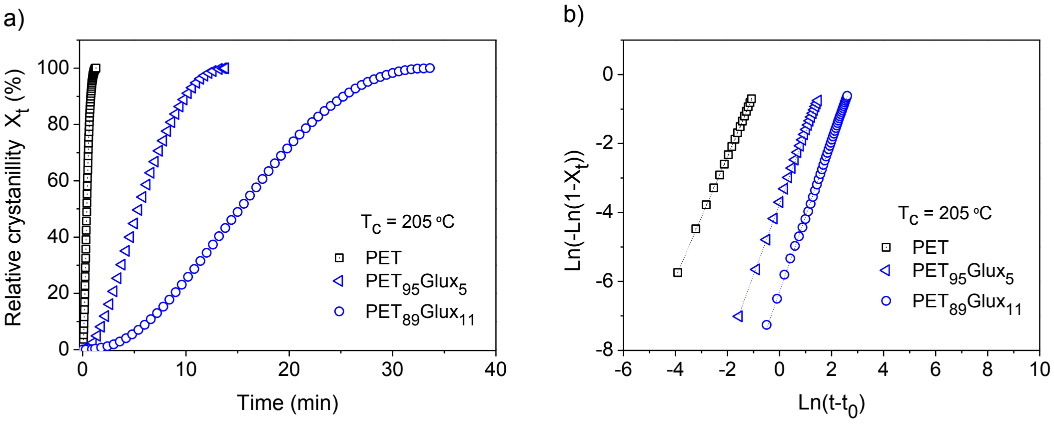


Figure 6. Compared isothermal crystallization at 205 ºC of PET, $PET_{95}Glux_5$ and $PET_{89}Glux_{11}$ copolyesters. a) Relative crystallinity *vs* crystallization time. b) Double logarithmic Avrami plot.

Structure

It has become evident by DSC that the crystallinity of the Glux containing copolyesters decays rapidly with the presence of Glux units (Table 3) to the point that they become apparently amorphous for Glux contents higher than ~10-15%. It has been shown before that such behavior should be interpreted as the logical consequence of the low crystallization rate caused by the Glux units. Such as delay for crystallizing may be motivated by a diminished chain mobility or/and a difficulty in chain packing. A preliminary analysis of the crystal structure occurring in these copolyesters will help in understanding better the molecular reasons standing behind their crystallization behavior.

The powder WAXS profiles obtained from annealed samples of those copolyesters that were shown to be semicrystalline by DSC ($PET_{95}Glux_5$, $PET_{89}Glux_{11}$, $PE_{92}Glux_8T$ and $PE_{87}Glux_{13}T$) together with that arising from PET are compared in Figure 7 with indication of the most conspicuous Bragg spacings therein observed. A detailed account of the all detected spacings in these diffractograms is afforded in the ESI file.

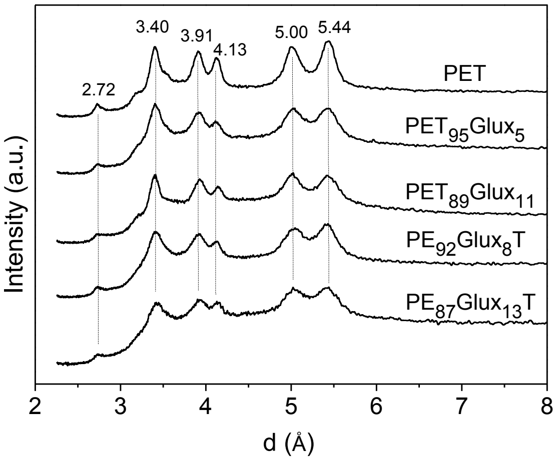


Figure 7. WAXS profiles of PET and the indicated PE_xGlux_yT and PET_xGlux_y copolyesters polyesters recorded from annealed powder samples.

All profiles exhibit well defined peaks characteristic of an ordered state corroborating therefore the semicrystalline nature of these copolyesters. Crystallinity degrees measured from these profiles oscillated between 0.3 and 0.5, which are figures well below that of PET (0.7), and that are in agreement with the melting enthalpy values measured by DSC (Table 3). What is really remarkable in this picture is the extremely similitude in both spacing and relative intensity showed by the profiles. It can be therefore inferred without reservation that all the analyzed polyesters are sharing the same crystal structure, which is by the way the well known triclinic structure of PET[40]. It is more than reasonable to assume that crystallization will involve only homogeneous ethylene terephthalate (ET) segments with exclusion of Glux units, which must be therefore segregated to the amorphous phase. Since the average length of the ET homogeneous segments will decrease with copolymerization, copolyesters containing high amounts of Glux units would no crystallize because they would be unable to render crystallites with the minimum critical size required to be stable. Segregated crystallization is a frequent phenomenon happening in copolyesters[41], and that has been reported to occur in other sugar-based polyesters studied previously by us.[35-37]

Stress-strain behaviour

A preliminary evaluation of the mechanical properties of Glux containing copolyesters has been carried out by tensile testing. The $PE_{79}Glux_{21}T$, $PE_{72}Glux_{28}T$ and $PE_{64}Glux_{36}T$, which distinguished in affording resistant films by casting, were essayed. PE_xGlux_yT copolyesters with lower contents in Glux afforded brittle films and the same happened with all the PET_xGlux_y copolyesters. Apparently, the molecular weights of these unmanageable copolyesters are below the entanglement critical value which is expected to be higher than for those copolyesters exempted of crystallinity. The stress-strain curves recorded from the essayed copolyesters are compared with that of PET in Figure 8 and the parameters measured in these essays are accessible in the ESI file. The Young modulus was observed to increase with the content in Glux as it does the elongation to break too. *E* values were slightly above 10^3 MPa whereas ε remained below 30%. Apparently the presence of Glux in the PET chain does not impoverish appreciably the mechanical behaviour of the polyester as far as a restricted interval of compositions is considered; out of the given composition limits, the Glux containing polyesters were unable to form consistent films, because either they are crystalline or have too low molecular weights, and the mechanical properties could not be evaluated in such cases. This is particularly applicable to the homopolyesters.

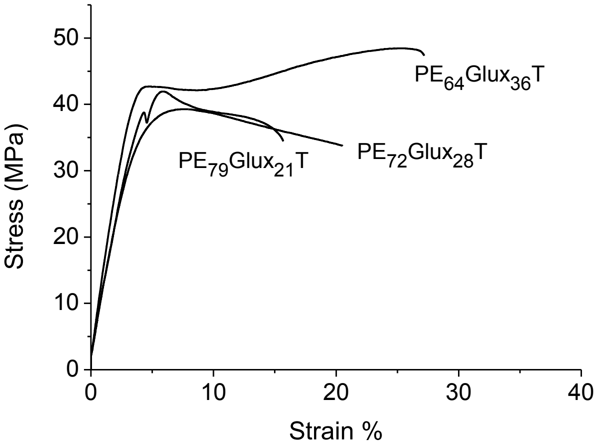


Figure 8. Stress-strain curves of PE_xGlux_yT copolyesters and PET[37c].

6.3.4. Hydrolytic and enzymatic degradability

The resistance of aromatic polyester to be hydrolyzed either chemically or enzimatically is a well-known fact.[42] The degradation time for PET films under 100% relative humidity and wet soil conditions has been estimated to be about 45 years.[43] It is also known that the insertion of sugar-derived units in aromatic polyesters enhances their hydrophilicity and consequently makes them more prone to the attack of water and the action of hydrolytic enzymes. To evaluate the effects that the incorporation of Glux-diol and Glux-diester exerts on the hydrolytic and enzymatic degradation of PET, the weight and molecular weight changes taking place in a selection of copolyesters incubated under different conditions were monitored.

PET, $PE_{72}Glux_{28}T$, $PE_{20}Glux_{80}T$ and $PET_{79}Glux_{21}$ were selected for this study. This selection allowed a comparison in terms of the amount of sugar inserted in the copolyester as well as for the type of unit that is replaced. First the hydrodegradability of these copolyesters in aggressive medium was estimated by incubation of the samples in aqueous buffer pH 2.0 at 80 ºC. Secondly, the action of lipases was evaluated by incubating the samples in phosphate saline at pH 7.4 with porcine lipases added. Results from these essays are compared in Figures 9 and 10 where the changes taking place in weight and molecular weight are plotted against incubation time. In general the hydrolysis rate increased moderately with copolymerization. It was observed that loses in sample weight were less noticeable than decays in molecular weight, which is presumably due to the scarce solubility of the polymer fragments originated by degradation. A comparative SEM inspection of the samples before and after incubation revealed morphological changes on the surface (ESI file) consistent with the degradation results obtained from weighting and GPC analyses. The conclusions drawn from this degradation study are the following:

a) The insertion of Glux units enhanced the hydrolysis of PET, the effect being stronger for higher degrees of replacement (compare results for $PE_{72}Glux_{28}T$ and $PE_{20}Glux_{80}T$).

b) The enhancing effect is more pronounced when the terephthalate unit was replaced in the polyester (compare results for $PE_{72}Glux_{28}T$ to $PET_{79}Glux_{21}$).

c) Degradation happened without alteration of bicyclic structure of Glux according with the high stability of the methylene acetal against acids and bases.

c) The action of lipases on the degradability of these copolyesters was found to be mild but noticeable compared to that exerted on PET which remains perfectly unaltered after incubation.

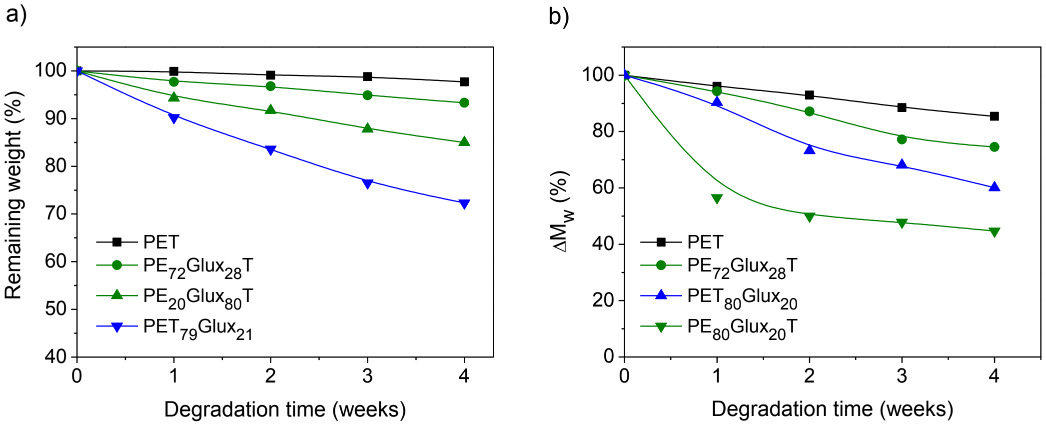


Figure 9. Remaining weight (a) and weight-average molecular weight (b) *vs.* time for PET and some of its Glux-containing copolyesters incubated in aqueous buffer at pH 2.0 and 80 ºC.

In summary it can be said that the insertion of Glux units made PET more prone to undergo hydrolysis and conferred it a certain degree of biodegradability. The enhanced susceptibility displayed by the PET copolyesters containing Glux units is a positive factor favouring a possible chemical recycling of these materials. On the contrary, this behaviour raises some concerns about the integrity of the polymer if used in prolonged contact with liquids at low pH. A detailed degradation study of the alterability of these copolyesters under conditions mimicking those intended to be applied in their utilization as drink containers would be needed to appraise their potential in the beverages bottle sector.

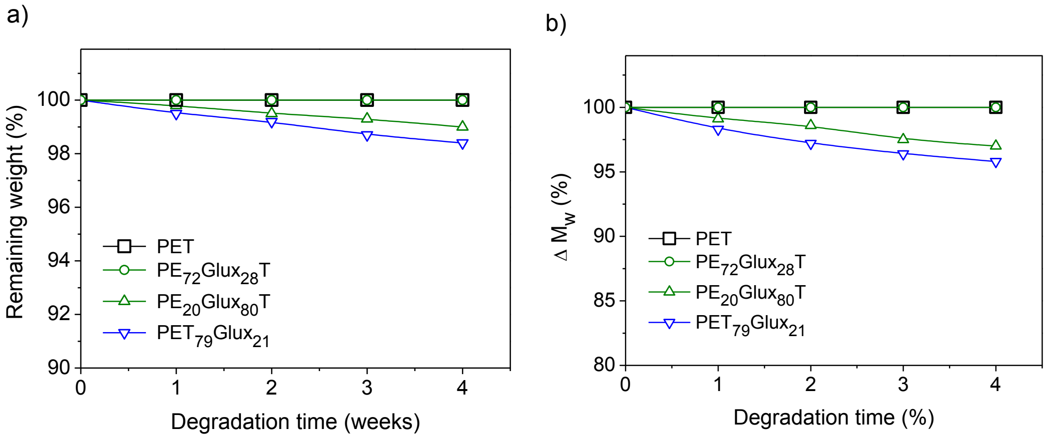


Figure 10. Remaining weight (a) and weight-average molecular weight (b) *vs.* time for PET and some of its Glux-containing copolyesters when incubated in physiological buffer in the presence of enzymes.

6.4. Conclusions

2,3:4,5-di-*O*-methylene-D-glucitol and dimethyl 2,3:4,5-di-*O*-methylene-D-glucarate are bicyclic difunctional compounds derived from D-glucose that can be successfully used as comonomers in the synthesis of polyesters. These compounds are synthesized using 1,5-D-gluconolactone as starting material, a food additive that is prepared by bacterial fermentation of the well accessible D-glucose. They distinguish from other cyclic acetalized sugar diols and diesters previously used by us in the preparation of polyesters, in that they lack molecular symmetry. The partial replacement in the polymerization feed of either ethylene glycol or dimethyl terephthalate by the acetalized glucitol or the dimethyl glucarate, respectively, led to random PET copolyesters with adjustable compositions and suitable molecular weights, and that are thermally stable up to above 300 ºC. The copolyesters containing more than 10-15% of sugar-derived units are mostly amorphous and those displaying crystallinity were found to adopt the same crystal structure than PET. The most outstanding merit of these new bicyclic sugar-based monomers is their capacity to raise notably the T_g of PET when they are inserted in the chain by replacing either the diol or the diacid units in relatively small amounts. It is also remarkable that the mechanical properties of PET do not decay significantly and that its degradability and biodegradability were clearly enhanced with the incorporation of these monomers. Unfortunately, the homopolyesters based on these compounds could not be attained with the same molecular weight as the copolyesters so the comparative evaluation of their basic properties could not be accomplished.

6.5. References

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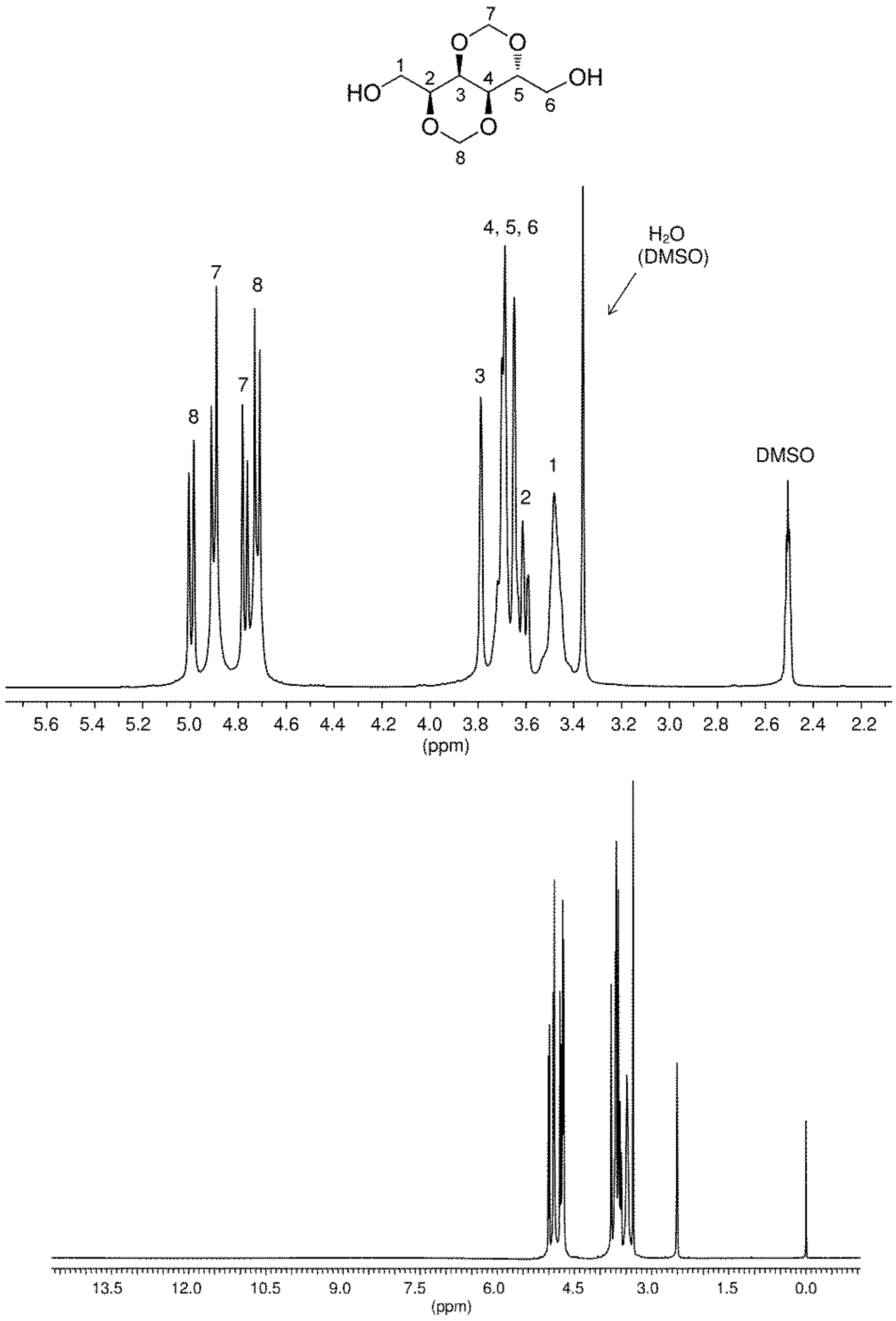
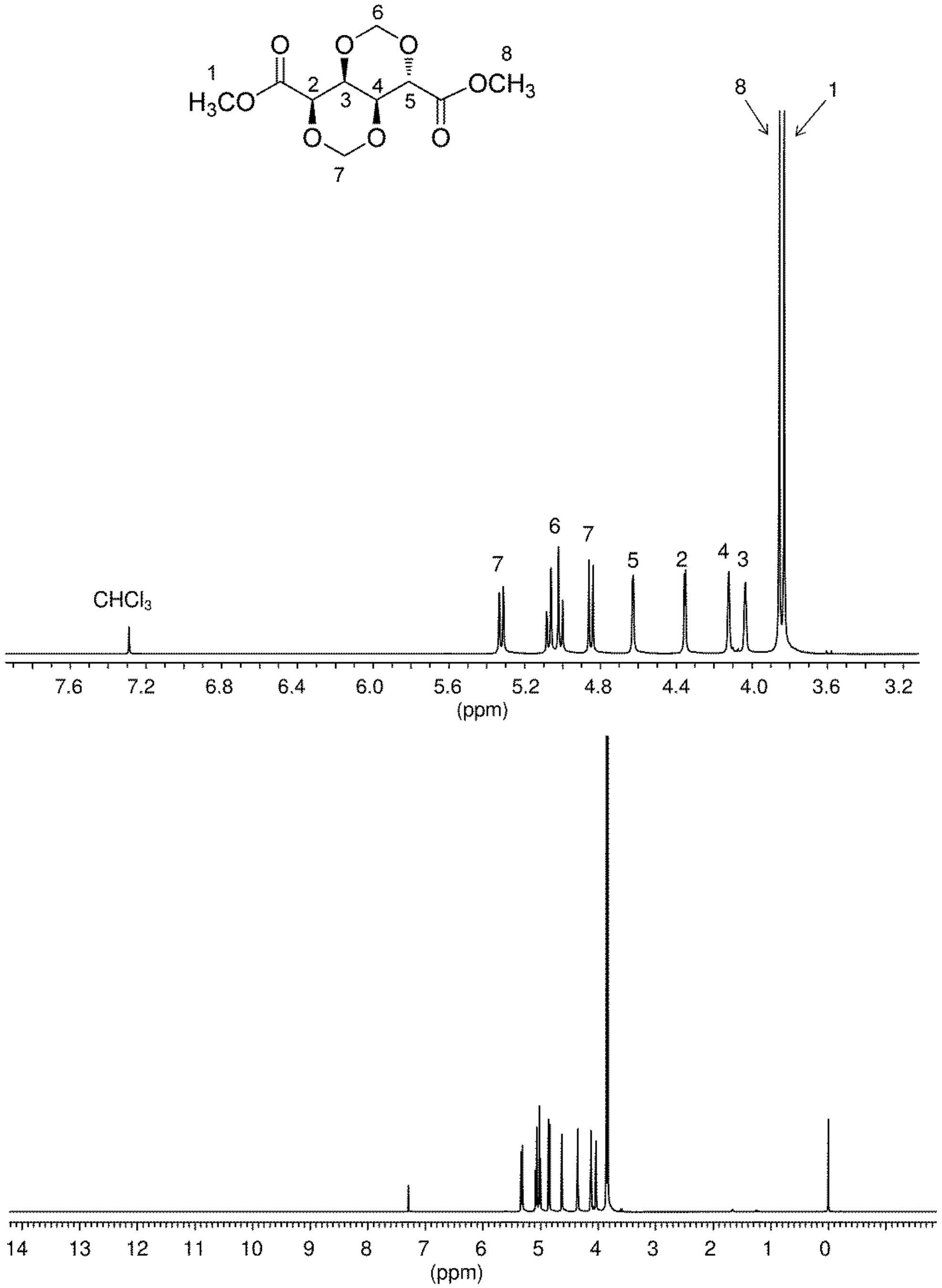
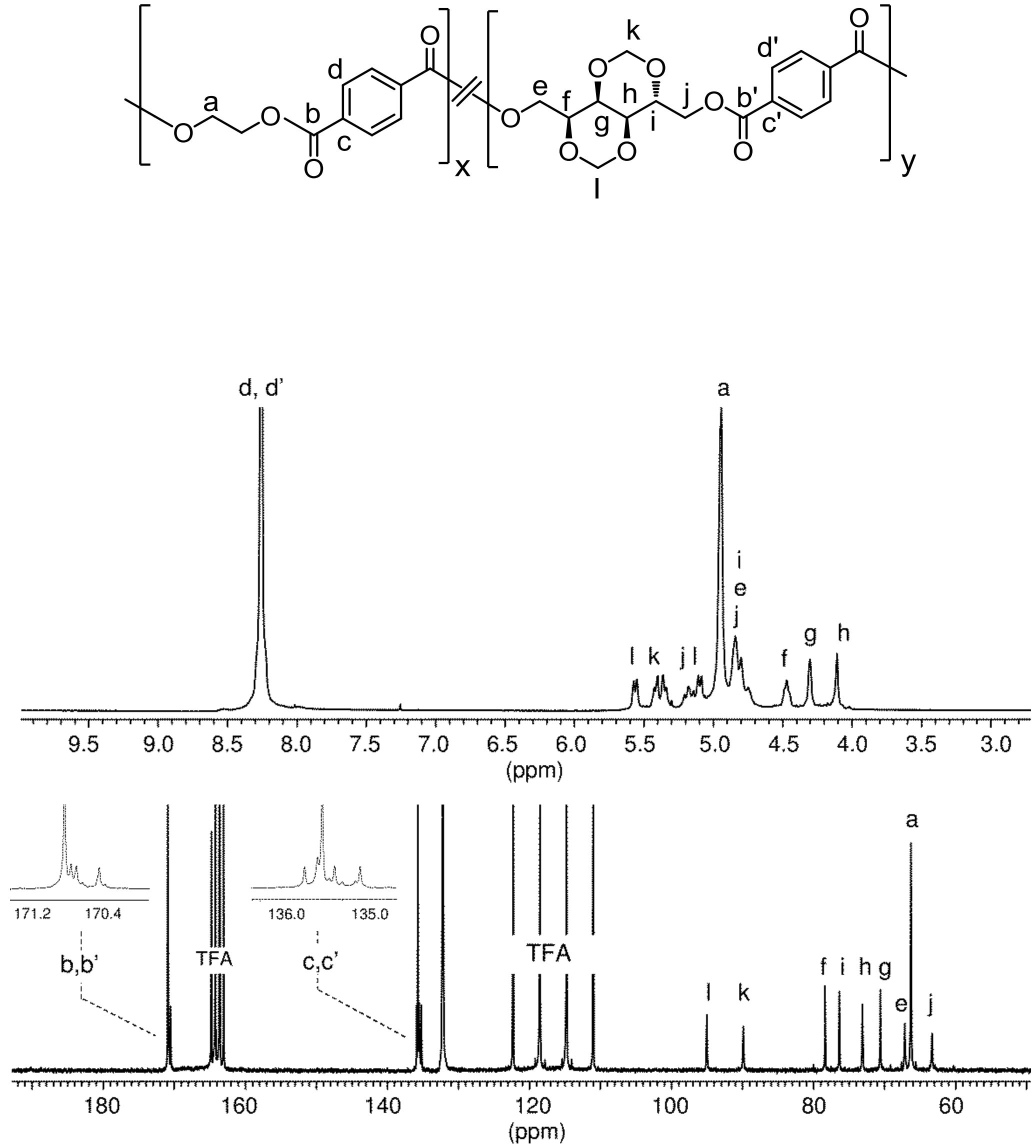
Supporting information



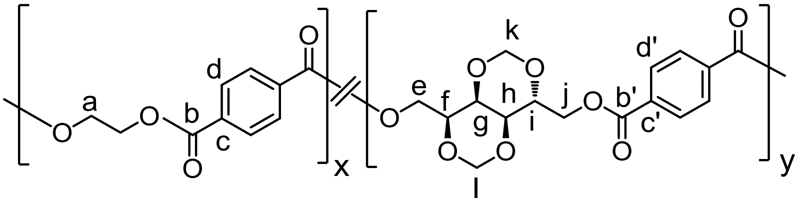
SI-Figure 1. ^{1}H NMR spectra of 2,4:3,5-di-*O*-methylene-D-glucitol (Glux-diol). Bottom: The whole spectrum. Top: Enlarged region containing compound signals with assignments.

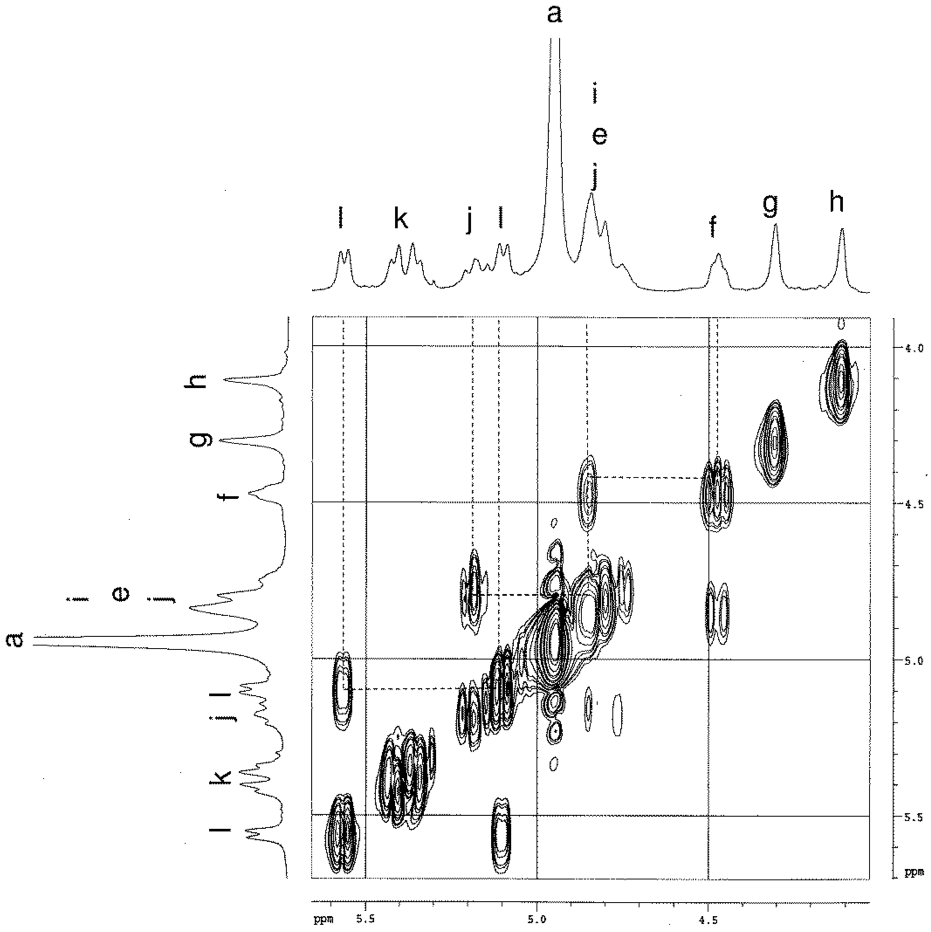


SI-Figure 2. ^{1}H NMR spectra of dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester). Bottom: The whole spectra; Top: Enlarged region containing compound signals with assignments.

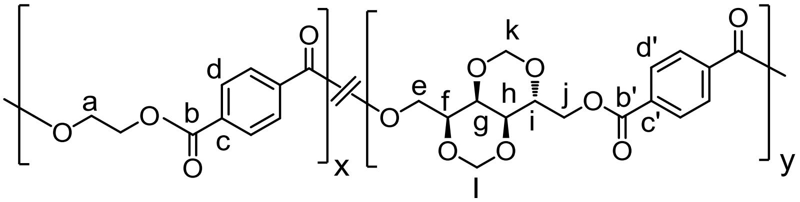


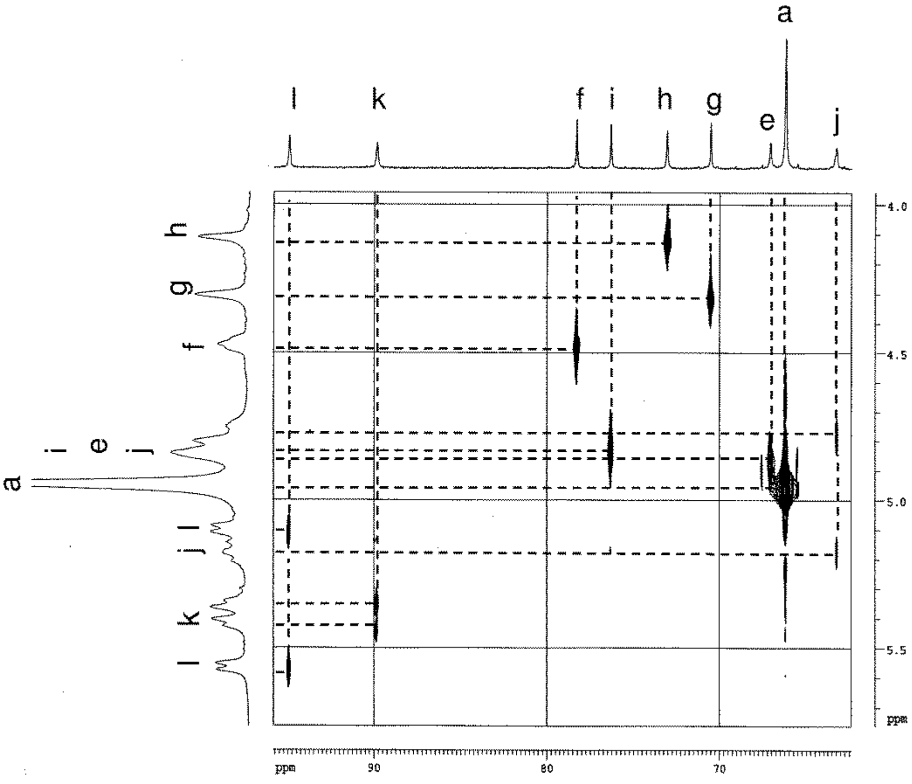
SI-Figure 3. ^{1}H (top) and ^{13}C (bottom) NMR spectra of PE$_{64}$Glux$_{36}$T copolyester.



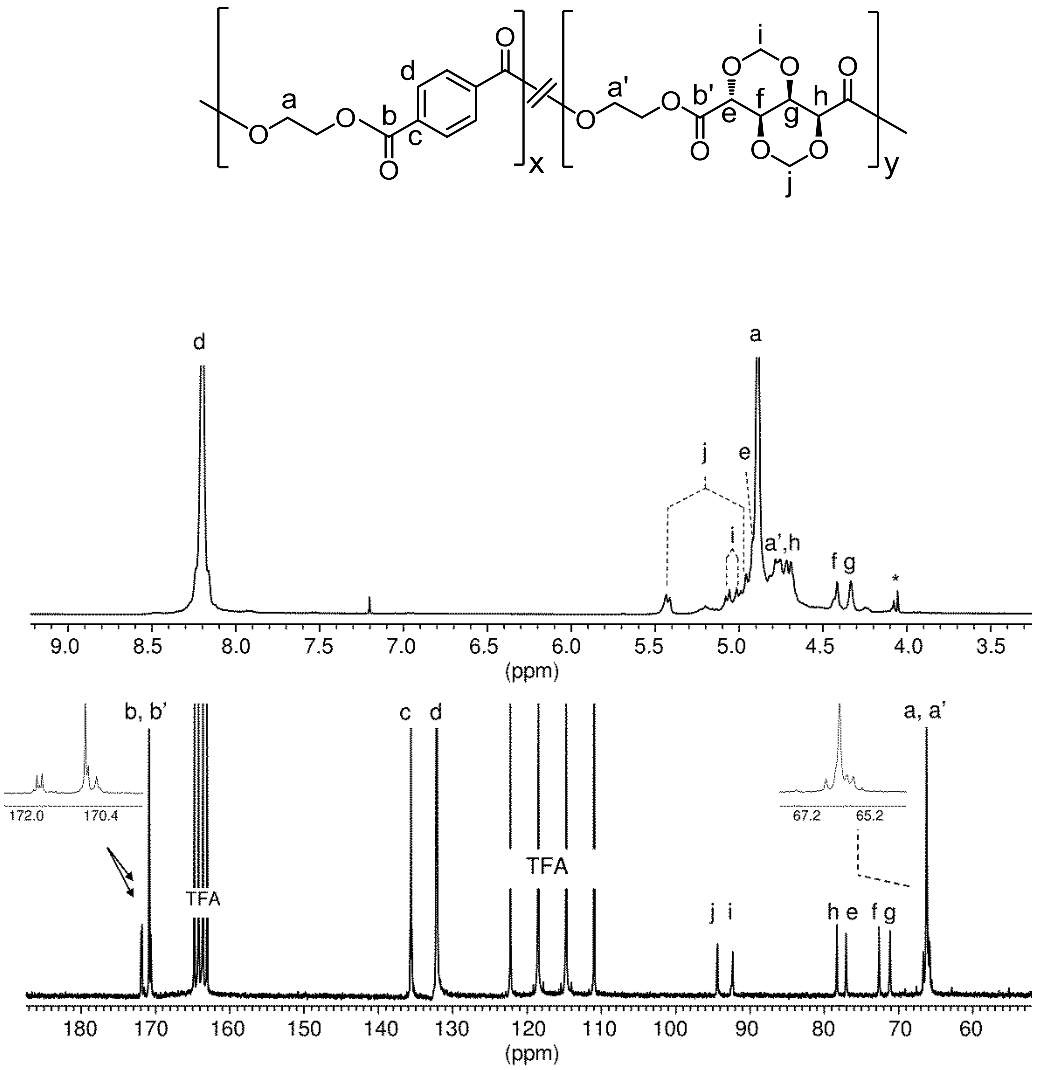


SI-Figure. 4. a) COSY ^{1}H-^{1}H NMR spectra of PE$_{64}$Glux$_{36}$T copolyester.

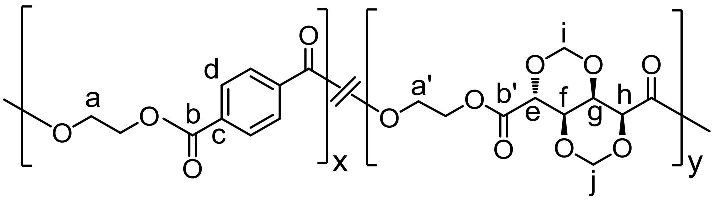


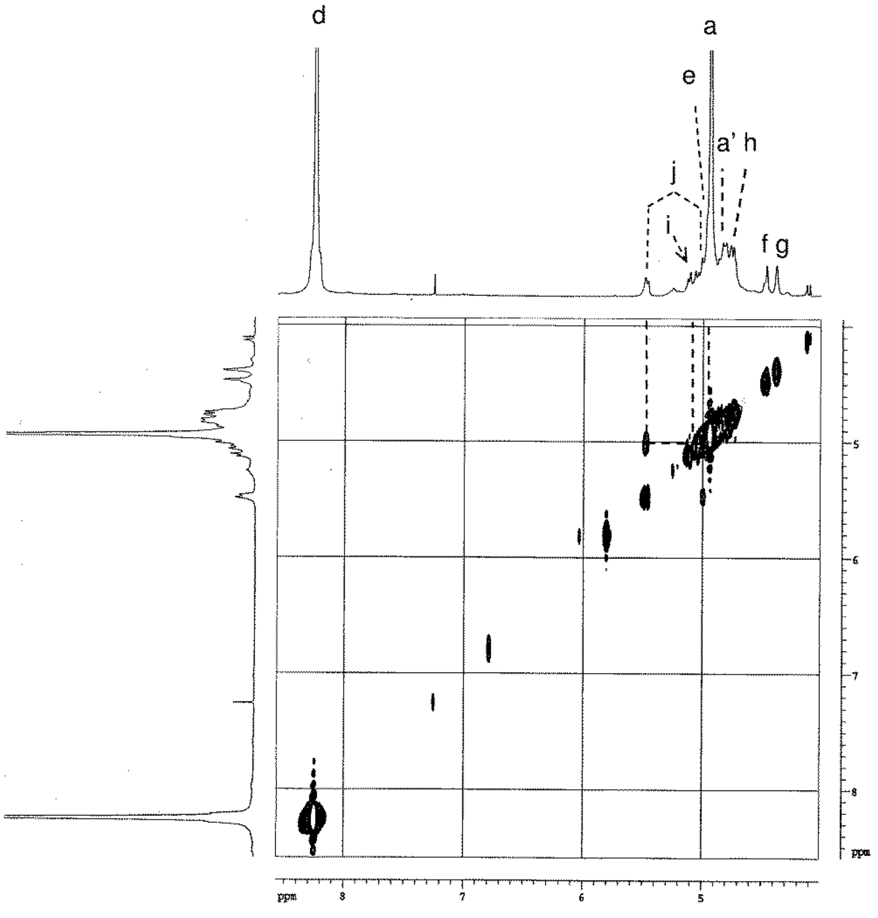


SI-Figure. 5. ^{1}H-^{13}C HETCOR NMR spectra of $PE_{64}Glux_{36}T$ copolyester.

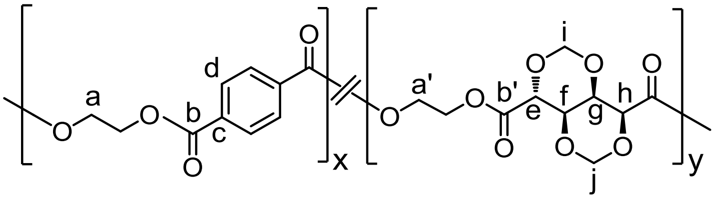


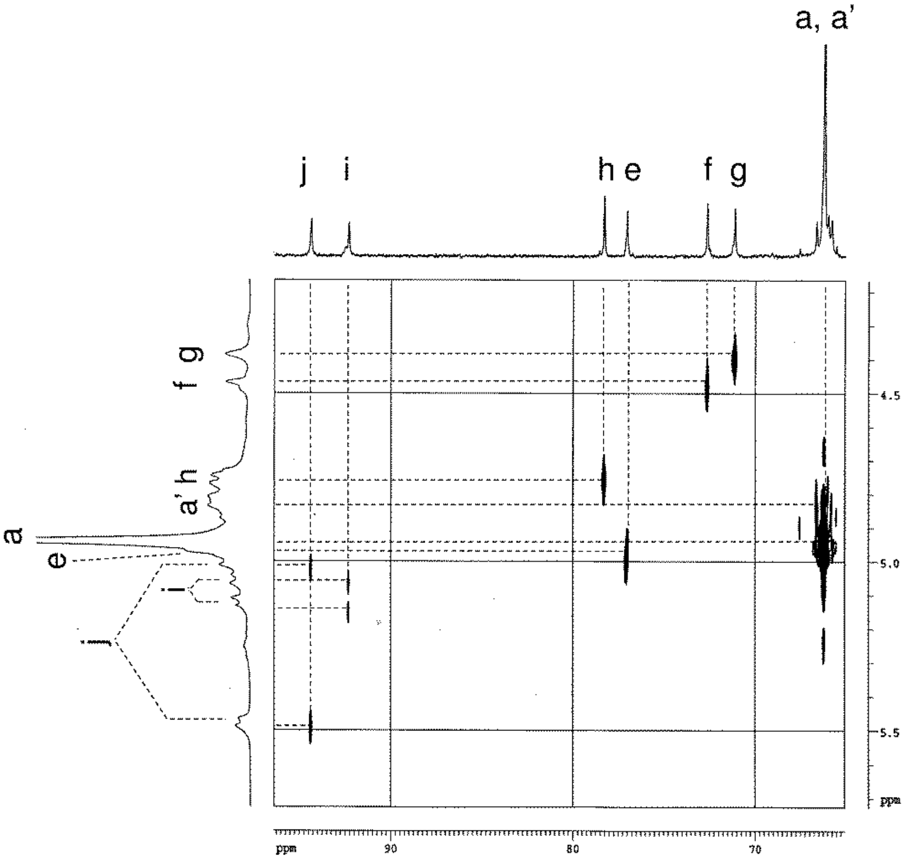
SI-Figure 6. ^{1}H (top) and ^{13}C (bottom) NMR spectra of PET$_{79}$Glux$_{21}$ copolyester. (* OCH$_3$ end group).





SI-Figure 7. COSY H-^{1}H NMR spectra of PET$_{79}$Glux$_{21}$ copolyester.





SI-Figure 8. ^{1}H-^{13}C HETCOR NMR spectra of PET$_{79}$Glux$_{21}$ copolyester.

Composition calculations

Although the signals corresponding to EG and Glux units are overlapped, the signal due to the aromatic terephthalate protons appears well resolved at lower field. Using the area of this signal and the area of the group of signals due to EG and Glux, it was possible to calculate the copolyester composition using the following simple expressions.

PE_xGlux_yT :

Area of aromatic protons= K (4x+4y)

Area of EG and Glux protons= K (4x+12y)

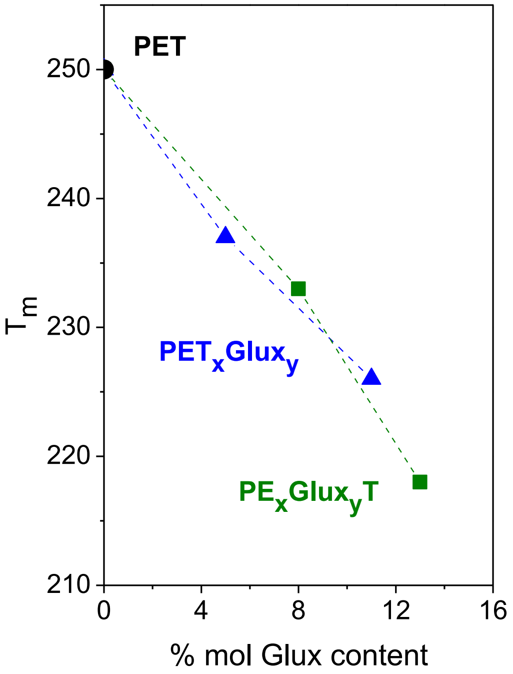
x+y= 100

PET_xGlux_y :

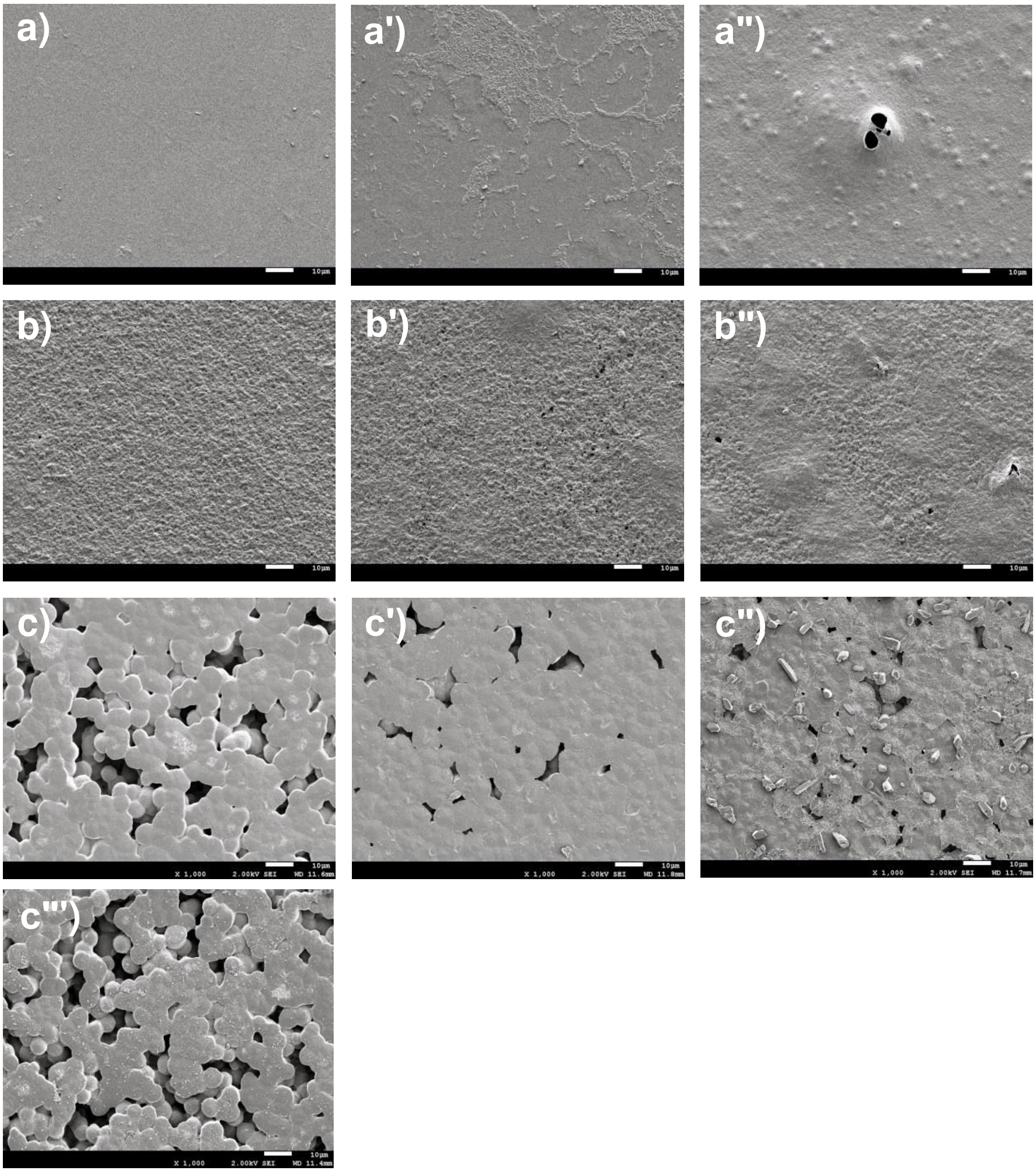
Area of aromatic protons= K (4x)

Area of EG and sugar protons= K (4x+12y)

x+y= 100



SI-Figure 9. T_m values as a function of the content in Glux units.



SI-Figure 10. SEM micrographs of films of $PE_{72}Glux_{28}T$ (a), $PE_{20}Glux_{80}T$ (b) and $PET_{79}Glux_{21}$ (c). After incubation in the presence of enzymes at pH 7.4 (a',b',c'), and after hydrolytic degradation at pH 2, 80 º C (a'',b'',c''). c''': Control of and $PET_{79}Glux_{21}$ incubated at pH 7.4 but without enzymes added.

SI-Table. 1. Powder X-ray diffraction data of polyesters.

Polyester	d_{hkl} [a] (Å)								X_c [b]
PET	5.44 s	5.00 s	4.13 s	3.91 s	3.55 w	3.40 s	3.19 m	2.72 m	0.63
PET$_{95}$Glux$_{5}$	5.43 s	5.02 s	4.13 s	3.92 s	3.55 w	3.40 s	3.19 w	2.72 m	0.45
PET$_{89}$Glux$_{11}$	5.43 s	5.03 s	4.14 s	3.92 s	-	3.40 s	3.19 w	2.72 m	0.37
PE$_{92}$Glux$_{8}$T	5.42 s	5.03 s	4.14 s	3.92 s	-	3.41 s	-	2.73 m	0.42
PE$_{87}$Glux$_{13}$T	542 s	5.03 s	4.15 s	3.92 s	-	3. 43 s	-	2.73 m	0.33

[a] Bragg spacings measured in powder diffraction patterns obtained from annealed samples. Intensities visually estimated as follows: m, medium; s, strong; w, weak.

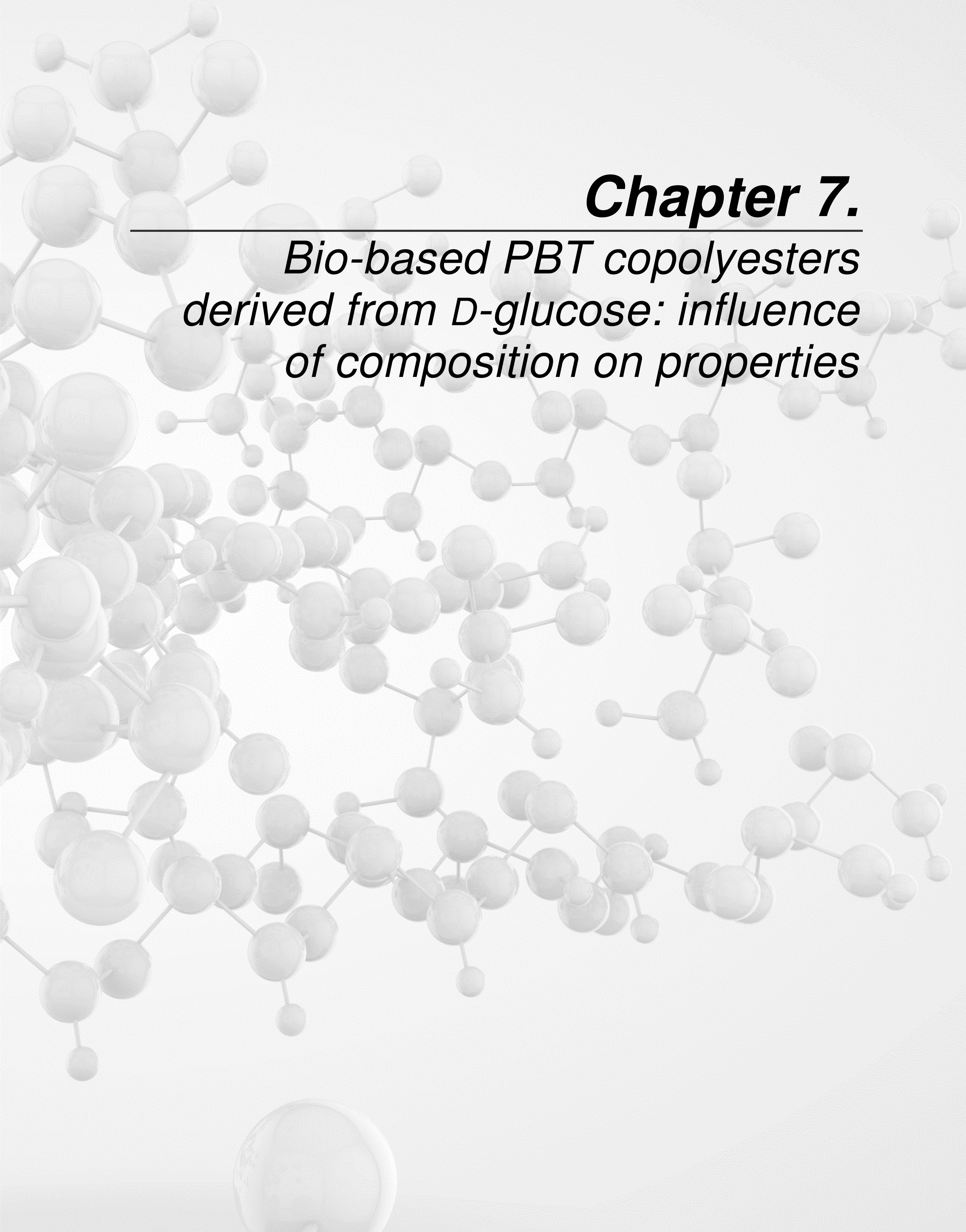
[b] Crystallinity index calculated as the quotient between crystalline area and total area. Crystalline and amorphous areas in the X-ray diffraction pattern were quantified using PeakFit v4.12 software.

SI-Table 2. Mechanical properties.

Copolyester	Elastic modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PET[a]	1032±52	45±7	23±5
PE$_{79}$Glux$_{21}$T	1040±47	48±5	27±3
PE$_{72}$Glux$_{28}$T	1070±50	41±7	20±2
PE$_{64}$Glux$_{36}$T	1080±40	39±6	16±2

Chapter 7.

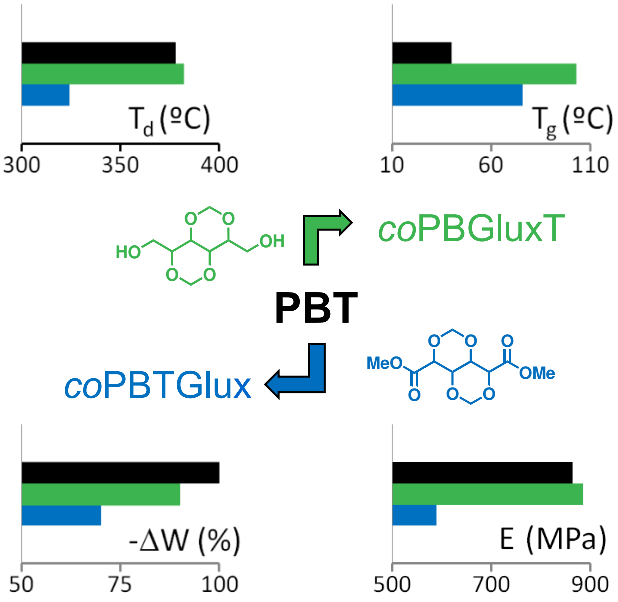
Bio-based PBT copolyesters derived from D-glucose: influence of composition on properties



Bio-based PBT copolyesters derived from D-glucose: influence of composition on properties

Abstract

Two series of bio-based PBT copolyesters were obtained by polycondensation in the melt of 2,4:3,5-di-*O*-methylene-D-glucitol (Glux-diol) or dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester) with 1,4-butanediol and dimethyl terephthalate. The glucose-based bicyclic compounds used as comonomers were synthesized from commercially available 1,5-D-gluconolactone. The prepared PBT copolyesters had weight-average molecular weights in the 30,000-50,000 range, they had a random microstructure, and they were stable above 300 ºC. The copolyesters containing less than 30% of sugar-based units were semicrystalline and were found to adopt the triclinic structure of PBT. These copolyesters with low contents in Glux were able to crystallize from the melt but at lower rates than PBT. The T_g of PBT steadily increased with the incorporation of Glux units in the polyester chain with an increasing ratio of ~1.7 ºC or ~1 ºC per %-Glux point, depending on which unit, the diol or the diacid, was replaced. The copolyesters hydrolyzed at higher rates than PBT, and those containing glucarate units displayed an appreciable susceptibility towards biodegradation.



Publication derived from this work:

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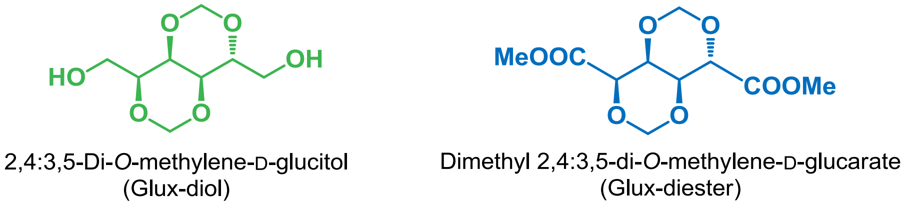
7.1. Introduction

The interest for polymers from renewable resources that are able to replace fossil-derived plastics is growing greatly.[1-3] Prospective studies predict that the worldwide yearly production capacity of bio-based plastics will increase from 0.36 Mt in 2007 up to ~3.5 Mt in 2020.[4] Although this trend extends to every class of polymers, it is particularly applicable to those obtained by polycondensation. Polyesters and, more specifically aromatic polyesters, are priority in this regard because both their great industrial significance and the easy accessibility to bio-resources suitable for their production. Two approaches are currently followed in the development of renewable aromatic polyesters. One consists of developing bio-based procedures leading to those monomers traditionally used in their production and that are currently obtained from petrochemicals.[5-7] Commercially viable routes to such compounds are not yet available and the ultimate success in these efforts is hardly predictable. The second approach is focused on the synthesis of polyesters and copolyesters made from novel monomers which are obtained by chemical modification of natural-occurring compounds. This option may lead to renewable polymers with properties improved respect to those displayed by the traditional ones. Carbohydrates are very suitable resources to provide bio-based monomers useful for polycondensation,[8-11] and among them, 2,5-furandicarboxylic acid (FDCA) appears to be an excellent replacement for terephthalic acid in the production of aromatic polyesters.[12-15] Other sugar-based cyclic compounds that are being intensively examined are the bicyclic diols based on 1,4:3,6-dianhydrohexitols. Among them, the diol derived from D-glucitol, known as isosorbide, is by far the most extensively studied and the only one that is commercially accessible.[16-19] Cyclic acetalized alditols and aldaric acids prepared from C4 and C6 sugars have recently emerged as a third option for the preparation of bio-based polyesters. These compounds are readily available from commercial carbohydrates by applying a relatively easy chemistry. Diverse monocyclic and bicyclic acetalized diols and dimethyl esters with *threo*, *galacto, manno* and *gluco* configuration have been reported for the preparation of polyesters including certain poly(terephthalate)s.[20-21] The main advantage offered by these monomers in general is their capacity to maintain or even to rise the glass-transition temperature of the parent polyesters without significant detriment of other properties.

In this work we wish to report on bio-based copolymers of poly(butylene terephthalate) (PBT) produced from bicyclic monomers derived from D-glucose. PBT is a leading polyester qualified as a medium performance-engineering thermoplastic that is daily produced in big amounts by polycondensation in the melt from 1,4-butanediol and dimethyl terephthalate. PBT melts around 225 °C and displays the exceptional property of crystallizing very fast from the melt, a feature that makes it the material of choice for goods manufactured by injection molding. Since PBT may absorb only small amounts of water (less than 0.1%), its resistance to hydrolysis is very strong and its accessibility to the action of enzymes is extremely restricted. The high environmental durability of PBT is an additional merit of this polyester when it is used for long-life applications.

However not all the attributes of PBT are of entire satisfaction when new application perspectives are considered for this material. Its melting temperature is too high for end use at room temperature since an energetic surplus has to be unnecessarily paid for processing. In contrast, its low glass-transition temperature (below 40 ºC) precludes its use in high temperature applications, as for example hot-filling containers or sterilized bottles for beverages. Moreover its great resistance to be degraded by atmospheric and biological agents together with its non-renewable origin, qualifies this polyester as an environmentally unfriendly material. 2,4:3,5-di-*O*-methylene-D-glucitol (Glux-diol) and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester) (Scheme 1) are the bicyclic acetalized compounds chosen in this work to be used as comonomers of 1,4-butanediol and dimethyl terephthalate acid, respectively, to prepare novel bio-based PBT copolyesters. The structure of these diacetals consists of a C6-segment backbone with four asymmetric carbons in D-*gluco* configuration forming part of the two fused 1,3-dioxane rings and bearing two hydroxyl or two methoxycarbonyl functions at the end positions. PBT copolyesters containing diacetalized cyclic units with *manno* and *galacto* configuration[23-25] as well as PET copolyesters containing Glux units[26] have been recently reported by us. The Glux diacetals distinguish from their *manno* and galacto isomers in that they lack molecular symmetry and are stiffer, and in consequence less crystalline copolyesters with higher T_g could be expected from them. The relatively greater natural abundance of the raw material from which they come is an additional merit of Glux monomers.



2,4:3,5-Di-*O*-methylene-D-glucitol (Glux-diol)

Dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester)

Scheme 1. Chemical structure of the bicyclic diacetals used as comonomers.

7.2. Experimental section

7.2.1. Materials and methods

Materials

1,4-butanediol (BD) (99%), dimethyl terephthalate (DMT) (99%), dibutyl tin oxide (DBTO, 98%) were purchased from Sigma-Aldrich. *Irganox 1010* and *Irgafos 126* antioxidants samples were generously gifted by BASF. Sodium trifluoroacetate (98%) used to stabilize 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and lipase from porcine pancreas (triacylglycerol lipase activity: 15-35 units/mg) were also purchased from Sigma-Aldrich. Solvents used for purification and characterization, such as chloroform, trifluoroacetic acid (TFA), methanol, diethyl ether and dichloracetic acid (DCA) were purchased from Panreac, and all they were of either technical or high-purity grade. All the reagents and solvents were used as received without further purification.

Intrinsic viscosities were measured in DCA with an Ubbelohde microviscometer thermostated at 25 ± 0.1 ºC using polymer concentrations in the 0.3 to 1 g·dL^{-1} range. Molecular weights were determined by GPC using a Waters apparatus equipped with a RI detector. 100 µL of sample solution (0.1% w/v) were injected and chromatographed using HFIP stabilized with sodium trifluoroacetate at a flow rate of 0.5 mL·min^{-1}. A set of a cross-linked polystyrene Styragel column (HR5E Water, 7.8x300 mm) preceded by a filtering pre-column was used. Molecular weights were estimated against monodisperse PMMA standards.

^{1}H and ^{13}C NMR spectra were recorded using a Bruker AMX-300 spectrometer operating at 300.1 and 75.5 MHz, respectively, and they were internally referenced with tetramethylsilane. Samples for ^{1}H and ^{13}C analyses were prepared by dissolving ~ 10 and 50 mg of polymer, respectively, in 1 mL of either TFA or a (9:1) $CDCl_3$:TFA mixture. Sixty-four scans were recorded for ^{1}H, and between 5,000 and 15,000 scans were taken for ^{13}C with 32 and 64 K data points and relaxation delays of 1 and 2 s, respectively. Two-dimensional spectra (2D) as ^{1}H-^{1}H homonuclear (COSY) and ^{13}C-^{1}H heteronuclear shift correlation (HETCOR) were recorded by means of the *cosy* and *hxco* pulse sequences implemented in the Bruker NMR instrument package. All the experiments were carried out at 25 ºC.

Thermogravimetric analyses were performed on a Perkin-Elmer TGA 6 thermobalance. Samples with a weight around 10 mg were heated at a rate of 10 ºC·min^{-1} within the temperature range of 30-600 ºC under an inert atmosphere.

Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Pyris 1 apparatus using 4-6 mg samples, which were heated/cooled at a rate of 10 ºC·min^{-1} under a nitrogen flow of 20 mL·min^{-1}. Temperature and enthalpy calibrations were made using indium and zinc as standards. The melting temperature (T_m) was taken as the maximum of the endothermic peak appearing on heating traces. For the estimation of the glass transition temperature (T_g), heating traces were recorded at 20 ºC·min^{-1} from samples rapidly cooled from the melt; T_g was taken as the temperature for the inflexion point of the shift in the base line.

Powder wide angle X-ray diffraction (WAXD) was carried out on a PANalyticalX'Pert PRO MPD θ/θ diffractometer with Cu-Kα radiation (λ = 0.1542 nm). Samples either coming directly from synthesis or after being subjected to annealing treatment were analyzed.

The mechanical behavior of polymers was evaluated by tensile assays carried out on a Zwick 2.5/TN1S tensile machine. The Young's modulus, yield strength, and elongationat break were measured at a stretching rate of 30 mm·min^{-1} at 23 ºC. For these measurements, 5 mm-width and ~150 µm-thick rectangular samples were tested with a distance of 10 mm between testing marks. Specimens were cut from polymer films prepared by casting from a 100 g·L^{-1} solution in either $CHCl_3$ or a mixture of $CHCl_3$:HFIP (5:1).

7.2.2. Synthesis of polyesters

2,4:3,5-di-*O*-methylene-D-glucitol (Glux-diol) and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester) used as monomers were prepared from commercial 1,5-D-gluconolactone as described in full detail elsewhere.[26]

The polyesters were synthesized by melt polymerization in two-steps, transesterification and polycondensation. The homopolymers, poly(butylene terephthalate) (PBT), poly(glucitylene terephthalate) (PGluxT), and poly(butylene glucarate) (PBGlux), were obtained from the two-component mixtures made of the corresponding diol and diacid monomers: 1,4-butanediol or 2,4:3,5-di-*O*-methylene-D-glucitol and dimethyl terephthalate or 2,4:3,5-di-*O*-methylene-D-glucarate. For the preparation of copolyesters, the reaction mixtures consisted of three components, *i.e.*1,4-butanediol, dimethyl terephthalate and either 2,4:3,5-di-*O*-methylene-D-glucitol or 2,4:3,5-di-*O*-methylene-D-glucarate,for PB_xGlux_yT andPBT_xGlux_y, respectively. In these abbreviations the *x* subscript refers to the mol percentage (%-mol) of 1,4-butylene or terephthalate units, and the *y* subscript refers to the %-mol of Glux units, either glucitylene or glucarate, in the respective series of copolyesters. An excess of diols respect to diesters was used in all cases in order to ensure the complete transesterification of methyl ester end groups. Dibutyl tin oxide (0.5% mol DBTO respect to the diester) was added to the mixture of monomers to act as catalyst. In previous work it was found that addition of small amounts of *Irganox 1010* (0.1 % w/w) and *Irgafos126 (0.3* % w/w*)* antioxidants was very effective to minimize degradation of the thermally-sensitive sugar-derived monomers.[26] The same procedure was therefore applied in the present case.

The polymerization reaction was performed in a three-necked, cylindrical-bottom flask provided with a mechanical stirrer, a nitrogen inlet, and a vacuum distillation outlet. The transesterification reaction was carried out at temperatures between 160 and 200 ºC and under atmospheric pressure provided by a low nitrogen flow. The methanol released in this stage was continuously removed by distillation. For polycondensation, the temperature was increased several tens of degrees and the pressured diminished down to 0.03-0.06 mbar. Once the polymerization was finished, the reaction mixture was cooled to room temperature and the resulting solid mass was collected under a flow of nitrogen, dissolved in $CHCl_3$ or in a mixture of

$CHCl_3$:TFA (9:1), and the solution poured into an excess of methanol to remove low molecular weight species. The precipitated polymer was recovered by filtration, washed with methanol, and dried under vacuum.

PBT homopolyester. BD to DMT molar ratio: 2.2/1 Transesterification: 190 ºC, 2.5 h and 240 ºC, 0.5 h. Polycondensation: 260 ºC, 2 h.^{1}H NMR (TFA-*d_1*, 300 MHz), *δ* (ppm): 8.13 (s, *Ar*H), 4.50 (t, *J* = 5.1 Hz, O*CH_2*CH_2), 2.02 (t, *J* = 5.1 Hz,OCH_2*CH_2*). ^{13}C{^{1}H}-NMR ($CDCl_3$/TFA, 75.50 MHz), *δ* (ppm): 168.0 (C=O), 133.70 (*Ar*C), 129.9 (*Ar*C), 66.21(O*CH_2*CH_2), 25.10 (OCH_2*CH_2*).

PB$_x$Glux$_y$Tcopolyesters. The copolyesters were obtained by a similar procedure, with polymerization conditions slightly differing for each composition feed.

BDandGlux-diol mixture to DMT molar ratio: 1.1/1. Transesterification: 175 ºC, 2 h, 200 ºC, 1.5 h. Polycondensation: 255 ºC, 1 h (for *y* between 3 and 11 %-mol), 250 ºC, 1,5-2 h (for *y* between 20 and 40 %-mol), 230 ºC, 3h (for y 50 %-mol) under a 0.03-0.06 mbar vacuum.

^{1}H NMR ($CDCl_3$/TFA, 300 MHz), *δ* (ppm): 8.14 (s, *Ar*H), 5.36 (d, *J* = 6.8 Hz, OCH_2O), 5.19 (s, OCH_2O), 5.00-4.88 (m, OCH_2, d, *J* = 6.8 Hz, OCH_2O,), 4.75-4.45 (m, *J* = 6.2 Hz, O*CH_2*CH_2, OCH_2, CH), 4.23 (t, *J* = 5.1 Hz, CH), 4.03 (s, OCH_2), 3.85 (s, OCH_2), 2.04 (t, OCH_2*CH_2*). ^{13}C{^{1}H}-NMR ($CDCl_3$/TFA, 75.5 MHz), *δ* (ppm): 168.20-166.90 (C=O), 134.20-132.85 (*Ar*C), 129.98(*Ar*C), 92.88 (OCH_2O), 88.07 (OCH_2O), 75.72 (CH), 73.89 (CH), 70.79 (CH), 67.75 (CH), 66.29 (O*CH_2*CH_2), 64.88 (OCH_2), 61.32 (OCH_2), 25.13 (OCH_2*CH_2*).

PGluxThomopolyester. 2,4:3,5-di-*O*-methylene-D-glucitol to dimethyl terephthalate molar ratio: 1.5/1. Transesterification: 160 ºC, 2.5 h. 180 ºC, 1 h. Polycondensation: 200 ºC, 1 h and 235 ºC, 2 h.

^{1}H NMR (TFA-*d_1*, 300 MHz), *δ* (ppm): 8.23 (s, ArH), 5.12-5.50 (2dd, *J* = 6.6 Hz, OCH_2O), 5.21-4.93 (m, CH_2, CH), 4,54 (m, CH), 4,3 (m, CH), 4.11 (m, CH).^{13}C{1H}-NMR (TFA-*d_1*, 75.5 MHz), *δ* (ppm): 170.50 (C=O), 135.0-131.9 (*Ar*C), 95.01 (OCH_2O), 89.93 (OCH_2O), 78.44 (CH), 76.40 (CH), 73.12 (CH), 70.62 (CH), 67.01 (CH_2), 63.33 (CH_2).

PBT$_x$Glux$_y$copolyesters. 1,4-butanediol to dimethyl terephthalate and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate diesters mixture: 2.2/1. Transesterification: 175 ºC, 2 h, 200 ºC, 1.5 h. Polycondensation: 250 ºC, 2h (for *y* between 5 and 30 %-mol), 230 ºC, 5.5 h (for *y* 40 %-mol) under a 0.03-0.06 mbar vacuum.

^{1}H NMR ($CDCl_3$/TFA, 300 MHz), *δ* (ppm): 8.13 (s, *Ar*H), 5.35 (d, *J* = 6.8 Hz, OCH_2O), 5.20-5.00 (2dd, *J* = 6.2 Hz, OCH_2O), 4.89 (d, *J* = 6.8 Hz, OCH_2O), 4.75 (s, CH), 4.65-4.42 (m, *x*-O*CH_2*CH_2, CH), 4.42-4.28 (m, *y*-O*CH_2*CH_2), 4.24 (s, CH), 4.15 (s, CH), 2.15-1.70 (m, -OCH_2*CH_2*,). ^{13}C{^{1}H}-NMR ($CDCl_3$/TFA, 75.5 MHz), *δ* (ppm): 169.3-168.0 (C=O), 133.73-129.96 (*Ar*C), 92.32 (OCH_2O), 90.16 (OCH_2O), 76.25 (CH), 74.97 (CH), 70.30 (CH), 68.68 (CH), 66.90-65.90 ($O\mathit{CH_2}CH_2$), 25.40-24.50 ($OCH_2\mathit{CH_2}$).

PBGluxhomopolyester. 1,4-butanediol to dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate molar ratio: 2.2/1 Transesterification: 165 ºC, 5 h. Polycondensation: 170 ºC, 7 h.

^{1}H NMR ($CDCl_3$/TFA, 300 MHz), δ (ppm): 8.13 (s, *Ar*H), 5.35 (d, J = 6.5 Hz, OCH_2O), 5.20-4.95 (2dd, J = 6.3 Hz, OCH_2O), 4.90 (d, J = 6.5 Hz, OCH_2O), 4.75 (s, CH), 4.65-4.45 (m, CH), 4.45-4.20 (m, $-O\mathit{CH_2}CH_2$, CH), 4.12 (s, CH), 1.79 (m, $-OCH_2\mathit{CH_2}$).^{13}C{^{1}H}-NMR ($CDCl_3$/TFA, 75.5 MHz), δ (ppm): 172.5-171.3 (C=O), 92.31 (OCH_2O), 90.21 (OCH_2O), 76.25 (CH), 74.98 (CH), 70.29 (CH), 68.74 (CH), 66.90-66.10 ($O\mathit{CH_2}CH_2$), 24.70 ($OCH_2\mathit{CH_2}$).

7.2.3. Hydrolytic and enzymatic degradation assays

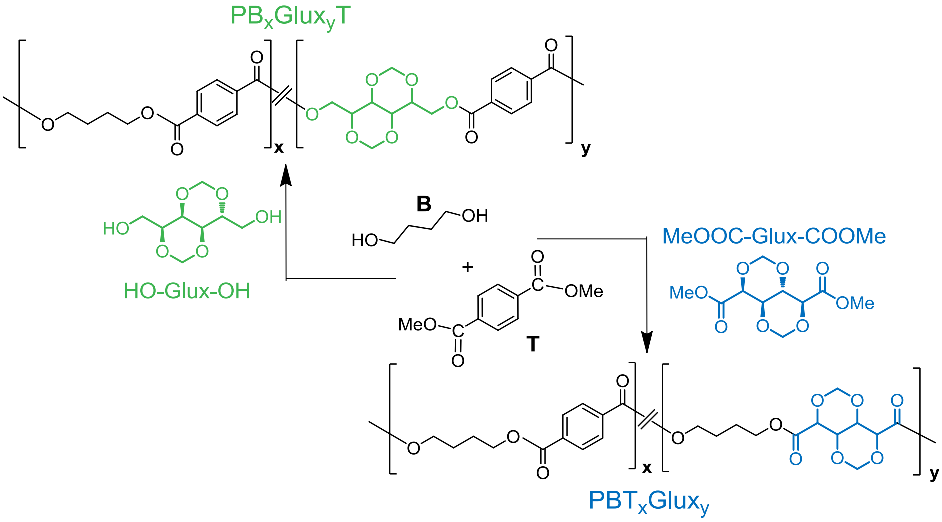
For degradation study, polymers films were prepared as mentioned above but with a thickness of ~200 µm. 10 mm-diameter disks were cut, dried under vacuum to constant weight (20-30 mg), and immersed in the incubating medium for a total period of one month. Hydrolytic degradation was performed at 80 ºC in sodium citric acid pH 2.0, and enzymatic degradation at 37 ºC in pH 7.4 sodium phosphate buffer containing 10 mg of porcine pancreas lipases.The disks were withdrawn from the buffer solution at scheduled periods of time and washed carefully with distilled water. After drying under vacuum to constant weight, they were analyzed by NMR and GPC.

7.3. Results and discution

7.3.1. Polyesters synthesis

The Glux-based polyesters studied in this work were synthesized by polycondensation in the melt which is the procedure usually applied in the industry for the high-scale production of aromatic polyesters. Two copolyester series, PB_xGlux_yT and PBT_xGlux_y, covering a wide range of compositions in Glux units, as well as the homopolyesters PBT, PGluxT and PBGlux were prepared. The essential difference between the two series relies on the type of unit, diol or diacid, that is replaced in each case by Glux, *i.e*. 1,4-butylene by 2,4:3,5-di-*O*-methylene-D-glucitylene and terephthalate by 2,4:3,5-di-*O*-methylene-D-glucarate in the PB_xGlux_yT and PBT_xGlux_y series, respectively. The reactions involved in these syntheses are formulated in Scheme 2.

The results obtained in these syntheses are presented in Table 1. After purification the copolyesters were obtained in yields close to 80-90 % with intrinsic viscosities in the 0.60-0.99 $dL \cdot g^{-1}$ range. Their weight-average molecular weights determined by GPC ranged between 49,000 and 28,000 $g \cdot mol^{-1}$ with dispersities oscillating in the narrow range of 2.3 to 2.5. It should be noted that homopolyesters entirely made of either glucitylene or glucarate units were attained with much lower molecular weights. It is worth to compare these results with those reported for the synthesis of PET-Glux copolyesters, *i.e* .copolyesters made by using ethylene glycol as alkanediol, which were named PE_xGlux_yT and PET_xGlux_y.[26] Whereas yields and polydispersities are perfectly comparable for the two families, molecular weights are significantly higher for the PBT derived copolyesters here reported. The higher chain mobility of PBT copolyesters provided by the more flexible butylenes segments makes easier the reaction between chain ends, and therefore enhances the growing of the polymer chains in the last polycondensation stage.



Scheme 2. Polymerization reactions leading to PB_xGlux_yT and PBT_xGlux_y.

The chemical constitution of the polyesters was ascertained by NMR spectroscopy; a detailed description of the NMR data is given in the Experimental Section, and ^1H and ^{13}C spectra of representative members of each series, as well as the 2D NMR spectra (*cosy* and *hetcor*) used for the assignment of the peaks are provided in the Electronic Supplementary Information document (ESI) linked to this paper (SI-Figs. 1-6).

The comonomeric composition of the PB_xGlux_yT copolyesters was determined by comparing the integrated signals at 5.5-3.7 ppm arising from methylene and methyne protons contained in the two repeating units of the copolyester (4Hx+12Hy) to the signal at 2.4 ppm (4Hx) that exclusively corresponds to butylene units. For the PBT_xGlux_y copolyesters the composition determination was similarly made but considering the methylene and methyne signals (4Hx+16Hy) at 5.5-4.0 ppm arising from the repeating units and the aromatic signal (4Hx) emerging from the phenylene ring. The percentage of sugar units present in the copolyester was estimated by applying simple proportion calculations. It was found that the content of Glux units in PB_xGlux_yT copolyesters was essentially the same as in the feed whereas in the case of PBT_xGlux_y, they incorporated into the polymer in amounts slightly higher than expected.

Table 1.Composition and molecular weight of PB$_x$Glux$_y$T and PBT$_x$Glux$_y$.

Copolyester	Yield (%)	Composition								Molecular weight			
		Feed				Copolyester[a]							
		Diol		Diacid		Diol		Diacid					
		[B]	[Glux]	[T]	[Glux]	[B]	[Glux]	[T]	[Glux]	[η][b]	M_n[c]	M_w[c]	Đ[c]
PBT	90	100	0	100	0	100	0	100	0	0.91	17,300	41,500	2.4
PB$_x$Glux$_y$T													
PB$_{97}$Glux$_3$T	89	97	3	100	0	97	3	100	-	0.88	17,200	41,200	2.4
PB$_{94}$Glux$_6$T	87	94	6	100	0	94	6	100	-	0.70	15,000	34,500	2.3
PB$_{89}$Glux$_{11}$T	88	90	10	100	0	89	11	100	-	0.80	15,600	39,000	2.5
PB$_{80}$Glux$_{20}$T	90	80	20	100	0	80	20	100	-	0.85	17,800	41,100	2.3
PB$_{69}$Glux$_{31}$T	87	70	30	100	0	69	31	100	-	0.81	17,200	39,500	2.3
PB$_{59}$Glux$_{41}$T	89	60	40	100	0	59	41	100	-	0.81	16,500	39,500	2.4
PB$_{48}$Glux$_{52}$T	86	50	50	100	0	48	52	100	-	0.70	15,000	34,500	2.3
PGluxT	30	0	100	100	0	0	100	100	-	0.32	5,500	12,800	2.3
PBT$_x$Glux$_y$													
PBT$_{95}$Glux$_5$	90	100	0	95	5	100	-	96	4	0.99	20,200	48,500	2.4
PBT$_{90}$Glux$_{10}$	89	100	0	90	10	100	-	90	10	0.97	20,400	47,000	2.3
PBT$_{84}$Glux$_{16}$	88	100	0	85	15	100	-	84	16	0.85	17,100	41,100	2.4
PBT$_{80}$Glux$_{20}$	87	100	0	80	20	100	-	80	20	0.83	17,500	40,200	2.3
PBT$_{67}$Glux$_{33}$	85	100	0	70	30	100	-	67	33	0.75	15,600	37,500	2.4
PBT$_{55}$Glux$_{45}$	80	100	0	60	40	100	-	55	45	0.60	11,400	28,500	2.5
PBGlux	40	100	0	0	100	100	-	0	100	0.40	5,600	13,500	2.4

[a] Molar composition determined by integration of ^{1}H NMR spectra.

[b] Intrinsic viscosity in dL·g^{-1} measured in DCA at 25 ºC.

[c] Number and weight average molecular weights in g·mol^{-1}, and dispersities measured by GPC in HFIP against PMMA standards.

Such deviations are attributed to differences in the relative volatility or/and reactivity of the interplaying comonomers.

7.3.2. Microstructure of PB_xGlux_yT and PBT_xGlux_y copolyesters

The microstructure of the copolyesters was determined by ^{13}C NMR. In the case of the PB_xGlux_yT series, the sensitiveness of the non-protonated aromatic carbons to sequence distributions at the dyad level was taken for benefit. In Figure 1 the 134.2-132.8 ppm region containing the resonance signals produced by such carbons is shown with indication of the dyads from which the peaks arise. B-B, B-Glux/Glux-B and Glux-Glux dyads contents were calculated by integration of these peaks. From the integrated values, the number-average sequence lengths *n* of the butylene-terephthalate (BT) and glucitylene-terephthalate (GluxT) homogeneous sequences, as well as the degree of randomness *R*, were estimated for each copolyester by using the following equations:

$$n_A = (N_{AA} + \tfrac{1}{2}(N_{AB}+N_{BA})) / \tfrac{1}{2}(N_{AB}+N_{BA});$$

$$n_B = (N_{BB} + \tfrac{1}{2}(N_{AB}+N_{BA})) / \tfrac{1}{2}(N_{AB}+N_{BA})$$

$$R = (1/n_A) + (1/n_B)$$

A:*BT* and B:*GluxT* (PB_xGlux_yTcopolyesters) or *BGlux*(PBT_xGlux_ycopolyesters).

Regarding PBT_xGlux_ycopolyesters, the ^{13}C NMR spectra of this series showed complex signals for the 1,4-butylene units, revealing that in this case the methylene carbons are sensitive to sequence effects. Figure 2 shows the nine peaks appearing within the 69.6-68.4 ppm interval which correspond to the four types of dyads (TT, GluxT/TGlux, GluxGlux) that are possible along the copolyester chain. Applying the same methodology used above for PB_xGlux_yT, the *R* values were calculated for this series.

The microstructure parameters calculated for PB_xGlux_yT and PBT_xGlux_y copolyesters are listed in Table 2, indicating that the sequence distribution is essentially random for the whole range of compositions with values of *R* being very close to unity for both series. The plots of calculated dyad contents *vs*. copolyester compositions for the two series are depicted in Figures1c and 2c, respectively, and compared to the function that would result for ideal random copolyesters with the same compositions. These results are almost identical to those obtained in the analysis of PE_xGlux_yT copolyesters[26] indicating that chain growing takes place in these copolymerizations without preferential selection of the diol comonomer irrespective of its length. Unfortunately a similar comparison between the series containing glucarate units is not feasible because the microstructure for PET_xGlux_y copolyesters could not be determined due to overlapping of the signals required for analysis.

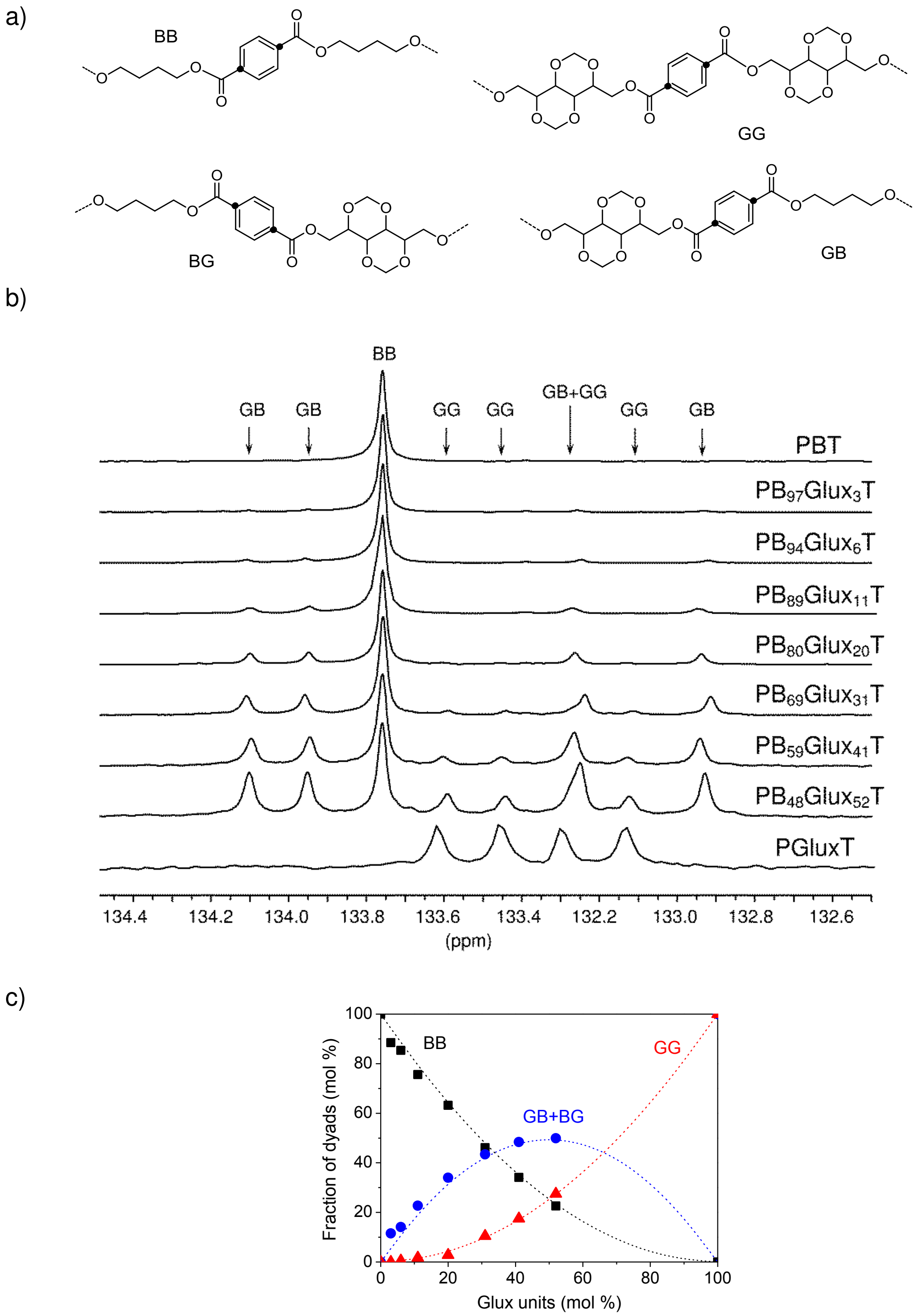


Figure 1. a) The four possible dyads occurring in PB$_x$Glux$_y$T copolyesters. b) The non-protonated aromatic carbon region in the ^{13}C NMR spectra of copolyesters and homopolyesters, c) Plot of dyad contents *vs.* copolyester compositions. Dashed lines represent the theoretically calculated contents for random copolyesters.

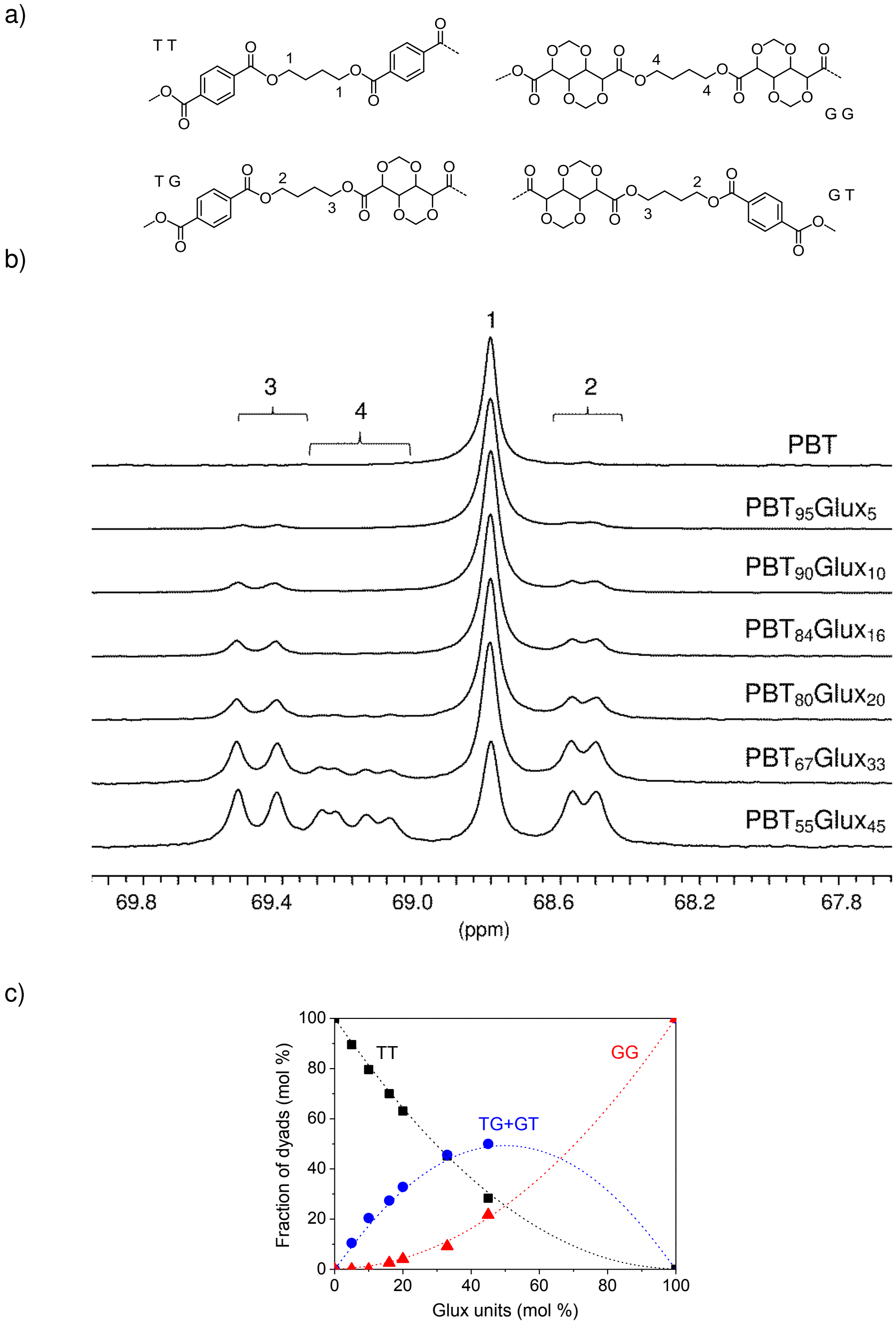


Figure 2. a) The four possible dyads occurring in PBT$_x$Glux$_y$ copolyesters. b) ^{13}C NMR spectra in the region of the α-methylenes of the butylene segment of PBT$_x$Glux$_y$ copolyesters and homopolyesters. c) Plot of dyad contents *vs.* copolyester compositions. Dashed lines represent the theoretically calculated contents for random copolyesters.

Table 2. Composition and microstructure of PB$_x$Glux$_y$T and PBT$_x$Glux$_y$ copolyesters.

Copolyesters	Composition[a]		Dyad content (mol%)[b]			Sequence lenghts		R
	X_B	X_{Glux}	BB	GB/BG	GG	n_{BT}	n_{GluxT}	
PB$_{97}$Glux$_3$T	0.97	0.03	88.5	11.5	0.0	16.4	1.0	1.1
PB$_{94}$Glux$_6$T	0.94	0.06	85.4	14.1	0.5	13.1	1.1	1.0
PB$_{89}$Glux$_{11}$T	0.89	0.11	75.6	22.7	1.7	7.7	1.2	1.0
PB$_{80}$Glux$_{20}$T	0.80	0.20	63.2	34.0	2.8	4.7	1.2	1.0
PB$_{69}$Glux$_{31}$T	0.69	0.31	46.1	43.4	10.5	3.1	1.5	1.0
PB$_{59}$Glux$_{41}$T	0.59	0.41	34.1	48.4	17.5	2.4	1.7	1.0
PB$_{48}$Glux$_{52}$T	0.48	0.52	22.6	49.9	27.5	1.9	2.1	1.0
	X_T	X_{Glux}	TT	TG/GT	GG	n_{BT}	n_{BGlux}	R
PBT$_{95}$Glux$_5$	0.95	0.05	89.5	10.5	0.0	18.0	1.0	1.1
PBT$_{90}$Glux$_{10}$	0.90	0.10	79.6	20.4	0.0	8.8	1.0	1.1
PBT$_{84}$Glux$_{16}$	0.84	0.16	70.0	27.4	2.6	6.1	1.2	1.0
PBT$_{80}$Glux$_{20}$	0.80	0.20	63.1	32.8	4.1	4.9	1.2	1.0
PBT$_{67}$Glux$_{33}$	0.67	0.33	45.2	45.6	9.2	3.0	1.4	1.0
PBT$_{55}$Glux$_{45}$	0.55	0.45	28.3	50.0	21.7	2.1	1.9	1.0

[a]Calculated from the ^{1}H NMR spectra.

[b]Experimental values were obtained by means of the equations mentioned in the text and using the ^{13}C NMR data.

7.3.3. Thermal properties

First the thermal stability of PB$_x$Glux$_y$T and PBT$_x$Glux$_y$ copolyesters was comparatively studied by thermogravimetry under inert atmosphere. The TGA traces for the two series, as well as some illustrative derivative curves are depicted in Figure 3, and the parameters measured in these essays are listed in Table 3. As it is known, PBT is fairly heating resistant polyester that does not start to lose weight significantly until well above 350 ºC, to further decompose along a single stage that reaches its maximum rate about 400 ºC. As expected the thermal stability of the PBT-Glux copolyesters is dependent on their content in glucitylene or glucarate units but the influence of composition is different in each case. In the PB$_x$Glux$_y$T series, the thermal stability was found to increase steadily with the replacement of butylene units so that the T_d displayed by the homopolyester PGluxT is 420 ºC. On the other hand, PBT$_x$Glux$_y$ copolyesters showed a more complex behavior in their response to heating. In contrast with PB$_x$Glux$_y$T, the replacement of the terephthalate units by the glucarate units caused an unevenly decreasing effect in both

Table 3. Thermal properties of $\mathrm{PB_xGlux_yT}$ and $\mathrm{PBT_xGlux_y}$copolyesters.

Polyester	TGA			DSC								
					First Heating[e]		Cooling[e]		Second Heating[e]			
	T_d[a] (°C)	T_ds[b] (°C)	RW[c] (%)	T_g[d] (°C)	T_m (°C)	ΔH_m ($\mathrm{J \cdot g^{-1}}$)	T_c (°C)	ΔH_c ($\mathrm{J \cdot g^{-1}}$)	T_cc (°C)	ΔH_{cc} ($\mathrm{J \cdot g^{-1}}$)	T_m (°C)	ΔH_m ($\mathrm{J \cdot g^{-1}}$)
PBT	378	404	1	30	219	49	196	45	-	-	221	45
$\mathrm{PB_{97}Glux_3T}$	379	407	2	38	212	47	188	44	-	-	216	44
$\mathrm{PB_{96}Glux_6T}$	379	406	1	40	209	47	184	41	-	-	212	41
$\mathrm{PB_{89}Glux_{11}T}$	380	409	5	45	199	42	172	36	-	-	201	36
$\mathrm{PB_{80}Glux_{20}T}$	379	408	7	70	184	26	132	26	114	4	186	22
$\mathrm{PB_{69}Glux_{31}T}$	378	407	9	86	165	15	-	-	-	-	-	-
$\mathrm{PB_{59}Glux_{41}T}$	381	415	9	103	-	-	-	-	-	-	-	-
$\mathrm{PB_{48}Glux_{52}T}$	382	414	10	115	-	-	-	-	-	-	-	-
PGluxT	377	420	15	154	-	-	-	-	-	-	-	-
$\mathrm{PBT_{95}Glux_5}$	375	407	4	37	214	49	188	46	-	-	215	48
$\mathrm{PBT_{90}Glux_{10}}$	355	349/**401**	7	44	199	44	173	38	-	-	202	38
$\mathrm{PBT_{84}Glux_{16}}$	343	345/**401**	6	46	186	38	157	34	-	-	192	35
$\mathrm{PBT_{80}Glux_{20}}$	352	359/**406**	5	52	184	25	137	30	-	-	181	21
$\mathrm{PBT_{67}Glux_{33}}$	348	359/**405**	9	66	92/148	14/31	69	3	-	-	-	-
$\mathrm{PBT_{55}Glux_{45}}$	324	**337**/400	14	76	-	-	-	-	-	-	-	-
PBGlux	274	345	11	89	-	-	-	-	-	-	-	-

TGA: [a]Temperature at which a 10 % weight loss was observed in the traces recorded at 10 °C $\mathrm{min^{-1}}$; [b]Temperature of maximum degradation rate; [c]Remaining weight at 600ºC.

DSC: [d]The glass-transition temperature was taken as the inflection point of the heating traces of melt-quenched samples recorded at 20 °C $\mathrm{min^{-1}}$; [e]The melting (T_m), crystallization (T_c) and cold crystallization (T_cc) temperatures and their respective enthalpies (ΔH_m, ΔH_c) measured at heating/cooling rates of 10 °C $\mathrm{min^{-1}}$.

onset and maximum decomposition rate temperatures. Furthermore, decomposition was found to proceed along two well differentiated stages with decomposition rates taking place at the proximities of 350 and 400 ºC, respectively, the first one appearing as a shoulder of the second peak with an intensity evenly increasing with the content in Glux units. According to this behavior and to data recorded for the parent homopolyesters, it can be assumed that the two observed weight loss steps correspond to the decomposition of glucarate and terephthalate short sequences, respectively. Since the glucarate structure is more sensitive to heat than the terephthalate one, its presence in PBT_xGlux_y must be therefore the responsible for the lower thermal stability showed by these polyesters respect to both PBT and PB_xGlux_yT.

The TGA observations described above slightly differ from those previously reported for the PET-Glux copolyester family.[26] In that case a decrease in thermal stability was found to take place in both series upon the incorporation of Glux units although the effect was more pronounced and the decomposition process more complex in the PET_xGlux_y series. The very high T_d of PET, which is about 40 ºC higher than in PBT, may be the reason for not observing in PE_xGlux_yT the enhancing effect exerted by the Glux-diol units on PBT.

Thermal transitions taking place in these copolyesters were examined by DSC. Melting and crystallization temperatures were measured at heating from samples, either coming from synthesis or slowly crystallized from the melt. Glass transition temperatures were measured at heating from samples quenched from the melt.The first heating DSC traces recorded from pristine samples are shown in Figure 4 whereas all the other recorded traces are available in the ESI document (SI-Fig.7). Data afforded by these measurements are comparatively listed in Table 3. Copolyesters containing up to ~30 % of Glux units exhibited endothermic peaks characteristic of melting indicating not only that crystallinity of PBT is preserved after copolymerization but that they also retain the tendency of the homopolyester to crystallize from the melt. Nevertheless, both T_m and ΔH_m decreased significantly upon the insertion of either glucitylene or glucarate units. The T_m plots are compared in Figure 5a for the two series revealing an almost linear decreasing of the melting temperature with composition with a slope between 1.5 and 2. When the content of Glux units in the copolyesters was beyond 30%, no sign of melting or crystallization was detected on the heating-cooling traces. The same happens for the PBGlux and PGluxT homopolyesyters.

This behavior contrasts with that reported for the PBT copolyesters prepared from bicyclic diacetalized mannitol,[24] galactitol[23] and galactaric acid,[23] which exhibited appreciable crystallinity for much higher replacement degrees and even for their corresponding homopolyesters. Such differences most probably arise from the symmetric nature of the compounds with *manno* and *galacto* configuration compared to those with asymmetric *gluco* configuration. On the other hand, the depressing effect on crystallinity exerted by the incorporation of Glux units in PBT is less pronounced than in PET.[26]

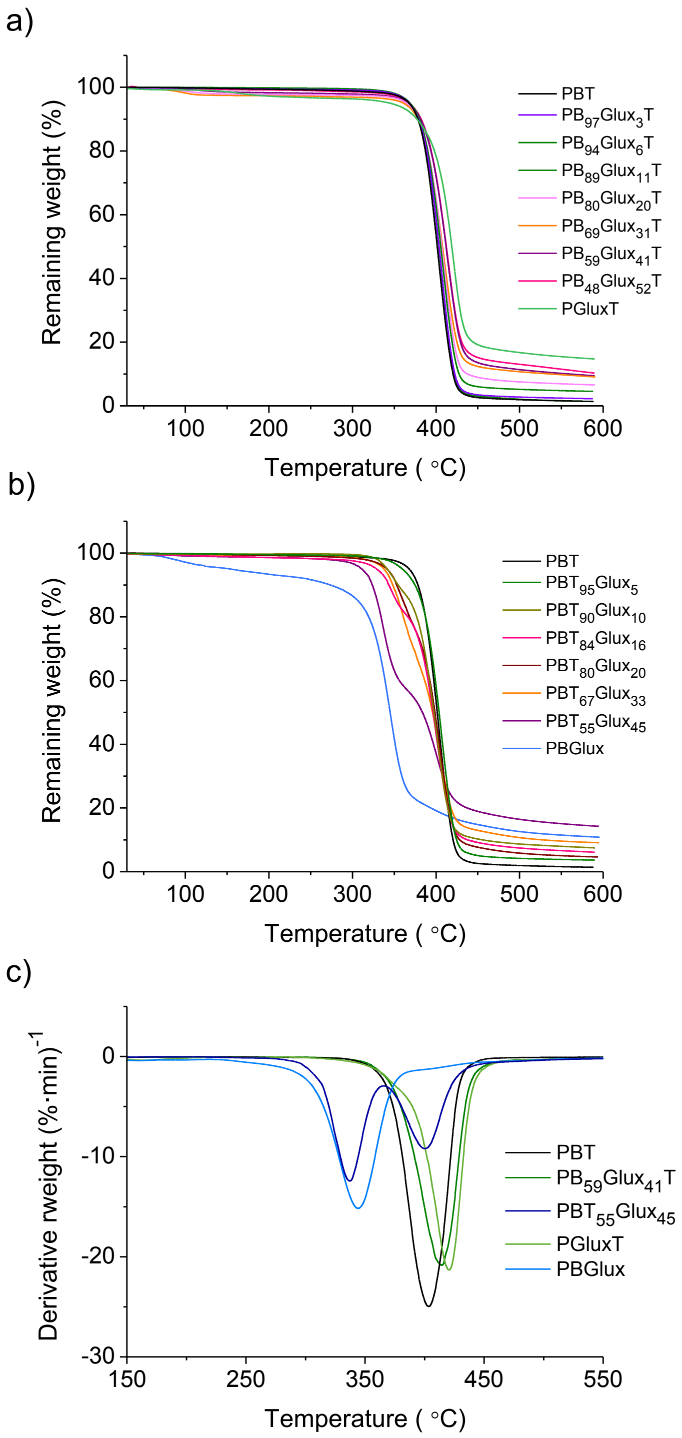


Figure 3. TGA traces of PB$_x$Glux$_y$T (a) and PBT$_x$Glux$_y$ (b) and compared derivative curves for a selection of cases (c).

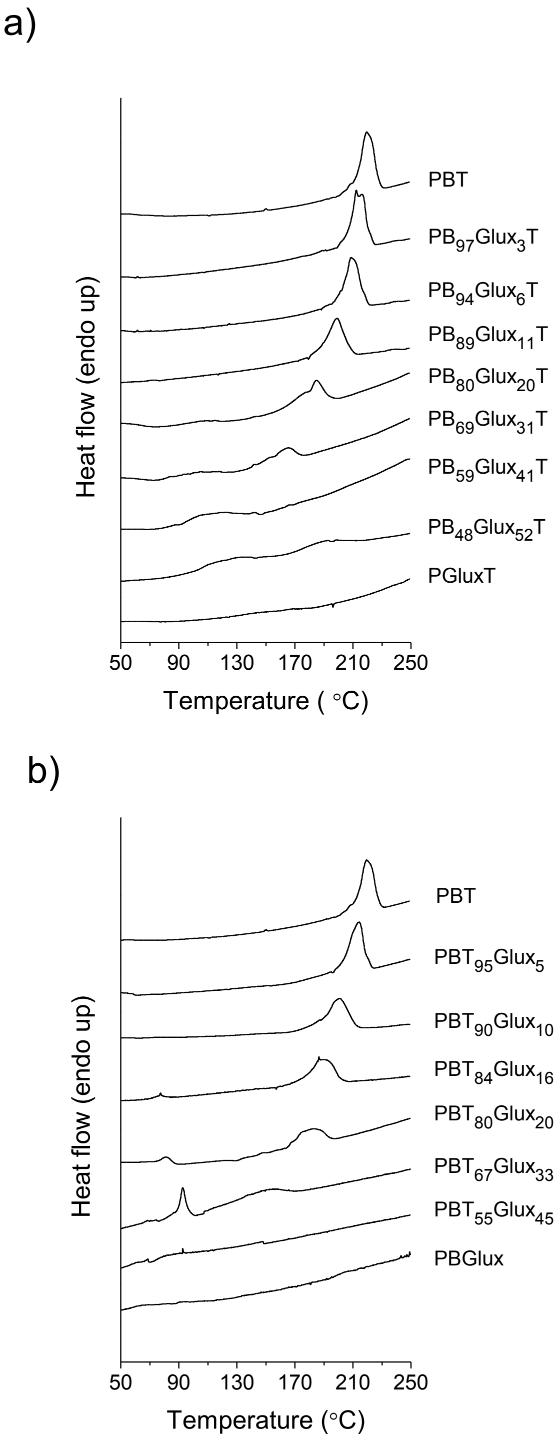


Figure. 4. DSC heating traces of PB_xGlux_yT (a) and PBT_xGlux_y(b)

In fact, both PE_xGlux_yT and PET_xGlux_y copolyesters were unable to display crystallinity for Glux contents above 11-13%. Such difference is not more than that the consequence of the lower ability of PET to crystallize compared to PBT because its more restricted chain mobility.

The incorporation of Glux in the chain of PBT, either as glucitylene or as glucarate moieties, enhanced significantly the glass-transition temperature. The variation of T_g for both series of copolyesters as a function of composition is plotted in Figure 5b. In both cases, the T_g steadily increased with the degree of replacement with a trend that nearly follows a straight line. The apparent deviations from the linear trend observed for PGluxT and PBGlux homopolyesters should be interpreted as being due, at least in part, to the much lower molecular weight attained for the homopolyesters. In the case of the PB_xGlux_yT series, the line slope is about 1.7 ºC per %-Glux point, which is slightly greater than that observed for terephthalate copolyesters containing diacetalized units derived from mannitol, and very close to that of copoly(isosorbide terephthalate)s. The high stiffness of the acetalized fused 1,3-dioxane bicyclic structure derived from D-glucitol will be the reason for the remarkable behavior found for PB_xGlux_yT. In the PBT_xGlux_y series, the incorporation of Glux units also enhanced T_g although in this case the increasing ratio was only about 1 ºC per %-Glux point. Nevertheless this result is not less exciting since the replacement of the terephthalate unit in aromatic polyesters usually leads to a decrease in T_g. As it can be seen in Table 3, the T_g of the PBGlux homopolyester is close to 90 ºC, which is about 60 ºC higher than that of PBT. This strongly contrasts with the decrease in T_g of near 20 ºC that is observed for the homopolyester PBGalx made from bicyclic diacetalized dimethyl galactarate.[23]

The homopolyesters made from 1,4-butanediol and 2,5-furandicarboxylic acid show T_g between 30 and 40 ºC depending on molecular weight.[14] Lastly, it is worth comparing the influence of Glux units on the T_g of PET with PBT. In the case pf PET incorporation of Glux also increases the T_g value but with lower intensity, the difference being less noticeable when the diol unit is the replacing one. This is expected since the replacement of the ethylene unit by Glux entails lesser relative increase in chain stiffness than when the butylene unit is replaced. Such differences vanish when the terephthalate unit is the replaced one; in this case the increase in chain stiffness resulting from the replacement must be expected to be very similar in both the PET_xGlux_y and PBT_xGlux_y series.

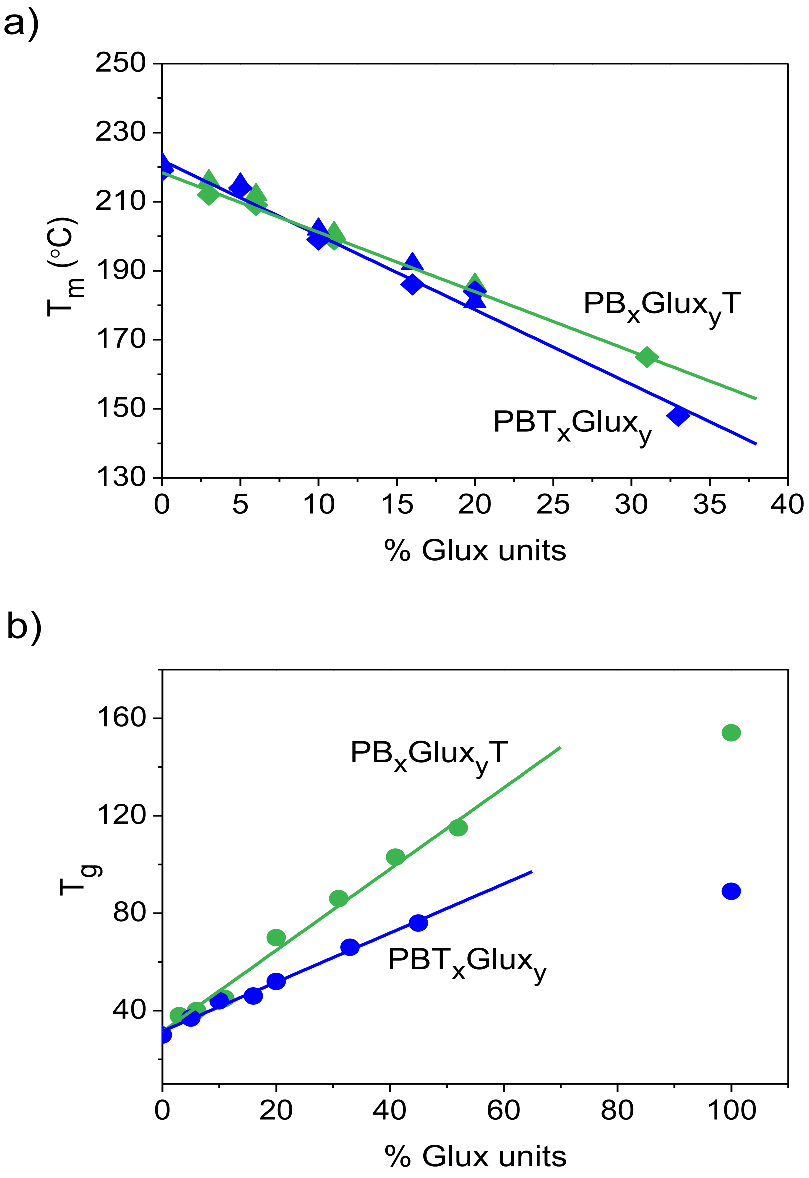


Figure 5. T_m (a) and T_g (b) values of PB_xGlux_yT and PBT_xGlux_y copolyesters as a function of the content in Glux units.

7.3.4. Isothermal crystallization

The exceptional high crystallization rate displayed by PBT upon cooling from the melt stands out as one of the most appreciate properties of this thermoplastic polyester as far as its use in injection molding is concerned. It is interesting therefore to appraise the effect of the presence of Glux units on the crystallizability of PBT. Comparing the isothermal crystallization kinetics of polyesters and copolyesters with different compositions under the same crystallization conditions is a very convenient and reliable method to evaluate the crystallizability. PB_xGlux_yT and PBT_xGlux_y with contents in Glux units below 20 % and 30%, respectively are able to crystallize upon cooling from the melt and they are suitable therefore for realizing this study. Unfortunately, not always is possible to fix a crystallization temperature common to copolyesters with different compositions because large differences in crystallization exist between them. Nevertheless, valuable conclusions can be drawn by indirect comparison of kinetics data provided that experiments are carried out within a narrow interval of temperatures.

In this study isothermal crystallizations of three PB_xGlux_yT (y = 3, 6 and 11) and two PBT_xGlux_y (y = 5 and 10) copolyesters, in addition to the PBT homopolyester, were comparatively studied in the 180-210 ºC interval. The evolution of the relative crystallinity, X_t, with crystallization time is depicted in Figure 6. The corresponding Avrami double logarithmic plots showing a linear correlation along the time intervals used for data analysis can be seen in the ESI document (SI-Fig. 8). From a glance of the X_t *vs t* plots it becomes clear that the insertion of Glux units in PBT causes a significant delay in its crystallization rate in both copolyesters series. The crystallization conditions used for each compound and the kinetics parameters resulting from the Avrami analysis of the experimental data are compared in Table 4. Conclusions drawn from a comparative inspection of the tabulated data are the following: a) The crystallization rate of each compound decreases with increasing temperature indicating that the process is controlled by nucleation. b) The depressing effect of copolymerization on crystallizability appears to be much more pronounced in the PB_xGlux_yT series. c) The axialite growing mechanism prevailing at low temperatures (*n* values close to 2) evolves towards spherulite formation at increasing crystallization temperatures (*n* values higher than 2.5 and even close to 3 in some cases).

The above results clearly show that the insertion of Glux in the PBT chain depresses the crystallizability of the polyester. Obviously, the distortion caused in the chain contour by the presence of the bulky bis(1,3-dioxane) structure in addition to the lack of stereoregularity inherent to the non-symmetric *gluco* configuration are responsible for the decrease observed in both crystallization rate and crystallinity of PBT copolyesters. The fact that this effect appears more pronounced in the case of the PB_xGlux_yT copolyesters is in full agreement with the greater increase observed in the T_g of this series. It should be therefore attributed to the relatively larger reduction in chain mobility that is produced when the flexible butylene units instead of the rigid terephthalate units are replaced by the bicyclic sugar units.

Comparison of these results with those reported for the isothermal crystallization of PET-Gluxcopolyesters is only feasible for the series made from Glux-diester since PE_xGlux_yT copolyesters were unable to crystallize from the melt whatever were their compositions.[26] Even in such case, comparison is not rigorous since crystallization temperatures were not the same for the two series. The only reliable conclusion that can be drawn therefore is that incorporation of Glux units in both PET and PBT chains slowed down the crystallization rate of the copolyesters, and that such effect is higher when the diol unit is the replaced unit.

Table 4. Isothermal crystallization data of PBT hompolyester and $PB_xGlux_yT$and PBT_xGlux_y copolyesters.

Polyester	T_c (ºC)[a]	ΔT (ºC)[b]	t_0 (min)[c]	$t_{1/2}$ (min)[d]	n[e]	-Lnk[e]
PBT	200	19	0.18	0.69	2.14	-0.99
	205	14	0.50	1.83	2.40	1.12
	210	9	1.59	11.51	3.03	7.37
$PB_{97}Glux_3T$	195	17	0.21	1.27	2.04	0.61
	200	12	0.67	4.22	2.53	3.59
	205	7	4.12	21.34	2.37	7.10
$PB_{94}Glux_6T$	190	19	0.21	0.98	1.99	-0.07
	195	14	0.54	2.95	2.44	2.50
	200	9	2.29	11.35	2.47	5.83
	205	4	6.45	54.49	2.55	10.10
$PB_{89}Glux_{11}T$	180	19	0.24	1.50	2.35	-0.90
	185	14	0.49	3.64	2.54	3.29
	190	9	1.73	9.62	2.89	6.30
$PBT_{95}Glux_5$	185	29	0.06	0.22	2.24	-3.63
	190	24	0.16	0.68	2.15	-0.98
$PBT_{90}Glux_{10}$	185	14	0.56	3.16	2.48	2.72
	190	9	1.60	7.71	2.57	5.00

[a] Crystallization temperature. [b] $\Delta T = T_m - T_c$. [c] Onset crystallization time.
[d] Crystallization half-time. [e] Avrami exponent (n) and kinetics rate constant (k).

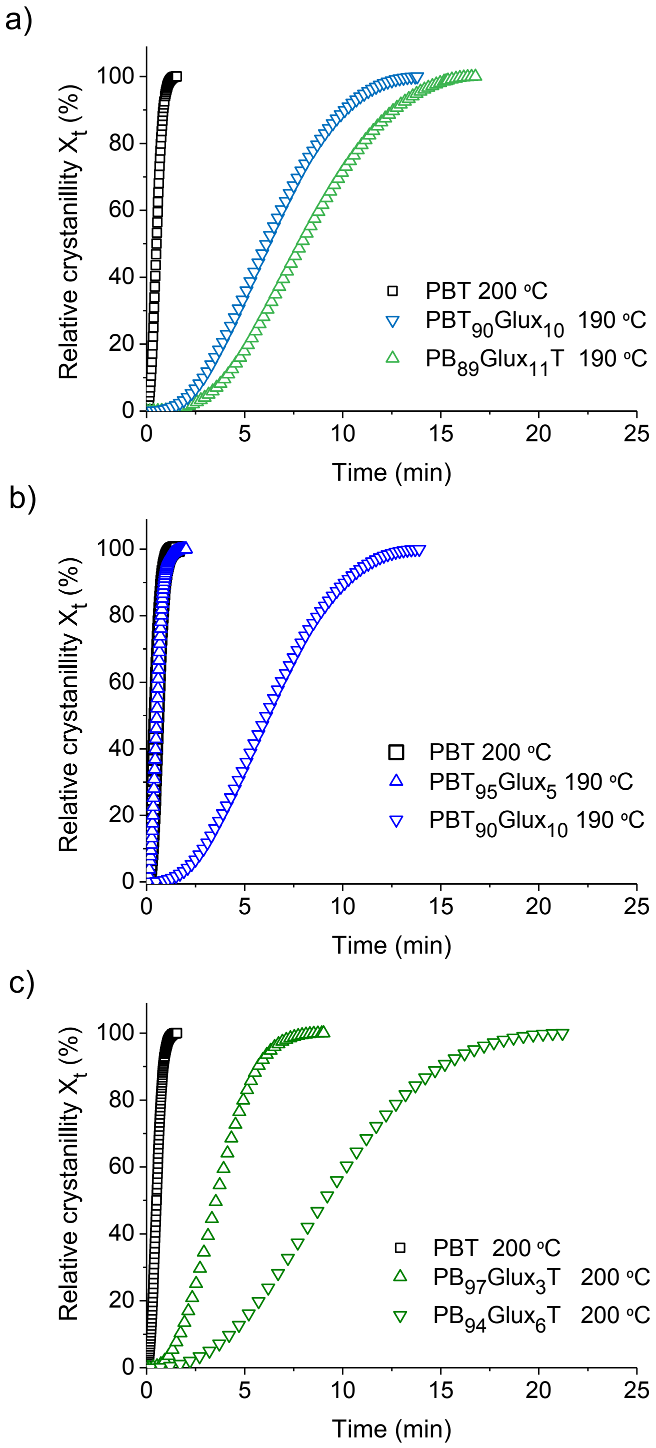


Figure 6. Isothermal crystallization of PB_xGlux_yT and PBT_xGlux_y copolyesters, and PBT homopolyester at the indicated temperatures. Relative crystallinity *vs*. time plot (a,b,c).

7.3.5. X-ray diffraction and stress-strain behaviour

Pristine samples of PB_xGlux_yT and PBT_xGlux_y copolyesters coming directly from synthesis produced poorly resolved scattering profiles (diffractograms available in ESI, Fig.9), which however were indicative of crystallinity for contents in Glux below 30% in agreement with the results obtained by DSC. Nevertheless after heating the samples at temperatures of about 20 ºC below melting for a few hours, well resolved diffraction patterns were obtained. The WAXS profiles registered from a selection of semicrystalline PBT-Glux copolyesters are compared to that of PBT in Figure 7. Apparently all the profiles including that of PBT are coincident in both peak positions and relative intensities which is demonstrative that the same crystal structure, which should be the triclinic crystal form known for PBT,[27] is adopted in all cases. A comparative table with a detailed account of the Bragg spacings measured on these patterns is provided in the ESI document (SI-Table 1). The ability of copolyesters with low contents in Glux units to crystallize in the same lattice of PBT can be understood by assuming that the bulky Glux units randomly distributed along the polymer chain are rejected from the crystal so that it becomes exclusively made up of PBT segments. For high contents in Glux, the homogeneous butylene terephthalate sequences do not reach the minimum length required to produce a stable crystallite and crystallization cannot occur. Such a crystallization behavior has been previously reported for other related sugar-based PBT and PET copolyesters, in particular for the PET copolyesters containing Glux units,[26] and interpreted in the same way.

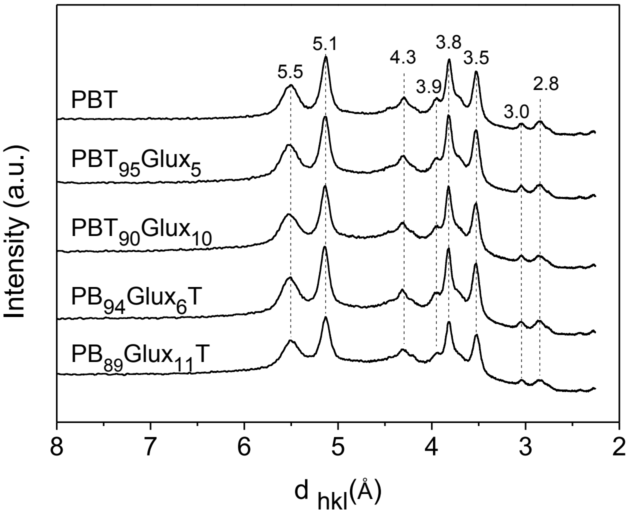


Figure7. a) Powder WAXS profiles of PB_xGlux_yT and PBT_xGlux_y copolyesters, and PBT recorded from samples previously subjected to heat treatment (see text).

The mechanical properties of PBT changed according to the type of copolyester and content of Glux. In general the presence of low amounts of Glux in PBT increased the brittleness of PBT. On the contrary, amorphous copolyesters with high contents in Glux were tougher than PBT and showed a stress-strain behavior different for the two series. The stress-strain curves obtained in tensile essays from copolyesters containing ~30% and ~ 40% of Glux for each series are depicted in Figure 8, and the mechanical parameter measured in these essays are afforded in the ESI document (SI-Table 2). In all cases the stress-strain behavior of PBT changed from brittle to ductile although the elongation to break was noticeably larger for the copolyesters containing glucarate units. The effect of copolymerization on the tensile behavior at low deformations appeared to be opposite for the two series with the elastic modulus and the maximum strength increasing in PB_xGlux_yT but decreasing in PBT_xGlux_ycopolyesters. The same behavior has been reported for Glux-containing PET copolyesters.[26]

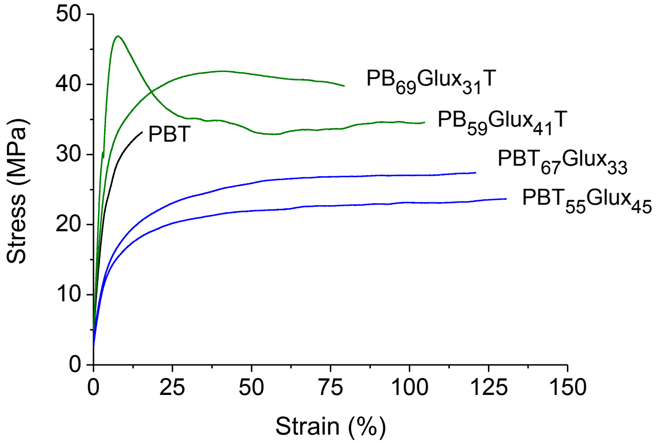


Figure 8. Stress-strain curves of PBT-Glux copolyesters and PBT.

7.3.6. Hydrolytic and enzymatic degradability

As it is common to aromatic polyesters, PBT is extremely reluctant to hydrolytic degradation even in the presence of enzymes. A higher sensitivity to hydrolysis would be desired for this polyester to minimize its environmental impact and also to expand its use in temporal applications. It is known for long time that the incorporation of sugar-based units in aromatic polyesters enhances their susceptibility to degradation by water and also makes them slightly vulnerable to certain hydrolases. It will be worthwhile therefore to include in this work a preliminary evaluation of the effects that the Glux units may exert on the hydrodegradability and biodegradability of PBT, as well as to assess if there are differences between PB_xGlux_yT, PBT_xGlux_y according to what is observed with other properties.

Hydrolytic degradation

For an estimation of the hydrodegradability of Glux-containing $PB_{59}Glux_{41}T$, $PBT_{55}Glux_{45}$ copolyesters as well as the PBT homopolyester were incubated in parallel in aqueous buffer at pH 2 and 80 ºC. The evolution of sample weight and polymer weight-average molecular weight with the incubation time is shown in the plots depicted in Figure 9. These plots reveal the enhancing effect that the presence of Glux has on the hydrolysis of PBT and also the higher sensitivity exhibited by the glucarate copolyesters in this regard. In fact, weight losses about 20% and 60% are observed for $PB_{59}Glux_{41}T$ and $PBT_{55}Glux_{45}$, respectively, after four weeks of incubation, in strong contrast with the inalterability shown by PBT. Also M_w is observed to decay in agreement with weight loss results. Apparent differences in the curve descents observed between the two plots, particularly as PBT is concerned, may be reasonably attributed to the non-complete solubility of the degradation products.

The enhancing effect exerted by the Glux units on the degradability of PBT was also observed on PET.[26] Although a close comparison between the two families is not feasible because the copolyester samples studied in each case have different compositions, some unequivocal conclusions can still be drawn. In both families the presence of Glux units increases the hydrodegradability of the polyester and also renders it susceptible to biodegradation. Also in the two families, the enhancing effect is much stronger when the Glux units replace the terephthalate units in the polyester. This parallelism is quite reasonable since it is the greater hydrolysis rate of the aliphatic ester group compared to the aromatic one, that motivates the greater degradability displayed by the PET_xGlux_y and PBT_xGlux_y series.

The NMR analysis of residual sample and degradation products solubilized in the aqueous incubating solution afforded evidences on the mechanism operating in the hydrolysis of the copolyesters. The ^1H NMR spectra registered from $PB_{59}Glux_{41}T$ and $PBT_{55}Glux_{45}$ after four weeks of incubation at 80 ºC and pH 2 do not show changes in the diacetal structure confirming the exceptional resistance of the bicyclic 1,3-dioxane structure to hydrolysis. On the contrary, they contain signals arising from polyester CH_2-OH end groups that progressively increase with time which is a verification of the splitting of the ester group. Moreover the spectra recorded from residual $PB_{59}Glux_{41}T$ did not exhibit appreciable changes in the comonomer composition whereas those taken from the $PBT_{55}Glux_{45}$ showed a continuous decrease in the glucarate unit content. Such contrasting behavior displayed by the two copolyesters is clearly reflected in Figure 9c where it is seen how the amount of glucitylene units in $PB_{59}Glux_{41}T$ remains almost constant along the incubation period whereas only 18 % of the initial glucarate units remained in the $PBT_{55}Glux_{45}$ residue. On the other hand, the ^1H NMR spectra registered from the aqueous solution used for PBT and $PB_{59}Glux_{41}T$ incubation did not show significant presence of degradation products whereas those obtained for $PBT_{55}Glux_{45}$ showed unequivocal signals

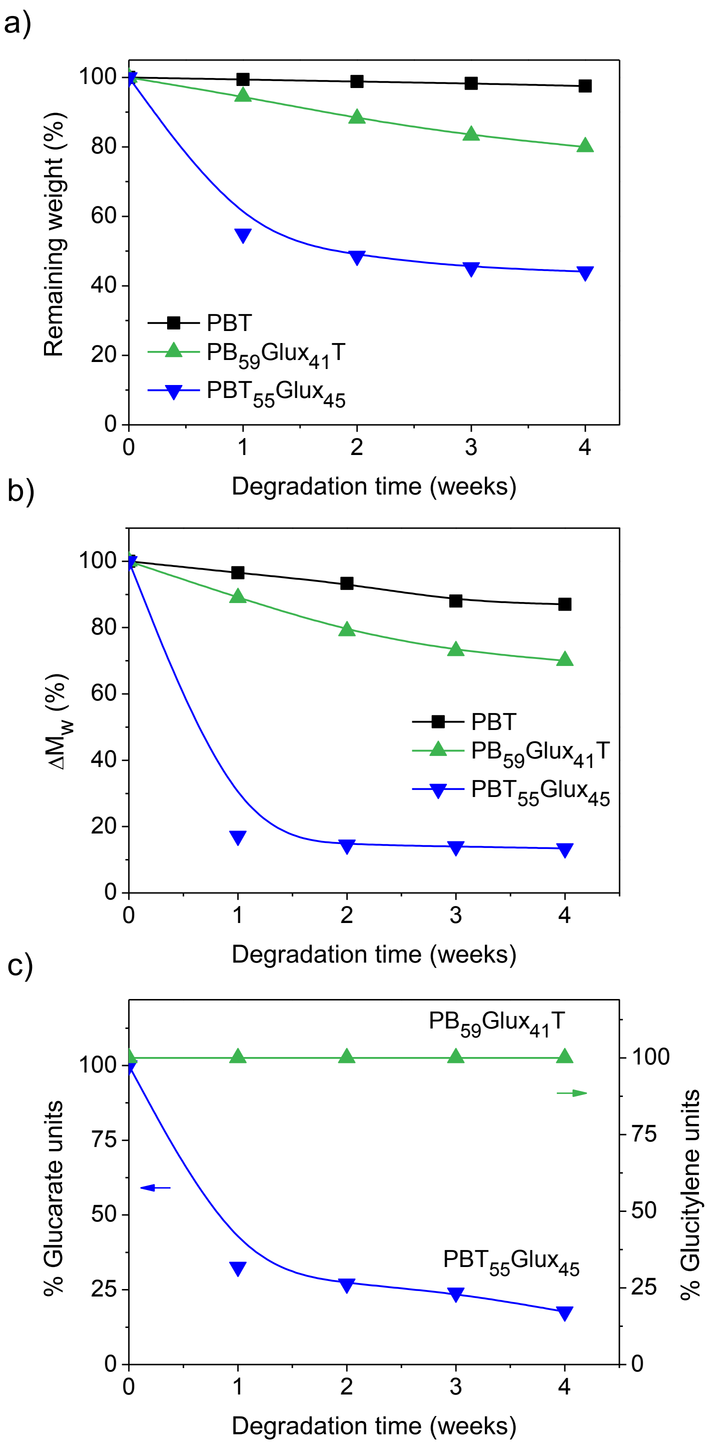


Figure 9. Degradation of $PB_{59}Glux_{41}T$, $PBT_{55}Glux_{45}$ and PBT at 80ºC, pH2. Remaining weight (a) molecular weight (b) *vs*. degradation time. c) Variation in the contents of glucitylene units and glucarate units in $PB_{59}Glux_{41}T$ and $PBT_{55}Glux_{45}$ respectively, with degradation time.

corresponding to the release of both 2,4:3,5-di-*O*-methylene-D-glucaric acid and 1,4-butanediol. All the NMR spectra used in this analysis have been included in the ESI document for examination (SI-Figs.10 and 11).

Enzymatic degradation

To evaluate the biodegradability of the Glux-containing PBT copolyesters, a degradation study in the presence of lipases was carried out. The changes taking place in sample weight and polymer weight-average molecular weight of PBT, PBT$_{55}$Glux$_{45}$ and PB$_{59}$Glux$_{41}$T incubated in aqueous pH 7.4 buffer at 37 ºC, with and without porcine pancreas lipase, are presented in Fig. 10. A first remarkable observation is that no changes were detected for PBT along the four weeks of incubation corroborating the well-known inertia of this polyester towards degradation by enzymes. The same result was found for the PB$_{59}$Glux$_{41}$T copolyester revealing that the influence of the glucitylene units on the biodegradability of PBT is negligible. On the contrary, an appreciable decay in both sample weight and molecular weight was displayed by the PBT$_{55}$Glux$_{45}$ copolyester with noticeable differences observed according to the essay was carried out in the presence or absence of enzymes. Thus the weight lost without added enzymes was only about 8% whereas it reached near 16% in the presence of lipases. The variations observed in the weight-average molecular weight were consistent with these results.

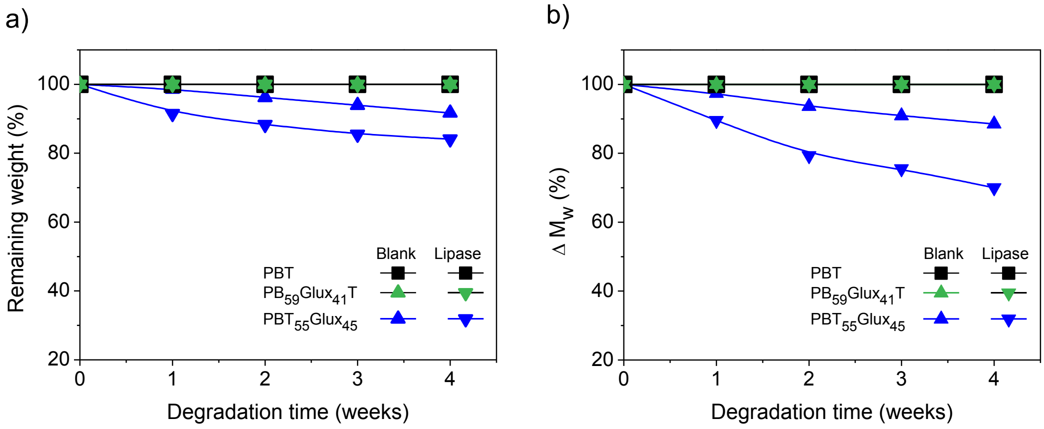


Figure 10. Enzymatic degradation of PB$_{59}$Glux$_{41}$T, PBT$_{55}$Glux$_{45}$ and PBT upon incubation at pH 7.4 at 37 ºC for 4 weeks. Remaining weight (a) molecular weight (b) *vs*. degradation time.

7.4. Conclusions

Two series of bio-based poly(butylene terephthalate) copolyesters, both of them with a random microstructure, have been successfully synthesized by polycondensation in the melt using bicyclic D-glucose-derived comonomers. One set was obtained by replacing 1,4-butanediol by 2,4:3,5-di-*O*-methylene-D-glucitol (Glux-diol) and the other by replacing dimethy terephthalate by dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester).

The incorporation of Glux units in the PBT chain gave rise to remarkable modifications in polymer properties which were depending on the functionality of such units. The presence of glucitylene units led to a significant increase in the thermal stability of PBT in contrast with the decrease produced when the bicyclic structure was inserted as glucarate units. The two copolyester series show crystallinity up to contents in Glux units about 30%, and copolyesters crystallized adopting the triclinic structure of PBT. Melting temperatures and enthalpies as well as crystallization rates decreased in both series with the Glux content but the depressing effect was more pronounced when the Glux-diester was the replacing comonomer.

The changes taking place in glass-transition temperatures are outstanding. The rigid bicyclic structure of Glux motivated a notable increase in the T_g of PBT whichever was the type of unit, diol or diacid, inserted in the copolyester. Increments in T_g of ~1.7 and ~1 ºC per %-Glux point were observed for copolyesters made from Glux-diol and Glux-diester, respectively. What it is really noteworthy is that T_g increased even when the terephthalate unit was the replaced unit; to our best knowledge, such effect has not precedent in aromatic copolyesters containing sugar-based units.

A last remarkable conclusion is that the Glux-containing copolyesters display higher sensitivity to hydrolysis than PBT, in particular those containing glucarate units, which in addition distinguished by their sensitivity to the action of lipases. This is certainly an important result because obtaining biodegradable aromatic polyesters by copolymerization is a strong challenge, particularly if the basic properties of the parents homopolyesters are wished to remain essentially preserved.

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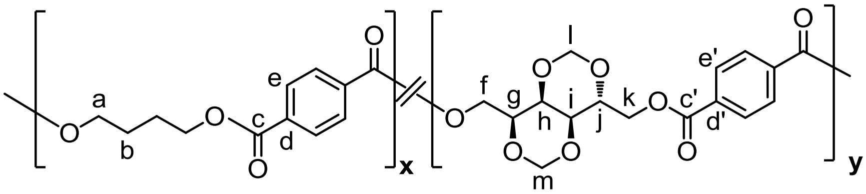
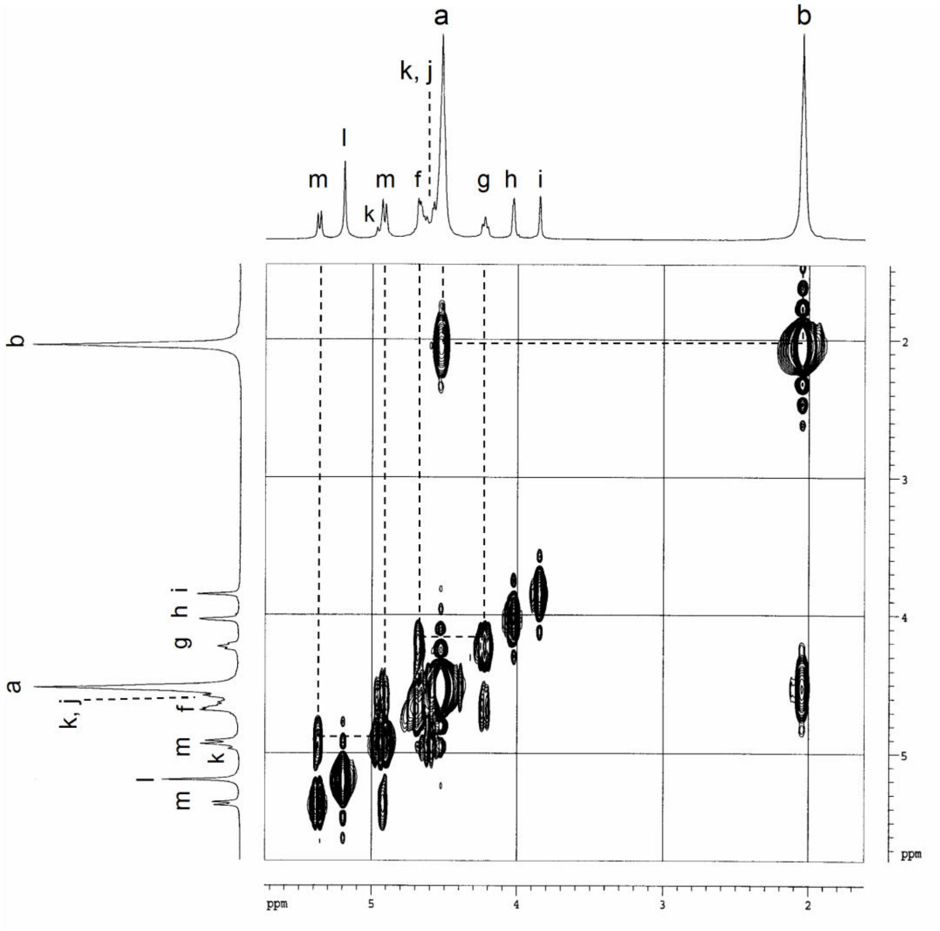
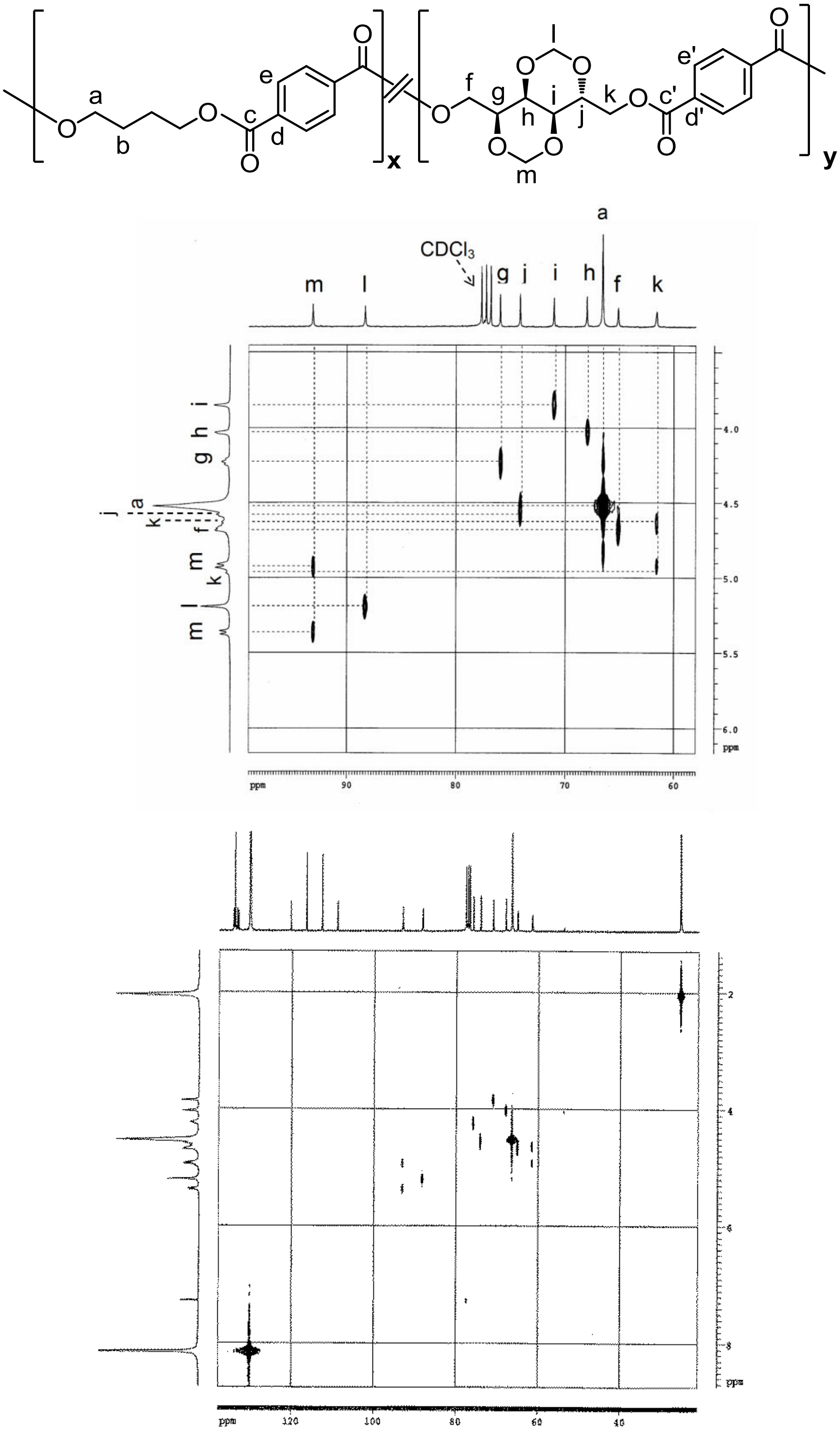
Supporting information

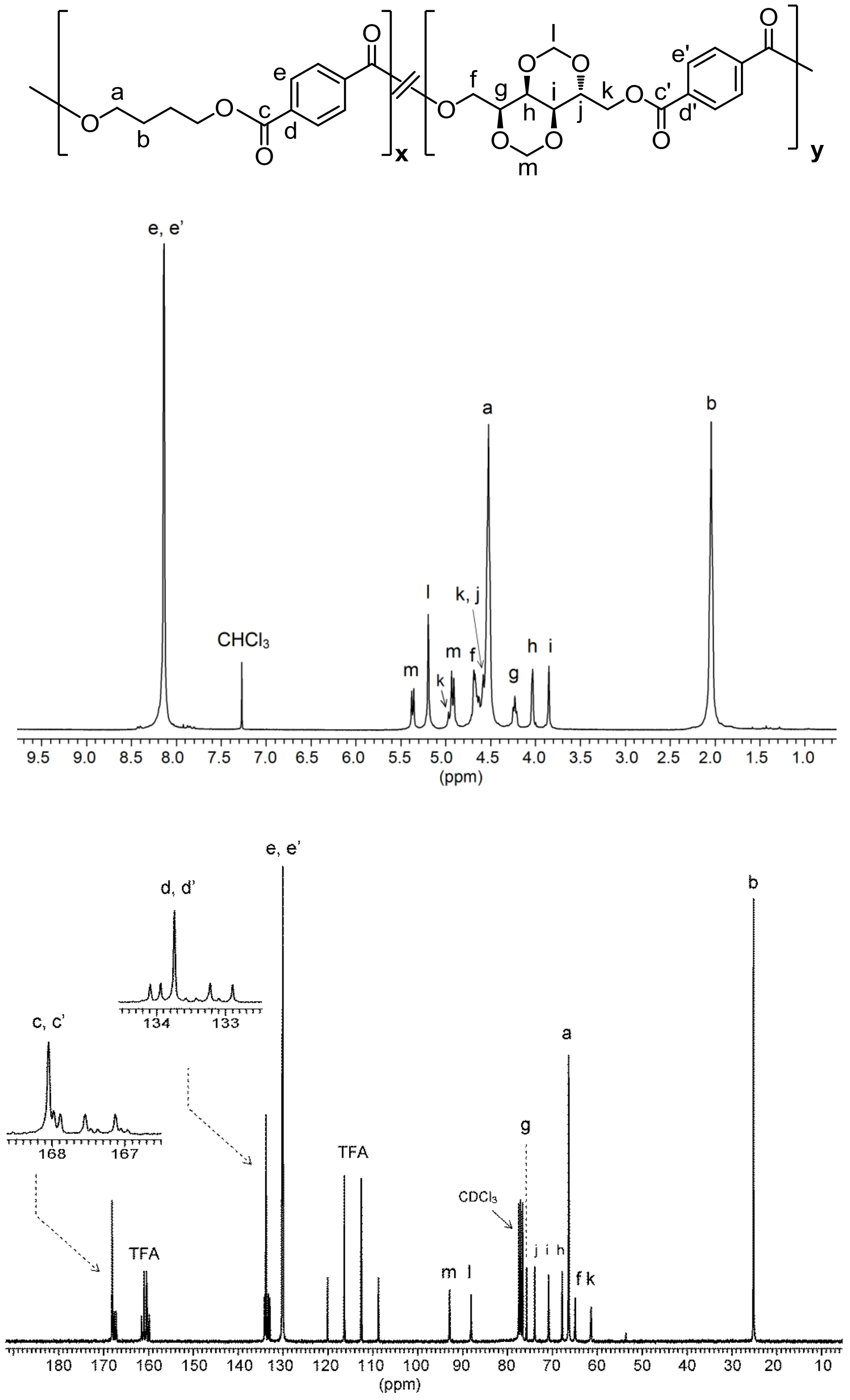




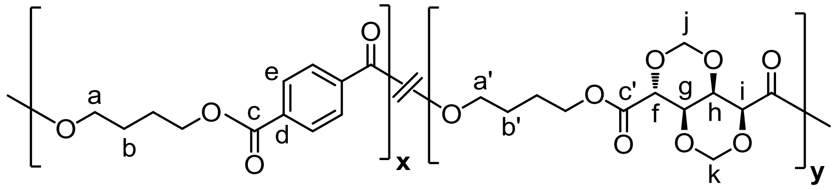
SI-Figure. 1. ^{1}H-^{1}H COSY NMR spectrum of PB$_{69}$Glux$_{31}$T copolyester.

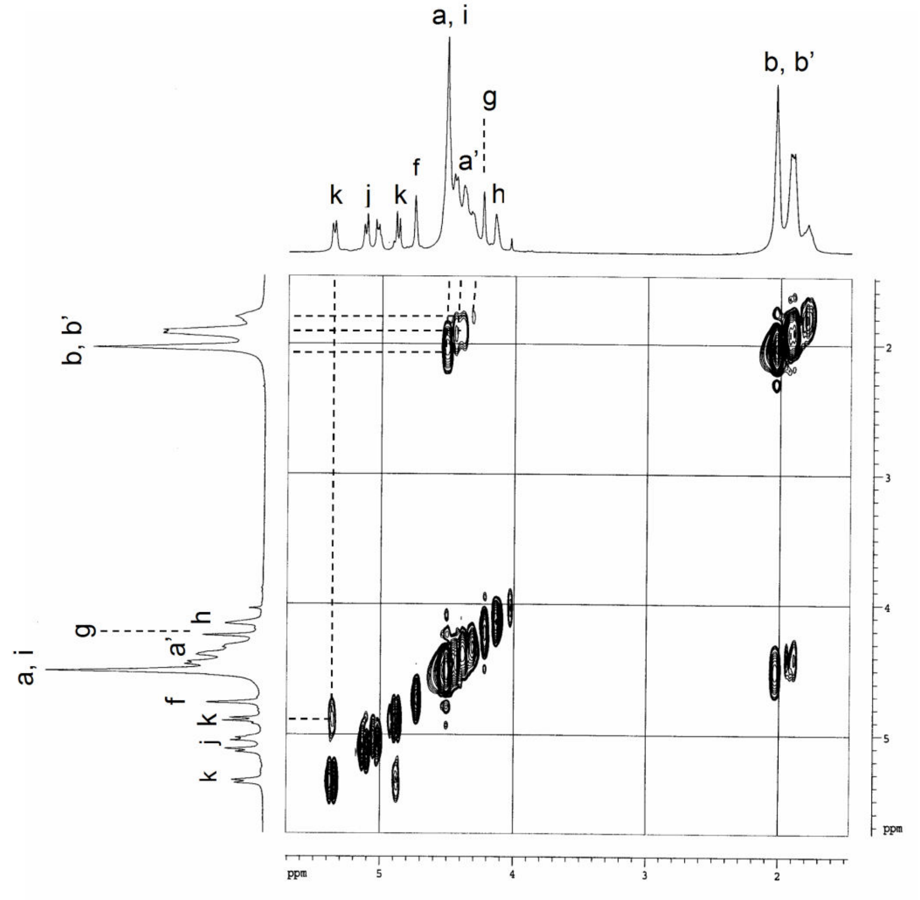


SI-Figure. 2. ^{1}H-^{13}C HETCOR NMR spectrum of PB$_{69}$Glux$_{31}$T copolyester (bottom) and enlarged region (top).

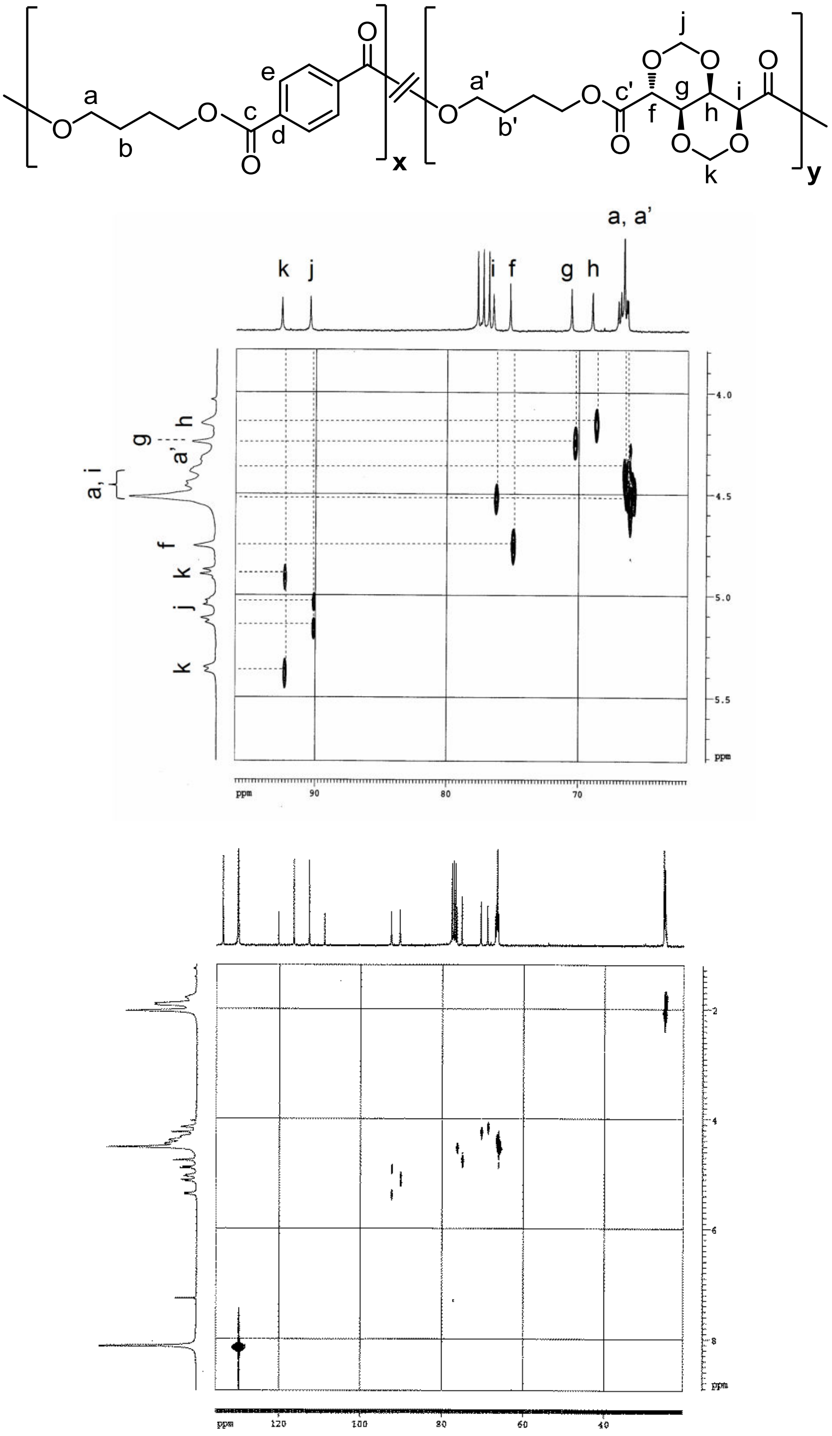


SI-Figure. 3. ^{1}H (top) and ^{13}C (bottom) NMR spectra of PB$_{69}$Glux$_{31}$T copolyester.

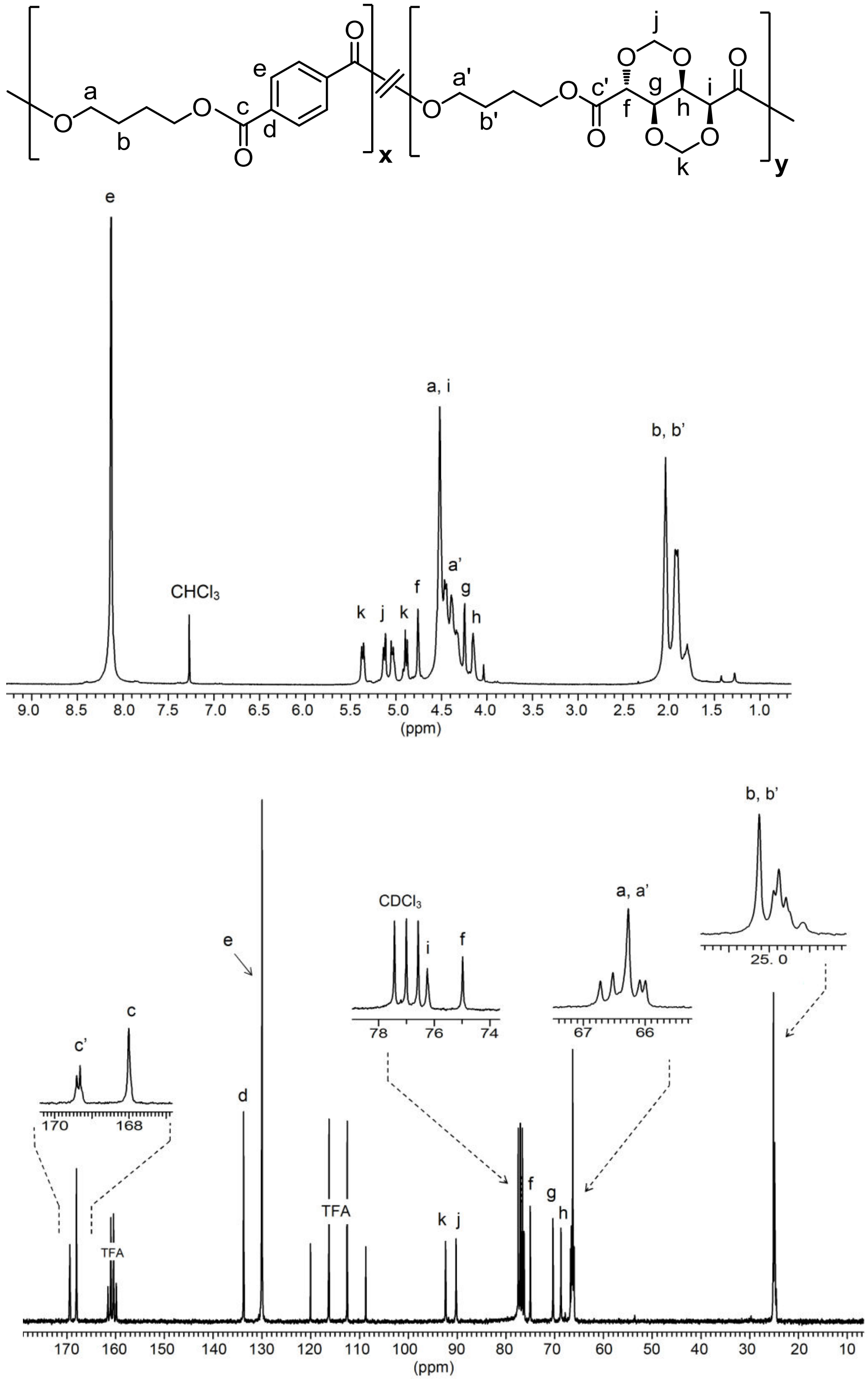




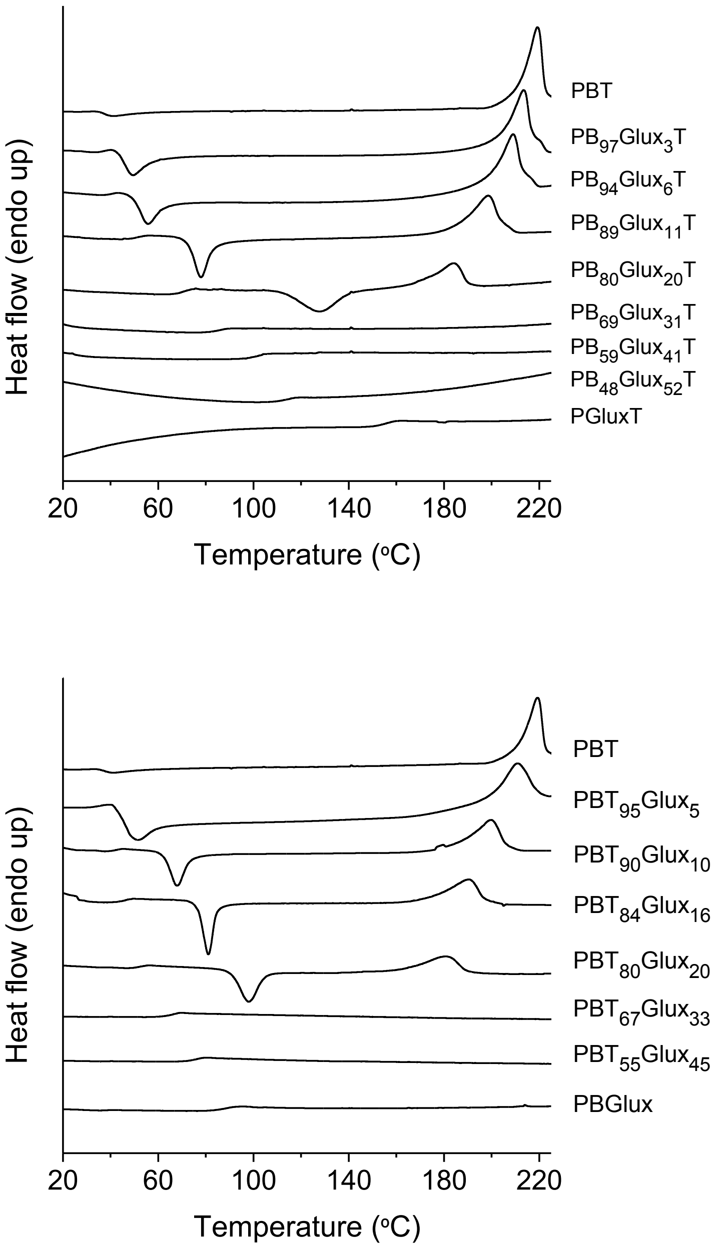
SI-Figure. 4. ^{1}H-^{1}H COSY NMR spectrum of $PBT_{67}Glux_{33}$ copolyester.



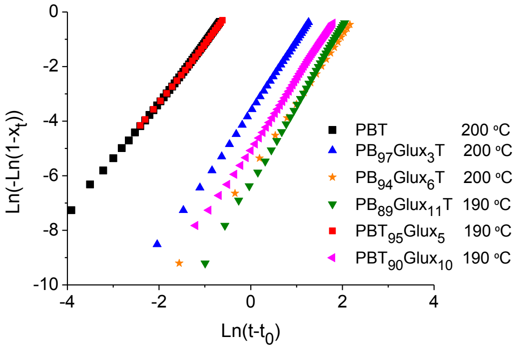
SI-Figure. 5. ^{1}H-^{13}C HETCOR NMR spectrum of PBT$_{67}$Glux$_{33}$ copolyester (top) and amplified region (bottom).



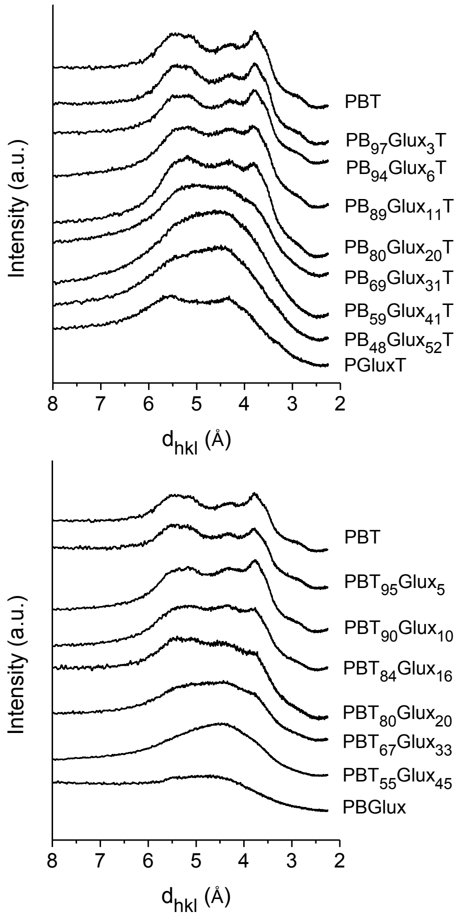
SI-Figure. 6. ^{1}H (top) and ^{13}C (bottom) NMR spectra of PBT$_{67}$Glux$_{33}$ copolyester.



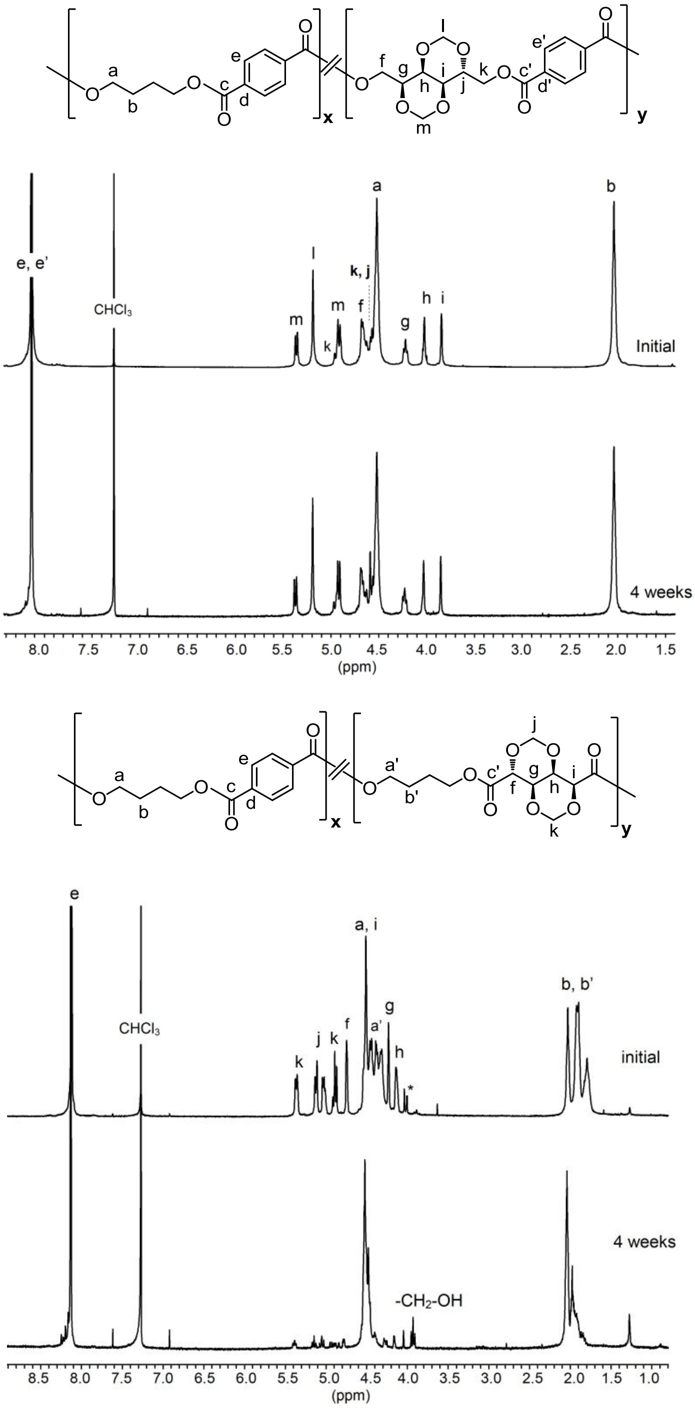
SI-Figure. 7. DSC traces of PB$_x$Glux$_y$T (a) and PBT$_x$Glux$_y$ (b) copolyesters recorded at heating from quenched samples for T_g observation.



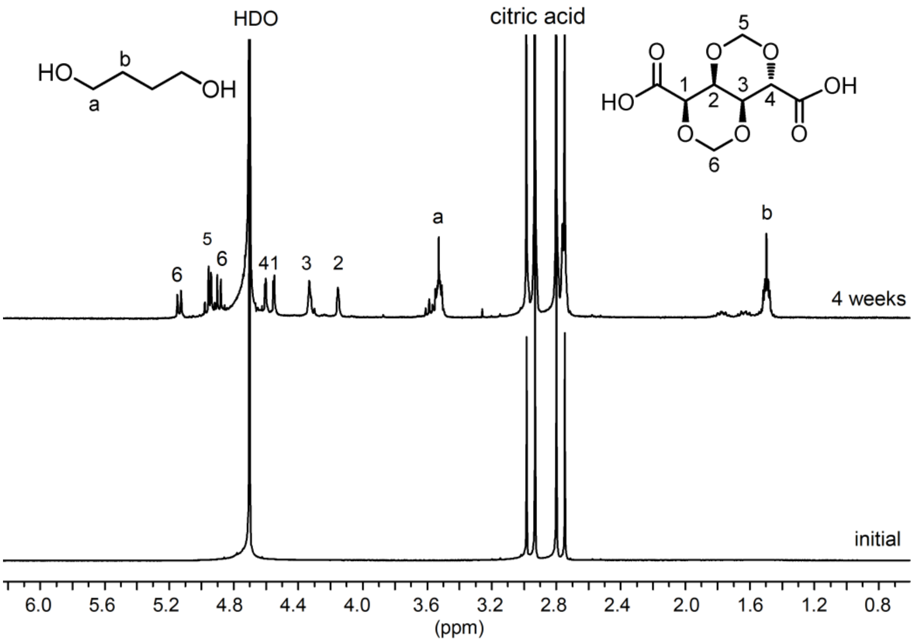
SI-Figure. 8. Double logarithmic plots of the isothermal crystallization of PB$_{97}$Glux$_3$T, PB$_{94}$Glux$_6$T, PB$_{89}$Glux$_{11}$T, PBT$_{95}$Glux$_5$, PBT$_{90}$Glux$_{10}$ copolyesters and PBT homopolyester at the indicated temperatures.



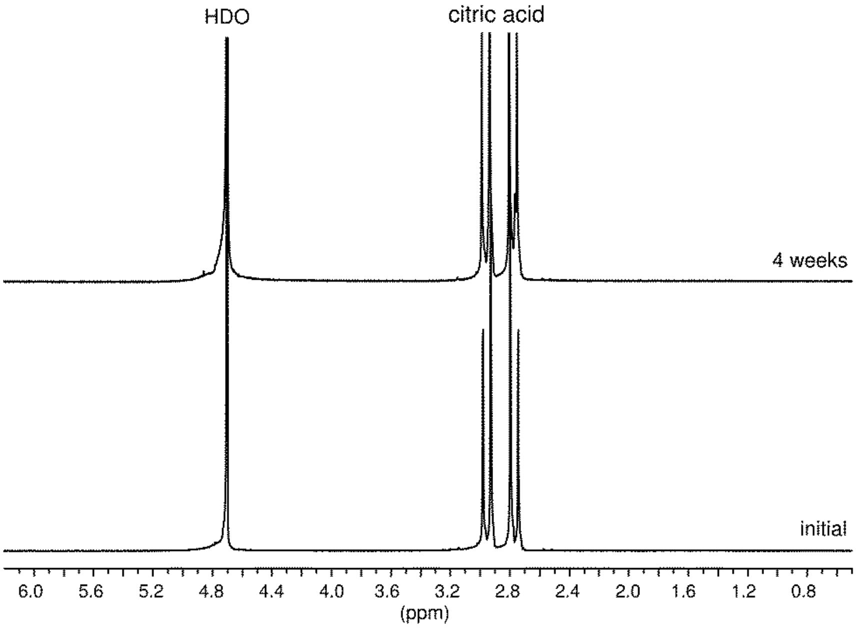
SI-Figure. 9. WAXS profiles of PB$_x$Glux$_y$T (top) PBT$_x$Glux$_y$ (bottom) copolymers and their respective parent homopolyesters recorded from powder samples without any previous thermal treatment.



SI-Figure.10. Compared ^{1}H NMR spectra of PB$_{59}$Glux$_{41}$T (a) and PBT$_{55}$Glux$_{45}$ (b) copolyesters before and after incubation (residue) in water at pH 2.0 at 80 ºC.



SI-Figure.11. ^{1}H NMR spectra in D_2O of the products released to the aqueous medium by PBT$_{55}$Glux$_{45}$ after incubation in water at pH 2.0 at 80 ºC for four weeks.



SI-Figure.12. ^{1}H NMR spectra of the aqueous medium after incubation of PB$_{59}$Glux$_{41}$T in water at pH 2.0 at 80 ºC for four weeks.

SI-Table 1. Powder X-ray diffraction data of polyesters.

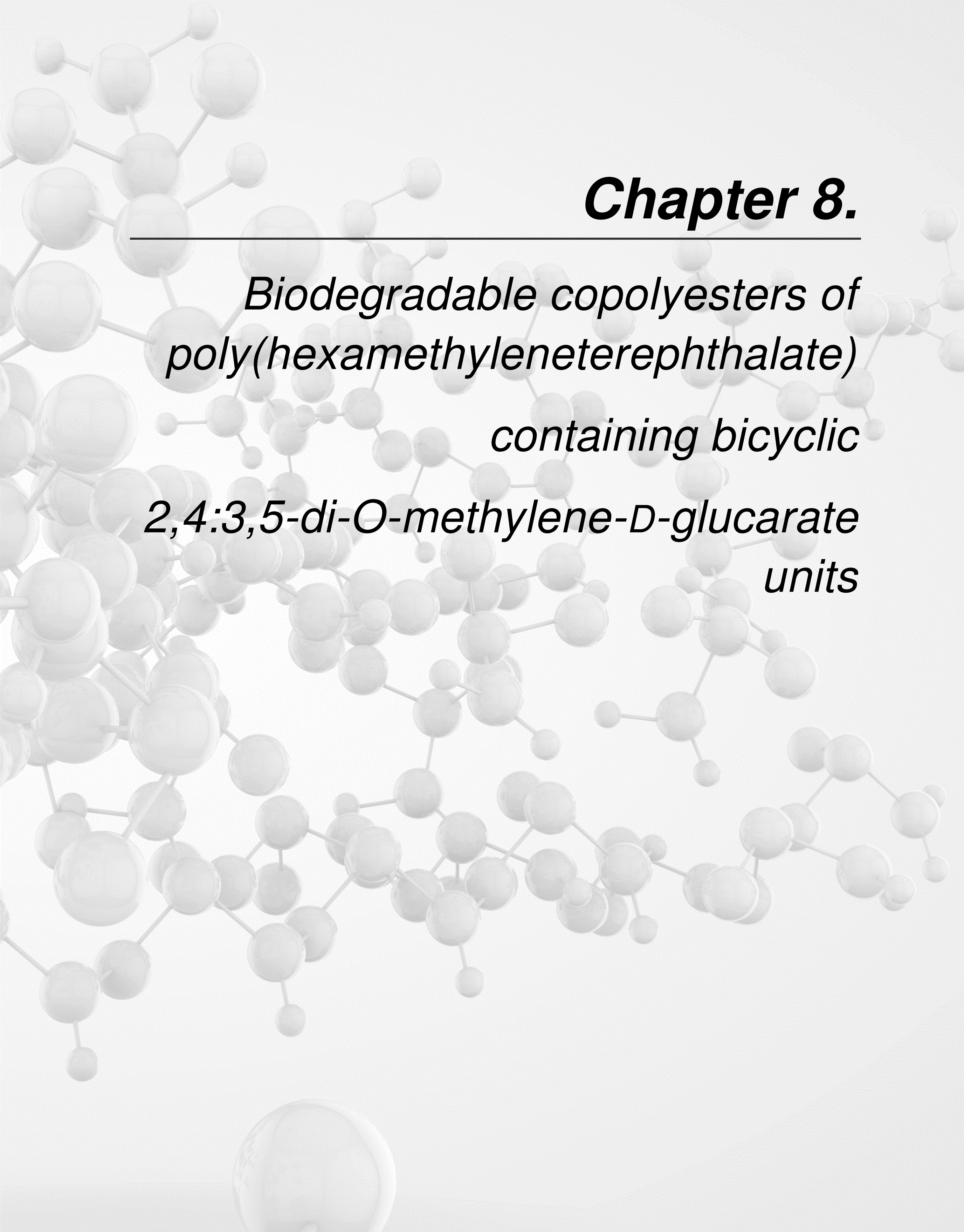
Polyester	d_{hkl} [a] (Å)										X_c [b]
PBT	5.50 s	5.13 s	4.45 w	4.29 s	3.95 m	3.81 s	3.69 w	3.52 s	3.04 w	2.84 m	0.70
PBT$_{95}$Glux$_{5}$	5.53 s	5.13 s	4.46 vw	4.29 s	3.95 m	3.82 s	3.69 w	3.52 s	3.04 w	2.84 m	0.66
PBT$_{90}$Glux$_{10}$	5.53 s	5.13 s	-	4.31 s	3.95 m	3.82 s	3.69 vw	3.52 s	3.04 w	2.85 m	0.60
PB$_{94}$Glux$_{6}$T	5.50 s	5.13 s	4.45 vw	4.31 s	3.95 m	3.82 s	3.69 w	3.52 s	3.04 w	2.85 m	0.63
PB$_{89}$Glux$_{11}$T	5.50 s	5.13 s	-	4.31 s	3.95 m	3.82 s	3.69 vw	3.52 s	3.04 w	2.85 m	0.49

[a] Bragg spacings measured in powder diffraction patterns obtained from annealed samples. Intensities visually estimated as follows: m, medium; s, strong; w, weak; vw, very weak.

[b] Crystallinity index calculated as the quotient between crystalline area and total area. Crystalline and amorphous areas in the X-ray diffraction pattern were quantified using PeakFit v4.12 software.

SI-Table 2. Mechanical properties.

Polyester	Elastic modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PBT	863±25	33±4	15±4
PB$_{69}$Glux$_{31}$T	885±17	41±5	79±9
PB$_{59}$Glux$_{41}$T	892±22	47±6	105±16
PBT$_{67}$Glux$_{33}$	590±20	27±5	121±15
PBT$_{55}$Glux$_{45}$	582±15	24±5	131±18



Chapter 8.

Biodegradable copolyesters of poly(hexamethyleneterephthalate) containing bicyclic 2,4:3,5-di-O-methylene-D-glucarate units

Biodegradable copolyesters of poly(hexamethylene terephthalate) containing bicyclic 2,4:3,5-di-*O*-methylene-D-glucarate units

Abstract

A set of copolyesters (PHT$_x$Glux$_y$) with compositions between 90/10 up to 50/50 in addition to the parent homopolyesters PHT and PHGlux, were prepared by melt polycondensation of 1,6-hexanediol (HD) with mixtures of dimethyl terephthalate (DMT) and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux). The copolyesters had M_w in the 35,000-45,000 range, their microstructure was random and they start to decompose under heating at temperatures well above 300 ºC. Crystallinty of PHT was repressed by copolymerization so that copolyesters containing more than 20% of sugar-based units were essentially amorphous. On the contrary PHT$_x$Glux$_y$ displayed a T_g that increased monotonically with composition from 16 ºC in PHT up to 73 ºC in PHGlux. Compared to PHT the copolyesters showed an accentuated susceptibility to hydrolysis and were sensitive to the action of lipases upon incubation under physiological conditions. The degradability of PHT$_x$Glux$_y$ increased with the content in Glux units.

Publication derived from this work:

C. Japu, A. Martínez de Ilarduya, A. Alla, M. G. García-Martín, J. A. Galbis and S. Muñoz-Guerra, “Biodegradable copolyesters of poly(hexamethylene terephthalate) containing bicyclic 2,4:3,5-di-*O*-methylene-D-glucarate units”, *to be submitted.*

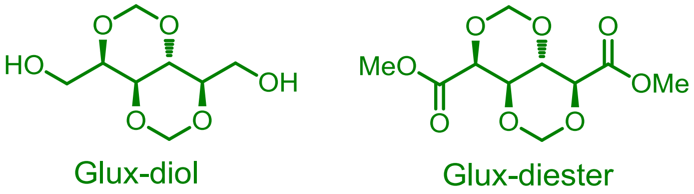
8.1. Introduction

Aromatic polyesters are high performance thermoplastic polymers with excellent thermal and mechanical properties and high chemical resistance. Poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are the best known members of the family due to their wide use in a large variety of industrial applications.[1] However the high resistance to hydrolysis of these polyesters makes more difficult their chemical recycling, hinders the environmental elimination of their residues, and limits their use in short-time applications. This together with the petrochemical origin of the monomers commonly used in their synthesis make that aromatic copolyesters are considered unfriendly materials. Their modification by replacing totally or partially the aromatic units by aliphatic ones coming from renewable resources, in order to render them more sustainable and even biodegradable, is an issue of great interest nowdays.[2,3]

The utilization of naturally-occurring carbohydrates for producing polymers[4,5] will reduce their dependence on petroleum and contribute to minimize the impact of the use of plastics on the environment. However, one major disadvantage of using carbohydrate derivatives for polycondensation is their excess of reactive functional groups, which upon polycondensation would lead to undesirable branched and cross-linked products. Consequently, defunctionalization or protection reactions of the exceeding functional groups are usually required to produce linear polycondensates.[6,7] Among carbohydrate-based monomers, those with a cyclic structure are particularly interesting since they combine their sustainability with their capability to improve some properties related to polymer chain stiffness like the glass transition temperature.[8-11] Furan 2,5-dicarboxylic acid (FDCA),[12-14] which has been reported as a potential alternative to replace terephthalic acid in PET and PBT, and 1,4:3,6-dianhydrohexitols, especially isosorbide,[15-17] are outstanding examples that distinguish because they are commercially available. Very recently it has been reported the synthesis of aliphatic and aromatic polyesters from monocyclic and bicyclic acetalized alditols or aldaric acids by melt polycondensation.[18-20] Most of these copolyesters showed high T_g values and/or an enhanced susceptibility to biodegradation.

Poly(hexamethylene terephthalate) (PHT) is an aromatic polyester that doesn´t have industrial application to date although it is used in telechelic form as soft segment in the synthesis of some patented polyurethanes.[21,22] This polyester has lower T_m and T_g than PET and PBT due to the high chain flexibility provided by the hexamethylene segment, and displays a high resistance to hydrolysis and biodegradation. Recently different aromatic-aliphatic copolyesters derived from PHT with enhanced degradability and biodegradability have been prepared by ring-opening polymerization of cyclic hexamethylene terephthalate oligomers with either caprolactone[23] or *p*-dioxanone.[24] These copolyesters appeared to be sensitive to hydrolysis and those containing more than 10% of caprolactone units were readily degraded by lipases under physiological conditions.

Several works dealing with PHT copolyesters containing cyclic units based on acetalized aldaric acids have been published recently.[19,20a] The replacement of terephthalic acid by the monocyclic 2,3-*O*-methylene-acetal of tartaric acid[19] or by the non-fused bicyclic 2,3:4,5-di-*O*-methylene-acetal of galactaric acid[20a] in polycondensation led to PHT copolyesters with enhanced biodegradability although their glass transition temperatures were slightly depressed. On the contrary, PHT copolyesters obtained by partial replacing of 1,6-hexanediol by 2,4:3,5-di-*O*-methylene-D-glucitol (Glux-diol),[25] not only were biodegradable but they displayed much higher T_g than PHT. The Glux structure consists of a C6-segment backbone with four asymmetric carbons in D-*gluco* configuration forming part of the two fused 1,3-dioxane rings (Scheme 1). This structure has proven to be effective to increase the T_g of both PET and PBT when it is inserted in the polyester either as diol or as diacid. Therefore the bicyclic dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester) stands out as an excellent candidate to improve the properties of PHT regarding both degradability and thermal behavior. The purpose of this work is to explore the suitability of the Glux unit to render partially sustainable and degradable PHT with increased T_g when it is inserted in the polyester chain as diacid unit. The PHT copolyesters are obtained by copolymerization in the melt of 1,6-hexanediol and mixtures of dimethyl terephthalate and Glux-diester by copolymerization. The aim is to open doors for PHT in applications that are not covered today by other aromatic polyesters.



8.2. Experimental section

8.2.1. Materials and methods

Materials

1,6-hexanediol (HD) (99%), dimethyl terephthalate (DMT) (99%), dibutyl tin oxide (DBTO, 98%) were purchased from Sigma-Aldrich. *Irganox 1010* and *Irgafos 126* antioxidants were generous gifts from BASF. Sodium trifluoroacetate (98%) used to stabilize 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and Lipase from porcine pancreas (triacylglycerol lipase activity: 15-35 units/mg) was also purchased from Sigma-Aldrich. The solvents used for purification and characterization, such as chloroform, trifluoroacetic acid (TFA), methanol, diethyl ether, dichloracetic acid (DCA) and HFIP, were high purity grade and used as received.

Dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate monomer (Glux-diester) was prepared by oxidation of 2,4:3,5-di-*O*-methylene-D-gluconic acid with potassium permanganate and esterification with methanol. This synthesis was described elsewhere in full detail.[8a]

Methods

Intrinsic viscosities were measured in DCA using an Ubbelohde microviscometer thermostated at 25 ± 0.1 ºC. Polymer solution concentrations ranged from 0.3 to 1 $g \cdot dL^{-1}$.

Molecular weights were determined by GPC using a Waters equipment provided with a RI detector. HFIP containing sodium trifluoroacetate (6.8 $g \cdot L^{-1}$) was the mobile phase. 100 µL of 0.1% (w/v) sample solution were injected and chromatographed with a flow of 0.5 $mL \cdot min^{-1}$. HR5E Water linear Styragel column (7.8 x 300 mm) packed with cross-linked polystyrene and protected with a pre-column were used. Molar mass averages and their distributions were calculated against PMMA standards.

^{1}H and ^{13}C NMR spectra were recorded using a Bruker AMX-300 spectrometer operating at 300.1 and 75.5 MHz, respectively and running the samples at 25 ºC. The spectra were internally referenced with tetramethylsilane. Samples were prepared by dissolving the polymer in deuterated chloroform. For ^{1}H and ^{13}C analyses were used ~10 and 50 mg of sample in 1 mL of solvent, respectively. Sixty-four scans were recorded for ^{1}H, and between 5,000 and 15,000 scans were taken for ^{13}C with 32 and 64 K data points and relaxation delays of 1 and 2 s, respectively. Two-dimensional spectra (2D) as ^{1}H-^{1}H homonuclear (COSY) and ^{13}C-^{1}H heteronuclear shift correlation (HETCOR) were recorded by means of the *cosy* and *hxco* pulse sequences, respectively, implemented in the Bruker NMR instrument package.

Thermogravimetric analysis was carried out in a nitrogen atmosphere with a Perkin-Elmer TGA6 thermobalance. Polymer samples with an approximate mass of 10 mg were degraded between 30 to 600 ºC at a heating rate of 10 $ºC \cdot min^{-1}$.

The thermal behavior of the polymers was examined by differential scanning calorimetry (DSC) using a Perkin-Elmer Pyris 1 apparatus. Thermograms were obtained from 4-6 mg samples under a nitrogen flow of 20 $mL \cdot min^{-1}$. Indium and zinc were used as standards for temperature and enthalpy calibrations. The melting temperature (T_m) was taken as the maximum of the endothermic peak appearing on heating traces recorded at 10 $ºC \cdot min^{-1}$, and the glass transition temperature (T_g) was taken as the inflection point seen on heating traces recorded at 20 $ºC \cdot min^{-1}$ from samples quenched from the melt. X-ray diffraction profiles were recorded on the PANalyticalX'Pert PRO MPD θ/θ diffractometer using the Cu-Kα radiation of wavelength 0.1542 nm from powder samples after a previous annealing treatment.

8.2.2. Synthesis of polyesters

The polyesters studied in this work were prepared by two-step bulk polymerization consisting of transesterification followed by polycondensation.

PHT_xGlux_y copolyesters were obtained from three-component mixtures of 1,6-hexanediol (HD), dimethyl terephthalate (DMT) and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux) with the selected composition. In the abbreviated name of these copolyesters *x* and *y* subscripts indicate the mol percentages (%-mol) of terephthalate and 2,4:3,5-di-*O*-methylene-D-glucarate units, respectively. The corresponding homopolyesters PHT and PHGlux were obtained from HD with DMT and Glux respectively.

A 2.2:1 molar ratio of HD to the diesters comonomeric mixtures and dibutyl tin oxide (DBTO) (5 mmol of catalyst per mole of diester) were used. It was found in previous work that addition of small amounts of commercial antioxidants *Irganox 1010* (0.1 % w/w) and *Irgafos126* (0.3 % w/w) was very effective to minimize degradation of the thermally-sensitive sugar-derived monomers. Therefore they were also added here to the initial reaction mixture.

The polymerization reaction was performed in a three-necked, cylindrical-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum distillation outlet. The apparatus was vented with nitrogen several times at room temperature in order to remove the air and avoid oxidation during the polymerization. Transesterification reactions were carried out under atmospheric pressure assisted with a low nitrogen flow at temperatures between 170 and 200 ºC. Polycondensation reactions were left to proceed at temperatures higher than those used for transesterification and under a 0.03-0.06 mbar vacuum. When polymerization was finished, the reaction mixture was cooled to room temperature, and the atmospheric pressure was recovered with nitrogen to prevent degradation. The collected solid mass was dissolved in chloroform and precipitated in an excess of methanol in order to remove unreacted monomers and formed oligomers. Finally, the polymer was separated by filtration, extensively washed with methanol, and dried under vacuum. The conditions used for the synthesis of homopolyesters and copolyesters are detailed as it follows:

PHT homopolyester.1,6-hexanediol to dimethyl terephthalate, molar ratio: 2.2/1 Transesterification reactions at 180 ºC for 2 h and polycondensation reactions at 240 ºC for 2.5 h under a 0.03-0.06 mbar vacuum.

^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm): 8.08 (s, *Ar*H), 4.36 (t, O$\mathbf{CH_2}$$CH_2CH_2$), 1,82 (q, $OCH_2$$\mathbf{CH_2}$$CH_2$), 1.54-1.63 (m, $OCH_2CH_2$$\mathbf{CH_2}$).^{13}C{^{1}H}-NMR ($CDCl_3$, 75.50 MHz), δ (ppm): 165.8 (C=O), 134.0-129.0 (*Ar*C), 65.20 (O$\mathbf{CH_2}$$CH_2CH_2$), 28.50 ($OCH_2O$$\mathbf{CH_2}$$CH_2$), 25.67 ($OCH_2OCH_2$$\mathbf{CH_2}$).

***PHT$_x$Glux$_y$* copolyesters.** The copolyesters were obtained by a similar procedure, with polymerization conditions slightly differing for each composition feed. In all cases the 1,6-hexanediol to the mixture of dimethyl terephthalate and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate diesters was 2.2/1.

PHT$_{90}$Glux$_{10}$ and PHT$_{85}$Glux$_{15}$. Transesterification reactions at 175 ºC for 3 h under low nitrogen flow and polycondensation reactions at 230 ºC for 3h under a 0.03-0.06 mbar vacuum.

PHT$_{81}$Glux$_{19}$ and PHT$_{70}$Glux$_{30}$. Transesterification reactions at 175 ºC for 3 h under low nitrogen flow and polycondensation reactions at 200 ºC for 3,5 h under a 0.03-0.06 mbar vacuum.

PHT$_{60}$Glux$_{40}$ and PHT$_{50}$Glux$_{50}$. Transesterification reactions at 170 ºC for 5 h and polycondensation reactions at 190 ºC for 5-6 h under a 0.03-0.06 mbar vacuum.

^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm): 8.07 (s, *Ar*H), 5.30, 4.83 (dd, OCH_2O), 5.12-4.96 (2dd, OCH_2O), 4.59(s, CH), 4.50-4.30 (m, *x*-O**CH$_2$**CH_2CH_2, CH), 4.30-4.15 (m, *y*-O**CH$_2$**CH_2CH_2), 4.09 (s, CH), 4.02 (s, CH), 1.98-1.64 (m, OCH_2**CH$_2$**CH_2), 1.64-1.30 (m, OCH_2CH_2**CH$_2$**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.5 MHz), δ (ppm): 168.6-165.3 (C=O), 134.05-129.41 (*Ar*C), 92.52 (OCH_2O), 90.06 (OCH_2O), 76.46 (CH), 75.06 (CH), 70.39 (CH), 68.65 (CH), 66.0-65.0 (O**CH$_2$**CH_2CH_2), 29.0-28.0 (OCH_2**CH$_2$**CH_2), 26.0-25.0 (OCH_2CH_2**CH$_2$**).

***PHGlux* homopolyester.** 1,6-hexanediol to dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate molar ratio: 2.2/1 Transesterification reactions at 170 ºC for 5 h and polycondensation reactions at 170 ºC for 7 h.

^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm): 5.28, 4.78 (dd,OCH_2O), 5.10-4.90 (m, OCH_2O), 4.57 (bs, CH), 4.40-4.30 (m, CH), 4.30-4.15 (m, O**CH$_2$**CH_2CH_2), 4.08 (bs, CH), 4.00 (bs, CH), 1.68 (m,OCH_2**CH$_2$**CH_2).^{13}C{^{1}H}-NMR ($CDCl_3$, 75.5 MHz), δ (ppm): 168.5-167.1 (C=O), 92.48 (OCH_2O), 90.02 (OCH_2O), 76.38 (CH), 75.01 (CH), 70.31 (CH), 68.64 (CH), 66.0-65.20 (O**CH$_2$**CH_2CH_2), 28.25 (OCH_2**CH$_2$**CH_2), 25.15 (OCH_2CH_2**CH$_2$**).

8.2.3. Hydrolytic and enzymatic assays

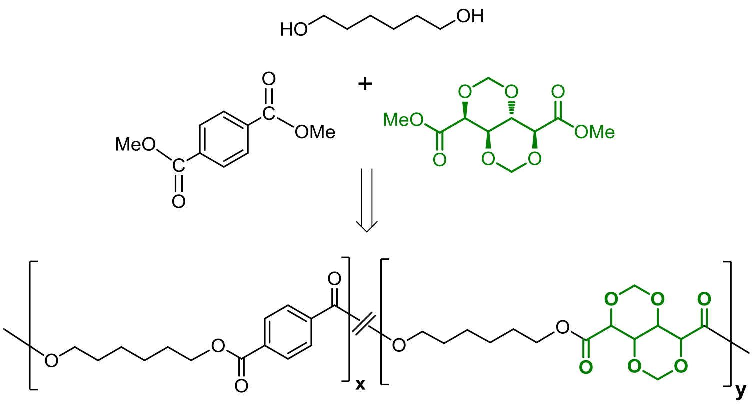
Both hydrolytic and enzymatic degradation essays were carried out on films of polyesters and copolyesters with a thickness of about 200 μm which were prepared by casting either from chloroform solutions with a concentration of about 100 mg mL^{-1}. The films were cut into 10 mm diameter disks and dried under vacuum to constant weight, which finally remained between 20 and 30 mg. The disks were individually immersed in vials containing 10 mL of either sodium citric acid buffer pH 2.0 (hydrolytic degradation), or sodium phosphate buffer pH 7.4 containing 10 mg of porcine pancreas lipases (enzymatic degradation), and left incubating at 37 ºC (pH 7.4) and 80 ºC (pH 2) for four weeks. The buffered enzyme solution was replaced every 72 h to maintain the enzyme activity. After scheduled periods of time, the disks were withdrawn from the incubation medium, washed thoroughly with distilled water, and dried to constant weight.

8.3. Results and discussion

8.3.1. Polyesters synthesis and microstructure of PHT$_x$Glux$_y$ copolyesters

Synthesis

The synthesis approach followed in this work for the preparation of the PHT$_x$Glux$_y$ copolyesters was the two-step melt polycondensation of 1,6-hexanediol (HD) with mixtures of dimethyl terephthalate (DMT) and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux), as it is depicted in Scheme 2. The polymerization system was the mixture of monomers, DBTO catalyst and the antioxidants (*Irganox 1010* and *Irgafos 126*) in total absence of solvents in order to imitate as far as possible the conditions that usually apply in the industrial practice. A slight excess of diols respect to diesters was used to ensure the complete transesterification of all methyl ester groups necessary for allowing the growth of the polymer chain.



Scheme 2. Polymerization reactions leading to PHT$_x$Glux$_y$.

In the first stage of transesterification which was carried out under atmospheric pressure, oligomers were formed with subsequent releasing of methanol. In the second stage, the oligomers were polycondensated at temperatures in the 190-230 ºC range under high vacuum with removal of the exceeding diols. Lower temperatures and longer reaction times were used for copolyesters with higher contents in Glux to prevent the decomposition of the sugar-based compounds. The same procedure was used for the synthesis of the parent homopolyesters PHT and PHGlux. The polymerization reaction was considered finished when the stirring was impeded by the high viscosity attained in the reaction mixture. Then the reaction mixture was dissolved in chloroform and the solution poured into methanol to precipitate the polyester which was recovered by filtration in yields close to 80-90%.

Table 1. Molar composition, molecular weight and microstructure of polyesters.

Polyester	Yield (%)	Composition[a]				Molecular weight				Microstructure
		Feed		Copolyester						
		[T]	[Glux]	[T]	[Glux]	$[\eta]^{b}$	M_n^{c}	M_w^{c}	$Đ^{c}$	R^{d}
PHT	90	100	0	100	0	1.33	21,900	50,300	2.3	-
$PHT_{90}Glux_{10}$	89	90	10	90	10	1.14	18,100	43,500	2.4	1.12
$PHT_{85}Glux_{15}$	88	85	15	85	15	0.89	19,400	42,600	2.2	1.01
$PHT_{81}Glux_{19}$	87	80	20	81	19	0.88	18,400	42,400	2.3	1.00
$PHT_{70}Glux_{30}$	85	70	30	70	30	0.65	15,800	36,400	2.3	1.01
$PHT_{60}Glux_{40}$	80	60	40	60	40	0.64	15,600	36,300	2.3	0.99
$PHT_{50}Glux_{50}$	80	50	50	50	50	0.62	16,300	35,900	2,2	0.99
PHGlux	40	0	100	0	100	0.50	9,500	20,000	2.1	-

[a] Molar composition determined by integration of ^{1}H NMR spectra. T: terephthalate units; Glux: glucarate units.
[b] Intrinsic viscosity in dL·g^{-1} measured in DCA at 25 ºC.
[c] Number and weight average molecular weights in g·mol^{-1}, and dispersities measured by GPC in HFIP against PMMA
[d] Randomness degree of copolyesters calculated on the basis of ^{13}C NMR analysis.

The chemical constitution and composition of PHT_xGlux_y copolyesters were ascertained by NMR spectroscopy. As it is illustrated in Figure 1 for the case of $PHT_{70}Glux_{30}$ copolyester, all signals appearing in both ^{1}H and ^{13}C NMR spectra were properly assigned according to the expected chemical structure. 2D NMR *cosy* and *hector* spectra were used to support the signal assignment (these spectra are provided in the Supporting Information file as Figures SI-1 and SI-2). The compositions of the copolyesters were calculated by integration of the signals arising from the two comonomeric units and they were found to be quite close to those of the corresponding feeds. Viscosimetry and molecular weight data estimated by GPC of all the synthesized polyesters are given in Table 1. As it is seen the resulted copolyesters were obtained with satisfactory molecular weights with weight-average values comprised in the 35,900-43,500 g·mol^{-1} interval. Their intrinsic viscosities ranged between 0.62 and 1.14 dL·g^{-1}. Whereas the homopolyester PHT was obtained with the highest M_w and $[\eta]$, the values for the homopolyester

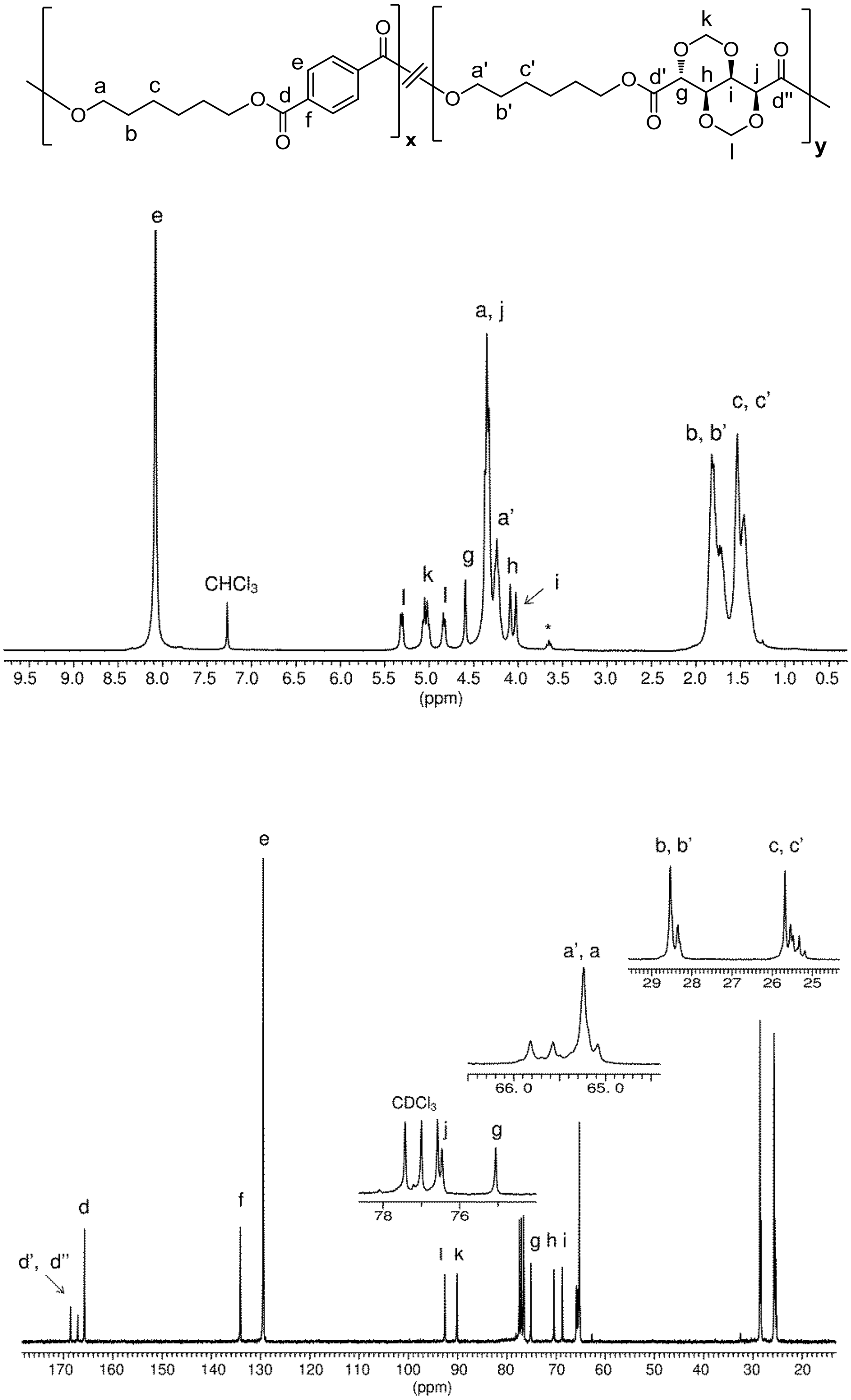


Figure 1.^{1}H (top) and ^{13}C (bottom) NMR spectra of PHT$_{70}$Glux$_{30}$ copolyester.

PHGlux were 20,000 g·mol^{-1} and 0.5 g·dL^{-1} respectively, in agreement with the trend observed for the whole series in which the polymer size diminishes monotonically with the content in Glux units.

Microstructure

The microstructure of $\mathrm{PHT}_x\mathrm{Glux}_y$ copolyesters was analyzed by ^{13}C NMR spectroscopy and their degrees of randomness (*R*) were determined. This was accomplished by taking benefit from the fact that the methylene carbons of the oxyhexamethylene units are sensitive to sequence distribution effects. In Figure 2 the ^{13}C NMR region containing the signals due to the second methylenes of the hexamethylene segment of $\mathrm{PHT}_x\mathrm{Glux}_y$ copolyesters are shown. These signals are split in four peaks due to sequence effects associated to the four types of dyads (TT, GluxT/TGlux, GluxGlux) that are possible along the copolyester chain. By Lorentzian deconvolution of the peaks using the Win NMR software and according to Randall,[26] the number average sequence lengths *n* of hexamethylene terephthalate (HT) and hexamethylene-glucarate (HG) units could be calculated and as well as their degree of randomness (*R)*. The equations used and the results obtained from these calculations are detailed in ESI (eq. SI-1 and Table SI-1). It was found that the sequence distribution in all $\mathrm{PHT}_x\mathrm{Glux}_y$ copolyesters is nearly random with values of (*R)* very close to unity.

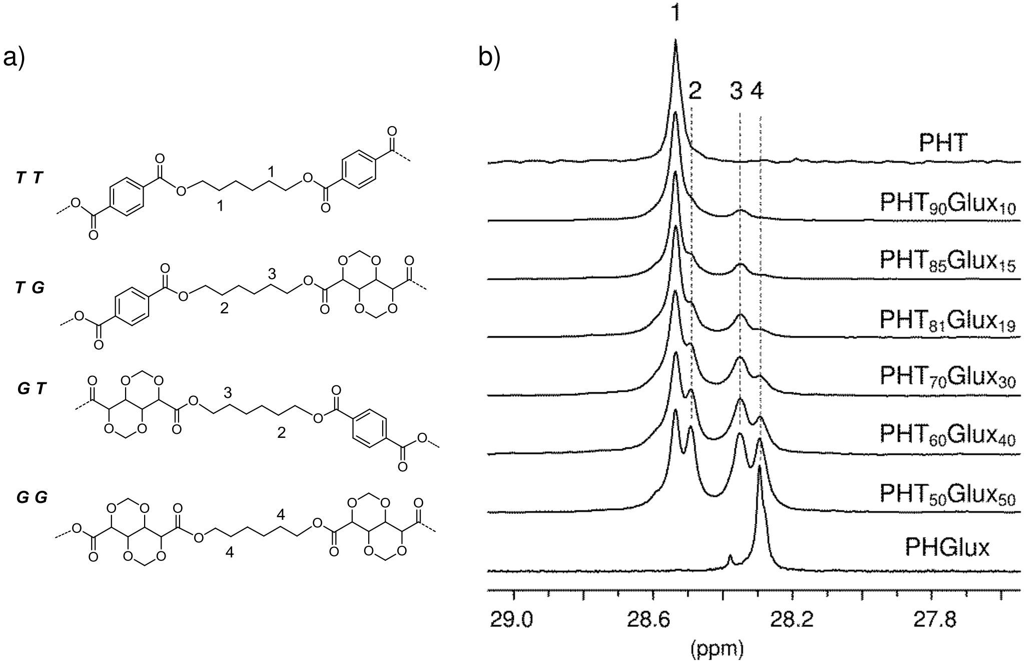


Figure 2. a) The four possible dyads occurring in $\mathrm{PHT}_x\mathrm{Glux}_y$ copolyesters. b) ^{13}C NMR spectra in the region of the second methylene (labeled as 1, 2, 3 and 4 in the top figure for the respective dyads) of the hexamethylene segment for $\mathrm{PHT}_x\mathrm{Glux}_y$ copolyesters and homopolyesters.

8.3.2. Thermal properties and X-ray diffraction

The TGA traces of PHT$_x$Glux$_y$ copolyesters and PHT and PHGlux homopolyesters, as well as a selection of illustrative derivative curves registered under an inert atmosphere are comparatively depicted in Figure 3. The onset temperatures and the temperatures of the maximum decomposition rate together with the weight remaining after heating at 600 ºC, are listed in Table 2. All the polyesters started to decompose above ~320 ºC and the decomposition process was found to proceed along two well differentiated stages with decomposition rates taking place at the proximities of 350 and 400 ºC respectively. The large great sensitivity to heating exhibited by PHGlux compared to PHT is the logical consequence of the decreasing thermal stability observed for the PHT$_x$Glux$_y$ with increasing contents in glucarate units. This behavior is not surprising at all since it has been repeatedly observed for other aromatic copolyester series prepared from cyclic acetalized aldaric acids.[8,20a] It continues being remarkable that the response to heat of PHT$_x$Glux$_y$ copolyesters is just opposite to that given by the PH$_x$Glux$_y$T copolyesters made from similar cyclic acetalized sugar units but inserted in the polyester chain as dioxyglucitylene units.[25]

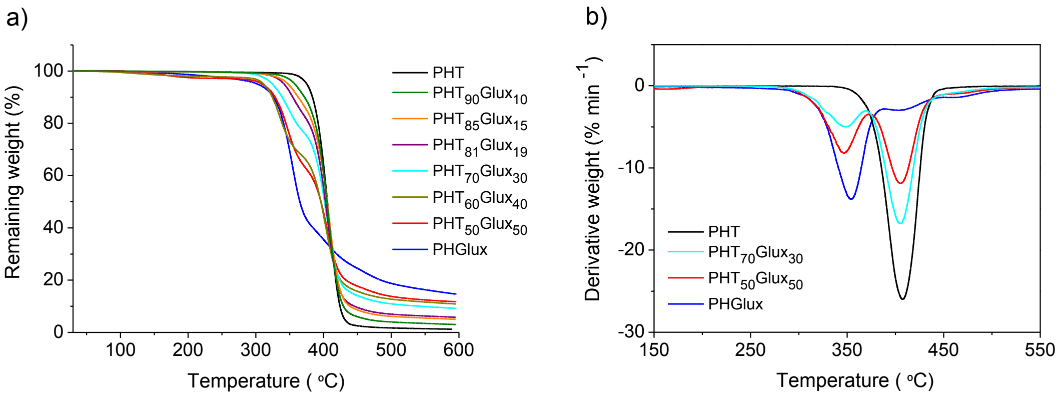


Figure 3. TGA traces of PHT$_x$Glux$_y$ (a) and derivative curves for a illustrative selection of cases (b) registered under an inert atmosphere.

The DSC analyses revealed that the incorporation of sugar units in the chain of PHT induced significant changes in glass-transition and melting temperatures of PHT. Melting and crystallization temperatures were measured by heating the samples coming from the synthesis and then cooling from the melt and data provided by these measurements are listed in Table 2. The DSC traces of the PHT$_x$Glux$_y$ copolyester series together with the parent homopolyesters are depicted in Figure 4. The glass transition (T_g) for all polyesters was clearly detected in the heating DSC traces of samples previously quenched from the melt (Figure 4b). It can be noticed that T_g steadily increased as terephthalate units were replaced by the glucarate ones, going from 16 ºC for PHT up to 50 ºC for $PHT_{50}Glux_{50}$ and attaining 70 ºC in the homopolyester PHGlux where the replacement is 100%. It is apparent that the bicyclic fused dioxane structure present in the 2,4:3,5-di-*O*-methylene-D-glucarate unit increases the stiffnes of the polyester chain with the consequent increasing in T_g. This is an outstanding result because the insertion of aliphatic units in aromatic polyesters usually leads to a notable decrease in T_g.[27,28] In the case of PHT, such depressing effect on T_g has been reported to occur in random copolyesters prepared by ROP from p-dioxanone[24] and ε-caprolactone.[23] This is also the usual result found for terephthalate copolyesters containing cyclic acetalized dicarboxylate units other than glucarate units.[9a,20a] Specifically PHT copolyesters with terephthalate units partially replaced by 2,3-di-*O*-methylene-L-threarate[19] or by 2,3:4,5-di-*O*-methylene galactarate[20a] units show T_g appreciably lower than the homopolyester. On the contrary, the T_g of both PET and PBT copolyesters is increased in their

Table 2. Thermal properties of PHT, PHGlux and PHT_xGlux_y copolyesters.

Polyester	TGA			DSC								
					First Heating[e]		Cooling[e]		Second Heating[e]			
	T_d[a] (°C)	T_{ds}[b] (°C)	RW[c] (%)	T_g[d] (°C)	T_m (°C)	ΔH_m ($J\cdot g^{-1}$)	T_c (°C)	ΔH_c ($J\cdot g^{-1}$)	T_{cc} (°C)	ΔH_{cc} ($J\cdot g^{-1}$)	T_m (°C)	ΔH_m ($J\cdot g^{-1}$)
PHT	384	407	1	16	144	35	111	-28	-	-	139	29
$PHT_{90}Glux_{10}$	372	407	3	20	127	27	86	-28	-	-	131	25
$PHT_{85}Glux_{15}$	363	357/**407**	5	21	56/**120**	3/**26**	-	-	55	15	121	24
$PHT_{81}Glux_{19}$	354	356/**405**	6	24	66/**112**	9/**24**	-	-	76	17	113	17
$PHT_{70}Glux_{30}$	339	349/**405**	9	34	68/95	13/7	-	-	-	-	-	-
$PHT_{60}Glux_{40}$	324	334/**403**	11	42	67	20	-	-	-	-	-	-
$PHT_{50}Glux_{50}$	328	346/**405**	12	50	65	10	-	-	-	-	-	-
PHGlux	326	**354**/405/ 466	15	73	-	-	-	-	-	-	-	-

[a] Temperature at which a 10% of weight loss was observed in the TGA traces recorded at 10 °C min^{-1}.
[b] Temperature of maximum degradation rate.
[c] Remaining weight at 600ºC.
[d] Glass-transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 ºC·min^{-1}
[e] Melting (T_m), crystallization (T_c) and cold crystallization (T_{cc}) temperatures and enthalpies (ΔH_m, ΔH_c) measured by DSC recorded at heating/cooling rates of 10 °C min^{-1}.

copolyesters containing 2,4:3,5-di-*O*-methylene glucarate units which corroborates the unique enhancing T_g effect exerted by the bicyclic fused 1,3-dioxane structure with *gluco* configuration.[8] The evolution of T_g with composition is plotted in Figure 5 for several series of PHT copolyesters to appreciate the particular effect exerted by Glux units on this transition.

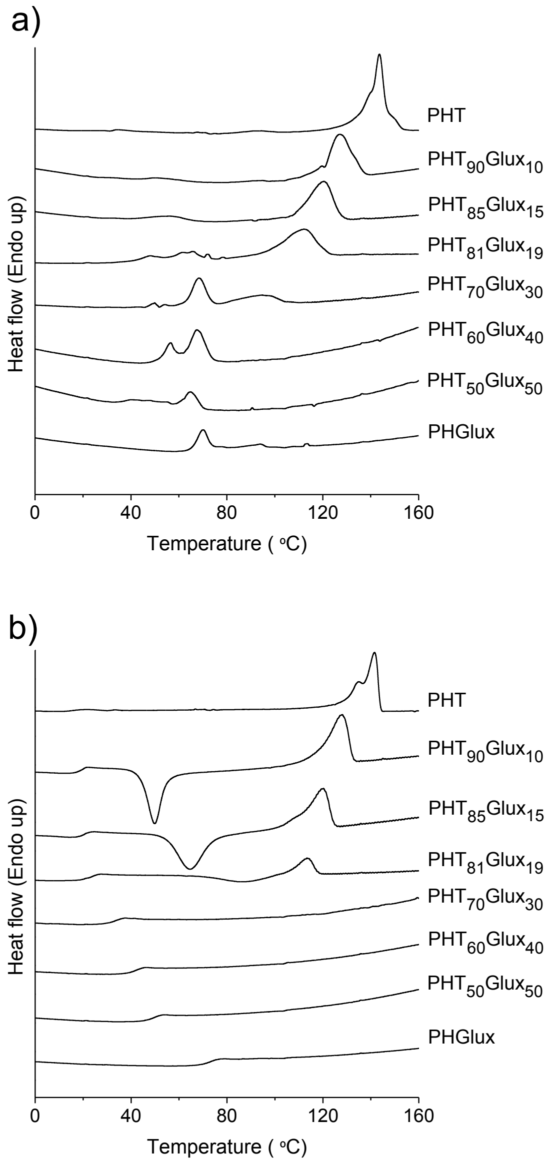


Figure 4. (a) DSC heating traces of PHT_xGlux_y copolyesters samples coming directly from synthesis (a), and samples quenched from the melt for T_g observation (b).

Although the first heating DSC scans of copolyesters pristine samples showed the presence of endothermic peaks meaning that they are semicrystalline (Figure 4), only $PHT_{90}Glux_{10}$ was able to crystallize upon cooling from the melt. Comparison of melting temperatures and enthalpies of PHT_xGlux_y with those of PHT homopolyester (Table 2) led to conclude that the insertion of Glux units in PHT gives rise to a decrease in both T_m and ΔH_m. It was noticed also that the melting endotherm produced by the copolyesters with more than 20% of content in Glux units exhibits peak multiplicity whereas the trace of the PHGlux homopolyester shows an only endothermic peak at 73 ºC. This peak can't be attributed to melting because PHGlux has a T_g about 70 ºC and does not produce crystalline scattering by WAX but to an enthalpic relaxation process that takes place immediately below the glass-transition.[29] The multiple peak observed for copolyesters should be interpreted therefore as due to melting of crystallite populations differing in crystallite sizes that were generate under more or less defective crystallization conditions.[30]

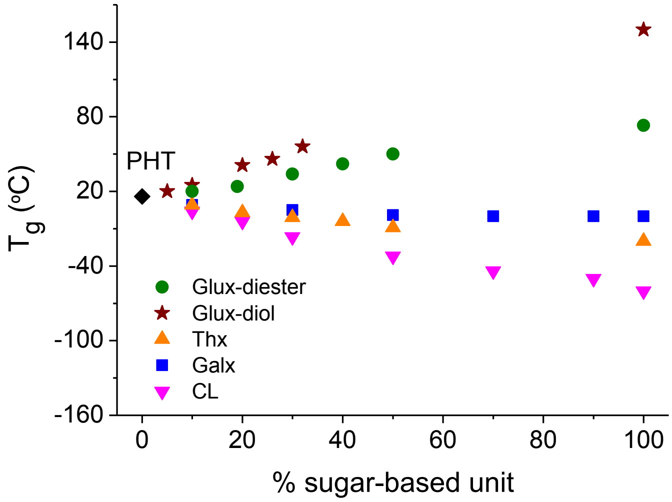


Figure 5. Glass-transition temperature versus composition for PHT copolyesters containing 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester), 2,3:4,5-di-*O*-methylene-galactarate (Galx),[20a] 2,3-di-*O*-methylene-L-threarate (Thx),[19] 2,4:3,5-di-*O*-methylene-D-glucitol (Glux-diol)[25] and ε-caprolactone (CL).[23]

X-ray diffraction

The powder WAXS profiles of $PHT_{90}Glux_{10}$, $PHT_{81}Glux_{19}$ and $PHT_{60}Glux_{40}$ copolyesters as well as of PHT and PHGlux homopolyesters recorded from annealed samples are depicted in Figure 6. What is apparent in these profiles is the decreasing in crystalline scattering that ensue the increasing content in Glux units. As expected the high crystallinity of PHT is hampered by the insertion of the bulky bicyclic units in the polyester chain. The homopolyester PHGlux, which is entirely made of Glux units, appears to be amorphous in spite of its homogeneous constitution. This result is in line with those previously attained for poly(ethylene glucarate) and poly(butylene glucarate) (PEGlux and PBGlux) but in manifest contrast with the remarkable crystallinity observed for PHThx[19] and different alkylene polygalactarates including PHGalx.[20a] The lack of molecular symmetry inherent to the *gluco* configuration compared to *threo* (C2) and *galacto* (I) may be reasonably invoked to explain the observed differences.

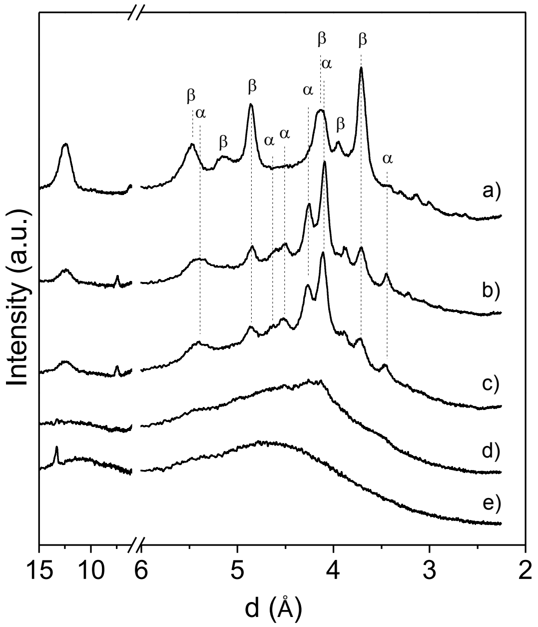


Figure 6. WAXS profiles recorded from powder samples of PHT and PHGlux homopolyesters (a and e, repectively) and copolyesters PHT$_{90}$Glux$_{10}$ (b), PHT$_{81}$Glux$_{19}$ (c), and PHT$_{60}$Glux$_{40}$ (d).

It is well known that PHT adopts three crystal forms designated as *α*, *β* and *γ*[31-34] depending on crystallization conditions. The *α*-form is monoclinic whereas both *β* and *γ* forms are triclinic but differ to each other in the *b* dimension. The diffraction pattern of PHT shown in Figure 6 is characteristic of the *β*-form whereas those of copolyesters containing 10 and 20% of glucarate units show reflections of both *α* and *β* forms, *α* being the predominant later. The Bragg spacings measured on these profiles are detailed in the Supplementary Information file (SI-Table2). As it has been reported in several previous occasions dealing with aromatic copolyesters containing sugar residues, the crystallinity present in PHT$_{90}$Glux$_{10}$ and PHT$_{81}$Glux$_{19}$ is associated to crystallites exclusively made of homogeneous sequences of HT units whereas HGlux units are segregated to the amorphous phase.[8,9,25] Beyond 20% of content in Glux units crystallinity is lost because the HT sequences are too short as to produce stable crystallites.

Although $PHT_{60}Glux_{40}$ exhibits several reflections, they are unidentifiable and of so low intensity that this copolyester can be considered essentially amorphous.

8.3.3. Hydrolytic and enzymatic degradability

The resistance of aromatic polyesters to be hydrolyzed either chemically or enzymatically is a well-known fact.[35] It has been reported that the degradation rate of aliphatic-aromatic copolyesters is mainly determined by the content in terephthalate units and that these copolyesters may be biodegradable with up to 60%-mol of aromatic units.[36] It is known also that the insertion of sugar-based units in aromatic polyesters is effective in enhancing their susceptibility to hydro- and biodegradation. Various papers showing this effect have been recently reported.[8,19,20,25,37] In this work the effect that the insertion of glucarate units in the PHT chain have on the hydrolytic and enzymatic degradability of the polyester is evaluated in order to compare with other similar systems previously reported. For this study two copolyesters with different content in Glux units, $PHT_{70}Glux_{30}$, $PHT_{50}Glux_{50}$, were examined in addition to PHT which is taken for reference.

First the water degradability under aggressive conditions was estimated by incubation of the samples in aqueous buffer pH 2 at 80 ºC. The changes taking place in sample weight and molecular weight along an incubation period of four weeks are plotted against time in Figure 7. As it was expected no weight loss was observed for PHT under these conditions; the extremely high reluctance of this polyester to hydrolysis has been reported by us in recent related papers.[19,20a,25] On the contrary, the two copolyesters showed appreciably degradation after four weeks of incubation with weight losses of 35% and 54% for $PHT_{70}Glux_{30}$ and $PHT_{50}Glux_{50}$ respectively. Also M_w was observed to decay in agreement with weight loses results. ^1H MNR spectra timely registered from residual $PHT_{50}Glux_{50}$ incubated at pH 2 are depicted in Figure 8a and those registered from $PHT_{70}Glux_{30}$ are included as supporting information material (Figure SI-3). The ^1H MNR spectra of both copolyesters showed signals of $-CH_2OH$ end groups of the polyester indicative of the decrease in molecular weight that was taking place. They also revealed a progressive decreasing of Glux units in the degraded copolyester along incubation with a loss of almost 80% of sugar units at the end of the experiments (Figure 8b). On the other hand, no changes in the structure of the diacetal were noticed which confirmed previous reports in which the high resistance of the bicyclic 1,3-dioxane structure to hydrolysis even in aggressive conditions was appraised.[37] The ^1H MNR spectrum taken from the aqueous solution at the end of the incubation period showed unequivocal signals evidencing the release of 2,4:3,5-di-*O*-methylene-D-glucaric acid and 1,6-hexanediol (Figure 9) whereas no signals arising from terephthalic acid were detected most likely because of the insolubility of this aromatic compound in the aqueous medium. It can be concluded therefore that hydrolysis of the copolyesters took place mainly by breaking of the carboxylate groups associated to the glucarate units and that the material left after degradation essentially consisted of 1,6-hexamethylene terephthalate oligomers.

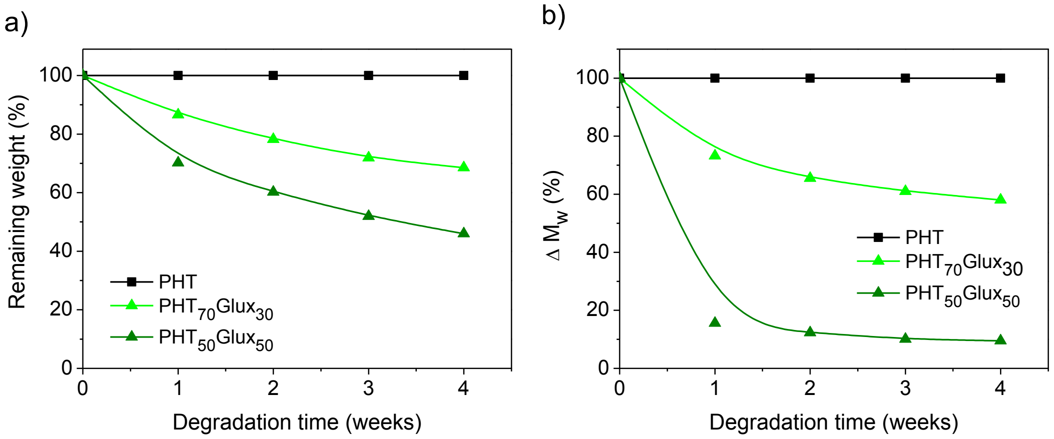


Figure 7.Hydrolytic degradation of $PHT_{70}Glux_{30}$, $PHT_{50}Glux_{50}$ and PHT at 80ºC, pH 2. Remaining weight (a) molecular weight (b) *vs.* degradation time.

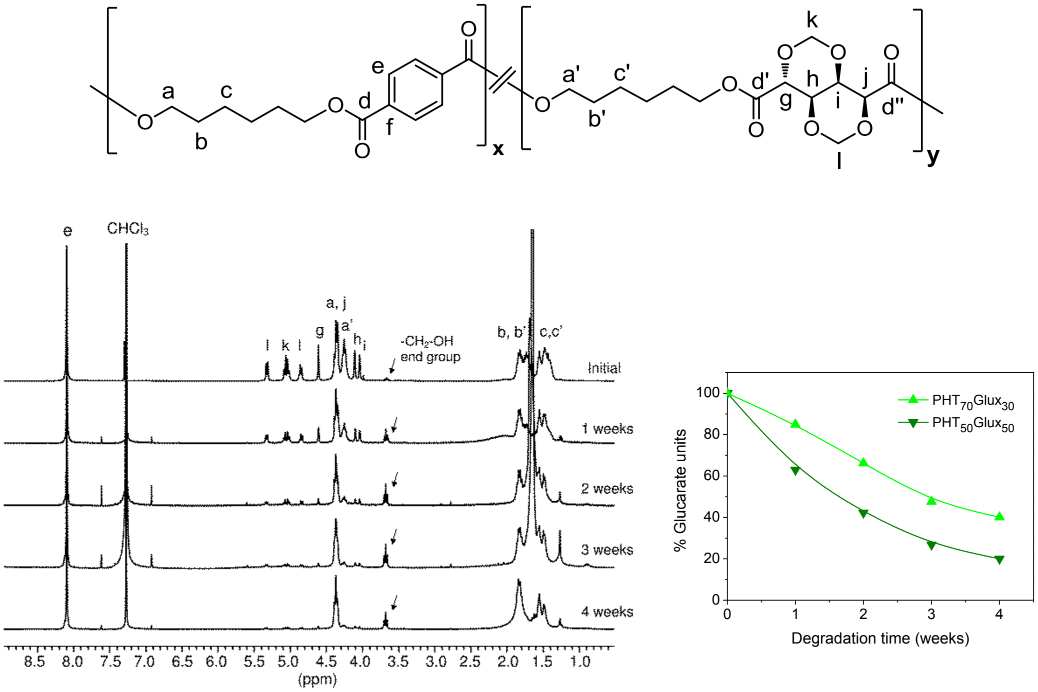


Figure 8. Compared ^{1}H NMR after incubation with water at pH 2.0 at 80 ºC and initial spectra of $PHT_{50}Glux_{50}$ copolyester (left) and representation of glucarate content*s vs.* incubation time (right).

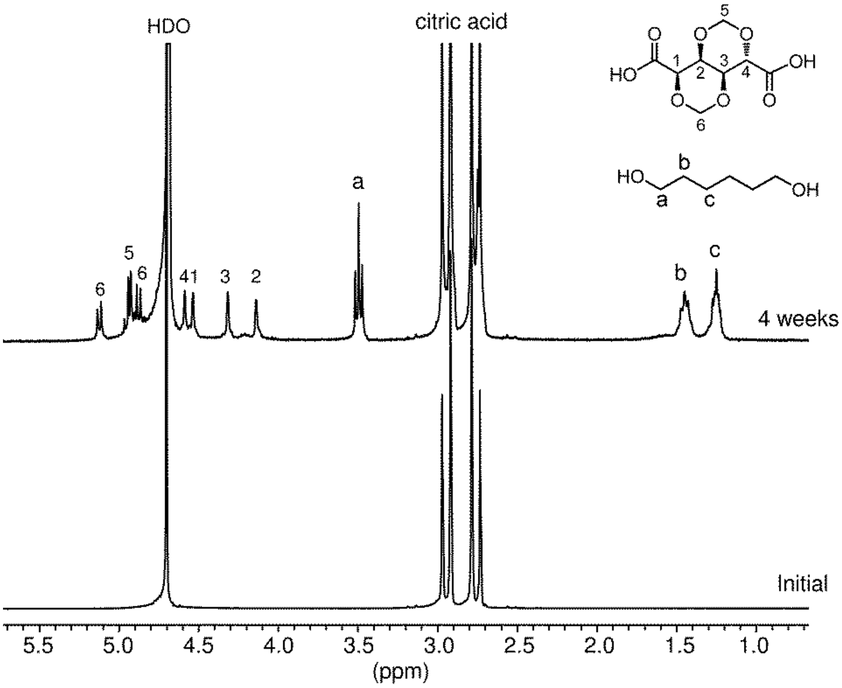


Figure 9.^{1}H NMR spectra in D_2O of the products released to the aqueous medium after incubation of $PHT_{50}Glux_{50}$ at pH 2.0 at 80 ºC for four weeks.

The second part of this study was addressed to evaluate the biodegradability of the Glux-containing PHT copolyesters. For this purpose $PHT_{70}Glux_{30}$, $PHT_{50}Glux_{50}$ and PHT discs were incubated in aqueous pH 7.4 buffer with and without added porcine pancreas lipase for a period of four weeks at 37 ºC. The changes taking place in sample weights and molecular weights of the polyesters over the whole period of incubation are plotted in Figure 10. No changes at all were detected for PHT confirming once more the high resistance of this polyester to enzymatic degradation. In contrast, both $PHT_{70}Glux_{30}$ and $PHT_{50}Glux_{50}$ showed losses of about 10% and 14% of the initial weight at the end of the incubation time. The fact that weight losses observed upon incubation in the absence of lipase were only ~3-5% is taken as demonstrative of the positive response of these copolyesters to enzymatic action. The variations detected in M_w were also noticeable and in full agreement with the changes observed in the remaining weight.

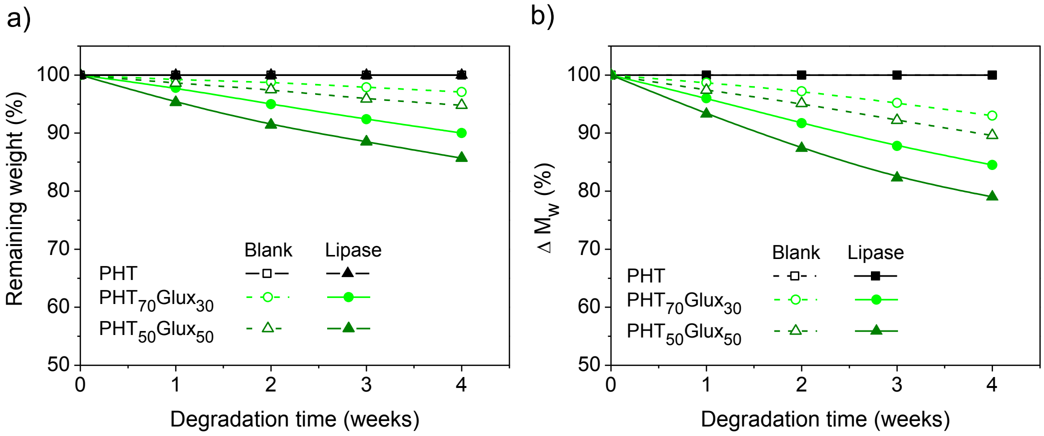


Figure 10. Enzymatic degradation of PHT$_{70}$Glux$_{30}$, PHT$_{50}$Glux$_{50}$ and PHT upon incubation at pH 7.4 at 37 ºC for 4 weeks.Remaining weight (a) molecular weight (b) *vs*. degradation time.

8.4. Conclusions

The bicyclic compound dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester) has been shown to be a suitable monomer to replace dimethyl terephthalate in the polycondensation with 1,6-hexanediol to produce random PHT copolyesters. Although the molecular weights of the copolyesters decrease with the content in Glux units, their values remain satisfactory over the whole range of compositions which attains up to 50%-mol. Also their resistance to heating diminishes with the incorporation of the sugar derived units but the stability is in all cases high enough as to allow the processing of the copolyesters by thermal processes. The copolyesters display crystallinity only for low contents in Glux units but their T_g increases continuously with the incorporation of such units. Whereas PHT is almost inalterable by water, the copolyesters shows appreciable susceptibility to hydrolysis which is enhanced in the presence of enzymes. Compared to other PHT copolyesters containing other cyclic diacetalized aldarate units, the PHT copolyesters made from Glux-diester are distinguished by displaying degradability and biodegradability along with increased T_g. The effects of Glux on PHT are similar to those reported for PET and PBT and corroborate the unique ability of the Glux unit to produce biodegradable aromatic copolyesters with high T_g. The novel synthesized copolyesters are of interest as materials with potential in biomedical applications for temporal use.

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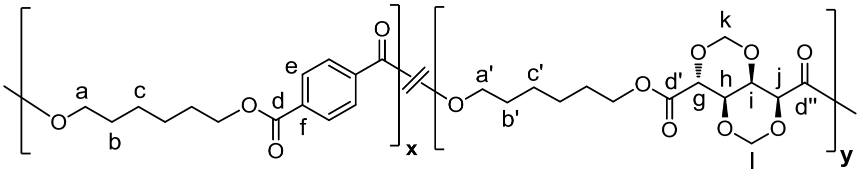
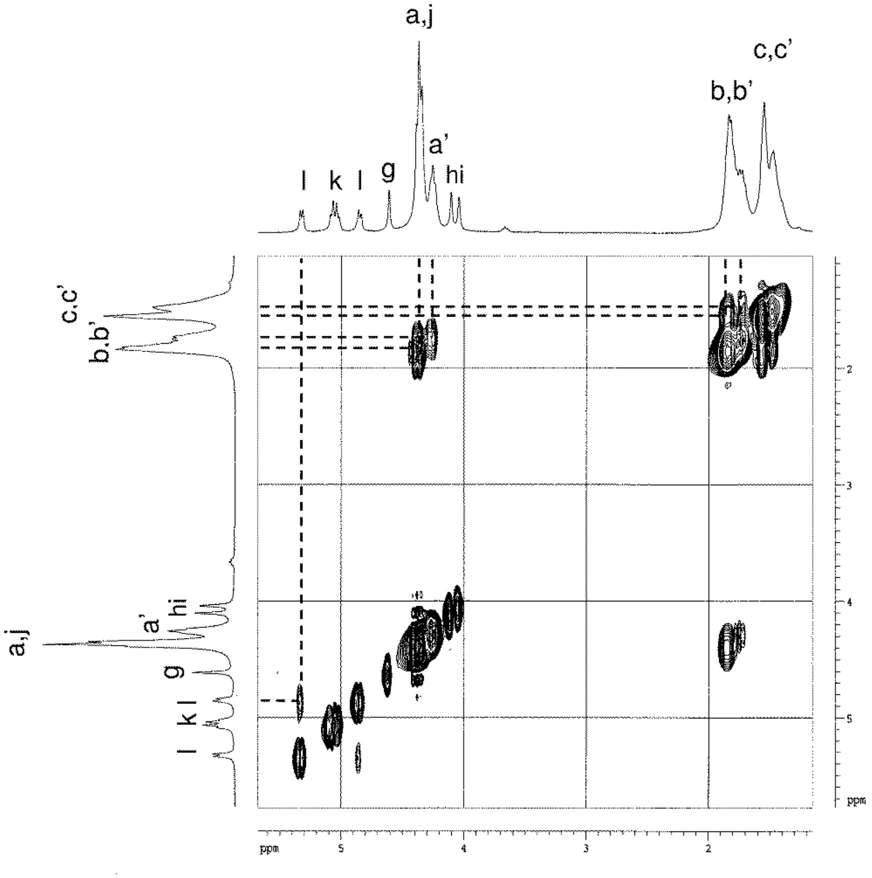
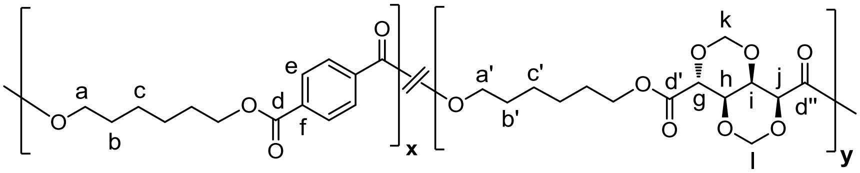
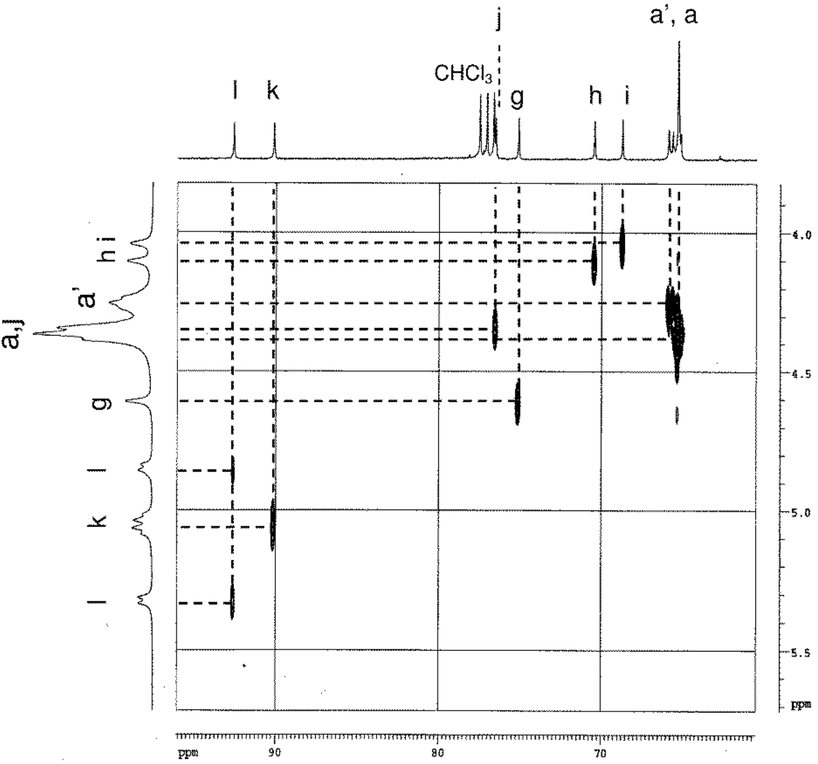
Supporting information



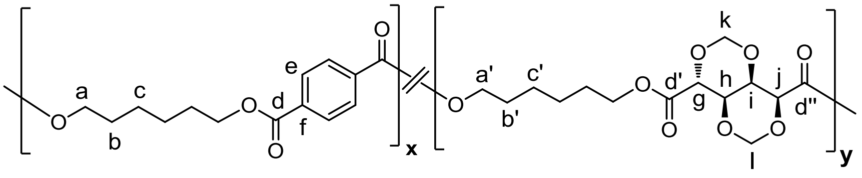


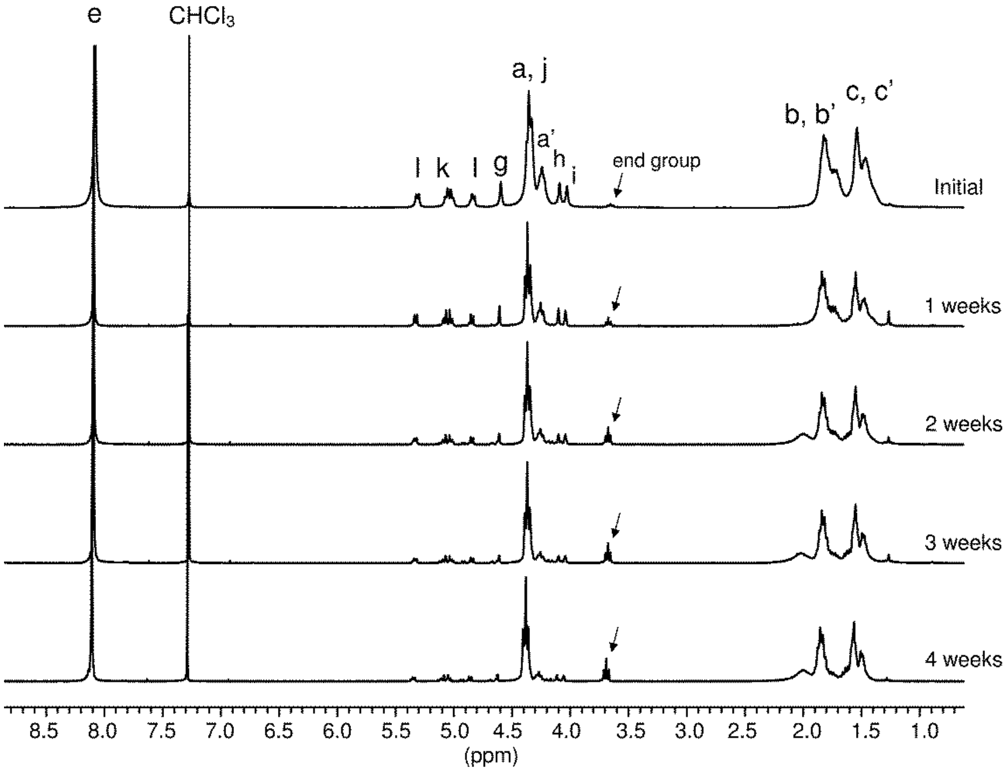
SI-Figure 1. COSY ^{1}H-^{1}H NMR spectra of PHT$_{70}$Glux$_{30}$ copolyester.





SI-Figure 2. ^{1}H-^{13}C HETCOR NMR spectra of PHT$_{70}$Glux$_{30}$ copolyester.





SI-Figure 3. Compared ^{1}H NMR after incubation with water at pH 2.0 at 80 ºC and initial spectra of $PHT_{70}Glux_{30}$ copolyesters.

Equations for the calculation of number average sequence lengths *n* of hexamethylene-terephthalate (HT) and hexamethylene-glucarate (HGlux) and the degree of randomness *R*.

$$n_{HT} = (N_{TT} + ½ (N_{TG}+N_{GT})) / ½ (N_{TG}+N_{GT}$$

$$n_{HGlux} = (N_{GG} + ½ (N_{TG}+N_{GT})) / ½ (N_{TG}+N_{GT})$$

$$R = (1/n_{HT}) + (1/n_{HGlux})$$

Eq. 1.

SI-Table 1. Composition and microstructure of the PHT_xGlux_y copolyesters.

Copolyesters	Composition[a]		Dyad content (%)[b]			Number average sequence lenghts		*R*
	X_T	X_{Glux}	TT	TG/GT	GG	n_{HT}	n_{HGlux}	
$PHT_{90}Glux_{10}$	0.90	0.10	78.3 (81.0)	21.7 (18.0)	0.0 (1.0)	8.22 (10.0)	1.0 (1.11)	1.12 (1.00)
$PHT_{85}Glux_{15}$	0.85	0.15	71.3 (72.25)	26.5 (25.5)	2.2 (2.25)	6.67 (6.38)	1.18 (1.17)	1.01 (1.00)
$PHT_{81}Glux_{19}$	0.81	0.19	64.8 (65.61)	31.8 (30.78)	3.4 (3.61)	5.07 (5.26)	1.21 (1.23)	1.00 (1.00)
$PHT_{70}Glux_{30}$	0.70	0.30	48.9 (49.0)	42.6 (42.0)	8.5 (9.0)	3.29 (3.33)	1.4 (1.43)	1.01 (1.00)
$PHT_{60}Glux_{40}$	0.60	0.40	36.8 (36.0)	47.6 (48)	15.6 (16)	2.55 (2.50)	1.66 (1.67)	0.99 (1.00)
$PHT_{50}Glux_{50}$	0.50	0.50	26.2 25.0	49.8 50.0	24.0 25.0	2.05 (2.0)	1.96 (2.0)	0.99 (1.00)

[a] Calculated from the ^1H NMR spectra.

[b] Experimental values were obtained by means of the equations mentioned in the text and using the ^{13}C NMR data. Theoretical values (in parentheses) were calculated on the basis of a statistical distribution using the copolyester composition data given in this Table.

SI-Table 2. Powder X-ray diffraction data of annealed polyesters

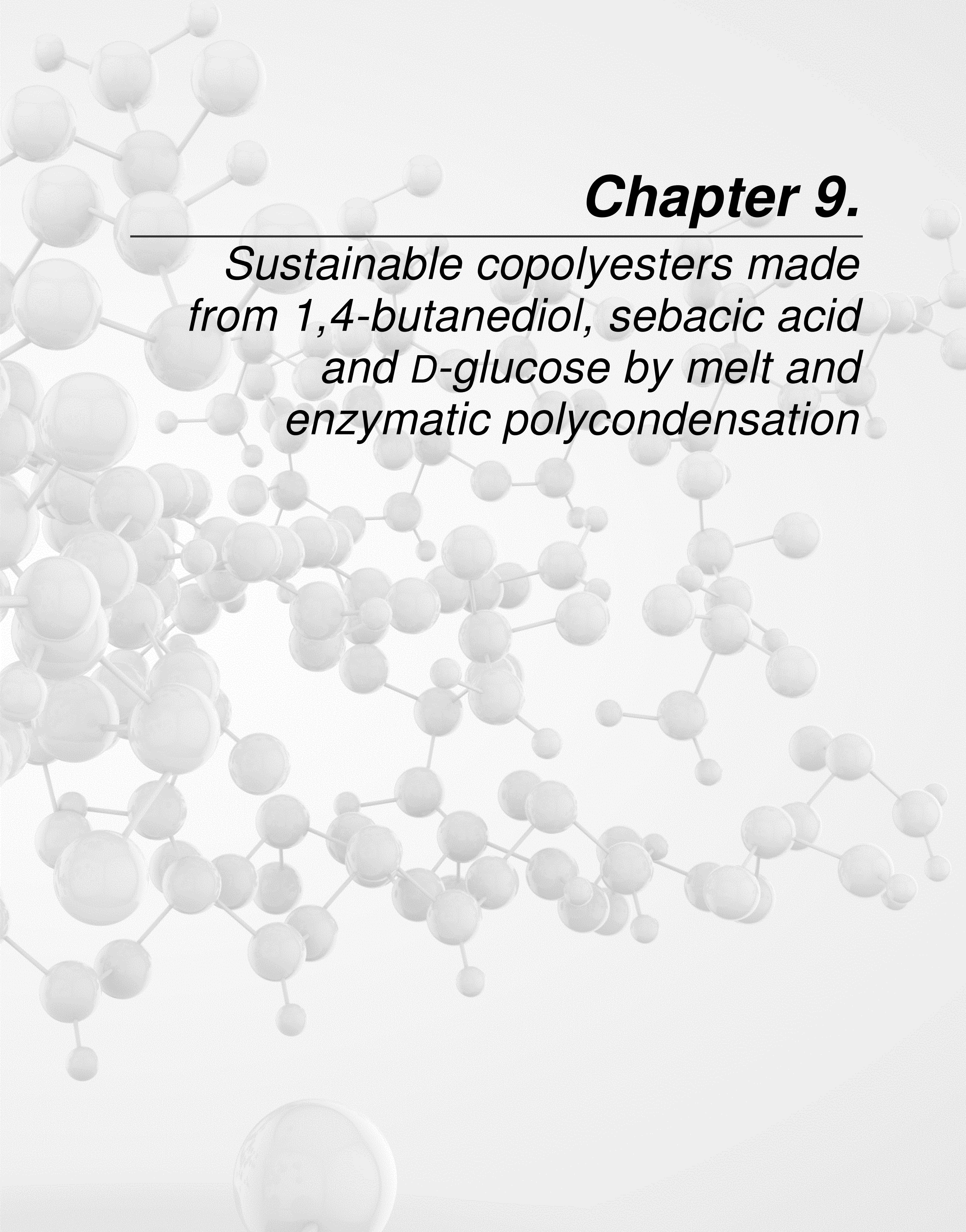
Polyester	*d*(Å)													X_c^b
Crystalline form	β	α	β	β	α	α	α	β	α	β	α	β	α	
PHT	5.47 s		5.15 m	4.85 s				4.13 s		3.94 w		3.71 s		51
PHT$_{90}$Glux$_{10}$		5.39 m		4.85 w	4.62 w	4.50 w	4.25 s		4.09 s		3.87 w	3.71 m	3.44 w	35
PHT$_{80}$Glux$_{20}$		5.39 m		4.85 w	4.63 w	4.51 w	4.25 s		4.10 s		3.87 w	3.71 w	3.44 w	35
PHT$_{60}$Glux$_{40}$						4.51 vw	4.25 vw	4.13 vw					3.44 vw	-

Bragg spacings measured on powder diffraction patterns obtained from annealed samples. Intensities visually estimated as follows: s, strong; m, medium; w, weak; vw: very weak.

[b] Crystallinity index calculated as the quotient between crystalline area and total area of WAXS profiles. Crystalline and amorphous areas were quantified using PeakFit v4.12 software.

Chapter 9.

Sustainable copolyesters made from 1,4-butanediol, sebacic acid and D-glucose by melt and enzymatic polycondensation



Sustainable copolyesters made from 1,4-butanediol, sebacic acid and D-glucose by melt and enzymatic polycondensation

Abstract

Biotecnologically accesible 1,4-butanediol and vegetal oil-based diethyl sebacate were copolymerized with bicyclic acetalized D-glucose derivatives both by melt polycondensation at high temperature and by enzymatic polycondensation in solution at mild temperatures mediated by supported *Candida antarctica*. Two series of random copolyesters (PB_xGlux_ySeb and $PBSeb_xGlux_y$) were prepared differing in which D-glucose derivative (Glux diol or Glux diester) was used as comonomer. The three parent homopolyesters PBSeb, PBGlux and PGluxSeb were also prepared by the two procedures. Both methods were found to be effective for polymerization although significant higher molecular weight were achieved by melt polycondensation. The thermal properties displayed by the copolyesters were largely dependent on their content in Glux units. The thermal stability of PBSeb was retained after copolymerization with Glux or even slightly increased whereas crystallinity and melting temperature were largely depressed. On the contrary, the glass-transition temperature noticeably increased with the presence of Glux. PGluxSeb distinguished in displaying higher T_g and T_m than PBSeb because a different crystal structure is adopted by this polyester. The degradability of PBSeb was enhanced by copolymerization, in particular the biodegradation assisted by lipases.

Article in preparation.

9.1. Introduction

The growing interest in the preparation of new chemicals and materials from renewable resources is leading to the development of a number of sustainable and biodegradable polymers that intend to replace those ones traditionally produced from fossil fuels.[1,2] Aliphatic polyesters are a family of biodegradable polymers that can be processed into various forms such as films, fibers and injection-molded devices.[3-5] Outstanding examples are poly(butylene succinate) (PBS), poly(L-lactic acid) (PLA), poly(*ε*-caprolactone) (PCL), poly(hydroxy alkanoate)s (PHA) among others. Some of these polyesters have found utility in the packaging sector and many of them have been intensively investigated for their potential as biomaterials to be used in the manufacture of temporal prostheses.

In this work the synthesis of novel aliphatic copolyesters entirely made from monomers of renewable origin is described. Mixtures of 1,4-butanediol, diethyl sebacate, and the bicyclic di-*O*-methylene diacetal of either D-glucitol or dimethyl D-glucarate are polycondensated in the melt to afford two series of copolyesters, namely PB_xGlux_ySeb and $PBSeb_xGlux_y$. In these acronymous, x and y denote the molar content of the copolyesters in butylene (B), sebacate (Seb) and glucose derived units (Glux), the later being either glucytilene ot glucarate units depending on whether the glucitol or dimethyl glucarate derivative is the used comonomer.

1,4-Butanediol is a very popular monomer that is extensively used in the synthesis of important polyesters. The traditional production of this diol is based on the use of petrochemical acetylene as raw material. Recently new processes based on direct fermentation of glucose or on hydrogenation of bio-succinic acid offer the opportunity to produce bio-based, renewable 1,4 butanediol.[6] Sebacic acid is an aliphatic dicarboxylic acid readily available from castor oil.[7] From the synthetic point of view, sebacic acid is preferred over short chain dicarboxylic aliphatic acids because intramolecular condensation leading to cyclization is in this case conveniently overcome. In the human body, sebacic acid is an intermediate product of the ω-oxidation of long chain monocarboxylic acids. The excellent biocompatibility exhibited by this diacid has made that the Food and Drug Administration (FDA) of USA has approved its use in the manufacture of biomaterials. Sebacic acid-based polyesters have found various applications both in the biomedical field as biodegradable delivery systems,[8-12] and in the packaging industry as component of blends for films.[13,14] The D-glucose derivatives used in this work are 2,4:3,5-di-*O*-methylene acetals of D-glucitol and D-glucaric acid aldaric compounds. The structure of these diacetals consists of a C6-segment backbone with four asymmetric carbons forming part of the two fused 1,3-dioxane rings and bearing two hydroxyl or methoxycarbonyl functions at the end positions. These bicyclic compounds are known to confer stiffness to polymer chains and to increase therefore the T_g of aliphatic copolyesters.[15]

Biodegradability is a distinguishing property of aliphatic polyesters that should be retained when modifications on the structure of the polymers are carried out with the purpose of improving other aspects of the material. The susceptibility of the polyester to biodegradation is enhanced when crystallinity is depressed and/or hydrophilicity is increased. The ability of the Glux units to enhance the biodegradability of polyesters and to increase at the same time their glass-transition temperature (T_g) is a well proven fact that has been recently reported for a number of cases. Other monocyclic and bicyclic, either independent or fused, diols or diacids derived from L-tartaric,[16] D-galactose,[17a] and D-mannose[17b] are known to be able of exerting a similar effect on both aliphatic and aromatic polyesters.

Poly(butylene sebacate) (PBSeb) has a T_g of -62 ºC, which is a very low value as to allow the use of the polyester in applications requiring a minimum of stiffness in the material.[18] In the light of the experience accumulated in the preparation of copolyesters containing sugar-based cyclic acetalized units, the replacement of either the diol or the diacid unit in PBSeb by Glux is expected to increase the T_g of the polyester without detriment of their biodegradability. Furthermore, given the bio-based origin of such comonomers, the sustainability of the polyester will remain ensured.

9.2. Experimental section

9.2.1. Materials and methods

Materials

2,4:3,5-Di-*O*-methylene-D-glucitol (Glux-diol) and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester) were synthesized following the procedure reported by Japu et al.[15] Diethyl sebacate (98%), 1,4-Butanediol (99%), and the catalyst dibutyl tin oxide (DBTO, 98%) were purchased from Sigma Aldrich. *Irganox 1010* and *Irgafos 126* antioxidants were generous gifts from BASF. Sodium trifluoroacetate (98%) used to stabilize 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and lipase from porcine pancreas (triacylglycerol lipase activity: 15-35 units/mg) was also purchased from Sigma-Aldrich. The solvents used for polycondensation, purification and characterization, such as diphenyl ether, chloroform, trifluoroacetic acid (TFA), methanol, diethyl ether, dichloracetic acid (DCA) and HFIP, were high purity grade and used as received. Lipase acrylic resin from *Candida Antarctica* (CALB) was purchased from Sigma Aldrich and it was dried under vacuum for 48 h previous to use.

Methods

Intrinsic viscosities were measured in DCA using an Ubbelohde microviscometer thermostated at 25 ± 0.1 ºC. Polymer solution concentrations ranged from 0.3 to 1 $g{\cdot}dL^{-1}$. Molecular weights were determined by GPC using a Waters equipment provided with a RI detector. HFIP containing sodium trifluoroacetate (6.8 g·L^{-1}) was the mobile phase. 100 µL of 0.1% (w/v) sample solution were injected and chromatographed with a flow of 0.5 mL·min^{-1}. HR5E Water linear Styragel column (7.8 x 300 mm) packed with cross-linked polystyrene and protected with a pre-column were used. Molar mass averages and their distributions were calculated against PMMA standards.

^{1}H and ^{13}C NMR spectra were recorded using a Bruker AMX-300 spectrometer operating at 300.1 and 75.5 MHz, respectively and running the samples at 25 ºC. The spectra were internally referenced with tetramethylsilane. Samples were prepared by dissolving the polymer in deuterated chloroform. For ^{1}H and ^{13}C analyses were used ~ 10 and 50 mg of sample in 1 mL of solvent, respectively. Sixty-four scans were recorded for ^{1}H, and between 5,000 and 15,000 scans were taken for ^{13}C with 32 and 64 K data points and relaxation delays of 1 and 2 s, respectively. Two-dimensional spectra (2D) as ^{1}H-^{1}H homonuclear (COSY) and ^{13}C-^{1}H heteronuclear shift correlation (HETCOR) were recorded by means of the *cosy* and *hxco* pulse sequences, respectively, implemented in the Bruker NMR instrument package.

Thermogravimetric analysis was carried out in a nitrogen atmosphere with a Perkin-Elmer TGA 6 thermobalance. Polymer samples with an approximate mass of 10 mg were degraded between 30 to 600 ºC at a heating rate of 10 ºC·min^{-1}.

The thermal behavior of the polymers was examined by differential scanning calorimetry (DSC) using a Perkin-Elmer Pyris 1 apparatus. Thermograms were obtained from 4-6 mg samples under a nitrogen flow of 20 mL·min^{-1}. Indium and zinc were used as standards for temperature and enthalpy calibrations. The melting temperature (T_m) was taken as the maximum of the endothermic peak appearing on heating traces recorded at 10 ºC·min^{-1}, and the glass transition temperature (T_g) was taken as the inflection point seen on heating traces recorded at 20 ºC·min^{-1} from samples quenched from the melt.

X-ray diffraction profiles were recorded on the PANalytical X'Pert PRO MPD θ/θ diffractometer using the Cu-Kα radiation of wavelength 0.1542 nm from powder samples coming directly from synthesis.

9.2.2. Synthesis of polyesters by melt polycondensation

The homopolyesters were prepared from two-component mixtures with the following compositions: poly(butylene sebacate) (PBSeb) from 1,4-butanediol and diethyl sebacate; poly(glucitylene sebacate), (PGluxSeb) from 2,4:3,5-di-*O*-methylene-D-glucitol (Glux-diol) and diethyl sebacate, poly(butylene glucarate) (PBGlux) from 1,4-butanediol and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate. PB_xGlux_ySeb copolyesters were obtained from three-component mixtures made of 1,4-butanediol, 2,4:3,5-di-*O*-methylene-D-glucitol and diethyl sebacate with the selected composition. In the abbreviated name of these copolyesters *x* and *y* subscripts indicate the mol percentages (%-mol) of butylene and 2,4:3,5-di-*O*-methylene-D-glucitylene units, respectively. In turn PBSeb$_x$Glux$_y$ copolyesters were obtained from three-component mixtures of 1,4-butanediol, diethyl sebacate and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate with the selected composition. In this case *x* and *y* subscripts refer to mol percentages of sebacate and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate units, respectively.

The reactions were performed in a three necked, cylindrical-bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a vacuum distillation outlet. In the both series it was used an excess of diol to diester and dibutyl tin oxide (DBTO) was added as a catalyst (0.6 mol% respect to diester). The apparatus was vented with nitrogen several times at room temperature in order to remove air and avoid oxidation during the polymerization. Transesterification reactions were carried out under a low nitrogen flow at the selected temperature. Polycondensation reactions were left to proceed at the selected temperature under a 0.03-0.06 mbar vacuum. Then, the reaction mixture was cooled to room temperature, and the atmospheric pressure was recovered with nitrogen to prevent degradation. The resulting polymers were dissolved in chloroform and precipitated in excess of methanol in order to remove unreacted monomers and formed oligomers. Finally, the polymer was collected by filtration, extensively washed with methanol, and dried under vacuum. These powdered samples coming directly from synthesis, were used throughout for the characterization performed in this work. The detailed conditions used for the synthesis of homopolyesters and copolyesters are the following:

PBSeb homopolyester. BD to diethyl sebacate molar ratio:1.5/1. Transesterification: 180 ºC, 3h. Polycondensation: 205 ºC, 2.5 h.

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 4.09 (bt, $-O\mathit{CH_2}CH_2$), 2.29 (t, $-OCOCH_2$), 1.70 (bt, $-OCH_2\mathit{CH_2}$), 1.61 (m, $-OCOCH_2\mathit{CH_2}$), 1.30 (s, $-OCOCH_2CH_2\mathit{CH_2CH_2}$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.5 MHz), δ (ppm): 173.7 (C=O), 63.6 (OCH_2), 34.2 ($-OCOCH_2$) 29.0 ($OCOCH_2CH_2\mathit{CH_2CH_2}$), 25.3 ($-OCH_2\mathit{CH_2}$), 24.9 ($-OCOCH_2\mathit{CH_2}$).

PB$_x$Glux$_y$Seb copolyesters. BD and Glux-diol mixture to diethyl sebacate molar ratio: 1.2/1.
PB$_{90}$Glux$_{10}$Seb: Transesterification: 170 ºC, 3.5 h. Polycondensation: 170 ºC, 5 h.
PB$_{80}$Glux$_{20}$Seb: Transesterification: 145 ºC, 7 h. Polycondensation: 145 ºC, 8 h.
PB$_{71}$Glux$_{29}$Seb: Transesterification: 140 ºC, 14 h. Polycondensation: 140 ºC, 10 h.
PB$_{65}$Glux$_{35}$Seb: Transesterification: 135 ºC, 18 h. Polycondensation: 135 ºC, 15 h.

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 5.21 (d, OCH_2O), 5.00 (s, OCH_2O), 4.78 (d, OCH_2O), 4.51-4.21 (m, $-O\mathit{CH_2}CH$ (Glux)), 4.16 (m, CH), 4.10 (bt, OCH_2 (B)), 3.87 (bt, CH), 3.73 (bs, CH), 3.56 (bs, CH), 2.29 (m, $-OCOCH_2$), 1.70 (bm, $-OCH_2\mathit{CH_2}$), 1.61 (m, $-OCOCH_2\mathit{CH_2}$), 1.30 (s, $-OCOCH_2CH_2\mathit{CH_2CH_2}$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.5 MHz), δ (ppm): 173.5-173.3 (C=O), 92.9

(OCH_2O), 88.4 (OCH_2O), 75.6 (CH), 73.8 (CH), 71.0 (CH), 67,3 (CH), 63.7 (OCH_2), 63.1 (OCH_2), 60.4 (OCH_2), 34.2-34.0 ($-OCOCH_2$), 29.1 (CH_2), 25.4 (CH_2), 24.9-24.8 (CH_2).

PBSeb$_x$Glux$_y$ copolyesters. BD to diethyl sebacate and Glux-diester mixture: 1.5/1. Transesterification: 175 ºC, 4.5-15 h. Polycondensation: 175 ºC, 10-24 h. The reaction times increased with de % Glux content.

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 5.30 (d, OCH_2O), 5.06-4.99 (2dd, OCH_2O), 4.83 (d, OCH_2O), 4.59 (bs, CH), 4.33 (bs, CH), 4.27 (bt, OCH_2 (Glux)), 4.09 (m, OCH_2 (B), CH), 4.02 (bs, CH), 2.28 (t, $-OCOCH_2$), 1,75-1.66 (m, $-OCH_2\mathit{CH_2}$), 1.60 (m $-OCOCH_2\mathit{CH_2}$), 1.29 (s, $-OCOCH_2CH_2\mathit{CH_2CH_2}$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.5 MHz), δ (ppm): 173.8-167.1 (C=O), 92.5 (OCH_2O), 90.1 (OCH_2O), 76.4 (CH), 75.4 (CH), 70.3 (CH), 68.7 (CH), 65.5-63.4 (OCH_2), 34.2 (CH_2) 29.1 (CH_2), 25.3-25.1 (CH_2), 24.9 (CH_2).

PBGlux homopolyester. 1,4-butanediol to dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate molar ratio: 2.2/1 Transesterification: 170 ºC, 8 h. Polycondensation: 170 ºC, 8 h. ^{1}H NMR ($CDCl_3$/TFA, 300 MHz), δ (ppm): 5.35 (d, OCH_2O), 5.20-4.85 (2dd, OCH_2O), 4.90 (d, OCH_2O), 4.74 (s, CH), 4.50-4.70 (m, CH), 4.52-4.20 (m, $-O\mathit{CH_2}CH_2$, CH), 4.12 (s, CH), 1.79 (s, $-OCH_2\mathit{CH_2}$). ^{13}C{^{1}H}-NMR ($CDCl_3$/TFA, 75.5 MHz), δ (ppm): 172.5-171.3 (C=O), 92.3 (OCH_2O), 90.2 (OCH_2O), 76.2 (CH), 75.0 (CH), 70.3 (CH), 68.7 (CH), 66.9-66.1 ($O\mathit{CH_2}CH_2$), 24.7 ($OCH_2\mathit{CH_2}$).

9.2.3. Synthesis of polyesters by enzymatic polycondensation

In order to find the solvent adequate for the enzymatic polycondensation of mixtures containing Glux-diol, which was hampered by the low solubility of this compound in organic solvents, several high boiling point solvents were essayed taken as reference the preparation of the copolyester PB$_{90}$Glux$_{10}$Seb. Reaction conditions used in these previous essays and obtained results are summarized in Table 1.

Table 1. Polymerization reaction of PB$_{90}$Glux$_{10}$Seb in different solvents.

Copolymer	Solvent		
	Dodecane	Diethylene glycol dimethyl ether (Diglyme)	Diphenyl ether
PB$_{90}$Glux$_{10}$Seb	No reaction	No reaction	Polymerization
Reaction conditions: 10% wt CALB, 10% molecular sieves, 90 ºC (5 hours, atmospheric pressure, 72 h p = 0.03-0.05 bar)			

The experimental details for the synthesis of PBSeb$_{90}$Glux$_{10}$ were the following: 0.2 g of CALB (10 wt % of total monomer), 5.78 mmol of diethyl sebacate (1.345 g), and 5.78 mmol of Glux-diol (0.1516 g), 5.85 mmol of BD (0.5277 g) and molecular sieves (~1.5 g) were mixed with

6 mL diphenyl ether. The mixture was magnetically stirred and heated at 85ºC. The reaction was carried out under N_2 atmospheric pressure for the 5 h to convert the monomers to oligomers. In the second step, the pressure was reduced to 0.1 bar during 12 h and after that it was reduced to below 0.04 for 72 h. The mild vacuum was only to eliminate the ethanol that forms in the transesterification reaction. At the end of reaction the mixture was dissolved in chloroform and then filtered to remove the enzyme catalyst and the molecular sieves. The chloroform solution was slowly added to methanol under stirring to precipitate the copolyester as a white crystalline product. These conditions were then used for the synthesis of other copolyesters and homopolyesters.

9.3.4. Hydrolytic and enzymatic assays

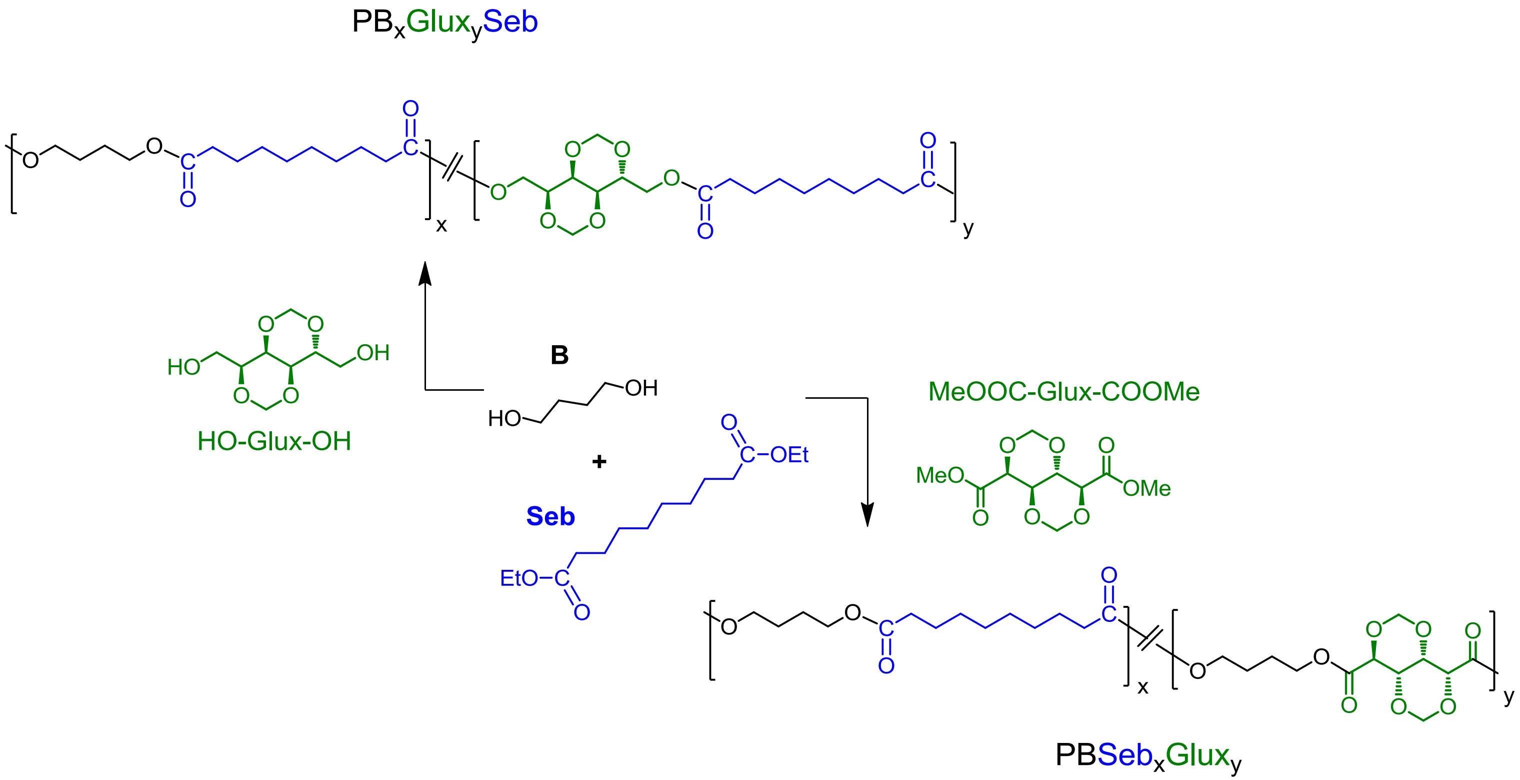
Both hydrolytic and enzymatic degradation essays were carried out on films of polyesters and copolyesters with a thickness of about 200 µm which were prepared by melt compression followed by quenching into ice-cold water. The films were cut into 10 mm diameter disks and dried under vacuum to constant weight, which finally remained between 20 and 30 mg. The disks were individually immersed in vials containing 10 mL of either sodium citric acid buffer pH 2.0 (hydrolytic degradation), or sodium phosphate buffer pH 7.4 containing 10 mg of porcine pancreas lipases (enzymatic degradation), and left incubating at 37 ºC for four weeks. The buffered enzyme solution was replaced every 72 h to maintain the enzyme activity. After scheduled periods of time, the disks were withdrawn from the incubation medium, washed thoroughly with distilled water, and dried to constant weight.

9.3. Results and discussion

9.3.1. Melt polycondensation-synthesis and microstructure

In this work two series of copolyesters of PBSeb using as comonomers 2,4:3,5-di-*O*-methylene acetals derived from D-glucose here were synthesized (Scheme 1). The difference between the two series lies in which unit, diol or diacid, was replaced in PBSeb by the Glux unit. The polymerizations reactions took place in the melt in the total absence of solvents in order to imitate as far as possible the conditions usually applied in the industrial practice.

In the synthesis of the PB_xGlux_ySeb series, BD monomer was replaced by Glux-diol so poly(butylene-*co*-glucitylene sebacate) copolyesters with contents in Glux units from 10 to 35% were prepared in addition to the homopolyester made entirely of Glux units. In the first step, transesterification of diethyl sebacate leading to B_xGlux_ySeb oligomers was accomplished at temperatures between 135-170 ºC under atmospheric pressure with formation of ethanol, which



Scheme 1. Polymerization reactions leading to PB$_x$Glux$_y$Seb and PBSeb$_x$Glux$_y$.

was removed by distillation. During the transesterification step it was noticed that the “solubilty” of Glux-diol in the system wasn´t complete, so some time was needed until the the reaction mixture became homogenous. As the monomers reacted it could be noticed that the appearance of reaction mixture was changing from transparent to opaque. The oligomers containing glucitylene units were insoluble and “precipitated” from the system. Since Glux sugar monomer or oligomers containing are not miscible, they were directly exposed to the necessary temperature and then it was lowered gradually according to composition to minimize thermal degradation. Polycondensation of the oligomers leading to PB_xGlux_ySeb copolyesters took place in the second step at 130-170 ºC under vacuum with releasing of excess of diols. It was noticed a change of the appearance of the mass from opaque to transparent as the reaction was evolving.

For comparison purposes, the parent homopolyesters were also prepared. PBSeb was obtained from 1,4-butanediol and diethyl sebacate using the same polycondensation procedure as for copolyesters. Unfortunately the synthesis of PGluxSeb homopolyester was not possible by melt polymerization because the monomers were not miscible between them even when the temperature was increased. Glux-diol monomer still remained solid although the temperature was increased. PGluxSeb could however be prepared in solution by enzymatic polymerization as it will be discussed below. On the other hand, for the synthesis of the $PBSeb_xGlux_y$ copolyesters, the diethyl sebacate was replaced by Glux-diester so poly(butylene sebacate-*co*-glucarate) copolyesters with contents in Glux units from 9 to 50% were prepared. Reactions took place at 175 ºC applying longer reaction times as the Glux-diester content increased. Since in this case BD and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate were miscible, the PBGlux homopolyester could be synthesized in the melt. Synthesis results obtained for the two series are compared in Table 1. All copolyesters were prepared in yields around 80-90 % after purification with intrinsic viscosities of 0.53-0.87 $dL \cdot g^{-1}$, weight-average molecular weights between 25,000 and 41,100 g mol^{-1} and polydispersities in the 2.2-2.4 range.

The chemical constitution of the polyesters was ascertained by NMR spectroscopy. The illustrative ^1H and ^{13}C spectra of representative members of each series are shown in Figures 1 and 2. The 2D NMR spectra (*cosy* and *hetcor*) used for the assignment of the peaks are provided in the Electronic Supplementary Information (Figures SI-1 to 4) document linked to this paper. The co-monomeric composition of the PB_xGlux_ySeb copolyesters was determined by comparing the integrated signals at 4.55-3.50 ppm arising from protons contained in the two repeating units of the copolyester (4Hx+8Hy) to the signals at 5.3-4.7 ppm (4Hy) that exclusively correspond to acetals of Glux units. For the $PBSeb_xGlux_y$ copolyesters the composition determination was similarly done but considering the signals (4Hx+12Hy) at 5.4-4.0 ppm arising from the Glux repeating units and the signal at 2.3 ppm emerging from the protons of sebacate units (4Hx). The percentage of sugar units present in the copolyester was estimated by applying simple proportion

Table 1. Composition and molecular weight of PB$_x$Glux$_y$Seb and PBSeb$_x$Glux$_y$.

Copolyester	Yield (%)	Composition								Molecular weight			
		Feed				Copolyester[a]							
		Diol		Diacid		Diol		Diacid					
		[B]	[Glux]	[Seb]	[Glux]	[B]	[Glux]	[Seb]	[Glux]	$[\eta]$[b]	M_n[c]	M_w[c]	$Đ$[c]
PBSeb	93	100	0	100	0	100	0	100	0	0.90	19,800	43,500	2.2
PB$_x$Glux$_y$Seb													
PB$_{90}$Glux$_{10}$Seb	89	90	10	100	0	90	10	-	-	0.87	17,900	41,100	2.3
PB$_{80}$Glux$_{20}$Seb	87	80	20	100	0	80	20	-	-	0.79	17,100	37,700	2.2
PB$_{71}$Glux$_{29}$Seb	85	70	30	100	0	71	29	-	-	0.86	17,800	41,000	2.3
PB$_{65}$Glux$_{35}$Seb	80	60	40	100	0	65	35	-	-	0.53	10,400	25,000	2.4
PGluxSeb*	70	0	100	100	0	0	100	-	-	0.40	5,600	11,200	2.0
PBSeb$_x$Glux$_y$													
PBSeb$_{91}$Glux$_9$	87	100	0	90	10	-	-	91	9	0.70	14,300	33,000	2.3
PBSeb$_{80}$Glux$_{20}$	86	100	0	80	20	-	-	80	20	0.74	15,800	34,900	2.2
PBSeb$_{72}$Glux$_{28}$	86	100	0	70	30	-	-	72	28	0.70	14,300	33,000	2.3
PBSeb$_{60}$Glux$_{40}$	83	100	0	60	40	-	-	60	40	0.50	10,200	23,400	2.3
PBSeb$_{50}$Glux$_{50}$	80	100	0	50	50	-	-	50	50	0.67	13,300	31,900	2.4
PBGlux	50	100	0	0	100	-	-	0	100	0.46	6,900	16,500	2.4

[a] Molar composition determined by integration of ^{1}H NMR spectra.

[b] Intrinsic viscosity in dL·g^{-1} measured in DCA at 25 ºC.

[c] Number and weight average molecular weights in g·mol^{-1}, and dispersities measured by GPC in HFIP against PMMA standards.

*Polymer synthesized by enzymatic polymerization.

calculations. It was found that the content of Glux units in PB$_x$Glux$_y$Seb copolyesters was lower than in the feed probably due to the poor miscibility of the monomers. In the case of PBSeb$_x$Glux$_y$ the content of sugar unit incorporated into the polymer was almost the same as in the feed.

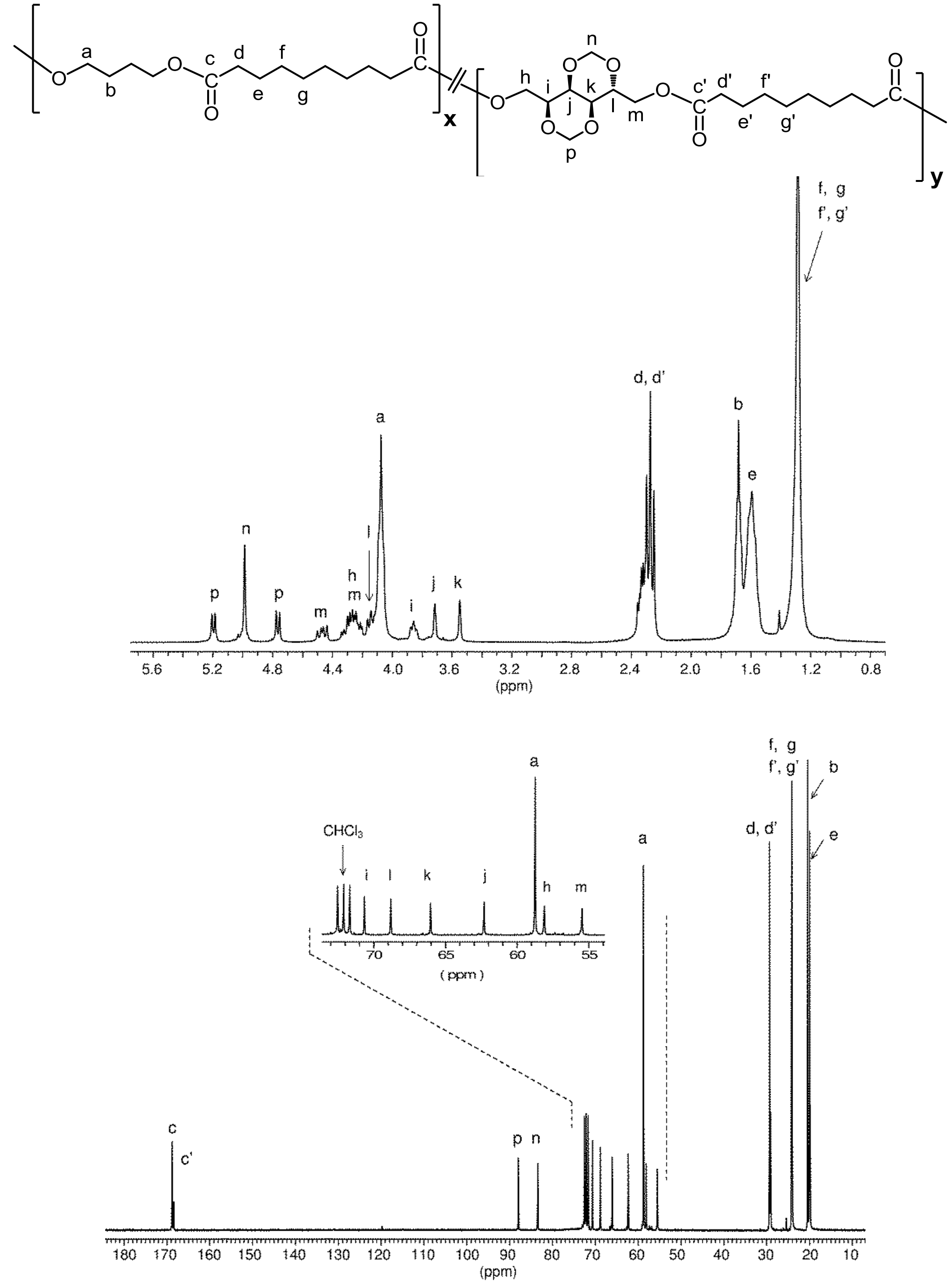


Figure 1. ^{1}H (top) and ^{13}C (bottom) NMR spectra of PB$_{71}$Glux$_{29}$Seb copolyester. (*) CH$_2$OH end groups

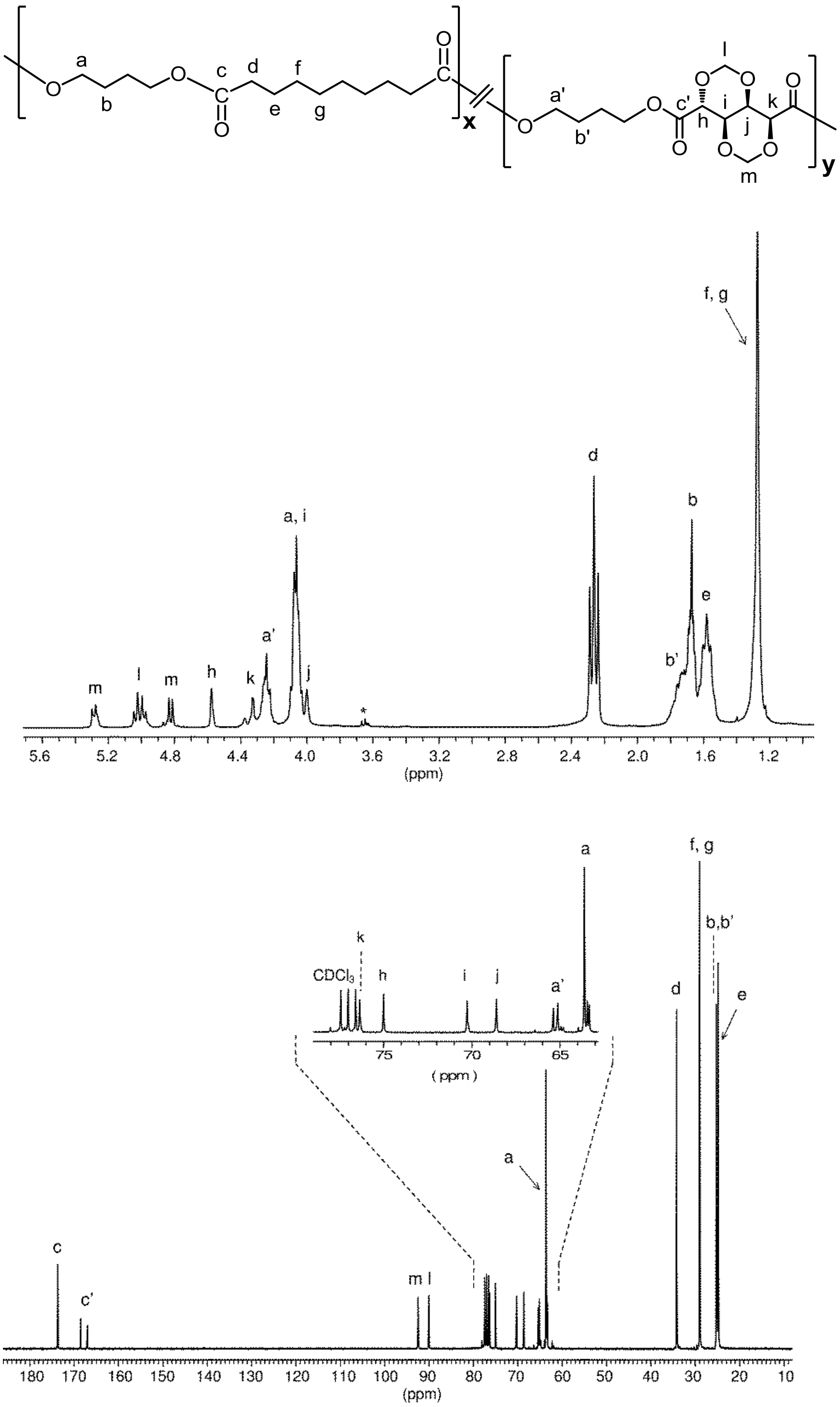


Figure 2. ^{1}H (top) and ^{13}C (bottom) NMR spectra of PBSeb$_{72}$Glux$_{28}$ copolyester.

Microstructure

The microstructure of the copolyesters was analyzed by ^{13}C NMR. In the case of the PB$_x$Glux$_y$Seb series, the microstructure could not be determined because of the large length of the sebacate unit weakens the environmental mutual effect of butylene and glucitylene units so the spectra of these copolyesters are no able to reveal comonomer sequence distributions. Regarding the PBSeb$_x$Glux$_y$ copolyesters, the ^{13}C NMR spectra of this series showed complex signals for the 1,4-butylene units, revealing that in this case the methylene carbons are sensitive to sequence effects. Figure 3 reveals 9 peaks, two of them overlapped, appearing within 65.6-63.3 ppm interval which correspond to the four types of dyads (SebSeb, GluxSeb/SebGlux, GluxGlux) that are possible along the copolyester chain. By Lorentzian deconvolution of the peaks using the WinNMR software could be calculated the number average sequence lengths *n* of butylene-sebacate (BS) and butylene-glucarate (BG) units and the degree of randomness (*R)* as well.

The equations used in this case for calculating the sequence lengths and randomness were the following:

$$n_{BS} = (N_{SS} + \tfrac{1}{2}(N_{SG}+N_{GS})) / \tfrac{1}{2}(N_{SG}+N_{GS})$$

$$n_{BGlux} = (N_{GG} + \tfrac{1}{2}(N_{SG}+N_{GS})) / \tfrac{1}{2}(N_{SG}+N_{GS})$$

$$R = (1/n_{BS}) + (1/n_{BG})$$

The results from these calculations (Table 2) showed that the sequence distribution in PBSeb$_x$Glux$_y$ copolyesters is random with values of *R* very close to unity.

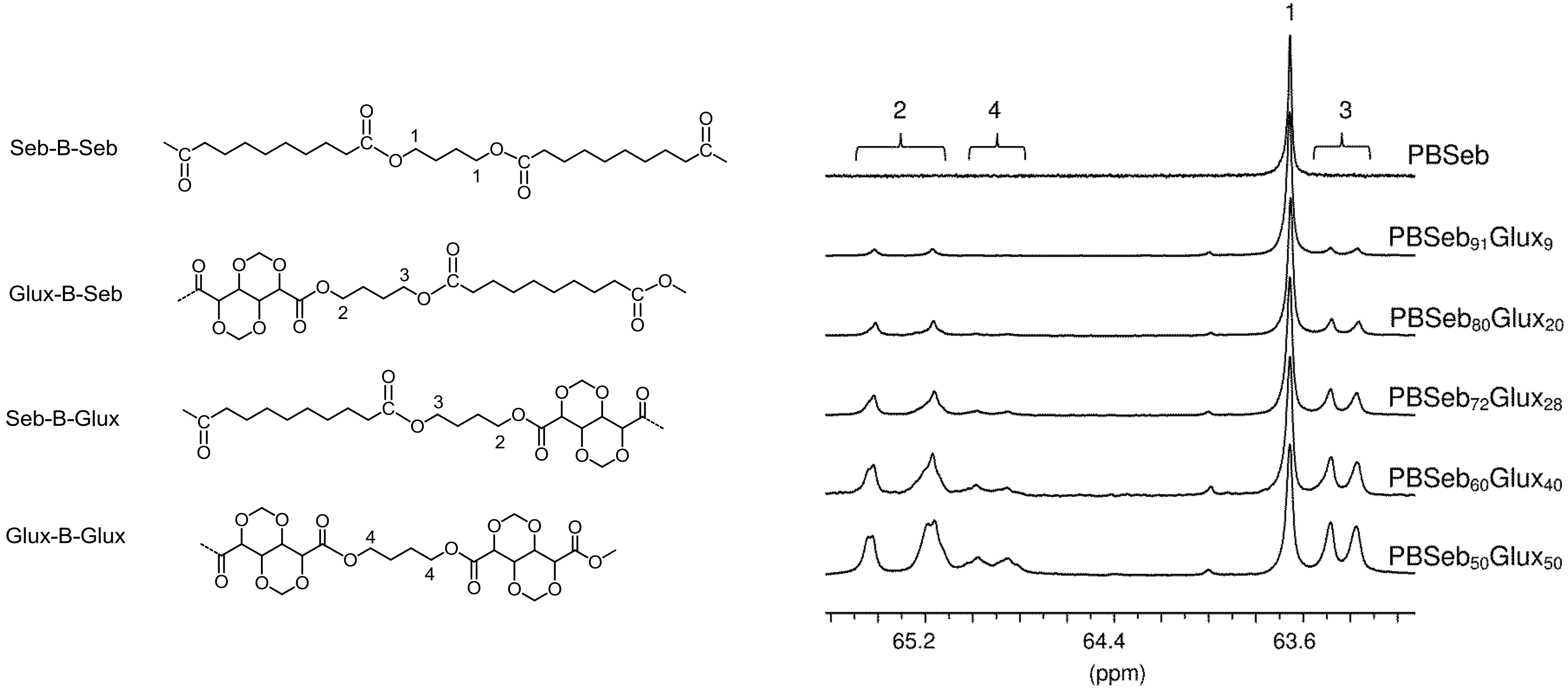


Figure 3. a) The four possible dyads occurring in PBSeb$_x$Glux$_y$ copolyesters. b) ^{13}C NMR spectra in the region of the first BD methylene for PBSeb$_x$Glux$_y$ copolyesters and homopolyesters.

Table 2. Composition and microstructure of the PBSeb$_x$Glux$_y$ copolyesters.

Copolyestes	Composition^a		Dyad content (%)^b			Number average sequence lenghts ^{b}		R
	X_{Seb}	X_{Glux}	SS	SG/GS	GG	n_{BS}	n_{BGlux}	
PBSeb$_{91}$Glux$_9$	0.91	0.09	81.3 (82.81)	18.7 (16.38)	0.0 (0.81)	9.69 (11.15)	1.0 (1.10)	1.01 (1.0)
PBSeb$_{80}$Glux$_{20}$	0.80	0.20	63.3 (64.0)	32.5 (32.0)	4.2 (4.00)	4.90 (5.0)	1.26 (1.25)	0.99 (1.0)
PBSeb$_{72}$Glux$_{28}$	0.72	0.28	49.1 (51.84)	42.3 (40.32)	8.6 (7.84)	3.32 (3.57)	1.40 (1.39)	1.01 (1.0)
PBSeb$_{60}$Glux$_{40}$	0.60	0.40	34.0 (36.0)	48.5 (48.0)	17.5 (16.0)	2.40 (2.50)	1.72 (1.67)	1.0 (1.0)
PBSeb$_{50}$Glux$_{50}$	0.50	0.50	24.8 (25.0)	49.7 (50.0)	25.5 (25.0)	2.0 (2.0)	2.0 (2.0)	1.00 (1.0)

^{a}Calculated from the ^{1}H NMR spectra.

^{b}Experimental values were obtained by deconvolution of ^{13}C NMR peaks corresponding to the first oxybutylene carbon and by means of the equations mentioned in the text.

Theoretical values (in parentheses) were calculated on the basis of a statistical distribution using the copolyester composition data given in this Table.

The sort names of dyads are detailed as follows **SS**: Seb-B-Seb; **SG**: Seb-B-Glux; **GS**: Glux-B-Seb; **GG**: Glux-B-Glux. Number average sequence lengths *n* of buthylene-sebacate (BS) and buthylene-glucarate (BGlux).

R: Degree of randomness.

9.3.2. Enzymatic synthesis with *Candida antarctica*

Given the bio-based character of the system under study and the vulnerability of Glux monomers to high temperatures, the *s*ynthesis of the polyesters and copolyesters described above was attempted by polycondensation catalyzed by *Candida antarctica* lipase.

First, an exploratory series of essays varying in solvent, temperature, and enzyme amount were carried out for the preparation of PB$_{90}$Glux$_{10}$Sb in order to optimize synthesis conditions. From these experiments it was concluded that diphenyl ether was the suitable solvent for these polymerizations because the initially non soluble Glux-diol became solubilised after 5 h of reaction. At preselected time intervals during the transesterification step there samples were withdrawn and analyzed by NMR to follow the evolution of monomers with time. No significant changes were observed after 2 h of reaction and the persistence of signals corresponding to diethyl sebacate indicated that the reaction was very slow. It was noticed also that raising the amount of either solvent or enzyme did not affect the reaction and made more difficult the recovery of the polymer by precipitation. The yields were in the range of 10-20 %. A summary of the conditions essayed and results obtained are provided in Table S-1 of the ESI file.

The optimized results achieved in the synthesis of the two series of copolyesters containing Glux units are presented in Table 3. All copolyesters were prepared in yields around 30-70 % after purification with intrinsic viscosities oscillating between 0.3 and 0.44 dL·g^{-1}, weight-average molecular weights at the proximities of 10,000 g mol^{-1} and polydispersities around 2. Molecular weights and yields for PBSeb$_x$Glux$_y$ were slightly lower than for PB$_x$Glux$_y$Seb copolyesters, the two parameters decreasing monotonically with the glucarate content in both series. In line with such results, the synthesis of PBGlux homopolyester was not feasible. A sound explanation for the poorer reactivity observed for Glux-diester is that the proximity of the bulky fused cycles to the carboxylate function hinders the access of this group to the active site of the enzyme.

The composition of the copolyesters was determined by NMR by using the same approach followed for the analysis of the same copolyesters prepared by melt polycondensation which was described in the previous section. In both series the content of the copolyesters in Glux units was lower than in the feeds used for their preparation, which is consistent with the relative lower reactivity expected for the functions neighboring bulky groups. The microstructure of PBSeb$_x$Glux$_y$ copolyesters was elucidated by ^{13}C NMR in the same way as it was made before with those prepared by melt polycondensation allowing a comparison between the two series. Values for number average sequence lengths and randomness degrees for enzymatically produced PBSeb$_x$Glux$_y$ copolyesters are given in Table S-2 in the ESI document. *R* values very close to unity were found for all the examined compositions indicating that, similarly to copolyesters obtained by bulk polycondensation, the comonomer distribution in the copolyester chain is essentially random.

In Figure 4, the ^{13}C NMR peaks used for microstructure determination are compared for two copolyesters prepared by each method with practically the same composition. The extremely close similarity between the two spectra illustrate vividly that the same microstructure is shared by the two copolyesters. Since the microstructure of the PB$_x$Glux$_y$Seb series cannot be determined, a similar study was not feasible for this series.

Table 3.Composition and molecular weight of PB$_x$Glux$_y$Seb and PBSeb$_x$Glux$_y$ prepared by enzymatic polymerization.

Copolyester	Yield (%)	Composition								Molecular weight			
		Feed				Copolyester^a							
		Diol		Diacid		Diol		Diacid					
		[B]	[Glux]	[Seb]	[Glux]	[B]	[Glux]	[Seb]	[Glux]	$[\eta]^b$	M_n^c	M_w^c	$Đ^c$
PBSeb	80	100	0	100	0	100	0	100	0	0.53	6,900	13,100	1.9
PB$_x$Glux$_y$Seb													
PB$_{92}$Glux$_{8}$Seb	73	90	10	100	0	90	10	-	-	0.44	5,600	12,400	2.2
PB$_{87}$Glux$_{13}$Seb	74	80	20	100	0	87	13	-	-	0.41	5,500	11,500	2.1
PB$_{78}$Glux$_{22}$Seb	72	70	30	100	0	78	22	-	-	0.43	5,900	12,400	2.1
PB$_{74}$Glux$_{26}$Seb	71	60	40	100	0	74	26	-	-	0.40	5,400	11,200	2.2
PB$_{70}$Glux$_{30}$Seb	71	50	50	100	0	70	30	-	-	0.38	4,800	10,500	2.2
PGluxSeb	70	0	100	100	0	0	100	-	-	0.40	5,600	11,200	2.0
PBSeb$_x$Glux$_y$													
PBSeb$_{93}$Glux$_{7}$	70	100	0	90	10	-	-	93	7	0.42	5,600	11,700	2.1
PBSeb$_{85}$Glux$_{15}$	68	100	0	80	20	-	-	85	15	0.39	5,300	11,700	2.2
PBSeb$_{73}$Glux$_{27}$	60	100	0	70	30	-	-	73	27	0.38	5,000	10,600	2.1
PBSeb$_{66}$Glux$_{34}$	40	100	0	60	40	-	-	66	34	0.37	4,700	10,400	2.2
PBSeb$_{55}$Glux$_{45}$	35	100	0	50	50	-	-	55	45	0.30	4,000	8,800	2.2

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

^{b}Intrinsic viscosity in dL·g^{-1} measured in DCA at 25 ºC.

^{c}Number and weight average molecular weights in g·mol^{-1}, and dispersities measured by GPC in HFIP against PMMA.standards.

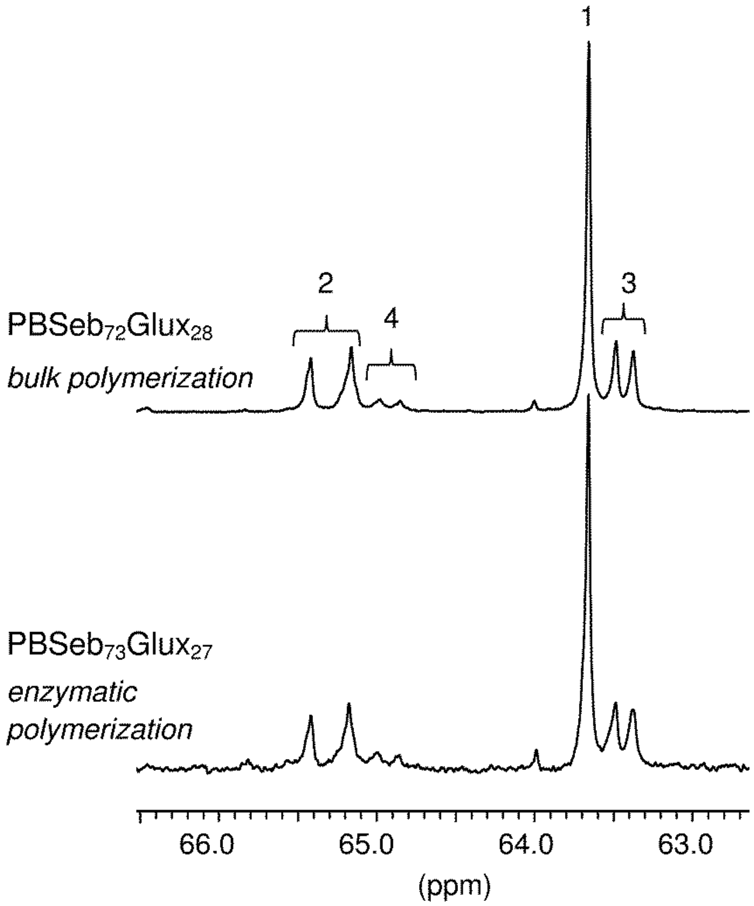


Figure 4. ^{13}C NMR spectra in the region of the first BD methylenes for two PBSeb$_x$Glux$_y$ copolyesters prepared by melt polycondensation and enzymatic polymerization, respectively.

9.3.3. Thermal properties

The thermal behaviour of the PB$_x$Glux$_y$Seb and PBSeb$_x$Glux$_y$ series that were prepared by melt polycondensation has been comparatively studied by TGA and DSC; the thermal parameters resulting from these analyses are given in Table 3 where the corresponding data for the parent homopolyesters PBSeb, PGluxSeb and PBGlux are also included for reference.

The TGA traces recorded from the whole sets of PB$_x$Glux$_y$Seb and PBSeb$_x$Glux$_y$ copolyesters are comparatively depicted in Figure. 5. The derivative curves of PBSeb, PGluxSeb and PBGlux are shown in Figure 5c. Thermal decomposition of PBSeb was observed to occur in a single stage with the maximum rate taking place at 421ºC ($^{max}T_d$). Decomposition of

PB_xGlux_ySeb copolyesters takes place also in one stage at temperatures steadily increasing as butanediol units are replaced by glucitylene units achieving a ${}^{max}T_d$ of 427 ºC for a 35% of substitution degree. PGluxSeb showed a high thermal stability with ${}^{max}T_d$ of 432 in spite that its molecular weight was no high. These results evidence that the incorporation of Glux-diol units in the PBSeb chain enhanced the thermal stability of the resulting copolyesters.

On the other hand $PBSeb_xGlux_y$ copolyesters showed a more complex behavior in their response to heating. In contrast with PB_xGlux_ySeb, the replacement of the sebacate units by the glucarate units had a slight decreasing effect in both onset and maximum decomposition rate temperatures. Furthermore, decomposition was found to proceed along two well differentiated stages with decomposition rates taking place at the proximities of 350 and 410 ºC, respectively. In the first stage the appearance of a shoulder that increased with the glucarate content was observed. According to this behavior and taking into account the TGA data for the parent homopolyesters, it can be interpreted that the two observed decomposition steps observed for these copolyesters correspond to the decomposition of glucarate and sebacate sequences.

The first heating DSC traces of the two series of copolyesters registered from the two series of copolyesters are depicted in Figure 6. Endothermic peaks representative of melting are observed for all composition in the PB_xGlux_ySeb series including the homopolyester PGluxSb although with a decreasing trend in both temperature and enthalpy as the content in glucitylene units is increasing. The same trend is observed for the $PBSeb_xGlux_y$ series although in this case the depressing effect of the incorporation of Glux units is more pronounced. In fact, no sign of melting was detected for the copolyester $PBSeb_{50}Glux_{50}$ and neither for the homopolyester PBGlux.

The crystal structure present in these copolyesters was examined by XRD, and the powder WAXS registered from semicrystalline samples are shown in Figure 7. The crystalline structure adopted by PBSeb which is characterized by two sharp reflections at 3.63 and 4.17 Å seems to be retained in all the copolyesters for whatever composition. As it has been repeatedly reported for other copolyesters containing bicyclic acetalized alditylene or aldarate units,[15,17] the presence of crystallinity in these systems can be reasonably accounted by assuming that only the homogeneous sequences of PBSeb are integrating the crystal phase whereas those segments containing Glux units are rejected to the amorphous phase. Conversely, the homopolyester PGluxSeb shows a rather different diffraction profile consisting of broad peaks centered on 15, 4.9 and 4.4 Å indicating the presence of a different crystal structure. Particularly interesting is the scattering observed in the low angle region of this profile which is indicative of a repeating distance compatible with the molecular chain periodicity calculated for the PGluxSeb molecule.

Table 3. Thermal properties of PBSeb, PGluxSeb, PBGlux, and the PB_xGlux_ySeb, $PBSeb_xGlux_y$ copolyesters.

Polyester	TGA			DSC								
					First Heating[e]		Cooling[e]		Second Heating[e]			
	T_d[a] (°C)	T_{ds}[b] (°C)	RW[c] (%)	T_g[d] (°C)	T_m (°C)	ΔH_m ($J\cdot g^{-1}$)	T_c (°C)	ΔH_c ($J\cdot g^{-1}$)	T_{cc} (°C)	ΔH_{cc} ($J\cdot g^{-1}$)	T_m (°C)	ΔH_m ($J\cdot g^{-1}$)
PBSeb	395	421	3	-62*	65	101	50	82	-	-	65	88
PB_xGlux_ySeb												
$PB_{90}Glux_{10}Seb$	393	420	5	n.d.	56	85	39	63	-	-	56	67
$PB_{80}Glux_{20}Seb$	393	419	5	n.d.	49	64	23	46	-	-	45	49
$PB_{71}Glux_{29}Seb$	397	423	5	-14	42	42	-	-	-3	12	34	32
$PB_{65}Glux_{35}Seb$	401	427	2	n.d.	40	36	-9	10	1	11	33	28
*PGluxSeb	398	432	6	28	119	32	80	33	-	-	118	30
$PBSeb_xGlux_y$												
$PBSeb_{91}Glux_9$	381	372/**418**	3	n.d.	56	81	34	62	-	-	54	62
$PBSeb_{80}Glux_{20}$	361	367/**417**	3	n.d.	50	61	21	43	-	-	48	43
$PBSeb_{72}Glux_{28}$	356	367/**419**	6	-31	43	45	-	-	4	20	35	26
$PBSeb_{60}Glux_{40}$	364	385/**419**	3	-25	43	17	-	-	-	-	-	-
$PBSeb_{50}Glux_{50}$	330	348/**417**	13	-4	-	-	-	-	-	-	-	-
PBGlux	274	345	11	77	-	-	-	-	-	-	-	-

[a]Temperature at which a 10 % weight loss was observed in the TGA traces recorded at 10 °C min^{-1}. [b]Temperature of maximum degradation rate. [c]Remaining weight at the 600ºC. [d]Glass-transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 °C min^{-1}. [e]Melting (T_m) and crystallization (T_c) temperatures and their respective enthalpies (ΔH_m, ΔH_c) measured by DSC at heating/cooling rates of 10 °C min^{-1}; T_{cc}, ΔH_{cc} – cold crystallization. *Polymer synthesized by enzymatic polymerization. *Data for T_g of PBSeb is taken from literature.[15]

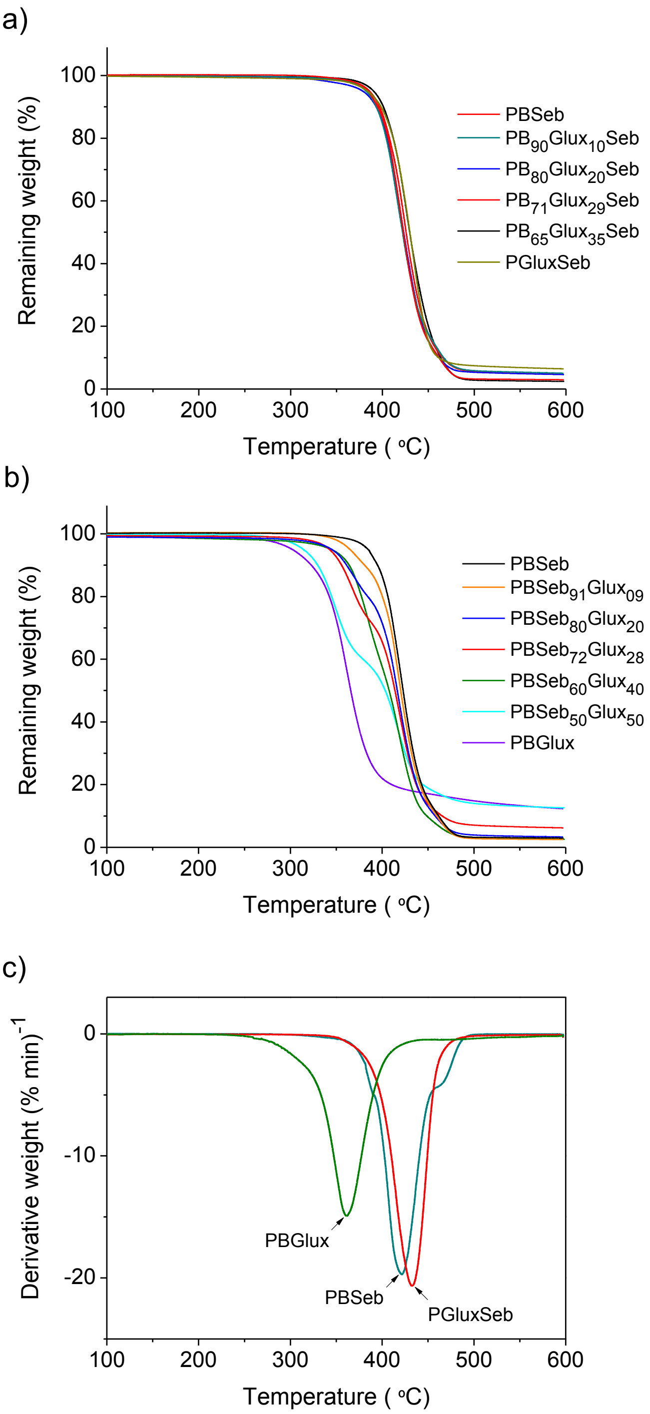


Figure 5. TGA traces of PB_xGlux_ySeb (a) and $PBSeb_xGlux_y$ (b) and compared derivative curves for homopolyesters (c).

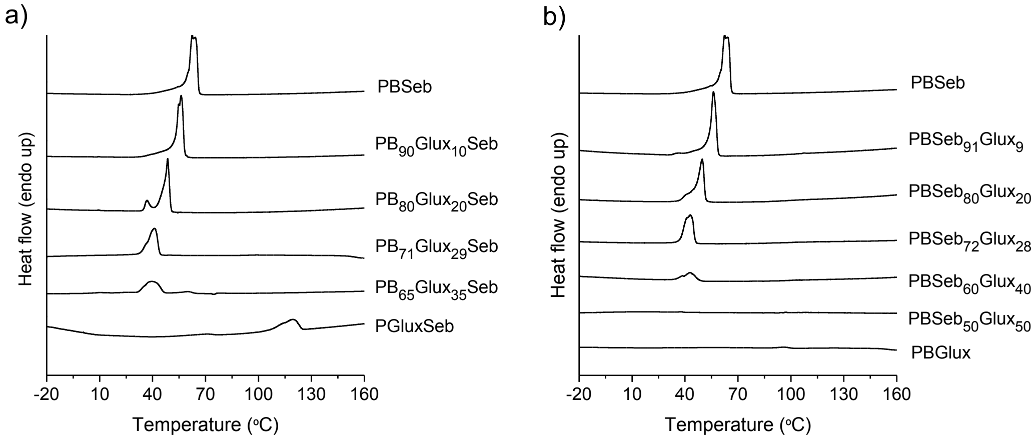


Figure 6. DSC melting traces of PB_xGlux_ySeb (a) and $PBSeb_xGlux_y$ (b).

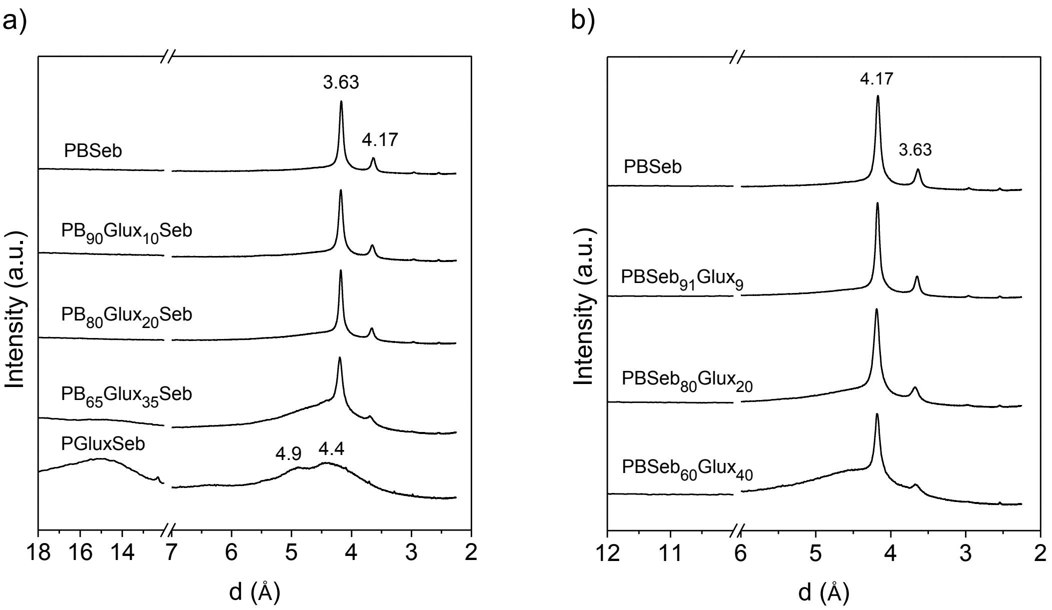


Figure 7. WAXS profiles for selected semicrystalline copolyesters of PB_xGlux_ySeb (a) and $PBSeb_xGlux_y$ (b) series recorded from powder samples without any previous thermal treatment.

In order to observe in the DSC traces the inflections corresponding to T_g, copolyester samples were quenched from the melt at -100 ºC and then heated up to 150 ºC. The traces registered for the two series are depicted in Figure 8 which reveals that the crystallization of the polymer was not repressed by quenching. In consequence, T_g were poorly observed or even unobserved, and since their values are influenced by crystallinity their comparison is scarcely reliable. The T_g data measured by DSC are given in Table 3 for those cases in which observation was feasible. In spite that no data are accessible for a good number of cases, it can be concluded that a significant increase in T_g is caused by the insertion of the Glux units in the two series. The results obtained for the homopolyester PGluxSeb is worth of attention. This polyester has a T_g of 28 ºC and a T_m of 119 ºC, which are very convenient values regarding thermal behavior and processing.

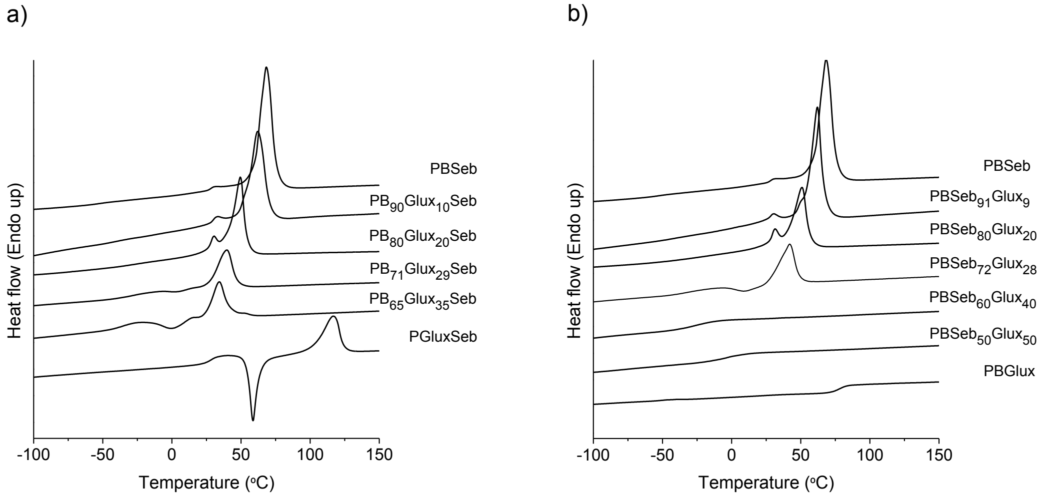


Figure 8. DSC traces of PB_xGlux_ySeb (a) and $PBSeb_xGlux_y$ (b) copolyesters quenched from the melt for T_g observation.

9.3.4. Biodegradation and hydrolytic degradability

To evaluate the effects that the incorporation of Glux (glucitylene or glucarate) units exerts on biodegradability and hydrolytic degradability of aliphatic polyesters, the $PB_{90}Glux_{10}Seb$, $PB_{71}Glux_{29}Seb$, $PBSeb_{91}Glux_9$ copolyesters obtained by melt polycondensation were selected out for a comparative degradation study. $PB_{90}Glux_{10}Seb$, $PB_{71}Glux_{29}Seb$ belong to the same series of copolyesters but differ in the content in glucitylene units. $PBSeb_{91}Glux_9$ copolyesters belong to the other series and have approximately the same content in Glux units as $PB_{90}Glux_{10}Seb$. PBSeb homopolyester was also tested in parallel for comparison purposes.

The study was first addressed to evaluate the biodegradability of Glux-containing of the copolyesters. The degradation experiments were carried out by incubating the copolyesters in aqueous pH 7.4 buffer at 37 °C with and without porcine pancreas lipase for four weeks. The changes taking place in sample weights and molecular weights of the samples along the period of incubation are shown in the two plots depicted Figure 9.

After 4 weeks of incubation in the presence of porcine pancreas enzyme $PB_{90}Glux_{10}Seb$, $PB_{71}Glux_{29}Seb$, $PBSeb_{91}Glux_9$ copolyesters lost around 10, 15, and 8 % respectively, whereas no changes were noticed for PBSeb. The plots of Figure 9 revealed the enhancing effect that the presence of Glux has on the hydrolysis of PBSeb, and also the more pronounced decay in molecular weight that follows the same tendency. Although PBSeb did not display any mass loss, the GPC results showed that it was degraded in the presence of enzyme, but the degradation products were not soluble in the medium and remained attached to the sample. $PB_{71}Glux_{29}Seb$ was the highest degraded one in the presence of lipase. Conversely, the weight losses observed for all copolyesters when incubated in the absence of lipase was only between 3 and 5%.

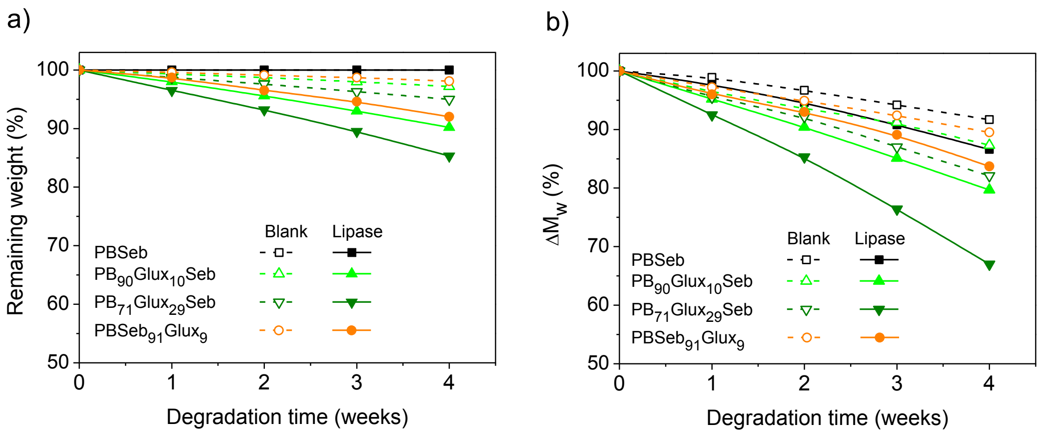


Figure 9 Enzymatic degradation of selected polyesters upon incubation at pH 7.4 at 37 ºC for four weeks. Remaining weight (a) molecular weight (b) *vs*. degradation time.

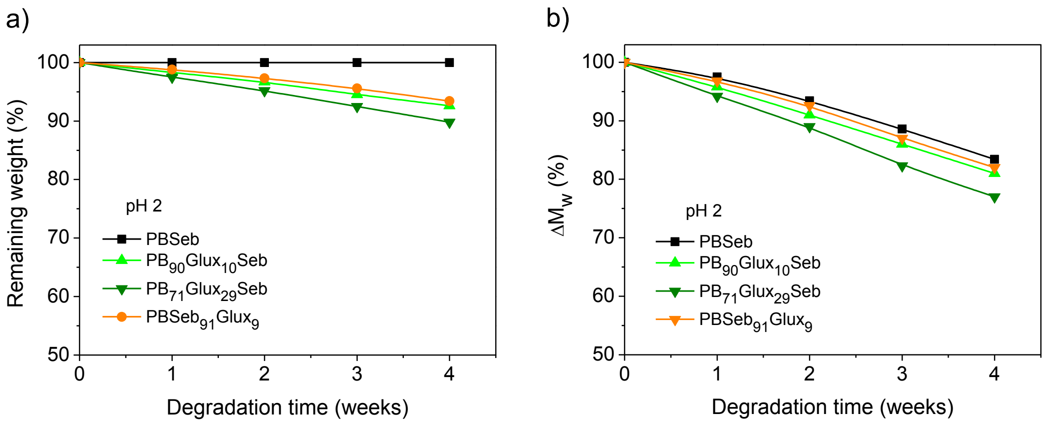


Figure 10. Hydrolytic degradation of selected polyesters at 37 ºC, pH 2. Remaining weight (a) molecular weight (b) *vs*. degradation time.

In the second part of the study the hydro-degradability of these polyesters under rather aggressive conditions was estimated by incubation of the samples in aqueous buffer pH 2 at 37 ºC. The evolution of sample weight and molecular weight with the incubation time is shown in the plots depicted in Figure 10. After the incubation period $PB_{90}Glux_{10}Seb$, $PB_{71}Glux_{29}Seb$, $PBSeb_{91}Glux_{9}$ copolyesters lost around 7, 10, and 6.6 % respectively, whereas no changes were noticed for PBSeb. It is really striking the fact that the Glux copolyesters degraded more in presence of lipase than when were subjected to hydrolytic degradation in aqueous pH 2 buffer at 37 °C. This is contrary to all observations previously reported on sugar containing copolyesters and contrary to PBSeb homopolyester that was more sensible to hydrolytic degradation.

Representative SEM micrographs for $PB_{90}Glux_{10}Seb$, $PB_{71}Glux_{29}Seb$ copolyesters subjected to degradation under different conditions are shown in Figures 11 and 12, and those for $PBSeb_{91}Glux_{9}$ and PBSeb are provided in the SI document.

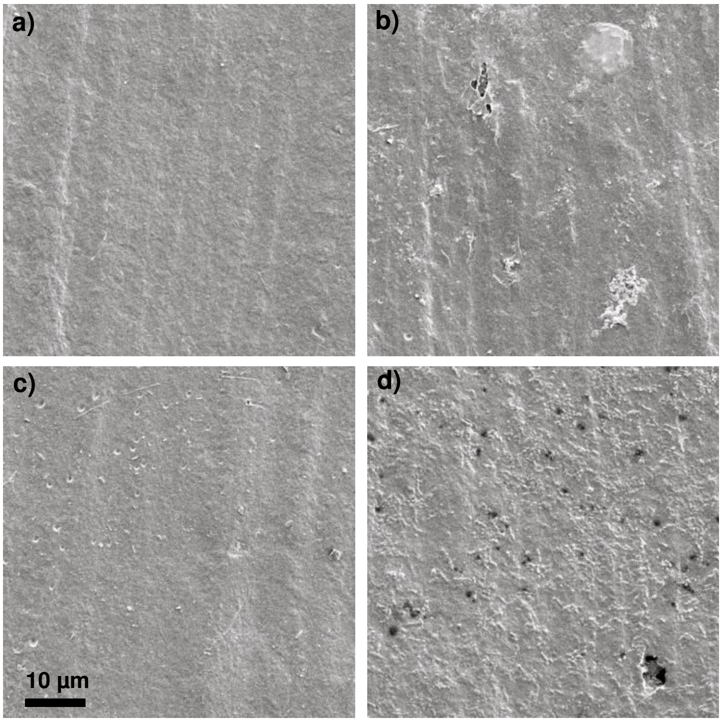


Figure 11. SEM micrographs of $PB_{90}Glux_{10}Seb$: initial sample (a); after incubation at pH 2 for four weeks (b); after incubation at pH 7.4 for four weeks without (c) and with (d) porcine pancreas lipase

9.4. Conclusions

A set of bio-based monomers has been used as platform for the synthesis of copolyesters by both melt polycondensation and enzymatic polymerization in solution. Aliphatic compounds (1,4-butanediol and diethyl sebacate) were combined with bicyclic acetalized D-glucitol and dimethyl D-glucarate (Glux-diol and Glux-diester) to produce two series of copolyesters (PB_xGlux_ySeb and $PBSeb_xGlux_y$) containing up to 50% of sugar-based units and that differ to each other in which Glux derivative (diol or diester) was used as comonomer for polymerization. Also the three parent homopolyesters (PBSeb, PBGlux and PGluxSeb) were prepared by both procedures.

The enzymatic procedure has proven to be effective to afford copolyesters with weight-average molecular weights of around 10,000 and dispersities about 2. On the other hand the melt polycondensation method was able to render polyesters with M_w of up to near 40,000 and dispersities between 2 and 2.4. In both cases the molecular weight decreased with the content in Glux units so the lowest values were attained for PBGlux and PGluxSeb and the microstructure of the copolyesters was almost random for whichever composition. Compared to the homopolyester PBSeb, it was observed that the insertion of Glux units increased the resistance to heat in the PB_xGlux_ySeb but caused a slight impoverishing of the thermal stability of $PBSeb_xGlux_y$ series. Both the initial crystallinity and melting temperature of PBSeb were depressed upon insertion of Glux units whether they are diol or diacid but this effect was more noticeable in the $PBSeb_xGlux_y$ series. On the contrary a unequivocal increase in T_g with the content in Glux units was observed for the two series of copolyesters. The crystal structure of PBSeb was preserved in the crystalline copolyesters.

The degradability of PBSeb was noticeably enhanced by the presence of Glux units in its copolyesters. Not only the easiness to be hydrolyzed increased but they appear to be particularly degradable in the presence of lipases. The homopolyester PGluxSeb made of Glux-diol and diethyl sebacate deserves particular attention. In spite of being obtained with a rather low molecular weight (M_w/M_n =11,200/5,600) it is more thermally stable than PBSeb, has melting and glass-transition temperatures of 119 and 28 ºC and is able to crystallize from the melt with almost full reproducibility of its initial crystallinity. Further efforts addressed to attain this polyester with higher molecular weight and to assess its biodegradability and mechanical properties should be made in a near future to evaluate its potential as a biodegradable bio-based thermoplastic of interest in the biomedical field.

9.5. References

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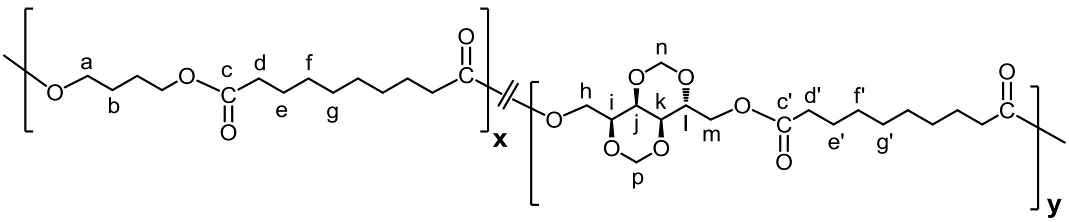
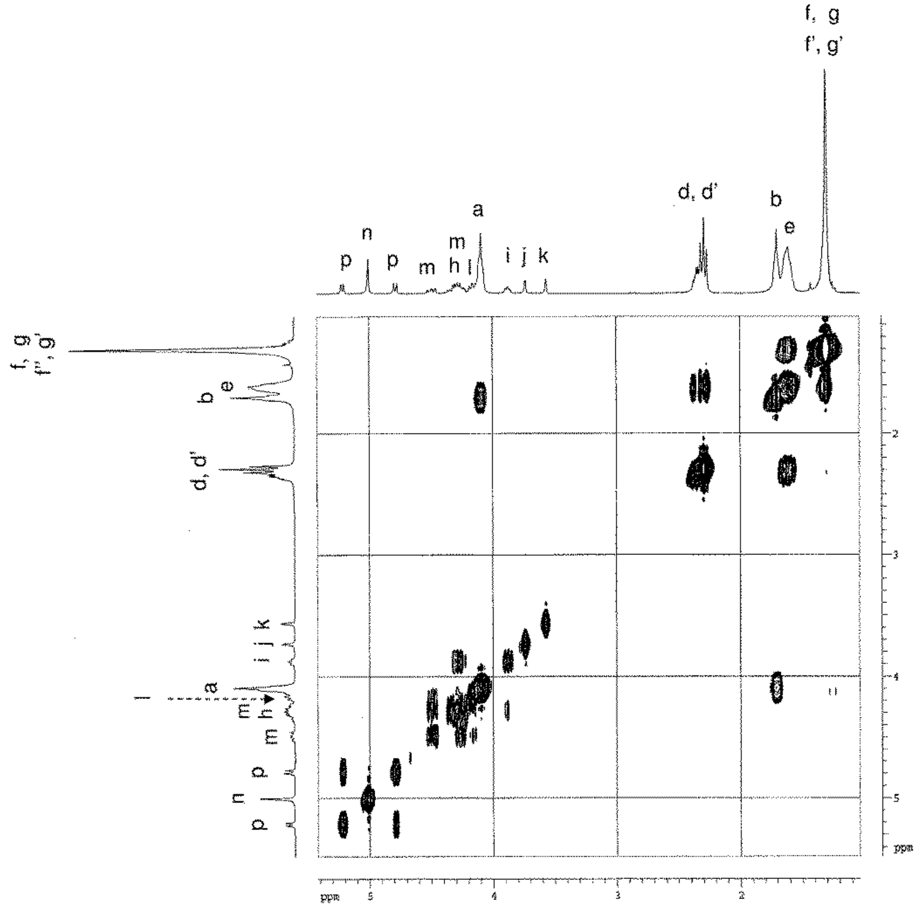
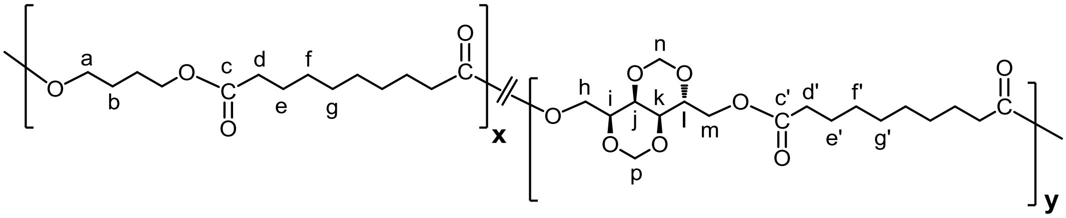
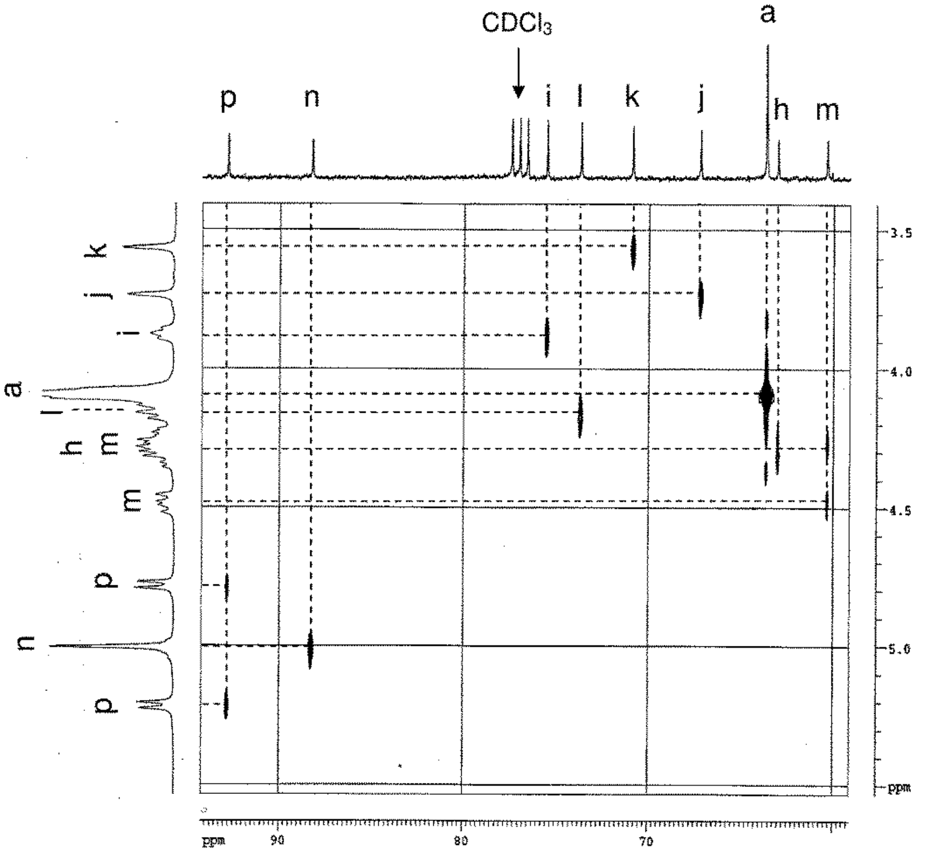
Supporting information



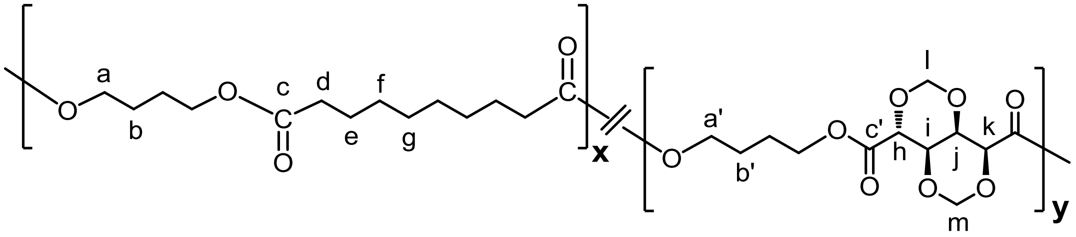


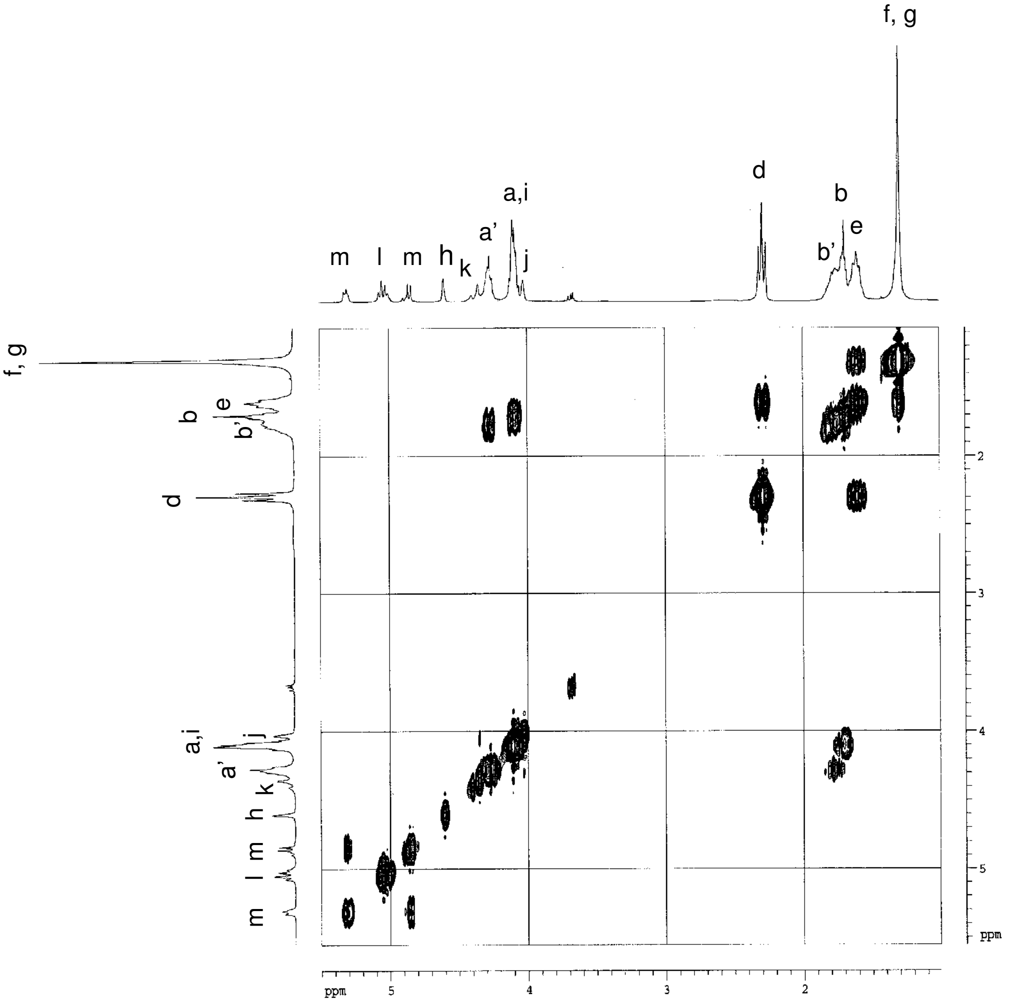
SI-Figure 1. COSY ^{1}H-^{1}H NMR spectra of PB$_{71}$Glux$_{29}$Seb copolyester.



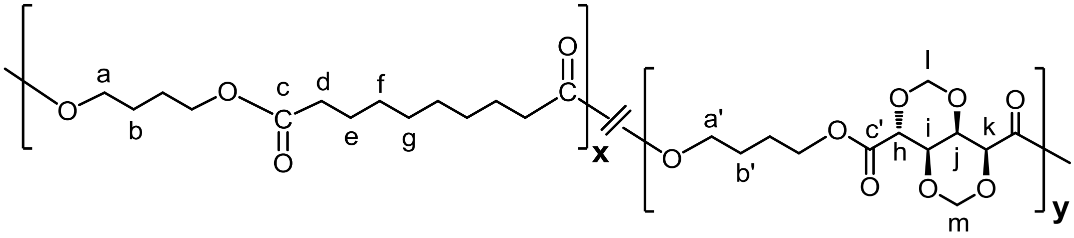


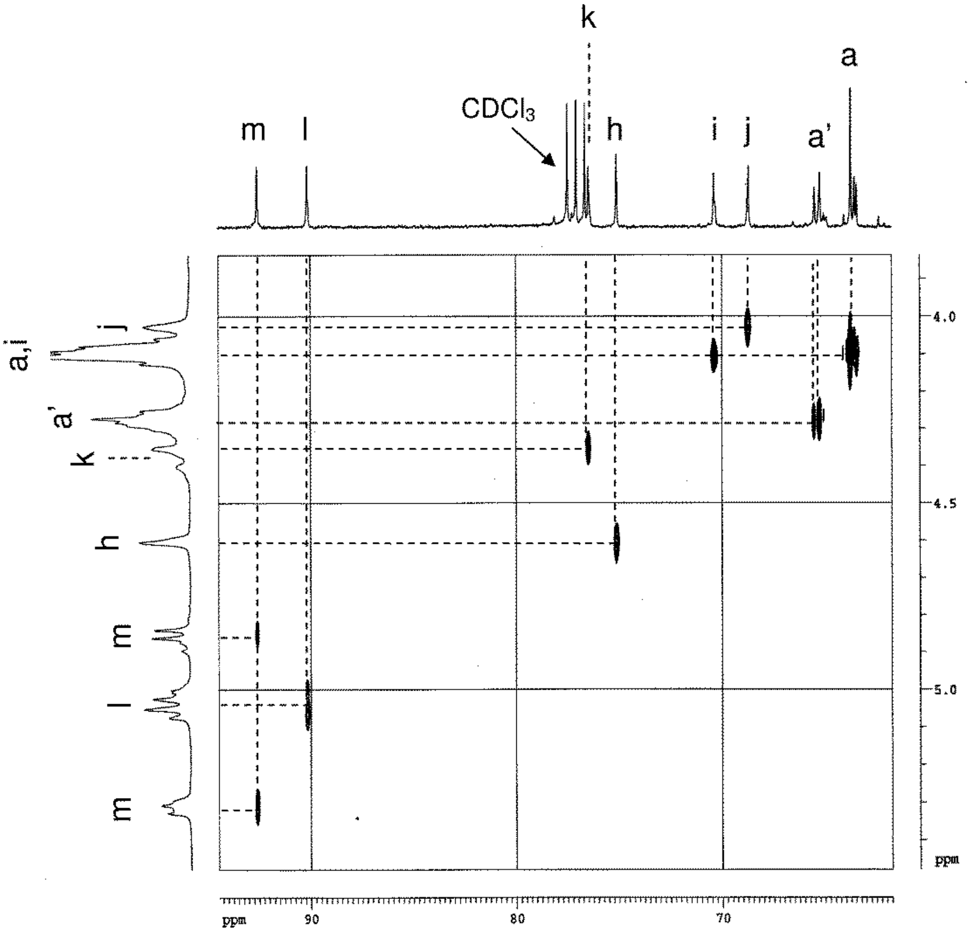
SI-Figure 2. ^{1}H-^{13}C HETCOR NMR spectra of PB$_{71}$Glux$_{29}$Seb copolyester (amplified region)



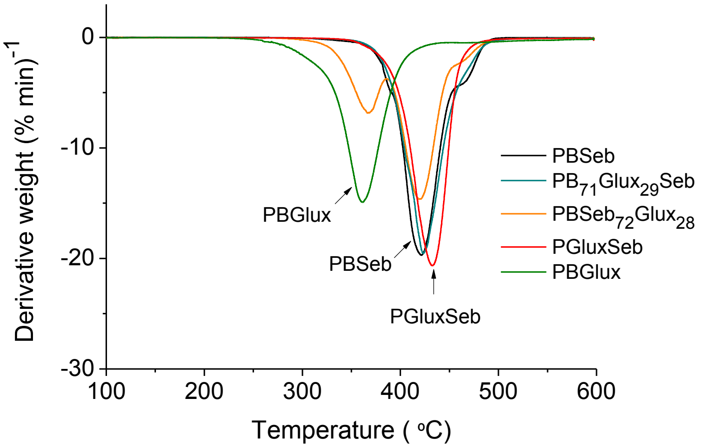


SI-Figure 3. COSY ^1H-^1H NMR spectra of $PBSeb_{72}Glux_{28}$ copolyester.

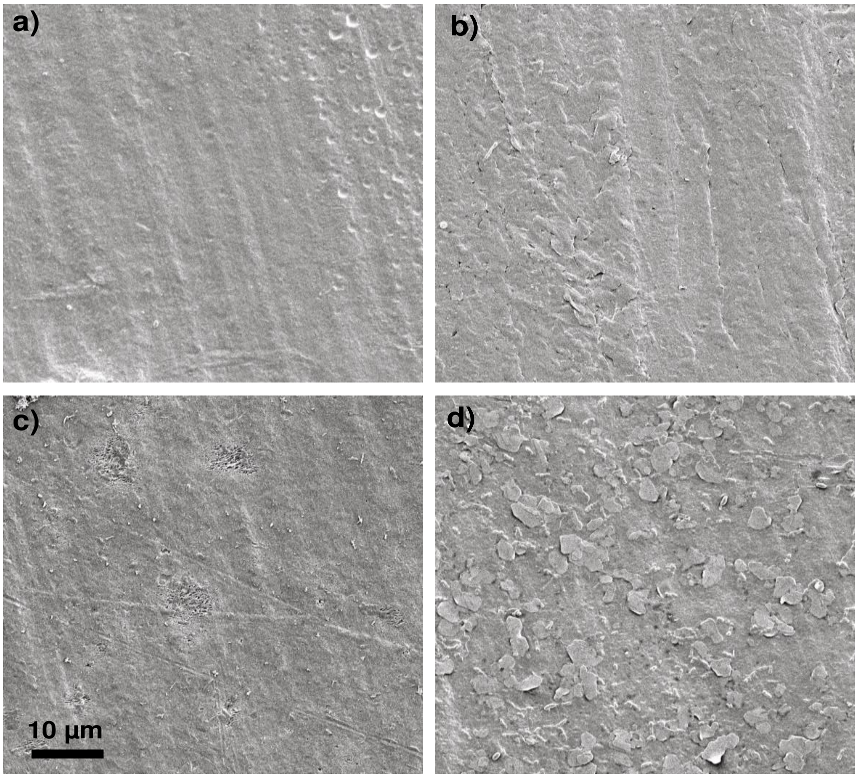




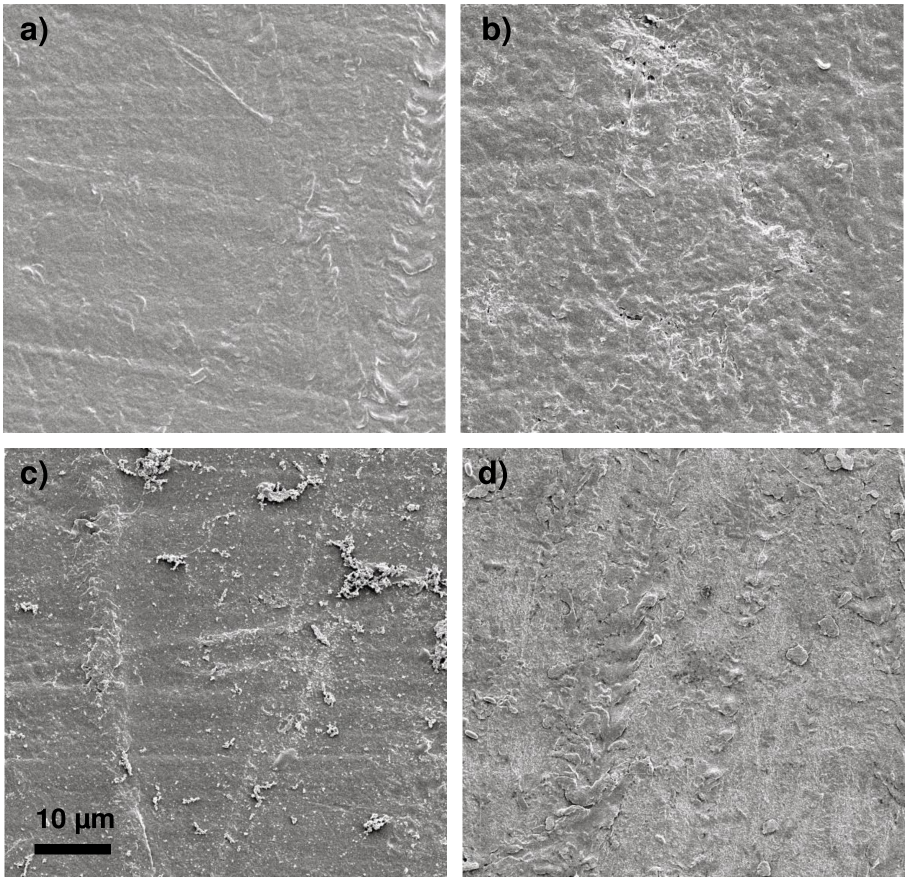
SI-Figure 4. ^1H-^{13}C HETCOR NMR spectra of PBSeb$_{72}$Glux$_{28}$ copolyester (amplified region).



SI-Figure 5. TGA compared derivative curves for a selection of cases.



SI-Figure 6. SEM micrographs of PBSeb: initial sample (a); after incubation at pH 2 for four weeks (b); after incubation at pH 7.4 for four weeks without (c) and with (d) porcine pancreas lipase.



SI-Figure 7. SEM micrographs of $PBSeb_{90}Glux_{10}$: initial sample (a); after incubation at pH 2 for four weeks (b); after incubation at pH 7.4 for four weeks without (c) and with (d) porcine pancreas lipase.

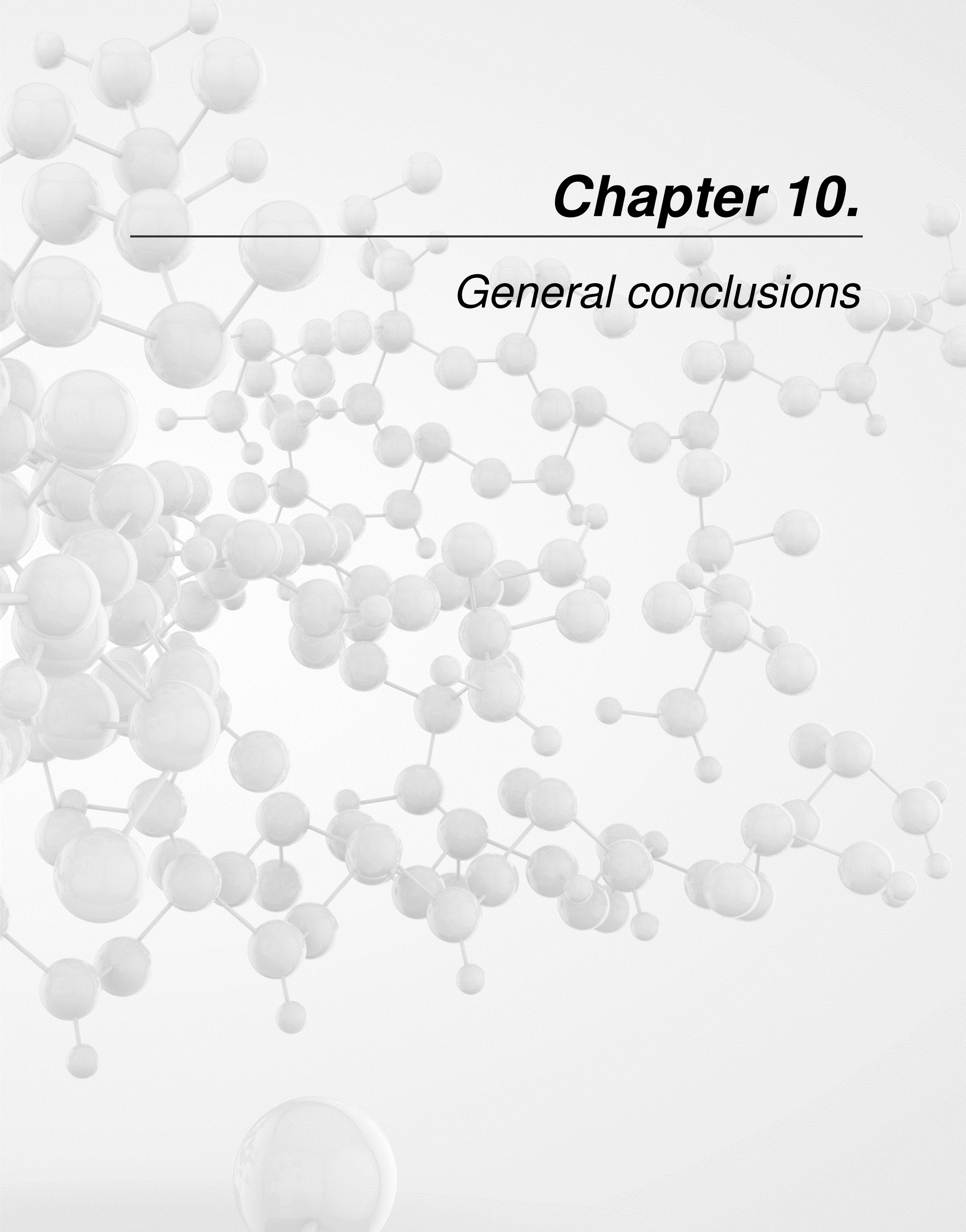
SI-Table 1. Compared molecular weights of $PB_{90}Glux_{10}Seb$ in different reaction conditions.

Reaction conditions		10 % wt CALB vs total amount of monomers	20 % wt CALB *vs* total amount of monomers					
		1) 90 ºC/ 5h 2) 95 C/72h	1) 90 ºC / 24 h 2) 90 ºC / 24 h			1) 90 ºC / 24 h 2) 95 ºC/ 72 h		
		$5\boldsymbol{X}$	$3\boldsymbol{X}$	$5\boldsymbol{X}$	$7\boldsymbol{X}$	$3\boldsymbol{X}$	$5\ \boldsymbol{X}$	$7\ \boldsymbol{X}$
Molecular weights	M_n	*6300*	5200	5000	5100	5000	5100	5200
	M_w	9100	6700	6500	6500	7000	6400	6400
	PD	1.4	1.3	1.3	1.3	1.4	1.3	1.2

GPC measurement was performed in THF solvent.

Chapter 10.

General conclusions



As it was demonstrated along this thesis, cyclic acetalized carbohydrate based monomers derived from tartaric acid and D-glucose are a good option for the preparation of bio-based polyesters with improved properties. Below are described briefly the most important conclusions extracted from this Thesis.

✓ There were synthezied PHT copolyesters containing tartrate sugar units with satisfactory molecular weights and without apparent discoloration. The copolymerization of the tartrate and terepthalate diesters took place at random with not perceivable rejection of neither of the two comonomers. The copolyesters, and even the homopolyester entirely made of tartrate units, were semicrystalline evidencing the capability of the 1,3-dioxolane ring to be accommodated in the polyester crystal lattice. However, both melting temperature and enthalpy decreased with the presence of the tartrate units as crystallization rate did as well. Also T_g diminished in the same sense, which is consistent with the lower stiffness of the 1,3-dioxolane cycle compared to the 1,4-phenylene ring. The extremely inertness toward hydrolysis characteristic of PHT was markedly weakened by the insertion of the tartrate units, which were evidenced to be very prone to undergo hydrolysis and even the material still arrived to be susceptible to the action of enzymes.

✓ Two cyclic compounds containing the 1,3-dioxolane structure, 2,3-di-*O*-methylene-L-threitol (Thx-diol) and 2,3-di-*O*-methylene-L-threarate (Thx-diester) may be successfully used for the synthesis of partially sustainable PET copolyesters through a methodology similar to that usually applied at industrial scale. Copolyesters containing Thx-diester units are significantly less stable to heat than PET, whereas those made of Thx-diol have a stability comparable or even slightly higher than that of PET. The replacement of terephthalate by threarate units entails a decrease in the T_g of PET. On the contrary, terephthalate copolyesters containing threitylene units have the same or even slightly higher T_g than PET, exicting result because thermal stability and T_g are enhanced whereas crystallizability is depressed, a behavior that is in full accord with what is required to PET for some specific applications.

✓ The bicyclic compound 2,4:3,5-di-O-methylene-D-glucitol (Glux) has been successfully used as comonomer of 1,6-hexanediol for the synthesis of poly(terephthalate)s copolyesters by polycondensation in the melt. In spite of the asymmetrical structure of Glux, all the copolyesters are semicrystalline although their crystallinity diminishes as their content in Glux increases. Copolyester melting temperatures span from 80 to 150 ºC, and those with lower contents in Glux are able to crystallize from the melt; since they are well stable to heat up to temperatures above 350 ºC, these partially bio-based copolyesters are suitable to be used as thermoplastic materials. An outstanding feature of these novel copolyesters is their relatively high T_g, which ranges between 20 and 60 ºC with values increasing with the content in Glux. Another merit is their susceptibility to biodegradation at low rates.

✓ 2,3:4,5-di-*O*-methylene-D-glucitol and dimethyl 2,3:4,5-di-*O*-methylene-D-glucarate are bicyclic difunctional compounds derived from D-glucose that can be successfully used as comonomers in the synthesis of PET copolyesters. The partial replacement in the polymerization feed of either ethylene glycol or dimethyl terephthalate by the acetalized glucitol or the dimethyl glucarate, respectively, led to random PET copolyesters with adjustable compositions and suitable molecular weights, and that are thermally stable up to above 300 ºC. The copolyesters containing more than 10-15% of sugar-derived units are mostly amorphous and those displaying crystallinity were found to adopt the same crystal structure than PET. The most outstanding merit of these new bicyclic sugar-based monomers is their capacity to raise notably the T_g of PET when they are inserted in the chain by replacing either the diol or the diacid units in relatively small amounts. It is also remarkable that the mechanical properties of PET do not decay significantly and that its degradability and biodegradability were clearly enhanced with the incorporation of these monomers.

✓ Two series of bio-based poly(butylene terephthalate) copolyesters, both of them with a random microstructure, have been successfully synthesized by polycondensation in the melt using bicyclic D-glucose-derived comonomers. One set was obtained by replacing 1,4-butanediol by 2,4:3,5-di-*O*-methylene-D-glucitol (Glux-diol) and the other by replacing dimethy terephthalate by dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester). The incorporation of Glux units in the PBT chain gave rise to remarkable modifications in polymer properties which were depending on the functionality of such units. The presence of glucitylene units led to a significant increase in the thermal stability of PBT in contrast with the decrease produced when the bicyclic structure was inserted as glucarate units. The changes taking place in glass-transition temperatures are significant. What it is really noteworthy is that T_g increased even when the terephthalate unit was the replaced unit; to our best knowledge, such effect has not precedent in aromatic copolyesters containing sugar-based units. A last remarkable conclusion is that the Glux-containing copolyesters display higher sensitivity to hydrolysis than PBT, in particular those containing glucarate units, which in addition distinguished by their sensitivity to the action of lipases.

✓ A set of bio-based monomers has been used as platform for the synthesis of copolyesters by both melt polycondensation and enzymatic polymerization in solution. Aliphatic compounds (1,4-butanediol and diethyl sebacate) were combined with bicyclic acetalized D-glucitol and dimethyl D-glucarate (Glux-diol and Glux-diester) to produce two series of copolyesters (PB_xGlux_ySeb and $PBSeb_xGlux_y$) containing up to 50% of sugar-based units and that differ to each other in which Glux derivative (diol or diester) was used as comonomer for polymerization. The enzymatic procedure has proven to be effective to afford copolyesters with weight-average molecular weights of around 10,000 and dispersities about 2. On the other hand the melt polycondensation method was able to render polyesters with M_w of up to near 40,000 and dispersities between 2 and 2.4. Both the initial crystallinity and melting temperature of PBSeb were depressed upon insertion of Glux units whether they are diol or diacid but this effect was more noticeable in the PBSebxGluxy series. On the contrary a unequivocal increase in T_g with the content in Glux units was observed for the two series of copolyesters. The crystal structure of PBSeb was preserved in the crystalline copolyesters. The degradability of PBSeb was noticeably enhanced by the presence of Glux units in its copolyesters. Not only the easiness to be hydrolyzed increased but they appear to be particularly degradable in the presence of lipases.

Patents

S. Muñoz-Guerra, C. Lavilla, C. Japu, M. G. García Martín, A. Alla, A. Martínez de Ilarduya, E. Benito, J. A. Galbis, “Síntesis de homopoliésteres y copoliésteres aromáticos y alifáticos, obtenidos a partir de derivados de alditoles y ácidos aldáricos diacetalizados, mediante policondensación”, ES2383079 Patent (2013).

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1. C. Japu, A. Alla, A. Martínez de Ilarduya, M. G. García-Martín, E. Benito, J. A. Galbis and S. Muñoz-Guerra, “Bio-based aromatic copolyesters made from 1,6-hexanediol and diacetalized D-glucitol”, *Polym. Chem.*, 2012, **3**, 2092-2101.

2. C. Japu, A. Martínez de Ilarduya, A. Alla and S. Muñoz-Guerra, “Bio-based poly(hexamethylene terephthalate) copolyesters containing cyclic acetalized tartrate units”, *Polyme*r, 2013, **54**, 1573-1582.

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5. C. Japu, A. Alla, A. Martínez de Ilarduya, S. Muñoz-Guerra, “Bio-based poly(ethylene terephthalate) copolyesters made from cyclic monomers derived from tartaric acid”, *Polymer*, 2014, **55**, 2294-2304.

6. C. Japu, A. Martínez de Ilarduya, A. Alla, M. G. García-Martín, J. A. Galbis and S. Muñoz-Guerra “Biodegradable copolyesters of poly(hexamethylene terephthalate) containing bicyclic 2,4:3,5-di-*O*-methylene-D-glucarate units”*. To be submitted.*

7. C. Japu, K. Loos, A. Martínez de Ilarduya, A. Alla and S. Muñoz-Guerra, “Sustainable copolyesters made from 1,4-butanediol, sebacic acid and D-glucose by melt and enzymatic polycondensation”. *Article in preparation*

8. S. Muñoz-Guerra, C. Lavilla, C. Japu and A. Martínez de Ilarduya, “Renewable terephthalate polyesters from carbohydrate-based bicíclic monomers”, *Green Chemistry*, 2014, **16**, 1716-1739.

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1. C.Japu, A. Alla, A. Martínez de Ilarduya, E. Benito, M. G. García-Martín, J. A. Galbis and Sebastián Muñoz Guerra, “Aromatic Polyesters from Cyclic Diacetalized Glucose. Poster at X Jornadas de Carbohidratos. Granada (Spain), 15th-18th September 2010.

2. C.Japu, A. Alla, A. Martínez de Ilarduya, E. Benito, M.G. García-Martín, J. A. Galbis and Sebastián Muñoz Guerra, “Aromatic Copolyesters from Cyclic Diacetalized Glucose”. Poster at the European Polymer Congress-XII GEP Congress. Granada (Spain), 26th June-1st July 2011.

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