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Carbohydrate-based bicyclic compounds, isohexides and diacetalized alditols and aldarates, are suitable polycondensation monomers to prepare partially renewable aromatic copolyesters displaying a satisfactory pattern of basic properties, and enhanced Tg and hydrodegradability.

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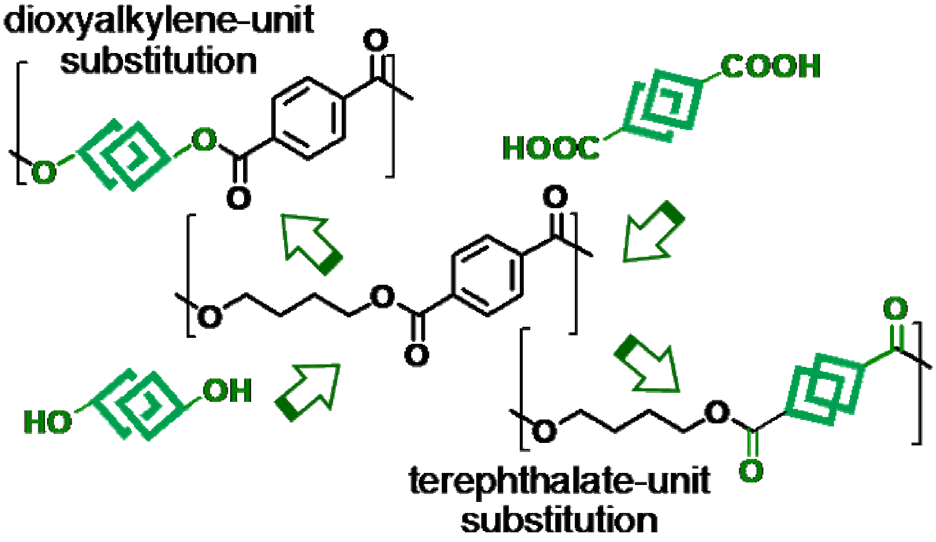

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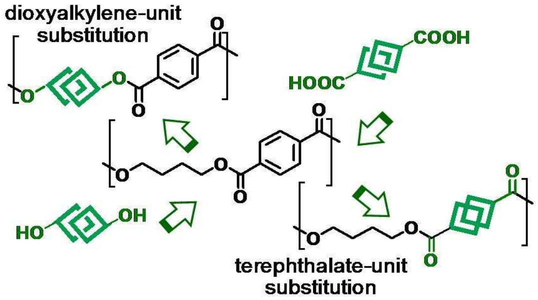

Renewable terephthalate polyesters from carbohydrate-based bicyclic monomers

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Abstract

Poly(alkylene terephthalate)s, PET and PBT in particular, are materials of great relevance and growing projection in the thermoplastic field but that are today almost totally produced from fossil resources. The current huge consumption of these polyesters requires urgent actions addressed to make them renewable by using naturally-occurring raw materials. Among the different approaches that are being followed to develop bio-based poly(terephthalate)s, that making use of bicyclic carbohydrate-derived difunctional compounds as building-blocks is receiving much attention in these last years because partially renewable polyesters with high T_g may be thus obtained. This review presents a critical account of the terephthalate homopolymers and copolymers that have been synthesized using the two types of carbohydrate-based bicyclic monomers, isohexides and diacetals, explored up to date. The properties displayed by the novel bio-based poly(terephthalate)s in relation to the bicyclic structure of the used monomers are comparatively reviewed and their potential as emergent materials for thermoplastic applications is evaluated.

1. Introduction

The amount of plastics today produced in the world is around 250 Mtons per year with a yearly average growth of about 10%.[1] Nearly the half of the plastic consumption is used in short-term applications with the unavoidable environmental damage caused by the resulting wastes.[2,3] Depletion of fossil reserves is another factor that contributes to aggravate the concern about the current situation. Also price fluctuations of petrochemical feedstock constitute an additional disturbing cause although it is true that industry has been traditionally able to deal with this issue.

Recycling technology has emerged as an effective reply to environmental problems associated to plastic handling. Significant increases in the recycling rates of polymers are taking place, with facilities and changes in legislation that now permit even recycling of food contact polymers. Thus the recollected amount of post-consumer PET bottles and the new clean recycling technologies, which are able to decontaminate post-consumer contaminants to concentration levels of virgin PET materials, make nowadays possible the bottle-to-bottle recycling of PET.[4,5] Recycling is especially suitable when recovery of the used material can be carried out without excessive difficulty, otherwise costs associated to used material recollection and primary classification would make economically prohibitive the application of this technology.

Anyhow there is unanimity in accepting that these undesirable impacts could be reduced by using plastics that are sustainable, *i.e.* plastics produced from renewable sources and susceptible to be degraded by the environment under controlled conditions. The replacement of traditionally petrochemical plastics by the bio-based plastics, popularly called bioplastics, is a matter of fact that is taking place at a rate in great part determined by a number of factors that include state policy, crude oil prices, feedstock cost competition and consumer acceptance. The forecasted total production capacity of 12 million tons by 2020 - a tripling of 2011 levels- evidences the increasing importance of bio-based plastics.[1]

From a technological perspective, the replacement rate is strongly depending on which kind of plastic is involved. In fact, the change is being particularly noticeable in polycondensates, more specifically in polyesters, due to the relatively higher accessibility to the bio-based monomers required for polycondensation. Moreover synthetic methods in polyesters are well developed,[6] and the large amount of knowledge coined on these polymers,[7,8] which is ready available from the accessible literature, provides the necessary criteria for the appropriate monomer selection. Although the starting monomers of most published polyesters are hydrocarbon-based, they can be useful points of learning on the structure-property relationship in new polyesters made from bio-based monomers.[9]

Plant oils[10] and carbohydrates[11] stand out as the most relevant feedstock affording bio-based plastics, either as raw materials for the chemical synthesis of new monomers or simply as carbon sources for biological processes leading to monomers or even to polymers directly. Microbial poly(hydroxy alkanoate)s as well as poly(lactic acid) are polyesters produced from natural-occurring resources that are known for almost a century,[12,13] but it is in these last two decades when the interest for bio-based polyesters generated by chemical synthesis has shot up.[14,15] Flexible building difunctional monomers as alkanediols and aliphatic dicarboxylic acids suitable for the synthesis of aliphatic polyesters are becoming increasingly available at industrial scale from either carbohydrate or oleochemical sources, and some of them have been definitely incorporated in the industrial production of commercial polycondensates.[16] On the contrary, the development of bio-based rigid monomers needed for the production of high performance thermoplastics is still in its commencement in spite of the growing interest on sustainable engineering polymers. First studies on the use of bio-based bicyclic compounds as building-blocks for the synthesis of renewable polymers were carried out at the early nineties of the last century.[17,18] This approach was realizable largely due to the availability of isosorbide (Is), a bicyclic anhydride-diol derived from D-glucose used as substrate for the production of medicaments of interest in the treatment of cardiovascular disorders.[19,20] Since then a good amount of exploratory work as well as a number of studies closer to the industrial realization, have been addressed to the development of polyesters, polyamides, polycarbonates and polyurethanes using isosorbide as bio-based monomer.[21] These investigations were rapidly extended to embrace several stereoisomers of isosorbide and some of their derivatives bearing modified functions. It is actually remarkable that no bio-based bicyclic compounds other than isohexides had been investigated in this regard along the past two decades, a fact that doubtlessly reflects the difficulty to access to such kind of compounds. Nevertheless, in these last few years a new class of bicyclic compounds suitable for polycondensation and also derived from carbohydrates has emerged with decision. These compounds are methylene diacetals of some common alditols and aldaric acids, and according to the results obtained in the pioneering works carried out by Muñoz-Guerra *et al*., which will be discussed later on, they stand today for a valid option towards renewable polycondensates. The purpose of this review is to compare in detail the two classes of carbohydrate-based bicyclic (CBB) compounds, isohexides and diacetals, today suitable as monomers for the production of polycondensates, more specifically of the aromatic polyesters poly(alkylene terephthalate)s, regarding polymerization results and basic properties of their respective resulting polymers. The conceptual axis around which revolves this study is depicted in Scheme 1.

carbohydrates

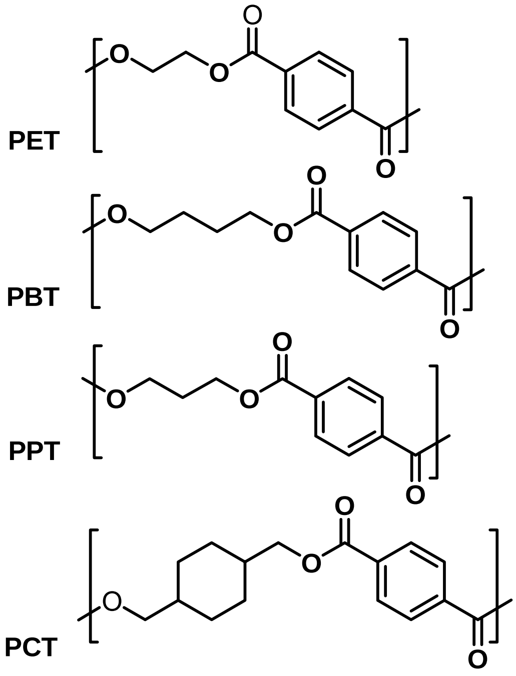
bicyclic
diols and diacids

terephthalate
polyesters

Scheme 1. The review's concept.

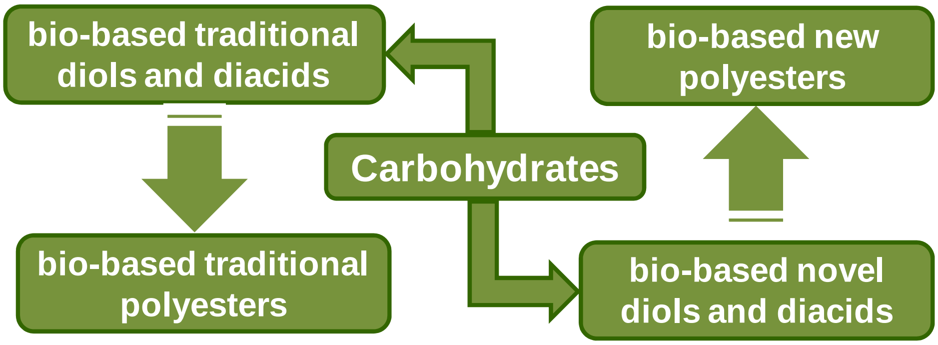
2. Poly(alkylene terephthalate)s: the bio-based approaches

The polyester class embraces a large number of aliphatic and aromatic polymers covering a wide diversity of behaviors that range from thermoset resins to semicrystalline thermoplastics in addition to liquid-crystalline materials. Linear polyesters combining aromatic and aliphatic moieties in the constitutional repeating unit stand out among polyesters for their good general behavior and noteworthy thermal and mechanical properties. Such features enable these aromatic polyesters for a broad range of applications not accessible to other common thermoplastics materials as polyolefins, polyvinyls or polyacrylics. The most extended by far aromatic polyesters are poly(alkylene terephthalate)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.[7a] The chemical structure of the most representative poly(alkylene terephthalate)s is depicted in Scheme 2. PET accounts for 8% of the global polymer production[22] 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.[23] 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.[6] 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.



Scheme 2. Chemical formulae of top poly(alkylene terephthalate)s.

The huge amounts of poly(alkylene terephthalate)s that are handled nowadays have generated the logical concerns about their environmental impact, that together with the increased price of fossil feedstock, have motivated an intensive research focused on the development of sustainable replacing products. An illustrative example of the attention paid to this issue and the progress attained in the last years is that two of the main world beverage companies have reported that they would be using only renewable resources for the production of PET bottles since the beginning of this decade. As it is depicted in Scheme 3, two approaches are followed for the development of bio-based aromatic polyesters.[16] The conservative one consists of creating novel synthesis routes from renewable sources to produce the same monomers that are currently being used in the industrial production of poly(alkylene terephthalate)s obtained from petrochemical feedstock. Obviously, the use of these bio-based monomers does not entail differences in terms of polymer synthesis and properties with those coming from petroleum since the resulting polymers are chemically indistinguishable. The second approach is based on the synthesis of new monomers from natural resources to replace, either partially or totally, those of petrochemical origin used in the production of aromatic polyesters. In this case, novel polymers more or less different from the traditional ones will be produced according to the chemical structure of the bio-based monomer. The merit afforded by this approach arises from the possibility of creating new products that while retaining the general pattern of behavior of the existing ones, are able to display improved properties in selected aspects of technical interest.



Scheme 3. The two routes to bio-based polyesters.

2.1. Bio-based routes to conventional monomers for poly(alkyl terephthalate)s

A good number of the monomers implied in the production of the most important aromatic polyesters have been reported to be accessible from renewable feedstock. Whereas some of them are being currently produced at ton levels many others are still in a very incipient state of development.

Ethylene glycol. Microbial ethanol for application as biofuel is produced at the multimillion ton scale from starch and from sugar. Bioethanol can be readily dehydrated to ethylene using different catalysts.[24] 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.[25] Coca-Cola Co. introduced in 2009 the PlantBottle as the first recyclable PET bottle using up to 30% bio-based ethylene glycol.

1,3-Propanediol. The production of bio-based 1,3-propanediol has been developed and commercialized by the joint venture DuPont Tate & Lyle LLC, with a annual capacity of 45,000 tons. In nature yeasts first ferment glucose to glycerol and then microbes ferment glycerol to 1,3-propanediol. 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.[26]

1,4-Butanediol. Genomatica Inc. (San Diego, USA) has developed a sucrose-based process for the manufacture of 1,4-butanediol by an engineered microorganism.[16] On the other hand, 1,4-butanediol can be also produced by catalytic hydrogenation of bio-based succinic acid which is obtained by fermentation of corn-derived glucose.[27] However, most 1,4-butanediol is still produced nowadays from petrochemical feedstock.

1,10-Decanediol. This diol has been reported as a bio-based derivative of castor oil.[28] The treatment of castor oil with strong bases at elevated temperatures and in the presence of catalysts produces sebacic acid and 2-octanol preferably. Sebacic acid can be then converted into 1,10-decanediol by hydrogenation.

Terephthalic acid. Bio-based PTA has been reported as potentially being produced from *p*-xylene generated by depolymerization of lignin.[29] Another route to bio-based PTA uses the limonene oil present in citric fruits as raw material.[30,31] Recently, the production of PTA from limonene has been patented.[32] 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,[33] well below what is needed to meet the current production of poly (terephthalate)s (only PET production for bottles amounted 13 Mtons in 2009)[34]. Although considerable progress is being attained in this synthesis,[31] the cost of the implied technology and the difficult accessibility to limonene lead to presuming that a substantial replacement of petrochemical PTA by the bio-based one will be not feasible at short term.

2.2. Terephthalate polyesters from carbohydrate-derived non bicyclic monomers

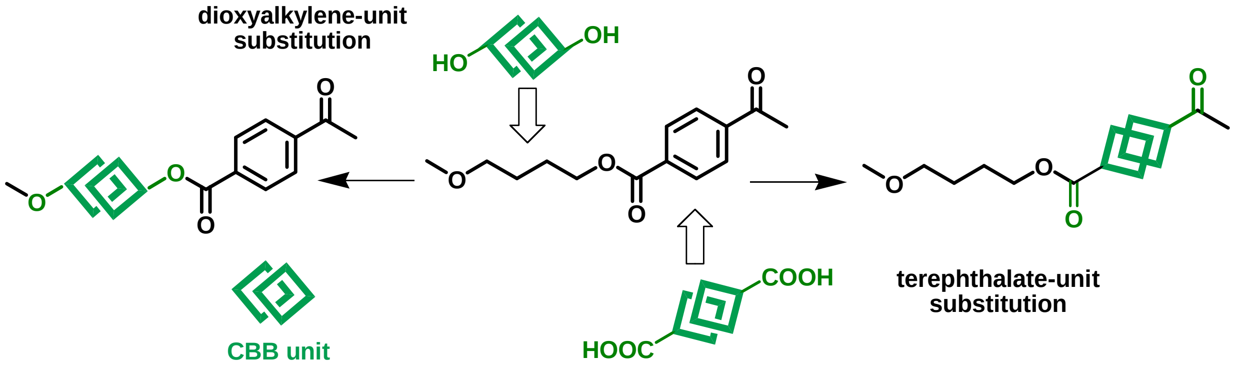
The synthesis of aromatic polyesters, specifically of poly(terephthalate)s, using carbohydrate-based acyclic *O*-protected monomers has been recently explored. Thus poly(ethylene terephthalate) (PET), poly(ethylene isophthalate) (PEI) and poly(butylene terephthalate) (PBT) have been chemically modified by insertion of different *O*-methyl alditols. Firstly, a series of PET copolyesters containing 2,3-di-*O*-methyl-L-threitol were prepared and duly characterized.[35] Later PET and PEI analogues with total replacement of the ethylene glycol units by 2,3,4,5-tetra-*O*-methyl-hexitols having either D-*manno* or *galacto* configurations were synthesized.[36] Polyesters analogous to PET, PEI and PBT have also been prepared by using 2,3,4-tri-*O*-methyl-L-arabinitol and 2,3,4-tri-*O*-methyl or 2,3,4-tri-*O*-benzyl ethers of L-arabinitol and xylitol.[37] PBT copolyesters based on *O*-methyl aldaric acids as L-arabinaric and galactaric acids were also prepared and characterized.[38]

The use of monocyclic acetalized compounds in the preparation of aromatic copolyesters has been also reported. Recently, Japu *et al*. have prepared and characterized a copolyester series of poly(terephthalate)s using dimethyl 2,3-di-*O*-methylene-L-tartrate, a monocyclic acetalized dimethyl aldarate derived from L-tartaric acid, and 1,6-hexanediol as diol comonomers.[39] These semicrystalline copolyesters displayed significant hydrodegradability when they were incubated in aqueous buffer, and also certain biodegradability when were subjected to the action of lipases.

2,5-furandicarboxylic acid (FDCA), a furan derivative obtained from different carbohydrate sources, has recently gained particular attention as a suitable monomer for replacing terephthalic acid for step-growth polymerization. Moore and Kelly initially explored the scope and limitations of FDCA in polycondensation reactions and synthesized a series of polyesters based on FDCA and several diols.[40] However, due to the limited availability of high-purity FDCA, the research interest in this field declined in the following years. Recent developments in the catalytic routes toward high-purity FDCA allowed the preparation of larger amounts of this compound in high purity, and renewed the interest for this compound for the production of sustainable polycondensates. The use of FDCA to obtain bio-based polyesters has been extensively studied in the last years.[41-44] FDCA has been used in conjunction with ethylene glycol to synthesize poly(ethylene 2,5-furandicarboxylate) (PEF), *i.e.* the furan analogue of PET. When PET and PEF with similar molecular weights are compared it is observed that the replacement of the terephthalate unit by the furanoate one leads to a decrease in the melting temperature, whereas not significant differences are appreciated in the glass-transition temperature.[45] In fact the T_g and T_m reported for a PEF with M_w/M_n of 44,500/22,400, which are values comparable to those of commercial PET, are 80 ºC and 215 ºC, while T_g and T_m values commonly reported for PET fall within the 75-85ºC and 250-260 ºC ranges, respectively. The same considerations apply to the polymer homologues bearing 1,4-butanediol units, *i.e*. PBF and PBT.[46] The angle between the carboxylic acid groups, which defines the degree of linearity of the monomer, is 180º in terephthalic acid whereas it ranges from 129.4º (X-ray diffraction) to 133.6º (DFT) and hence closer to the value of 120º found for isophthalic acid.[47] Although the use of both terephthalic acid and FDCA results in a similar T_g of their corresponding polyesters, the lack in monomer linearity in the latter has significant depressing effects on crystallinity.[48]

3. Terephthalate polyesters from carbohydrate-based bicyclic monomers

Aromatic polyesters of industrial relevance like PET, PBT and other poly(terephthalate)s distinguish in displaying a relatively high T_g, which in combination with their crystallinity, results in a very satisfactory pattern of mechanical behavior.[7a] Such properties derive from the stiffness that the plate-like phthalate units confer to the polyester chain otherwise highly flexible due to the low energy barrier for the C-O-C linkage rotation. The substitution of the exceptionally rigid phthalate units in aromatic polyesters by acyclic or even mono-alicyclic units unavoidable entails a severe decreasing in chain stiffness with the consequent impoverishment of thermal and mechanical properties. On the contrary, bicyclic monomers, particularly those consisting of fused rings, are characterized by a high molecular rigidity that along with their great voluminosity are able to restrict the polymer chain movement as much as aromatic units do. In these last years, it has been shown that both bicyclic dianhydrides and diacetalized sugar-derived compounds are incorporated into the aromatic polyester chains retaining or even increasing the T_g of the resulting copolyesters. The incorporation of the CBB units can be made by replacing either the dioxyalkylene or the terephthalate units in the aromatic polyester (Scheme 4). Obviously, the enhancing effect on T_g becomes much more pronounced when the aliphatic moiety of a poly(alkylene phthalate) is the replaced unit.

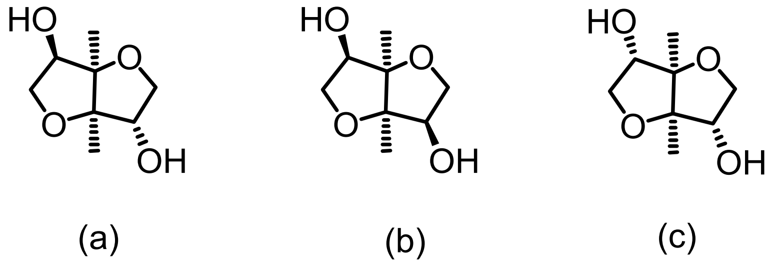


Scheme 4. Two routes towards polyesters containing CBB units.

In addition to the satisfactory effect on T_g and the sustainable quality that the utilization of these carbohydrate-derived compounds bestows to the resulting polyesters, they also enhance the polyester susceptibility to degradation regarding both chemical and biological hydrolytic processes. The precise effect that copolymerization exerts on each one of these properties is determined, in addition to the degree of substitution, by both the structure of the bicyclic compound and the particular constitution of the counterparts integrated in the polyester chain. Finally it is necessary to remark that synthetic aspects concerning both monomers and polymers are of primary importance in the overall evaluation of the new bio-based polyesters. Synthesis outcomes significantly depend on the nature of the bio-based comonomer and the global composition of the system, the differences being particularly significant when isohexides and diacetalized compounds are compared.

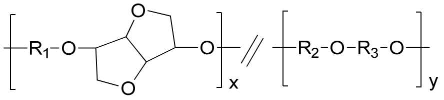
3.1. Terephthalate polyesters from isohexides

1,4:3,6-Dianhydrohexitols, such as isosorbide, isomannide and isoidide (Scheme 5) have been used in the last thirty years for the synthesis of different condensation polymers,[18,21,47,48] such as polyesters, polyamides, polyurethanes and polycarbonates as well for orthogonal chemistry.[49] Representative terephthalate polyesters and copolyesters synthesized from these monomers are shown in Table 1.



Scheme 5. Chemical structure of isosorbide (a), isomannide (b) and isoidide (c).

Table 1. Terephthalate polyesters containing isohexide units



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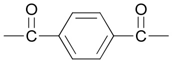
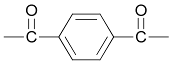
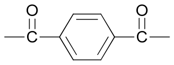
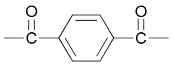
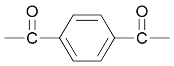
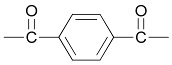
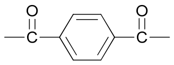
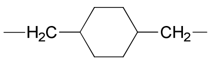
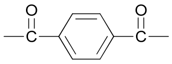
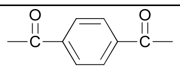
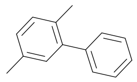
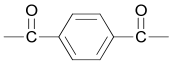
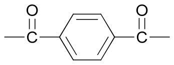
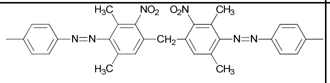
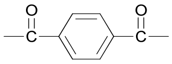
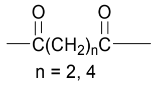
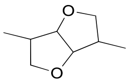
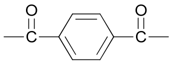
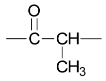
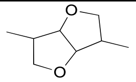
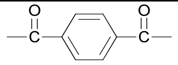
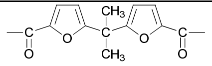
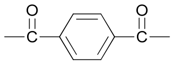
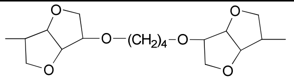
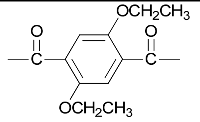
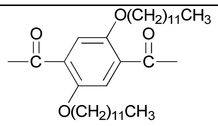
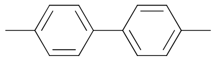
	-	-	17,50-52a
		$—CH_2CH_2—$	53-56
		$—CH_2CH_2CH_2CH_2—$	57-59
		$—CH_2CH_2—$ 	56
			60
			61
	 $\overset{O}{\overset{\|}{C}}(CH_2)_n\overset{O}{\overset{\|}{C}}$ n = 2, 4		62
	 $\overset{O}{\overset{\|}{C}}-\underset{CH_3}{CH}$		63
		$—CH_2CH_2—$	64
-			65
	-	-	50
	-		66

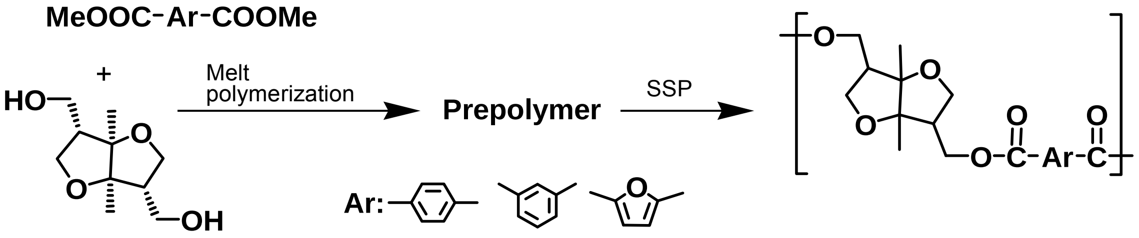
A largely appreciated feature of these bicyclic diols is their ability to increase the T_g when they are replacing totally or partially the aliphatic diol used in the synthesis of polyesters or copolyesters. In Table 2 the main thermal transitions of the most common poly(alkylene terephthalate)s and the poly(terephthalate)s made from isosorbide (PIsT) and from isoidide (PIiT) are compared. As it is expected, an increase in the number of methylene units produces a decrease in both melting and glass-transition temperatures of poly(alkylene terephthalate)s. On the other hand, the T_g of PIsT and PIiT stand at a much higher level exceeding the T_g of PET in more than 100 ºC when high molecular weight isohexide polyesters are concerned (in bold). The molecular symmetry of the isohexide is reflected in the crystallinity degree of the polyester; PIsT is an amorphous material due to the non-stereoregular structure of the chain, whereas PIiT is semicrystalline with a melting temperature of 261 ºC, which is not far from that of PET.

Table 2. Compared main thermal transitions of terephthalate polyesters

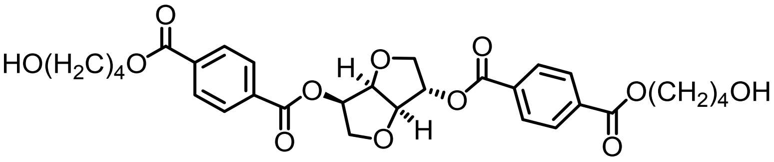
Polyester	**T_g (ºC)**	**T_m (ºC)**	**References**
PET	78	256	7b
PBT	45	220	7c
PHT	10	143	67
PIsT	147-**205**	-	17,50,52b,55,59,63
PIiT	153-**209**	261	50,52b

A severe drawback of isohexides is their low reactivity in polycondensation reactions due to the secondary nature of their two hydroxyl groups, and in the case of isosorbide, also due to their different steric position respect to the bicycle frame (*endo* and *exo* positions).[21,52a] This is in fact the reason invoked by different authors to explain the deficient incorporation of isosorbide in PET[56] or PBT[58,59] copolyesters when prepared by the classical two-step melt polycondensation process. Charbonneau et al.[68] reported 16 examples of synthesis of aromatic copolyesters varying in the 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 to isohexides. A new catalytic system based in 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.[54] Also a trivalent bismuth catalyst has been claimed for preparing the same copolyesters at reduced polycondensation temperatures with lower raw material losses.[69] Hayes et al.[70] 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 6) via melt and solid state polycondensation (SSP).[43] A macrodiol made from isosorbide diesterified by a terephthalate derivative (Scheme 7), has been used for the synthesis of PBT copolyesters via solid-state polymerization with a blocky microstructure, and molecular weight and thermal properties improved respect to those obtained by polycondensation in the melt.[57,59] Storbeck *et al.* reported the synthesis of high molecular weight aromatic polyesters based on isosorbide, isomannide and isoidide by polycondensation in solution with terephthaloyl chloride and 2,5-diethoxyterephthaloyl chloride.[50] It was observed that the T_g of the 2,5-diethoxy substituted poly(terephthalate)s was around 70 ºC lower than those of non-substituted ones, a reasonable result according to the free volume increase caused by the presence of the ethoxy side groups. Chatti *et al.* synthesized a diol-ether of isosorbide that was made to react with terephthaloyl chloride to produce aromatic poly(ether-ester).[65] It was observed that the reaction proceed five times faster under microwave irradiation.



Scheme 6. Synthesis of aromatic polyesters from 2,5-dimethanol isoidide.[43]



Scheme 7. Isosorbide macromonomer used for the modification of PBT by SSP.[57]

The glass-transition temperature as well as the melting temperature and crystallinity in PET or PBT copolymers containing isosorbide can be conveniently tuned by composition. Figure 1 shows the evolution of these two thermal transitions with the isosorbide content in PET and PBT copolyesters.[55,57] Amorphous PET copolyesters with a T_g around 100 ºC are obtained when the content in isosorbide reaches 20 mol-%.

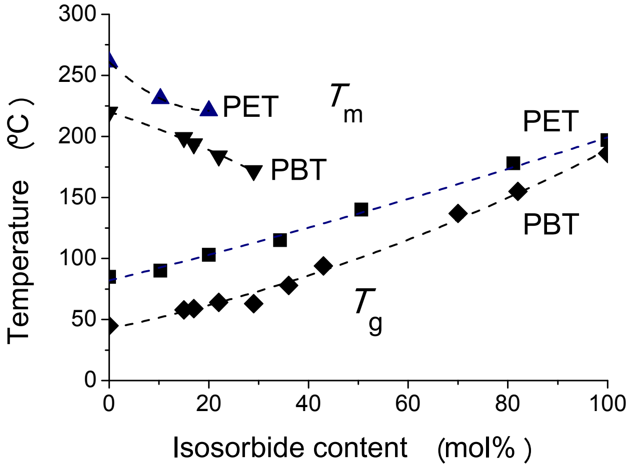
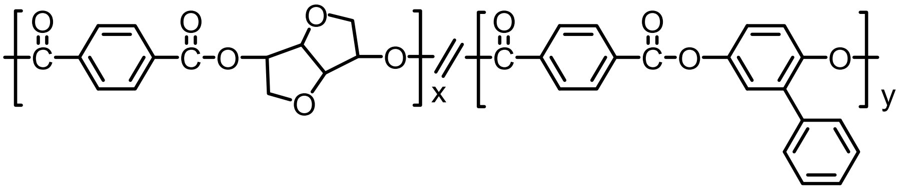


Figure 1. Melting (triangles) and glass-transition (squares) temperatures of PET and PBT random copolyesters as a function of molar content of isosorbide.[55,57]

Discoloration is frequently a serious inconvenient of poly(terephthalate)s containing isosorbide because a well transparent colourless appearance is essential for many applications. Adelman et al.[71] prepared PET copolyesters with low content of diethyleneglycol and low colour using suitable bases such as tetramethylammonium hydroxide (TMAH) in combination with germanium oxide catalyst (GeO_2) in the polymerization reaction. They claimed that these copolyesters were suitable for making bottles, hot-fill containers, films, sheets, etc. In another related work, it was observed that the use of primary antioxidants such hindered phenols, and secondary antioxidants such trivalent phosphorous compounds were able to improve the final colour of these copolymers.[72]

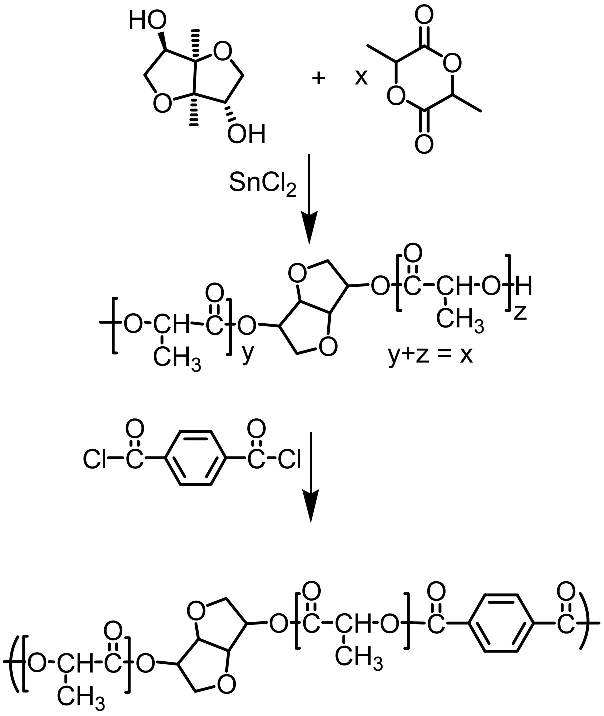
Aromatic terpolyesters containing isosorbide display thermal properties highly depending on composition in cyclic units. Quintana *et al.* prepared series of random PET terpolyesters containing variable amounts of 1,4-cyclohexanedimethanol (CHDM) and isosorbide.[56] The glass-transition temperature of 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 104-127 ºC according to the terephthalate/furoate and ethyleneglycol/isosorbide ratios with good thermal stability and enhanced solubility in common solvents.[64]

The stiff nature of isosorbide allows its use as monomer for the synthesis of rigid polymer chain with liquid crystal properties and several examples are given in the literature. If isosorbide is partially replaced in PIsT by aromatic diols such as phenyl-hydroquinone, cholesteric thermotropic materials with good thermal stability can been obtained (Scheme 8).[60] Its replacement by monomers containing azobenzene mesogenic groups allowed the synthesis of liquid crystal copolyesters with high glass-transition temperatures and good thermal stability useful for the preparation of materials for nonlinear optical applications.[61] On the other hand, the reaction of 2,5-bis(dodecyloxy)terephthaloyl chloride with mixtures of isosorbide and 4,4'-dihydroxybiphenyl lead to the synthesis of thermotropic 2,5-disubstituted terephthalate copolyesters displaying Grandjean textures for 10% contents in isosorbide units.[66]



Scheme 8. Chemical structure of thermotropic liquid crystalline copolyesters.[60]

Very recently several works dealing with aliphatic-aromatic copolyesters containing isosorbide have appeared. The partial replacement of the terephthalate units in PIsT by aliphatic ones leads to aliphatic-aromatic copolyesters with lower glass-transition temperatures and lower thermal stability but with enhanced biodegradability.[62,63] Kricheldorf *et al*. prepared biodegradable isosorbide terephthalate copolyesters containing lactate units by polycondensation of the oligomer obtained from lactide and isosorbide with terephthaloyl chloride (Scheme 9); the segmented lactate-terephthalate copolyesters had glass-transition temperatures within the 90-180 ºC range decreasing linearly with the composition in lactate units.[63] Aliphatic-aromatic copolyesters obtained from mixtures of lactic and terephthalic acids with ethylene glycol and isosorbide are claimed to show excellent thermal and color properties; these copolyesters have been recently patented for uses as films, sheets, and optical products.[73]



Scheme 9. Synthesis of copolyesters from isosorbide, L-lactide and terephthaloyl chloride.[63]

3.2. Terephthalate polyesters from bicyclic diacetalized monomers

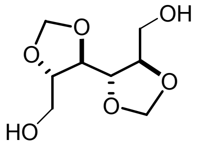
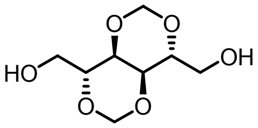
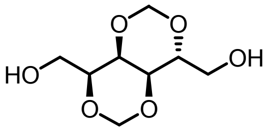
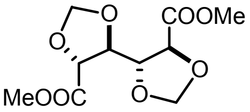
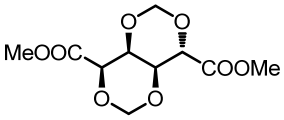
In principle, the utilization of CBB acetals as monomers in the synthesis of polyesters pursues the same basic objectives than those attained when isohexides are the replacing compounds. Thus fully or partially renewable polymers with improved thermal properties, satisfactory mechanical behavior and enhanced hydrodegradability compared to the parent polyesters are intended. Depending on which family of CBB compounds, isohexides or diacetals, the polyesters come from, not only significant differences in their basic properties but also remarkable dissimilarities in synthesis are appreciable. Whereas diacetalized alditols are highly reactive primary alcohols, isohexides are secondary diols and consequently, their reactivity in esterification reactions is relatively low due to both the attenuated nucleophilicity of the hydroxyl group and negative steric effects. From the point of view of accessibility, both diacetal diacids and diols derivatives may be prepared in most cases by a comparable synthetic chemistry which makes feasible therefore the replacement of either the diacid or the diol unit in the polyester. On the contrary, the synthesis of isohexides bearing carboxylate groups is only feasible after considerable chemical modifications in the firstly generated dianhydride diol. The relatively inaccessibility to carboxyl-functionalized isohexides explains the highly preferential (almost exclusive) use that is made of these compounds as diols.

The most severe shortcoming of the bicyclic diacetals compounds compared to isosorbide is out of question the much more complicated procedures required for their synthesis. Their preparation not only involves more chemicals and reaction steps but also needs the use of rather hazard compounds as paraformaldehyde. Such synthetic advantage of isosorbide over diacetals is not readily extensible to other isohexides since additional reactions are needed to convey the appropriate stereochemical conversions of isosorbide. Recent advances in this direction make use of ruthenium catalyst for an efficient epimerization of isosorbide into isoidide.[74] It should be remarked in favor of the diacetalized monomers that no attention has been given to date to the optimization of the synthesis of this family of compounds focused on their scaling up with industrial purposes. It is not unreasonable therefore to presume that these syntheses will become more affordable in the future by simplifying the procedure and reducing the utilization of hazardous reagents and solvents. The chemistry history is rich in cases in which, compounds initially difficult to synthesize became finally amenable at industrial scale because their use was indispensable for new valuable applications.

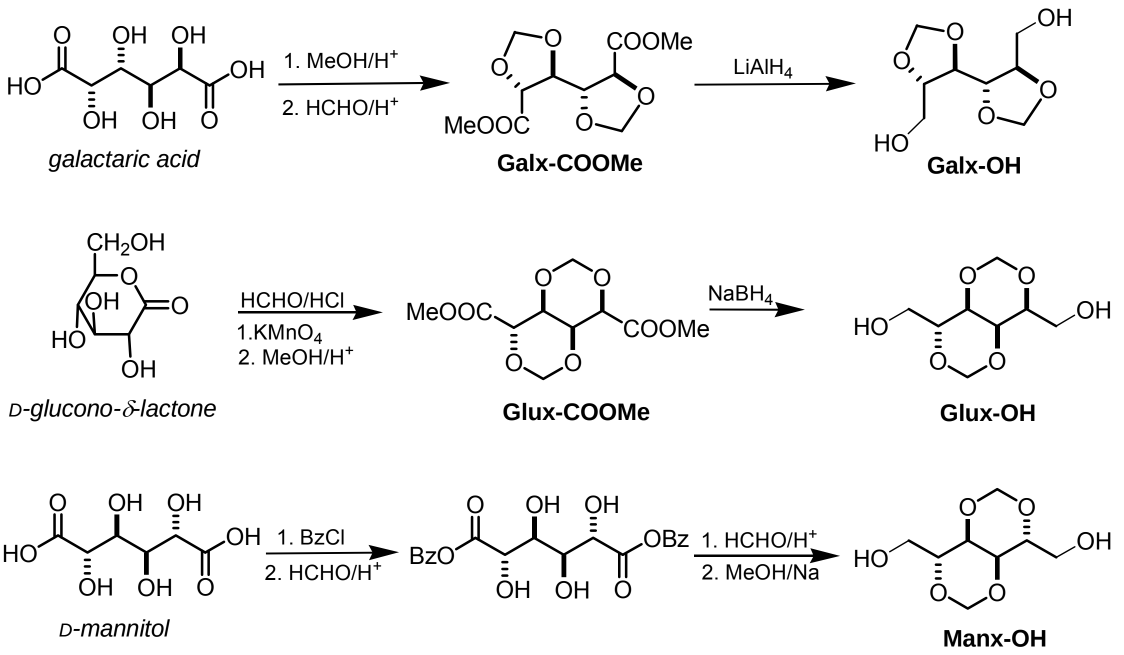
3.2.1. Bicyclic diacetalized diols and diacids

The studies carried out up to date on terephthalate copolyesters containing CBB acetalized units have made use of an assortment of diacetalized C6-alditols and C6-dimethylaldarates differing in the configuration of the sugar moiety. *Galacto*, *manno* and *gluco* have been the stereochemical structures investigated so far. The criteria applied for selection obey mainly to synthesis simplicity, accessibility of the starting material and structural features of the diacetalized monomers. The whole collection of these monomers with information of the most relevant characteristics regarding their use as polycondensation monomers is presented in Table 3.

Table 3. Main features of bicyclic acetalized alditols and methyl aldarates.

Sugar configuration	**Galx**	**Manx**	**Glux**
Chemical name	2,3:4,5-di-*O*-Methylene-galactitol (**Galx-OH**)	2,4:3,5-di-*O*-Methylene-D-mannitol (**Manx-OH**)	2,4:3,5-di-*O*-Methylene-D-glucitol (**Glux-OH**)
Chemical structure			
Chemical name	Dimethyl 2,3:4,5-di-*O*-methylene-galactarate (**Galx-COOMe**)		Dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (**Glux-COOMe**)
Chemical structure			
Cycle structure	1,3-Dioxolane	1,3-Dioxane	1,3-Dioxane
Symmetry	I	C_2	1
Function stereo positions	-/-	*exo*/*exo*	*exo*/*endo*
Melting point	100-102/ 106-107 ºC	139-140 ºC	192-194/157-158 ºC
Synthesis ref.	75,76	77,83a	78,79,84b
Natural source	D-Galactose	D-Fructose	D-Glucose

The synthetic routes followed for the preparation of the bicyclic acetalized monomers are depicted in Scheme 10. The two monomers with *galacto* configuration, 2,3:4,5-di-*O*-methylene-galactitol (Galx-OH) and dimethyl 2,3:4,5-di-*O*-methylene-galactarate (Galx-COOMe), are prepared from commercially available galactaric acid (mucic acid). The procedure consists essentially in the acetalization of the four secondary hydroxyl groups of methyl galactarate with paraformaldehyde followed by reduction of the carboxylate groups. A similar route is followed for the synthesis of the *gluco* monomers Glux-OH and Glux-COOMe, in this case using commercial D-glucolactone as starting material. The synthesis of the *manno* diol Manx-OH is carried out from D-mannitol by acetalization of the previously prepared 1,6-di-*O*-benzoyl derivative and subsequent removal of the protecting group. All the diacetalized diols and dimethyl esters are crystalline compounds that are easily isolated and purified. The synthesis of dimethyl mannarate (Manx-COOMe) in the amounts required for exploring its potential as polycondensation monomer presented insurmountable difficulties that have prevented its inclusion in the studies carried out so far.

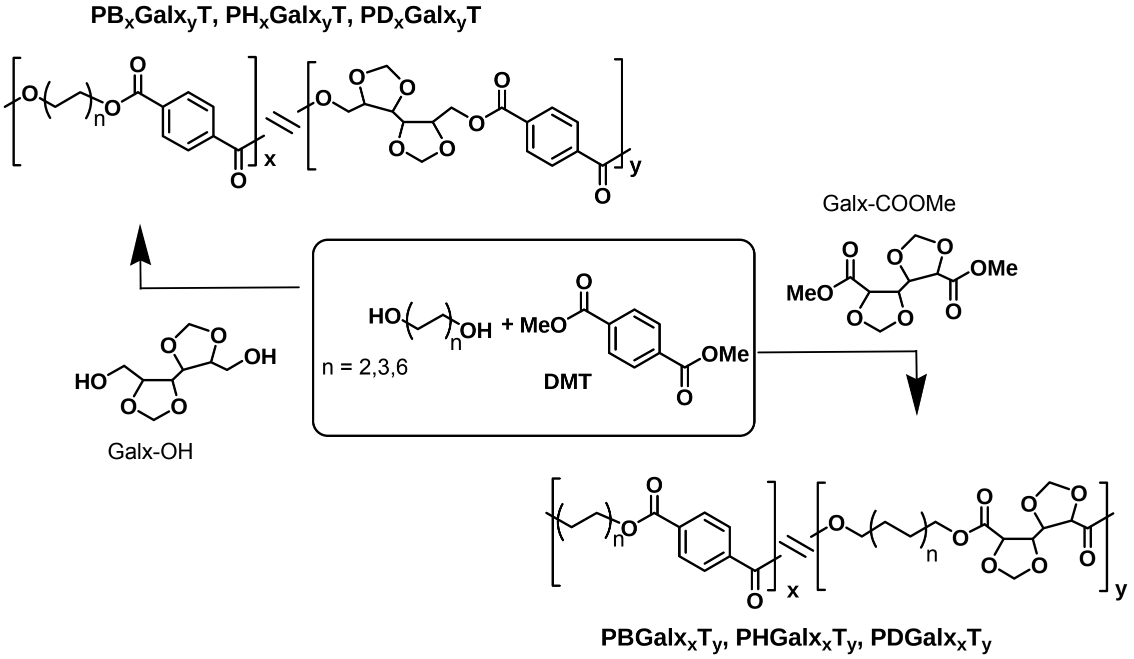


Scheme 10. Synthetic routes leading to CBB diacetalized monomers.

The CBB diacetalized diols and dimethyl esters are bifunctional compounds suitable for the generation of linear polycondensates; the four secondary hydroxyl groups present in the genuine sugars are blocked as quite stable 5- or 6-membered cyclic acetals. The cycloacetal is a widely recognized structure for its high efficiency in protecting hydroxyl and carbonyl groups under neutral or basic conditions but readily removable by acidic hydrolysis. The cyclic methylene acetals distinguish however in that they are reluctant to hydrolysis under any condition so their removal is not feasible by the usual methods. Furthermore they all are highly stable to heat, which together with their good chemical stability make them fully appropriate for permanent monomer protection. Whereas the Manx and Glux compounds share the same bicyclic structure made of two fused 1,3-dioxane rings that confers to the molecule a high stiffness, the diacetal arrangement adopted by the *galacto* configuration consists of two independent 1,3-dioxolane rings linked by a single C-C bond which allows certain molecular flexibility. Molecular symmetry is another structural feature differentiating these compounds. Whereas diols and diesters with *galacto* configuration are centrosymmetric and those with *manno* configuration have a C_2 axis, the *gluco* monomers lack of any symmetry element. As a consequence only the polyesters generated from Galx and Manx monomers would be able to display chain stereoregularity. A second consequence of such differences in symmetry is that the two reactive functions remaining in the diacetalized compounds (hydroxyl or methylcarboxylate) have the same spatial orientation (*exo*-*exo*) respect to the bicyclic frame in the symmetrical compounds whereas they are *exo* and *endo* in the *gluco* structure. The different spatial arrangement between the two functions attached to the monomer rings might be reflected in a dissimilar reactivity with possible consequences in chain growing, as it is known to happen in isosorbide-derived polycondensates.[21,52,80] In the diacetalized compounds such differences are alleviated due to the high reactivity inherent to the primary character of the hydroxyl groups as well as to their farther distance from the cyclic structure.

3.2.2. Galactose-derived terephthalate polyesters

The *galacto* compounds 2,3:4,5-di-*O*-methylene-galactitol (Galx-OH) and dimethyl 2,3:4,5-di-*O*-methylene-galactarate (Galx-COOMe) have been used as comonomers of a variety of aliphatic diols and dimethyl terephthalate (DMT), respectively, to produce an assortment of polyesters and copolyesters with the general formulae depicted in Scheme 11. The synthesis results and more significant properties of the Galx containing polyesters are given in Table 4.



Scheme 11. Synthesis of polyesters and copolyesters containing Galx units.

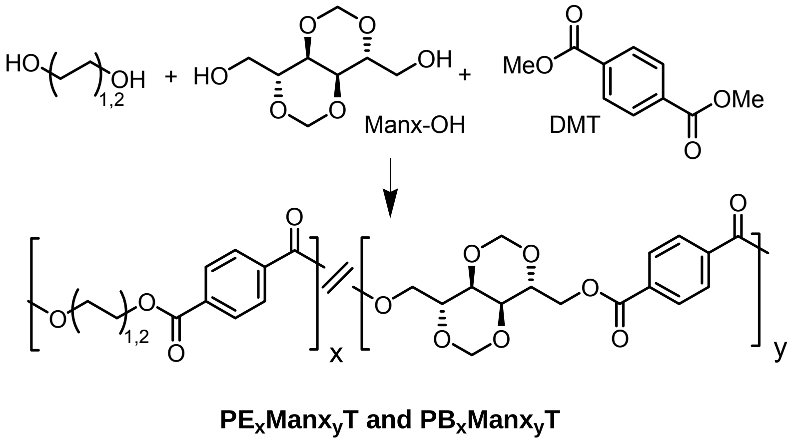
The copolyester series made from mixtures of Galx-COOMe and DMT and 1,4-butanediol (BD), 1,6-hexanediol (HD) or 1,12-dodecanediol (DD) were described by Lavilla *et al.*[81a,b] They were prepared by melt polycondensation using the protocol previously set up for the polymerization of Galx-COOMe with aliphatic diacids and diols.[82a] Polymerization conditions were adapted to the volatility of Galx-COOMe, and the more active dibutyl tin oxide (DBTO) was the catalyst of choice instead of the commonly used titanium (IV) tetrabutoxide (TBT). By this method, random PBT_xGalx_y copolyesters with pretty high molecular weights (M_w ranging between 30,000 and 42,000 g·mol^{-1}) were obtained in good yields as white powders. Most of these copolyesters were able to crystallize from the melt with almost full recovering of the initial crystallinity and slightly diminished melting temperatures. All PBT_xGalx_y displayed crystallinity upon precipitation from solution, and they retained the crystal structure of the PBT homopolyester. In all cases, the T_g steadily decreased as the terephthalate units were replaced by the galactarate ones, due to the less rigid structure of the non-fused *galacto* unit compared to the aromatic one. Accordingly, decay in the elastic moduli and tensile strength was reported. The thermal stability also decreased with the degree of replacement. Hydrolytic degradation and biodegradation essays performed on some of these polyesters demonstrated that hydrolysis was largely enhanced by copolymerization and brought into evidence the capacity of the galactarate units for making aromatic polyesters susceptible to biodegradation.[81c]

Random copolyesters PB_xGalx_yT containing the Galx structure as diol unit were prepared by copolymerization of mixtures of Galx-OH and BD units with DMT by polycondensation in the melt using the same catalyst as before.[81b] In this case milder reaction temperatures (160 ºC) were initially applied to minimize volatilization of Galx-OH and to control accurately the incorporation of the diols into the copolyester chain. Although all the copolyesters were semicrystalline only those containing up to 20% of Galx units were able to crystallize from the melt. It was found that, at difference to what happens with PBT_xGalx_y, the incorporation of the sugar as diol units in the PBT chain led to an increase in thermal stability. Furthermore, the presence of the Galx units in PB_xGalx_yT increased the glass-transition temperature and the mechanical moduli, since in this case the substitution of the alkanediol by Galx-OH makes stiffer the polymer chain. Although PB_xGalx_yT copolyesters were not biodegradable in the presence of lipases, the presence of the Galx as diol units also enhanced the hydrodegradability of PBT.[81c]

3.2.3. Mannose-derived terephthalate polyesters

Bio-based PET and PBT copolyesters were prepared when the bicyclic *manno* diol Manx-OH was made to react with mixtures of DMT and EG or BD, respectively. Polycondensations were conducted in the melt, also using DBTO as catalyst.[83] The chemical formulae of these Manx-containing polyesters and copolyesters (PE_xManx_yT

and PB_xManx_yT) are depicted in Scheme 12. The synthesis results and more significant properties of the Manx containing polyesters are given in Table 5.



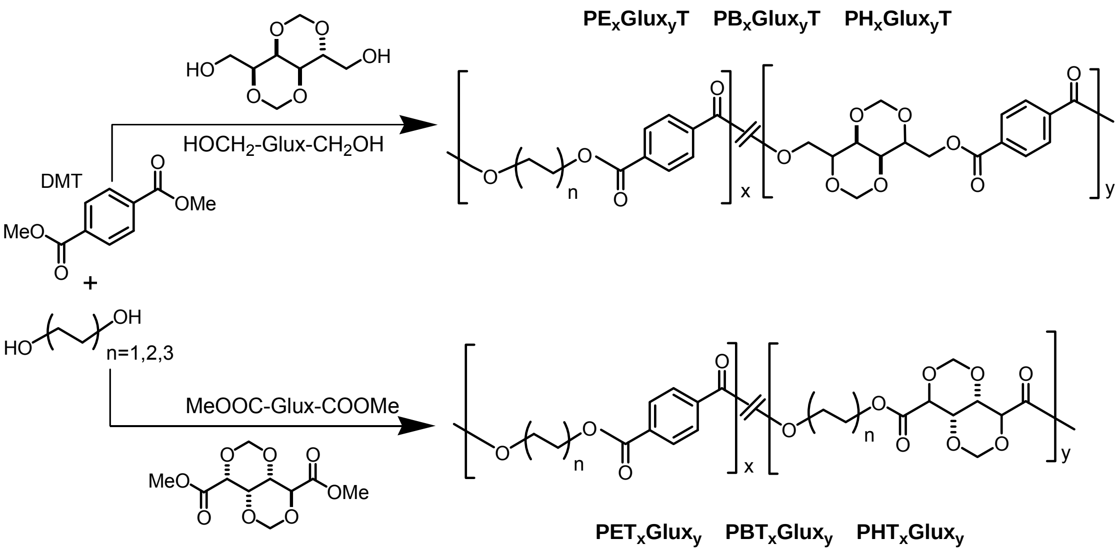
Scheme 12. Synthesis of polyesters and copolyesters containing Manx units.

Taking into account the same consideration as in previous cases, reaction temperatures were kept as low as possible, starting at 160 ºC and increasing up to the value required to prevent crystallization of the formed oligomers. Within each series, lower temperatures and longer reaction times were used for copolyesters with higher contents in Manx units. The random copolyesters were obtained in good yields and molecular weights (M_w) between 33,000 and 51,000 g·mol^{-1}. Molar compositions very close to those of the feed ratio were obtained for all the PB_xManx_yT copolyesters. Conversely, the content of in Manx units in the PE_xManx_yT series was found to be in all cases higher than in their corresponding feeds; such a preference was attributed to losses of the more-volatile ethylene glycol provided that EG and Manx-OH react at a similar rate. PE_xManx_yT and PB_xManx_yT copolyesters containing up to 14% and 40%, respectively, of Manx units were semicrystalline, but only the latter were able to crystallize from the melt provided that their content in Manx does not go beyond 20%.The thermal stability of the PManxT homopolyester, *i.e.* with all the aliphatic diol units replaced by Manx-OH, was found to be intermediate between those of PBT and

PET. Accordingly, thermal stability in the PB_xManx_yT series increased when BD was replaced by the Manx units, whereas the trend was opposite in the PE_xManx_yT series. It is worthy to mention however that in the latter the decreasing in the thermal stability is very slightly with the decomposition temperature decreasing around 20 ºC in the most detrimental case. In both series, the glass-transition temperature and also the mechanical moduli steadily increased upon incorporation of Manx units. Neither PE_xManx_yT or PB_xManx_yT were degraded by enzymes but both of them showed enhanced susceptibility to hydrolysis compared to their respective parent homopolyesters.

3.2.4. Glucose-derived terephthalate polyesters

2,4:3,5-di-*O*-Methylene-D-glucitol (Glux-OH) and dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-COOMe) are the two CBB acetalized compounds derived from D-glucose that have been used so far for the synthesis of polyesters and copolyesters by reaction with DMT and EG, BD or HD as comonomers. The chemical route applied for these syntheses is depicted in Scheme 13. The synthesis results and more significant properties of the Glux containing polyesters are given in Tables 6 and 7.



Scheme 13. Synthesis of polyesters and copolyesters containing Glux units.

Glux-OH was used as comonomer of HD in the reaction with DMT in the melt to produce a set of random copolyesters (PH_xGlux_yT) with Glux contents ranging from 5 to 32%-mole.[84a] The polymerization was performed in two steps in the presence of TBT catalyst. Since Glux-OH is highly sensitive to temperature it was necessary to adjust the reaction conditions according to composition to minimize thermal degradation. Nevertheless PH_xGlux_yT copolyesters were thermally stable up to nearly 370 ºC. All PH_xGlux_yT copolyesters were semicrystalline with melting temperatures decreasing from 144 ºC to 84 ºC and only those containing 5 and 10% of Glux units were able to crystallize upon cooling from the melt. T_g notably increased with the incorporation of sugar diol going from 8 ºC in PHT to near 60 ºC in the copolyester containing 32%-mole of Glux. Compared to PHT, PH_xGlux_yT copolyesters showed not only an enhanced susceptibility to hydrolysis but also an appreciable biodegradability in the presence of lipases. The Glux-COOMe was used in turn as comonomer of DMT in the polycondensation with HD in the melt to produce random copolyesters PHT_xGlux_y with contents in glucarate units up to 50% and molecular weights (M_w) between 20,000 and 50,000 $g \cdot mol^{-1}$ and dispersities within the 2.1-2.4 range. These copolyesters started to decompose at lower temperature than their analogs made from Glux-OH. Interestingly, the T_g of PHT increased steadily with copolymerization attaining 50 ºC for a 50% of substitution in glucarate units.

Glux-OH and Glux-COOMe have been later copolymerized with EG and DMT, respectively, by polycondensation in the bulk to produce PET copolyesters PE_xGlux_yT and PET_xGlux_y as well as their parent homopolyesters with 100% of substitution.[84b] Since higher temperatures were required in the synthesis of PET copolyesters and given the susceptibility to heat of the Glux compounds, the polymerization process was assisted in this case by addition of antioxidants (*Irganox 1010* and *Irgafos 126*) and using DBTO instead of TBT as catalyst.

The PET copolyesters with either the diol or the diacid counterpart partially replaced by Glux were obtained in 89-90% yields and had molecular weights in the

20,000-40,000 g·mol^{-1} range, white color and a random microstructure. Thermal decomposition of the PE$_x$Glux$_y$T copolyesters started to be detectable above 350 ºC following a single stage profile identical to PET. Conversely PET$_x$Glux$_y$ copolyesters exhibited a more complex behavior involving a remarkable lower stability and a two-stages decomposition process at temperatures around to 350 ºC and 450 ºC, respectively. Nevertheless, these copolyesters remained essentially unaltered upon heating at 300 ºC, and therefore they are still suitable for being processed by melting. Compared to PET, these copolyesters exhibited a higher hydrolysis rate and an appreciable susceptibility towards biodegradation.

The incorporation of Glux units in the chain of PET, either as dioxy or as dicarboxylate units, altered significantly the thermal transitions of the polyester. Since the Glux structure is quite rigid, bulky and asymmetric, its restrictive effect on mobility and packing hampers the ordering of the chains to form crystalline domains. Nevertheless PE$_x$Glux$_y$T and PET$_x$Glux$_y$ copolyesters containing up to ~ 10 to 15% of Glux units were semicrystalline, probably because at such low concentrations, the sugar units are selectively rejected from the crystalline phase. Accordingly, the powder WAXS profiles of these copolyesters indicated that they adopt the same triclinic crystal structure as PET[85] with very small deviations in the crystallographic parameters. As expected, melting of these copolyesters occurred at temperatures notably lower than in PET and involved much smaller associated enthalpies and only those containing glucarate units were able to crystallize upon cooling from the melt but at much lower rates than PET.

The enhancing effect of Glux on T_g was very apparent and really interesting. In PE$_x$Glux$_y$T copolyesters T_g attained a value of 154 ºC for the homopolyester, which is almost double the value of PET. In the PET$_x$Glux$_y$ series, the increase in T_g was rather less noticeable because the stiff aromatic ring is replaced in this case. Such change 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. According to such enhancement in T_g and their poor crystallinity, the stress-strain curves of PE_xGlux_yT copolyesters showed an increase in Young's modulus and also in the elongation to break with the Glux content with the consequent increase in toughness.

Finally, the two series of PBT copolyesters, PB_xGlux_yT and PBT_xGlux_y, with contents in Glux units up to 50% have been prepared by polycondensation in the melt of Glux-OH and Glux-COOMe with BD and DMT, PB_xGlux_yT and PBT_xGlux_y.[84c] After purification, the copolyesters were obtained in yields close to 80-90% with M_w in the 28,000-47,000 $g \cdot mol^{-1}$ range, and dispersities between 2.3 and 2.5. The thermal stability of these PBT copolyesters was found to be dependent on their content in Glux units but with opposite effect in each case. In the PB_xGlux_yT series, the thermal stability was found to increase steadily with the replacement of the butylene units whereas PBT_xGlux_y copolyesters showed a complex decomposition behavior at heating that takes place in two well differentiated stages with maximum decomposition rates at the proximities of 350 and 400 ºC. The Glux-containing copolyesters displayed higher sensitivity to hydrolysis than PBT, in particular those containing glucarate units which additionally distinguished by their sensitivity to the action of lipases.

PBT copolyesters containing up to ~30% of Glux units were semicristalline exhibiting endothermic peaks characteristic of melting and crystallizing in the triclinic structure of the parent PBT. Both PB_xGlux_yT and PBT_xGlux_y with contents in Glux units below 20% and 30%, respectively, were able to crystallize upon cooling from the melt. The influence of Glux units on crystallizability was evaluated by a comparative isothermal crystallization study. It was found that the crystallization rate decreased with the insertion of the sugar units with a more pronounced depressing effect in the PB_xGlux_yT series.

The effect of copolymerization on the glass-transition temperatures was very remarkable in these copolyesters. The T_g was found to increase at a ratio of 3 and 1.5 ºC per %-Glux point in the copolyesters made from Glux-OH and Glux-COOMe, respectively. To our knowledge such an enhancing effect has not parallelism in any other bio-based aromatic copolyester series studied to date.

4. Comparative analysis of bio-based terephthalate polyesters containing carbohydrate-based bicyclic units

Experimental data accessible in the literature have been used to compare the different bio-based poly(terephthalate)s containing CBB units, isohexides and diacetals, that have been reported so far. Comparison has been made regarding those basic aspects more relevant to the potential development of the polyesters such as synthesis results, thermal properties, mechanical behavior and degradability.

4.1 Synthesis aspects: Molecular weight and copolyesters composition

It is widely known that the preparation of high molecular weight polyesters is frequently very challenging and even unfeasible in a good number of cases. This is a critical issue in the potential of poly(terephthalate)s since molecular weight is the first parameter limiting their possible applications. The utilization of sugar-derived monomers in the synthesis of aromatic polyesters by melt-polycondensation adds difficulty to the problem because the relatively high sensitivity of these compounds to heat.

The molecular weights attained for the different copolyesters containing CBB units are compared in Figure 2 for similar compositions and polymerization conditions. In plots a) and b), terephphthalate copolyesters made from isosorbide are compared to those made from diacetalized diols for the ethylene and butylene series, respectively.

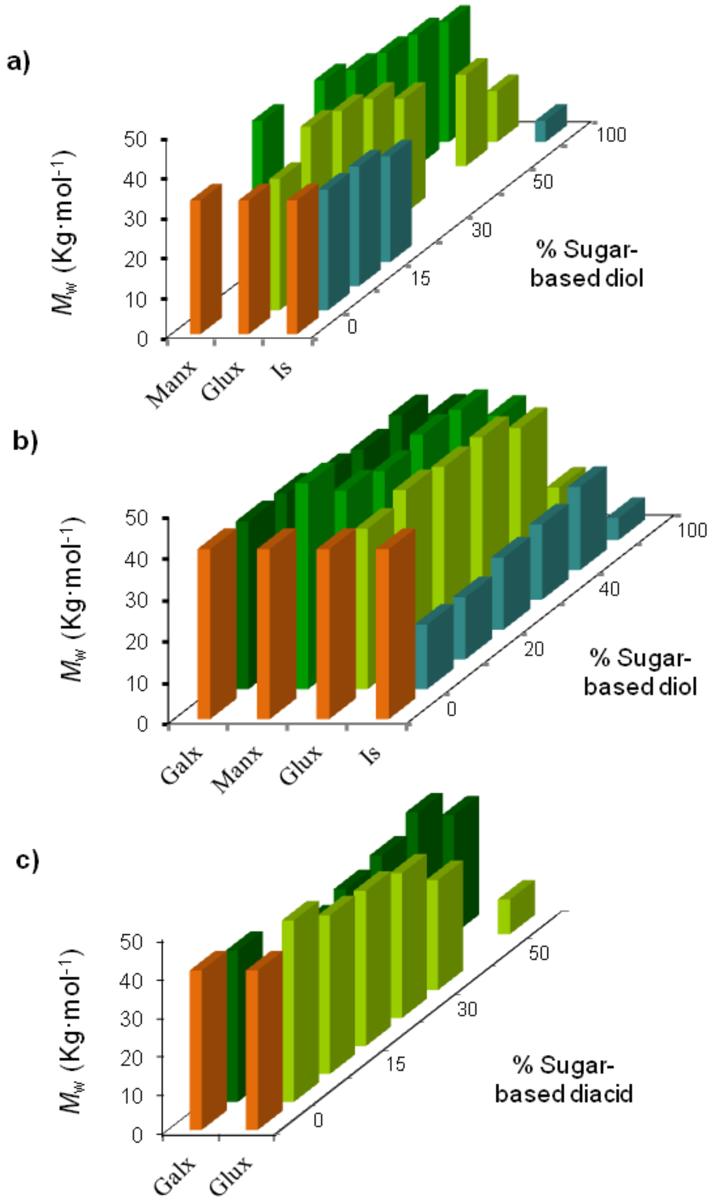


Figure 2. Molecular weight of polyesters and copolyesters containing different BCC units with different compositions. (a) PET copolyesters from BCC diols; (b) PBT copolyesters from BCC diols; (c) PBT copolyesters from BCC diacids.[56,59,81b,83,84b,c]

In both series (PET and PBT) comparing results are similar as far as isosorbide polyesters are concerned. Whereas molecular weights of range similar to PET and PBT are attained for the CBB diacetalized units containing copolyesters, significantly lower values are reported for those containing isosorbide. Such differences must be attributed to the lower reactivity of the secondary hydroxyl groups of isosorbide compared to that of the primary ones present in Galx-OH, Manx-OH and Glux-OH. The low reactivity of Is in melt polycondensation is a well known issue that has been severally reported.[21,58,86] Polycondensation in solution has been shown to be a suitable method to obtain Is containing copolyesters with higher molecular weights but it is not appropriate for industrial application.[6] Recently, Sablong *et al.* reported the incorporation of isosorbide into PBT via solid-state polymerization leading to higher molecular weight copolyesters,[57] however the copolyesters prepared by this method have a blocky microstructure and the amount of comonomer that may be inserted in the initial homopolyester is restricted to a few tens percent.

The c) plot in Figure 2 only includes results for polyesters PBT_xGalx_y and PBT_xGlux_y which were made by copolymerization of DMT with the methyl diacetalized aldarates Galx-COOMe and Glux-COOMe. Unfortunately no experimental data on copolyesters containing diacid units derived from isosorbide are found in the accessible literature. The purpose of this plot is to compare the influence of the CBB structure on molecular weight when the terephthalate is the replaced unit in the bio-based copolyester. Galx and Glux compounds not only differ in the stereochemical configuration but mainly in the arrangement (loose or fused bicycle) that is adopted by the diacetal structure. In both series, copolyesters show satisfactory molecular weights although higher values were attained in the PBT_xGlux_y series for low contents in CBB units whereas the opposite was found as far as copolyesters enriched in such units are concerned.

A second issue important for the appraisal of the synthesis process is the correspondence between the comonomeric composition used in the feed with that present in the resulting copolyester. The influence of the comonomeric system on this aspect is brought out in the plots included in Figure 3. The content of the copolyesters in Is units was found to be in all cases significantly lower than in their corresponding feeds, with losses ranging 20-30% and 10-40% in PET and PBT based copolyesters, respectively (plots a and b). Such discrepancy is attributed again to the higher reactivity of the hydroxyl groups of the replaced alkanediols compared to those of isosorbide.

Conversely, differences observed when the acetalized diols are used as comonomers were almost negligible in most of cases with the largest deviation being observed for $PB_{90}Manx_{10}T$ in which a loss of near 10% was detected. The primary hydroxyl groups of Galx-, Glux- and Manx-diols are able to react at a rate similar to those of EG and BD minimizing differences in the incorporation of the bicyclic comonomers into the copolymer for kinetics reasons. The fact that similar results are obtained for the CBB diacetalized monomers regardless their configuration corroborates that the reactivity of the primary hydroxyl groups of Galx, Manx and Glux is not affected by the cyclic structure which changes from the 2,3:4,5 arrangement in the Galx-OH to the 2,4:3,5 one in both Manx-OH and Glux-OH. The efficiency in the incorporation displayed by the CBB diacetalized diols is shared by diacetalized diesters. In fact, as it is illustrated in the plot c of Figure 2, the monomer, either Galx-COOMe or Glux-COOMe, is fully incorporated in the copolymer at whichever feed composition except for the copolyester $PBT_{90}Galx_{10}$ in which the amount of monomer lost is close to 13%. It is striking the fact that the largest losses take place for $PBT_{90}Galx_{10}$ and $PB_{90}Manx_{10}T$, two structurally different PBT-based copolyesters but sharing the same composition in units. A possible explanation for this result could be the possible stripping of the monomer caused by the large amounts of BD that are released for such compositions.

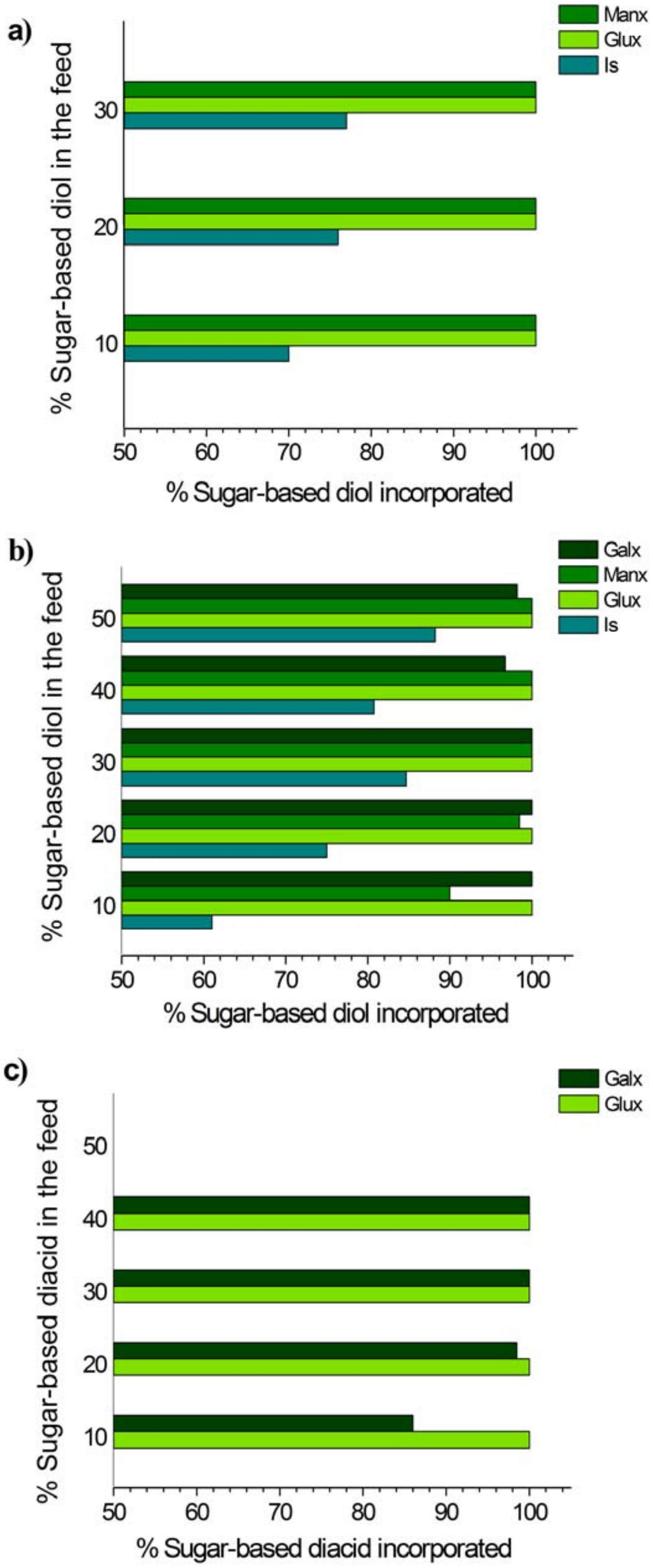


Figure 3. Percentage of the different CBB monomers incorporated in the copolyester for different feed compositions. (a) PET copolyesters from sugar diols; (b) PBT copolyesters from sugar diols; (c) PBT copolyesters from sugar diacids.[56,59,81b,83,84b,c]

4.2. Thermal and mechanical properties

4.2.1. Thermal stability

As it should be expected, the stability to heat of poly(terephthalate)s, and particularly of PET and PBT, is modified with the incorporation of bicyclic units in the polyester only in a moderate extent, and the sense of the change is depending on whether the diol or diacid unit is replaced. An overview of such changes is provided in the plot depicted in Figure 4 where the onset decomposition temperature is represented for PET and PBT copolyesters containing 30% of the different CBB comonomers that have been used. In general it can be said that the resistance to heat diminished with the insertion of CBB units and that such effect is stronger when the diacid is the replacing unit. On the other hand, no significant differences exist when copolyesters made from CBB diol monomers are compared. Nevertheless note that the temperature scale of Figure 4 starts at 300 ºC which is indicative of the high thermal stability that is preserved in all these compounds whatever their composition.

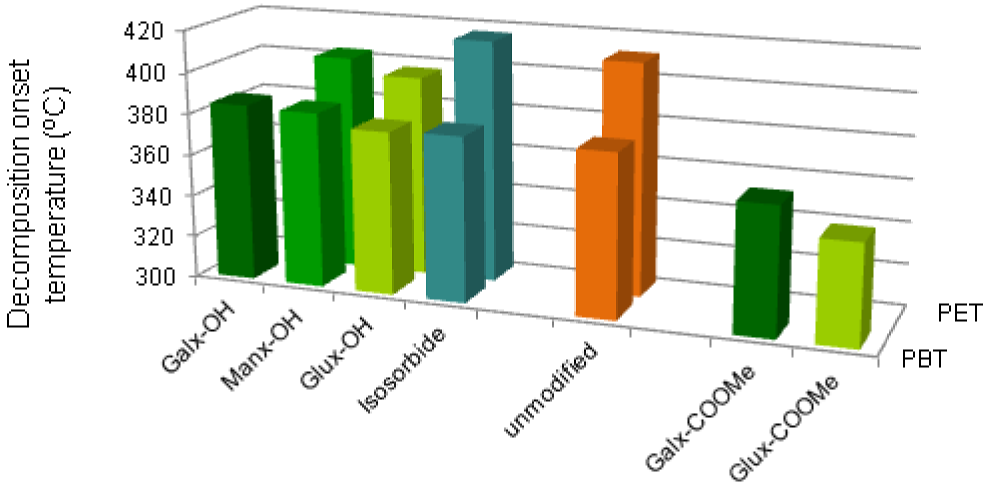


Figure 4. Changes in the onset decomposition temperature (10% of weight loss) of PET and PBT for bio-based copolyesters containing 30% of the indicated CBB units.[56,59,81b,83,84b,c]

4.2.2. Influence of composition on T_g

The changes that take place in the T_g of PET and PBT upon copolymerization using CBB monomers are comparatively represented in the plots included in Figure 5. It can be said in general that the replacement of the alkylene units in the poly(alkylene terephthalate) chain by the bicyclic units gives rise to a steady increase in T_g with the degree of substitution. The magnitude of such increment depends not only on composition but also on the constitution of the replacing bicyclic unit. At first glance it could be inferred that the bicyclic anhydride structure of isosorbide is the most effective in raising the T_g of the polyesters. However some considerations must be taken into account for drawing a trustier conclusion since data coming from different sources are being compared. Note that the higher T_g values reported for Is containing copolyesters correspond to polymers obtained by polycondensation in solution. Given the known high sensitivity of T_g to molecular weight,[21] such differences should be attributed to the larger molecular weights obtained by this method. Moreover the values reported for Is containing poly(terephthalate)s obtained in solution were recorded from semicrystalline samples and therefore expected to be higher than when recorded from amorphous quenched samples. In fact, T_g values reported for PBT copolyesters containing Is units are lower and comparable to those reported for the copolyesters made from acetalized bicyclic diols.

Among CBB diacetalized compounds, those consisting of a fused structure (Manx and Glux) are clearly more efficient in enhancing the T_g than that made of two independent cycles (Galx). On the contrary, differences in configuration do not seem to have relevant consequences on the effect exerted on T_g; variations produced in both PET and PBT series by Manx and Glux are comparable with a slight difference in favor of Glux. A feature of the T_g *vs.* % sugar-content plots deserving attention is the decreasing in the slope observed in the data trend displayed by both Manx and Glux containing PET copolyesters (also shown by PBT copolyesters but less clearly) when the CBB unit content attains about 30-40%. Such a deviation is most likely due to the decreasing in molecular weight attained for such compositions, which cannot be avoided when melt polymerization is the method used for their synthesis.

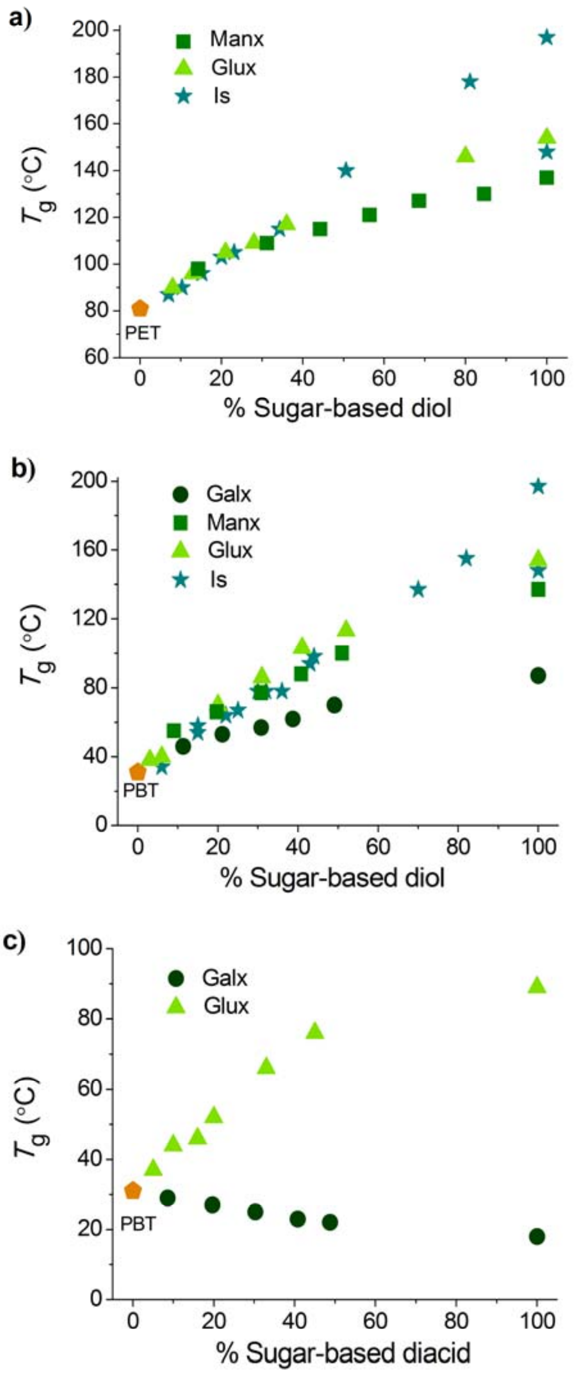


Figure 5. T_g *vs*. composition plots for the indicate copolyester series. (a) PET copolyesters from CBB diols; (b) PBT copolyesters from CBB diols; (c) PBT copolyesters from CBB diacids.[55-59,81b,83,84,b,c] The two values of T_g plotted in a) and b) for PIsT correspond to the polyester obtained in solution[58] and from the melt.[59]

The influence exerted by the Glux units on T_g deserves particular comments. The changes in T_g observed for PET, PBT and PHT upon insertion of Glux units both as diol and diacid within the 5-30% range are depicted in Figure 6. The pertinent conclusion of general validity that is drawn from the inspection of this plot is that T_g of the polyesters increases steadily with the content in Glux units in the three series and whether they are replacing the diol or the diacid units, and that such increasing is more pronounced as the length of the alkylene segment is longer. The relative increasing depends also on which type of unit is replaced, with changes being greater when the diol is the exchanged unit. Nevertheless the increase in T_g caused by the presence of the Glux structure is very noticeable in all cases attaining values similar or even higher than those obtained when Is is the replacing unit and slightly higher than for Manx. What it is really remarkable is that the replacement of the terephthalate units by the bicyclic glucarate units enhances the T_g of the polyester, an effect that is common to the three poly(alkylene terephthalate)s investigated so far. Whether such effect could be exerted also by Is or Manx units is not known since no terephthalate copolyesters containing these structures as diacid units have been synthesized yet. Furthermore data reported for poly(alkylene terephthalate)s copolyesters made from Galx-COOMe indicate that T_g decreases in all cases (Figure 5c).

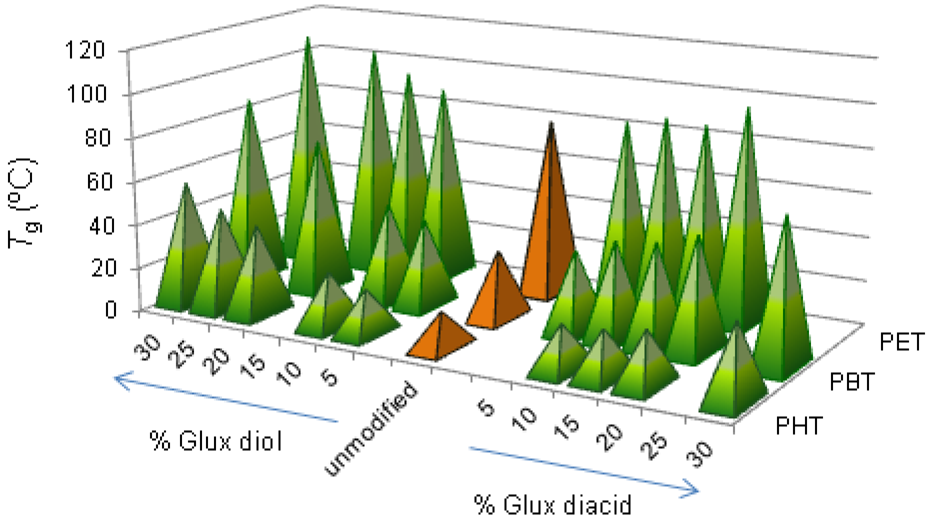


Figure 6. T_g values of PET, PBT and PHT copolyesters made from Glux-OH and Glux-COOMe for different compositions.[84]

4.2.3. Crystallinity and crystallizability

The presence of rigid bulky units, such as the BCC units that are object of this review, in the polyester chains hinders the chain movement and packing, and therefore depresses the crystallinity. In fact, all the random copolyesters containing BCC units reported so far are amorphous or display a diminished crystallinity with melting temperatures noticeably lower than the parent homopolyesters.

It is a generally observed fact that T_m of terephthalate copolyesters containing BCC units steadily decays with the degree of substitution. In Figure 7 comprehensive plots comparing the T_m of all the homopolyesters and copolyesters of PET and PBT synthesized so far using CBB monomers are depicted. These plots reveal that the effect of the content in CBB units on melting is scarcely depending on their structure.

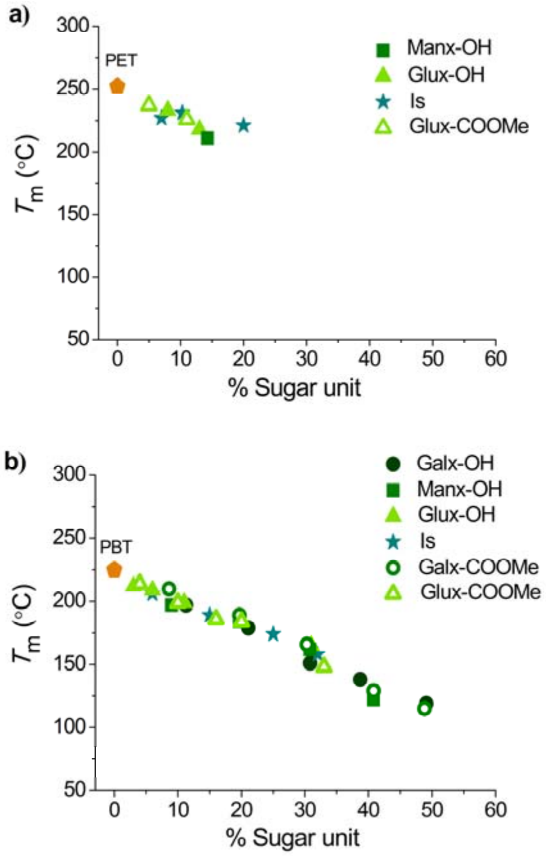


Figure 7. T_m values as a function of composition for the indicated PET (a) and PBT (b) copolyesters containing CBB units.[55-59,81b,83,84b,c]

The potential as bio-based thermoplastics of modified PET and PBT copolyesters is strongly depending on their crystallizability, *i.e*. their capacity for crystallizing measured in terms of crystallization rate and attainable crystallinity degree. A number of isothermal crystallization studies carried out with a diversity of copolyesters containing CBB diacetalized units have demonstrated that crystallizability is depressed by copolymerization,[82-84] in an extent that increases with the content in such units and with their molecular rigidity. Nevertheless a very eloquent parameter to reveal the relative tendency of these copolyesters to crystallize is the maximum composition in CBB at which crystallinity is detected in samples prepared under similar conditions, either upon cooling from the melt or upon precipitation from solution. The plot shown in Figure 8 has been built using such data. It is apparent that the tendency to crystallize is much more pronounced in PBT than in PET, whether homopolyesters or copolyesters are concerned. This behavior is a consequence of the different flexibility between the butylene and ethylene containing polymer chains, which is a widely recognized characteristic distinguishing the two polyesters. Difference in chain mobility is also the reason for the much higher crystallizability found for isocompositional samples prepared by precipitation from solution compared to those prepared by cooling from the melt; since the crystallization rate of poly(terephthalate)s is a viscosity controlled phenomenon, the impeded mobility of the chains in the molten state is the reason for the slower crystallization rate observed under such conditions.

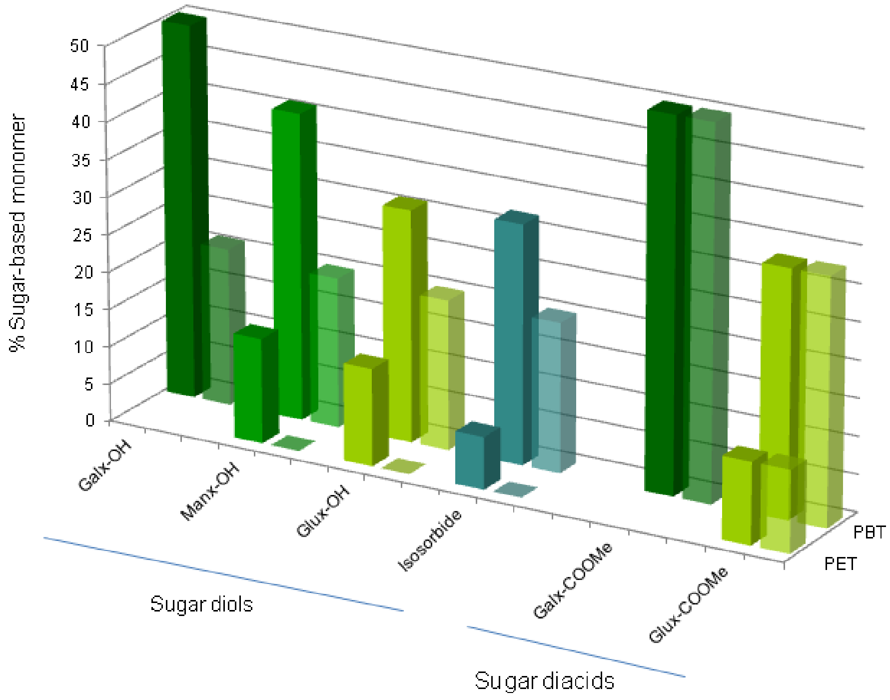


Figure 8. Maximum %-content in CBB units affording crystalline copolyesters. Results are grouped in pairs for each CBB; the more and less solid colors of each pair refer to samples cooled from the melt and precipitated from solution, respectively.[56,59,81b,83,84b,c]

4.2.4. Stress-strain behavior

No study devoted to the evaluation of the mechanical properties of terephthalate polyesters or copolyesters containing isosorbide was found in the accessible literature. A recent study carried out on copolycarbonates in which bisphenol A is replaced by isosorbide in different degrees is the nearest reference dealing with this issue. In these systems, the elastic modulus of the copolyesters increases with the content in Is units, and its value may be tuned by changing the composition.[87] Regarding copolyesters containing CBB diacetalized units, although the accessible information on the mechanical behavior of these compounds is much greater, the reported data are preliminary and they do not cover all the synthesized copolyesters series. Standardized measurements extended to the whole set of series would be required to have a reliable evaluation of the influence of the presence of CBB units in poly(terephthalate)s.

Elastic modulus data reported for PET and PBT based copolyesters containing CBB diacetalized units are plotted against composition in Figure 9. In both cases, the E value is retained or even slightly increased with the incorporation of the CBB units as far as the diol is the replaced unit. The effect is almost the same for the different unit configurations. Conversely, copolyesters in which the terephthalate unit is replaced by CBB units display a steadily decrease in E with the increasing degree of replacement. Regarding elongation at break, a reduction in ductility is produced by copolymerization in most of cases so the stress-strain behavior usually changed from ductile to brittle whichever is the series considered.

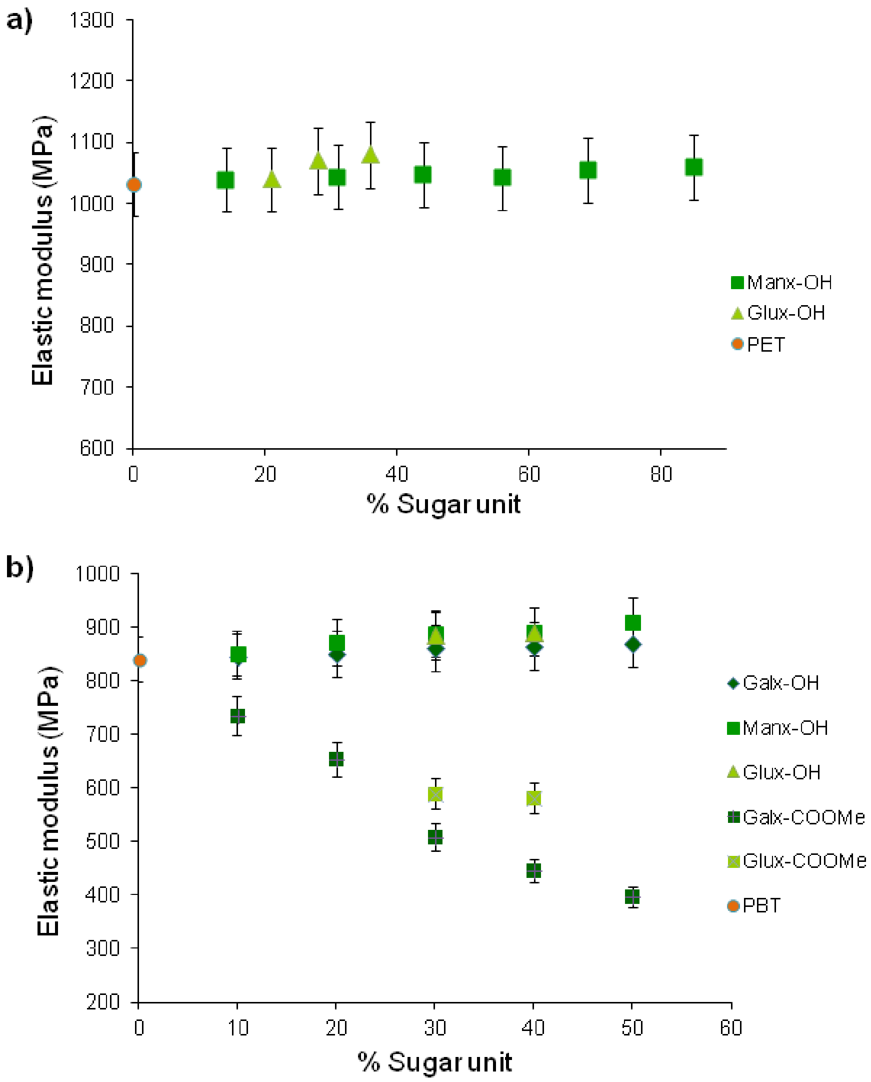


Figure 9. Elastic modulus as a function of composition for the indicated PET (a) and PBT (b) based copolyesters.[81,83,84b,c]

4.3. Degradability

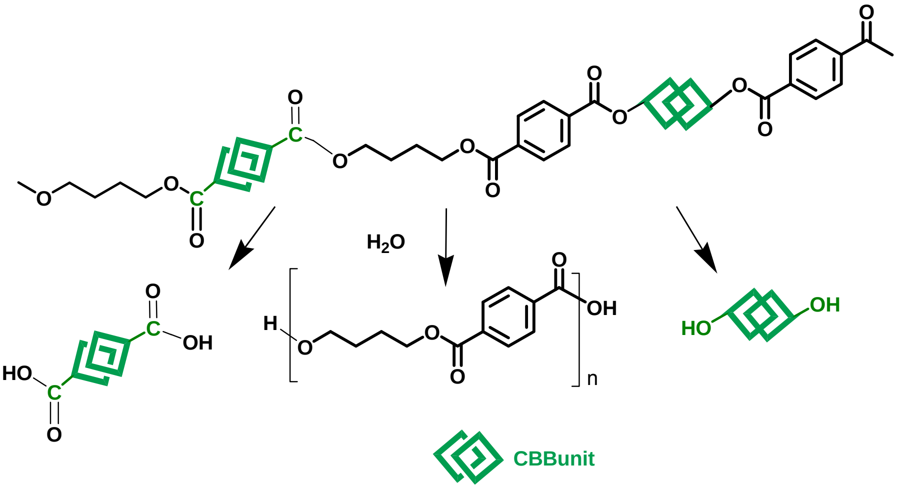
Hydrolysis of terephthalate polyesters under room conditions is an extremely slow reaction hardly perceivable by ordinary analytical methods. In practice hydrolysis of these polyesters is usually run at a pressure of a few MPa and temperatures of 200-300°C. Under environmental conditions PET bottles exposed to 45-100% relative humidity at 20°C last between 30 and 40 years for a 50% property loss.[88] Hydrolysis of polyesters in the solid state is a complex process highly dependent on chain mobility and permeability.[89,90] High values of glass-transition temperature and crystallinity make aromatic polyesters resistant to hydrolysis since chain mobility is greatly reduced and the material hardly permeable. The approach commonly followed to improve the hydrodegradability of polyterephthalates consists of incorporating hydrolyzable units in the backbone by either copolymerization or transesterification by reactive blending.[91]

Several works published in the last decade have shown that the incorporation of sugar-derived units in poly(terephthalate)s enhanced their hydrodegradability. The hydrolytic degradation of a series of homo- and copolyesters analogous to PET and PEI based on *O*-methyl protected L-arabinitol, xylitol, D-mannitol and galactitol were relatively fast at temperatures 10 ºC above their respective T_g. The hydrolysis of copolyesters took place preferentially by cleavage of the ester groups of the sugar units.[92] The hydrolytic degradation of PBT copolyesters containing up to 50% of *O*-methyl protected pentitols derived from L-arabinose and D-xylose was also studied.[37b] It was shown that these copolyesters were much more sensitive to hydrolysis than was PBT. In all these cases, the reduction in both T_g and crystallinity taking place upon copolymerization is very probably the factor causing the enhancing effect.

No data on the influence of isosorbide on the susceptibility of poly(terephthalate)s toward hydrolysis are available. Conversely most of the terephthalate copolyesters containing CBB diacetalized units synthesized to date have been examined regarding their hydrodegradability.[81a,c,82-84]

Several general conclusions are drawn from the results obtained upon incubation in aqueous media under different conditions. In contrast to poly(alkylene terephthalate) homopolyesters which are fully resistant to water attack at neutral pH and room temperature, most of the poly(terephthalate)s containing CBB diacetalized units appear to be lightly vulnerable to hydrolysis in a degree that varies with comonomer composition, length of the alkylene segment and nature of the replacing unit. Largest differences in the hydrolysis enhancing effect are observed when the same CBB unit is inserted in the polyester as diacid or diol with maximum weight losses of 15-20% being observed for PBT copolyesters containing Galx-COOMe units. Under greater degrading aggressive conditions (basic or acid pH and high temperature), the enhancing effect of the CBB units on hydrolysis is also manifested even with higher intensity than under physiological conditions.

Degradation of the sugar containing poly(terephthalate) copolyesters takes place preferentially by hydrolysis of the ester groups involving aldarate or alditol units and leaving practically unchanged the alkylene terephthalate linkages (Scheme 14). No alteration of the acetal structure is observed in any case and under any condition. Consequently, the resulting products of the degradation process are mainly alkylene terephthalate oligomers and isolated acetalized aldaric acids and alditols. The greater hydrophilicity of the sugar moieties and their specific localization in the amorphous phase are thought to be responsible for the higher vulnerability to water attack displayed by the links.



Scheme 14. Hydrolysis of poly(terephthalate) copolyesters containing CBB units.

The reluctance of poly(alkylene terephthalate)s to biodegradability is a widely known fact. The enzymatic activity on these polyesters is inhibited by their aromatic nature which caused a very stringent molecular mobility. Most of strategies applied to render poly(terephthalate)s biodegradable consist of inserting flexible aliphatic segments of recognized biodegradability such as polyglycolic, polycaprolactone or polysuccinate.[91] The effect of Is units on the biodegradability of poly(terephthalate)s copolyesters has not been specifically evaluated. On the contrary, several examples of the biodegradability displayed by these polyesters upon insertion of CBB acetalized units have been afforded in the recent literature. Particularly remarkable are the results observed for PBT, which is fully inert to enzymatic action, but upon insertion of Galx-COOMe or Glux-COOMe units losses 20-30% and 10-15% of weight, respectively, after several weeks of incubation in the presence of lipases. Interestingly, no degradation was detected in PBT copolyesters when the Galx or Glux units were inserted as diol units.

5. Conclusions

The work accumulated in the last two decades, and more particularly in these last few years, has provided a considerable amount of published data on the synthesis, characterization and basic properties of aromatic polyesters and copolyesters made of carbohydrate-based bicyclic (CBB) monomers. Two types of CBB compounds, dianhydrides and diacetals, both of them derived from naturally-occurring hexoses have been explored to date. The diol isosorbide derived from D-glucose is by far the most investigated dianhydride despite that its isomer isoidide is receiving lately increasing attention. In the synthesis of polyesters, isohexides are mostly used as diols due to the difficulty entailed in the conversion of their secondary hydroxyl groups into carboxylic groups. Diacetalized CBB compounds with *galacto*, *manno* and *gluco* configuration have been systematically explored, most of them as both diols and diacids.

Both dianhydride and diacetalized CBB compounds have been used as comonomers of alkanediols in melt-polycondensation leading to poly(terephthalate) homopolyesters and copolyesters. Higher molecular weight polymers with better adjustable compositions are however attained using diacetalized compounds due to the higher reactivity of their primary hydroxyl groups. The insertion of CBB units in poly(terephthalate)s diminishes slightly their thermal stability, the effect being more pronounced when the diacid is the replacing unit. Also the melting temperature, crystallinity and crystallizability are depressed to the point that copolyesters with high degrees of substitution become amorphous. Noticeably semicrystalline copolyesters with low to moderate contents in CBB units retain the triclinic crystal structure of their corresponding parent poly(alkylene terephthalate)s with the sugar moieties segregated from the ordered phase. Undoubtedly the most relevant outcome resulting from the incorporation of CBB units in terephthalate polyesters is modification of the glass-transition temperature. An almost linear increase in T_g is produced by replacing the diol units in poly(alkylene terephthalate)s by any CBB diol units, the effect being less pronounced when the substituent is a non-fused ring structure. The CBB acetalized monomers with *gluco* configuration were revealed to be unique in affording copolyesters with enhanced T_g whether they are replacing diol or diacid units in the polyester. As a logical consequence the copolyesters containing BCC units display higher mechanical moduli and are more brittle than their parent poly(alkylene terephthalate)s.

The resistance of terephthalate polyesters to hydrolysis is weakened when they incorporate CBB acetalized units, the effect being more perceivable when the terephthalate unit is the replaced one. Biodegradability is also significantly enhanced by copolymerization with CBB acetalized monomers. Hydrolysis of copolyesters containing CBB units takes place preferably by splitting of the ester linkages in which the sugar moieties are involved.

6. Outlook

The review of the published results on polyesters containing CBB units shows that both isohexides and the bicyclic diacetals of six-carbon alditols or aldaric acids are building-blocks suitable for the preparation of partially renewable poly(terephthalate)s using the methods typically applied in the industry. The CBB containing copolyesters are comparable in their basic behavior to their parent poly(alkylene terephthalate)s and even able to display enhanced properties of interest for certain demanding applications.[93-95] Until the advent of CBB diacetalized compounds, isohexides were the unique renewable rigid diols capable of altering beneficially the polymer properties when incorporated into poly(terephthalate)s. Whereas the beneficial effects derived from the intrinsic rigidity of the bicyclic structure are beyond question given their industrial relevance, other issues, like reduced reactivity and thermal stability are severe drawbacks that affect the suitability of CBB compounds, with particular incidence in isohexides. These deficiencies have to be properly addressed before the implementation of these monomers at large industrial scale, and notable efforts are being made today in this regard. The application of novel organic catalysts able to speed the polycondensation reaction with the consequent reduction of residence times are hoped to be of great help to overcome such limitations.

Nevertheless the synthesis of CBB compounds appears to be the main shortcoming for the short- or medium-term development of terephthalate copolyesters containing CBB units, especially as far as diacetalized compounds are concerned. Whereas isosorbide has reached today a production level at medium industrial scale, the synthesis of the diacetalized alditols and aldaric acids implies laborious procedures that require considerable simplification in order to be acceptable for large consumptions. The design of a simple synthetic route towards CBB acetalized monomers is really challenging since the acetalization reaction entails the use of carbonyl compounds, specifically formaldehyde derivatives, for which no many options are today available.

The advancing rate of modern strategies addressed to producing PTA and alkanediols from renewable feedstock is a fact that will surely have significant incidence on the development of CBB based poly(terephthalate)s. If the aim is just to replace the high-consumption petrochemical poly(terephthalate)s, *i.e.* PET, PBT, PPT, by their bio-based mimics, the advantages afforded by such strategies are out of question; no property discrimination between polyesters will be feasible because their origin, and no differences will be perceived in processing and application. On the other hand, polyesters made from CBB compounds will be favorites in the case that products with novel specific properties combined with a bio-based character were desired. The poly(terephthalate)s reviewed in this paper afford a paradigmatic example of such approach; in these compounds the partial replacement of the classical petrochemical monomers by the carbohydrate-derived ones not only benefits their sustainability but also enhances their thermal properties regarding novel high-performance applications; in addition a certain biodegradability is attained, which can be an additional advantage for certain specific uses.

A last point deserving comment is that related to the EU REACH regulation (Registration, Evaluation, Authorization, and Restriction of Chemicals) that will start to apply to new monomers from 2018 onwards when their production exceeds one ton per year.[96] Given the bio-origin of the CBB compounds they would be advantageously positioned for attaining authorization of use in front of competitors coming from fossil feedstock, a feature that will certainly benefit the potential development of these monomers.

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Table 4. Polyesters and copolyesters containing CBB diacetalized dioxy and dicarboxylate units of *galacto* configuration.

Polyester	Molar composition[a]				Molecular weights			Thermal properties				Mechanical properties	
	X_B / $X_{Galx\text{-}diol}$		X_T / $X_{Galx\text{-}diester}$		$[\eta]^b$	$M_w{}^c$	$Đ^c$	$T_d{}^d$ (°C)	$T_g{}^e$ (°C)	$T_m{}^f$ (°C)	$\Delta H_m{}^f$ ($J \cdot g^{-1}$)	Elastic modulus (MPa)	Elongation at break (%)
	Feed	Copolyester	Feed	Copolyester									
PBT	-	-	100/0	100/0	0.93	41,300	2.4	371	31	223	56	841±15	14±3
$PB_{90}Galx_{10}T$	90/10	89/11			0.91	40,800	2.5	372	46	197	37	846±18	11±2
$PB_{80}Galx_{20}T$	80/20	79/21			0.90	40,300	2.4	373	53	179	26	850±23	10±3
$PB_{60}Galx_{40}T$	60/40	61/39			0.65	36,500	2.5	377	62	138	15	865±25	7±1
$PB_{50}Galx_{50}T$	50/50	51/49			0.69	37,600	2.4	379	70	119	9	869±24	5±1
PGalxT	0/100	0/100			0.50	30,500	2.5	382	87	-	-	953±22	3±1
$PBT_{90}Galx_{10}$			90/10	91/9	0.84	39,200	2.4	368	29	210	43	735±17	19±3
$PBT_{80}Galx_{20}$			80/20	80/20	0.70	31,500	2.2	361	27	189	29	653±15	23±4
$PBT_{70}Galx_{30}$			70/30	70/30	0.72	33,400	2.3	347	25	166	22	509±11	26±3
$PBT_{50}Galx_{50}$			50/50	51/49	0.75	38,800	2.5	333	22	115	10	397±8	34±5
PBGalx			0/100	0/100	0.52	30,800	2.4	328	18	122	35	162±5	45±5
PHT			100/0	100/0	0.95	47,900	2.8	370	18	142	34	610±15	14±2
$PHT_{90}Galx_{10}$			90/10	89/11	0.67	30,500	2.1	362	9	133	33	563±12	21±3
$PHT_{50}Galx_{50}$			50/50	50/50	0.68	35,800	2.8	335	1	65	14	327±9	188±7
$PHT_{30}Galx_{70}$			30/70	29/71	0.66	33,000	2.5	333	0	50	13	260±7	147±6
$PHT_{10}Galx_{90}$			10/90	10/90	0.69	41,300	2.7	327	0	71	13	176±5	49±4
PHGalx			0/100	0/100	0.60	40,300	2.3	327	0	73	16	158±4	54±5
PDT			100/0	100/0	1.06	37,200	2.3	373	-6	119	57	432±11	24±3
$PDT_{90}Galx_{10}$			90/10	90/10	0.84	30,500	2.0	363	-9	116	54	389±8	26±3
$PDT_{50}Galx_{50}$			50/50	49/51	0.92	38,700	2.5	336	-19	80	35	261±6	283±12
$PDT_{30}Galx_{70}$			30/70	30/70	0.74	31,700	2.1	334	-19	69	33	220±6	245±9
$PDT_{10}Galx_{90}$			10/90	10/90	0.77	30,800	2.1	333	-22	82	41	172±5	33±5
PDGalx			0/100	0/100	0.81	41,200	2.5	329	-22	88	44	155±4	59±4

[a] Determined by NMR. [b] Intrinsic viscosity ($dL \cdot g^{-1}$) measured in dichloroacetic acid at 25 °C. [c] Weight average molecular weights in $g \cdot mol^{-1}$ and dispersities measured by GPC in HFIP against PMMA standards. [d] Onset temperature for 5% weight loss observed by TGA under nitrogen flow at 10 °C min^{-1}. [e] Glass-transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 °C min^{-1}. [f] Melting temperature and enthalpy measured by DSC at heating rates of 10 °C min^{-1}. [g] Young's modulus and elongation at break measured at a stretching rate of 30 $mm \cdot min^{-1}$ at 23 ºC.

Table 5. Polyesters and copolyesters containing CBB diacetalized dioxy units of *manno* configuration.

Polyester	Molar composition[a] $X_A/X_{\text{Manx-diol}}$		Molecular weights			Thermal properties				Mechanical properties	
	Feed	Copolyester	$[\eta]^b$	$M_w{}^c$	$Đ^c$	$T_d{}^d$ (°C)	$T_g{}^e$ (°C)	$T_m{}^f$ (°C)	$\Delta H_m{}^f$ ($J\cdot g^{-1}$)	Elastic modulus (MPa)	Elongation at break (%)
PET	100/0	100/0	0.67	33,600	2.3	384	81	252	44	1032±52	23±5
$PE_{86}Manx_{14}T$	90/10	86/14	0.80	41,600	2.5	391	98	211	3	1038±48	11±4
$PE_{56}Manx_{44}T$	70/30	56/44	0.70	36,300	2.5	388	115	-	-	1047±41	5±2
$PE_{31}Manx_{69}T$	50/50	31/69	0.68	34,700	2.4	388	127	-	-	1055±37	2±1
$PE_{15}Manx_{85}T$	30/70	15/85	0.60	33,100	2.5	382	130	-	-	1059±40	2±1
PBT	100/0	100/0	0.93	41,300	2.4	371	31	223	56	841±15	14±3
$PB_{90}Manx_{10}T$	90/10	91/9	1.18	51,200	2.5	371	55	197	34	852±13	12±3
$PB_{80}Manx_{20}T$	80/20	80/20	0.84	41,000	2.5	372	66	184	26	871±25	9±2
$PB_{60}Manx_{40}T$	60/40	59/41	0.83	40,100	2.4	376	88	122	5	891±19	5±2
$PB_{50}Manx_{50}T$	50/50	49/51	0.77	38,900	2.4	377	100	-	-	909±26	3±1
PManxT	0/100	0/100	0.51	30,200	2.3	378	137	-	-	1067±29	2±1

[a]Determined by NMR; A refers to EG or BD.[b]Intrinsic viscosity ($dL\cdot g^{-1}$) measured in dichloroacetic acid at 25 °C. [c]Weight average molecular weights in $g\cdot mol^{-1}$ and dispersities measured by GPC in HFIP against PMMA standards. [d]Onset temperature for 5% weight loss observed by TGA under nitrogen flow at 10 °C min^{-1}. [e]Glass-transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 °C min^{-1}.[f]Melting temperature, and enthalpy measured by DSC at heating rates of 10 °C min^{-1}.[g]Young's modulus and elongationat break measured at a stretching rate of 30 $mm\cdot min^{-1}$at 23 °C.

Table 6. Polyesters and copolyesters containing CBB diacetalized dioxy units of *gluco* configuration.

Polyester*	Molar composition[a] $X_A/X_{\text{Glux-diol}}$		Molecular weights			Thermal properties				Mechanical properties	
	Feed	Copolyester	$[\eta]^b$	$M_w{}^c$	$Đ^c$	$T_d{}^d$ (°C)	$T_g{}^e$ (°C)	$T_m{}^f$ (°C)	$\Delta H_m{}^f$ ($J\cdot g^{-1}$)	Elastic modulus (MPa)	Elongation at break (%)
PET	100/0	100/0	0.68	32,100	2.5	411	81	250	44	1032±52	23±5
$PE_{87}Glux_{13}T$	90/10	87/13	0.84	40,100	2.5	406	96	218	21	n.d.	n.d.
$PE_{79}Glux_{21}T$	85/15	79/21	0.78	38,000	2.5	403	105	-	-	1040±47	27±3
$PE_{72}Glux_{28}T$	80/20	72/28	0.72	35,000	2.4	396	109	-	-	1070±50	20±2
$PE_{64}Glux_{36}T$	70/30	64/36	0.65	29,000	2.4	396	117	-	-	1080±40	16±2
$PE_{20}Glux_{80}T$	30/70	20/80	0.42	23,000	2.4	386	146	-	-	n.d.	n.d.
PBT	100/0	100/0	0.91	41,500	2.4	378	30	219	49	863±25	15±4
$PB_{89}Glux_{11}T$	90/10	89/11	0.80	39,000	2.5	380	45	199	42	n.d.	n.d.
$PB_{80}Glux_{20}T$	80/20	80/20	0.85	41,100	2.3	379	70	184	26	n.d.	n.d.
$PB_{69}Glux_{31}T$	70/30	69/31	0.81	39,500	2.3	378	86	165	15	885±17	79±9
$PB_{59}Glux_{41}T$	60/40	59/41	0.81	39,500	2.4	381	103	-	-	892±22	105±16
$PB_{48}Glux_{52}T$	50/50	48/52	0.70	34,500	2.3	382	113	-	-	n.d.	n.d.
PHT	100/0	100/0	0.83	46,000	2.3	360	8	144	34	n.d.	n.d.
$PH_{95}Glux_5T$	95/5	95/5	0.86	47,500	2.2	373	20	136	29	n.d.	n.d.
$PH_{90}Glux_{10}T$	90/10	90/10	0.68	31,400	2.1	371	25	133	31	n.d.	n.d.
$PH_{81}Glux_{19}T$	80/20	81/19	0.65	33,000	2.2	375	41	118	22	n.d.	n.d.
$PH_{74}Glux_{26}T$	70/30	74/26	0.34	16,000	2.5	366	46	119	12	n.d.	n.d.
$PH_{68}Glux_{32}T$	60/40	68/32	0.29	12,400	2.5	367	56	84	9	n.d.	n.d.
PGluxT	0/100	0/100	0.32	12,800	2.3	377	154	272	15	n.d	n.d

[a] Determined by NMR; A refers to EG, BD or HD. [b] Intrinsic viscosity ($dL\cdot g^{-1}$) measured in dichloroacetic acid at 25 °C. [c] Weight average molecular weights in $g\cdot mol^{-1}$ and dispersities measured by GPC in HFIP against PMMA standards. [d] Onset temperature for 10% weight loss observed by TGA under nitrogen flow at 10 °C min^{-1}. [e] Glass-transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 °C min^{-1}. [f] Melting temperature and enthalpy measured by DSC at heating rates of 10 °C min^{-1}. [g] Young's modulus and elongation at break measured at a stretching rate of 30 $mm\cdot min^{-1}$ at 23 ºC. n.d.= not determined. *Polyesters synthesized using DBTO as catalyst except for PH_xGlux_yT polyesters for which TBT was used.

Table 7. Polyesters and copolyesters containing CBB diacetalized dicarboxylate units of *gluco* configuration.

Polyester*	Molar composition[a] $X_T/X_{\text{Glux-diester}}$		Molecular weights			Thermal properties			
	Feed	Copolyester	$[\eta]$[b]	M_w[c]	$Đ$[c]	T_d[d] (°C)	T_g[e] (°C)	T_m[f] (°C)	ΔH_m[f] ($J \cdot g^{-1}$)
PET	100/0	100/0	0.68	32,100	2.5	411	81	250	44
PET$_{95}$Glux$_{5}$	95/5	95/5	0.52	26,000	2.2	393	85	237	30
PET$_{89}$Glux$_{11}$	90/10	89/11	0.50	25,100	2.3	361	89	226	27
PET$_{84}$Glux$_{16}$	85/15	84/16	0.60	30,000	2.2	347	88	-	-
PET$_{79}$Glux$_{21}$	80/20	79/21	0.57	28,500	2.2	323	98	-	-
PEGlux	0/100	0/100	0.27	9,000	2.4	262	112	-	-
PBT	100/0	100/0	0.91	41,500	2.4	378	30	219	49
PBT$_{90}$Glux$_{10}$	90/10	90/10	0.97	47,000	2.3	355	44	199	44
PBT$_{80}$Glux$_{20}$	80/20	80/20	0.83	40,200	2.3	352	52	184	25
PBT$_{67}$Glux$_{33}$	70/30	67/33	0.75	37,500	2.4	348	66	148	31
PBT$_{55}$Glux$_{45}$	60/40	55/45	0.60	28,500	2.5	324	76	-	-
PBGlux	0/100	0/100	0.40	13,500	2.4	274	89	-	-
PHT	100/0	100/0	1.33	50,300	2.3	384	16	144	35
PHT$_{90}$Glux$_{10}$	90/10	90/10	1.14	43,500	2.4	372	20	127	27
PHT$_{81}$Glux$_{19}$	80/20	81/19	0.88	42,400	2.3	354	24	112	24
PHT$_{60}$Glux$_{40}$	60/40	60/40	0.64	36,300	2.3	324	42	67	20
PHT$_{50}$Glux$_{50}$	50/50	50/50	0.62	35,900	2.2	328	50	65	10
PHGlux	0/100	0/100	0.50	20,000	2.1	326	73	-	-

[a] Determined by NMR. [b] Intrinsic viscosity ($dL \cdot g^{-1}$) measured in dichloroacetic acid at 25 °C. [c] Weight average molecular weights in $g \cdot mol^{-1}$ and dispersities measured by GPC in HFIP against PMMA standards. [d] Onset temperature for 10% weight loss observed by TGA under nitrogen flow at 10 °C min^{-1}. [e] Glass-transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 °C min^{-1}. [f] Melting temperature and enthalpy measured by DSC at heating rates of 10 °C min^{-1}. *Polyesters synthesized using DBTO as catalyst.