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Abstract

Utilization of carbohydrate derivatives for polymer synthesis has been paid much attention not only because of the huge abundance of resources but also because of the promising biodegradability and biocompatibility of the polymers obtained from them. Of the different natural resources, carbohydrates stand out as highly convenient raw materials because they are inexpensive, readily available, and provide great functional diversity.

Poly(butylene succinate) (PBS) and its copolymers are a family of biodegradable polymers with excellent biodegradability, thermoplastic processability and balanced mechanical properties.

In this work, copolyesters of PBS were synthesized by taking different feed molar ratio of 2,3-di-O-methylene-L-threitol to 1,4-butanediol with dimethyl succinate, and 2,3-di-O-methylene dimethyl tartrate to dimethyl succinate with 1,4-butanediol. Chemical characterization of copolymers was carried out by NMR, FT-IR, viscosimetry and GPC. The number average molecular weights (Mn) of the polymers were found to vary in the range of 615×10^{3} g·mol^{-1}. The physical properties of PBS materials varied in a wide range depending on their composition.

The thermal behavior and the mechanical properties of these polyesters were evaluated and compared with PBS. The PBS copolyesters showed higher glass transition (T_g) and low melt temperatures (T_m) as compared to the parent polyester. T_g varies from -37 to 13 °C depending on the feed ratio of the comonomers. Regarding the mechanical properties, the introduction of cyclic acetal groups caused an increase in the elongation at break of the polyesters, and produced a reduction in the elastic modulus and tensile strength at the same time.

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Acronyms

BD: 1,4-butanediol

DBTO: dibutyl tin oxide

DSC: differential scanning calorimetry

FT-IR: Fourier transformed infrared spectroscopy

GPC: gel permeation chromatography

HFIP: hexafluoroisopropanol

Mn: number average molecular weight

Mw: weight average molecular weight

IV: intrinsic viscosity

NaTFA-HFIP: sodium trifluoroacetate-hexafluoroisopropanol

NMR: nuclear magnetic resonance

PBS: poly(buthylene succinate)

PMMA: poly(methyl methacrylate)

Thx-COOMe: 2,3-di-*O*-methylene dimethyl tartrate

Thx-CH₂OH: 2,3-di-*O*-methylene-L-threitol

PBSₙThxₘ; poly(butylene succinate-*co*-butylene-2,3-di-*O*-methylene tartrate) copolyesters

PBₙThxₘS: poly(butylene succinate-*co*-2,3-di-*O*-methylene-L-threitylene succinate) copolyesters

PThxS: poly(2,3-di-*O*-methylene-L-threitylene succinate)

PLA: polylactic acid

PP: polypropylene

HDPE: high-density polyethylene

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LDPE: low-density polyethylene

PBSA: poly(butylene succinate-*co*-butylene adipate)

T_c: crystallization temperature

TFA-*d*: deuterated trifluoroacetic acid

T_g: glass-transition temperature

TGA: thermogravimetry

T_m: melting temperature

TMS: tetramethylsilane

1. Introduction

The biodegradable polymers are polymers which are capable to degrade by the concourse of enzymes. The replacement of the common plastic by biodegradable plastics is a route to diminish the pollutant effect of those, in the environment. Biodegradable plastics can be treated like organic waste and they could be placed in the sanitary deposits, where its degradation would realize in short periods of time.

The biodegradability of the plastic depends on the chemical structure of the material and the composition of the final product, not only on the raw material used for its manufacture. As any other commercial plastic, the biodegradable materials must fulfill a series of requests focused to the function to which they are destined.

L-Tartaric acid is one of the most frequently used starting materials and their synthetic versatility has resulted in an amazing array of products made available by well-developed synthetic procedures. The chemistry of these hydroxy acids was developed over a period of more than one hundred years.[1] In a broad sense, tartaric acid finds countless applications in industry and in basic research. Its industrial applications include pharmaceutical formulations, dental materials, ceramics, paints, electrochemical coatings and piezoelectronic devices.[1] It has also attracted a great deal of interest as a substrate for synthesis of functional polymers based on carbohydrates.

L-Tartaric acid is a natural product mainly obtained from a large variety of fruits. Since the investigations of tartaric acid-based polyamides by Ogata *et al.*[2] in the 1970s, various classes of polymers containing tartaric acid have been reported. Kuramoto et al. [3] synthesized polyesters or polyurethanes having pendant carboxyl groups by polycondensation of dibenzyl L-tartrate with dicarboxylic chlorides or diisocyanates, respectively. Muñoz-Guerra *et al.*[4-6] reported the synthesis of a series of stereoregular polyamides and poly(ester amide)s derived from tartaric acid, and their hydrolytic degradability.[5] Acemoglu *et al.*[7] synthesized water-soluble poly(hydroxyalkylene carbonate)s from L-tartaric acid derivatives, and found that they degraded into monomers and smaller oligomers by *in vitro* and *in vivo* hydrolysis. As an extension of the series of our studies on biodegradable polymer synthesis based on renewable resources, novel polycarbonates containing pendant functional groups have been synthesized from 1,4:3,6-dianhydrohexitols and L-tartaric acid derivatives.

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Aliphatic polyesters are an interesting class of materials in that they hold great promise in biomedical and pharmaceutical applications. Aliphatic polyesters are known to be the most promising category of biodegradable polymers and environmentally benign materials. [8,9,10]

For example, aliphatic polyesters, like poly(lactide)(PLA), poly(ε-caprolactone) (PCL), poly(glycolide) (PGA), and poly(β−hydroxy butyrate) (PHB) have shown the highest potential as biodegradable and biocompatible polymers.[10,11,12] Poly(butylene succinate) and its copolymers are a family of biodegradable polymers with excellent biodegradability, thermoplastic processability and balanced mechanical properties, which has a wide temperature window for thermoplastic processing.[13]
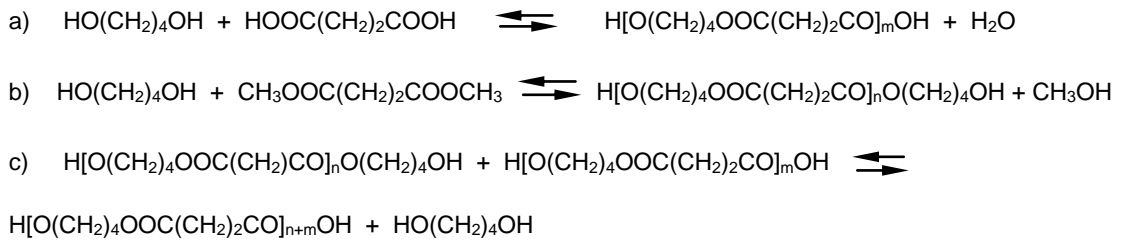
Due to increasing concerns on sustainable development and the impact of materials on the environment, biodegradable materials have attracted intensive interest in the past decades. Among them, poly(butylene succinate) exhibits balanced performance in thermal and mechanical properties as well as thermoplastic processability compared with other common plastics, as shown in Table 1.[14–16] Via copolymerization with other dicarboxylic acids or diols, the properties of PBS can be varied in a wide range, which is a promising advantage for various applications. Ever since the pioneering of Carothers in 1931 [17], massive efforts have been devoted to investigate the synthesis and properties of PBS and its copolymers.

Table 1. Physical properties of PBS and PBSA compared with PLA and some commodity plastics [14].

Items	PLA	PBS	PBSA[a]	PP	HDPE	LDPE
Glass transition temperature (ºC)	55	-32	-45	-5	-120	-120
Melting point (ºC)	170-180	114	96	163	129	110
Heat distortion temperature (ºC)	55	97	69	110	82	49
Tensile strength	66	34	19	33	28	10
Elongation at break (%)	4	560	807	415	700	300
Izod impact strength (J·m^{-1})	29	300	>400	20	40	>400
Degree of crystallinity (%)		35-45	20-30	56	69	49

[a]PBSA poly(butylene succinate-*co*-butylene adipate)

The synthesis of PBS can be separated into two steps: The first step is esterification of succinic acid and 1,4 butanediol (BD) or transesterification of dimethyl succinate and BD to obtain oligomers, the second step is polycondensation of the oligomers to remove BD to form high-molecular weight PBS [13].

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a) $HO(CH_2)_4OH + HOOC(CH_2)_2COOH \rightleftarrows H[O(CH_2)_4OOC(CH_2)_2CO]_mOH + H_2O$

b) $HO(CH_2)_4OH + CH_3OOC(CH_2)_2COOCH_3 \rightleftarrows H[O(CH_2)_4OOC(CH_2)_2CO]_nO(CH_2)_4OH + CH_3OH$

c) $H[O(CH_2)_4OOC(CH_2)CO]_nO(CH_2)_4OH + H[O(CH_2)_4OOC(CH_2)_2CO]_mOH \rightleftarrows$

$H[O(CH_2)_4OOC(CH_2)_2CO]_{n+m}OH + HO(CH_2)_4OH$

Scheme 1. Chemical formulations of PBS synthesis: (a) Esterification of succinic acid and 1,4-butanediol or (b) transesterification of dimethyl succinate and 1,4-butanediol to obtain oligomers. In the following stage, oligomers are polycondensed to produce the final PBS resin.

Dependence of the thermal properties and the degree of crystallinity of several PBS copolymers on the comonomer content is presented in Figure 1. Whatever, the type of the comomoner, melting point and the degree of crystallinity of PBS copolymers decrease with increasing comonomer content in the studied range from 0 to 40 mol%.[13]
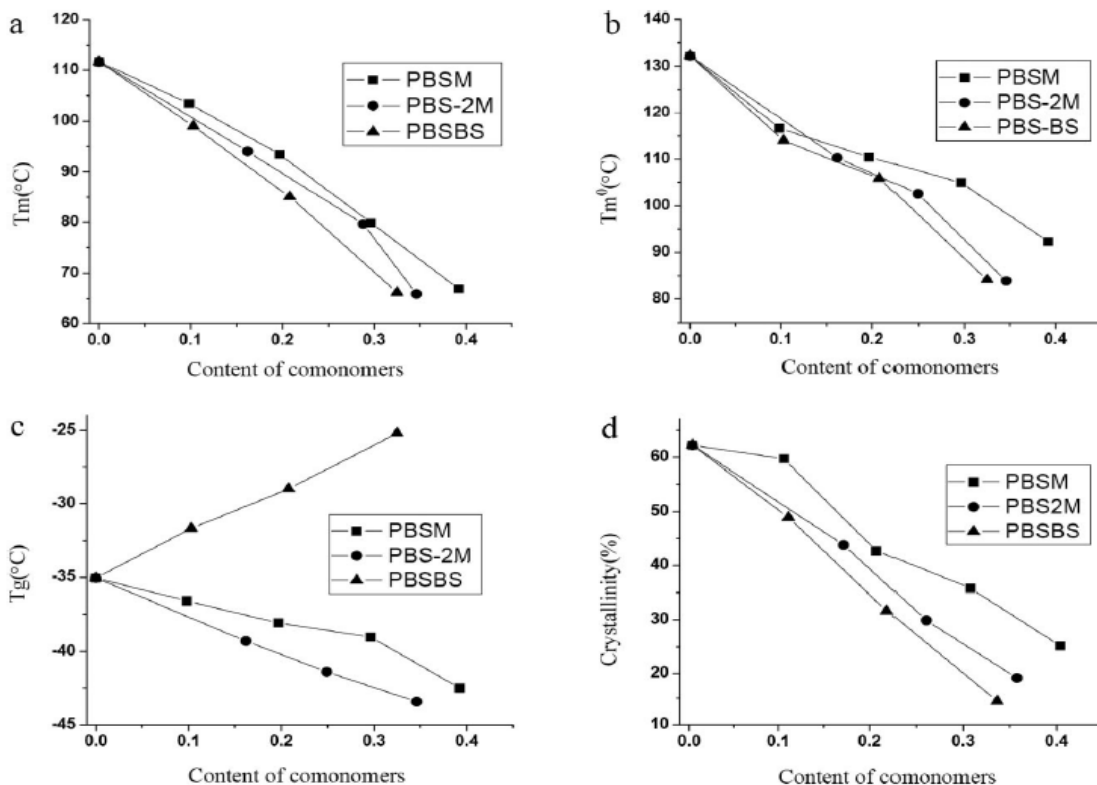

Figure1. Dependence of the physical properties of PBS copolymers on the content of comonomer units. (a) melting point; (b) equilibrium melting point, (c) glass transition temperature; (d) degree of crystallinity. PBSM: poly(butylene succinate-*co*-butylene methylsuccinate); PBS-2M: poly(butylene succinate-*co*-butylene dimethylsuccinate); PBSBS: poly(butylene succinate-*co*-butylene phenylsuccinate).

The biodegradation rate of PBS copolymers varies with the chemical structure, the condensed state structures (such as the degree of crystallinity and specimen size) and the biodegradation environment. The biodegradation profile of PBS copolymer films with a

similar degree of crystallinity in the activated sludge was investigated, results presents below.

Table 2. Parameters of PBS and its copolymers used for biodegradation study. [16]

Item[a]	M_w (x10^4 g·mol^{-1})	Content of copolymer (mol%)	Crystallinity (%)	Film thickness (µm)
PBS	6.44	0	62.2	150
PBSA-20	4.42	22.6	53.9	150
PBSM-20	3.58	19.7	42.7	150
PBS-2M-20	4.32	16.2	43.8	150
PBSBS-20	5.48	20.8	34.9	150

a) PBSA-20: poly(butylene succinate-*co*-20 mol% butylene adipate); PBSM-20: poly(butylene succinate-*co*-20 mol% butylene methylsuccinate); PBS-2M-20: poly(butylene succinate-*co*-20 mol% butylene dimethylsuccinate); PBSBS-20: poly(butylene succinate-*co*-20 mol% butylene phenylsuccinate).

For PBS copolymers with substituted succinic acid as the comonomer, at the same comonomer content of 20 mol%, the biodegradation rate at the first stage follows the order: poly(butylene succinate-*co*-butylene methyl succinate) ≈ poly(butylene succinate-*co*-butylene dimethyl succinate)> poly(butylene succinate-*co*-butylene adipate)> poly(butylene succinate-*co*-butylene phenyl succinate)> poly(butylene succinate).[13] Compared to aliphatic copolyesters with the same comonomer content, PBS copolymerized with aromatic comonomers revealed slower biodegradation rates. However, PBS copolyesters with 20 mol% aromatic comonomers still showed higher biodegradation rates in the activated sludge during the first three weeks. For aliphatic copolyesters, the biodegradation rate enhances with an increase of the comonomer content below 40 mol%, resulting from the decreased degree of crystallinity.[18] For aliphatic-aromatic copolyesters, the biodegradation rate slows down with an increase in the aromatic content in the range of 10–70 mol%.[19] Consequently, the biodegradation rate of PBS can be tailored via copolymerization with different types and contents of comonomer units to meet various requirements.

In general, copolymerization leads to a decrease in melting point, degree of crystallinity, tensile strength and modulus; at the same time, elongation at break and impact strength improves with copolymerization when the content of comonomer units is less than 30 mol%. Effect of copolymerization on biodegradation rate depends on the type of comonomer: copolymerization with aliphatic comonomers results in a faster biodegradation rate in activated sludge, while that with aromatic comonomers leads to a slower biodegradation rate. The melt strength of PBS is considerably enhanced by long-chain branching, meeting the demands posed by film blowing processes. PBS resins for extrusion, injection molding, thermoforming, fiber spinning and film blowing have been commercialized.[13] It has been

utilized to produce fast food packages, bottles, supermarket bags, flushable hygiene products, mulch film and compost bags, etc.[14–16] PBS oligomers can also be used as building blocks of polyurethane elastomers as well.[20]

A type of cyclic carbohydrate-derived monomers are those generated by intramolecular acetalization of alditols and aldaric acids. Thus polyamides and polyurethanes have been prepared from 2,3-*O*-methylene-threaric acid and 2,3-*O*-methylidene threitol[21] respectively.

The most common *O*-protecting groups of the secondary hydroxyl groups of the alditol monomers ether groups. The ether group is of course the most resistant *O*-protecting group of alditol monomers under the polycondensation reaction conditions, and also the most difficult to remove from the resulting polymers.[22]

Within the framework of systematic research to explore the potential of sugar-based polymers, Muñoz-Guerra along with Galbis *et al.* have employed various *O*-methyl alditol derivatives to prepare novel polymers, as well as chemical modification of other well-known materials. Poly(ethylene terephthalate) (PET), poly(ethylene isophthalate) (PEI), poly(butylene terephtalate) (PBT) have been chemicaly modified by insertion of a series of *O*-methyl alditols. Among them, 2,3-di-*O*-methyl-L-threitol was inserted into PET [23] and the preparation of PET and PEI analogues by total replacement of the ethylene glycol (EG) units with 2,3,4,5,-tetra-*O*-methyl-hexitols having D-*manno* and D-*galacto* configurations.[24] They also obtained analogues to PET, PEI, and PBT by using 2,3,4,-tri-*O*-methyl-L-arabinitol or 2,3,4,-tri-*O*-methyl-xylitol [25, 26]. The *O*-methyl-alditol monomers used are easily obtained from the respective comercially available diethyl L-tartrate, pentoses, and hexitols.[24,27, 28]

2,3-Diprotected L-threitols are the most frecuently used derivatives of L-threitol; they include both 2,3 acetal and 2,3-di-*O*-alkyl derivatives. Their popularity stems from their direct availability from suitably protected tartrates and from the well-established synthetic routes for converting these compounds to other unprotected and protected derivatives of threitol.[1]

Symmetrically substituted 2,3-acetals (2,3-*O*-isopropylidene protected threitol) is readily available by reduction of 2,3-*O*-isopropylidene tartrates with either LiAlH$_4$ or NaBH$_4$; in the letter case the successful reduction of the ester group is made possible by the activating effect of the α-C-O bonds.[1]

A variety of carbohydrate-based linear polyesters [29] of the poly(alkylene dicarboxylate) type were obtained by polycondensation reactions of the alditols 2,3,4-tri-*O*-methyl-L-arabinitol and 2,3,4,-tri-*O*-methyl-xylitol, and aldaric acids 2,3,4-tri-*O*-methyl-L-arabinaric acid and 2,3,4-tri-*O*-methyl xylaric acid. Butanediol and adipic acid were also used as comonomers. Copolyesters

of the poly(alkylene-*co*-arylene dicarboxylate) type were obtained using bisphenols as comonomers. Chemical polycondensation reactions were conducted in bulk or in solutions. Enzymatic polycondensation reactions of adipic acid with the above-mentioned alditols were carried out successfully using Lipozyme and Novozyme 435. The hydrolytic degradations of some of these polyesters were also described.

Bioerodible polymers having pendant functional groups are of particular interest, since they are capable of covalent pro-drug formation. Acemoglu *et al.*[30] prepared biodegradable poly(hydroxyalkylene carbonate)s from the optically active and racemic 2,3-*O*-isopropylidene-threitol and 2,4:3,5-di-*O*-isopropylidene-L-mannitol with diethyl carbonate in the presence of dibutyl tin oxide. The isopropylidene groups of the polycarbonates were hydrolyzed, and derivations were made on the hydroxy groups to obtain esters, orthoesters, and carbamates. The deprotected polycarbonates were water-soluble, and degraded in a few weeks by a mechanism in which hydroxy groups were shown to participate.
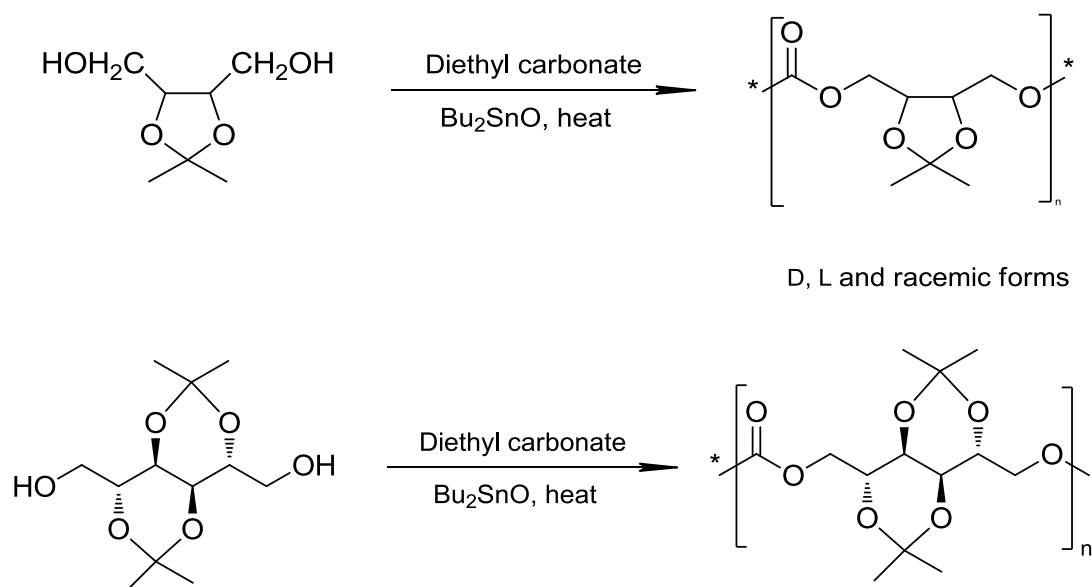

Figure 2. Biodegradable poly(hydroxyalkylene carbonate)s, synthesized from the optically active and racemic 2,3-*O*-isopropylidene-threitol and 2,4:3,5-di-*O*-isopropylidene-L-mannitol with diethyl carbonate in the presence of dibutyl tin oxide.

The first apparently cholesteric polyester derived from an alditol such as 1,2:5,6-di-*O*-isopropylidene-D-mannitol was reported by Chiellini *et al.*[31]. Surprinsingly, an acidolytic deprotection yielded a seemingly thermotropic polyester.

Cristina Lavilla and Cristina Japu are studing within their respective PhD. projects, polimerizations using carbohydrate-based bicyclic diols, 1,4:3,6-dianhydro-D-glucitol (isosorbide, Is), 2,3:4,5-di-*O*-methylene-galactitol (Galx) and 2,4:3,5-di-*O*-methylene-D-mannitol (Manx), 2,4:3,5-di-*O*-methylene-D-glucitol (Glux).[32]

1,4:3,6-Dianhydro-D-glucitol (Is) is the dianhydride generated in the dehydration of D-glucitol (sorbitol). Sorbitol is prepared by hydrogenation of D-glucose coming from cereal starch. (Is) is the only bicyclic carbohydrate-based monomer commercially available today at an industrial level.[33] It is composed of two *cis*-fused nearly planar tetrahydrofuran rings with a dihedral angle of 120° and the 2- and 5-hydroxyl groups in *endo* and *exo* positions, respectively.

2,3:4,5-Di-*O*-methylene-galactitol (Galx) is obtained from galactaric acid by acetalization of the four secondary hydroxyl groups with paraformaldehyde and subsequent reduction. The structure of Galx consists of two non-fused 1,3-dioxolane rings with the two primary hydroxyl groups in *exo* positions. Contrary to isosorbide, Galx is centrosymmetric so its two free hydroxyl groups display the same reactivity since they are spatially undistinguishable.

2,4:3,5-Di-*O*-methylene-D-mannitol (Manx) is obtained by acetalization of 1,6-di-*O*-benzoyl-D-mannitol followed by hydrolysis of the benzoxy groups. Manx consists of two fused 1,3-dioxane rings and possesses a twofold axis of symmetry and, similarly to Galx, the two primary hydroxyl groups are in *exo* positions and display the same reactivity.

2,4:3,5-di-*O*-methylene-D-glucitol (Glux) may be readily prepared from commercially available1,5-D-gluconolactone. Glux is termally stable and greatly resistant to hydrolysis in both basic and acid medium. Since it lacks any symmetry elements and the two hydroxyl groups display similar reactivity, it will enter in the polymer chain with two different orientations producing *aregic* and therefore non-stereoregular polyesters.

As seen above, carbohydrates stand as an extremely important natural source of monomers for the synthesis of polycondensates, and in particular of polyesters. However, the efforts devoted to this purpose have not been to date as large as it could be expected, probably due to the chemical complexity implied in the preparation of adequate monomers. The high current interest in the increasing use of naturally-occurring monomers, for replacing oil-based compounds in the production of synthetic polymers, will contribute doubtlessly to stimulate the research in this area.
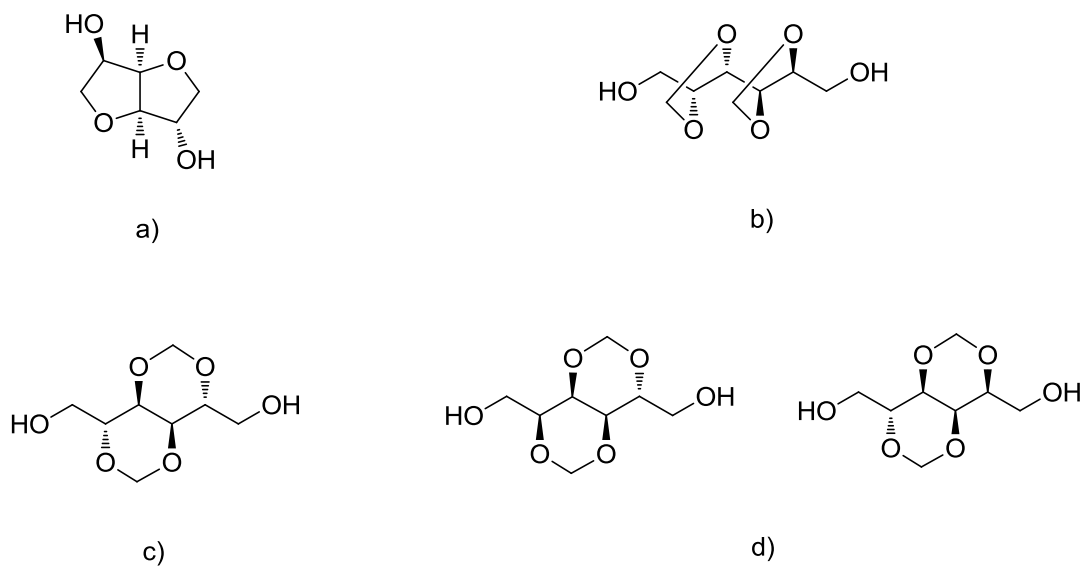
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Figure 3. Chemical structure of 1,4:3,6-Dianhydro-D-glucitol (a), 2,3:4,5-Di-*O*-methylene-galactitol (b), 2,4:3,5-Di-*O*-methylene-D-mannitol (c), pair view of the chemical structure of 2,4;3,5-di-*O*-methylene-D-glucitol rotated 180° around the view axis(d).

2. Project aims

This Final Master Work is addressed to the research and development of poly(butylene succinate)- copolyesters containing cyclic acetalized tartrate units.

A first aim of this project is to prepare cyclic monomers derived from carbohydrates, like 2,3-di-*O*-methylene dimethyl tartrate (Thx-COOMe) and 2,3-di-*O*-methylene-L-threitol (Thx-CH$_2$OH). From these monomers, two classes of polyesters were synthesized, the first by polycondensation of mixtures of dimethyl 2,3-di-*O*-methylene tartrate, dimethyl succinate with 1,4-butanediol and the second by reaction of mixtures of 2,3-di-*O*-methylene-L-threitol and 1,4-butanediol with dimethyl succinate. The second aim is studying the influence of the incorporation of the sugar-based comonomers, physical, mechanical (tensile test), thermal properties (glass transition and melting temperature), including crystallinity and crystallizability. All these properties were compared with those displayed by polybutylene succinate. To achieve the final goal of this TFM, the following specific objectives had been established:

- To prepare the cyclic monomers: 2,3-di-*O*-methylene dimethyl tartrate and 2,3-di-*O*-methylene-L-threitol.

- To synthesize the homopolyesters: poly(butylene succinate) and poly(2,3-di-*O*-methylene-L-threitylene succinate).

- To synthesize poly(butylene succinate-*co*-butylene-2,3-di-*O*-methylene tartrate) copolyesters.

- To synthesize poly(butylene succinate-*co*-2,3-di-*O*-methylene-L-threitylene succinate) copolyesters.

- To characterize all the sinthesized polyesters by NMR, FT-IR, viscosimetry and GPC.

- To study comparatively the thermal properties of polyesters by TGA and DSC.

- To evaluate comparatively the isothermal crystallization of polyesters.

- To evaluate comparatively their mechanical properties by tensile testing.

3. Experimental section

3.1. Materials

The monomer 2,3-di-*O*-methylene-L-threitol, 2,3-di-*O*-methylene dimethyl tartrate were produced by synthesis described below in chapter 3.2.

The reagents 1,4-butanediol (97 %), dimethyl succinate (> 99 %), and the catalyst dibutyl tin oxide (DBTO, 98 %), were purchased from Sigma-Aldrich.

Solvents used for purification, synthesis and characterization, as chloroform, methanol and diethylether, dichloroacetic acid, trifluoroacetate-hexafluoroisopropanol, all of either technical or high-purity grade, were purchased from Panreac y were used as received without further purification.

3.2. Synthesis of monomers

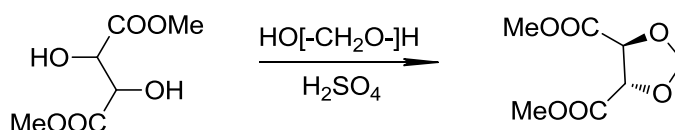### 3.2.1. Synthesis of 2,3-di-*O*-methylene-L-threitol

The procedure to obtain the product was described by Seebach *et al.* [34] To ice bath cooled dispersion of LiAlH$_4$ (11 g, 0.3 mol) in dried diethyl ether (200 mL) was added dropwise solution of 2,3-di-*O*-methylene dimethyl tartrate (25 g, 0.13 mol) in dried diethyl ether (130 mL) under intensive stirring under inert atmosphere. The mixing was left stirring overnight at room temperature. The flask was reintroduced in ice bath to add dropwise successively water (10 mL), 15% NaOH solution (10 mL), water (60 mL). The mixture was left stirring for one hour at room temperature, filtered and extensively washed with warm acetone. The filtrates were pooled, concentrated, and distilled under vacuum (100-110 °C (0.01 mBar)). The 2,3-di-*O*-methylene-L-threitol was obtained as a yellowish oil (9.5 g, 53 % yield).
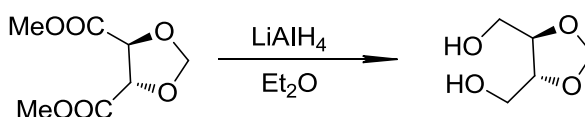
Scheme 3.2.1. Synthesis of 2,3-di-*O*-methylene-L-threitol from 2,3-di-*O*-methylene dimethyl tartrate.

3.2.2. Synthesis of 2,3-di-*O*-methylene dimethyl tartrate

In flask with dimethyl tartrate (40 g, 0.225 mol) at 60°C was added dropwise paraformaldehyde (40 g), dissolved in 40 ml of 98%-H_2SO_4. The reaction mixture was shaken for 6-8 hours at the same temperature and then extracted en chloroform. The extract was concentrated, washed extensively with water and ammonium hydroxide, distilled (84-86 °C, 0.05 mm) to give 16 g of methylene derivative. The 2,3-di-*O*-methylene dimethyl tartrate was obtained as a transparent liquid. Yield based on L-tartaric acid: 40%.
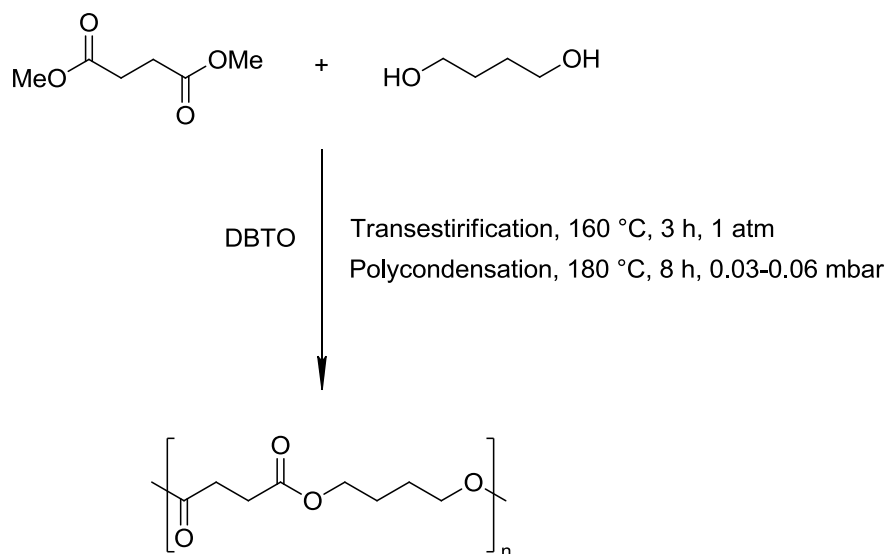

Scheme 3.2.2. Synthesis of 2,3-di-*O*-methylene dimethyl tartrate from dimethyl tartrate

3.3. Polyesters synthesis method

3.3.1. Synthesis of poly(butylene succinate) (PBS)

Synthesis of PBS is separated into two steps: the first step is transesterification of dimethyl succinate and BD to obtain oligomers, the second step is polycondensation of the oligomers to remove BD to form high-molecular weight PBS.

Dimethyl succinate (2.12 g, 0.0145 mol), 20% excess of 1,4 butanediol (1.568 g, 0.0174 mol) were introduced in a three-necked, cylindrical bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a vacuum distillation outlet. The reactants were stirred to a homogeneous mixture and dibutyl tin oxide (0.02165 g, 0.6 mol% respect to monomers), was added as catalyst. Transesterification reactions were carried out under a low nitrogen flow for a period of 3 h at 160 ºC. The temperature was then increased to 180 ºC, and polycondensation was performed at this temperature for 8 h, under a 0.03-0.06 mbar vacuum. After that, the reaction mixture was cooled to room temperature, and atmospheric pressure was recovered with nitrogen flow to prevent degradation. The solid mass was dissolved in chloroform, and the polymer was precipitated with methanol, collected by filtration, extensively washed with methanol, and dried under vacuum (yield 84%).

Scheme 3.3.1. Synthesis of PBS.

3.3.2. Synthesis of PB$_m$Thx$_n$S copolyesters: Copolymerization of 1,4-butanediol and 2,3-di-*O*-methylene-L-threitol with dimethyl succinate.
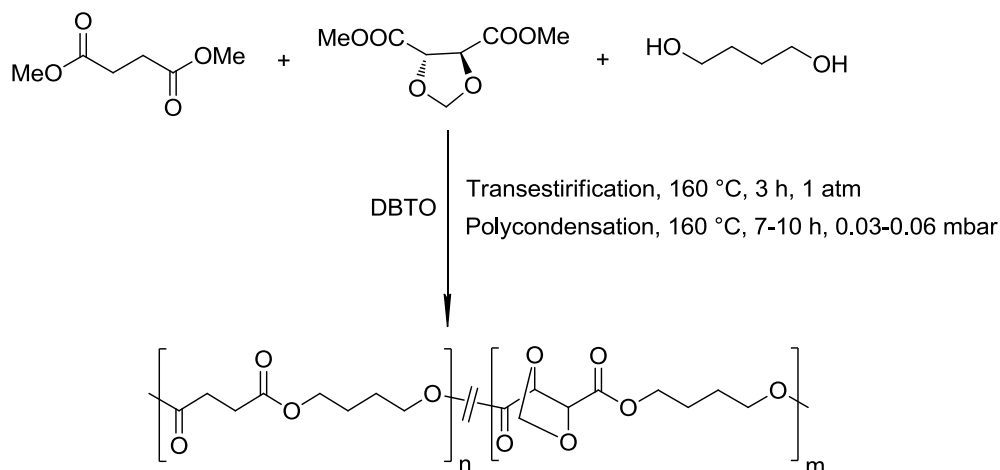
The copolyesters were synthesized by bulk polycondensation. Dimethyl succinate, 1,4-butanediol and 20% molar excess of 2,3-di-*O*-methylene-L-threitol were taken in a Schlenk tube equipped with a mechanical stirrer with a Dean Stark apparatus and condenser under nitrogen atmosphere. The reactants were stirred to a homogeneous mixture and dibutyl tin oxide (0.6 mol% respect to monomers) was added as catalyst. In the first step (esterification), the reaction mixture was heated at 140-160 °C for 3-7 h, till almost the theoretical amount of methanol was collected in the side arm of Dean Stark apparatus. In the second step (polycondensation), the Dean Stark apparatus was removed and a vacuum (0.03–0.06 mbar) was applied and the reaction mixture heated at 140-180°C for 5–10 h till the stirring ceased. The cooled reaction mixture was then dissolved in a minimum amount of chloroform, was precipitated with methanol, collected by filtration, extensively washed with methanol, and dried under vacuum.
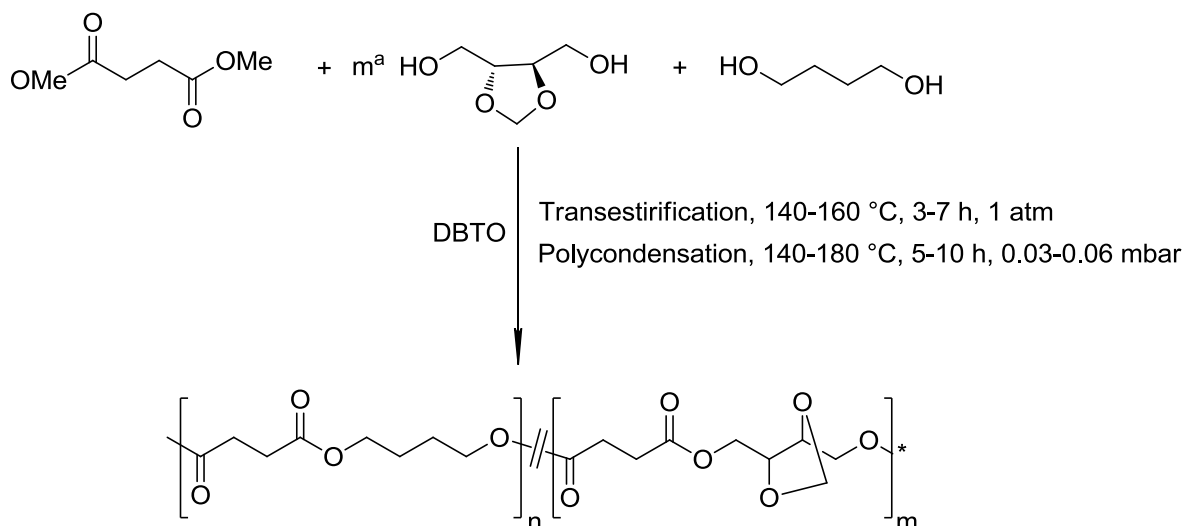
Scheme 3.3.2. Synthesis of poly(butylene succinate-*co*-2,3-di-*O*-methylene threitylene succinate), m^a: PB$_{95}$Thx$_5$S, PB$_{80}$Thx$_{20}$S, PB$_{60}$Thx$_{40}$S stoichiometric ; PB$_{40}$Thx$_{60}$S, PB$_{20}$Thx$_{80}$S-20% molar excess of 2,3-di-*O*-methylene-L-threitol respect to dimethyl succinate.

3.3.3. Synthesis of PBS$_m$Thx$_n$ copolyesters: Copolymerization of dimethyl succinate and 2,3-di-*O*-methylene dimethyl tartrate with 1,4-butanediol.

Dimethyl succinate, of 2,3-di-*O*-methylene dimethyl tartrate and 20% molar excess of 1,4-butanediol were taken in a Schlenk tube equipped with a mechanical stirrer with a Dean Stark apparatus and condenser under nitrogen atmosphere. The reactants were stirred to a homogeneous mixture and dibutyl tin oxide (0.6 mol% respect to monomers) was added as catalyst. In the first step, the reaction mixture was heated at 160°C for 3 h, till almost the theoretical amount of methanol was collected in the side arm of Dean Stark apparatus. In the second step, the Dean Stark apparatus was removed and a vacuum (0.03–0.06 mbar) was applied and the reaction mixture heated at 160°C for 7–10 h till the stirring ceased. The cooled reaction mixture was then dissolved in a minimum amount of chloroform, was precipitated with methanol, collected by filtration, extensively washed with methanol, and dried under vacuum.

Scheme 3.3.3. Synthesis of poly(butylene succinate-*co*-butylene-2,3-di-*O*-methylene tartrate).

3.3.4. Synthesis of poly(2,3-di-*O*-methyl-L-threitylene succinate) (PThxS).

Dimethyl succinate (0.6765 g, 0.00463 mol) and 20% molar excess of 2,3-di-*O*-methylene-L-threitol (0.7444g, 0.00555 mol) were taken in a Schlenk tube equipped with a mechanical stirrer with a Dean Stark apparatus and condenser under nitrogen atmosphere. The reactants were stirred to a homogeneous mixture and dibutyl tin oxide (0.6 mol% respect to monomers) was added as catalyst. In the first step, the reaction mixture was heated at 140°C for 7 h. In the second step, the Dean Stark apparatus was removed and a vacuum (0.03–0.06 mbar) was applied and the reaction mixture heated at 140°C for 8 h till the stirring ceased. The cooled reaction mixture was then dissolved in a minimum amount of chloroform, was precipitated with methanol, collected by filtration, extensively washed with methanol, and dried under vacuum (yield 69%).
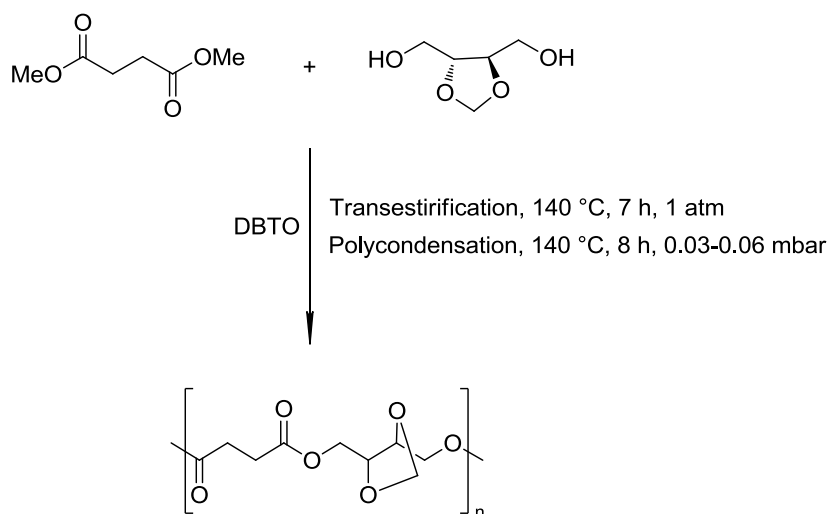
Scheme 3.3.4. Synthesis of poly(2,3-di-*O*-methylene-L-threitylene succinate).

3.4. Characterization methods

3.4.1. Nuclear Magnetic Resonance (NMR)

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer at 25.0 ºC operating at 300.1 and 75.5 MHz, respectively. Polyesters were dissolved either in deuterated chloroform or in a mixture of chloroform/deuterated trifluoroacetic acid (TFA-*d*) (1/1), and spectra were internally referenced to tetramethylsilane (TMS). About 10 and 50 mg of sample dissolved in 1 mL of solvent were used for ^{1}H and ^{13}C NMR, respectively. Sixty-four scans were acquired for ^{1}H and 1,000-10,000 for ^{13}C with 32 and 64-K data points as well as relaxation delays of 1 and 2 s, respectively.

3.4.2. Intrinsic Viscosity (IV)

Intrinsic viscosities of polyesters dissolved in dichloroacetic acid were measured in capillary viscosimeter at 25.00 ± 0.01 ºC.

3.4.3. Gel Permeation Chromatography (GPC)

Gel permeation chromatograms were acquired at 35.0 ºC with Waters equipment provided with a refraction-index detector. The samples were chromatographed with 0.05 M sodium trifluoroacetate-hexafluoroisopropanol (NaTFA-HFIP) using a polystyrene-divinylbenzene packed linear column with a flow rate of 0.5 mL·min^{-1}. Chromatograms were calibrated against poly(methyl methacrylate) (PMMA) monodisperse standards.

3.4.4. Fourier Transformed Infrared Spectroscopy (FT-IR)

The measurements were carried out using the technique of infrared attenuated total reflection (ATR) in a Jasco 4100 FT-IR spectrophotometer, coupled with an ATR accessory Specac MKII, with a single reflection Golden Gate diamond, ZnSe lenses and a high stability temperature driver West6100+. The absorbance of the sample was recorded in the range of 4000-550 cm^{-1} accumulating 32 scans for each run.

3.4.5. Differential Scanning Calorimetry (DSC)

The thermal behavior of polyesters was examined by DSC using a Perkin Elmer DSC Pyris1. DSC data were obtained from 3 to 5 mg samples at heating/cooling rates of 10 ºC·min⁻¹ under a nitrogen flow of 20 mL·min⁻¹. Indium and zinc were used as standards for temperature and enthalpy calibration, respectively. The glass-transition temperatures were determined at a heating rate of 20 ºC·min⁻¹ from rapidly melt-quenched polymer samples. The treatment of the samples for isothermal crystallization experiments was the following: the thermal history was removed by heating the sample up to 150 ºC and left at this temperature for 5 min, and then it was cooled at 20 ºC·min⁻¹ to the selected crystallization temperature, where it was left to crystallize until saturation.

3.4.6. Thermogravimetry (TGA)

Thermogravimetric analyses were performed under a nitrogen flow of 20 mL·min⁻¹ at heating rate of 10 ºC·min⁻¹, within a temperature range of 30 to 600 ºC, using a Perkin Elmer TGA 6 Thermogravimetric Analyzer. Sample weights of about 10-15 mg were used in these experiments.

3.4.7. Stress-strain testing

Films for mechanical properties with a thickness of ~200 µm were prepared by casting from a chloroform solution at a concentration of 100 g·L⁻¹. The tested samples were cut into strips with a width of 3 mm while the distance between testing marks was 10 mm. The tensile strength, elongation at break and Young's modulus were measured at a stretching rate of 30 mm·min⁻¹ on a Zwick 2.5/TN1S testing machine coupled with a compressor Dalbe DR 150, at 23 ºC. Each sample was measured five times.

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4. Results and discussion

4.1. Synthesis and characterization

The 2,3-di-*O*-methylene dimethyl tartrate was obtained by procedure described in chapter 3.2.2 as a transparent liquid 9.5 g with 53 % yield. The 2,3-di-*O*-methylene-L-threitol was obtained by procedure, described in chapter 3.2.1. as a yellowish oil (40 % yield). ^{1}H RMN spectras (Figure 4.1.1, 4.1.2) given below show that obtained substances are pures.
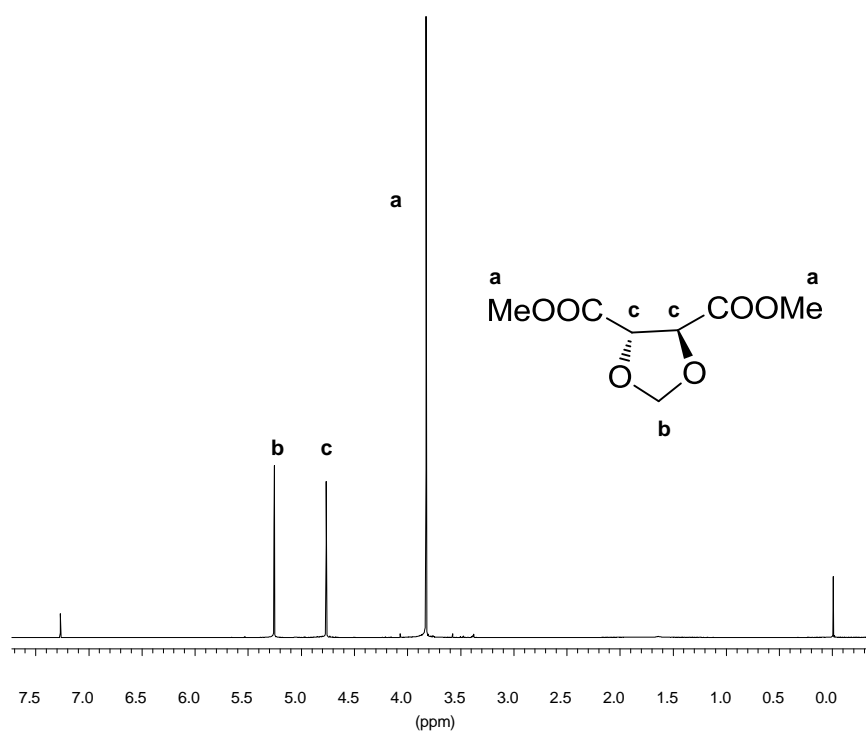

Figure 4.1.1.^{1}H NMR spectra of 2,3-di-*O*-methylene dimethyl tartrate (300 MHz, CDCl$_3$): (a) 3.82, (c) 4.76, (b) 5.25.
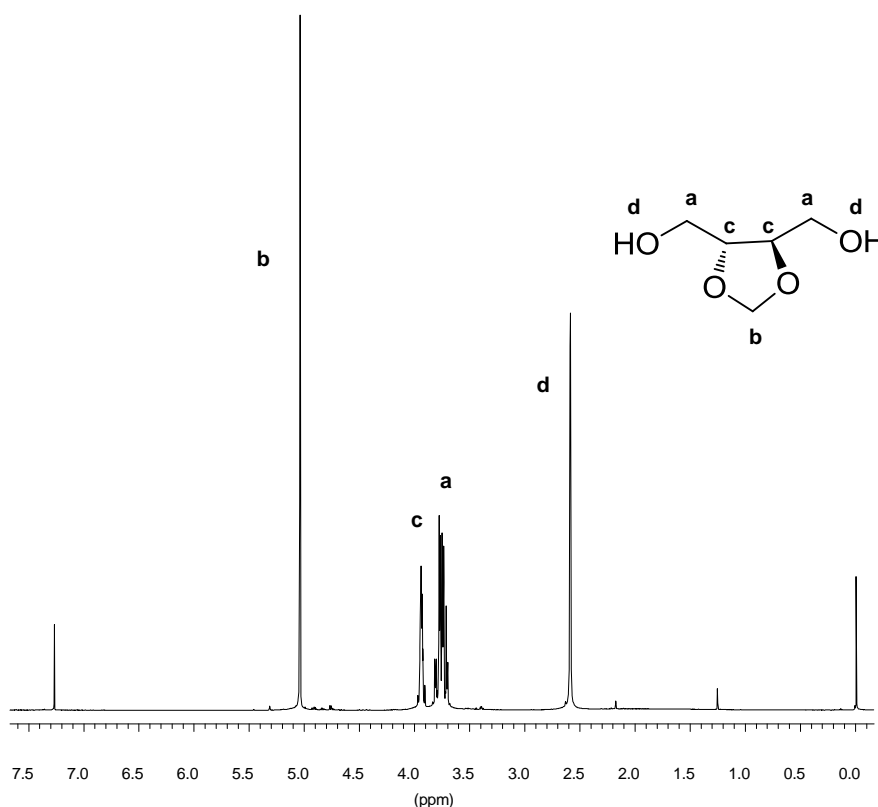
Figure 4.1.2.^{1}H NMR spectra of 2,3-di-*O*-methylene-L-threitol (300 MHz, CDCl$_3$): (d) 2.58, (a) 3.74-3.77; (c) 3.93;(b) 5.03.

PBS polyesters were obtained by the procedure depicted in chapters 3.3. Transesterification reactions were performed for 3-7 h at 140-160 ºC under nitrogen flow, and polycondensation reactions were carried out for 5-10 h at 140-180 ºC under vacuum (0.03-0.06 mbar). DBTO was used as catalyst, and the reagents were not introduced stoichiometrically, because at these conditions the volatilization of diols took place. This fact was justified by the observation that during the reaction the diol was partially removed from the flask by the nitrogen stream and by the vacuum. It is well-known that a precise stoichiometric balance between the two reactive groups is needed for reaching high conversions and highmolecular weights; therefore, the stoichiometric excess of the diol was elevated to 20%. GPC analyses showed that polyesters were obtained with weight-average molecular weights from 16800 to 34400 and number-average molecular weights between 5800 and 15300 with polydispersity degrees from 2.19 to 2.95. Intrinsic viscosities ranged from 0.41 to 0.8 dL·g^{-1}.

Table 4.1.1. Molecular weights of polyesters.

Polyester	$[\eta]^a$ dL·g^{-1}	M_n^b	M_w^b	D^b
PBS	0.8	15368	34450	2.24
PB$_{95}$Thx$_5$S	0.78	13775	30454	2.87
PB$_{80}$Thx$_{20}$S	0.76	12611	27923	2.21
PB$_{60}$Thx$_{40}$S	0.58	11938	29299	2.19
PB$_{40}$Thx$_{60}$S	0.41	11372	26393	2.45
PB$_{20}$Thx$_{80}$S	0.44	9888	27567	2.32
PThxS	0.41	8629	25482	2.78
PBS$_{90}$Thx$_{10}$	0.55	5848	16821	2.87
PBS$_{70}$Thx$_{30}$	0.71	12061	28131	2.33

[a] Intrinsic viscosity measured in chloroform at 25 ºC.
[b] Determined by GPC in HFIP against PMMA standards.

The experimental conditions used for the synthesis of PBS and its copolyesters are summarized and compared in Table 4.1.2. It can be observed that with increase of amounts of sugar, speed of reactions decrease, polymerization lasts more, applied temperatures decrease too due to thermal sensitivity of acetal groups presence in structure of monomers.

Table 4.1.2. Compared experimental conditions of polimerization of polyesters.

Polyester	Excess of BD (%-mole)	Excess of Thx-CH$_2$OH (%-mole)	1st step		2nd step		
			T (°C)	t (h)	T (°C)	t (h)	Vacuum (mbar)
PBS	20		160	3	180	8	0.06-0.1
PB$_{95}$Thx$_5$S	20		160	3	180	5	0.03-0.06
PB$_{80}$THx$_{20}$S		stoichiometric	160	3	180	5	0.03-0.06
PB$_{60}$Thx$_{40}$S		stoichiometric	160	3	180	7	0.03-0,06
PB$_{40}$Thx$_{60}$S	-	20	140	6	140	7	0.03-0.06
PB$_{20}$Thx$_{80}$S	-	20	140	7	140	7	0.03-0.06
PThxS	-	20	140	7	140	8	0.03-0.06
PBS$_{90}$Thx$_{10}$	20		160	3	160	7	0.03-0.06
PBS$_{70}$Thx$_{30}$	20		160	3	160	10	0.03-0.06

Below represented ^{1}H NMR spectra of PBS, poly(butylene succinate-*co*-2,3-di-*O*-methylene-L-threitylene succinate) copolyesters and poly(2,3-di-*O*-methylene-L-threitylene succinate).

Figure 4.1.3. Compared ^{1}H NMR spectra of PBS, poly(butylene succinate-*co*-2,3-di-*O*-methylene-L-threitylene succinate) copolyesters, poly(2,3-di-*O*-methylene-L-threitylene succinate).

If spread the signal between 28.7 and 29.3 ppm, which correspond to -CH$_2$- of succinate units in ^{13}C NMR spectras, the present peak will bend into 4 peaks. Such bending is caused by distribution of integrated sequences by deconvolution. These signals determines the content of the 4 possible dyads (BB, BT/ TB, TT). With these values, we can determine the average sequence length and degree of random of the copolymer, using follow expressions:

$$\overline{n}_B = \frac{BB + 0.5(BT + TB)}{0.5(BT + TB)}$$ **Equation 4.1.1.**

$$\overline{n}_T = \frac{TT + 0.5(TB + BT)}{0.5(TB + BT)}$$ **Equation 4.1.2**

$$R = 1/\overline{n}_{B} + 1/\overline{n}_T$$ **Equation 4.1.3.**

Figure. 4.1.4. Comparative NMR ^{13}C spectra showing the -CH$_2$- signals .

Table 4.1.3. Data of average length of sequences.

Copolyester	Average length of sequences		Degree of randomness, R
	$\overline{n}_B$	$\overline{n}_T$	
PB$_{95}$Thx$_5$S	18.6	1	1.05
PB$_{80}$Thx$_{20}$S	4.5	1.3	0.99
PB$_{60}$Thx$_{40}$S	2.5	1.7	0.98
PB$_{40}$Thx$_{60}$S	1.8	2.2	1.01
PB$_{20}$Thx$_{80}$S	1.3	3.5	1.06

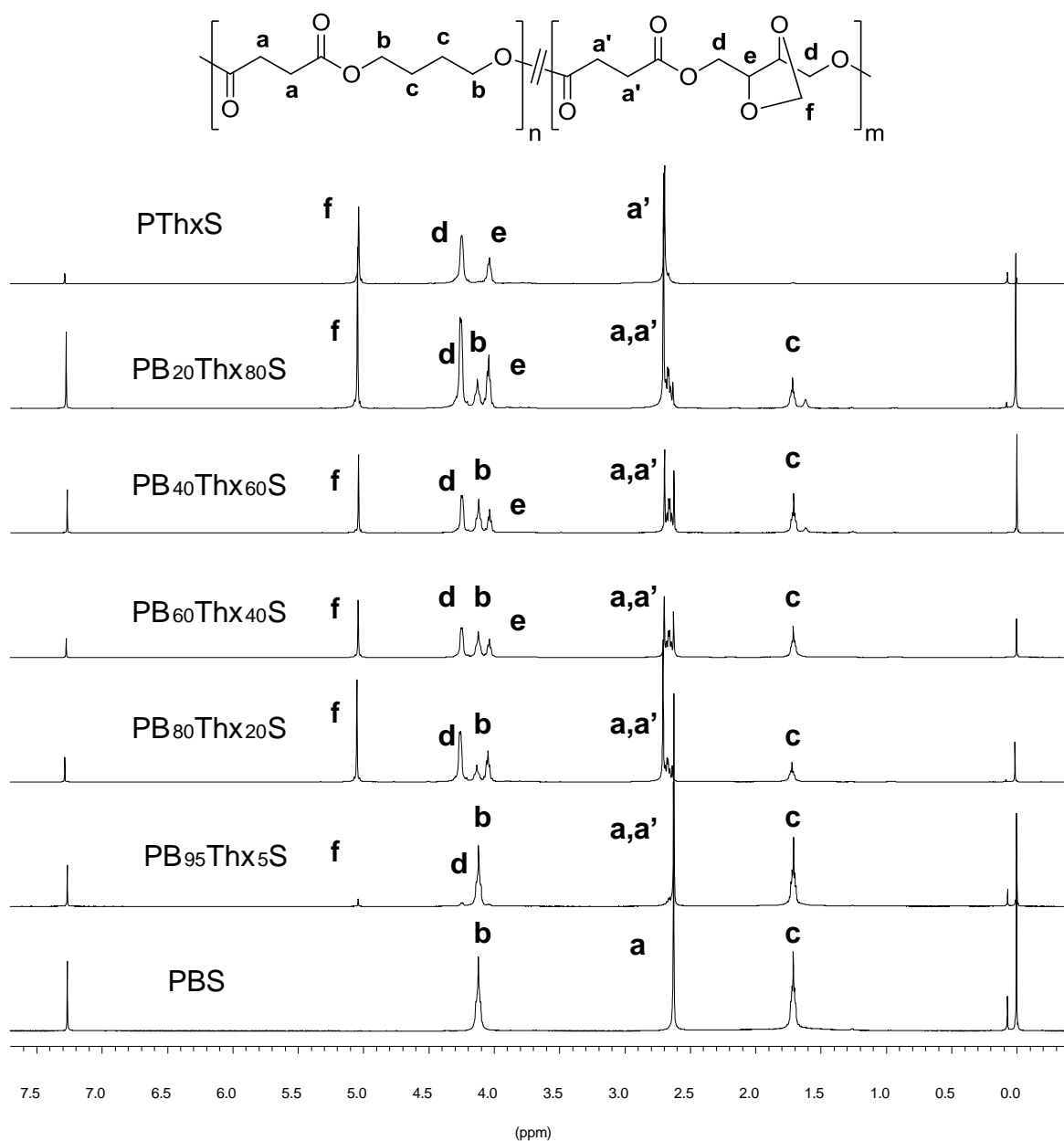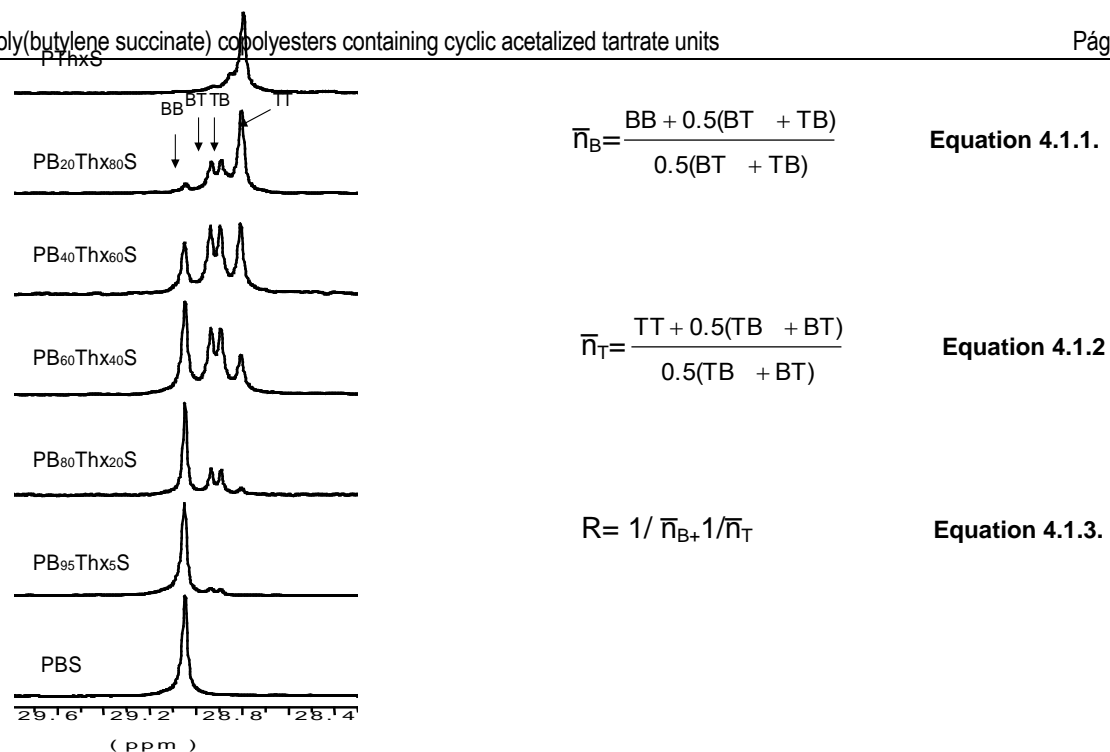Infrared spectra of PBS, poly(butylene succinate-*co*-2,3-di-*O*-methylene-L-threitylene succinate) copolyesters and poly(2,3-di-*O*-methylene-L-threitylene succinate) are very similar. As illustrated in Figure 4.1.5, the C-H stretching bands appearing in the 3000-2850 cm^{-1} region, the C-H bending band appearing at 1470 cm^{-1}. The bands related to cyclic acetals appear in the 1170-1050 cm^{-1} region (C-O-C asymmetric stretching) and in the 950-925 cm^{-1} region (C-O-C symmetric stretching). Furthermore, the infrared spectra exhibit the characteristic ester-stretching bands at about 1730 (C=O), and 1150-1050 (CO-O). Band at 790 cm^{-1} arises from the butylene vibration group.
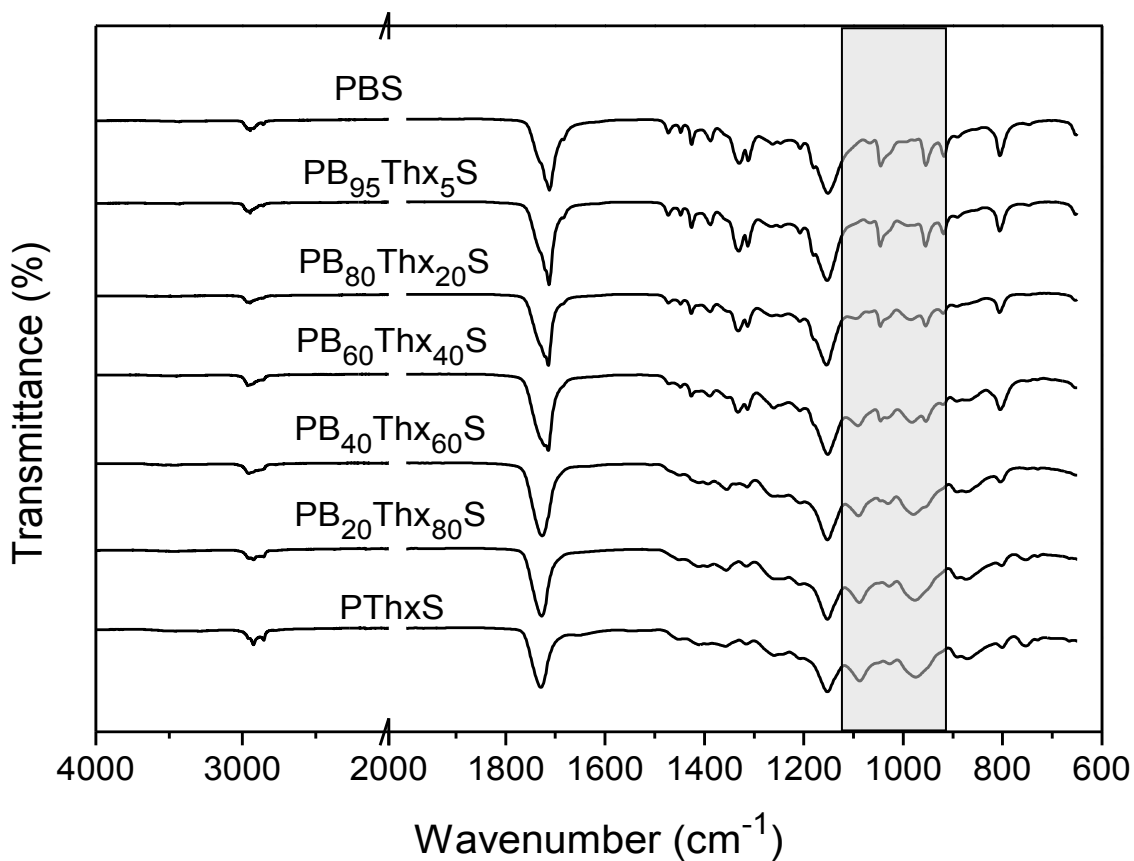
Figure 4.1.5. Compared FT-IR spectra for PBS, poly(butylene succinate-*co*-2,3-di-*O*-methylene-L-threitylene succinate) copolyesters and poly(2,3-di-*O*-methylene-L-threitylene succinate). In shadows, the absorption of (C-O-C) groups.

^{1}H NMR spectra of PBS, poly(butylene succinate-*co*-butylene-2,3-di-*O*-methylene tartrate) copolyesters is presented below.

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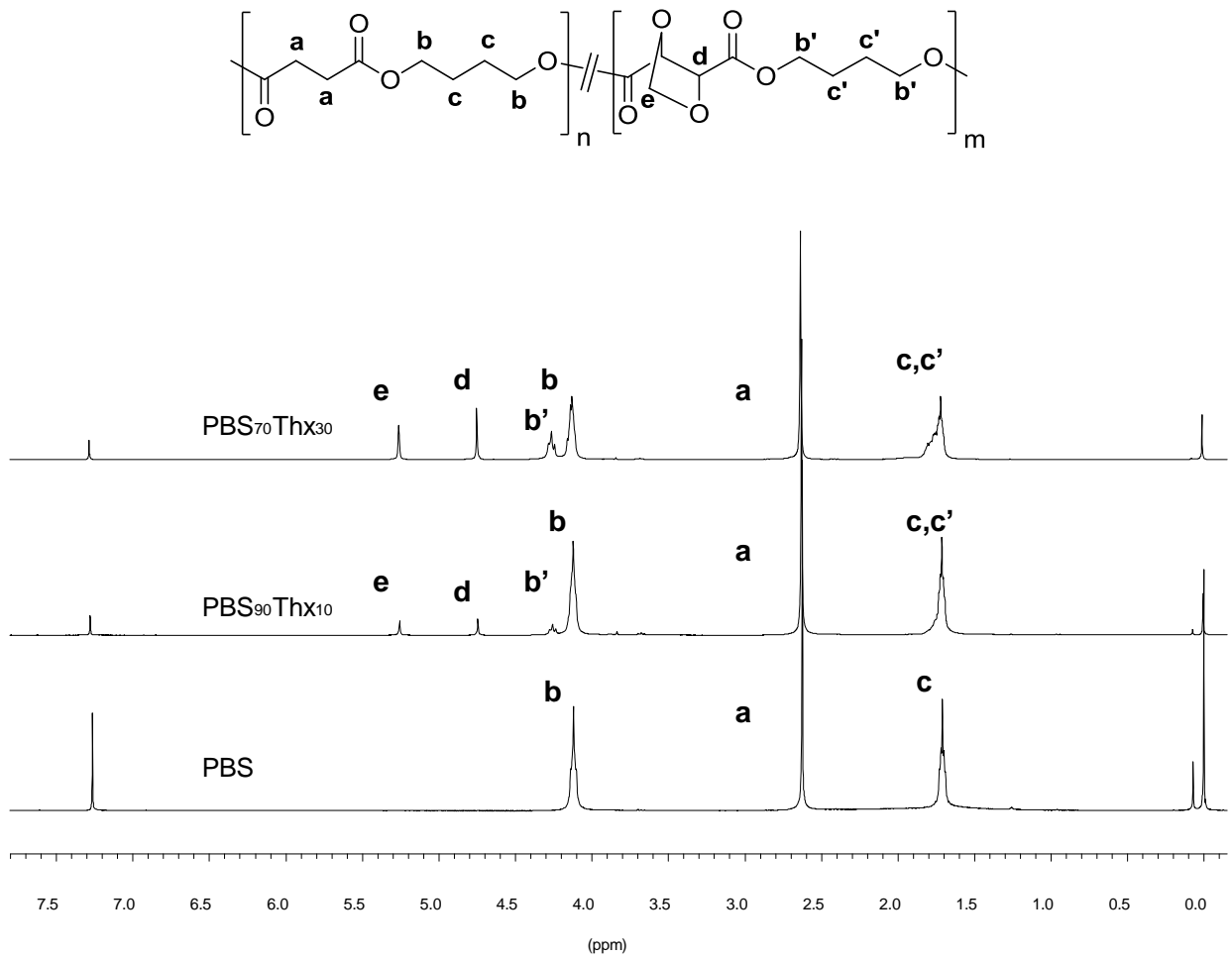
Figure 4.1.6. Compared ^{1}H NMR spectra of PBS, poly(butylene succinate-*co*-butylene-2,3-di-*O*-methylene tartrate) copolyesters.

Enlarging the signal appearing between 24.95 and 25.35 ppm in the ^{13}C NMR spectra , which correspond to -O-CH$_2$- of 1,4-butanediol units, allows to observe 4 peaks (Figure 4.1.7). These signals indicate the content of the 4 possible dyads. With these values, we can determine the average sequence length and degree of random of the copolymer.

$$\overline{n}_s = \frac{SS + 0.5(ST + TS)}{0.5(ST + TS)}$$

Equation 4.1.4.

$$\overline{n}_T = \frac{TT + 0.5(TS + ST)}{0.5(TS + ST)}$$

Equation 4.1.5.

$$R = 1/\overline{n}_s + 1/\overline{n}_T$$

Equation 4.1.6.
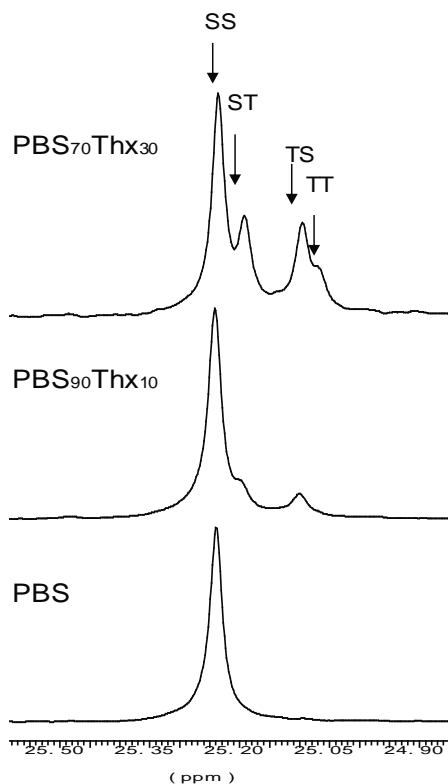
Figure 4.1.7. Comparative ^{13}C NMR spectra in the 24.9-25.5 region showing the -O-CH$_2$ signals.

Table 4.1.4. Data of average length of sequences.

Copolyester	Average length of sequences		Degree of randomness, R
	$\overline{n}_s$	$\overline{n}_T$	
PBS$_{90}$Thx$_{10}$	8.9	1	1.11
PBS$_{70}$Thx$_{30}$S	3.6	1.7	0.87

Infrared spectra of of PBS, poly(butylene succinate-*co*-butylene-2,3-di-*O*-methylene tartrate) copolyesters shows the C-H stretching bands appearing in the 3000-2850 cm^{-1} region, the C-H bending band appearing at 1470 cm^{-1}. The bands related to cyclic acetals appear in the 1170-1050 cm^{-1} region (C-O-C asymmetric stretching) and in the 950-925 cm^{-1} region (C-O-C symmetric stretching). Furthermore, the infrared spectra exhibit the characteristic ester-stretching bands at about 1730 (C=O), and 1150-1050 (CO-O). Band at 790 cm^{-1} arises from the butylene vibration group.
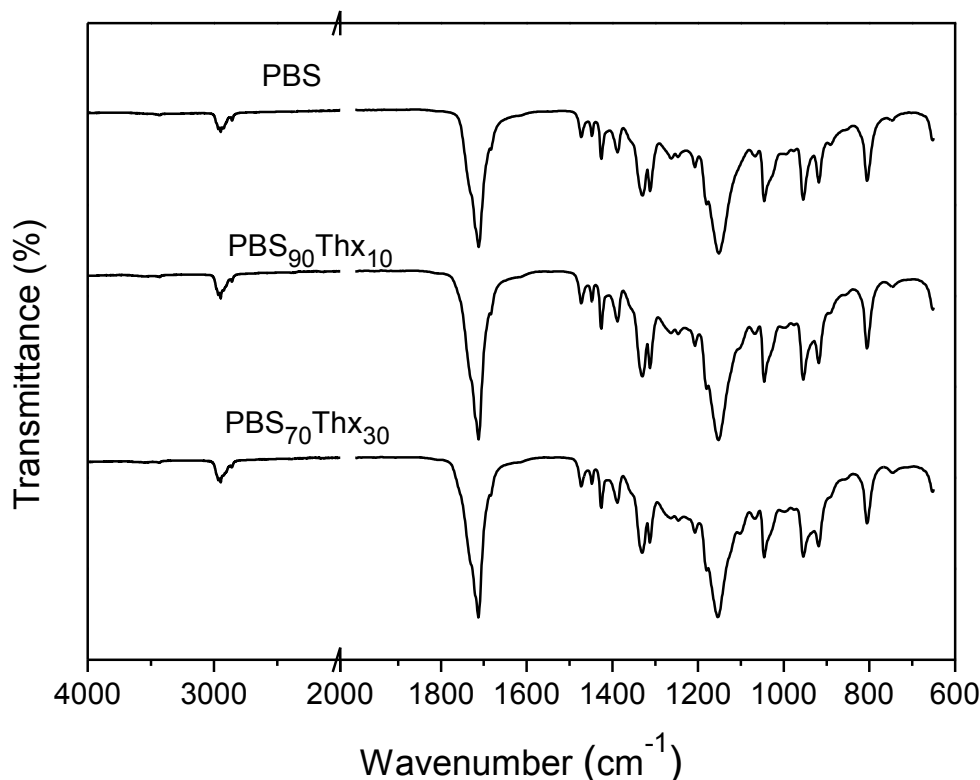
Figure 4.1.8. Compared FT-IR spectra for PBS, poly(butylene succinate-*co*-butylene-2,3-di-*O*-methylene tartrate) copolyesters.

4.2. Thermal properties

4.2.1. Melting and glass transition temperature

Synthesized copolymers were analyzed using differential scanning calorimetry. This study allowed us to determine the glass transition temperature (T_g) and melting temperature (T_m) and to observe how the copolymers (Thx-COOMe), (Thx-CH$_2$-OH) affect to thermal properties of copolyesters.

DSC traces for PB$_{95}$Thx$_5$S, PBS$_{90}$Thx$_{10}$ upon heating and cooling are shown in Figure 4.2.1. Glass-transition temperatures *(Tg)* were determined from rapidly melt-quenched samples and are listed in Table 4.2.3. The glass transition temperatures of PB$_n$Thx$_m$S polyesters vary from -33 to 7 ºC, while PBS$_n$Thx$_m$ polyesters are between -35 and -28 ºC. The glass transition happens in amorphous polymers; whose chains are not arranged in ordered crystals, even though they are in the solid state. But even crystalline polymers will have

some amorphous portion. That's why the same sample of a polymer can have both a glass transition temperature and a melting temperature. So the PBS has low T_g due to few presence of amorphous part. With increasing amounts of sugar-based units in the copolyesters, the T_g goes up and the crystalinity decreases. This effect can be seen in table 4.2.3.
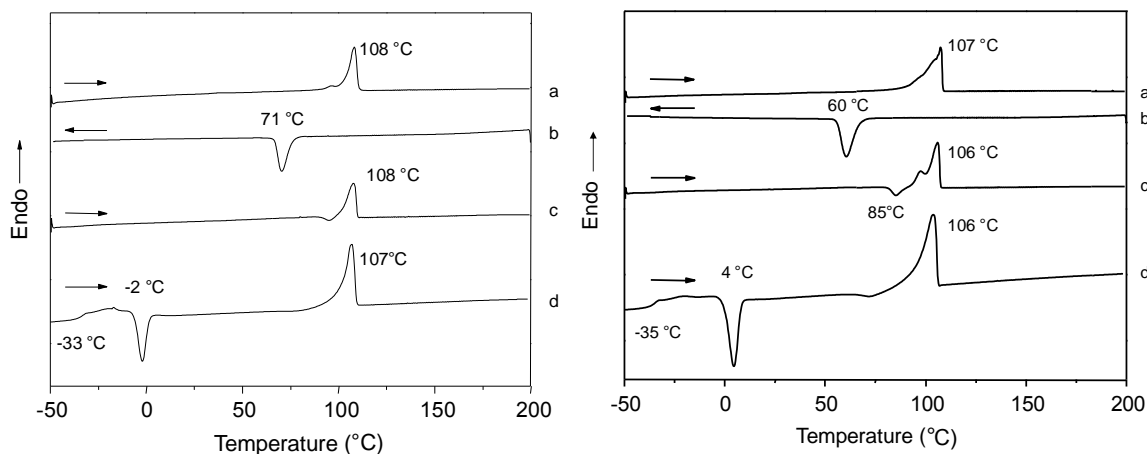
Figure 4.2.1. DSC traces for PB$_{95}$Thx$_5$S (left), PBS$_{90}$Thx$_{10}$ (right): (a) Heating at 10 ºC·min^{-1}, (b) Cooling at 10 ºC·min^{-1}, (c) Second heating at 10 ºC·min^{-1}, (d) Heating at 20 ºC·min^{-1} of a sample quenched from the melt.

Melting temperatures decrease with increasing amounts of sugar-based monomers in the structure of copolyesters. The same trend is observed for the enthalpy. The decreasing of T_m reflects a smaller crystallite size motivated by the lack of regularity of the copolymer chain. The decreasing of enthalpy is doubtless due to the lower crystalizability of the copolyester. It is evidenced by the kinetics study, that will be described below.

Figure 4.2.2. DSC melting traces for samples of PB$_n$Thx$_m$S (left), PBS$_n$Thx$_m$(right).

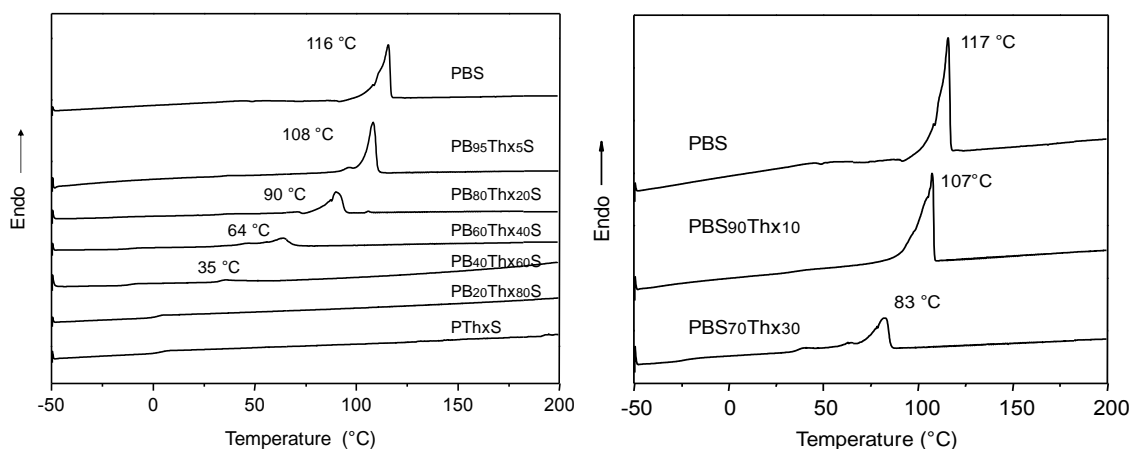T_m is given by the classical relationship $T_m = \Delta H_m / \Delta S_m$, where ΔH_m and ΔS_m are the enthalpy and entropy of melting, respectively. Therefore, T_m can be regarded in a first approximation as a measure of both intermolecular interactions (ΔH_m), and chain flexibility (ΔS_m). It must be stressed that melting temperature of semicrystalline polymers is also influenced by other factors such as molar mass, degree of crystallinity, and crystallite size.

4.2.2. Compared crystallization kinetics

This study was carried out in order to evaluate the effect of incorporating of sugar units in the crystallization kinetics of the copolyesters, which as previously noted, cause the reduction of the melting temperature and average enthalpy.

A popular method for obtaining kinetics data known as isothermal crystallization is based on rapidly cooling the sample from the melt to the crystallization temperature and then measuring the heat evolved while the sample is held isothermal. The most applied model for studying of isothermal crystallization is the Avrami model.[35]

In Differential Scanning Calorimetry, heat flow is measured as a function of time and temperature. When a material crystallizes, a measurable amount of heat is evolved, appear an exothermic peak in the DSC thermal curve. The shape of this peak is directly related to the kinetics of crystallization. Two fundamental properties which can be measured in a DSC are the reaction rate of growth of crystal, which is related to the amount of heat flow at any given time and temperature, and level of crystallization, which is measured as the amount of heat evolved (enthalpy) from the beginning of reaction until the selected time and temperature. May be considered that the isothermal crystallization is reasonably well studied and physically described by Avrami equation.[36] The Avrami equation relates the fraction or amount of uncrystallized polymer that remains after time *(t-t₀)* during an isothermal processes to its growth rate parameter, *k*, and Avrami index, *n*.

$$X_c = 1 - \exp(-k(t-t_0)^n) \qquad \text{Equation 4.2.1.}$$

The value of *n* is associated to the nucleation type present during the experiment (e.g., sporadic or instantaneous) and also to the dimension of the crystalline structures [37,38], so the Avrami index *n* can be considered simply as the sum two terms:

$$n = n_d + n_n \qquad \text{Equation 4.2.2.}$$

n_d is the dimensionality part (values integers equals to 1, 2 and 3 only): has the value of 1 for needle-shaped-like crystals, 2 for plates-like crystals , and 3 for spheres-like crystals. The time dependence of the nucleation is represented by n_n. In principle its value should be either 0 or 1, where 0 corresponds to instantaneous nucleation and 1 to sporadic nucleation. For example, a descript polymeric system with $n>3$ indicates a spheroidal grown ($n_d=3$) in which additional nucleation sites sporadically appear with time ($n_n>0$), if the same system result with $n=3$, possibly indicates a spheroidal grown in which all the nucleation sites appear initially in the process ($n_n=0$).

With this interpretation, in the present study the dimensionality is the same for all samples, 2 ($n_d=2$) where they differ is in the sporadic growth; therefore, we can observe that the addition of sugar-based units promotes the instantaneous growth and provide nucleation sites, since the values of n_n decreases from 0.74 ($n = 2.74$) to 0.7 ($n = 2.07$).

On the other hand, we can consider that the relationship dimensionality-nucleation type is more complex. That is, if we consider that the values of n_n and n_d are not independent of each other but they have more complex form. We can establish classifications for to explain more flexible values of n, such values of less than 1 and greater than 4, for example. In this adress Michell *et al.*[38] presented interpretations intervals for classifying the experimental values of *n*.

Instantaneously nucleated spherulites should yield an Avrami index of 3 (experimental values of 2.5–3.4 are considered a good approximation), while sporadically nucleated spherulites should exhibit an Avrami index of 4 (values of 3.5-4.4 are also considered a good approximation). Avraim index 2 (values of 1.5-2.4), structure 2D instantaneously nucleated. Avrami indexes in the order of 1 (<1.5) or lower indicate a dramatic change in the order of the crystallization kinetics (an Avrami index of 1 would be equivalent to a first order crystallization kinetics). It can be considered that the PBS 85°C is instantaneously nucleated spherulites, while PBS at 90 °C y $PB_{95}Thx_5S$ with Avrami index of 2 are structure 2D instantaneously nucleated.

The table 4.2.2. shows the values obtained from the Avrami fit: the parameters *k, n* and the predicted half-crystallization time,[39] is the time needed for the 50% relative transformation to the semi-crystalline state. If we denote the absolute time *t* as the time at which the temperature reaches the desired crystallization temperature, a certain time could elapse before crystallization starts, t_0, and this time must be subtracted from the absolute time or, in other words, time count must start from time equal to t_0. In this table can be observed the reaction take more time in to start when is added the sugar units. In the same table can be observe that

the growth rate parameter is higher en case of PBS. It is well know that the overall crystallization is a process that depends on temperature, the overcooling applied is causes that the speed of crystallization become more slow at 90 than 85 °C.

Table 4.2.2. Isothermal crystallization data for PBS and PB$_{95}$Thx$_5$S.

Polyester	T_c °C	t_0 min	$t_{1/2}$ min	n	-log$k$	$T_m{}^a$ °C
PBS	85	0.23	1.94	2.74	0.80	101/114
PBS	90	0.5	5.33	2.36	1.94	104/114
PB$_{95}$Thx$_5$S	85	0.41	6.16	2.20	2.11	100/108
PB$_{95}$Thx$_5$S	90	1.24	19.51	2.07	3.02	103/108

[a]Multiple melting peak.

Not often used directly Avrami equation as presented above. The common and more useful form is rearranging and applying logarithmic to both sides:

$$\log[-\ln(1 - X_c)] = \log k + n\log(t - t_0)$$

Equation 4.2.3.

This represent the line equation, then ploting $\log(t - t_0)$ vs. $\log[-\ln(1 - X_c)]$ can be determined the parameters *n* and *k*, see Figure 4.2.2.
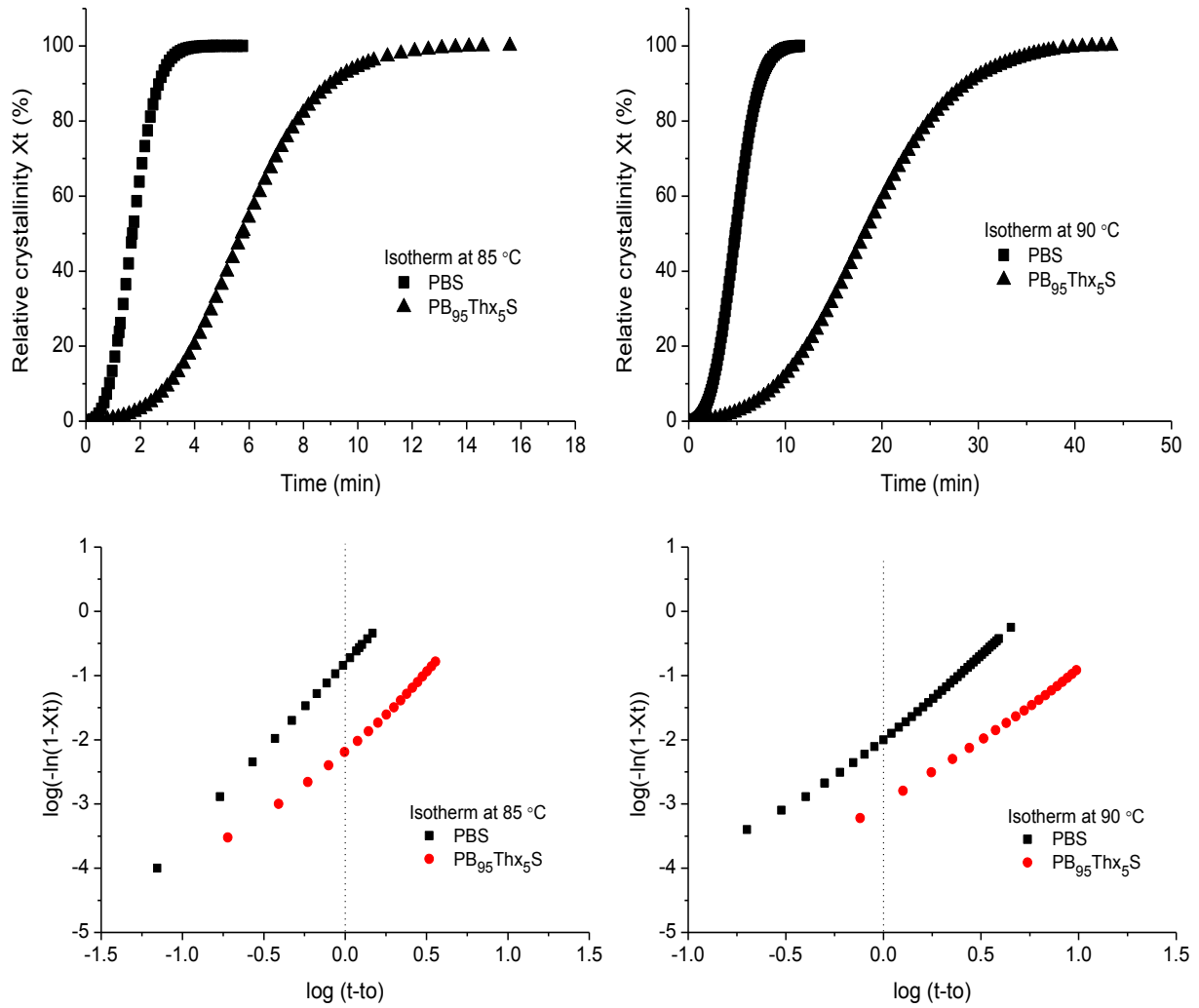
Figure 4.2.2. Isothermal crystallization of PBS and PB$_{95}$Thx$_5$S at 85 ºC (left), 90 °C (right).

4.2.3. Thermal stability

To evaluate the thermal stability of PB_nThx_mS and PBS_nThx_m polyesters, TGA analyses were performed in the 30-600 ºC temperature range under a nitrogen atmosphere. The TGA traces are compared in Figure 4.2.3. This analysis demonstrates that the thermal stability decreases with increasing of sugar content. The registration of temperature at which PB_nThx_mS polyesters lost 5 % shows decreasing from 329 ºC and 245 ºC (Table 4.2.3.). Temperature for maximum decomposition rate (T_d) and the remaining weight at 600 ºC do not significally change by molecular weight o introduction of cyclic acetal groups.
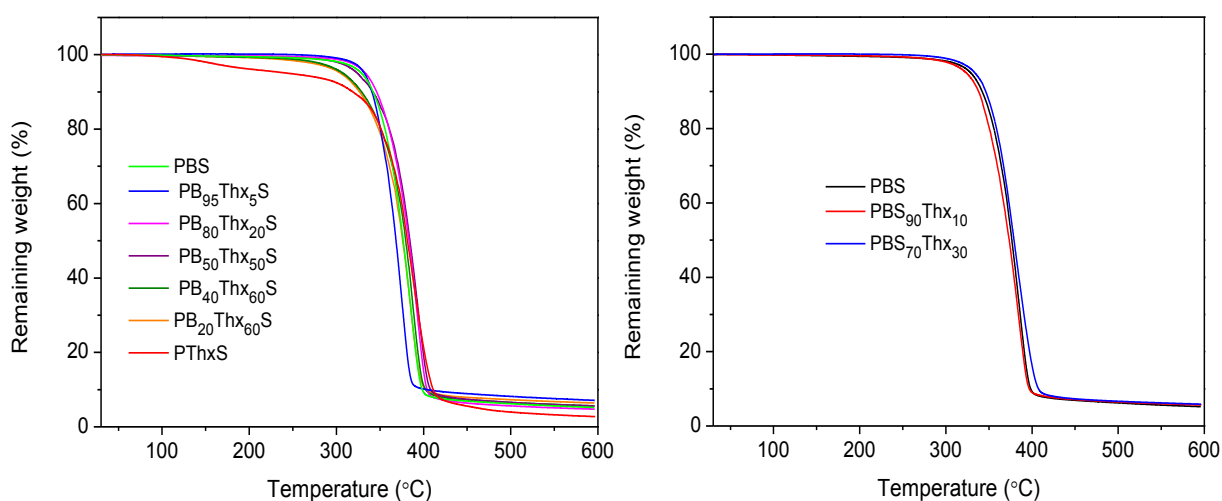

Figure 4.2.3. TGA traces of PB_nThx_mS (left) and PBS_nThx_m (right).

Table 4.2.3. Thermal properties of PB_nThx_mS and PBS_nThx_m polyesters.

Polyester	First heating[b]			Cooling[b]	Second heating[b]			TGA		
	$T_g{}^a$ (°C)	T_m (°C)	ΔH_m J·g^{-1}	T_c (°C)	T_c (°C)	T_m (°C)	ΔH_m J·g^{-1}	$T_{d5\%}{}^c$ (°C)	$T_{d\,max}{}^d$ (°C)	RW^e
PBS	-37	117	82	75	98	115	63	329	386	5
$PB_{95}Thx_5S$	-33	108	73	71	95	108	56	332	375	7
$PB_{80}Thx_{20}S$	-24	90	4	39	74	90	42	333	392	5
$PB_{60}Thx_{40}S$	-13	64	31	-	-	-	-	324	394	6
$PB_{40}Thx_{60}S$	-8	35	6	-	-	-	-	308	387	6
$PB_{20}Thx_{80}S$	7	-	-	-	-	-	-	304	384	6
PThxS	13	-	-	-	-	-	-	245	386	3
$PBS_{90}Thx_{10}$	-35	107	82	60	85	106	67	324	386	6
$PBS_{70}Thx_{30}$	-28	83	35	-	35	80	33	334	380	6

[a]Glass-transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 ºC·min^1.
[b]Melting (T_m) and crystallization (T_c) temperatures, melting enthalpy (ΔH_m) measured by DSC at heating/cooling rates of 10 ºC·min^{-1}.
[c]Temperature at which 5 % weight loss was observed.
[d]Temperature for maximum degradation rate.
[e]Remaining weight at 600 ºC

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4.3. Mechanical properties

Table 4.3. summarizes the data obtained from the stress-strain curves. Elastic modulus decrease from 535 to 75 MPa. The higher rigidity of PBS copolyesters observed in case of minimum content of acetal rings, which increased significantly the T_g.

Tensile strengths were in the range 5-33 MPa respectively; whereas elongations at break ranged from 9-50 %. It can be noted that the introduction of acetal rings also caused an sufficiently decrease in tensile strength and a considerably increasing of elongation break. But in case of polyester, which contain in its structure 20% of sugar shows low elongation at break, which could be caused of defect of structure of sample. The stress-strain curves are presented in Figure 4.3.
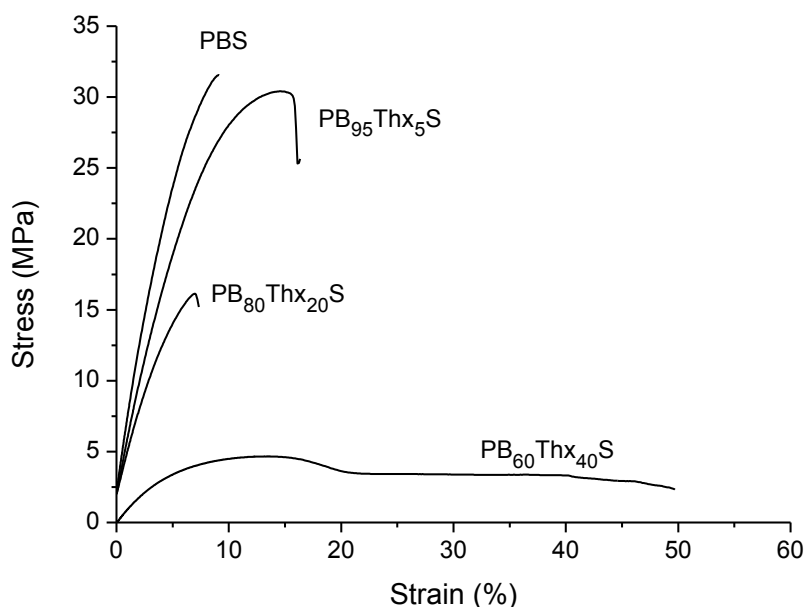

Figure 4.3 . Stress-strain curves for PBS and its copolyesters.

Table 4.3. Mechanical properties of polyesters.

Polyester	T_m °C	ΔH_m J·g^{-1}	Elastic modulus (MPa)	Tensile strength (MPa)	Elongation at break %
PBS	114	55	535	33	9
PB$_{95}$Thx$_5$S	108	59	410	28	26
PB$_{80}$Thx$_{20}$S	92	50	288	16	7
PB$_{60}$Thx$_{40}$S	65	33	75	5	50

5. Conclusions

- The cyclic monomers 2,3-di-*O*-methylene dimethyl tartrate and 2,3-di-*O*-methylene-L-threitol were prepared. The homopolyesters poly(butylene succinate) and poly(2,3-di-*O*-methylene-L-threitylene succinate), as well as the copolyesters-poly(butylene succinate-*co*-butylene-2,3-di-*O*-methylene tartrate) and poly(butylene succinate-*co*-2,3-di-*O*-methylene-L-threitylene succinate), were successfully synthesized from them. Samples of all the polyesters and copolyesters were characterized by NMR, FT-IR, viscosimetry, GPC. GPC analyses showed that polyesters were obtained with weight-average molecular weights from 16800 to 34400 and number-average molecular weights between 5800 and 15300 with dispersity degrees from 2 to 3. Intrinsic viscosities ranged from 0.41 to 0.8 $dL \cdot g^{-1}$.

- The glass transition temperatures of PB_nThx_mS polyesters varied from -33 to 7 ºC, while in PBS_nThx_m polyesters it oscillates between -35 and -28 ºC. Melting temperatures decrease with increasing amounts of sugar-based monomers in the structure of copolyesters.

- Crystallization kinetic study was carried out in order to evaluate the effect of incorporating of sugar units in the crystallization of the copolyesters. The addition of sugar-based units promotes the instantaneous growth and provide nucleation sites. It can be observed that the growth rate parameter is lower in the case of $PB_{95}Thx_5S$.

- TGA analyses demonstrate that the thermal stability of copolymers decreases with increasing of sugar content. The registration of temperature at which PB_nThx_mS polyesters lost 5 % shows decreasing from 329 ºC and 245 ºC. Temperature for maximum decomposition rate (T_d) and remaining weight at 600 ºC do not significantly changed by molecular weight o introduction of cyclic acetal groups.

- Elastic modul decrease from 534 to 75 MPa. The higher rigidity of PBS copolyesters observed in case of minimum content of acetal rings. Tensile strengths were in the range 5-33 MPa respectively; whereas elongations at break ranged from 9-50,%. It can be noted that the introduction of acetal rings also caused a notable decrease in tensile strength and a considerably increasing of elongation break.

6. References

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