Ionic copolyesters and their nanocomposites: synthesis, characterization and properties

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Summary

A polymer containing small amounts of ionic groups either along the polymer backbone chains or as pendant groups is defined as ionomer. As originally proposed by Eisenberg, the interaction between ionic groups leads to the formation of multiplets containing a small number of ion pairs, and also to ionic clusters, which constitute a second phase made of many multiplets as well as portions of the hydrocarbon chains. These ionic structures have been shown to act as strong electrostatic cross-links, which provide altered physical properties, such as enhanced mechanical properties and high melt viscosity, among others. The improvement in mechanical properties of the ionomer has been reported to be related to the strength of the electrostatic cross-links, which can be varied by changing the size and type of the counterions present in the ionomer.

Both aromatic polyesters as poly(ethylene terephthalate) and poly(butylene terephthalate) and aliphatic polyesters as poly(butylene succinate), poly(hydroxyl alkanoate)s and poly(lactic acid), are polymeric materials widely used today. Their most familiar applications are in clothing, food packaging and water and carbonated soft drinks bottles. Major part of biodegradable synthetic polymers are polyesters, and in particular, aliphatic polyesters. Monomers for the latter can be synthesized from renewable resources. Biodegradable polyesters play a key role in medical applications due to their biodegradability and versatile synthesis able to afford tailored properties; they are currently employed as biomaterials for medical purposes such as surgical sutures, scaffolds, screws and reinforcing plates as well as controlled release drug carriers, since they are biocompatible and non-toxic.

This thesis is focused to the chemical modification of aromatic and aliphatic polyesters through the incorporation of various concentration and different ionic groups. We synthesized poly(hexamethylene terephthalate) and poly(butylene succinate)-based ionomers and investigated the effects of the ionic substitution on physical properties, crystallization rates and hydrodegradability of these polyester ionomers. In addition, we also studied the influence of the ionic interaction with nanoclays in the formation of ionomers-based nanocomposites.

This thesis embodies a multidisciplinary task work that includes synthesis, spectroscopy characterization, evaluation of thermal and mechanical properties, hydrolytic degradation and nanocomposites preparation: the synthesis procedure of copolyesters was made in all cases by polycondensation in melt-phase. Different conditions of temperature, catalyst and time required were used for each family of copolyesters depending on both the stability and the reactivity of the comonomers involved in the synthesis. The copolyesters synthesized incorporated sulfonated, ammonium, trimethylammonium and tributylphosphonium ionic groups into their chains. The hydrolytic degradation results suggest that the insertion of sulfonated groups in the copolyesters make them more hydrophilic allowing better solvation and an easier attack of water on the ester groups.

Nanocomposites with nanoclays were obtained by using different approaches for mixing and in some cases by making use of compatibilizers. Octadecyltrimethylammonium, 1,12-dodecylenediammonium salts and a terpolyester ionomer were used for compatibilization. The clay was used either unmodified or modified with alkylammonium soaps. Results obtained by the different procedures were compared and the effect of the compatibilizers on the mixing efficiency and composite properties were evaluated.

Characterization was carried out by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, FTIR spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and thermogravimetry analysis (TGA). The changes in crystal structure upon copolymerization were followed by small angle X-ray diffraction (SAXD) and the changes in hydrodegradability by GPC and ^{1}H NMR.

Glossary

A-DMG·Cl	L-glutamic acid dimethyl ester hydrochloride
BD	1,4-Butanediol
CALB	Candida Antarctica lipase B
$CDCl_3$	Deuterated chloroform
CL or CLNa	Unmodified sodium montmorillonite-Cloisite Na
CL30B	Modified montorillonite-Cloisite 30B
$Đ$	Dispersity
DBG	Dibutylene glycol
DBTO	Dibutyl tin oxide
DHG	Dihexylene glycol
DMF	*N,N'*-dimethylformamide
DMS	Dimethyl succinate
DMSI	Sodium salt of dimethyl 5-sulphoisophthalate
DMSO	Dimethyl sulfoxide
DMT	Dimethyl terephthalate
DSC	Differential scanning calorimetry
E	Young's modulus
ε_{max}	Elongation at break
FTIR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
GA	Glutaric acid
HBr	Hydrobromic acid
HD	1,6-Hexanediol
M_n	Number average molecular weight
M_w	Weight average molecular weight
MMT	Montmorillonite
η	Intrinsic viscosity
NMP	1-methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
PBS	Poly(butylene succinate)
$PBS_xG^{I}_y$	Poly(butylene succinate-*co*-ammonium chloride glutarate)

PBS$_x$G$_y$G$^{I}_{z}$	Poly(butylene succinate-*co*-glutarate-co-2-trimethylammonium chloride glutarate)
PB$_x$PP$_y$S	Poly(butylene-*co*-2-methyl-2(tributylphosphonium bromide)-methyl propylene succinate)
PBS$_x$SS$_y$	Poly(butylene succinate-*co*-sulfonated succinate)
PLA	Poly(lactic acid)
PET	Poly(ethylene terephthalate)
PBT	Poly(butylene terephthalate)
PHSI	Poly(hexamethylene 5-sulfoisophthalate)
PHT	Poly(hexamethylene terephthalate)
PHT$_x$SI$_y$	Poly(hexamethylene terephthalate-*co*-5-sulfoisophthalate)
PPD	2,2-(dihydroxymethyl)propyl-tributylphosphonium bromide
RW	Remaining weight
SA	Succinic acid
Sc(NTf$_2$)$_3$	Scandium (III) trifluoromethane sulfonimide
SDMS	Sulfonated dimethyl succinate
SI	5-sodium sulfoisophthalate units or supporting information file
T_c	Crystallization temperature
T_d	Temperature of maximum decomposition rate
$^{o}T_d$	Onset decomposition temperature
T_g	Glass transition temperature
T_m	Melting temperature
TBT	Titanium (IV) tetrabutoxide
TFA	Trifluoroacetic acid
THF	Tetrahydrofurane
TGA	Thermogravimetric analysis
TMA-DMG·I	2-(*N,N,N*-trimethyl ammonium) dimethyl glutarate iodide
TMAGA·Cl	2-(*N,N,N*-trimethyl ammonium) glutaric acid chloride
ΔH_m	Melting enthalpy
σ_{max}	Maximum tensile stress
12A$_2$·2HCL	1,12-dodecanediamine dihydrochloride
18ATMA·Br	Octadecyltrimethylammonium bromide

Index

Chapter III. Polyesters containing anionic groups 37

Chapter I.

Introduction

1. General introduction

Ionic forces have a significant and critical role attributed by nature not only in the formation of the inorganic world of mineral and silicate glasses, but also in life cycles, where ionic interactions of biopolymers are responsible for vital biomembrane processes.[1] The concept of ionic interactions has been successfully applied in order to modify the properties of polymers, and thus to achieve a most versatile group of known materials. The study of ionic interactions in polymer systems represents one of the liveliest areas of research activity in modern polymer science. The industrial interest is due to the fact that ionic interactions permit the control of the physical properties of polymers, even at low ionic concentrations.

Ionomers are long chain polymers that contain ionic groups, usually occurring as side chain substituents attached to some of the monomeric units of the non-ionic backbone chains. They can be prepared from a wide variety of polymers and copolymers, including rubbery ones such as polybutadiene, glassy ones such as polystyrene and poly(methyl methacrylate), and partially crystalline ones such as polyethylene and polypropylene. In many ionomers, the ionic groups are distributed randomly along the hydrocarbon chain, but in some of them, such as the telechelic ionomers, the ionic groups are situated only at the chain ends.

This particular class of ion-containing polymers known as ionomers constitutes a large family of polymers which a diversity of applications. These applications are based on the thermoreversible character of the physical crosslinks and to the specific mechanical properties resulting from their microstructure. The interaction between the ionic groups in the polymer matrix modifies and strengthens the intermolecular forces and leads to a physical type of cross-linking. The change in properties of ionomers in the solid state is due to the clustering of ion pairs in a medium of low dielectric constant. Polymers with strongly interacting groups are of great interest due to their unusual properties caused by the ability to microphase segregation in bulk and in solution. This peculiarity leads to high probability of self-organization with the formation of various types of nano and microstructures.

Two types or ionic aggregates are proposed to exist according to ion content: a) below a certain ion content, multiplets consisting of a small number of ion pairs, which work as physical crosslinks, and b) above that critical ion content, clusters consisting not only of ion pairs but also of portions of hydrocarbon chains, which bear many of the characteristics of microphase separation. Ionic crosslinks are not as strong or stable as covalent crosslinks because they can be overcome by applying a high temperature. This feature may, be however a valuable attribute of ionomers because it means that, unlike covalently cross linked polymers or thermosets, they can be processed into desirable shapes by conventional methods, such as compression molding, injection molding, and extrusion.

Ion-containing polymers provide a way of modifying various properties by controlling molecular structure through the utilization of ionic interactions. By controlling the many variables that are involved such as the ion content, degree of neutralization, nature of counterion, thermal treatment, presence of plasticizing agents and additives, it is possible to prepare ionomers that have a wide range of properties suitable for industrial applications such as molded thermoplastic products, thermoplastic elastomers, films, compatibilizing agents, and membranes for various industrial uses.

One method of modifying the chemical structure of polyesters for improved physical properties involves the introduction of an additional functional group, which combines and enhances the advantages of both components: the polyester and the particular functional group. Because chemical structures are being better defined by new synthetic approaches as well as a better understanding of polymerization mechanisms, an ever expanding array of applications are being explored in important areas such as optical electronics, adhesion and coatings, high performance materials, and biotechnology. The incorporation of network structures into the backbone is of particular interest for new biodegradable materials, since they are expected to afford better physical and chemical properties, such as resistance to heat and the presence of other chemicals.

The present work of this thesis is divided in six chapters. Chapter I contains a general introduction to the subject, the thesis aims and a literature review of the polymers related to those studied in this thesis. Chapter II summarizes the general materials and methods used in this research. Chapter III describes the synthesis, characterization and properties evaluation study carried out on aliphatic and aromatic polyesters containing anionic groups. Chapter IV is focused on the study of aliphatic polyesters containing cationic groups, synthesis, characterization and evaluation of their properties. Chapter V covers the preparation of ionomers polyesters based-nanocomposites made with modified and unmodified montmorillonite using different compatibilizers, Chapter VI summarized the general conclusions of the performed research.

2. Objectives

The main objective of this thesis is to incorporate different pendant ionic groups such as sulfonated, ammonium, trimethylamonium and tri-*n*-butylphosphonium into the chains of aliphatic and aromatic polyesters by melt polycondesation to promote the ionic interactions in the obtained polyesters and nanocomposites in order to modify the mechanical properties and hydrolytic degradation.

This main objective is achieved through several specific objectives:

- Synthesis and characterization of sulfonated poly(hexamethylene therephtalate). Chemical structure, thermal analysis, mechanical properties and hydrolytic degradation of these copolyesters.
- Synthesis and characterization of poly(butylene succinate) ionomers containing sulfonate units. Evaluation of the thermal and mechanical properties and their hydrolytic degradation.
- Enzymatic polymerization and characterization of poly(butylene succinate) ionomers containing ammonium groups. Thermal analysis and tests activity of CALB in presence and absence of ammonium and trimethyl ammonium groups. Evaluation of these cationic ionomers as biocides.
- Synthesis and characterization of poly(butylene succinate)-based phosphonium bromide ionomers. Evaluation of their thermal and mechanical properties and ionic coupling with sulfonated PBS ionomer.
- Synthesis and characterization of poly(butylene succinate) ionomers containing glutarate units both unmodified and modified with a trimethylammonium group to be used as compatibilizer in PBS/montmorillonirte nanocomposites prepared by melt extrusion. Structure and evaluation of thermal and mechanical properties of nancomposites compared to ionomers.
- Preparation of nanocomposites of sulfonated poly(hexametylene terephthalate) ionomers with momtmorillonite using octadecyltrimethylammonium and 1,12-dodecylenediammonium salts as compatibilizers prepared by melt extusion. Their structural characterization and the evaluation of their thermal and mechanical properties.

3. Ionomers

Ionomers are defined as polymers having a small mole fraction (less than 15 mol-%) of ionic groups covalently bonded to the polymer backbone as pendant or end moieties. Polyelectrolytes also have ionic groups covalently bonded to the polymer backbone with the difference that the content of ionic groups is much higher (usually >80 mol-%). Polyelectrolytes are typically water-soluble, at least at some pH, and do not have the interesting solid-state properties, which is the main reason for the more commercial uses of ionomers.

The origin of the word ionomer dates back to 1965.[2] It was used for the first time to describe a class of thermoplastics (Surlyn, DuPont), consisting of ethylene and partly neutralized methacrylic acid. In 1965, Rees and Vaughan defined ionomers as olefin-based polymers containing a relatively small percentage of ionic groups, in which, strong ionic interchain forces play the dominant role in controlling properties. Later, Eisenberg and Rinaudo noticed that ionomers in solution sometimes showed a behavior very similarly to polyelectrolyte, especially in solvents with high dielectric constants. This confusion between polyelectrolytes and ionomers lead to a new definition by Eisenberg and Rinaudo in 1990; ionomers are polymers whose bulk properties are governed by ionic interactions in discrete regions of the material (ionic aggregates).[3] Schematic structures of common ionomers are shown in Figure 1.

Typically, ionomers are low dielectric copolymers comprised of nonionic repeat units and ionic groups. Alkali metals, alkaline earth metals and transition metals, for example, act as counter ions for these polymers. The distribution of these ionic groups along the backbone chain is an important variable. The ionic groups can be synthetically placed randomly or systematically within the primary polymer chain as end groups on polymer chains or as pendant groups in a copolymer.[4,5] Regardless of the ionic group placement, the groups facilitate the formation of ionic aggregates. The ionic aggregates act as effectively physical crosslinks, which give rise to ionomers with thermoplastic characteristics.

As bulk materials, ionomers have widespread applications in packaging, adhesive and coating technologies due to their excellent toughness, and compatibility with various solvents. Ionomers have also been processed into membranes for a variety of electrochemical devices thanks to their high ionic conductivity.

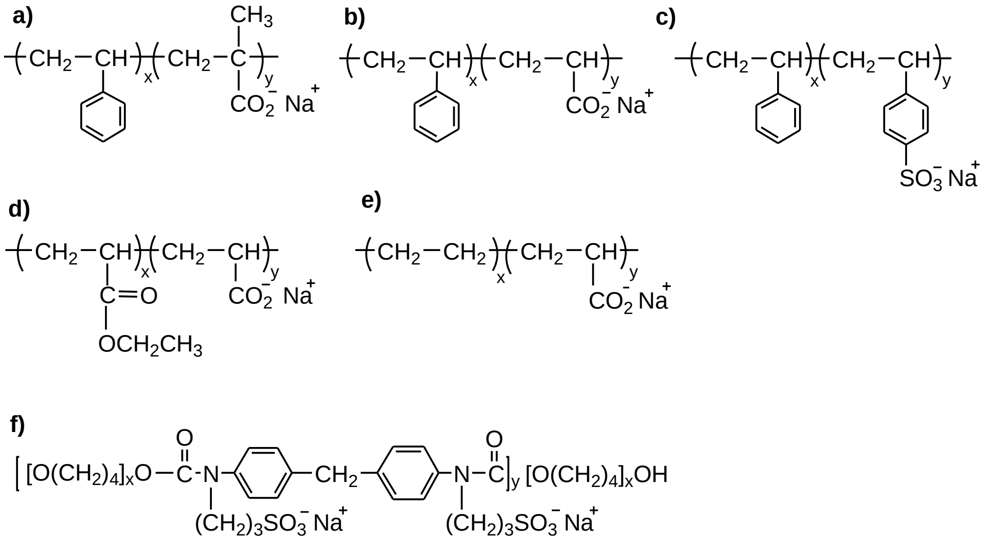


Figure 1. Structure of some common ionomers: (a) poly(styrene-*co*-sodium methacrylate), (b) poly(styrene-*co*-sodium acrylate), (c) poly(styrene-*co*-sodium styrenesulfonate), (d) poly(ethyl acrylate-*co*-sodium acrylate), (e) poly(ethylene-*co*-sodium acrylate), (f) sulfonated poly(urethane).

Ionomers are classified to the following main types: Ionones, monochelics, telechelic, block copolymers, random copolymers, glass-ionomers, zwitter-ionomers, etc.[6,7] Ionenes are materials where the ionic groups are part of the polymer backbone,[8] instead of being attached as a pendant group, *i.e.*, a quaternary ammonium or pyridinium ion is located on the backbone. The number of papers published on ionones is about 7% of that published on ionomers. Some ionenes have been studied for their bacteriostatic and bactericidal activity. Ionenes have applications in biomedical technologies such as gene transfection agents,[9] polymeric cancer drugs,[10] and antimicrobials.[11,12] A monochelic is the simplest type of ionomer consisting of a single ion placed at the end of a polymer chain. An example is polystyrene containing a terminal carboxylate anion and can be prepared by radical polymerization.[7,13] A telechelic, on the other hand, is typified by one ion at each end of a polymer chain. Materials of this type can also been synthesized by anionic polymerization or melt polymerization.[14-16] The most extensive studies of thelechelic are based on carboxylate ionomers.[17-19] Besides carboxylate end groups, the ionic ends can also consist of a sulfonate, a sulfate, and a borate.

Block copolymers are known in several forms. The AB type, in which one of the segments is nonionic and the other consists of repeating ionic units;[20] an ABA-type triblock[21] consists of one completely nonionic segment and another partly ionic segment. Another new type of block ionomer was synthesized by van Hest *et al*.[22] The acid form of the block copolymer consisted of a block of polystyrene with an acid functionalized poly(propylene imide) dendrimer. The term random ionomer denotes an ionomer in which the ionic species are randomly distributed along the chain.[23] These materials may be viewed as random copolymers and are prepared by either direct copolymerization or postpolymerization modification of a polymer. Polystyrene-based ionomers, in which the ionic groups are distributed randomly along the polymer chain, constitute an important class of ionomers and a great deal of research has been devoted to the study of their properties. One of the reasons for the interest in these materials is that the absence of crystallinity facilitates studies of the effects of the ion pairs on their physical properties.[24-26]

Most glassy ionomers are based on calcium aluminosilicate glasses.[27] The aluminosilicate poly(alkenoic acid) ionomer is prepared by melting a mixture of calcium oxide or fluoride, alumina and silica with aluminum phosphate and cryolite as flux at 1000-1500°C. These materials are used in dental cements, termed glass-ionomer cements. Several methacrylate-glass ionomer hybrid materials are now available for clinical use as restorative filling materials.[28] In the zwitter-ionomers the anion and cation are attached to each other and to the main chain. The first systematic study of a zwitter-ionomeric system was that of Graiver *et al*.,[29,30] who investigated copolymers of dimethylsiloxane and 4,7-diazaheptyl4,7-di(3-propanesulfonate) methylsiloxane. Other zwitter-ionomers based on polyvinylimidazolium sulphobetaine were studied by Salamone *et al*.[31]

4. Effect of ionic interactions

Four cases are chosen illustrate the effect of ionic interactions on the properties of ionomers; they involve the glass-transition temperature, mechanical properties, transport, and melt viscosity.

4.1. Glass transition temperature

The glass transition temperature (T_g) is one example of a property influenced by the polymer's ionic character. T_g is related to the amount of ionic groups in the ionomer. The concentration of present ionic groups dictates the extent of area with restricted mobility. At low ion content, no overlapping of the restricted mobility regions occurs and a single T_g is expected. This is because the few multiplets inter-dispersed among the bulk exhibit characteristics similar to the bulk material; the multiplets act only as crosslinks and do not exhibit behavior independent from the bulk. For a polymer with high ion content a large overlap of the restricted mobility regions is apparent and thus two T_g are expected, one for the multiplet domains and one for the bulk behavior.[32] The glass transition temperature of poly(phosphoric acid), $(HPO_3)_x$, is −10 °C, but the neutralization of the polymer with Na^+ increased the T_g to 280 °C;[33] in the case of the ionomer neutralized with Ca^{2+}, the T_g increased further to 520 °C. This is strictly an effect of ionic forces because, in all other characteristics, the three polymers are identical. Thus, it was concluded that the increase in the T_g was strictly ascribed to the neutralization of the acid groups and to the ionic interactions. Similar results were observed for acrylates,[34] and ionenes.[35]

4.2. Mechanical properties

The aggregates formation, whether multiplets or clusters, gives rise to novel physical properties in ionomers. Interactions between the ionic groups modifie and strengthen the intermolecular forces and lead to a physical type of crosslinking. The resulting network structure causes that the mechanical properties of the ionomer differ from the properties of the original non-ionic polymer,[36-38] and a broad range of properties can be observed by controlling the ion content and other variables.[39]

Modulus, yield strength, tensile strength, and clarity can be enhanced in partially neutralized ionomers based on poly(ethylene-co-methacrylic acid), for example, Surlyn resins, which, successfully introduced into the commercial market in the mid-1960s.

In the Figure 2 the storage modulus (*E'*) and loss tangent versus temperature for a series of poly(styrene-*co*-sodium methacrylate) ionomers of various ion contents are shown.[40,41] It is evident from Figure 2a that, as the ion content rises, the intensity of the cluster peak increases, while that the loss tangent peak at low temperature, which is associated with the multiplet-containing matrix, is disappearing. Therefore, at certain critical ion content, which is ±6 mol-% for this ionomer, the cluster phase becomes dominant over the multiplet-containing phase.

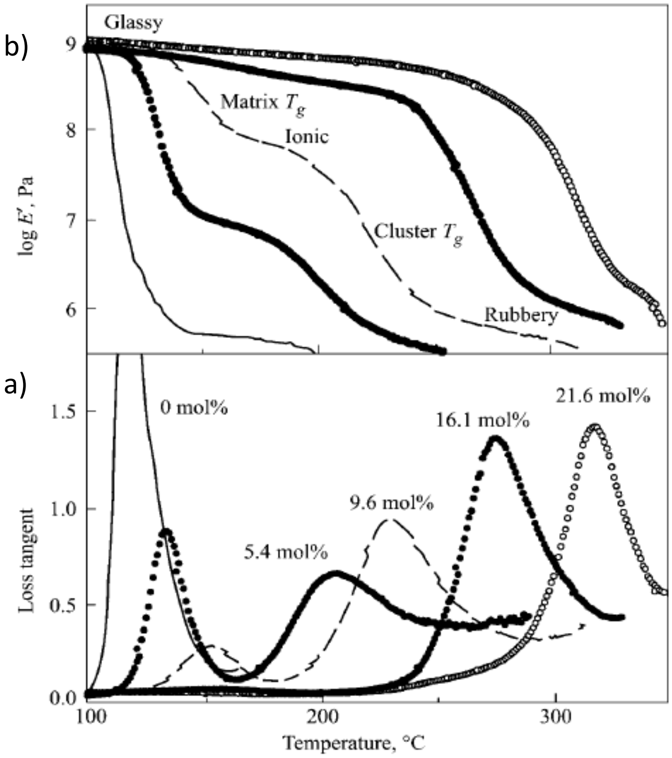


Figure 2. Storage modulus (*E*') and loss tangent measured as a function of temperature for P(S-*co*-MANa) ionomers.[40, 41]

The presence of ions also affects ionomer modulus significantly (Figure 2b). At 200 °C polystyrene is a viscous material the modulus of the 5.4 mol-% ionomer is ca

$10^{6.3}$ Pa, and that of the material containing 21.6 mol-% of ions is ca $10^{8.8}$ Pa. This behavior is in part due to an increase in the T_g of the ionomer. It should also be noted that for the ionomers of intermediate ion contents, the modulus value reflects two falls corresponding to the glass transition of the matrix phase and to the glass transition of the ion-rich phase.

4.3. Transport properties

The third case demonstrates the effect of ions on the transport properties of polymers, especially conductivity. Since their appearance, the DuPont Nafion materials, both sulfonate and carboxylate varieties[42-44] have been recognized as becoming conductive in the presence of water. The high conductivity has been attributed to the hydration of ionic aggregates, resulting in the formation of percolative ionic domains containing water that allow the ionomers' high conductance. These ionomers allow water transport and the diffusion of cations at a fast rate.

4.4. Melt viscosity

The fourth case illustrates the melt viscosity of ionomers as a function of the ion content. The melt viscosity depends on the type of counterion and the degree of neutralization in the polymer; four different zinc sulfonated EPDMs having the same Mooney viscosity, different ethylene/propylene composition, and different sulfonated distribution have been reported by Makowski *et al*.[45,46] The melt viscosity is substantially enhanced over that of the base EPDM at the zinc sulfonate level of 20 mEq/100g (or 0.6 mol-%). The melt viscosity of polystyrene homopolymer was found to be 400 Pa·s at 220 °C.[47] However, the melt viscosity of identical molecular weight polystyrene containing 3 mol-% of carboxylate ionic groups increased to 7×10^4 Pa·s. In the case of a sulfonated sample, the melt viscosity increased further to 9×10^7 Pa·s; as expected, the melt viscosity also increased with increasing ion content.

5. Structure of ionomers

The ions pairs show strong dipole-dipole attraction which leads to their association as dimers, trimers or higher-order aggregates. Einsenberg pointed out that it is useful to divide these ion-pair aggregates into two classes: multiplets and clusters. In 1970, it was suggested that ions in media of low dielectric constants form aggregates.[48] Associated pairs, triplets, quartets, etc, in which the charges are close to each other as much as it is physically possible, are referred as multiplets, and the the association of multiplets is called clusters, in which the multiplets are separated by nonionic material. The strength of electrostatic interaction between ion pairs and the ion content determine the proximity of ion pairs to one another and are are the critical parameters for multiplet formation. Geometric constraints of multiplets limit their size to 0.6 nm diameter; the characteristics of the host polymer such as low dielectric constant and low T_g favor ionic aggregation, whereas high dielectric constant and high T_g inhibit multiplet formation. Each ion pair in a multiplet effectively anchors the polymer chain at the point to which it is attached. Hence, the mobility of the polymer chain in the immediate vicinity of the multiplet is expected to be greatly reduced relative to that of a chain in the bulk polymer, with mobility increasing gradually with increasing distance from the multiplet.[23] Clusters are a collection of several multiplets that form a domain locally rich in ionic material but containing a significant fraction of non-ionic material as well. Clusters are envisioned to be of the order of 5 to 10 nm in diameter. The number of ionic groups existing in clusters is strongly dependent on polarity of the polymer matrix, ionic functionality and temperature. At low ion content with a low polarity matrix, only multiplets are probable, whereas cluster formation is favored by increasing ion contents.

This ion aggregation is probably the most outstanding feature in the study of ionomers, and is the fundamental basis of the discussion on morphology. The ionic aggregates, termed multiplets, frequently give rise to a pronounced peak in the small-angle region of the X-ray scattering profile (Figure 3.). However, the interpretation of this ionomer peak is not straightforward and has been a theoretical challenge; as a result, different models have been proposed. Furthermore, a wide range of ionomers have been investigated by techniques such as small angle X-ray,[26,49,50] and neutron scattering,[51] mechanical and dielectric measurements,[52,53] Mossbauer,[54] ESR,[55] IR,[56] Raman,[57] and NMR[58] spectroscopy, solution properties and electron microscopy.[59,60]

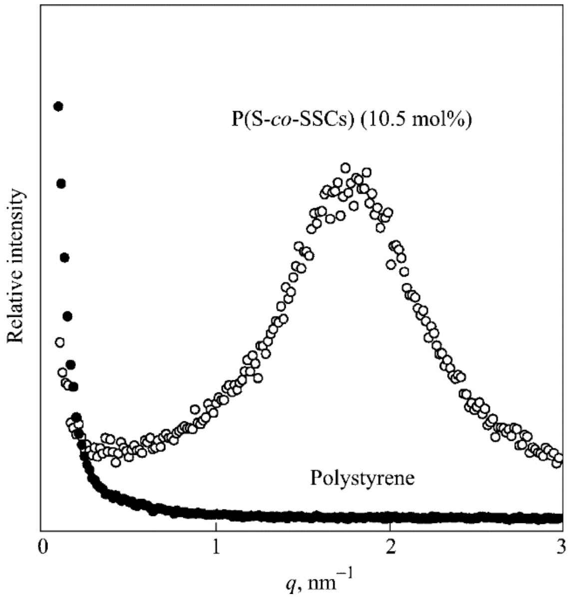


Figure 3. Small-angle X-ray scattering data for polystyrene and poly(styrene-*co*-cesium styrenesulfonate) ionomer containing 10.5 mol-% of ions.[61]

5.1. Hard-Sphere Model

In 1973, Marx *et al*. suggested that the SAXS peak is ascribed to the distance between ionic aggregates, which were taken to be small particles located on a paracrystalline lattice.[62] Later, Yarusso *et al*.[63] proposed a modified hard-sphere model in which the multiplets have a liquid-like order at a distance of closest approach, determined by the hydrocarbon layer attached and surrounding each multiplet. This model was in good agreement with the SAXS profiles and assumed the existence of multiplets of high electron density surrounded by a layer of hydrocarbon material of much lower electron density immersed in a medium of intermediate ion content, which was equivalent to a hard sphere diameter somewhat larger than that of the multiplet itself.

5.2. Core-Shell Model

In 1974, Macknight *et al.*[64] interpreted the small-angle X-ray scattering peak as resulting from the characteristic intraparticle distances. This model assumes that the ionomer pairs form a core that is surrounded by a shell of material of low electron density, which is in turn surrounded by another shell of somewhat higher electron density. The central core is taken to have a radius of 8-10 Å and to contain ~50 ion pairs. The hydrocarbon shell surrounding this multiplet is in the order of 20 Å. This model was elaborated in 1980. It was found that the SAXS profiles of the ethylene ionomers depended on sample elongation, and thus it was postulated that the ionic core might not be spherical but lamellar (Figure 4.).[65]

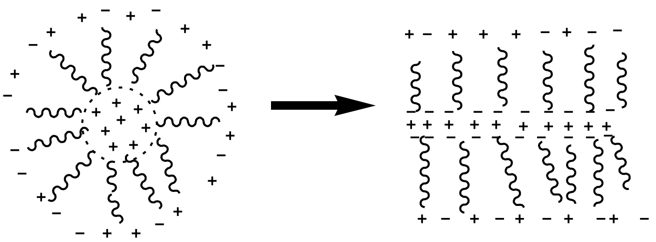


Figure 4. Intracluster Lamellar Shell core models.

5.3. EHM Model

The Eisenberg–Hird–Moore (EHM) model or multiplet-cluster model, incorporating both morphological and mechanical features; it is also based on the existence of ionic aggregates, *i.e.* multiplets.[23] The EHM model is shown in Figure 5. One of the novel features of the model is that the mobility of the material immediately surrounding the multiplet is reduced relative to that of the bulk material. There are several reasons for this behavior. One is the simple immobilization effect owing to the anchoring of chain to the multiplet. The mobility of a species is a function of its molecular weight. Anchoring a chain to multiplet increases the effective molecular weight of the segment adjacent to the multiplet and reduces the mobility.

As the ion content increases, the number of multiplets also increases, and regions of restricted mobility start to overlap and the sizes of these regions become large enough to exceed a threshold value for independent phase behavior. This overlapping of reduced mobility regions results in the appearance of a second T_g at a temperature higher than that of the normal T_g. As the ion content further increases, the clustered regions become dominant and may give rise to a continuous phase.

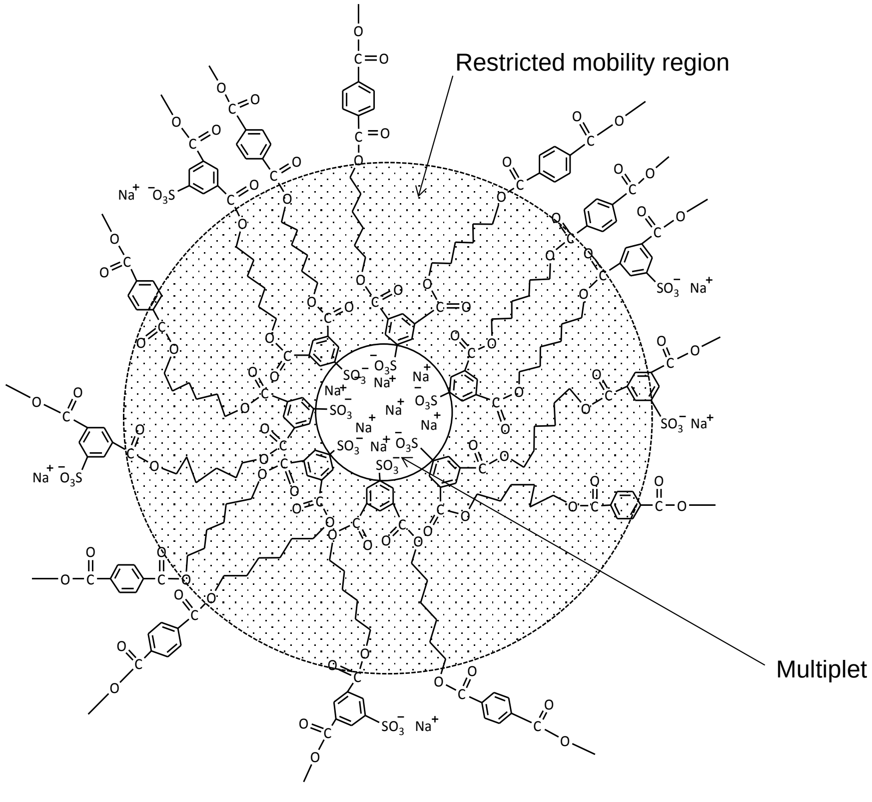


Figure 5. Representative scheme of a multiplet.

6. Ionomers synthesis

There are two main techniques of practical interest for the preparation of ionomers: copolymerization of minor amounts of functionalised monomer with the major comonomer, and direct functionalization of a preformed polymer.[66-68] Ionomers of commercial interest have either carboxylate or sulfonated groups as the ionic species. Other salts such as phosphonates, sulphates, thioglycolates, ammonium or pyridinium salts have been also reported.[69]

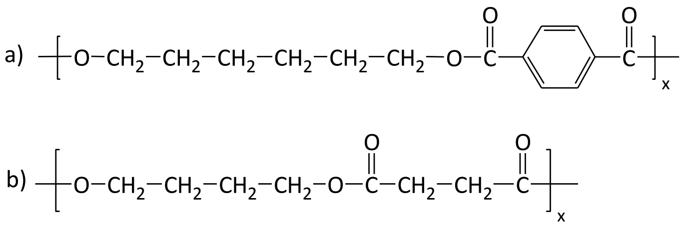
Carboxylate anions can be incorporated into ionomers by copolymerization with acrylic acid, methacrylic acid, maleic anhydride, or similar comonomers by free radical copolymerization. An alternative method of preparing carboxylate ionomers is via a postpolymerization reaction. This type of reaction is particularly suitable for aromatic substitutions, and a number of reactions have been developed for the carboxylation.[70-72] Weiss *et al*.[73-76] prepared ionomers by a free radical emulsion copolymerization of styrene and sodium sulfonated styrene. Allen *et al*.[77] obtained a copolymer of butylacrylate and sulfonated styrene. Salamone *et al*.[78-82] copolymerized styrene, methylmethacrylate, or butyl acrylate with a cationic-anionic monomer pair, 3-methacrylamido-propyltrimethylammonium and sulfonated trimethylammonium 2-acrylamide-2methylpropane.

The incorporation of sulfonic acids into polymers chains is also possible via copolymerization. In this case, the sulfonated group should be relatively distant from the site of the double bond, as its proximity affects the reactivity ratios considerably and might even make copolymerization impossible in some cases.[83] Furthermore, the strength of the sulfonic acid group reduces the solubility of the monomer, so that finding a common solvent becomes problematic. Despite these drawbacks, copolymerization of sulfonated monomers with nonionic organic monomers has been successfully achieved.[83]

The direct functionalization of preformed polymers has been the common method for the preparation of sulfonated ionomers. Makowski *et al*.[84] prepared lightly sulfonated polystyrene and ethylene-propylene-diene terpolymers by reaction with acetylsulfate in homogeneous solution. Bishop *et al*.[85] described the sulfonation of poly (ether ether ketone) (PEEK) with chlorosulfonic acid or sulfuric acid. Zhou *et al*.[86] prepared sulfonated cyclized *cis*-1,4-polyisoprene using acetylsulfate. Rahrig *et al*.[87] prepared sulfonated polypentenamer using a 1:1 complex of sulfur trioxide and triethyl phosphate in chloroform. Peiffer *et at*.[88] synthesized a copolymer of styrene-based polyampholyte, composed mainly of styrene with relatively low levels of 4-vinylpyridine and zinc neutralized sulfonated styrene. Huang *et al*.[89] prepared polyether-polyurethane zwitter-ionomers based on 4,4′-diphenylmethane diisocyanate, and *N*-methyl diethanolamine, with γ-propane sultone. Kennedy *et al*.[90-92] prepared linear and three arm star telechelic sulfonated polyisobutylene by heterogeneous sulfonation of an olefin-terminated polyisobutylene with acetyl sulfate.

7. Polyester ionomers

Polyesters are an important family of polymeric materials, which are widely used as fibers, engineering materials, containers, coatings, adhesives, and so on. These polymers are termed as aromatics or aliphatics polyesters depending on their structures (Figure 6.). The most important polyesters in the market are semiflexible semicrystalline polyesters, including poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). Moreover, aromatic polyesters are also widely used as engineering materials and aliphatic polyesters exhibit potential applications as biomaterials.



$$\left[O-CH_2-CH_2-CH_2-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C} \right]_x$$

Figure 6. Polyester**:** a) aromatic and b) aliphatic.

In recent years, the attention has focused on biodegradable materials for use in biomedical applications and as environmentally friendly materials. Aliphatic polyesters are an important class of biodegradable and hydrolysable polymers. The biodegradable polyesters developed up until now, however, are almost all linear polyesters. The incorporation of network structures into the backbone is of particular interest for new biodegradable materials, as they are expected to have better physical and chemical properties.[93]

7.1. Poly(ethylene terephthalate) (PET) ionomers

The incorporation of low amounts of ionic groups into PET effectively improve the mechanic performance and compatibility with other substrates.[94-96] These ionomers are widely used as textile filaments, packaging materials, optical and electronic materials, adhesives and coatings, high performance materials, and in biotechnology. Random PET ionomers (Figure 7.) are used to prepare dyeable fibers with basic dyes, and fibers with antipilling and antistatic properties.[95] With the incorporation of a small amount of interacting groups in PET, blends are made partially compatible and the formed dispersions are relatively fine. Because they are semicrystalline polymers, the glass transition temperature in the amorphous region is significantly affected by the presence of ionic groups. Two patents[97,98] claim the synthesis of sulfonated PET telechelic ionomers with the aim at increasing the dyeability of PET fibers and improving the manufacture of PET bottles through the extrusion blow molding process.

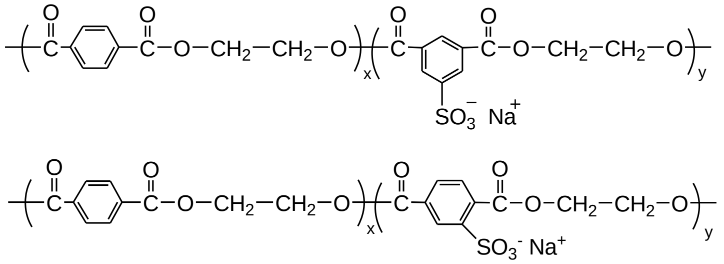


Figure 7. PET random ionomers.

Ostowska *et al*.[99-102] investigated ionic aggregates of PET ionomers using FT-IR spectroscopy and DSC, and they found a sharp change in ionic aggregates, when the ionic level was higher than 5 mol-%. Greener *et al*.[94] interpreted the rheological and dynamic-mechanic behaviors of PET random ionomers in terms of the restricted mobility model, which proposed that at the critical ion concentration (10 mol-%) the multiplets appear to form a distinct microphase (cluster). Yu *et al*.[103,104] prepared PETs with metal carboxylate end groups, which formed ionic aggregates. The presence of ionic aggregates acts as nuclear agents increasing the crystallization rate. Long *et al*. reported the synthesis of telechelic poly(ethylene terephthalate) ionomers containing terminal units derived from the sodium salt of 3-sulfobenzoic acid (SSBA) via melt polymerization techniques.[105] DSC analysis demonstrated that the presence of ionic end groups increased significantly the crystallization half time. Melt rheological analysis demonstrated that the ionic end groups increased the melt viscosity compared to non-ionomers at equivalent molecular weight, and ionic aggregation was more stable below 150 °C. Unal *et al.*[106] synthesized telechelic PET ionomers with phosphonium salt end groups, reporting greater thermal stabilities of phosphonium salts over ammonium salts.

7.2. Poly(butylene terephthalate) (PBT) ionomers

PBT ionomers have become very important semicrystalline thermoplastics for injection molding applications. PBT is an engineering thermoplastic resin displaying excellent melt processability, fast crystallization, and good mechanical properties. The synthesis, morphology, and mechanical properties of sulfonated poly(butylene terephthalate) and its unsulfonated analogs were comparatively studied by Gorda *et al*.[107] Stress-strain measurements were correlated with morphological results. Spherulitic morphology, with a Maltese cross at 45°C with respect to the crossed polars, was observed at low sulfonate levels (≤ 5.0 mol-%) whereas the cross rotated 45° to form a cross pattern at a higher ion contents. Chisholm *et al*.[108] reported hydrolytic stability of sulfonated poly(butylene terephthalate), indicating that hydrolysis was enhanced by the presence of ionic multiplets, which increased the amorphous content, absorb water, and perhaps exerted a medium effect on the hydrolysis of esters linkages associated with the ionic groups. Berti *et al*.[109] reported a detailed study of telechelic ionomers synthesis and the scale-up of the polymerization process along with the chemical and physical characterization of the prepared ionomers. They reported also a comparison with random PBT ionomers showing the improved thermo-mechanical and hydrolytic stability properties of telechelic ionomers. Later, Colonna *et al*.[110] reported the synthesis and characterization of imidazolium telechelic poly(butylene terephthalate) for antimicrobial applications. The influence of ionic comonomer units and ionic aggregation on the crystallization behavior and crystallite surface energies of poly(butylene terephthalate-*co*-5-sodiumsulfoisophthalate) ionomers containing 3 and 5 mol-% of 5-sodium sulfoisophthalate units was study by Page *et al*.[111]

7.3. Poly(butylene adipate) (PBA) ionomers

PBA ionomer is a biodegradable polymer which exhibits mechanical properties close to low density polyethylene.[112] PBA presents a slower biodegradation rate compared with other aliphatic polyesters with shorter methylene units between ester groups, such as poly(butylene succinate) and polyglycolide. The main objective pursued in several studies was to synthesize PBA ionomers with improved biodegradation rate and displaying acceptable mechanical and thermal properties. Yoo *et al*.[113] described the synthesis, characterization, and a preliminary degradation study of PBA ionomers prepared employing dimethyl 5-sulfoisophthalate sodium salt (DMSI). The hydrolytic degradation of the ionomers was drastically accelerated compared to PBA homopolymer because the presence of ionic moieties reduced the crystallinity and allowed easier moisture penetration, and thus improved their hydrolytic susceptibility. Anthierens *et al*.[114] synthesized and functionalized alkyne-containing poly(butylene adipate) through the copper catalyzed azide-alkyne click reaction with a quaternary phosphonium group. The resulting functionalized polyester was tested for antimicrobial activity both on the surface and in dispersion by a dynamic shake flask method. In both cases the polyester was found to significantly reduce the cell counts of *Escherichia coli*. Results showed that the antimicrobial activity was caused by the covalently attached quaternary phosphonium groups and not by freely available residues or unreacted alkyne groups.

7.4. Poly(butylene succinate) (PBS) ionomers

Copolymerization and blending are important methods for the improvement of the mechanical properties of polymers. Han *et al*.[115] synthesized poly(butylene succinate) based ionomers (PBSi) by bulk polimerization and confirmed that PBSi with 3 mol-% of ionic groups exhibited enhanced mechanical properties and melt rheological properties because of a physical cross-linkage effect by ion interaction. However, there are several problems affecting the physicochemical properties of polymers prepared by these methods. For instance, aliphatic copolyesters contain 10-30 mol-% of secondary monomers show significant melting point depression, due to imperfect lateral packing or isomorphism, adversely affecting the temperature range over which they can be used.[116] A series of poly(butylene succinate) ionomers containing 5-sodium sulfoisophthalate units were prepared by bulk polymerization of succinic acid and 1,4-butanediol in the presence of dimethyl 5-sulfoisophthalate sodium salt (DMSI) up to 5 mol-% of diacid monomer.[115,117,118] Han *et al*.[119] evaluated PBSi as a biomaterial and reported the crystallization behavior, the degradation behavior, and cellular interactions in vitro. They studied also the effects of ionic clusters on the crystallization process by using morphological observations and synchrotron small angle X-ray scattering (SAXS) analysis.

8. Polyester ionomer based-clay nanocomposites

Polymer-layered silicate nanocomposites have attracted great interest, both in industry and in academia, because of the improved properties exhibited when compared with pure polymer or conventional micro and macro-composites. These improvements can include increased moduli,[120,121] increased strength and heat resistance,[122] decreased gas permeability[123] and flammability,[124] and increased biodegradability of biodegradable polymers.[125] Toyota was the first company to develop and commercialize polymer nanocomposites. Their materials were based on nylon-6 as the polymer matrix, and the process for producing the nanocomposites consisted of: organically modifying sodium montmorillonite by exchanging the sodium ions with an amino acid salt, isolating the modified clay, and polymerizing caprolactam in the presence of the modified clay.[126]

Chisholm *et al*.[127] studied the effect of sodium sulfonated functionalization of poly(butylene terephthalate) on the properties of PBT/montmorillonite composites obtained by simple extrusion process. The results of the study clearly showed that organic modification of montmorillonite clay coupled with the modification of PBT with low levels (1.0-5.0 mol-%) of SO_3Na groups resulted in the production of highly exfoliated nanocomposites. The incorporation of as little as 1 mol-% of ionic content was found to significantly affect the morphology and achieved considerable exfoliation of the nanocomposites. The degree of exfoliation was found to be not strongly dependent on the amount of ionic incorporation. However, the mechanical properties were found to improve as the ionic content was raised. This was attributed to the increased interactions between the polymer matrix and the clay platelets. Li *et al*.[128] reported the synthesis of PET ionomer/MMT nanocomposites by *in situ* polymerization. The microstructure, morphology, and properties of the nanocomposites were studied with wide-angle X-ray diffraction, transmission electron microscopy, atomic force microscopy, differential scanning calorimetry, and thermogravimetric analysis, indicating that an increase in the $NaSO_3$ content improved the dispersion of organically modified montmorillonite in the sulfonated poly(ethylene terephthalate) (SPET) ionomer matrix. In these nanocomposites the dispersed layered silicates in the SPET matrix acted as nucleating agents for SPET crystallization improving its thermal stability.

Colonna *et al*.[129] synthesized telechelic ionomeric poly(butylene terephthalate) and obtained nanocomposites with organically modified clays. They were prepared by the melt intercalation technique both in a Brabender mixer and in twin screw-extruder. The presence of ionic groups tethered at the end of the polymer chains allowed the preparation of well-dispersed polymer-clay nanocomposites due to the formation of favorable electrostatic interaction between the polymer and the surface of the organically modified clays. Nanocomposite obtained using PBT with 3 mol-% of telechelic ionic groups and with 5% of clay presented a heat deflection temperature 48 °C higher than that of the commercial material. The presence of the clay also slightly increased the thermal and hydrolytic stability respect to standard PBT.

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Chapter II.

Materials and methods

1. Materials

Dimethyl terephthalate (DMT) (99+%), sodium salt of dimethyl 5-sulfoisophthalate (DMSI) (98%), hexanediol (HD) (97+%), 1,12-diaminododecane and octadecyltrimethylammonium bromide (18ATMA·Br), 1,4-butanediol (BD) (99%), dimethyl fumarate (DMF), sodium bisulfite, potassium tert-butoxide, iodomethane, 1,1,1-tris(hydroxymethyl) ethane, tri-*n*-butylphosphine and diethyl carbonate, glutaric acid (GA), L-glutamic acid dimethyl ester hydrochloride (A-DMG·Cl), and Lipasa acrylic resin from Candida antarctica (CALB) were purchased from Sigma-Aldrich. Succinic acid (SA) (99%), hydrochloric acid (37%), hydrobromic acid (HBr) (48%) and sodium hydrogen carbonate were obtained from Panreac. Dimethyl succinate (DMS) (98+%) was purchased from Merck-Schuchardt. Catalysts as tetra-butyl titanate (TBT) (Merck-Schuchardt), dibutyl tin oxide (DBTO, 98%) and scandium (III) trifluoromethanesulfonimide ($Sc(NTf_2)_3$) (Sigma-Aldrich) were used as received. The unmodified montmorillonite Cloisite-Na (CLNa) and the modified one Cloisite 30B (CL30B) (modified with *n*-alkyl-di(2-hydroxyethyl)-methylammonium, with *n* being a mixture of alkyl groups with 14, 16 and 18 carbon atoms), were supplied by Southern Clay Products. Solvents for purification and characterization, as trifluoroacetic acid, chloroform, diethyl ether, methanol, dichloroacetic acid, tetrahydrofurane, acetone, dimethyl sulphoxide, toluene, hexane, and acetonitrile, were all either technical grade or high-purity grade, and they were used as received.

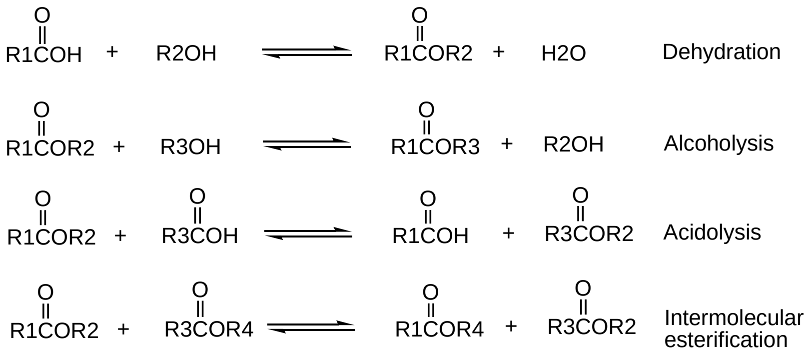
2. Synthesis of copolyester

2.1. Polycondensation

All copolyesters were synthesized by two step melt polycondensation process corresponding to esterification or/and transesterification and polycondensation reactions, respectively. In the first step the molecules join together resulting loss of small molecules as methanol or water. The second step leads to the formation of high molecular weight macromolecules. Polymerization conditions for the synthesis of copolyesters are described in each chapter.

2.1.1. Enzymatic polymerization

The most common lipase-catalyst used for polyester synthesis is Candida Antarctica lipase B (CALB), which was used in our synthesis. The enzymatic condensation reaction to form an ester using enzymes is composed of four modes of elemental reactions: dehydration, alcoholysis; acidolysis and intermolecular esterification (Scheme 1.). These reactions are reversible and like as the condensation polymerization with common catalyst, the by-products, as water or alcohol, are removed from the reaction mixture to shift the reaction equilibrium to the product side.[1]



Scheme 1. Four basic modes of elemental reactions of enzyme - catalyzed condensations.[1]

3. Measurements

NMR- NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at 300.1 MHz for ^{1}H and 75.5 MHz for ^{13}C. About 10 mg for ^{1}H or 50 mg for ^{13}C of polymer samples were dissolved in 1 mL of deuterated chloroform or a mixture of deuterated chloroform ($CDCl_3$) and trifluoroacetic acid (TFA) (7/3 v/v). 64 and 5,000-10,000 scans were acquired with 32- and 64-K data points and 1 and 2 seconds of relaxation delays for ^{1}H and ^{13}C respectively.

Intrinsic viscosities- Intrinsic viscosities of the copolyester dissolved in dichloroacetic acid were measured with and Ubbelohde viscometer thermostated at 25 ºC ± 0.1 ºC.

GPC- Gel permeation chromatograms were acquired at 35.0 °C with a Waters equipment provided with a refraction-index detector. 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. To prevent ionic aggregation, polyesters samples were previously dissolved in a mixture of chloroform/trifluoroacetic acid (1/1) and precipited with diethyl ether or methanol.

FT-IR- Infrared spectra were recorded from film samples obtained by hot-pressing using a Spectrum One FT-IR spectrometer equipped with an ATR diamond accessory. 8 scans at 2 cm^{-1} were collected for each sample.

TGA- Thermogravimetric analysis for polyesters was performed from 10-15 mg of sample under nitrogen flow of 20 mL min^{-1} at a heating rate of 10 ^{0}C min^{-1} and within a temperature range of 30 to 600 ^{0}C, using a Perkin-Elmer TGA6 or Mettler Toledo TGA/DSC 1 thermobalance. For nanocomposites, TGA measurements were carried out under an oxidative atmosphere over a temperature range of 30-800 ºC.

DSC- Calorimetric measurements were performed with a Perkin-Elmer Pyris1 DSC instrument provided with an intracooler device and they were calibrated with indium and zinc. Sample weights of about 3-6 mg were analyzed in a temperature range from -30 to 200 °C at heating and cooling rates of 10 °C min^{-1} under a nitrogen atmosphere. The T_g of the copolyesters was measured from amorphous samples at heating rate of 20 ºC min^{-1}.

UV-VIS- Absorbance measurements were performed using a UV-visible spectrophotometer UVmini-1240 with 5 nm bandwidth. Samples were dissolved in toluene.

XRD- The patterns of X-ray diffraction were recorded on the PANalytical X'Pert PRO MPD θ/θ diffractometer using the Cu Ka radiation of wavelength 0.1542 nm, and at BL11-NCD beamline at Alba Synchrotron from powdered samples coming from synthesis. The energy employed corresponded to a 0.1 nm wavelength and the spectra were calibrated with Chromium (III) oxide (Cr_2O_3). For the analysis of the PBS(PP-SS) complex requiring heating, X-ray diffraction was recorded from the sample introduced in a Lindemann glass capillary of 1.0 mm of diameter.

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Chapter III.

Polyesters containing anionic groups

1. Sulfonated poly(hexamethylene terephthalate) copolyesters: enhanced thermal and mechanical properties

Abstract

A series of poly(hexamethylene terephthalate-*co*-hexamethylene 5-sodium sulfoisophthalate) copolyesters containing from 5 to 50 mol-% of sulfonated units as well as the two parent homopolymers are prepared by melt polycondensation. The polyesters are obtained with high molecular weights, which decrease with the increased content of sulfonated units in the copolymer. Polyesters with 5 and 10 mol-% of sulfonated units are semicrystalline whereas for contents equal or above 20 mol-% they are unable to crystallize from the melt. Thermogravimetric analysis show that the thermal stability decreases with the content in sulfonated units. Isothermal crystallizations of semicrystalline copolyesters show that the insertion of the sulfonated units causes a reduction of crystallizability, most probably due to the occurrence of ionic aggregations. It is observed a synergistic effect on the mechanical properties for copolymers with contents of around 5 mol-% where the elongation at break increases drastically. Moreover, the hydrolytic degradation of the copolymer is enhanced with the content in sulfonated units.

1.1. Introduction

Polyelectrolytes and particularly ionomers are materials of great technological interest due to the fact that the ionic groups can interact with each other disturbing the supramolecular structure and modifying their physical and mechanical properties.[1-5] Several examples of random and telechelic copolyester ionomers derived from poly(ethylene terephthalate) (PET)[6-10] or poly(butylene terephthalate) (PBT)[11-13] have been reported, where the main changes that were observed by the insertion of the ionic groups were a reduction in crystallizability as well as an increase of the glass transition temperature. Additionally they showed an increase in the melt viscosity caused by the ionic interactions. These copolyester ionomers have been used with the aim of improving either the dying properties of polyester yarns[6] or their compatibility with other polymers[14,15] or nanoclays.[16-21] On the other hand poly(hexamethylene terephthalate) (PHT) is an aliphatic-aromatic polyester that present polymorphism with melting peaks between 110-140 ^{0}C. Although it can be used for applications such as polymer for laminating processes,[22] it has not been industrially developed. In these processes, a high melt-viscosity throughout a considerable temperature range above the melting temperature, as well as ad good adhesivity with the material to which it is to be joined are primary requirements.

With the aim at improving the thermal and mechanical behavior of PHT and increase its melt viscosity, and then to expand its potential applications, we undertook the study of PHT copolyesters that incorporate different amounts of 5-sodium sulfoisophthalate (SI) units. In this article we wish to report on the synthesis and on the spectroscopic characterization of such copolyesters, the evaluation of their thermal and mechanical properties and their hydrolytic degradability.

1.2. Experimental section

1.2.1. Synthesis of PHT_xSI_y copolyesters

DMT, DMSI and HD were introduced into a three-necked 250-mL round bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum-distillation outlet. Approximately 0.6 mmol catalyst per mole of aromatic monomer were used for the preparation of all these polyesters. A molar ratio 2.1:1 of HD to diesters was used for PHT and PHT_xSI_y copolyesters with SI unit contents above 10 mol-%, whereas a 1.5:1 molar ratio was used for the rest of copolyesters as well as for PHSI homopolymer. The temperature was then raised to 190 ^{0}C, and the mixture was stirred until all aromatic comonomers were dissolved in HD. The transesterification reaction was carried out at 190 ^{0}C under a low nitrogen flow for a period of 2-3 hours, along which methanol byproduct was distilled off. The polycondensation reaction was performed at 250-280 ^{0}C under reduced pressure (0.5-1 mbar) for 1.5-2 hours, until a high viscous liquid was obtained. The reaction mixture was cooled down to room temperature, and the atmospheric pressure was recovered with a nitrogen flow to prevent degradation. The final solid mass without further treatment was used for all characterization tasks.

1.2.2. Hydrolytic degradation

Hydrolytic degradation studies were made on amorphous films with a thickness of 200 μm obtained by hot pressing. The films were cut into disks of 10 mm diameter and about 50-70 mg weight. The disks were immersed in vials with 20 mL of deionized water (pH = 5.2) and left inside an oven at 60 ºC for several weeks. Samples were taken out every week and washed with distilled water previous to GPC and weight loss determinations.

1.3. Results and discussion

1.3.1. Synthesis, composition and microstructure of PHT_xSI_y copolyesters

The synthetic procedure followed in this work for the preparation of PHT_xSI_y copolyesters is depicted in Figure 1. The process consists of a two-step melt polycondensation process. The first step was carried out at 190 ^{0}C under a low nitrogen flow to promote the reaction of the mixture of DMT and DMSI with an excess of HD and subsequent removal of the released methanol. The second step was carried out at higher temperatures under vacuum to force the low molecular weight oligomers formed in the first step to react with each other to form a high molecular weight polymer with releasing of the excess of HD. To reduce secondary reactions leading to etherification of HD, which are favored by the presence of sulfonated units, a lower molar ratio HD/aromatic diesters has been used for contents of SI units above 10 mol-%. It was observed that the final melt viscosity increased gradually with the content of SI units, to the point that copolymers containing 50 mol-% of these units as well as the homopolymer PHSI were so viscous that stirring became almost impracticable at the end of reaction. In fact a rubber-like mass was attached to the agitator's impeller which prevented the axial flow of the material. It is well known that the sulfonate groups can interact forming ionic aggregates or clusters which act as thermoreversible cross-links.[7]

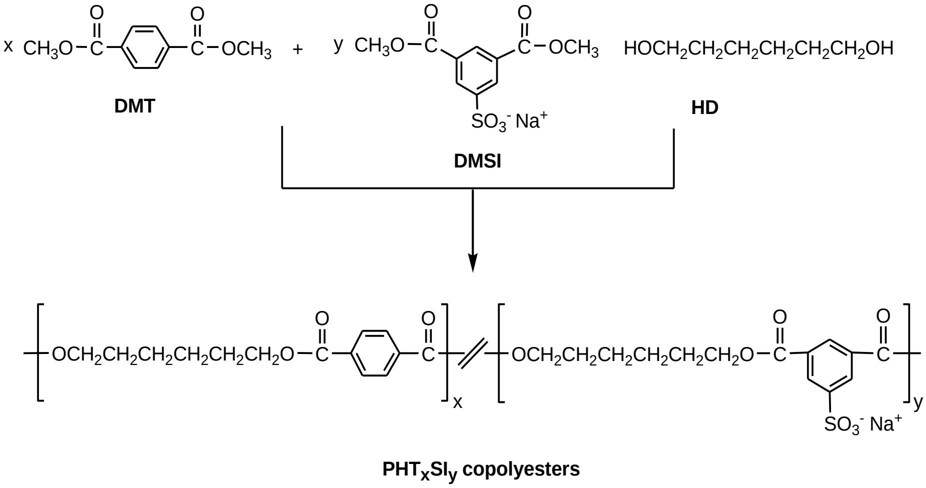

Figure 1. Outline of the synthesis route followed for the preparation of PHT$_x$SI$_y$ copolyesters examined in this work.

All the copolyesters were obtained as white or yellowish solid masses with high yields and molecular weights decreasing with the increased content in SI units (Table 1). The increase of the melt viscosity provoked by the interactions of ionic groups, which prevent the release of HD during polycondensation, seems to be the main factor responsible for such behavior.

To have a first approach to the chemical structure of the copolyesters and homopolyesters, FTIR spectra from solid samples were recorded and they are depicted in Figure 2. All spectra show bands in the region of 3000 cm^{-1} that correspond to the CH's stretching vibrations. At around 1710 cm^{-1} there is a prominent band that corresponds to the carbonyl ester group stretching vibration. As the content in SI units increases, two new bands at 1050 and 1160 cm^{-1} corresponding to the SO_2 asymmetric and symmetric stretching vibrations emerged. Additionally a new peak at 753 cm^{-1} arising from the S-O$^-$ bond appear in the copolymers with intensity increasing with the content of SI units in the copolymer.

Table 1. Composition and molecular weights of PHT, PHSI and PHT_xSI_y copolyesters.

	Copolymer composition[a]	Copolymer composition[b]		Molecular weights		
Polyester	T/SI	T/SI	DHG[c]	$[\eta]$[d]	M_w[e]	$Đ$[e]
PHT	100/0	100/0	0.1	0.75	21,300	2.2
$PHT_{95}SI_5$	95/5	94.9/5.1	1.0	0.74	22,000	2.3
$PHT_{90}SI_{10}$	90/10	90.1/9.9	2.5	0.56	19,000	2.3
$PHT_{80}SI_{20}$	80/20	80.6/19.4	2.5	0.57	19,500	2.4
$PHT_{70}SI_{30}$	70/30	72.3/27.7	1.1	0.48	20,000	2.4
$PHT_{60}SI_{40}$	60/40	63.6/36.4	2.7	0.48	17,800	2.1
$PHT_{50}SI_{50}$	50/50	51.0/49.0	2.0	0.45	19,750	2.5
PHSI	0/100	100/0	5.4	0.45	17,500	2.5

[a] Molar ratio in the feed.
[b] Determined from the aromatic proton resonances observed in the ^1H NMR spectra.
[c] Dihexylene glycol content (mol-%) calculated from ^1H NMR spectra.
[d] Intrinsic viscosity ($dL\cdot g^{-1}$) measured in dichloroacetic acid at 25 °C.
[e] Weigth-average molecular weight (M_w) and dispersity ($Đ$) determined by GPC

The chemical structure was further ascertained by NMR spectroscopy. Both ^1H and ^{13}C NMR spectra showed signals at different chemical shifts that allowed for the determination of copolyesters composition as well as for their chemical microstructure. The spectra registered from $PHT_{70}SI_{30}$ as a representative for the series, are shown in Figure 3 with the corresponding peak assignments. The chemical composition was determined by integration of the *f* and *g* signals of sulfoisophthalate units and the *f* signal of terephthalate units. As it can be observed in Table 1, there was a good correlation between feed and final copolyester compositions.

All copolyesters showed small signals in the ^1H NMR spectra at 3.7 ppm due to the presence of dihexyleneglycol units produced by the side etherification reaction between two units of hexyleneglycol. It has been reported before for the synthesis of PET copolyesters containing SI units that this side reaction is enhanced by the presence of sulfonated groups, where the presence of oligo(ethyleneglycol) units were detected for copolyesters containing more than 20 mol-% of SI units.[10] In the present case, the content of dihexyleneglycol units was within the range 1-3 mol-% for all compositions except for the PHSI homopolyester where the content was about 5.4 mol-%.

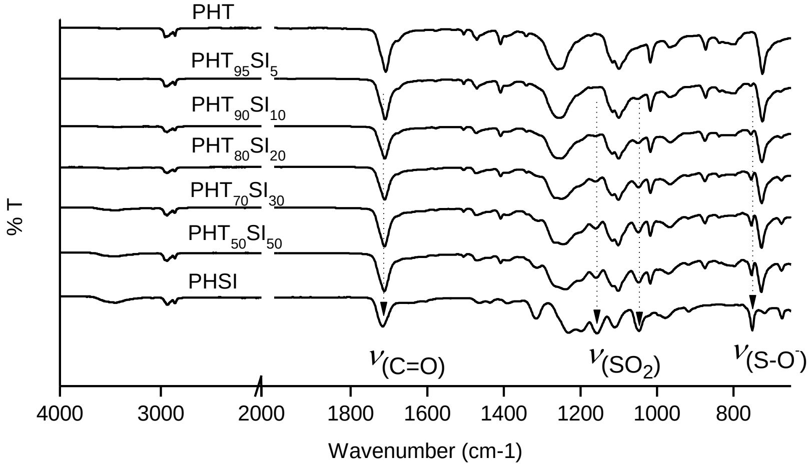

Figure 2. FTIR spectra of PHT$_x$SI$_y$ copolyesters and their parent homopolyesters with indication of the main stretching vibrations.

According to our previous satisfactory experience in the analysis of this type of copolyesters,[10] ^{13}C NMR was used for the study of the microstructure of PHT$_x$SI$_y$. The spectra of these copolyesters showed splitting in the signals of the first methylene of the hexamethylene segments (Figure 4). This splitting was interpreted as a consequence of sequence distribution of both aromatic units around it. Similar splitting was observed for PET copolyesters containing SI units where the signal due to oxyethylene carbons split into four peaks associated to the four possible dyads.[10] The integration of these peaks by means of Lorentzian deconvolution allowed the determination of the contents of different dyads, and by the application of simple expressions,[23] the number average sequence length and degree of randomness could be estimated (Table S1 of supporting information). The degree of randomness was close to 1 for all copolyesters, which indicates that they have a statistical distribution of terephthalate and sulfoisophthalate units along the polymer chain.

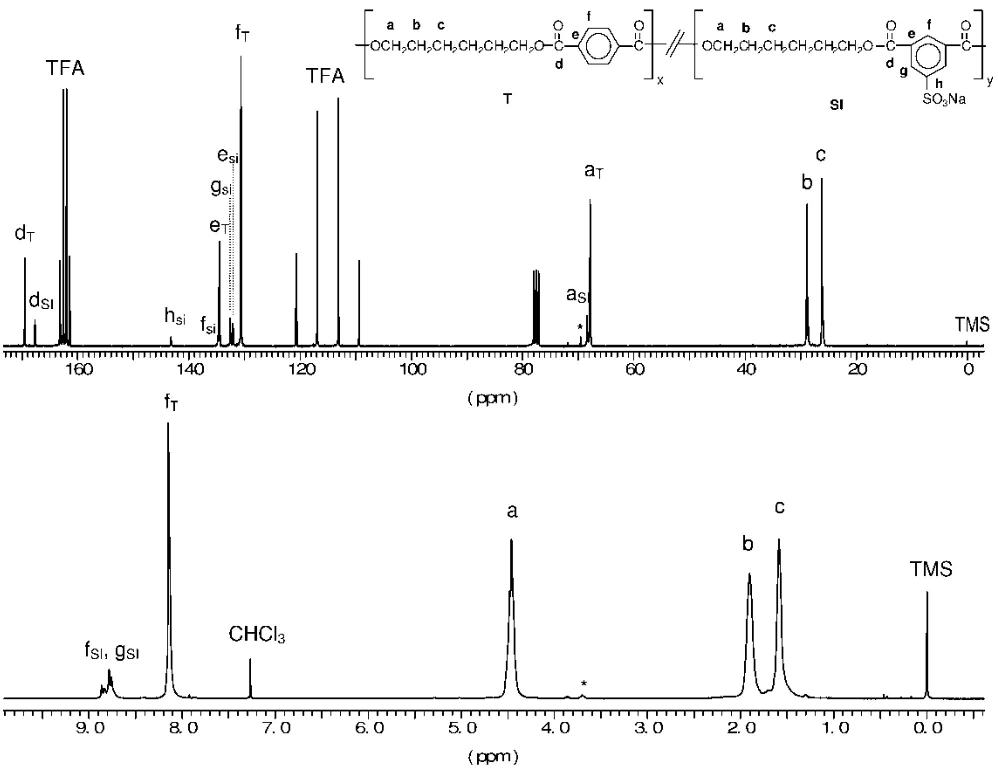

Figure 3. The 300.1 MHz ^{1}H NMR (bottom) and 75.5 MHz ^{13}C (top) spectra of PHT$_{70}$SI$_{30}$ recorded in a mixture of CDCl3/TFA (7/3). Peaks arising from dihexylene glycol units, which are present in small amounts in the polyesters, are labeled as (*).

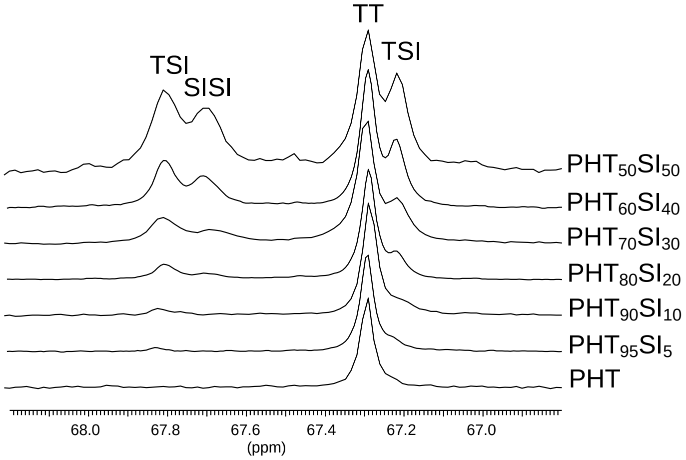

Figure 4. The 75.5 MHz ^{13}C NMR spectra of PHT$_x$SI$_y$ in the region corresponding to the oxymethylene carbons with dyad assignments.

1.3.2 Solubility

To evaluate the effect of the SI units on solubility, the behavior of the $PHT_{60}SI_{40}$ copolyester in a variety of solvents with different polarity was compared with that observed for the PHT and PHSI homopolymers (Table 2). A great difference in solubility was found according to the content in sulfonate groups. PHT was readily soluble in chloroform whereas PHSI and the copolyester only become swollen in this solvent. On the other hand, PHT was insoluble in water, while both PHSI and $PHT_{60}SI_{40}$ were soluble in hot water, in DMSO and in DMF. The increasing content of sodium sulfonate groups in PHT_xSI_y copolyesters improved the solubility of them in both polar protic or aprotic solvents, which was attributed to the solvation between the sodium sulfonate groups and the polar solvents which diminish the ionic associations. Similar observations have been reported in sulfonated polystyrene ionomers where the solubility behavior was attributed to preferential solvation of the metal sulfonate groups by the polar solvent and rationalized considering an equilibrium between solvated and aggregated species.[24]

Table 2. Compared solubilities[a] of PHT, PHSI, and $PHT_{60}SI_{40}$ copolyesters.

	Polyester		
Solvent	PHT	$PHT_{60}SI_{40}$	PHSI
Water	-	+	++
Ethanol	-	-	-
Diethyl ether	-	-	-
Acetone	-	-	-
THF	+	±	-
Chloroform	++	±	-
DMSO	-	++	++
DMF	-	++	+
NMP	+	++	++
TFA	++	++	++

[a] Estimated according to the method of Braun.[25] (-) Insoluble, (±) slightly swollen, (+) soluble on warming at 100 °C or at boiling point, (++) soluble at room temperature. THF = tetrahydrofuran; DMSO = dimethyl sulfoxide; DMF = *N,N´*-dimethylformamide; NMP = 1-methyl-2-pyrrolidone; TFA = trifluoroacetic acid

1.3.3. Thermal behavior

The effects provoked by the incorporation of SI units on the thermal properties were investigated by DSC and TGA. To evaluate the thermal stability of the polyesters, TGA measurements were carried out under nitrogen atmosphere in the 30-600 ^{0}C temperature range. It was observed that PHT degraded in a single step, whereas the copolyesters showed two or three steps, depending on the copolyester composition (Figure 5). Data collected from these polymers are summarized in Table 3, which shows that the thermal stability of copolyesters decreased with the content of SI units, although the copolymers did not show appreciable weight loss below 300 ^{0}C. On the other hand the remaining weight after the thermal degradation at 600 ^{0}C increased continuously with the content of SI units (Table 3).

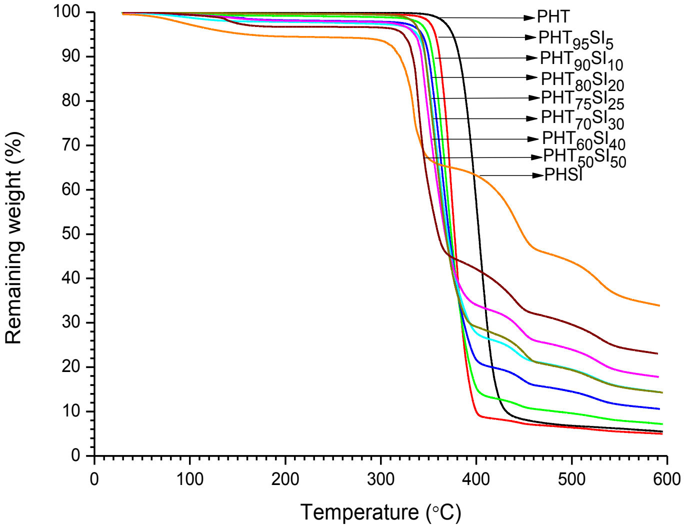

Figure 5. TGA traces of PHT_xSI_y copolyesters and their parent homopolyesters.

On the other hand DSC studies showed that copolyesters with SI contents equal or above 20 mol-% were unable to crystallize from the melt so they remain amorphous after cooling to room temperature (Figure 6).

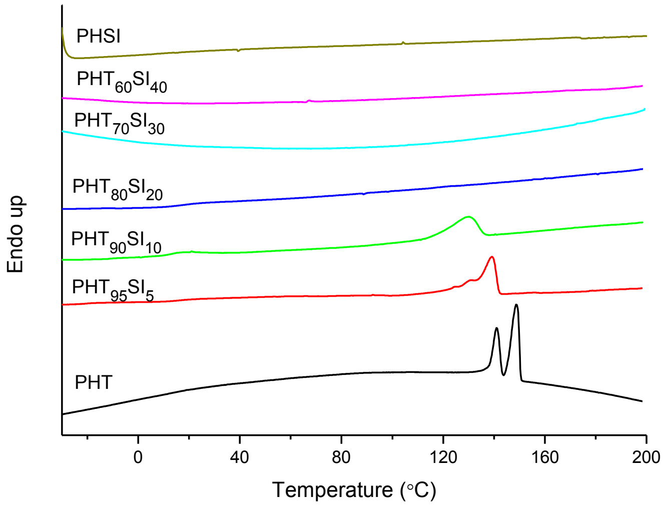

Figure 6. DSC thermograms (second heating) of PHT$_x$SI$_y$ copolyesters.

For semicrystalline copolyesters, the melting temperature and enthalpy decreased gradually with the content in SI units. On the other hand an increase of the glass transition temperature was observed with values within of the two PHT and PHSI homopolymer T_g's (11 and 78 ^{0}C, respectively) (Table 3). The reduction of crystallization and increase of the T_g must be caused by the ionic interactions between the sulfonated units, which will act as ionic cross-links causing a reduction of the chain mobility. This behavior is in accordance with the results of Eisemberg *et al*,[26,27] who reported that the T_g of ionomers increased linearly with the content of salt units.

Table 3. Thermal properties of PHT, PHSI and PHT_xSI_y copolyesters.

Polyester	T_g [a] (°C)	T_c [b] (°C)	T_m [c] (°C)	ΔH_m [c] (J g^{-1})	^oT_d [d] (°C)	T_d [e] (°C)	RW [f] (%)
PHT	11	122	148	38	371	403	5
$PHT_{95}SI_5$	14	76	139	31	356	**374**/444	5
$PHT_{90}SI_{10}$	14	-	130	21	350	**369**/444	7
$PHT_{80}SI_{20}$	19	-	-	-	346	**364**/447/525	11
$PHT_{70}SI_{30}$	31	-	-	-	341	**352**/449/522	15
$PHT_{60}SI_{40}$	43	-	-	-	339	**347**/447/529	18
$PHT_{50}SI_{50}$	52	-	-	-	327	**340**/439/531	24
PHSI	78	-	-	-	316	**334**/443/528	34

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

[b] Crystallization temperature was registered at cooling from 200 °C at 10 °C·min^{-1}.

[c] Melting temperature and enthalpy were registered at a heating rate of 10 °C·min^{-1} from samples crystallized as indicated in b.

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

[e] Temperatures of maximum degradation rates. In bold main degradation temperature.

[f] Remaining weight at 600 °C.

1.3.4. Isothermal crystallization

To evaluate the crystallizability of PHT_xSI_y copolyesters with regard to their composition, molten samples were isothermally crystallized at selected temperatures and the crystallization enthalpy was registered as a function of time. Figure 7 shows the evolution of the relative crystallinity versus crystallization time for both PHT and the crystallizable $PHT_{95}SI_5$ and $PHT_{90}SI_{10}$ copolyesters at two different temperatures. Unfortunately, it was not possible to register the crystallization enthalpy of PHT at these temperatures because the process is extremely fast in this case. Nevertheless, comparison of the registered data for the homopolyester and the copolyesters showed that the incorporation of SI units shifted the resulting sigmoid curves to longer crystallization times (Figure 7, left), which is a clear evidence that the presence of these units in the copolyester reduces the crystallizability. Estimation of Avrami parameters was accomplished by the representation of the double-logarithmic equation:

$$\log[-\ln(1-X_t)] = \log K + n \log (t-t_o)$$

Where X_t is the relative crystallinity developed at time t, t_o is the onset crystallization time, and K and n are the crystallization rate and the Avrami exponent, respectively. The resulting plots are shown in Figure 7 (right) and the crystallization parameters extracted from these figures are given in Table 4.

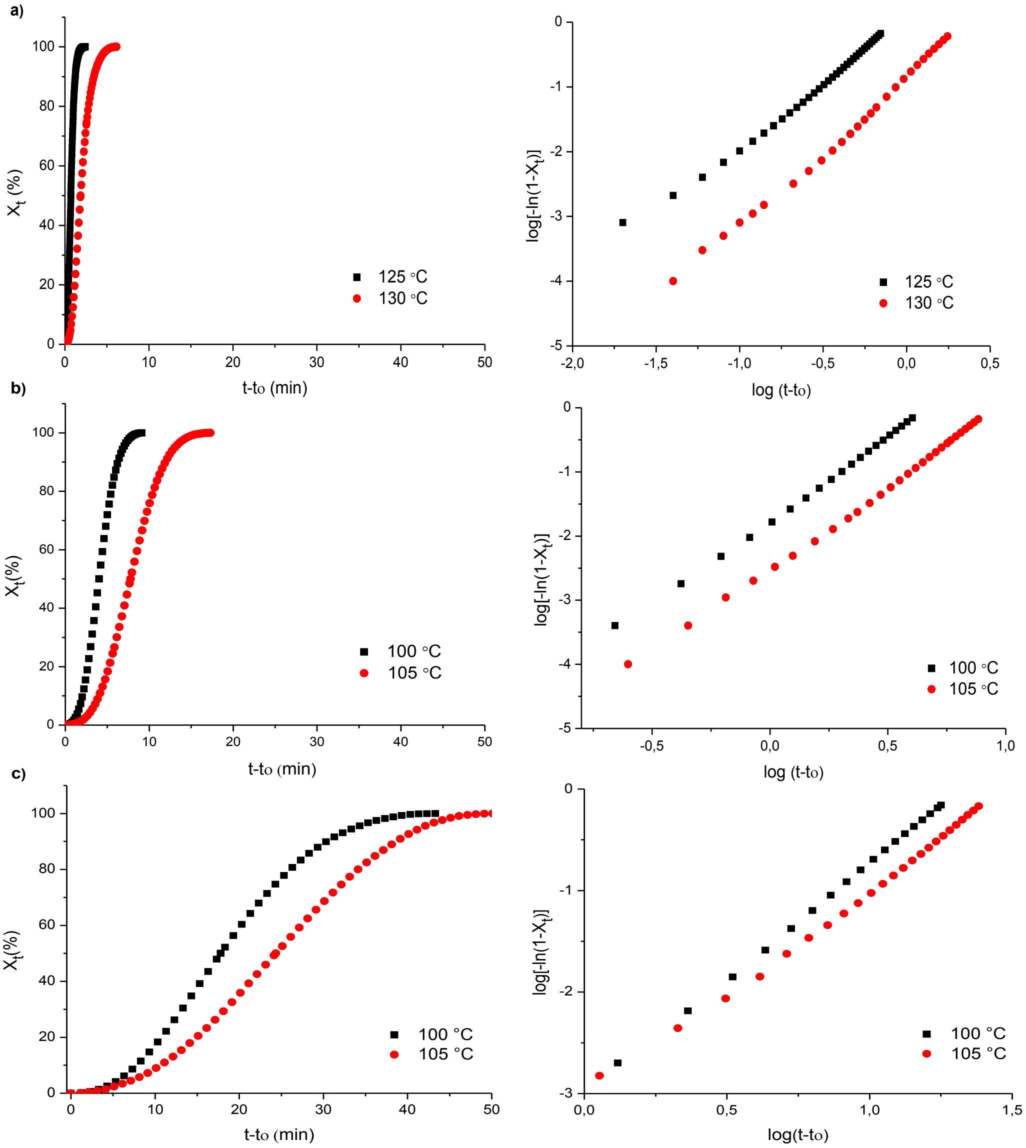

Figure 7. Relative crystallinity X_t versus crystallization time (left) and Avrami plots (right) for (a) PHT, (b) PHT$_{95}$SI$_5$, and (c) PHT$_{90}$SI$_{10}$ at the indicated temperature.

Table 4. Crystallization parameters of isothermally crystallized PHT and PHT_xSI_y copolyesters.

Polyester	T_c (ºC)	t_o[a] (min)	Avrami parameters[b]		
			n	log K	$t_{1/2}$ (min)
PHT	125	0.24	2.1	-0.1	0.95
	130	0.34	2.3	0.9	2.21
$PHT_{95}SI_5$	100	0.38	2.6	1.7	4.40
	105	0.75	2.6	2.5	8.53
$PHT_{90}SI_{10}$	100	1.69	2.3	3.0	19.49
	105	6.87	2.1	3.1	31.22

[a] Onset crystallization time .

[b] Avrami exponent n, constant of crystallization k (min^{-1}), and crystallization half-time $_{1/2}$.

1.3.5. Crystalline structure

The crystalline structure of copolyesters was preliminary examined by powder X-ray diffraction. It is well known that PHT may adopt three different crystalline structures, designated as α, β, and γ, depending on the thermal or solvent treatment, in which the polyester is arranged in a nearly fully extended conformation.[28-31] The powder diffraction profiles recorded from PHT and two selected copolyesters of the PHT_xSI_y series are compared in Figura 8. The most prominent Bragg spacings measured on such profiles are listed in Table S2 of Supporting Information. According to literature, the profile observed for PHT arises from a mixture of two β, β' triclinic forms; these crystalline forms differ only in the local conformational disorder around the terephthaloyl groups.[32] As it could be expected from its lower crystallinity revealed by DSC broader diffraction peaks were observed for the $PHT_{95}SI_5$ copolyester. Nevertheless the spacings associated to these peaks are the same as observed for PHT indicating that the same crystal structure must be adopted by the two polymers. On the other hand, a pattern consisting exclusively of diffuse scattering characteristic of amorphous material was observed for $PHT_{70}SI_{30}$ copolyester. These results are in agreement with those provided by DSC and corroborate that the insertion of SI units in PHT reduces significantly its crystallizability.

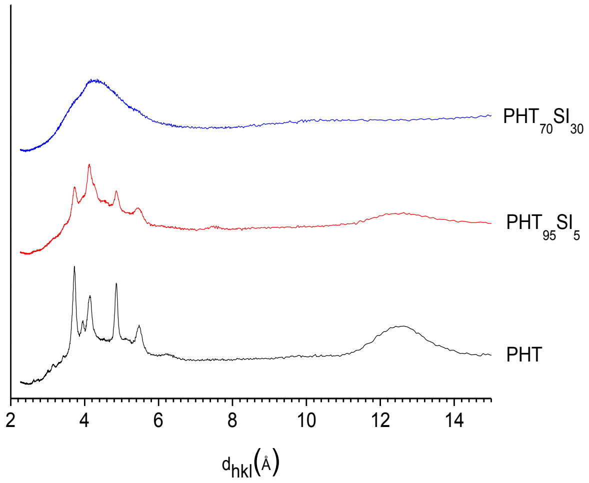

Figure 8. Powder WAXS diffraction patters of PHT, and the indicated PHT$_x$SI$_y$ copolyesters.

1.3.6. Mechanical properties

The mechanical parameters, such as the Young's modulus, the maximum tensile stress and the elongation at break are compared in Table 5. As it can be observed, the modulus increased gradually with the content in sulfonated units. The ionic interactions between the SI units, which restrict the mobility of the chains, seem to be again the main factor responsible for this behavior. On the other hand, the elongation at break also increased drastically for low contents of SI units (Figure S1 of Supporting Information). In fact this value is almost 30 times higher for PHT$_{95}$SI$_5$ than observed for pure PHT (Table 5). The formation of small aggregates taking place at low contents in SI units which act as reversible chain extenders could be the main factor for this striking increase in the ductility. At higher contents the clusters will act as defects, decreasing the deformation at break. However, for the copolymers with contents in SI units below 30 mol-%, there is an improvement of mechanical properties when compared to PHT.

Table 5. Tensile properties of PHT and PHT_xSI_y copolyesters.

Polyester	Young´s modulus E (MPa)	Maximum tensile stress σ_{max} (MPa)	Elongation at break ε_{max} (%)
PHT	539	26	16
$PHT_{95}SI_5$	550	29	569
$PHT_{90}SI_{10}$	700	30	200
$PHT_{80}SI_{20}$	759	31	170
$PHT_{70}SI_{30}$	814	32	125
$PHT_{60}SI_{40}$	908	37	24

1.3.7. Hydrolytic degradation

To evaluate the influence of the sulfonate groups on the stability of the polyesters, PHT and some selected copolyesters were incubated in water at 60 ^{0}C and pH 5.2. The hydrolytic degradation was comparatively evaluated for PHT and the PHT_xSI_y copolyesters containing 10 and 20 mol-% of SI units, respectively. The evolution of the sample weight and molecular weight with incubation time is shown in Figure 9. No significant changes were observed for PHT and $PHT_{90}SI_{10}$ whereas, a considerable reduction in both sample and molecular weights was observed for the $PHT_{80}SI_{20}$ copolyester, with nearly 45% of its original weight being lost upon seven weeks of incubation. Furthermore, sample weight lost was accompanied by a considerable falling in M_w, which was reduced in more than 50% value in such period of time. These results are an unambiguous indication that the insertion of the SI units enhances the hydrolytic degradability of PHT. The presence of these SI units in the copolyesters make them more hydrophilic allowing a better solvation by water as well as an easier attack on the ester groups. These results are in agreement with those reported by Gaona *et al.*[10] for PET copolyesters containing SI units, which revealed that the hydrodegradability of the copolyesters was very high as compared to PET.

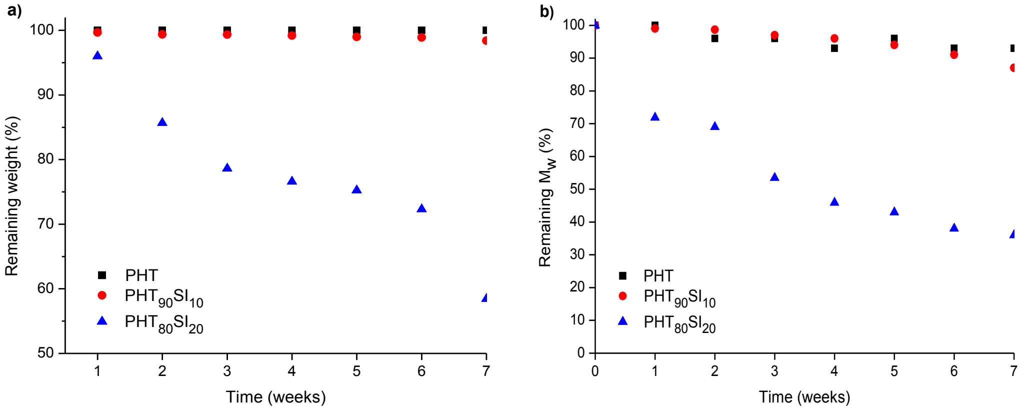

Figure 9. The evolution of (a) the remaining weight and (b) weight average molecular weight for PHT, and PHT$_x$SI$_y$ copolyesters as a function of incubation time.

1.4. Conclusions

A series of PHT derived copolyesters containing different amounts of sulfoisophthalate units has been prepared by melt phase polycondensation. Their weight average molecular weights oscillated between 17,500 and 22,000 g·mol^{-1}. The final composition attained in these copolyesters was almost the same than that of the feed. The copolyesters were semicrystalline for contents in SI units below 20 mol-%. An increase in the T_g from 11 ºC (PHT) to 78 ºC (PHSI) and a decrease in the melting temperature and enthalpy were observed for the copolyesters, which is attributed to both the irregularity introduced by the isophthalate units as well as to the unfavourable ionic interactions between the SI units. The mechanical properties were substantially improved for low contents in sulfonated units as compared to PHT, where the elongation at break was increased significantly. The copolyesters showed higher hydrodegradability than PHT with the degradation rate increasing with the content in sulfonated units.

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1.6. Supporting information

Table S1. Number-average sequence lengths and randomness of PHT$_x$SI$_y$ copolyesters.[a]

	Dyads (mol-%)			Number-Average Sequence Lengths		Randomness
Copolyester	T**H**T	T**H**SI	SI**H**SI	n_T	n_{SI}	R
PHT$_{95}$SI$_5$	91.6	8.4	0	22,8	1.0	1.04
PHT$_{90}$SI$_{10}$	82.8	15.7	1.6	11.5	1.2	1.08
PHT$_{80}$SI$_{20}$	66.2	27.7	6.1	5.8	1.4	0.86
PHT$_{70}$SI$_{30}$	52.9	34.5	12.6	4.1	1.7	0.82
PHT$_{60}$SI$_{40}$	42.6	43.9	13.9	2.9	1.6	0.95
PHT$_{50}$SI$_{50}$	27.2	46.8	26.1	2.2	2.1	0.93

[a] Experimental values were obtained by Lorentzian deconvolution of ^{13}C NMR spectra in the region of oxymethylene peaks. Number average sequence lengths and randomness were calculated using ref. 23.

Table S2. Powder X-ray diffraction data of PHT and PHT$_x$SI$_y$ copolyesters.

Copolyester	d^a (Å)													
PHT	12.6 (s)	6.2 (w)	5.5 (m)	4.9 (s)		4.1 (m)	3.9 (w)	3.7 (s)	3.4 (vw)	3.3 (vw)	3.2 (vw)	3.0 (vw)	2.7 (vw)	2.6 (vw)
PHT$_{95}$SI$_5$	12.5 (w)		5.5 (w)	4.9 (w)	4.3 (w)	4.1 (s)		3.7 (w)						
PHT$_{70}$SI$_{30}$					4.3 (m)									

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

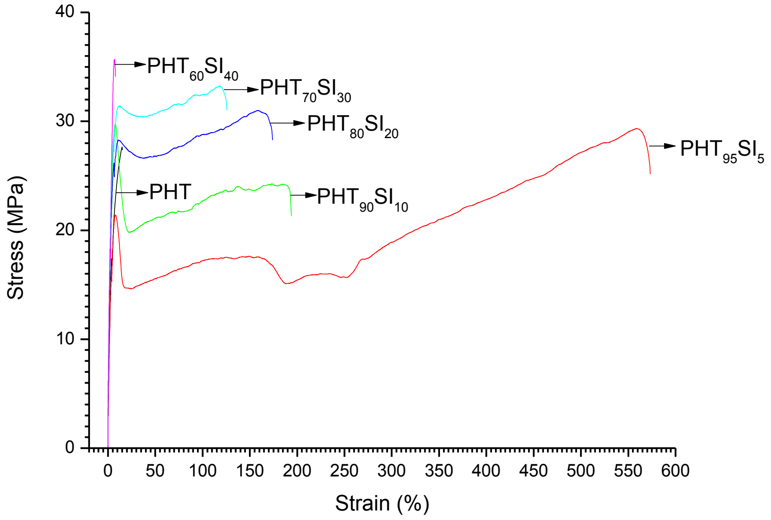


Figure S1. Stress-strain curves of PHT and PHT$_x$SI$_y$ copolyesters with the indicated compositions.

2. Poly(butylene succinate) ionomers with enhanced hydrodegradability

Abstract

A series of poly(butylene succinate) (PBS) ionomers containing up to 14 mol-% of sulfonated succinate units have been synthesized by polycondensation in the melt-phase. The copolyesters were obtained with weight average molecular weights oscillating between 33,000 and 72,000 g·mol^{-1}. All copolyesters were semicrystalline with melting temperatures and enthalpies decreasing and glass transition temperatures increasing with the content of ionic units. The thermal stability of PBS was slightly reduced by the incorporation of these units, and it was also found that the copolyesters were stiffer but also more brittle than PBS. The hydrolytic degradability of PBS was enhanced by copolymerization, an effect that was much more pronounced in basic media.

2.1. Introduction

The electrostatic effect exerted by the ionic groups on the packing of polymer chains strengthens the intermolecular forces and leads to physical cross-linking. Eisenberg and Rinaudo[1] proposed that the bulk properties of ionomers are governed by ionic interactions taking place in discrete regions of the material. In the recent decades, ionomers have been extensively investigated to examine their unique characteristic ionic aggregation as responsible for significant changes in physical properties such as glass-transition temperature, mechanical behavior, transport of gases, and melt viscosity.[2-6] According to the Eisenberg-Hird-Moore model, at increasing ionic concentrations the aggregates (multiplets) start to overlap to form the so called clusters.[7,8]

Biodegradable polymers are considered ideal materials for environmental protection and they are also of great interest for biomedical applications. Particular attention has been given to aliphatic polyesters due to their relatively easy synthesis, good biocompatibility and biodegradability, and acceptable overall pattern of properties.[9-13] Among them, poly(butylene succinate) (PBS) is nowadays one of the most appealing biodegradable polymer because it is fully sustainable, commercially available and exhibits a good balance of thermal and mechanical properties. Nevertheless a good amount of work still remains to be done on this polyester in order to optimize its synthesis and to attain the level of performance required by current advanced applications.

Copolymerization is one of the most important methods for modifying the physical properties of polyesters. However the random incorporation of a second monomeric unit unavoidably entails a significant depression in the melting temperature of crystalline polymers that may restrict to unacceptable values the temperature range over which the copolyester can be used.[14-17] In order to surpass this shortcoming, some authors have introduced the ionomer approach into the field of bio-based polyesters.[18,19] Han *et al.*[9,20] inserted ionic groups into the PBS main chain leading to an improved extensibility due to reduction of crystallinity as well as a noticeable modification in melt rheological properties due to the ionic interactions. PBS ionomers have been proposed as a solution for the brittleness and poor processability of other polymers. Park *et al.*[21] blended polylactic acid (PLA) with PBS ionomers with the aim of improving the shortcomings of PLA.

The aim of this work is to report on the effect of sodium 1,2-(dimethoxycarbonyl)ethanesulfonate as a comonomer on the properties of poly(butylene succinate). This comonomer is dimethyl succinate bearing a pendant sodium sulfonate group which makes the compound ionic and non-symmetric. The presence of this unit is expected to modify the properties of the polyester without much disturbing its packing in the solid state since its differences in size with the succinate unit are relatively small. Two papers have been previously reported on this type of copolyesters both of them dealing with very low content of ionic groups and focused exclusively on crystallization aspects.[22,23] In the present work, we have prepared a series of PBS copolyesters, abbreviated as PBS_xSS_y containing sulfonated succinate units (SS) in a range much wider than previously reported, *i.e*. from 3 to 15 mol-% and repressing the elimination of sodium sulfonate groups during reaction. The object is to evaluate how the basic properties of PBS and in particular hydrolytic degradability are affected by the incorporation of sulfonated succinate units, with special attention to copoylesters with high contents in ionic groups.

2.2. Experimental section

2.2.1. Synthesis of sulfonated dimethyl succinate

Sodium 1,2-(dimethoxycarbonyl)ethanesulfonate (sulfonated dimethyl succinate) (SDMS) was synthesized according to the procedure described elsewhere.[24] Dimethyl fumarate (5 g) and $NaHSO_3$ (8 g) were dissolved in a methanol/water solution (70/30 v/v) and were left under reflux at 80 °C for 8 h. Then, the reaction mixture was evaporated to dryness. The residue was extracted with DMSO, the liquid phase was concentrated and precipitated with a large amount of acetone, and the precipitate collected by filtration and dried under vacuum at 60 °C for 48 h. The structure of the SDMS comonomer was checked by NMR; both ^{1}H and ^{13}C NMR spectra with signals assignments are available in the supporting information file (Figure S1).

2.2.2. Copolymers synthesis

PBS and poly(butylene succinate-*co*-butylene sulfonated succinate) (PBS_xSS_y) copolyesters were prepared according to the synthetic route depicted in Scheme 1. It consisted of a two-step melt polycondensation procedure corresponding to esterification/transesterification and polycondensation reactions, respectively. A mixture SA, BD and SDMS with the selected composition and containing 0.6 % (w/w) of dibutyl tin oxide (DBTO) was charged into a 250 mL, three-necked, round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a distillation column. A molar ratio 2.1:1 of BD to SA or SA+SDMS was used for both PBS and PBS_xSS_y copolyesters. The esterification/transesterification reaction was carried out at 170 ºC under a nitrogen flow for a period of 6 h with continuous removal of the released water and methanol. Polycondensation reaction leading to PBS homopolymers was performed either at 240 ºC or 180 ºC for 3 h under a 0.03-0.006 mbar vacuum using DBTO as a catalyst. Two PBS samples differing in molecular weight (PBS1 and PBS2) were respectively obtained. Polycondensation reactions leading to PBS_xSS_y copolyesters were left to proceed at 190 ºC under high vacuum for 6-10 h depending on composition. The high viscous liquid finally formed was cooled down to room temperature and the atmospheric pressure was restored with a nitrogen flow to prevent degradation. If it is not specified, the final solid mass without further treatment was used for characterization and property evaluation.

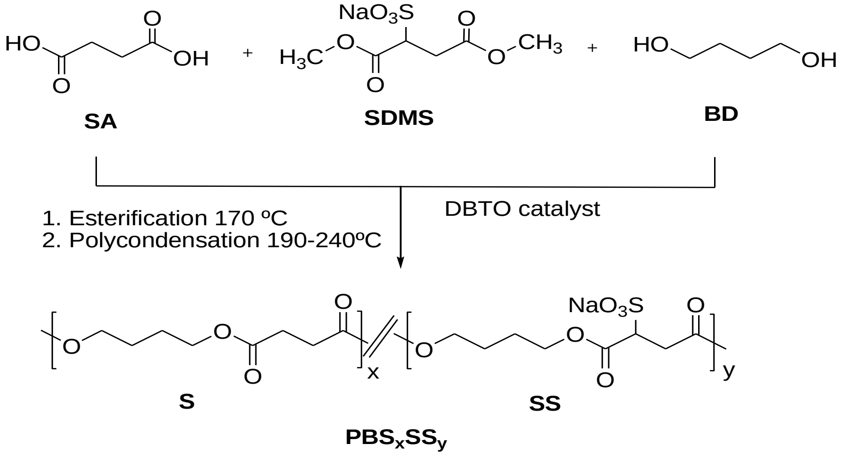
2.2.3. Hydrolytic degradation

The hydrolytic degradation essays for PBS and PBS_xSS_y samples were carried out in parallel using three different buffer solutions: citric acid (pH 4.0), sodium phosphate (pH 7.4) and sodium carbonate buffer (pH 10) at 37 ºC. The films were prepared by hot pressing at a temperature just below the melting point of the polymer. They were cut into 7 x 7 x 0.20 mm pieces. Samples were immersed in 10 mL of each buffer for 8 weeks. After a fixed period of time the samples were picked out and washed with distilled water and dried in a vacuum oven at room temperature to constant weight and finally analyzed by GPC. For NMR spectroscopy analysis samples of about 30 mg weight were immersed in NMR tubes containing the corresponding buffer in D_2O, and incubated under the same conditions. Both the products released to the incubating medium as well as the residue left after incubation were subjected to NMR analysis.

2.3. Results and discussion

2.3.1. Synthesis and chemical structure of PBS_xSS_y copolyesters

The synthesis pathway leading to the PBS_xSS_y ionomers is shown in Scheme 1. The procedure consists of two successive steps, the first one is an esterification/transesterification reaction leading to low molecular weight oligomers, and the second one is the polycondensation of the oligomers formed in the previous step to render the final copolyesters. The first step was carried out at 170 ºC with removal of the released water and methanol and the second one was carried out at higher temperatures under high vacuum to accelerate the transesterification reaction and to unbalance the equilibrium towards the formation of high molecular weight polymers by releasing of the excess of BD. The maximum temperature applied was 190 ºC because the β-elimination reaction of SS units with releasing of $NaHSO_3$ and concomitant generation of fumarate units starts to happen above this temperature.



Scheme 1. Polymerization reactions leading to PBS$_x$SS$_y$ copolyesters.

It was observed that the melt viscosity attained by the reaction mass increased gradually with the content of SS units as it should be expected for ionomers; it is widely known that sulfonate groups can interact to generate ionic aggregates or clusters which act as thermoreversible crosslinks.[25,26] Dibutyl tin oxide (DBTO) was the catalyst of choice. Initially, the synthesis of the copolymers was done with titanium (IV) tetrabutoxide (TBT) but the result was not satisfactory due to the decomposition of SS units and formation of copolyesters with very low intrinsic viscosities. DBTO allowed the reaction to proceed at lower temperatures and copolymers with significantly higher intrinsic viscosities could be then attained. All the copolyesters were obtained in high yields (higher than 90%) and molecular weights going down with increasing contents in SS units (Table 1). It should be noted that GPC measurements could be affected by ionic aggregations. Although one can expect that the treatment of samples with TFA previous to injection and the use of HFIP as the mobile phase will minimize the occurrence of ionic interactions, their complete absence cannot be fully ascertained.

However results afforded by GPC were very consistent with intrinsic viscosities measured in DCA which ranged between 0.74 and 1.18 dL·g^{-1} with values also decreasing as the content of the copolyester in SS units increased. Nevertheless, the clear conclusion that can be drawn from these data is that the polycondensation reaction is hindered in the presence of the dimethyl sulfonated succinate comonomer. One factor motivating the decrease in molecular weight is the limited temperature at which polycondensation has to be conducted in order to avoid the β-elimination reaction of sulfonate groups. A second factor is the increasing in melt viscosity of the mass reaction with the content of the forming copolyester in SS units, which hinders the volatilization of BD that is released in the polycondensation step.

Table 1. Composition and molecular weights of PBS homopolyester and PBS$_x$SS$_y$ copolyesters.

	Copolyester composition[a]	Copolyester composition[b]	Molecular weights		
Copolyester	S/SS	S/SS	$[\eta]^c$	M_w[d]	$Đ$[d]
PBS1[e]	100/0	100/0	1.33	112,000	2.2
PBS2[f]	100/0	100/0	1.0	45,600	2.5
PBS$_{97}$SS$_3$	97/3	97.9/2.1	1.18	72,000	2.5
PBS$_{95}$SS$_5$	95/5	96.1/3.9	1.03	39,000	2.4
PBS$_{92}$SS$_8$	92/8	92.8/7.2	1.02	38,000	2.4
PBS$_{90}$SS$_{10}$	90/10	90.9/9.1	0.94	35,000	2.2
PBS$_{85}$SS$_{15}$	85/15	86.2/13.8	0.74	33,000	2.1

[a] Molar ratio of comonomers in the feed.
[b] Composition of the copolyester (mol/mol) determined by ^{1}H NMR.
[c] Intrinsic viscosity (dL g^{-1}) measured in dichloroacetic acid at 25 ºC.
[d] Weight-average molecular weight (M_w) (g·mol^{-1}) and dispersity ($Đ$) determined by GPC.
[e] Sample prepared at a polycondensation temperature of 240 ºC.
[f] Sample prepared at a polycondensation temperature of 180 ºC.

The chemical structure and composition of PBS$_x$SS$_y$ copolyesters was ascertained by NMR. The ^{1}H and ^{13}C NMR spectra of PBS$_{85}$SS$_{15}$ are shown in Figure 1 as representative of the series. The content in SS units was determined by the ratio of the integrated NMR signals at 3.25 ppm for the CH$_2$ in the SS unit (signal e) and at 2.76 ppm for the two CH$_2$ in the succinate unit (signal c). Results are listed in Table 1 indicating that the content of copolyesters in sulfonated units was lower than in the feed. Differences are however small, around 10% in overall, and they must be attributed to the β-elimination reaction of sulfonated groups happening in the SS units. This side reaction was observed to be enhanced at higher temperatures;[22] as it is shown in the SI file (Figure S2), the peak corresponding to fumarate protons becomes clearly observed in the ^{1}H NMR spectra of a copolyester heated at 210 ºC for 30 min.

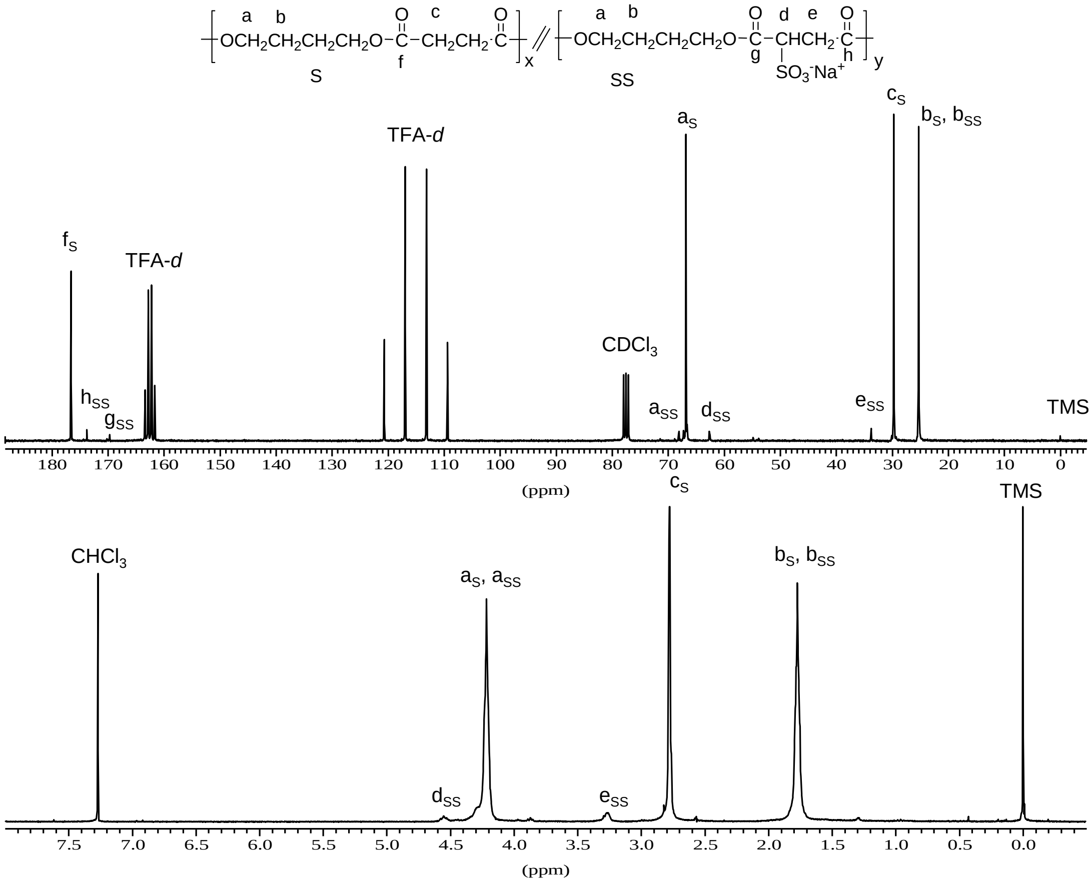


Figure 1. ^{1}H NMR (bottom) and ^{13}C NMR (top) of $PBS_{85}SS_{15}$ copolyester.

2.3.2. Thermal and mechanical properties

The effects exerted by the incorporation of SS units on the thermal properties of PBS were evaluated by DSC and TGA. The DSC data obtained for the whole PBS_xSS_y series examined in this work are collected in Table 2. The two samples of PBS showed practically the same T_g value of -37 ºC, which was found to increase up to -32 ºC with the content in SS units. Such slight but significant increase in T_g is supposedly caused by the ionic interactions taking place between the sulfonate groups, which are known to act as physical crosslinks that restrict the chain mobility. Eisenberg *et al.,*[27,28] reported a similar behavior for styrene-based ionomers, which contain ionic multiplets, each one was surrounded by a shell of restricted chain mobility. The restricted mobility region surrounding an isolated multiplet would be too small as to have a noticeable effect on the overall T_g of the polymer; but the multiplet itself would increase the T_g of the polymer by acting as a large cross-link. A similar effect has been reported by Im *et al*.[22,23] for the same copolyesters with low contents of SS units and attributed to the restricted chain mobility caused by the strong intermolecular association of ionic groups.

To evaluate the thermal stability of the polyesters, TGA measurements were carried out under a nitrogen atmosphere in the 30-600 ºC interval. The TGA traces of PBS_xSS_y copolyesters are shown in Figure 2a where the trace for PBS1 has been included for comparison, and data obtained therefrom are summarized in Table 2, which shows that the thermal stability of copolyesters decreased with the content in SS units. Thermal decomposition of PBS occurs in a single stage with maximum rate at about 405 ºC with a 1-2% of residual weight left upon heating at 600 °C. The insertion of SS units in PBS not only tends to decrease the decomposition temperature but also makes the process more complex. Up to four decomposition steps are detected in the PBS_xSS_y copolyesters with that happening at 390-400 ºC being much more prominent than the others (Figure 2b). The remaining weight after the thermal degradation at 600 ºC increased continuously with the content in SS units, which may be accounted by the metallic residue left in the decomposition of the SS units (Table 2).

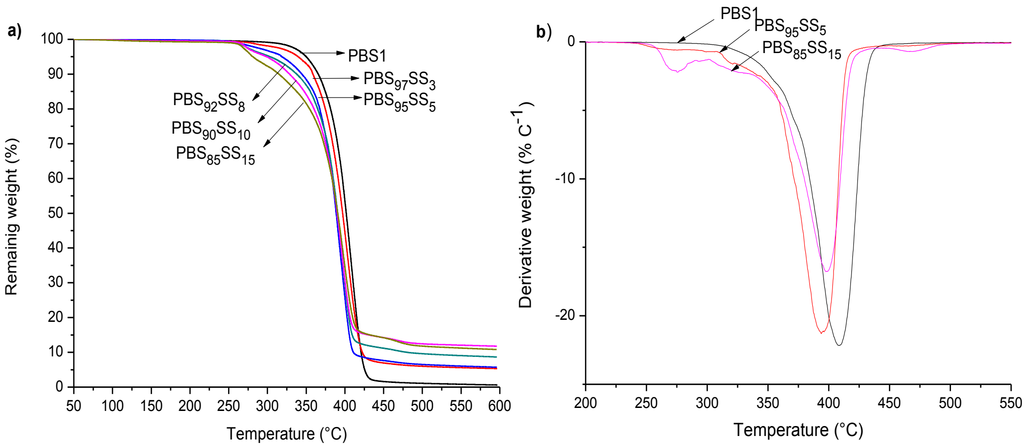


Figure 2. (a) TGA traces of PBS1 and PBS$_x$SS$_y$. (b) Derivative curves of PBS1 and a selection of PBS$_x$SS$_y$ copolyesters.

All PBS$_x$SS$_y$ copolyesteres are semicrystalline with melting temperatures and enthalpies slightly decreasing with the content in SS units. Since the random insertion of the second comonomer will diminish the chain regularity of PBS, a decrease in both crystallite size and crystallinity should be expected for the copolyesters. Nevertheless the effect is really moderate with a decay of T_m in less than 10 ºC for a content of 15 mol-% in SS units. The thermograms registered at the first heating from copolyester samples prepared by precipitation from $CHCl_3$ with methanol are shown in Figure 3. All they display well defined endothermic peaks characteristic of melting. Moreover, all the copolyesters were able to crystallize from the melt upon cooling at 10 ºC·min^{-1} with a good reproduction of melting at the second heating (Figure S3). Samples obtained by precipitation from solution are expected to be well crystallized and to display therefore high melting temperature and enthalpy. Samples used for the second heating were crystallized under much more unfavorable conditions. The small differences observed in both T_m and ΔH_m between first and second heating traces (Table 2) are indicative of the ability of these copolyesters to crystallize from the melt. In principle it could be thought that ionic clusters that have not been destroyed after melting may act as nucleating agents favoring the crystallization of the molten material, as it was reported for these copolyesters with low content of SS units.[22] In the present case however, the large supercooling observed for crystallization, which attains up to near 70 ºC, makes less probable such interpretation.

Table 2. Thermal and mechanical properties of PBS homopolymer and PBS$_x$SS$_y$ copolyesters.

				DSC					Stress-strain parameters[g]		
	$^{o}T_{d}$[a]	$^{max}T_{d}$[b]	RW[c]	T_g[d]	T_m[e]	ΔH_m[e]	T_c[f]	ΔH_c[f]	E	σ_{max}	ε_{max}
Copolyester	(ºC)	(ºC)	(%)	(ºC)	(ºC)	(Jg^{-1})	(ºC)	(Jg^{-1})	(Mpa)	(Mpa)	(%)
PBS1	363	408	1	-37	115 (114)	70 (74)	75	66	440±5	35±1	282±10
PBS2	356	405	3	-37	113 (114)	77 (67)	78	62	403±3	26±1	10±1
PBS$_{97}$SS$_3$	359	403	5.4	-36	113 (111)	90 (69)	71	65	480±10	36±2	121±3
PBS$_{95}$SS$_5$	344	399	6.0	-36	113 (111)	71 (66)	63	63	515±10	39±1	21±3
PBS$_{92}$SS$_8$	338	397	8.7	-34	111 (110)	61 (60)	54	57	860±5	42±1	9±1
PBS$_{90}$SS$_{10}$	328	396	12	-33	110 (108)	43 (56)	53	50	930±7	38±1	6±1
PBS$_{85}$SS$_{15}$	315	393	13	-32	106 (105)	53 (46)	36	25	1050±8	28±2	3±1

[a] Degradation temperature at which a 10% weight loss was observed in TGA traces at 10 ºC·min^{-1}.
[b] Temperature of maximum degradation rate.
[c] Remaining weight at 600 ºC.
[d] Glass transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 ºC·min^{-1}.
[e] Melting temperatures and enthalpies were registered at a heating rate of 10 ºC·min^{-1}. In parenthesis, values recorded in the second heating.
[f] Crystallization temperatures and enthalpies were registered at cooling from 200 ºC at 10 ºC·min^{-1}.
[g] Young's modulus, maximum tensile stress, maximum elongation at break measured at room temperature on a Zwick BZ2.5/TN1S.

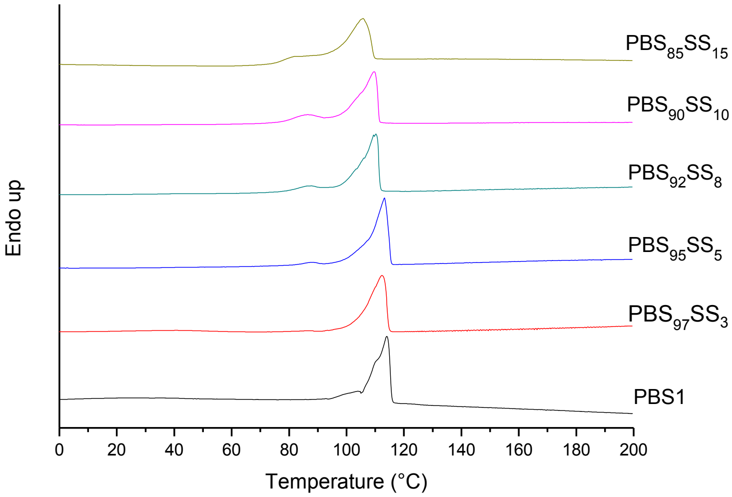


Figure 3. DSC thermograms (first heating) of PBS_xSS_y copolyesters and PBS1.

The basic mechanical parameters of the copolyesters registered in the tensile essays are presented in Table 2 together with those of PBS1 and PBS2 that have been included for comparison. The stress-strain curves experimentally registered are depicted in the Figure S4 of the SI file. Large differences in the mechanical parameters are observed between PBS1 and PBS2 according to what should be expected from their different molecular weights. Nevertheless, taking as reference PBS1 which has a molecular weight closer to copolyesters, it can be inferred that in overall the Young's modulus (*E*) increased steadily with the content in SS units whereas the elongation at break followed an opposite trend. $PBS_{97}SS_3$ deviates from this trend by showing a high elongation which can be explained taking into account both its very low content in SS units and its relative higher molecular weight. On the contrary, the influence of composition on the maximum stress is weak and it does not show a clear trend; it slightly increased with the content in SS units in the copolyester for values lower than 8 mol-% to then decrease for higher contents without apparent explanation. Noticeably, both $PBS_{90}SS_{10}$ and $PBS_{85}SS_{15}$ show an *E* modulus much greater than PBS but a much lower elongation at break. It can be unambiguously concluded from this preliminary study is that the insertion of ionic units in amounts above 5 mol-% makes the polyester more brittle because the elongation at break largely diminishes with the incorporation of SS units. This behavior is in accordance with the trend displayed by sulfonated units containing ionomers reported in previous works.[2,29]

2.3.3. Hydrolytic degradation

Polyester recycling is in the focus of current polymer research concerning sustainability. Chemical recycling leading to monomers (or oligomers) recovery for subsequent valorization is an actual alternative method to physical processes and PBS is a good candidate for hydrolysis recycling with regeneration of succinic acid.[30] Therefore to know the influence of comonomers on novel PBS copolyesters is a matter of unquestionable importance.

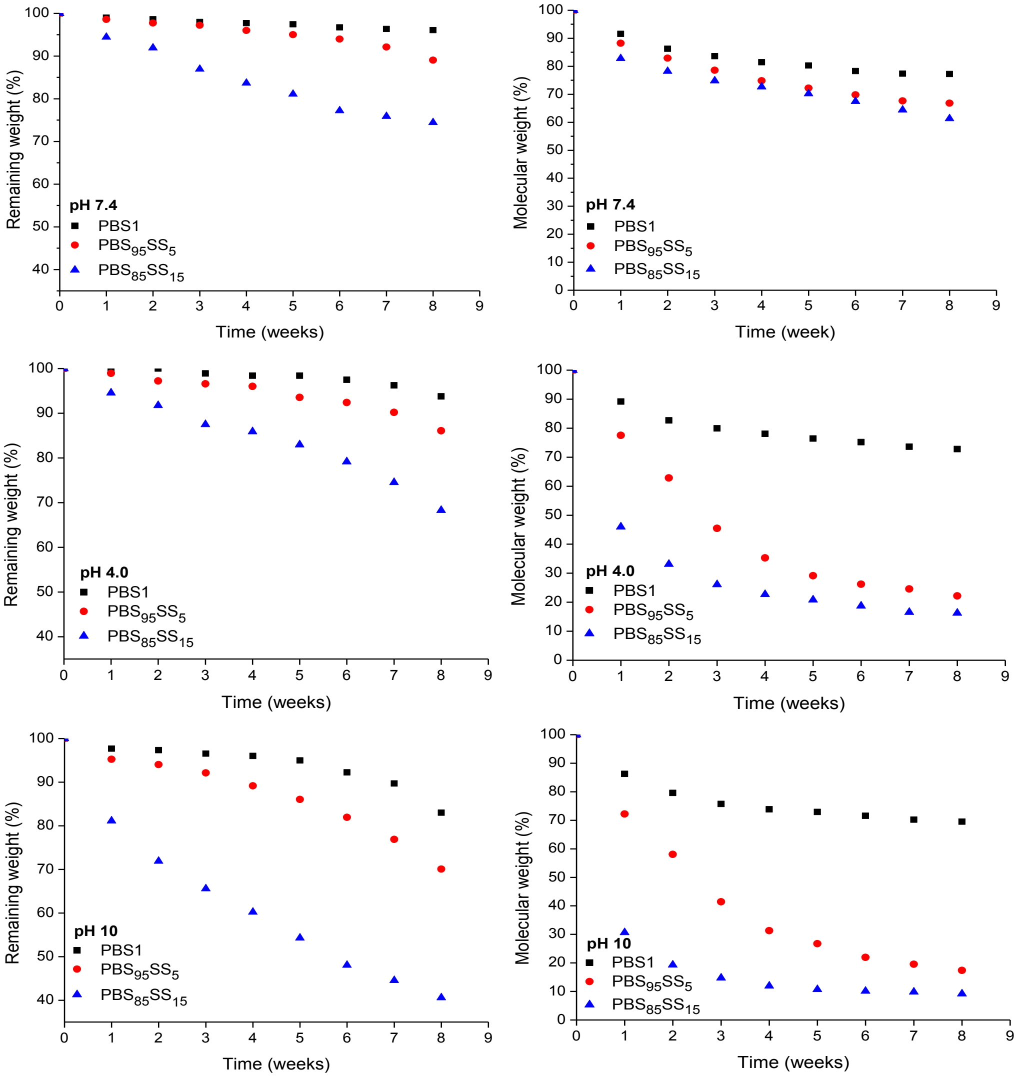


Figure 4. Evolution of sample remaining weight (left) and weight average molecular weight (right) for PBS1, $PBS_{95}SS_5$ and $PBS_{85}SS_{15}$ at pH 7.4, 4.0 and 10 (top to bottom) at 37 ºC, as a function of incubation time.

Accordingly, the effect exerted by the incorporation of SS units on the hydrolytic degradation of PBS has been evaluated under a variety of conditions. The copolyesters chosen for comparison with PBS were $PBS_{95}SS_5$ and $PBS_{85}SS_{15}$. They were incubated in pH 7.4 buffers at 37 °C and also at pH 4.0 and 10 to estimate their susceptibility to hydrolysis under both acidic and basic conditions. The degradation progress was monitored by following the weight loss and molecular weight decay of the residual sample as a function of the incubation time. These data are presented in Figure 4. After 8 weeks of incubation at pH 7.4, the M_w of samples with SS unit contents of 5 and 15 mol-% was 33% and 39% of the initial value, respectively whereas PBS decreased only in less than 20%. It becomes clear therefore from these results that the hydrolytic degradation is enhanced by increasing contents in SS units.

To gain insight into the degradation of the polyester chain at the molecular level, PBS, $PBS_{95}SS_5$ and $PBS_{85}SS_{15}$ polyesters were incubated at 37 °C in aqueous buffer at pH 4.0 and pH 10 and both the releasing fragments and the residual polymer were weekly analyzed over a period of two months. Changes taking place in sample weight and M_w of the three polyesters upon hydrolysis are comparatively depicted in Figure 4. A significant decay in both sample weight and molecular weight was observed for the PBS_xSS_y copolyesters. It was noticed that the hydrolytic degradation was drastically accelerated by increasing either ionic content or pH. Similar observations have been recently reported for PBS ionenes[31] as well as for other copolyesters containing sulfoisophthalic units[2,18,29] and such increase has been attributed to the enhancement of the hydrophilicity caused by the presence of the ionic groups.

Melting enthalpies displayed by PBS, $PBS_{95}SS_5$ and $PBS_{85}SS_{15}$ polyesters after incubation are compared in Figure 5. It is noteworthy to highlight that crystallinity of the three polyesters increased as degradation proceeded, with the highest values attained when samples were incubated in basic conditions. Such increase in crystallinity is indicative that hydrolysis has taken place preferably in the more permeable amorphous phase, as it is usually observed in semicrystalline polymers.[32]

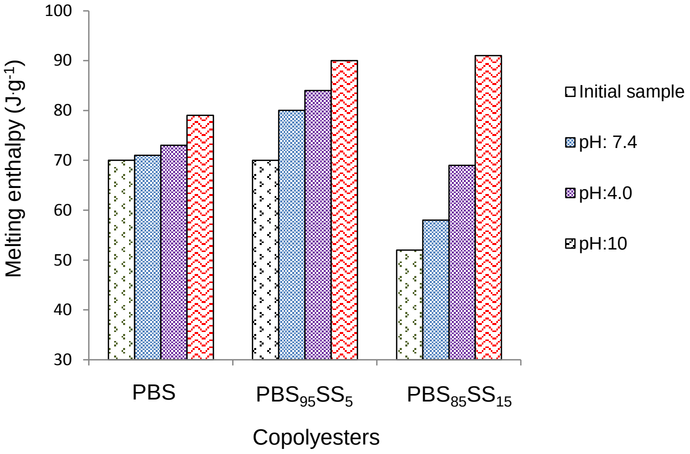


Figure 5. Melting enthalpies of PBS1, PBS$_{95}$SS$_5$ and PBS$_{85}$SS$_{15}$ after 8 weeks of incubation and initial samples.

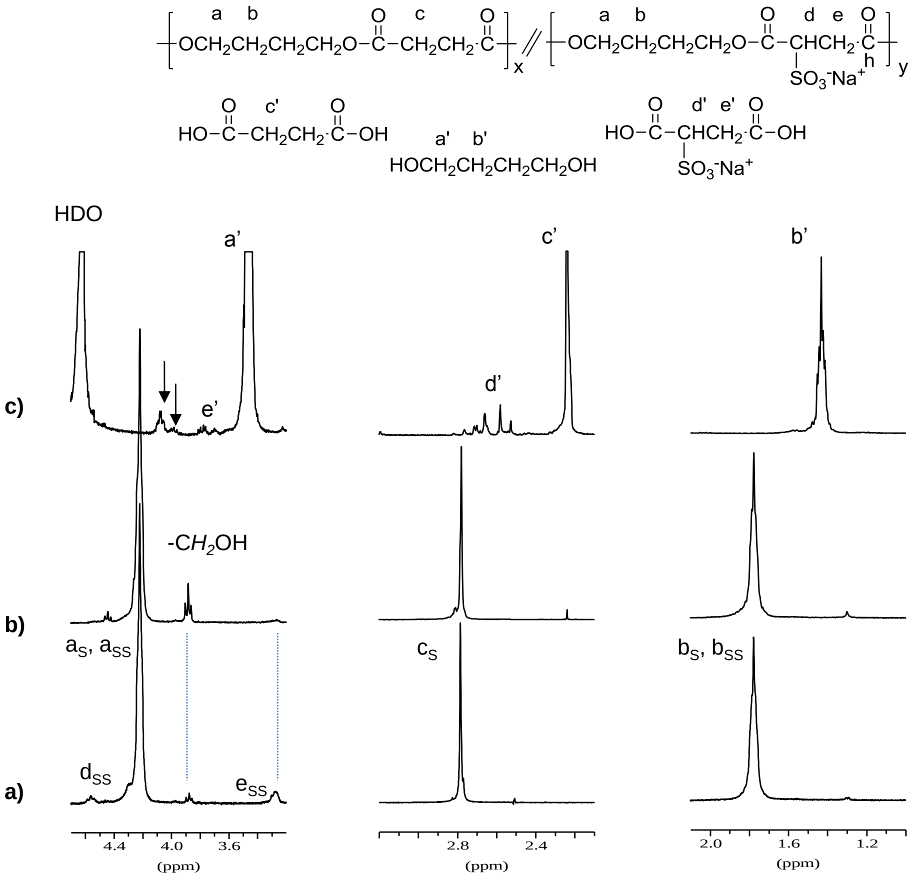


Figure 6. ^{1}H NMR spectra of PBS$_{85}$SS$_{15}$ (a), residue (b) and water soluble products (c) of PBS$_{85}$SS$_{15}$ degraded in aqueous buffer, pH 10 for 8 weeks. The arrows indicate signals arising from oligomers generated upon hydrolysis.

^{1}H NMR spectra of PBS$_{85}$SS$_{15}$ residue and of the products released to the incubation medium after 8 weeks of incubation are depicted in Figure 6. It can be observed that the signals due to sulfonate units (e$_{SS}$ and d$_{SS}$) almost disappeared in the degraded sample, and that signals arising from -CH$_2$OH end groups increased as a consequence of the hydrolysis process. The spectra of water soluble products showed signals corresponding to succinic and sulfonated succinic acids, 1,4-butanediol and short oligomers, which are more intense for samples incubated at basic pH where copolyesters underwent a more severe degradation.

The evolution of the content in sulfonated units of the residual PBS$_{85}$SS$_{15}$ with time for an incubation period of 8 weeks under the different essayed conditions is plotted in Figure 7. These results are consistent with those obtained by sample weighing and GPC measurements and reveal that degradation involves preferably the hydrolysis of the SS units. The drastically accelerated degradation observed at pH 10 is ascribed to both the higher hydrophylicity of the copolyester and to the faster and more efficient hydrolytic degradation process that takes place in copolyesters at basic pH.

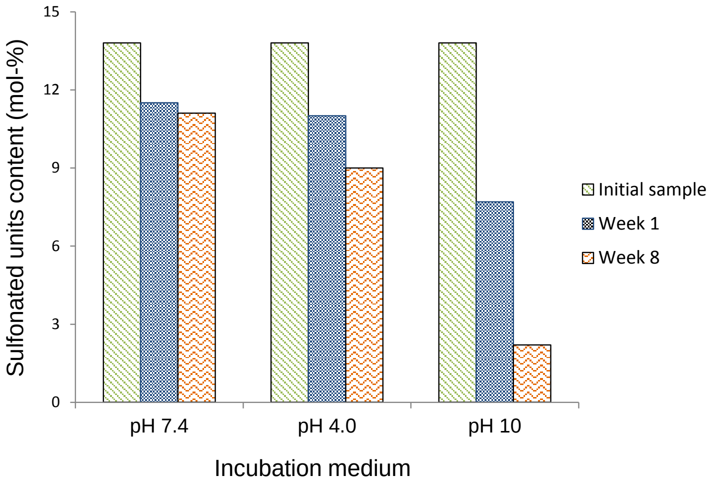


Figure 7. Evolution of the content in sulfonated units of the residual PBS$_{85}$SS$_{15}$ along incubation time.

2.4. Conclusions

High molecular weight PBS copolyesters containing amounts of ionic sulfonate groups up to ~15 mol-% were successfully synthesized by using sodium sulfonate dimethyl succinate as comonomer. Polycondensation was carried out in the melt phase following essentially the same procedure that is used for the industrial preparation of PBS although the reaction temperature had to be lower in order to prevent decomposition of the sulfonated compounds. The sulfonated diester entered effectively the growing polyester chain so that the compositions of the resulting copolyesters were quite close to those of the feed from which they were obtained. The weight-average molecular weights of the copolyesters were between 30,000 and 70,000, which is a range acceptable for most of their foreseeable applications. The changes in thermal properties of PBS due to copolymerization were not significant and the copolyesters continued to be thermally stable and semicrystalline, and they retained the ability to crystallize from the melt. Conversely, the mechanical behavior changed noticeably with both molecular weight and composition. In general copolyesters were stiffer and stronger but also more brittle than PBS. The hydrodegradability was enhanced by copolymerization, an effect that was more pronounced when the copolyester was incubated in basic medium. All the property modifications were more apparent as the content in sulfonated units increased and all the observed effects could be reasonably accounted by the specific molecular interactions that are expected to occur from the presence of ionic units in the PBS chain.

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2.6. Supporting information

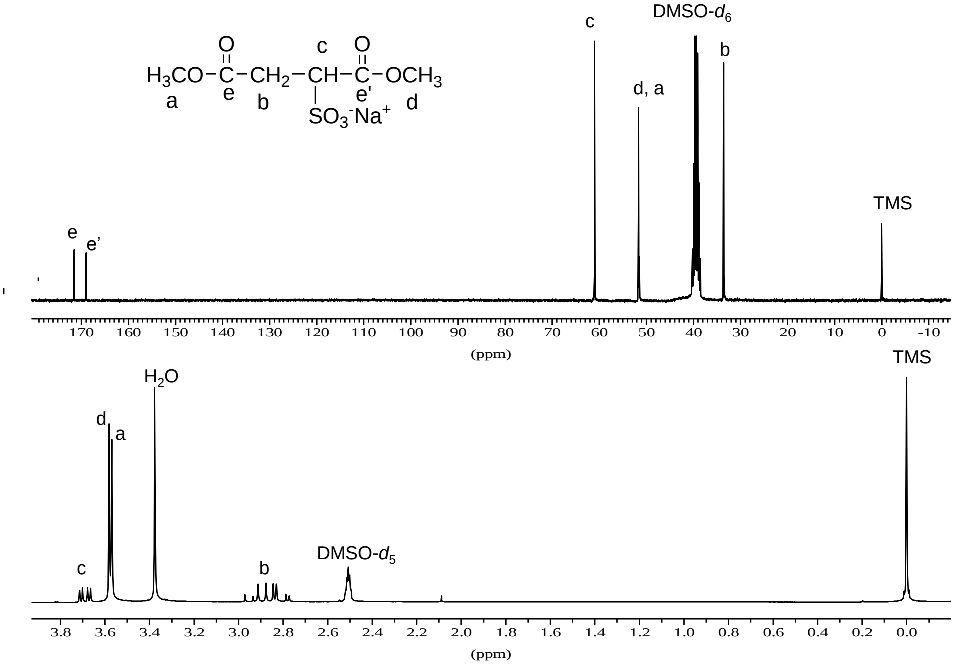


Figure S1. ^{1}H NMR (bottom) and ^{13}C NMR (top) spectra of SDMS

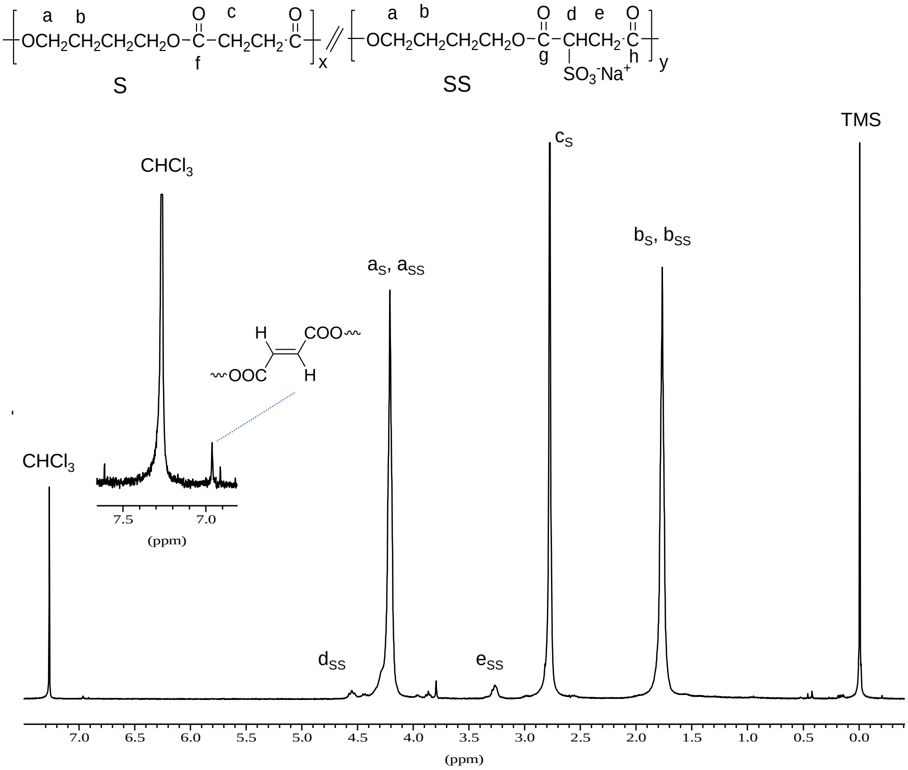


Figure 2S. ^{1}H NMR spectrum of $PBS_{85}SS_{15}$ copolyester after heating at 210 ºC during 30 minutes.

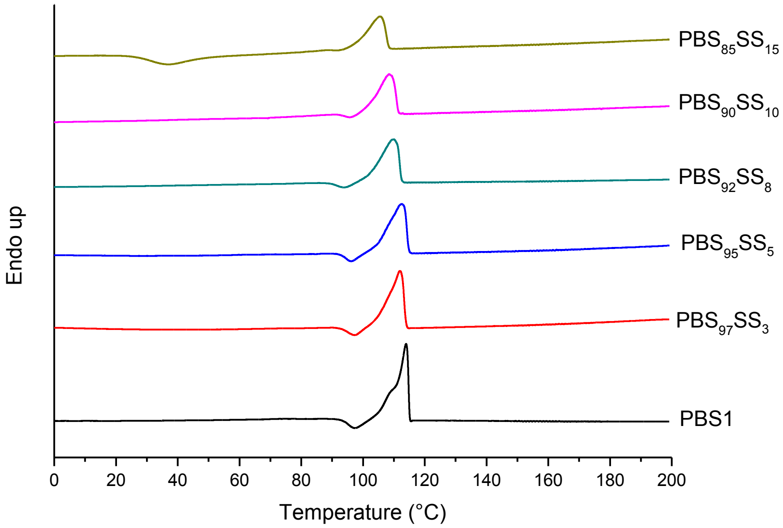


Figure S3. DSC thermograms (second heating) of PBS_xSS_y copolyesters.

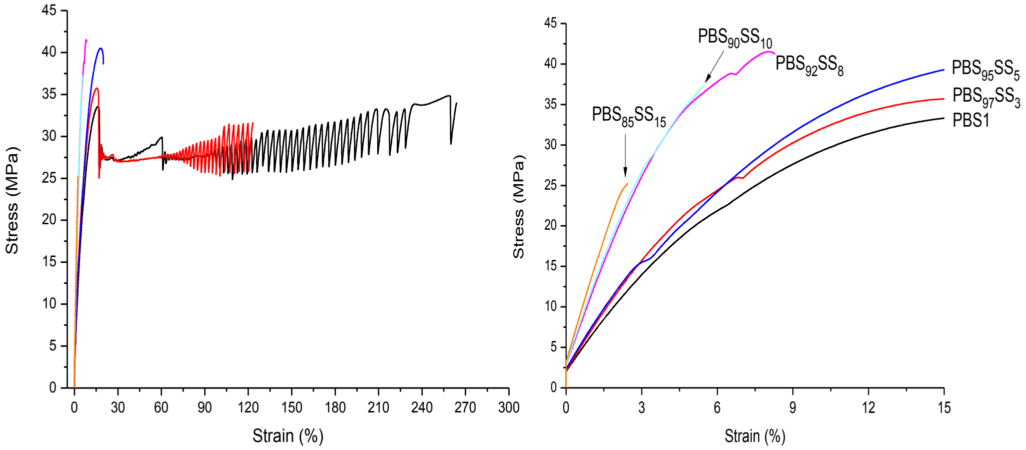


Figure S4. Stress-strain curve of PBS$_x$SS$_y$ copolyesters (left). Stress-strain expanded in the zone elastic deformation.

Chapter III.

Polyesters containing cationic groups

1. Enzymatic synthesis, characterization and biocide properties of poly(butylene succinate) ionomers containing ammonium groups

Abstract

Poly(butylene succinate) (PBS) of high molecular weight (M_n~35,000) was obtained by enzymatic polycondensation in the melt by using *Candida Antarctica* lipase B (CALB). Cationic PBS ionomers bearing ammonium side groups in addition to the homopolymer fully made of glutamic acid were prepared by the same procedure from mixtures of succinic and glutamic dimethyl esters with 1,4-butanediol. Enzyme activity tests showed that CALB retained more than 50% of its lipase function in the presence of ammonium groups. The PBS ionomers were non-water soluble polymers that showed good thermal stability. All they were semicrystalline with melting temperatures in the 115-75 ºC range and adopting the same crystal structure as PBS. The strong interactions of the ionic groups restricted largely the molecular mobility and caused a large increase in both melt viscosity and glass transition temperature of PBS copolyesters. Nevertheless, copolyester ionomers containing up to 16 mol-% of ammonium groups were able to crystallize from the melt. Antimicrobial activity results show that the PBS copolyesters with contents equal o above 50 mol-% of ionic groups were found to significantly reduce the cell counts of both gram-positive and gram-negative bacterias whereas they were poorly active against fungi.

1.1. Introduction

In the past three decades it has been a great progress in the use of enzymes in organic media to catalyze a wide variety of small-molecule transformations.[1-3] Also, the enzymatic polymerization has emerged as a new trend of increasing importance in macromolecular science[4-7] because it provides a new synthetic strategy for the synthesis of useful polymers, most of which are difficult to produce by means of conventional chemical catalysis. Since enzymatic polymerization allows generating polymers under mild reaction conditions without using toxic reagents, the method is regarded as environmentally friendly providing a good example of green polymer chemistry.

Recently, the interest in the synthesis of aliphatic polyesters has greatly increased due to the fact that they are among the most promising sustainable polymeric materials. Many polyesters may be synthesized from biobased resources and are designed with the purpose of improving the degradation rate[8-11] in order to be used in the biomedical field.[12-14] Poly(butylene succinate) (PBS) is a typical biodegradable polymer that has been traditionally produced using petroleum-based monomers. Recently PBS has emerged as a distinguished polyester mainly due to that its two monomers, succinic acid and 1,4-butanediol, are now accessible from renewable resources.[15] Moreover PBS displays a satisfactory pattern of thermal and mechanical properties that make it suitable for a wide range of end applications by using conventional melt processing techniques.[16]

The incorporation of small amounts of ionic groups in a polymeric chain gives rise to important changes in both physical and chemical properties. The charged polymer (ionomer or polyelectrolyte) is able to interact electrostatically with other ionic polymers and small charged molecules, and even with itself. In aliphatic polyester ionomers these properties may be combined with biodegradability to render materials of exceptional interest as drugs delivery systems, and in particular for their use in transfection technology.[10,17] Anionic PBS ionomers containing sulfonate groups have been recently studied by different authors and in some cases their potential as biomaterial has been evaluated.[9,18,19] On the other hand, the study of polyester cationic ionomers is in a much more backward state, in great part due to the difficulty found in the introduction of cationic groups into the polyester chain by melt polycondensation. To our knowledge, a recent paper published by us on PBS containing trimethyl ammonium side groups is the only reference on polyester cationic ionomers that is found in the accessible literature.[20] In this work, it was brought into evidence that the high temperatures applied for melt polycondensation promote the decomposition of the ammonium units and hinder the growing of the polymer chain.

Lipase-catalyzed polymerization is a recently developed method that allows to produce aliphatic polyesters under mild conditions in the absence of residual metals.[21] Polyesters produced by this means, and in particular PBS, are materials fully suitable for those bioapplications, in which a good biocompatible and biodegradable behavior is required.[22] The most common lipase used for polyester synthesis has been *Candida Antarctica* lipase B (CALB). The effects of substrate and solvent on polymer formation by CALB-assisted polycondensation were investigated by Mahapatro *et al*.[23] for a series of diacids and diols polymerized in solution and in bulk. It was found that reactions involving monomers that contain long alkylene segments displayed higher reactivity than those carried out with short diacids and diols. Nevertheless Azim *et al*.[5] reported the synthesis of PBS from homogeneous reaction mixtures of diethyl succinate and 1,4-butanediol and found that temperature played an important role in the attained polymer molecular weight. Sugihara *et al*.[24] succeeded in synthesizing PBS with a M_w around 130,000 by the lipase-catalyzed polymerization of butylene succinate cyclic oligomers.

Conventional antimicrobial agents, based on low-molecular-weight compounds with biocide activity, are easily susceptible to resistance and frequently result in environmental contamination and toxicity due to biocidal diffusion.[25,26] In comparison, antimicrobial polymeric materials provide a valid approach addressing these problems by promoting antimicrobial efficacy and reducing residual toxicity.[27,28] In addition, antimicrobial polymers possess chemical stability and non-volatility, presenting long-term activity.[29] Polymers containing covalently bonded antimicrobial moieties avoid the problem of the permeation of low-molecular-weight biocides from the polymer matrices. Such antimicrobial polymers promise long-term durability in an environmentally friendly way.[30,31] Among them, the antimicrobial polymeric materials containing quaternary ammonium and/or phosphonium salts are probably the most widely used and studied antimicrobial polymers.[32]

We wish to report here the enzyme-catalyzed melt polycondensation of high molecular weight PBS, as well as of PBS copolyester ionomers ($PBS_xG^I_y$) that incorporate different amounts of 2-aminoglutarate hydrochloride (G^I). We study the synthesis of these copolyesters by using CALB and the enzymatic activity is evaluated for the ammonium comonomers bearing either ammonium or trimethyl ammonium groups. The influence of the presence of the ammonium side groups in PBS on its thermal properties has been also examined. In addition, the biocidal effect of these PBS cationic copolyesters on bacterias (*Escherichia coli and Staphylococcus aureus*) as well as on fungi (*Candida albican*) ha been preliminary evaluated.

1.2. Experimental section

1.2.1. Synthesis of $PBS_xG^l_y$ copolyesters

Candida Antarctica lipase immobilized on macroporous acrylic resin (CALB) was dried under 0.1 mm-Hg at 25 ºC for 24 h. 2% (w/w) of CALB was transferred into a round-bottom flask containing dimethyl succinate, L-glutamic acid dimethyl ester hydrochloride (A-DMG·Cl) and 1,4-butanediol. A molar ratio 1.4:1 of BD to the total of diesters was used for the synthesis of PBS and $PBS_xG^l_y$ copolyesters. The reaction mixture was mechanically stirred under heating at 80 ºC for 72 h with a low nitrogen flow. Then a second 2% (w/w) CALB portion was added to the reaction mixture and the polycondensation reaction was initiated by raising the temperature to 90 ºC and reducing the pressure down to 40 mbar and these conditions maintained for 72 h. Finally a third 2% (w/w) portion of CALB was added and the temperature increased to 115 ºC and the pressure reduced to $1.6 \cdot 10^{-3}$ mbar and the reaction was left to proceed for another 72 h. The synthesis of both $PBS_{50}G^l_{50}$ and PBG^l required longer reaction time (300 h) and higher amounts of enzyme (a total of 10% w/w). Finally, a viscous mass was formed, and after cooling down to room temperature the atmospheric pressure was restored with a nitrogen flow to prevent degradation. The resulting solid mass was dissolved in chloroform and filtered using a fluoropore PTFE membrane with 0.5 µm pore size. After evaporating the chloroform, the final solid mass was used for all characterization tasks without further treatment.

1.2.2. CALB activity test

The enzyme activity was tested according to the procedure described by Schwab *et al*.[33] In this test, the transesterification reaction between *p*-nitrophenyl acetate (*p*NPA) and methanol in toluene to yield *p*-nitrophenol (*p*NP) is followed by spectroscopy. A mixture of CALB (10 mg) and toluene (20 mL) was stirred at 40 ºC and a solution of *p*-nitrophenyl acetate (5 mL, 7.25 mmol·L^{-1}) in toluene was added. Immediately following, methanol (20 µL) was added to the mixture. Each 5 minutes aliquots of 0.5 mL were withdrawn and they were dissolved in 9.5 mL of toluene. The *p*-nitrophenol concentration was determined by UV photospectrometry. $\varepsilon_{p\mathrm{NP}}$ (toluene, 304nm) = 9344,5 M^{-1} cm^{-1} and $\varepsilon_{p\mathrm{NPA}}$ (toluene, 304nm) = 2469.1 M^{-1} cm^{-1}. The enzyme activity *a* (nmol of substrate converted by 1 mg of CALB per minute) was calculated using equations 1 and 2.

$$c = \frac{n*Abs - \varepsilon_{pNPA}*C_{0pPNA}}{\varepsilon_{pNP} - \varepsilon_{pNPA}} \qquad \textbf{Eq. 1}$$

$$a = \frac{C*V*x}{M_{CALB}*t} \qquad \textbf{Eq. 2}$$

1.2.3. Antimicrobial activity

The antimicrobial activity was performed following the dynamic shake flask method described by Anthierens *et al*.[34] Lyophilized strains of the microorganisms from CECT (Colección Española de Cultivos Tipo, CECT) were resuspended in TSB (Tryptone Soy Broth) for *Escherichia coli* and *Staphylococcus aureus* and PDB (Potato Dextrose Broth) for *Candida albicans* following the CECT instructions. After 24 h of incubation at 37 ºC, allowed growing in broth and the plate culture in TSA (Tryptone Soy Agar) and PDA (Potato Dextrose Agar) respectively permitted the determination of initial concentration. The inoculated broths were incubated at 37 ºC for 24 h, after which they were diluted to approximately 10^{6} colony forming units (cfu) mL^{-1}. One milliliter of this was used to inoculate sterile erlenmeyers containing 100 mg of each sample ($PBS_{84}G^{I}_{16}$, $PBS_{50}G^{I}_{50}$, PBG^{I} and PBS) and 9 mL of physiological peptone solution [PPS: 8.5 g NaCl and 1 g bacteriological peptone (Oxoid, Hampshire, United Kingdom) per liter of water] to achieve an inoculation level of approximately 10^{5} cfu mL^{-1}. The pH of the PPS solution was adjusted to 5.81 with 0.2% hydrochloric acid for *Escherichia coli* and to 4.34 for *Staphylococcus aureus* and *Candida albicans.* Assays were conducted in a controlled temperature of 37 ºC and constant stirring (200 rpm).

Samples were extracted at periods of time of 20, 40, 60, 120, 480 and 1020 min; 100µL of each sample was cultured in TSA or PDA petri plates in duplicates and incubated for 24 h at 37 ºC, after which they were visually counted. Petri Plate Count Assay was used to determine the microorgasnism concentration expressed as cfu·mL^{-1}. Counts out of the 30-300 cfu range were discarded.

1.3. Results and discussion

1.3.1. Copolymerization of dimethyl succinate and 2-(N,N,N-trimethyl ammonium) dimethyl glutarate iodide with 1,4-butanediol

2-(*N,N,N*-trimethyl ammonium) dimethyl glutarate iodide (TMA-DMG·I) was successfully prepared by quaternization of L-glutamic acid dimethyl ester hydrochloride with methyl iodide.[35] All attempts made to copolymerize TMA-DMG·I and DMS with BD were unsuccessful because the transesterification reaction was unable to proceed neither in solution nor in the bulk. Increasing the temperature or reducing the pressure to favor the release of methanol did not afford any positive result. Neither increasing amounts of CALB produced any perceivable effect. To elucidate if the enzyme activity was affected by the reaction components, activity tests for CALB were carried out using *p*-nitrophenyl acetate as substrate in the presence and in the absence of TMA-DMG·I. The *p*-nitrophenol released in these essays along a period of 60 min of incubation is plotted against time in Figure 1. Whereas in the absence of TMA-DMG·I the hydrolysis of the substrate took place steadily, no reaction occurred in the presence of the quaternary ammonium salt. It can be concluded therefore that the polycondensation reaction could not proceed at a detectable rate because the enzyme was fully inhibited by TMA-DMG·I since the initial stage. This result contrasts with data reported by Lozano *et al*.,[36] who found that ionic liquids made of quaternary imidazolium salts were suitable for carrying out transesterification reactions mediated by CALB.

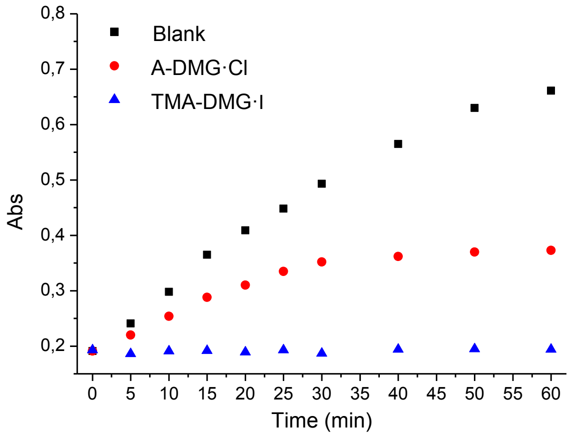
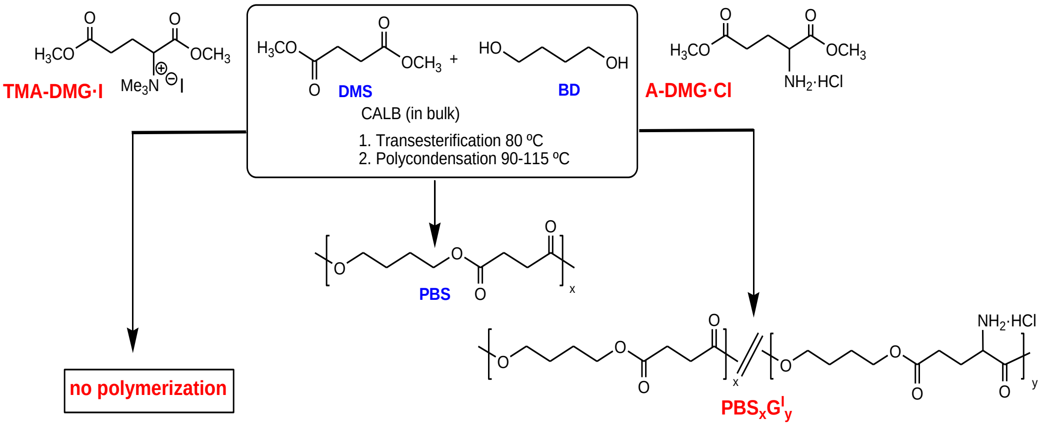


Figure 1. CALB activity test. Absorbance plotted against incubation time for the hydrolysis of *p*-nitrophenol acetate.

1.3.2. Copolymerization of dimethyl succinate and L*-glutamic acid dimethyl ester hydrochloride with 1,4-butanediol*

The route followed for the synthesis of PBS and $PBS_xG^I_y$ by polycondensation in the bulk catalyzed by CALB is depicted in Scheme 1. An excess of BD respect to the diesters was used to ensure the complete displacement of methanol and temperature was increased gradually in order to minimize the thermal decomposition of nitrogen compounds and the denaturation of the enzyme. It is known that enzymes in general are denaturated when they are exposed to temperatures above ~90 ºC, especially in aqueous environments.[33] The CALB was added to the reaction in three successive portions to maintain the enzymatic activity during the whole reaction time. The polycondensation was followed by ^1H NMR which indicated the advance of the transesterification reaction which was found to be complete in six days. Finally the oligomeric mixture was made to polycondensate at 115 ºC under a low pressure to favor the release of the excess of butanediol. As expected, the melt viscosity of the reaction mass increased with the content of G^I units due to the formation of ionic aggregates, which are known to act as simple thermoreversible crosslinks.[37,38] The preparation of $PBS_{50}G^I_{50}$ copolyester and PBG^I homopolyester required to increase both the reaction time and the amount of added enzyme content in order to attain molecular weights of the same range as those obtained for $PBS_xG^I_y$ with low contents in ionic groups.

Synthesis results are shown in Table 1 for both homopolyesters and copolyesters. PBS homopolyester was obtained with an intrinsic viscosity of 0.9 and a number-average molecular weight of 25,000-30,000 with a dispersity of around 2. This is an excellent result for the synthesis of this polyester by enzymatic polycondensation that proves the suitability of the applied procedure. In fact, the molecular weight of PBS prepared to date by such method are reported to be about 3,000.[5] The $PBS_xG^I_y$ copolyesters had M_n in the 13,000-4,000 range with dispersities above 2 and viscosities ranging from 0.36 to 0.60 $dL\cdot g^{-1}$. It was found that the molecular weights of the copolyesters steadily decreased with increasing contents in G^I units. Such trend can be attributed to the action of two disfavoring factors: a) the notable increase of melt viscosity with the increasing content in ionic groups, which makes the reaction mass to act as rubber that attaches to the stirrer impeller preventing the axial flow of the material and the subsequent release of BD, and b) the effect of L-glutamic acid dimethyl ester hydrochloride, that according to the enzyme activity test (Figure 1), partially inhibits the action of CALB. In fact, calculations by applying equation 2 gave lipase activity values of 90 and 52 nmol *p*NP m^{-1} mg^{-1} for the transesterification reaction according to it was performed in absence and presence of A-DMG·Cl, respectively.



Scheme 1. Synthesis route for the preparation of $PBS_xG^I_y$ copolyesters.

Table 1. Composition and molecular weights of PBS and $PBS_xG^I_y$ copolyesters.

	Copolyester composition		Molecular weights			
Copolyester	S/G^{Ia}	S/G^{Ib}	$[\eta]^c$	$M_n{}^d$	$M_n{}^e$	$Đ^d$
PBS	100/0	100/0	0.90	31,000	25,000	1.9
$PBS_{97}G^I_3$	97/3	97.6/2.6	0.60	11,000	13,000	2.1
$PBS_{90}G^I_{10}$	90/10	90.7/9.3	0.45	5,000	5,400	2.5
$PBS_{84}G^I_{16}$	84/16	85.7/14.3	0.40	4,500	5,500	2.6
$PBS_{50}G^I_{50}$	50/50	56/44	0.36	-	4,900	-
PBG^I	0/100	0/100	0.35	-	4,500	-

[a] Molar ratio of monomers in the feed.
[b] Molar composition of the copolyester determined by ^1H NMR.
[c] Intrinsic viscosity ($dL \cdot g^{-1}$) measured in dichloroacetic acid at 25 ºC.
[d] Number-average molecular weight (M_n) ($g \cdot mol^{-1}$) and dispersity ($Đ$) determined by GPC.
[e] Number-average molecular weight (M_n) ($g \cdot mol^{-1}$) determined by NMR end-group analysis.

Both the ^1H and ^{13}C NMR analysis ascertained the chemical structure and composition of the polyesters. The spectra registered from $PBS_{84}G^I_{16}$ as a representative for the series, are shown in Figure 2 with the corresponding peaks assignments. The chemical composition was determined by integration of *f* and *g* signals of ammonium glutarate units and the *b* signals of butylene units. As it can observed in Table 1, the amount of ammonium glutarate incorporated into the copolyester was slightly lower than that used in the feed, the difference being around 10% and practically constant along the whole series.

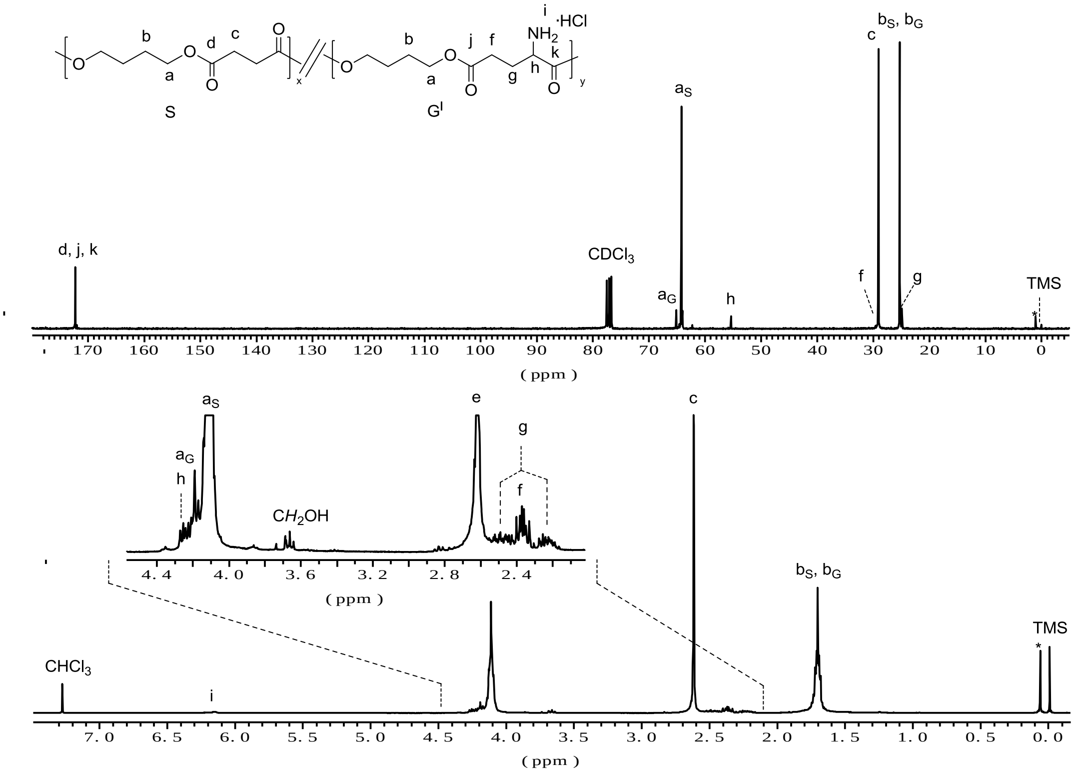


Figure 2. ^{1}H NMR (bottom) and ^{13}C (top) spectra of $PBS_{84}G^{I}_{16}$. (*) Methyl silicone impurity.

1.3.3. Thermal properties

The thermal behavior of homopolyesters and $PBS_xG^I_y$ copolyesters has been comparatively examined by TGA and DSC, and the thermal parameters estimated in this study are given in Table 2. The thermal stability was evaluated under inert atmosphere and the TGA traces recorded for the whole set of polyesters are shown in Figure 3. The comparative analysis of these traces indicates that the thermal stability of $PBS_xG^I_y$ copolyesters steadily decreases with the incorporation of G^I units so both onset (^oT_d) and maximum rate ($^{max}T_d$) decomposition temperatures, oscillate between the values displayed respectively by the parent homopolyesters PBS and PBG^I (Figure 3). In all cases decomposition took place essentially in one stage and the weight left after heating at 600 ºC increased with the ammonium content. Although the resistance to heat of the $PBS_xG^I_y$ ionomers is significantly lower than that of PBS, the ^oT_d -T_m

window is still wide enough as to allow their reversible melting and to be processed therefore by thermal methods.

Table 2. Thermal properties of PBS and PBG^{I} homopolyesters and PBS$_x$G$^{I}_y$ copolyesters.

Copolyester	TGA			DSC				
	$^{o}T_d{}^{a}$ (ºC)	$^{max}T_d{}^{b}$ (ºC)	RW^{c} (%)	$T_g{}^{d}$ (ºC)	$T_m{}^{e}$ (ºC)	$\Delta H_m{}^{e}$ (J·g^{-1})	$T_c{}^{f}$ (ºC)	$\Delta H_c{}^{f}$ (J·g^{-1})
PBS	376	408	0.9	-39	114 (113)	101 (68)	71	-69
PBS$_{97}$G$^{I}_{3}$	374	407	1.1	-37	114 (113)	96 (74)	70	-72
PBS$_{90}$G$^{I}_{10}$	369	406	3.2	-35	98, 107 (106)	58 (43)	53	-43
PBS$_{84}$G$^{I}_{16}$	367	406	1.8	-34	108 (108)	90 (72)	56	-71
PBS$_{50}$G$^{I}_{50}$	343	391	10	-27	77 (81)	63 (37)	-	-
PBG^{I}	292	342	16	-6	85	52 (-)	-	-

[a] Temperature at which a 10% weight loss was observed.
[b] Temperature of maximum degradation rate.
[c] Remaining weight at 600 ºC.
[d] Glass transition temperature measured for melt-quenched samples.
[e] Melting temperatures and enthalpies recorded from pristine samples; in parenthesis, values recorded at the second heating.
[f] Crystallization temperatures and enthalpies registered at cooling from 200 ºC at 10 ºC·min^{-1}.

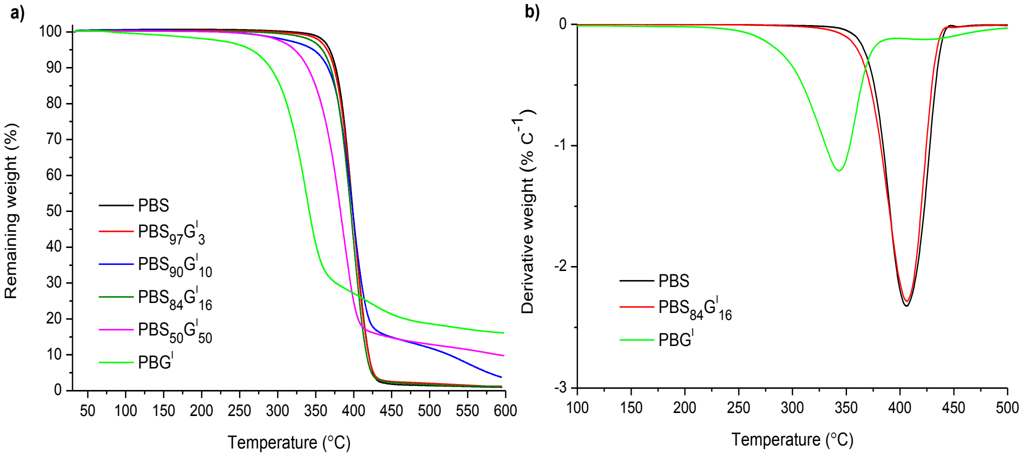


Figure 3. (a) TGA traces of PBS and PBG^{I} homopolyesters, and PBS$_x$G$^{I}_y$ copolyesters. (b) Derivative curves of PBS and PBG^{I} homopolyesters and PBS$_{84}$G$^{I}_{16}$ copolyester.

The heating DSC traces of the polyester samples that had been previously cooled by quenching from the melt showed the slope change characteristic of glass transition for all the studied compositions. The temperatures recorded for such changes revealed that the T_g of PBS steadily increased with the increasing content in G^I units so it goes up from −39 °C for PBS to -6 °C for PBG^I. According to Shohamy *et al.*[39] these results are fully consistent with the effect on T_g that is expected from the occurrence of ionic interactions. The first and second heating DSC traces of the polyester samples coming directly from synthesis are depicted in Figure 4. All $PBS_xG^I_y$ copolyesters as well as PBS and PBG^I homopolyesters produced first heating traces displaying endotherms characteristic of melting which are demonstrative that all they were semicrystalline (Figure 4a). Nevertheless, comparison of melting temperatures and enthalpies of $PBS_xG^I_y$ copolyesters with that of PBS brings into evidence that the insertion of G^I units gives place to a decrease in both T_m and ΔH_m. This is not surprising at all since the ionic side groups are expected to be unable to accommodate in the PBS crystal lattice. The WAXS profiles recorded from PBS and $PBS_xG^I_y$ copolyesters are compared in Figure 5. The crystal structure of PBS, which is characterized by three strong reflections (3.9, 4.0 and 4.5 Å), was not significantly affected by the presence of the ammonium glutarate units. On the contrary, the profile recorded for the PBG^I homopolymer is radically unlike any other revealing the presence of a completely different crystal structure.

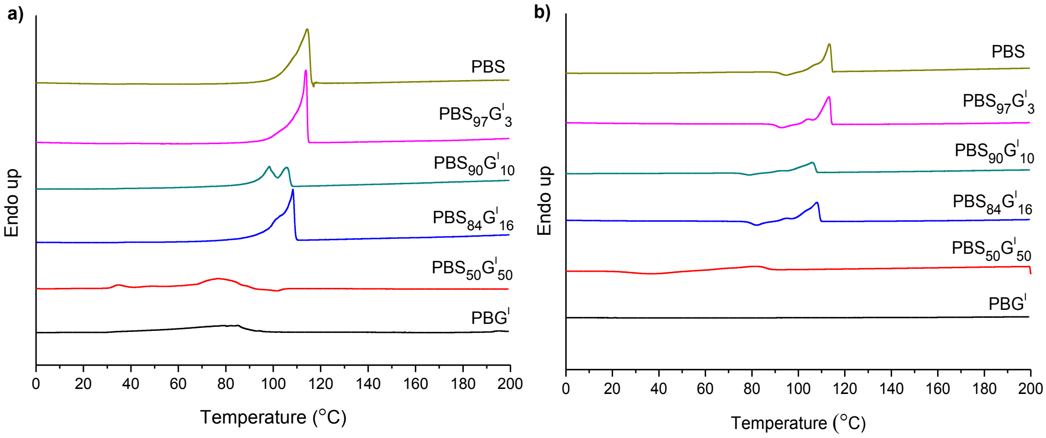


Figure 4. DSC heating traces of PBS and PBG^I homopolyeters and $PBS_xG^I_y$ copolyesters coming directly from synthesis. a) First heating. b) Second heating.

Last it is worth to comment how the crystallizability of PBS is modified by the incorporation of G^I units. Only copolyesters containing 16 mol-% of G^I units as maximum were able to crystallize from the melt and therefore to show melting at the second heating. No sign of crystallization was detected neither for $PBS_{56}G^{I}_{44}$ nor for the homopolyester PBG^I. This limitation is indicative of the depressing effect that the presence of the ammonium groups exerts on the crystallization rate of PBS. Such effect can be interpreted as a combination of two hindering factors, the incompatibility of BS and G^I units to crystallize within the same lattice and the high melt viscosity attained by the copolyester. The former is the simple consequence of the different constitution of the units, whereas the latter is caused by the strong ionic interactions that are characteristic for ionomers.

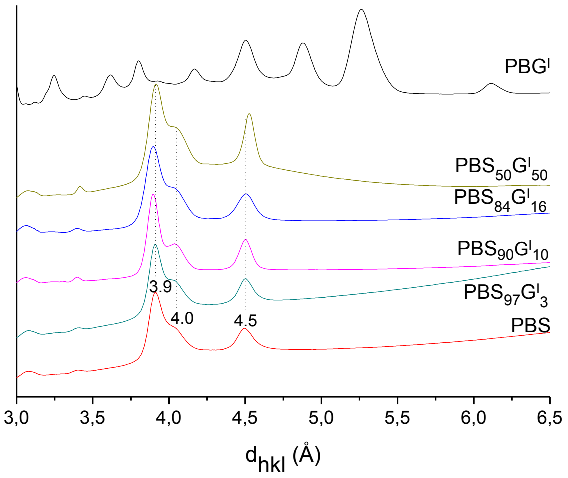


Figure 5. Powder WAXS profiles of PBS and $PBS_xG^{I}_{y}$ copolyesters coming directly from synthesis.

1.3.4. Antimicrobial activity

The antimicrobial activity of the PBS cationic copolyesters containing 16 and 50 mol-% together with the two parent homopolymers was tested on *Escherichia coli, Staphylococcus aureus* and *Candida albicans*. The results attained for the three microorganisms are shown in Figure 6; in the case of *E. coli,* the results revealed a drastic and fast decreasing bacteria viability until complete inactivation in a time of 40 min for PBG^I homopolyester. A decrease in microbial viability was also evident in the presence of the $PBS_{50}G^{I}_{50}$ copolyester, although longer time was now required to achieve a complete inactivation. Riva *et al.*[40] synthesized biodegradable poly(ε-caprolactone) by grafting of pendant ammonium salts by “click” chemistry; a biocidal effect of the quaternary ammonium salt-modified PCL was observed on *Escherichia coli.* They report a fast and complete inactivation of the *Escherichia coli* in 1 h using 126 mg of cationic PCL containing 30 mol-% of ammonium groups in 10 mL of the bacterial solution tested by the dynamic shake flask method. In our case, the $PBS_{50}G^{I}_{50}$ copolyester took a time of 480 min until complete inactivation. The copolyester containing 16 mol-% of ammonium groups did not present any antimicrobial effect showing a behavior similar to both the control and PBS. In fact, the physiological peptane solution (PPS) can be used as a substrate for microorganism growth, if inactivation is not enough. This could explain the growing of *Escherichia coli* after initial inactivation in the control, PBS and $PBS_{84}G^{I}_{16}$.

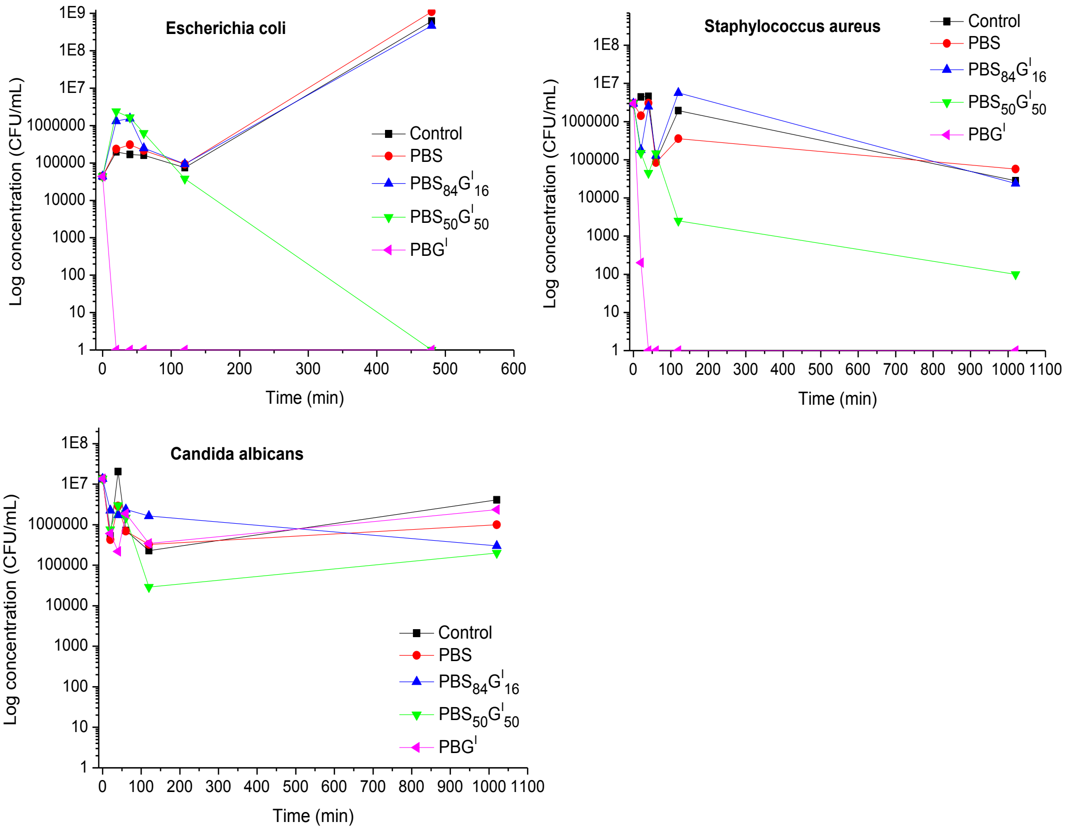


Figure 6. Cell counts of Escherichia coli, *Staphylococcus aureus* and *Candida albicans* during the dynamic shake flask experiment in contact with PBS, PBG^{I} homopolyesters and $PBS_{x}G^{I}_{y}$ copolyesters.

For *S. aureus*, a bacteria that is known to be much more resistant to any adverse factor, it was also observed a powerful and fast inactivation when PBG^I was present. After 2 h, the $PBS_{50}G^I_{50}$copolyester achieved a considerable reduction of the *S aureus* viability, effect that was more pronounced after 17 h. As it happened with *Escherichia coli*, $PBS_{84}G^I_{16}$copolyester did not show antimicrobial effect on *S. aureus* so the response was similar to that given by the control and PBS. According to what is observed for *E. coli*, an increase in the CFU values were expected for control, PBS and $PBS_{84}G^I_{16}$ due to the PPS. However, this increase was not as significant as in the *Escherichia coli,* one explanation can be that the use of PPS at a pH of 4.34 is slightly restrictive for the *S.aureus* growing.

Then assays carried out with *Candida albicans* showed a slight inactivation by the copolyester containing 16 and 50 mol-% of ammonium groups after 17 h. On the contrary no significant changes were observed for the PBG^I homopolyester which is a largely unexpected result without apparent explanation.

1.4. Conclusions

CALB enzymatic mediated polycondensation in the melt has been proved to be a suitable method to produce high molecular weight PBS under mild conditions. The method was also successfully applied to the copolymerization in the melt of dimethyl succinate, L-glutamic acid dimethyl ester hydrochloride and 1,4-butanediol to produce ionic PBS bearing ammonium side groups. The cationic PBS iononomers were obtained however with lower molecular weights compared to PBS. The homopolyester entirely made of glutamic acid was also obtained by the same method with a number-average molecular weight of about 5,000. On the contrary the method systematically failed when the trimethyl ammonium glutamic derivative was used as comonomer. Enzyme activity essays revealed that CALB was partially inactivated by the presence of glutamic acid and completely inhibited by the quaternized derivative.

The new PBS ionomers display a panel of properties that faithfully reflect the presence of the ammonium units in the polyester chain. Their thermal stability decreases respect to PBS but they continue to be heat resistant enough as to be able to be processed in the melt. They are semicrystalline and adopt the same crystal structure as PBS although their melting temperature and crystallinity decrease with the content in ionic groups. At moderate ionic contents they are able to crystallize from the melt under non-isothermal conditions. At difference to all other thermal properties but in parallel to melting viscosity, the T_g regularly increases in the ionomers going up from -39 ºC (PBS) to -6 ºC (PBG^I). Such an enhancing effect of composition is doubtless due the decreasing in chain mobility caused by strong ionic interactions.

The quaternary ammonium salt-modified PBS with contents equal o above 50 mol-% in ionic groups showed a high biocide effect against bacterias. The PBS$_{84}$G$^I_{16}$ copolyester appeared to be practically ineffective since it showed results similar to those observed for the control and the unmodified PBS. It is remarkable that the PBG^I homopolyester has a lethal effect on bacteria in very short times and that PBS$_{50}$G$^I_{50}$ copolyester even retains such biocide efficiency although requiring longer times.

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2. Poly(butylene succinate) ionomers containing phosphonium bromide units

Abstract

Poly(butylene succinate) ionomers copolyesters containing tributylphosphonium groups within the 3 to 14 mol-% range were synthesized by polycondensation in the melt-phase using as second diol 2,2-(dihydroxymethyl)propyl-tributylphosphonium bromide. The phosphonium-containing copolyesters were obtained with molecular weights ranging from 35,000 to 15,000 with values decreasing with increasing contents in phosphonium units. Although the thermal stability of PBS decreased in the ionic copolyesters, they are still able to withstand temperatures well above 250 ºC. All the copolyesters were semicrystalline with melting temperature and enthalpy decreasing with ionic composition. On the other hand, the glass-transition temperature and consequently, the elastic modulus and tensile strength increased with the content in phosphonium units. The high melt viscosity displayed by molten phosphonium PBS ionomers prevents them to crystallize upon cooling. Equimolar mixtures of phosphonium and sulfonated PBS copolyesters were prepared and shown to be able to crystallize from the melt due to the nucleating effect played by the ionic crystallites that are generated in the polymer coupling.

2.1. Introduction

Aliphatic polyesters are among the most promising materials that are suitable for the production of high performance environment friendly plastics. Poly(butylene succinate) (PBS) is a commercially available polyester that is produced by polycondensation of 1,4-butanediol and succinic acid, two traditionally petrochemical compounds that have become today accessible from natural resources. In addition to be sustainable and biodegradable, PBS displays an overall satisfactory pattern of properties including a suitable melting-crystallization behavior as well as good thermal and chemical resistance.[1,2] PBS is therefore a typical thermoplastic that can be processed by different methods such as extrusion, injection molding and thermoforming, and that may be blown in thin films or spun in long continuous fibers.[3,4] Its excellent processability makes it an outstanding candidate for a wide number of applications in both textile and plastic industries.[5-9]

Ionomers are rather unusual polymeric materials that contain minor amounts of anionic or cationic groups (less than 15 mol-%) and that tend to form aggregates displaying a reinforcing effect on the parent polymer.[10-12] Ionic association, even entailing a small concentration of ionic groups, greatly affects polymer physical properties, increasing both the elastic modulus and the glass transition temperature.[13,14] Some PBS ionomers containing anionic groups have been reported in the literature. PBS containing 5-sulfoisophthalate sodium units were prepared and reported to show improved extensibility and noticeable alteration of rheological properties.[15,16] Park *et al*.[17] used PBS ionomers to prepare blends with poly(lactic acid) with the aim at improving the properties of the later. More recently, sodium 1,2-(dimethoxycarbonyl)ethanesulfonate has been used as comonomer of dimethyl succinate to prepare PBS-sulfonate ionomers.[18-20] These ionomers have T_g noticeably higher than PBS and display an enhanced sensitivity towards hydrolytic degradation.

In this paper we wish to report on PBS ionomers containing quaternary phosphonium groups at the pendant sites. The insertion of phosphonium units in polymers is particularly attractive because they provide higher thermal stability and greater antimicrobial activity.[21-24] It has been observed furthermore that phosphonium salts find current application as flame retardants and thermal stabilizers.[25] Although the literature on phosphonium salt containing polymers is abundant very few has been published on polyesters. Anderson *et al*.[26,27] synthesized successfully poly(ethylene terephthalate-*co*-ethylene isophthalate) (PET-*co*-PEI) ionomers end-capped with butyl *p*-carboxyphenyl diphenylphosphonium bromide and observed that the molecular weight of copolyesters decreased with increasing amounts of end-capping agent. They also reported that dissociation of the ionic aggregates in these ionomers took place at temperatures close to 200 °C which pointed to a new route to melt processing of high-performance polymers. Anthierens *et al*.[28] reported on poly(butylene adipate) functionalized with an alkyltriphenylphosphonium group and showed its antimicrobial activity useful for applications in food packaging and for medical purposes.

In the present work the diol 2,2-(dihydroxymethyl)propyl-tributylphosphonium bromide (PPD) was copolymerized with succinic acid and 1,4-butanediol (BD) to obtain poly(butylene-*co*-propylene succinate) containing pendant quaternary phosphonium groups. The new cationic PBS ionomers are abbreviated as PB_xPP_yS where x and y subscripts refer to the mol-% in 1,4-butylene and 1,3-(2-methyl-2-methylenetributylammonium bromide) propylene units present in the copolyester. The synthesis and characterization of these ionomer copolyesters as well as the evaluation of their thermal and mechanical properties were carried out. The complex PBS(PP-SS) formed by ionic coupling interaction of the phosphonium PBS ionomer containing 15 mol-% of ionic units with an isocompositional sulfonated PBS ionomer previously described by us, has been also examined in this work.

2.2. Experimental section

2.2.1. Synthesis of 2-(bromomethyl)-2-methyl-1,3-propanediol

2-(Bromomethyl)-2-methyl-1,3-propanediol was synthesized according to the procedure described in the literature.[30] 1,1,1-Tris(hydroxymethyl)ethane (0.14 mol), diethyl carbonate (0.14 mol) and K_2CO_3 (0.6 mmol) were stirred and heated in a round-bottom flask at 130 ºC for two hours. A clear solution was formed and the pressure was reduced to 20 mbar to distill off all the ethanol generated in the reaction as well as any residual diethyl carbonate. The temperature was then increased to 200 ºC and 3-methyl-3-hydroxymethyloxetane was distilled under reduced pressure (2.1×10^{-3} mbar). Then, 7 mL of concentrated HBr were added dropwise to a stirred solution of 3-methyl-3-hydroxymethyloxetane (50 mmol) in THF (50 mL) placed within an ice bath. The ice was then removed and the reaction was allowed to proceed for 24 h. The solution was neutralized with 125 ml of saturated $NaHCO_3$ and extracted with diethyl ether. The organic phase was separated, dried with Na_2SO_4 anhydrous and the evaporated to dryness. The crude product was recrystallized from toluene. ^1H NMR spectra with their corresponding signals assignments are available in the Figure S1 of the supporting information file (SI).

2.2.2. Synthesis of 2,2-(dihydroxymethyl)propyl-tributylphosphonium bromide (PPD)

This compound was synthesized according with the procedure reported in the literature.[31] 2-(Bromomethyl)-2-methyl-1,3-propanediol (1.05 molar excess) was charged into a dry round-bottomed flask provided with a magnetic stir and purged with a low nitrogen flow. Tri-*N*-butylphosphine (3.7 mL) was added using a dry syringe and the reaction left to proceed at 100 ºC for 3 days under vigorous stirring. Unreacted reagents were distilled from the reaction mixture at 100 ºC and 2.1×10^{-3} mbar. The residual product was washed several times with diethyl ether and dried at 60 ºC under reduced pressure for 24 h. The chemical structure of 2,2-(dihydroxymethyl)propyl-tributylphosphonium bromide was confirmed by both ^{1}H and ^{13}C NMR spectra; these spectra with their corresponding signals assignments are available in the Figure S2 of SI.

2.2.3. Synthesis of poly(butylene succinate) ionomer copolyesters (PB_xPP_yS)

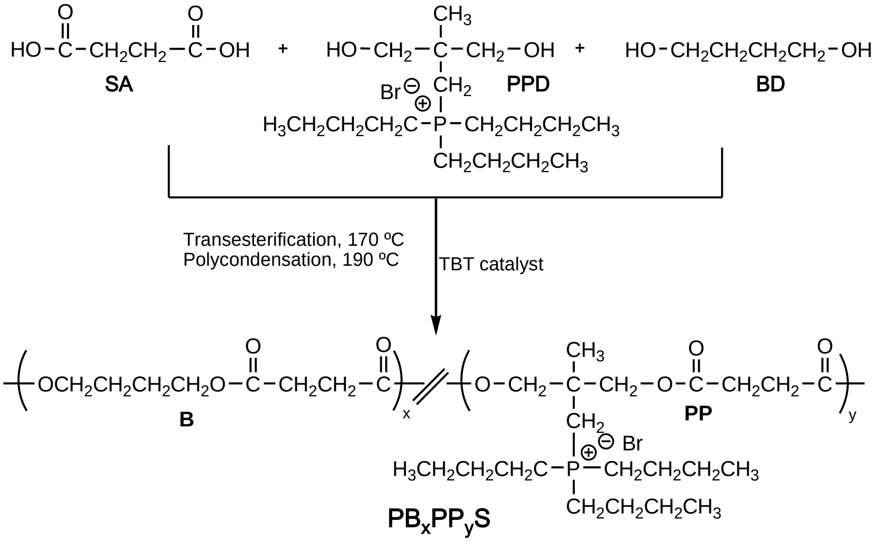
Poly(butylene succinate) ionomer copolyesters containing tributylphosphonium units (PB_xPP_yS) were obtained from succinic acid (SA) and mixtures of 2,2-(dihydroxymethyl)propyl-tributylphosphonium bromide (PPD) and 1,4-butanediol (BD) containing 3, 5, 8, 10 and 15 mol-% of PPD. The reactions were performed in a three necked, cylindrical-bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a vacuum-distillation outlet. An excess 1.4:1 of BD to SA was used and tetrabutyl titanate (TBT, 0.3 w/w % respect to monomers) was the catalyst of choice. Esterification reactions were carried out under a low nitrogen flow at 170 ºC during 8 h. Polycondensation reactions were left to proceed at 190 ºC under a $2.9 \cdot 10^{-3}$ mbar vacuum for 8 h. Finally, the reaction mixture was cooled to room temperature and the atmospheric pressure was recovered with ntrogen to prevent degradation. The resulting solid mass without further treatment was used for the characterization and property evaluation unless otherwise stated.

2.3. Results and discussion

2.3.1. Synthesis and composition

Phosphonium ionomer copolyesters (PB_xPP_yS) were successfully synthesized according to the procedure depicted in Scheme 1. The polymerization reaction was entirely performed in the melt in two successive stages. The first step was conducted at 170 °C and under a nitrogen flow to facilitate the removal of released byproducts. The second step was carried out at 190 ºC to promote the reaction between the oligomers formed in the first step and under high vacuum to favor the releasing of the excess of BD. This polycondensation temperature is significantly lower than that usually applied in the synthesis of PBS homopolyester because it was observed that thermal degradation of PP units due to the occurrence of β-elimination reaction was promoted at higher temperatures. It was also observed that a secondary reaction leading to etherification of BD took place in the presence of increasing PPD in the copolymerization feed. It is worthy to note that the final viscosity attained in the reaction mass increased gradually with the content of PP units as it should be expected from the ionomeric nature of the resulting polymer. A series of PB_xPP_yS copolyesters with contents in phosphonium units ranging from 3 to 15 mol-% in addition to the homopolyester PPPS made of PPD as only diol could be prepared by this procedure in high yields (<90%). Their most relevant characteristics of PB_xPP_yS are collected in Table 1 and compared to those of PBS.

The PBS sample used for reference in this work was obtained by a procedure similar to that used for the synthesis of PB_xPP_yS copolyesters. It had an intrinsic viscosity of 1.0 $dL \cdot g^{-1}$ and a weight-average molecular weight (M_w) of 45,600 with a dispersity of 2.5. On the other hand, the ionic PPPS homopolyester was obtained with an intrinsic viscosity of 0.31 $dL \cdot g^{-1}$ and M_w of 6,000 with a dispersity of 3. Accordingly the PB_xPP_yS copolyesters were obtained with intrinsic viscosities and molecular weights between those of PBS and PPPS and dispersities ranging from 2.0 to 2.5. It is apparent from these results that polymer molar mass tend to decrease with increasing contents in PP units. The reasons for such behavior are thought to be the difficulty for releasing the 1,4-butanediol because the relative low temperature at which polycondensation has to be carried out combined with the high viscosity attained in the molten reaction mixture, which increased with the content of the copolyester in phosphonium units.



Scheme 1. Chemical procedure applied for the synthesis PB_xPP_yS copolyesters.

Table 1. Composition and molecular weights of PBS homopolyester and PB_xPP_yS copolyesters.

	Copolyester composition[a]	Copolyester composition[b]	Diglycol content[c]	Molecular weights		
Copolyester	B/PP	B/PP	mol-%	$[\eta]^d$	M_w^e	$Đ^e$
PBS	100/0	100/0	-	1.00	45,600	2.5
$PB_{97}PP_3S$	97/3	97.1/2.9	1.8	0.68	35.000	2.1
$PB_{95}PP_5S$	95/5	95.2/4.8	2.7	0.64	26.000	2.2
$PB_{92}PP_8S$	92/8	92.7/7.3	3.9	0.54	22.000	2.2
$PB_{90}PP_{10}S$	90/10	90.4/9.6	3.9	0.49	20.000	2.3
$PB_{85}PP_{15}S$	85/15	86.1/13.9	2.9	0.44	15.000	2.4
PPPS	0/100	0/100	-	0.31	6000	3

[a] Molar ratio of comonomers in the feed.
[b] Composition of the copolyester (mol/mol) determined by ^1H NMR.
[c] Composition in glycol in mol-% determined by ^1H NMR
[d] Intrinsic viscosity ($dL \cdot g^{-1}$) measured in dichloroacetic acid at 25 ºC.
[e] Weight-average molecular weight (M_w) ($g \cdot mol^{-1}$) and dispersity ($Đ$) determined by GPC.

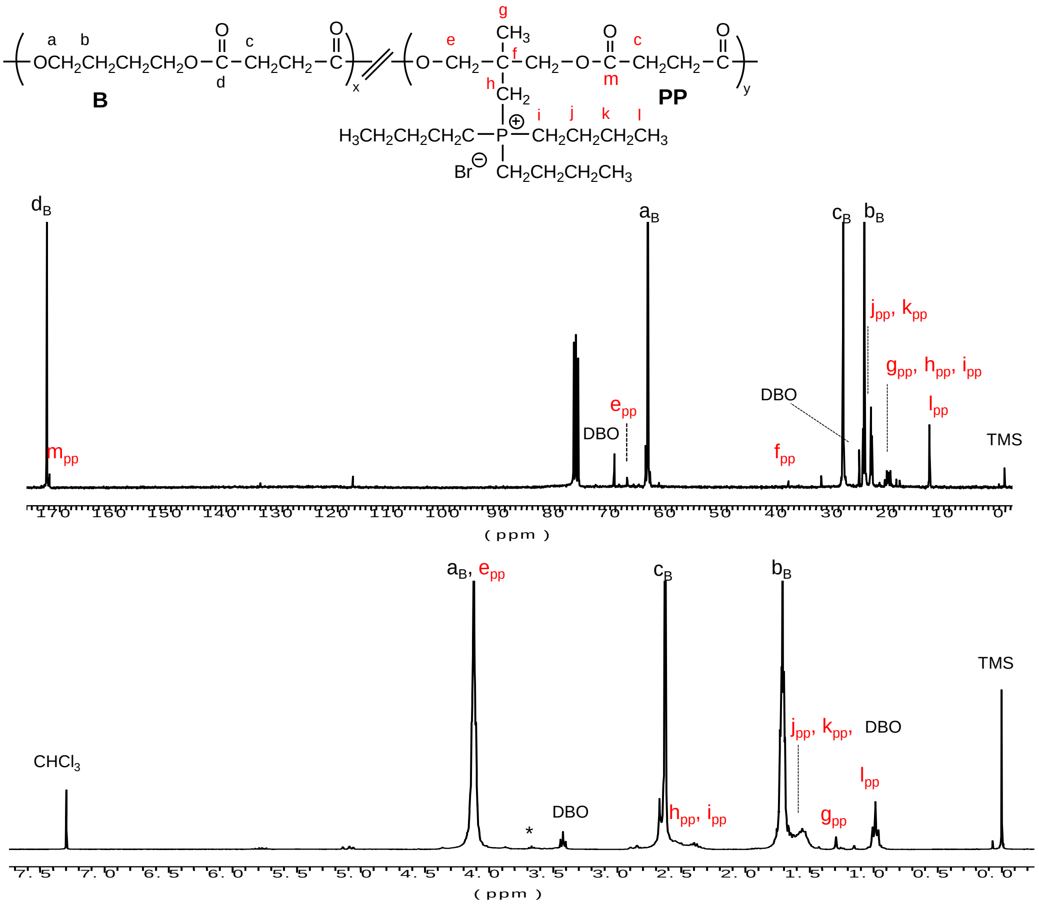


Figure 1. ^{1}H NMR (bottom) and ^{13}C NMR (top) spectra of $PB_{95}PP_{5}S$.

The chemical structure as well as the comonomer composition of PB_xPP_yS were ascertained by NMR spectroscopy. An accurate assignment of the ^{1}H and ^{13}C spectra associated to the different protons and carbons signals present in the copolyesters could be achieved by 2D heteronuclear shift correlation (HETCOR) analysis. Figure 1 shows the ^{1}H and ^{13}C NMR spectra of the $PB_{95}PP_{5}S$ as a representative of the whole series. All copolyesters showed a small signal in the ^{1}H NMR spectra at 3.42 ppm due to the presence of dibutyleneoxide (DBO) units produced by the etherification reaction between two hydroxybutyl units. The content in DBO of the resulting copolyesters oscillated along the 2-4 mol-% range following roughly a trend parallel to the content in phosphonium groups. The occurrence of this secondary reaction leading to the generation of ether groups in the polyester backbone was also reported for the synthesis of PET and PHT copolyesters containing sulfonated units.[14,32]

In those cases however, the content in dialkyleneglycol units in the copolyester achieved much higher values.

The content of the two comonomers in the copolyesters was determined by integration of the proton signals appearing around 0.9 and 4.1 ppm and making calculations that take into account that the latter is a complex signals including arising from both B and PP units. Copolyester compositions are compared with those used in the polymerization feeds for the whole series in Table 1. These data reveal that both diols enter in the growing polymer chain in the approximate same ratio that they had in the initial mixture with losses in PPD comonomer less than 10%.

2.3.2. Thermal and mechanical properties

The thermal behavior of PBS and PPPS homopolyesters and PB_xPP_yS copolyesters has been comparatively studied by TGA and DSC and the thermal parameters resulting from these analyses are given in Table 2. The thermogravimetry traces for the whole series together with the derivative curves for some selected cases are depicted in Figure 2. TGA results bring into evidence that the thermal stability of PBS is significantly reduced by the presence of the phosphonium units with both the onset and maximum rate decomposition temperatures decreasing with increasing contents in ionic groups. In fact the thermal decomposition of PB_xPP_yS copolyesters starts well below 300 ºC whereas in PBS it does above 350 ºC. It is also illustrative that PBS degrades in a single step while the copolyesters degrade through a complex mechanism that involves two or three decomposition stages, depending on their composition (Figure 2b). On the other hand, the remaining weight at 600 ºC of PB_xPP_yS with a content is of 3-5% without showing a clear dependence on the content in PP units.

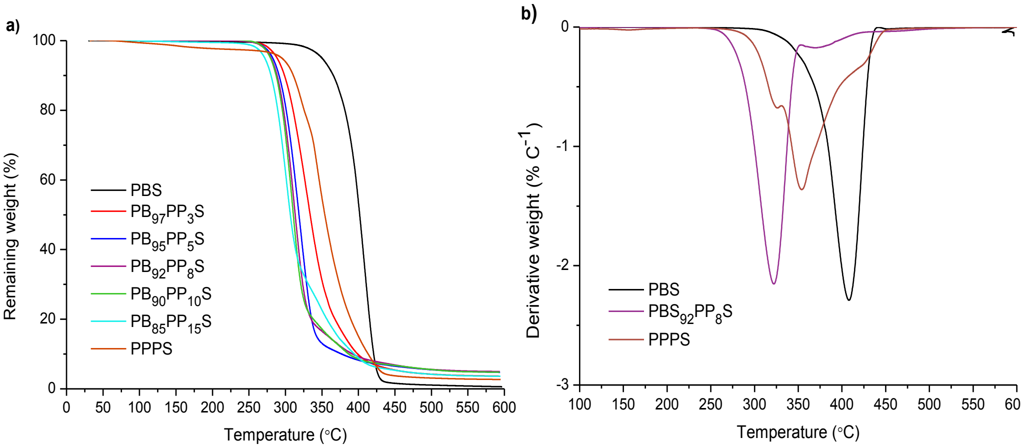


Figure 2. (a) TGA traces and (b) derivative curves of PBS and PPPS homopolyesters and $PB_{92}PP_8S$ copolyesters.

Data recorded by DSC from the PB_xPP_yS copolyesters as well as from PBS and PPPS homopolyesters, are collected in Table 2. According to what should be reasonably expected, the incorporation of ionic groups caused an increase in the T_g of PBS although this enhancing effect was only perceived for PP contents above 5 mol-% which is probably due to the contrary effect resulting from the reduced molecular weight of the copolyesters. The enhancing T_g effect exerted by the presence of phosphonium units is clearly evidenced however when PBS and PPPS homopolyesters are compared in this regard; PPPS has a T_g 8 ºC higher than PBS in spite that its molecular weight is about eight times lower. On the other hand, DSC traces recording at heating from the PB_xPP_yS copolyesters revealed that all they melted within the 94-111 ºC range with both melting temperature and enthalpy decreasing steadily with the content in PP units. Crystallization from the melt is was found to be only feasible for copolyesters with contents in PP units up to 10 mol-%, which is thought to be the consequence of the restricted chain mobility caused by ionic aggregation. All copolyesters included $PB_{85}PP_{15}S$ displayed melting at the second heating at temperatures quite close to those observed for melting at the first heating; $PB_{85}PP_{15}S$ remained uncrystallized after cooling but showed underwent cold-crystallization at the second heating. On the contrary, no heat exchange was detected in none of the DSC traces recorded from the PPPS homopolyester indicating the persistent absence of crystallinity in this polymer. This is a reasonably expected result not only from its largely restricted mobility but also of this polyester and the great bulkiness of the pendant alkylenetributyl phosphonium group. A heating-cooling-heating cycle is depicted in Figure 3a for the representative case of $PB_{95}PP_5S$, and the first heating traces recorded from the whole series are comparatively depicted in Figure 3b.

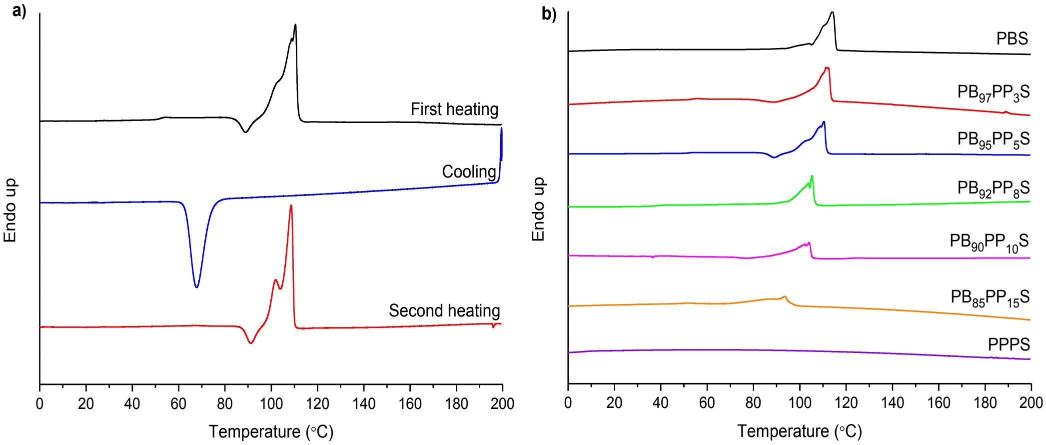


Figure 3. DSC heating traces of PB_xPP_yS copolyesters: a) heating-cooling cycle of $PB_{95}PP_5S$ and b) first heating traces compared for the whole series.

To complement DSC data, powder X-ray diffraction analyses were performed for PB_xPP_yS copolyesters with 5 and 15 mol-% in phosphonium units as well as for the PBS homopolyester. The X-ray diffraction profiles recorded from powdered samples coming directly from synthesis are compared in Figure 4; essentially, the same diffraction pattern including both peak spacing and intensity is shared by PBS and PB_xPP_yS copolyesters. The pattern is distinguished by the presence of three sharp strong reflections at 4.5, 4.1, and 3.9 Å indicating that the monoclinic crystal structure of PBS[33] is retained in the copolyesters. As it has been reported for a number of copolyesters containing minor amounts of one comonomer, the noticeable crystallinity attained in such systems is feasible because crystallites are formed exclusively from homogeneous polymer segments made up of the major comonomer whereas the minor comonomer is segregated to the amorphous phase;[34,35] this is in full agreement with the fact that crystal structure of the parent homopolyester is the same adopted by the copolyesters.

Table 2. Thermal and mechanical properties of PBS homopolyester and PB$_x$PP$_y$S copolyesters.

	TGA			DSC					Stress-strain parameters[g]		
	$^{o}T_d$[a]	$^{max}T_d$[b]	*RW*[c]	T_g[d]	T_m[e]	ΔH_m[e]	T_c[f]	ΔH_c[f]	*E*	σ_{max}	ε_{max}
Copolyester	(ºC)	(ºC)	(%)	(ºC)	(ºC)	(Jg^{-1})	(ºC)	(Jg^{-1})	(Mpa)	(Mpa)	(%)
PBS	356	405	3	-37	113 (114)	77 (67)	78	-62	403±3	26±1	10±0.5
PB$_{97}$PP$_3$S	301	**337**/391	4	-37	111 (111)	71 (67)	70	-60	583±10	28±1	8±0.3
PB$_{95}$PP$_5$S	294	**328**/387	5	-37	111 (109)	68 (66)	68	-59	736±30	29±1	5±0.5
PB$_{92}$PP$_8$S	288	**322**/373	5	-36	105 (104)	48 (56)	58	-53	893±40	19±2	1.4±0.3
PB$_{90}$PP$_{10}$S	288	**318**/356/383	5	-34	104 (102)	42 (35)	58	-35	-	-	-
PB$_{85}$PP$_{15}$S	283	**308**/352/401	4	-31	94 (89)	41 (32)	-	-	-	-	-
PPPS	310	325/**353**/423	3	-29	-	-	-	-		-	-

[a] Degradation temperature at which a 10% weight loss was observed in TGA traces at 10 ºC·min^{-1}.
[b] Temperature of maximum degradation rate.
[c] Remaining weight at 600 ºC.
[d] Glass transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 ºC·min^{-1}.
[e] Melting temperatures and enthalpies were registered at a heating rate of 10 ºC·min^{-1}. In parenthesis, values recorded in the second heating.
[f] Crystallization temperatures and enthalpies were registered at cooling from 200 ºC at 10 ºC·min^{-1}.
[g] Young’s modulus, maximum tensile stress and elongation at break measured at room temperature on a Zwick BZ2.5/TN1S.

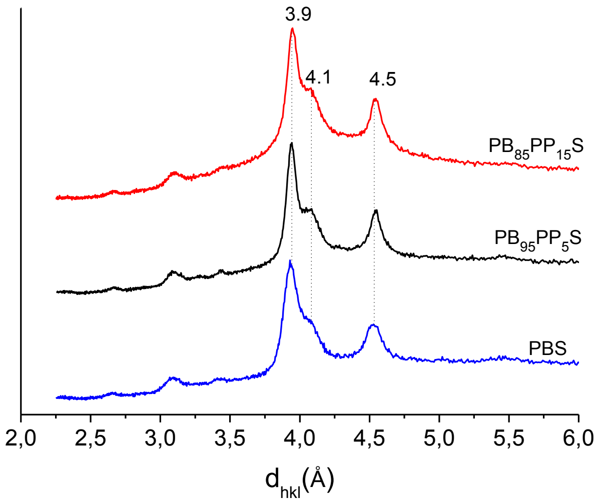


Figure 4. Powder XRD profiles of PBS and PB_xPP_yS copolyesters.

The tensile properties, such as Young's modulus (*E*), the maximum stress (σ_{max}), and the elongation at break (ε_{max}), were determined for amorphous samples of the copolyesters with PP contents equal or below 8 mol-%. Unfortunately, copolyesters containing above 8 mol-% of phosphonium units could not be evaluated because samples were too brittle. The stress−strain curves resulted from tensile essays are depicted in Figure 5 and the mechanical parameters measured therefrom are compared in Table 2. It was found that both the *E* modulus and σ_{max} increased with the content of PP units, whereas at the same time the ε_{max} decreased. It should be noticed that the *E* modulus of PBS increased more than 100% when only 8 mol-% of phosphonium units were incorporated in the chain. Such chain stiffness enhancing effect of the phosphonium units is really amazing and probably it is underestimated; greater *E* values should be expected if PBS and PB_xPP_yS copolyesters with similar molecular weight were compared.

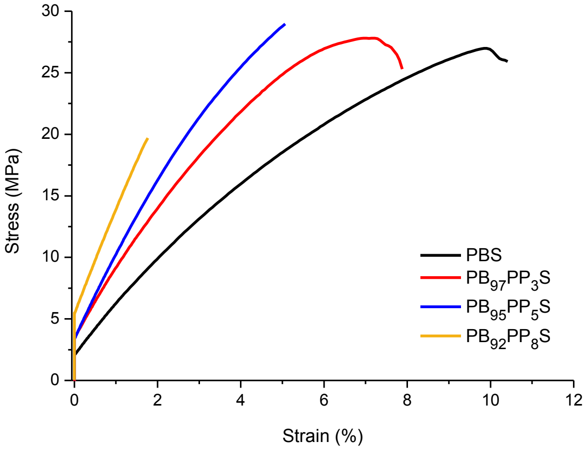


Figure 5. Stress−strain curves of PB_xPP_yS copolyesters.

2.3.3. Ionic coupling with anionic PBS ionomers

Coupling between polyelectrolytes of opposite sign is known to proceed with generation of a polymer heterocomplex stabilized by ionic interactions that distinguishes in displaying properties different to its individual components.[36-38] Anionic and cationic ionomers should be expected to interact ionically too although with not so noticeable results as with polyelectrolytes because the low charge content involved in such cases. In order to investigate this issue for PBS ionomers, the almost isocompositional ionomers $PB_{85}SS_{15}$ and $PB_{85}PP_{15}S$ were made to interact in a 1,1,1.3,3,3-hexafluoro-2-propanol solution and the structure and thermal behavior of the product resulting upon evaporation to dryness was examined by TGA, DSC and powder X-ray diffraction. Data collected in this study for the two ionomers as well as for the mixed compound PBS(PP-SS) are compared in Table 3. The thermal decomposition of the complex increased slightly with respect to the $PB_{85}PP_{15}S$ copolyester and no significant differences in melting temperature were observed between the complex and the isolated components. This is a reasonable result since the low concentration of ionic interactions will not affect crystallite size significantly. On the contrary the glass transition temperature was found to be higher in the complex as it should be expected from the ionic interactions taking place in the amorphous phase of the complex.

Table 3. Compared properties of sulfonated and phosphonium ionomers of PBS and their equimolar mixture

				TGA-DSC				Isothermal crystallization			WAXS
	Ionic (mol-%)	$[\eta]$[a] (dL·g^{-1})	M_w[b] (g·mol^{-1})	ºT_d[c] (ºC)	T_g[d] (ºC)	T_m[e] (ºC)	T_c[f] (ºC)	$t_{(1/2)}$ (min)	n	-log$K$	d (Å)
PBS$_{85}$PP$_{15}$S	13.9	0.44	15,000	283	-31	89	-	-	-	-	3.9, 4.1, 4.5
PBS$_{85}$SS$_{15}$	13.8	0.74	33,000	315	-32	106	-	3.8	2.1	1.4	3.9, 4.1, 4.5
PBS(PP-SS)	-	0.68	-	289	-29	104	48	1.9	1.9	0.5	3.9, 4.1, 4.5 (**2.9, 3.4**)

[a] Intrinsic viscosity (dL·g^{-1}) measured in dichloroacetic acid at 25 ºC.
[b] Weight-average molecular weight (M_w) (g·mol^{-1}) determined by GPC.
[c] Degradation temperature at which a 10% weight loss was observed in TGA traces at 10 ºC·min^{-1}.
[d] Glass transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 ºC·min^{-1}.
[e] Melting temperatures was registered at a heating rate of 10 ºC·min^{-1}.
[f] Crystallization temperatures and enthalpies were registered at cooling at 10 ºC·min^{-1}.

Nevertheless, the most obvious difference between the ionomers and the complex was observed for crystallization. As it is shown in Figure 6, no crystallization upon cooling from the melt at 10 ºC·min^{-1}could be detected for none of the two ionomers whereas a strong exothermic peak characteristic of crystallization was observed at 48 ºC for the complex. The exceptional capability of PBS(PP-SS) to crystallize from the melt is interpreted to be due to the nucleating effect exerted by the ionic microcrystallites present in the complex. To ascertain this effect, an isothermal crystallization experiment was comparatively carried out. After checking for optimum conditions, the temperature selected was 70 ºC in spite that at this temperature the crystallization of $PB_{85}PP_{15}S$ proceeded so slowly that enthalpy recording in the DSC was not practically feasible. The figures showing the relative crystallinity advance with time as well as the double logarithmic *T-t* plots are accessible in the SI file (Figure S3). Kinetics parameters resulting from the application of the Avrami approach (Table 3) revealed that crystallization of $PB_{85}SS_{15}$ took place with a $t_{(1/2)}$ approximately double than in the complex with no significant changes in the crystallization mechanism.

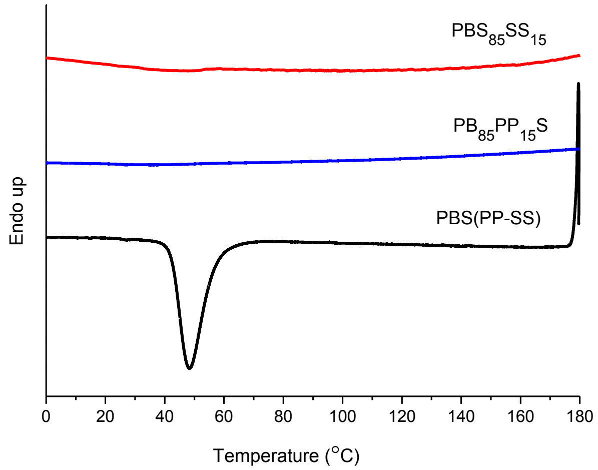


Figure 6. DSC traces registered at cooling from the melt for the ionomers and the complex.

The occurrence in the complex of microcrystallites integrated by sulfonate and phosphonium ions and their role as crystallization nucleating agent was brought into evidence by X-ray diffraction. The powder XRD profiles registered from the two ionomers and the complex at room temperature are compared in Figure 7. The three profiles display the pattern characteristic of PBS with strong peaks at 3.1, 3.9 and 4.5 Å indicating that the same crystal structure is adopted in the three cases. In addition, two peaks at about 3.4 and 2.9 Å were perceived in the trace recorded from PBS(PP-SS). These peaks are sharp and of low intensity as it should correspond to small well-done crystallites made of ionic motives. After heating at temperatures above melting, the XRD profile of the complex displayed, as expected, a broad scattering characteristic of amorphous material but with the two small peaks still appearing. After cooling the PBS crystalline diffraction was recovered so the final pattern became similar to the original one. It can be concluded therefore that ionic crystallites are preserved in the molten state and they will act therefore as effective nuclei in the crystallization of PBS.

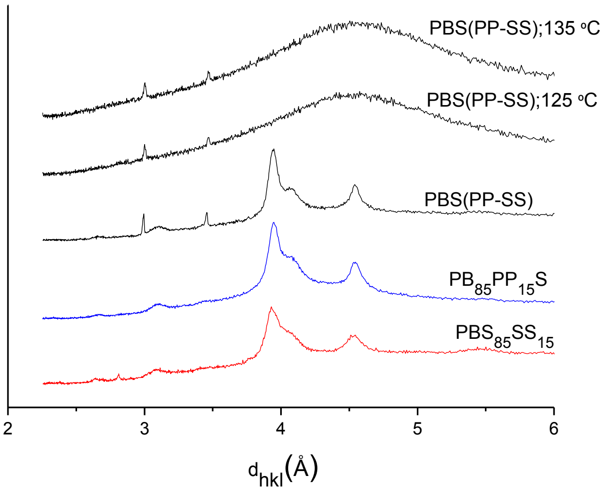


Figure 7. XRD profiles of $PBS_{85}SS_{15}$ and $PB_{85}PP_{15}S$ copolyesters and CPBS(PP-SS) complex. XRD profiles of PBS(PP-SS) was carried out at 125 and 135 ºC.

2.4. Conclusions

Phosphonium bromide poly(butylene succinate) ionomers were synthesized for the first time from succinic acid, 2,2-(dihydroxymethyl)propyl-tributylphosphonium bromide and 1,4-butanediol. Polycondensation could be conducted in the melt phase with careful adjustment of the reaction temperature used in the second polymerization step. Nevertheless, the molecular weight of the ionomers notably decreased as the content in phosphonium units increased. The thermal stability of PBS decreased with the content in phosphonium units but the resistance to heat of the copolyesters remained satisfactorily high without showing perceivable decomposition up to temperatures above 280 ºC. All PB_xPP_yS copolyesters were semicrystalline with melting temperatures and enthalpies slightly lower than for PBS. They were able to crystallize at cooling from the melt for contents in phosphonium units of 10 mol-% as maximum. The T_g of the ionomers steadily increased with the content in phosphonium groups displaying values between those of the parent polysuccinates made of one or the other diol, respectively. Both the elastic modulus and tensile strength of the copolyesters were found to increase with the content in phosphonium units but the elongation at break decreased. The thermal behavior observed is consistent with the presence of ionic aggregates located in the amorphous phase of crystallized material. It was demonstrated that 15 mol-% cationic PBS ionomers containing phosphonium units are able to couple with 15 mol-% anionic sulfonated PBS ionomers to produce a semicrystalline complex with similar T_m but higher T_g. The microcrystallites resulting from the interactions between oppositely charged ions in the complex were still present after melting so that they act as efficient nuclei in the crystallization of the ionomers from the molten state.

2.5. References

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2.6. Supporting information

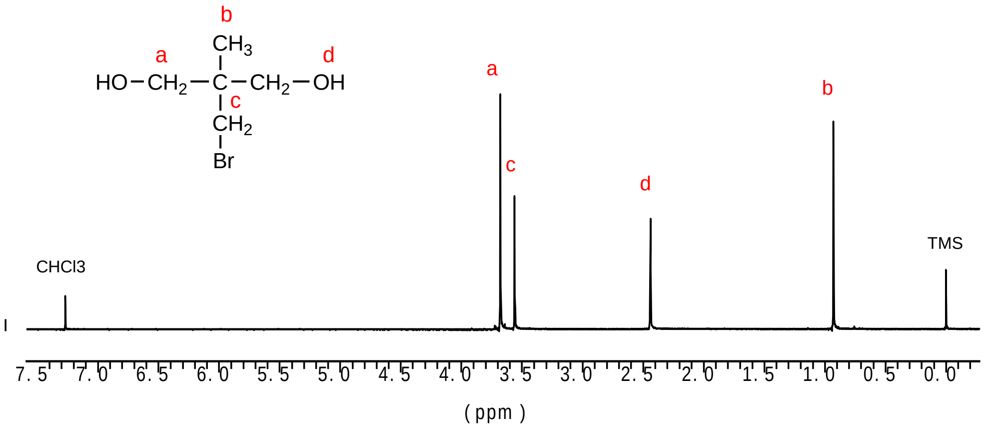


Figure S1. ^{1}H NMR spectrum of 2-(bromomethyl)-2-methyl-1,3-propanediol.

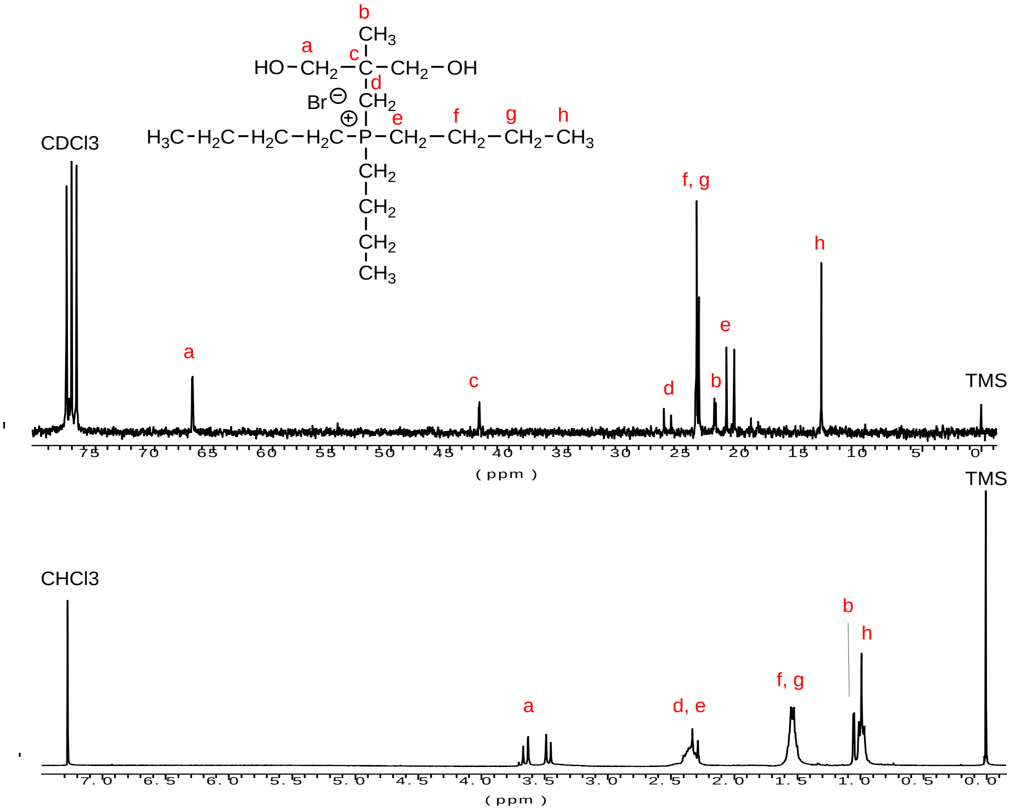


Figure S2. ^{1}H NMR (bottom) and ^{13}C NMR (top) spectra of 2,2-(dihydroxymethyl)propyl-tributylphosphonium bromide.

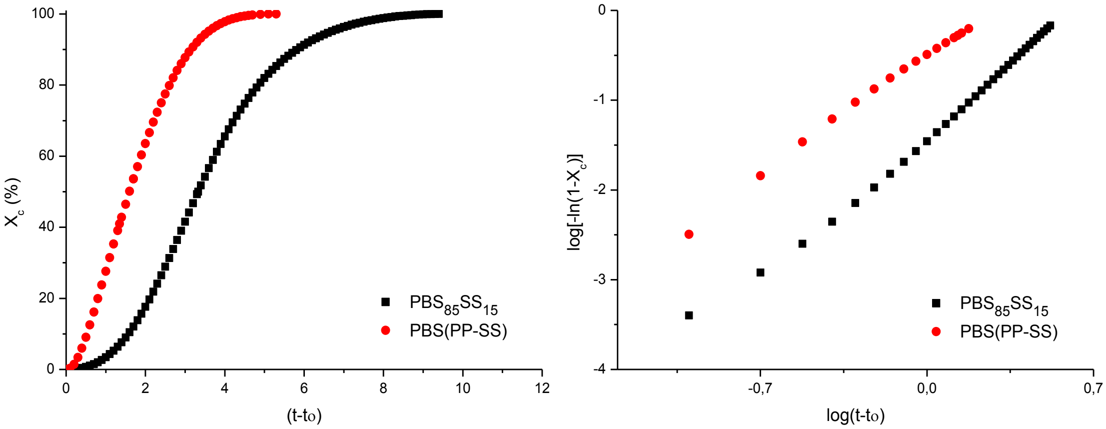


Figure S3. Isothermal crystallization of $PBS_{85}SS_{15}$ copolyester and PBS(PP-SS) complex at 70 ºC. Relative crystallinity versus time plot (a) and log−log plot (b).

Chapter V.

Ionomer polyesters-based nanocomposites

1. Poly(butylene succinate) ionomers and their use as compatibilizers in nanocomposites

Abstract

A series of low molecular weight poly(butylene succinate-*co*-glutarate-*co*-2-trimethylammonium chloride glutarate) terpolyester ionomers containing 35 mol-% of total glutarate units but varying in the content of charged units were synthesized by polycondensation at mild temperatures using a scandium catalyst. The terpolyester ionomers started to decompose at temperatures of > 175 ºC and all of them were semicrystalline and have glass transition temperature similar to poly(butylene succinate) (PBS). These terpolyesters were used to compatibilize the nanocomposites made of PBS-Cloisite (CL) prepared by melt extrusion. X-ray difraction revealed that an intercalated structure was present in these nanocomposites. The thermal properties of the three-component mixtures did not differ substantially from those of PBS·CL but the mechanical properties were significantly improved by addition of the ionomer, in particular tenacity. The beneficial effect afforded by the terpolyester ionomer was attributed to its ability for strengthening the binding between PBS and the nanoclay.

1.1. Introduction

Poly(butylene succinate) (PBS) is a well-known aliphatic polyester that is synthesized from succinic acid (SA) and 1,4-butanediol (BD) in a variety of grades to give response to a wide assortment of applications. This polyester exhibits a balanced performance in thermal and mechanical properties, as well as a thermoplastic processability comparable to other common plastics.[1-3] The production of the PBS monomers from renewable resources is rapidly advancing so that this polyester is breaking through other polyesters of widely recognized sustainability such as poly(lactic acid)[4] and poly(hydroxyalkanoate)s.[5] Today bio-based PBS is a good candidate to be ecofriendly used in high tonnage applications such as packaging, nonwovens, and mulch films. On the other hand, PBS is comparable to other biodegradable polyesters such as poly(ε-caprolactone) and poly(glycolic acid) regarding its potential as a biomaterial for temporal applications. Nevertheless the T_g and mechanical behavior of PBS are far from what it would be desirable, in particular when aromatic polyesters are concerned, a drawback that is hampering its penetration in some fields traditionally occupied by fossil fuel derived thermoplastics.

Layered silicate nanocomposites have been proposed as a good option to improve the physical properties of aliphatic polyesters and they are emerging as the next generation of biodegradable materials.[6-8] Someya *et al*.[8] prepared nanocomposites made of PBS and organo-modified montmorillonites by melt intercalation and subsequent injection molding. These nanocomposites displayed a high degree of intercalation and showed tensile and flexural moduli higher than PBS but lower tensile strength. Ray *et al.*[9] reported on the same type of nanocomposites prepared by simple melt extrusion. Also, a good intercalation of the silicate layers into the polymeric matrix was attained by this method and the nanocomposites also exhibited remarkably improved mechanical properties in both solid and melt states compared with neat PBS. Nevertheless, all PBS nanocomposites containing nanoclays are found to be significantly less tough than the polyester because flowing at high deformations becomes largely restricted, an effect that is a commonly observed in polymer nanocomposites. Strikingly, this effect is not observed in nanocomposites of poly(butylene succinate-*co*-adipate) made of Cloisite 30B obtained by melt-extrusion, which exhibited substantial increase in both stiffness and elongation at break compared to the copolyester.[10] It seems, therefore, that a high degree of intercalation is not enough to provide a general improvement of the mechanical behavior of nanocomposites of PBS but that a deeper interaction between polymer and silicate has also to be attained.

The ionomer concept has been also employed to improve some aspects of the mechanical behavior of polymers and in particular to get better interactions with charged fillers in nanocomposites.[11,12] Han *et al*.[13,14] reported a series of PBS ionomers containing 5-sodium sulfoisophthalate units prepared by bulk polycondensation. The presence of small amounts of sulfonate groups in PBS provided higher melt viscosity and improved certain thermal and mechanical properties significantly. However the ionomer structure unavoidably entails a decrease in crystallinity, an effect that is especially detrimental for aliphatic polyesters displaying low or moderate glass transition and melting temperatures, as it is the case of PBS.

In this work, an ionomer is designed and synthesized to be used as compatibilizer in PBS/cloisite (CL) nanocomposites prepared by melt extrusion. The ionomer is a PBS terpolyester ($PBS_xG_yG^I_z$) containing minor amounts of glutarate units both unmodified and modified with a trimethylammonium group attached to the α-backbone carbon. It is expected that this ionomer is capable of interacting strongly with the nanoclay creating an in situ organomodified montmorillonite with good accessibility to PBS. Several nanocomposite compositions varying in the ionomer content and the PBS/compatibizer or the PBS/nanoclay ratios have been prepared and their thermal and mechanical properties were comparatively evaluated to appraise the effect of the compatibilizer on the PBS/CL nanocomposites.

1.2. Experimental section

1.2.1. Synthesis of 2-(*N,N,N*-trimethylammonium)-glutaric acid chloride (TMAGA·Cl).

2-(*N,N,N*-trimethylammonium)-glutaric acid chloride was synthesized according to the general procedure described in the literature for quaternization of amines.[15] Efficient quaternization of L-glutamic acid dimethyl ester was attained by using iodomethane in methanol. The reaction was carried out by stirring a mixture of 20 g of iodomethane, 4 g of $NaHCO_3$ and 1 g of glutamic acid dimethyl ester in 100 mL of methanol at room temperature for 24 h. The residue left after evaporation to dryness of the reaction mixture was extracted with $CHCl_3$ and the extract was evaporated to give a solid that was crystallized from chloroform-hexane solution (80/20). The obtained 2-(*N,N,N*-trimethylammonium) dimethyl glutarate iodide (TMA-DMG·I) was subjected to basic hydrolysis. The hydrolysis process was monitored by NMR by following the decreasing of the methoxy proton signal so that the reaction was considered to be finished when no trace of this group was observed in the spectra, which took about 5 h. The aqueous basic solution was acidified with concentrated HCl and then evaporated to dryness at 40 ºC. The solid residue was extracted with acetone and TMAGA·Cl was recovered from the extract upon evaporation.

1.2.2. Synthesis of $PBS_xG_yG^I_z$ terpolyesters

Poly(butylene succinate-*co*-glutarate-*co*-2-trimethylammonium glutarate chloride) ($PBS_xG_yG^I_z$) terpolyesters were prepared according to the synthetic route shown in Scheme 1. A mixture of the three diacids (SA, GA and TMAGA·Cl), 1,4-butanediol and catalyst ($Sc(NTf_2)_3$) with the adjusted proportions was dissolved in acetonitrile (3 mL) in a three-necked cylindrical round-bottomed flask equipped with a mechanical stirrer. The acetonitrile was used to obtain a good mixture of the monomers. A molar ratio of 1:1 of BD to the total of diacids with 0.3 mol-% of $Sc(NTf_2)_3$ with respect to the monomers was used. The esterification reaction was left to proceed at 80 ºC under a nitrogen atmosphere for a period of 35-40 h along which water and acetonitrile were continuously distilled out. Then, the polycondensation reaction was initiated by raising the temperature up to 90 ºC and reducing the pressure down to 0.03 mbar. After 100 h, a viscous mass was formed which was cooled down to room temperature and the atmospheric pressure in the flask was restored with a nitrogen flow to prevent degradation. The final solid mass was used for characterization and properties evaluation without any further treatment.

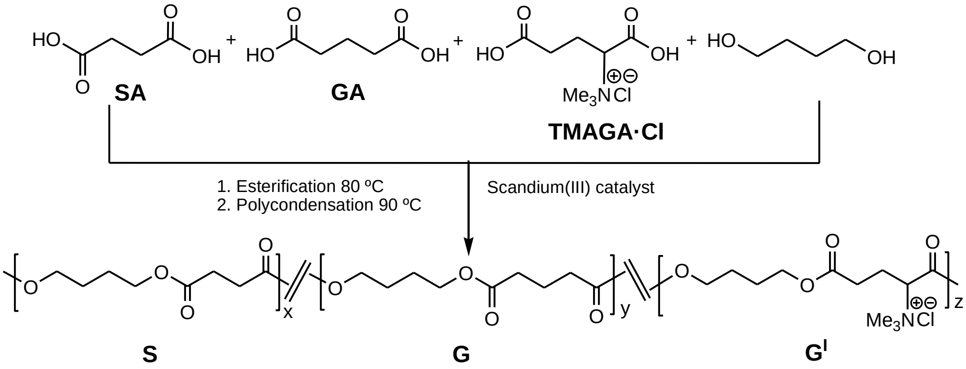
1.2.3. Preparation of $PBS\cdot CL\cdot w\%(PBS_{65}G_{20}G^I_{15})$ nanocomposites

The mixtures of PBS and $PBS_{65}G_{20}G^I_{15}$ terpolyester ionomer at concentrations of 5, 10 and 20% w/w, all of them containing 3% w/w of CL were extruded in a miniextruder machine at a temperature 10 °C above the melting temperature of PBS for a residence time of 20 min and with the screw rotating rate fixed at 75 rpm.

1.3. Results and discussion

1.3.1. Synthesis and chemical characterization of $PBS_xG_yG^I_z$ terpolyester ionomers

The synthesis pathway leading to the $PBS_xG_yG^I_z$ terpolyester ionomers is shown in Scheme 1. Acetonitrile was the solvent of choice as it afforded a homogeneous mixture of the initial reaction mixture. The procedure consists of two successive steps: (1) an esterification reaction leading to low-molecular-weight oligomers and (2) the polycondensation of the oligomers formed in the previous step to render the final terpolyesters. The first step was carried out at 80 ºC with the removal of the released water and acetonitrile and the second one was carried out at higher temperatures under high vacuum to speed up the esterification reaction and to favor the removal of water to unbalance the equilibrium toward the formation of high-molecular-weight polymers. Scandium (III) trifluoromethane sulfonimide was chosen as a catalyst according to recent literature,[16] as it has been reported to be active at relatively low temperatures. In fact, the use of low-reaction temperatures is an essential requirement for these polycondensations to proceed successfully as temperatures of > 100 ºC promote the thermal decomposition of TMAGA·Cl. All the terpolyesters were obtained in high yields (~90%) but with rather low molecular weights (Table 1). The intrinsic viscosity of $PBS_xG_yG^I_z$ ranged between 0.41 and 0.44 dL g^{-1}.



Scheme I. Polymerization reactions leading to $PBS_xG_yG^I_z$ terpolyesters.

The chemical structure and composition of $PBS_xG_yG^I_z$ terpolyesters was ascertained by NMR spectroscopy assisted by COSY 2D NMR spectrum for signal assignment. The ^1H and ^{13}C NMR spectra of $PBS_{65}G_{25}G^I_{10}$ are shown in Figure 1 as a representative of the series. The chemical composition was determined by the integration of signals appearing at ~2 ppm for the central CH_2 of the glutarate unit, at ~3.3 ppm for the CH_3 of the trimethylammonium glutarate unit and at ~2.7 ppm arising from the CH_2 of the succinate unit.

Table 1. Composition and molecular weights of PBS and $PBS_xG_yG^I_z$ terpolyesters.

	Composition		Molecular weight		
Copolyester	$S/G/G^{Ia}$	$S/G/G^{Ib}$	$[\eta]^c$	$M_w{}^d$	$Đ^d$
PBS	100/0/0	100/0/0	1.33	112,000	2.2
$PBS_{65}G_{32}G^I_3$	65/32/3	66.4/31/2.6	0.43	10,300	2.1
$PBS_{65}G_{30}G^I_5$	65/30/5	64.3/29.7/5.9	0.44	10,600	2.2
$PBS_{65}G_{27.5}G^I_{7.5}$	65/27.5/7.5	65.6/27.8/6.6	0.42	10,400	2.3
$PBS_{65}G_{25}G^I_{10}$	65/25/10	67/24.8/8.2	0.41	10,200	2.5
$PBS_{65}G_{20}G^I_{15}$	65/20/15	67.8/19.9/12.3	0.41	9,500	2.5

[a] Molar ratio of monomers in the feed.
[b] Molar composition of the terpolyester determined by ^1H NMR.
[c] Intrinsic viscosity ($dL\cdot g^{-1}$) measured in dichloroacetic acid at 25 ºC.
[d] Weight-average molecular weight (M_w) ($g\cdot mol^{-1}$) and dispersity (*Đ*) determined by GPC.

The results are summarized in Table 1, which shows that the content of the terpolyesters in trimethylammonium glutarate units was, in general, slightly lower than in the feed. The small differences must be attributed to the elimination of the trimethylammonium taking place by effect of heating during the polycondensation reaction.

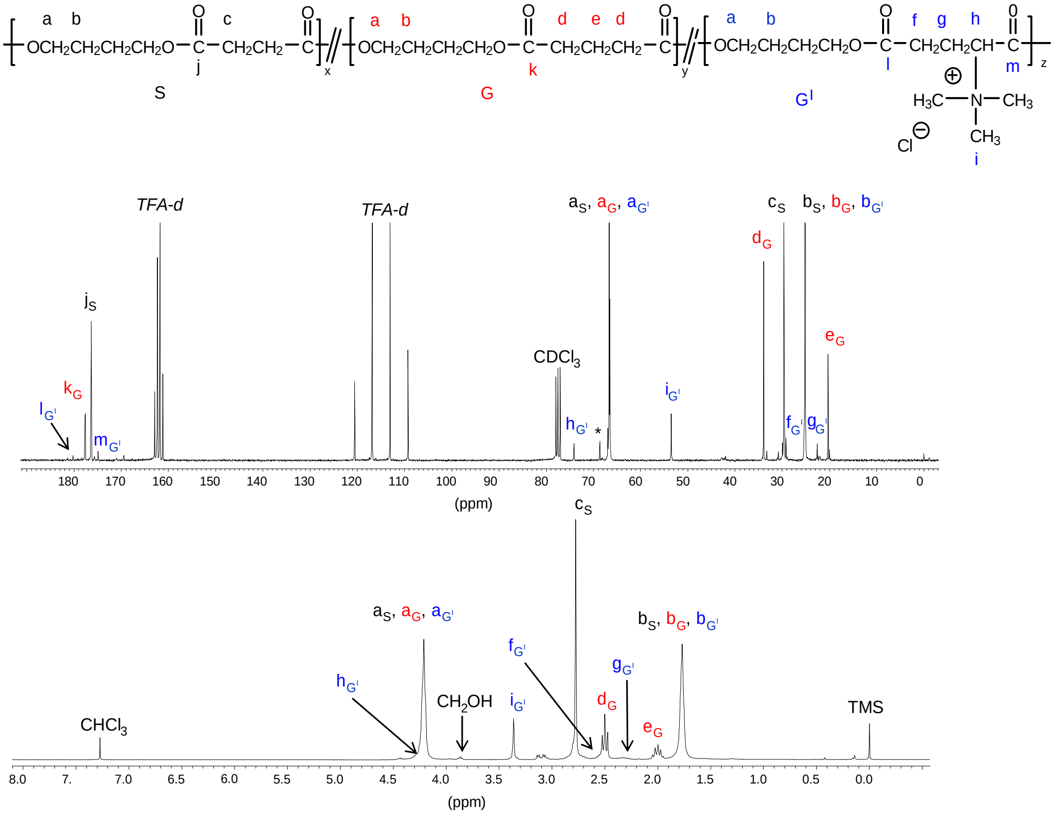


Figure 1. ^{13}C NMR (top) and ^{1}H NMR (bottom) of $PBS_{65}G_{25}G'_{10}$ terpolyester. Asterisk indicates CH_2OH end groups.

1.3.2. XRD analysis

The crystalline structure of the copolyesters and the dispersion degree of the nanocomposites was examined by XRD. The representative XRD profiles are shown in Figure 2 together with that produced by CL for comparison. The diffraction pattern of CL is well known to consist of a main reflection close to 1.0-1.1 nm corresponding to the interlayer spacing together with a series of wide-angle reflections arising from the aluminum silicate crystalline lattice.[17] On the other hand, semicrystalline PBS is characterized by a diffraction pattern containing three strong reflections at 0.45, 0.40, and 0.39 nm produced by the monoclinic crystal structure adopted by this polyester.[18] The XRD profiles obtained from the nanocomposites both from PBS alone and from PBS blended with 20% of either the PBSG copolyester or the PBSGG^{I} ionomer are very similar, and all of them display the reflection characteristic of PBS indicating that the crystalline structure of the homopolyester is fully retained not only in the copolyesters but also in the mixtures with the clay. The presence of the intercalated structure in the nanocomposites is evidenced by the displacement toward smaller angle observed for the ~1.0 nm montmorillonite peak which appears in the mixtures around 1.25 nm. As the intensity and position of this peak is practically the same for the three samples, it can be concluded that a similar intercalation degree is attained in the three cases.

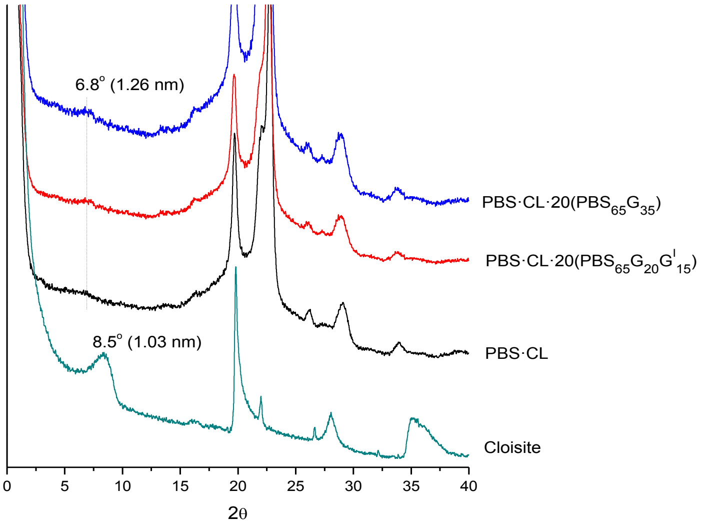


Figure 2. Powder XRD profiles recorded from nanocomposites and CL.

1.3.3. Thermal properties

The effect exerted by the incorporation of glutarate units on the thermal properties of PBS was assessed by TGA and DSC. TGA essays addressed to evaluate the thermal stability were conducted under a nitrogen atmosphere in a temperature range of 30-600 ºC. The TGA heating traces registered for $PBS_xG_yG^I_z$ terpolyesters are shown in Figure 3a together with the trace obtained for PBS that is included for comparison. Derivative curves showing the maximum decomposition rates for PBS and the $PBS_{65}G_{20}G^I_{15}$ are compared in Figure 3b. The characteristic decomposition data afforded by TGA are summarized in Table 2, which reveals that the thermal stability of the terpolyesters is significantly lower than that of PBS with the ${}^{o}T_d$ going down near to

90 ºC for the polymer containing 35% of glutarate units. Although a decrease in molecular weight will be in part responsible for the loss of thermal stability observed for the terpolyesters, it is unquestionable that decomposition temperatures, both the onset and the maximum rate, decrease steadily with the content in G ad G^I units. Furthermore, the insertion of glutarate units makes that decomposition proceeds through two stages with maximum decomposition rates at around 355 and 400 ºC, respectively, whereas PBS decomposes in one single step at 408 ºC. It is concluded therefore that the insertion of G and G^I units in PBS not only decreases its thermal stability but also makes the decomposition mechanism more complex.

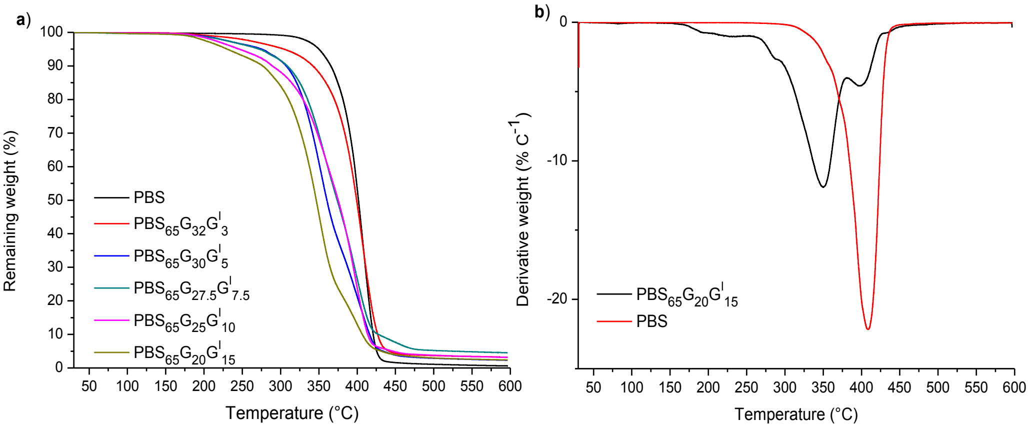


Figure 3. TGA traces of PBS and $PBS_xG_yG^I_z$ terpolyesters (a). Derivative curves of PBS and $PBS_{65}G_{20}G^I_{15}$ (b).

For the determination of the thermal stability of the nanocomposites, the measurements of TGA were carried out under an oxidative atmosphere over a temperature range of 30-800 ºC. The TGA traces recorded from nanocomposites made from PBS containing CL with and without compatibilizer are shown in Figure 4, and the decomposition data afforded by this analysis are compared in Table 2. The results reveal that the addition of 3% of CL slightly modifies the thermal stability of PBS but has a significant beneficial effect on the thermal behavior of the ionomer terpolymers. In fact, the onset decomposition temperature of PBS·CL containing 3% of nanoclay is 7 ºC higher than that of PBS, whereas the maximum decomposition rate temperature is essentially the same. Such slightly beneficial effect of the clay on the thermal stability of PBS has been previously reported.[19] When the $PBS_{65}G_{20}G^I_{15}$ terpolyester is added to the PBS·CL mixture, the resulting nanocomposites show a single decomposition process practically undistinguishable from that observed for PBS·CL (Figure 4b). Furthermore the $^{max}T_d$ observed for these three-component nanocomposites hardly change with the content in ionomer. What is particularly relevant is the behavior observed for the onset temperature which was found to be about 40 ºC higher than those of the isolate terpolyester ionomers. The fact that the TGA traces of the three-component nanocomposites do not show any sign characteristic of their ionomeric counterpart leads to the conclusion that the interaction of the PBS with the terpolyester in the presence of CL must be highly efficient.

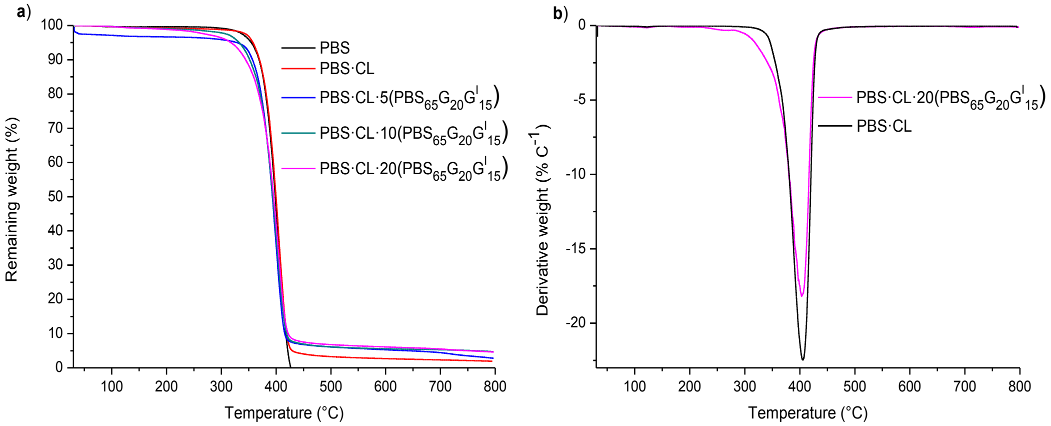


Figure 4. TGA traces of PBS and PBS·CL·w%$PBS_xG_yG^I_z$ nanocomposites (a). Derivative curves of PBS and PBS·CL·20%$PBS_{65}G_{20}G^I_{15}$ nanocomposite (b).

The DSC data obtained for the $PBS_xG_yG^I_z$ series studied in this work are summarized in Table 2. The values of T_g of $PBS_xG_yG^I_z$ terpolyesters increased from -45 to -38 with the content in trimethylammonium glutarate units and T_g values of PBS·CL·w%$PBS_{65}G_{20}G^I_{15}$ showed an almost imperceptible decrease with the increase of ionomer content. The DSC traces obtained from the terpolyester series upon heating the molten samples are comparatively shown in Figure 5. All $PBS_xG_yG^I_z$ are semicrystalline with melting temperatures and enthalpies increasing slightly with the content in trimethylammonium groups but always significantly lower than the values measured for PBS. On the other hand, the crystallizability of the terpolyesters, estimated on the basis of the crystallization temperature and enthalpy, was also found to be considerably lower than that of PBS. Furthermore, it is worthy to note the depression appearing on the second heating trace of $PBS_{65}G_{25}G^I_{10}$ at around 15 ºC owing to the occurrence of cold crystallization. As summarized in Table 2, the crystallization enthalpy of this polyester is considerably low and therefore a large amount of uncrystallized material remained after cooling. No sign of cold crystallization was detected for any other polyester. Interestingly, the DSC behavior of the three-component nanocomposites regarding both melting and crystallization, did not differ substantially from that of PBS neither in the presence nor the absence of compatibilizer. What can be inferred from these results is that the nucleating effect exerted by the nanoclay is determinant of the crystallization process of PBS either in the presence or absence of ionomer.

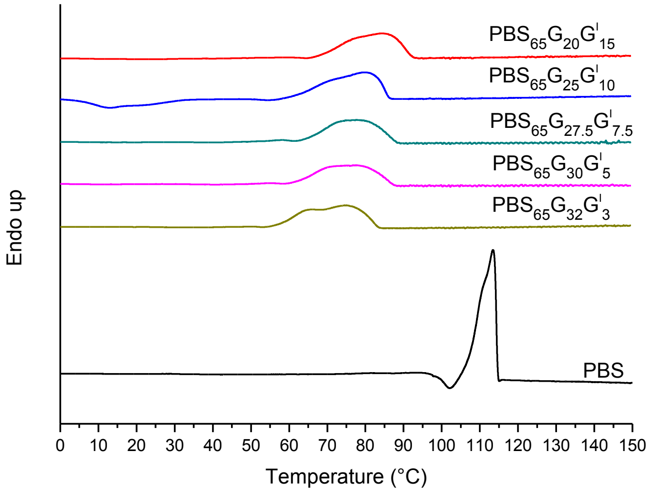


Figure 5. DSC thermograms (second heating) $PBSxG_yG^I_z$ terpolyesters.

Table 2. Thermal and mechanical properties of PBS homopolymer and $PBS_xG_yG^I_z$ terpolyesters.

	TGA			DSC					Stress-strain parameters[g]		
	$^{o}T_d$[a]	$^{max}T_d$[b]	RW[c]	T_g[d]	T_m[e]	ΔH_m[e]	T_c[f]	ΔH_c[f]	E	σ_{max}	ε_{max}
Terpolyester	(ºC)	(ºC)	(%)	(ºC)	(ºC)	(Jg^{-1})	(ºC)	(Jg^{-1})	(Mpa)	(Mpa)	(%)
PBS	363	408	1	-37	115 (114)	70 (74)	75	66	440±5	35±1	282±10
$PBS_{65}G_{32}G^I_3$	342	408	2.1	-45	71 (75)	51 (39)	26	39	149±2	2.23±0.3	0.30±0.1
$PBS_{65}G_{30}G^I_5$	310	**352**/400	2.3	-41	74 (78)	51 (34)	30	37	152±3	2.66±0.5	0.42±0.3
$PBS_{65}G_{27.5}G^I_{7.5}$	309	357/**395**	3.2	-40	76 (78)	52 (34)	31	36	165±5	3.12±0.3	0.76±0.2
$PBS_{65}G_{25}G^I_{10}$	291	356/**395**	3.4	-38	82 (82)	54 (44)	25	44	174±6	3.34±0.2	0.87±0.4
$PBS_{65}G_{20}G^I_{15}$	276	**350**/398	2.8	-38	82 (83)	55 (38)	35	38	266±3	5.05±0.3	1.46±0.4
Nanocomposite											
PBS·CL	370	**406**	2	-38	114 (113)	61 (48)	90	60	607±7	41±4	16±0.5
PBS·CL·5($PBS_{65}G_{20}G^I_{15}$)	356	**400**	2.7	-38	114 (113)	61 (60)	88	58	713±15	50±2	25±3
PBS·CL·10($PBS_{65}G_{20}G^I_{15}$)	353	**401**	4.8	-40	114 (113)	60 (57)	85	59	747±15	49±3	109±20
PBS·CL·20($PBS_{65}G_{20}G^I_{15}$)	345	**404**	4.9	-40	115 (113)	60 (57)	85	59	731±10	48±5	144±15
PBS·CL·10($PBS_{65}G_{35}$)	350	**403**	2.7	-39	114 (113)	55(54)	80	56	550±10	39±1	40±5
PBS·CL·20($PBS_{65}G_{35}$)	349	**401**	2.9	-39	114(113)	53(52)	78	52	560±15	44±1	60±5

[a] Degradation temperature at which a 10% weight loss was observed in TGA traces at 10 ºC·min^{-1}. [b] Temperature of maximum degradation rate (in bold main degradation temperature). [c] Remaining weight at 600 ºC for the terpolyester. Remaining weight at 800 ºC for the nanocomposites. [d] Glass transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 ºC·min^{-1}. [e] Melting temperatures and enthalpies were registered at a heating rate of 10 ºC·min^{-1}. In parenthesis, values recorded in the second heating. [f] Crystallization temperatures and enthalpies were registered at cooling from 200 ºC at 10 ºC·min^{-1}. [g] Young's modulus, maximum tensile stress and maximum elongation at break measured at room temperature on a Zwick BZ2.5/TN1S.

1.3.4. Stress-strain mechanical behavior

The mechanical parameters of the terpolyesters and nanocomposites are listed in Table 2 and the stress-strain curves of the latter are shown in Figure 6 together with that of PBS. It is apparent that the mechanical behavior of the ionomer terpolyesters is largely poorer than that of PBS, which is undoubtedly consequence of their low molecular weight.

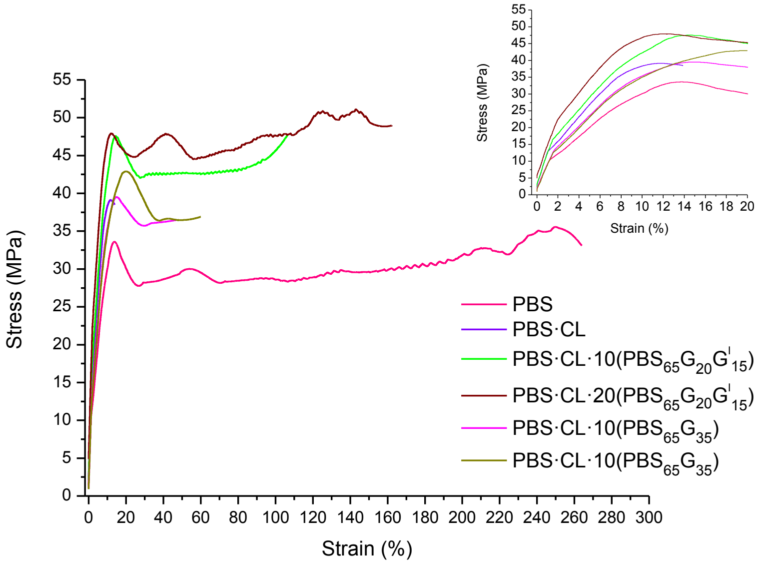


Figure 6. Stress-strain traces of nanocomposites. The curve obtained from PBS is also included for comparison

Nevertheless, the Young's modulus (E), elongation at break (ε_{max}) and maximum tensile stress (σ_{max}) of terpolyesters tend to increase steadily with the content in G^{I} units bringing into evidence the positive effect of the presence of charges on mechanical properties, an effect that has been repeatedly reported for other related systems.[13] On the other hand, the nanocomposite prepared by extruding PBS with 3% of CL shows enhanced Young's modulus and maximum tensile stress but a largely reduced deformation at break. This is a result commonly found for those nanocomposites that are unable to attain the exfoliated state.[20,21] The addition of the ionomer $PBS_{65}G_{20}G^{I}_{15}$ as compatibilizer was shown to clearly improve the mechanical parameters of the nanocomposite of PBS. Not only the modulus and yield increased but also, in particular, the ductility was greatly enhanced. In fact, the nanocomposite containing 20% of ionomer could be stretched about 10 times more than the nanocomposite without compatibilizer. The comparison with the nanocomposites containing the copolyester $PBS_{65}G_{35}$, that is containing the same amount of glutarate units but without ammonium groups, was very enlightening. The presence of such copolyester in PBS·CL produced a moderate increment of ε_{max} but also an impoverishing of E and σ_{max}, a result that can be partially explained by taking into account the possible lowering effect that the relatively more flexible poly(butylene succinate-*co*-glutarate) has on T_g. What it is concluded is that the ionomer is capable of producing a positive effect on mechanical properties of the nanocomposites of PBS with CL. This result, although preliminary, is of great relevance as it brings out the suitability of using PBS copolyester ionomers to optimize the preparation of the nanocomposites of PBS, an approach that offers a wide assortment of technical possibilities.

1.4. Conclusions

$PBS_xG_yG^I_z$ terpolyesters, all of them containing 35 mol-% of total glutarate and trimethylammonium glutarate units but varying in the ratio in which these two units are present, were synthesized by polycondensation using a scandium catalyst. All these terpolyesters were fairly stable to heat and were semicrystalline. Their T_g was close to that of PBS but they showed much poorer mechanical properties, a behavior that is the logical consequence of their low molecular weights. The use of these terpolyesters as compatibilizers in the preparation of nanocomposites made of PBS and CL gave outstanding results. Their presence in the nanocomposites in minor amounts gave rise to a significant increase in the Young modulus and the stress to yield and in particular to a large increment in the elongation to break. The capacity of such terpolyester ionomers to enhance the mechanical properties of PBS·CL nanocomposites must be attributed to their unique binding effect based on a combination of their good compatibility with PBS and their strong ionic interaction with the anionically charged layer surfaces of CL.

1.5. References

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2. Nanocomposites of sulfonated poly(hexamethylene terephthalate) ionomers

Abstract

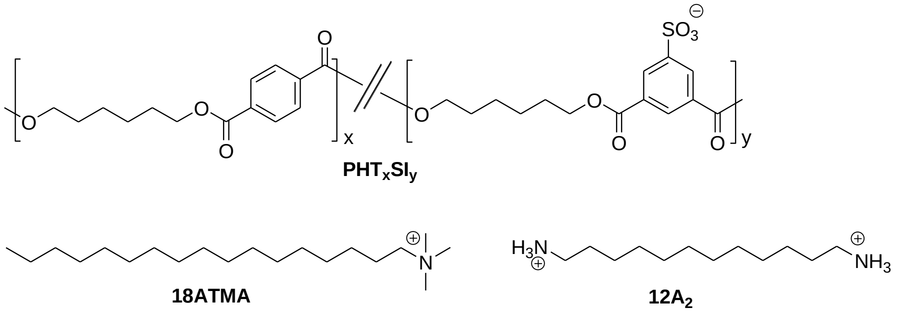
Sulfonated poly(hexamethylene terephthalate) (PHTSI)/montmorillonite (CLNa or CL30B) nanocomposites containing from 1.5 to 5% of clay were prepared by two procedures: a) Melt extrusion of either PHTSI/CL30B or 18A·PHTSI/CL30B previously prepared by coupling PHTSI with octadecyltrimethylammonium surfactant (18A). b) Mixing of PHTSI/CLNa and dodecilenediammonium ($12A_2 \cdot 2HCl$) solution in THF and precipitation with methanol. The objective was to evaluate the influence of the use of compatibilizers and montmorillonite modification on the properties of the resulting nanocomposites. In all cases the thermal stability of the nanocomposites slightly diminished compared to that of the copolyester ionomer. Nanocomposites prepared with the addition of compatibilizers (18A·PHTSI·wCL30B and $12A_2$·PHTSI·wCLNa) displayed extensive intercalation or even exfoliation and the elastic modulus of PHTSI significantly increased in the three series of nanocomposites. Conversely, the elongation to break of the nanocomposites was dramatically reduced in all cases.

2.1. Introduction

Traditionally, polymeric materials have been filled with a diversity of synthetic and natural inorganic compounds in order to improve their properties, or simply to reduce costs. The utilization of inorganic nanoparticles as filler to enhance the polymer performance has attracted great interest, both in industry and in academia, because they often exhibit remarkable improvement in materials properties when compared with virgin polymer or conventional micro and macro-composites. These improvements can include high moduli,[1,2] increased strength and heat resistance,[3] decreased gas permeability[4,5] and flammability,[6,7] and increased biodegradability of biodegradable polymers.[8] Much of the work in this area has been focused on polymeric nanocomposites derived from layered silicates such as montmorillonite. Examples of polymer matrices that have been utilized for the production of montmorillonite-containing nanocomposites include nylon-6,[9] polyimide,[10] polycaprolactone,[11] unsaturated polyesters,[12] epoxy resins,[13] and poly(dimethylsiloxane).[14] This family of materials exhibits enhanced properties at very low filler level, usually below 5 wt%. The melt intercalation process is one of the most studied since permits the straightforward preparation of nanocomposites by melt extrusion of the polymer with the silicate. However, in order to improve the compatibility of the polymer with the clay, it is usually necessary to modify the sodium montmorillonite by exchanging the sodium ions with amino acid salts or quaternary ammonium salts bearing long alkyl chains.[15] With this process, the ion exchange between sodium cations and the ammonium cations increases the spacing between the silicate layers and makes the galleries between the layers more organophilic, facilitating the intercalation of the clay with polymer chains. In fact, the degree of property improvement is dependent on the morphology of nanocomposite; with a greater degree of exfoliation of clay platelets usually resulting in optimal property improvement.

Polymer nanocomposites comprised of a semicrystalline polymer matrix like PET and PBT are particularly attractive due to the dramatic improvement in heat distortion temperature and modulus provided by the nanoparticle reinforcement. The main problem in the production of PET/MMT nanocomposites is to achieve a satisfactory degree of exfoliation. Melt processing combined with organo modifier to enhance affinity between the polyester and the clay has been the methodology mostly applied. In some studies compatibilizers such as pentaerythrytol and maleic anhydride have been used in an attempt to increase the exfoliated morphology.[16] PET and PBT ionomers have been also used with montmorillonite to prepare nanocomposites.[17,18] Chisholm *et al*.[17] studied the effect of sodium sulfonate functionalization of poly(butylene terephthalate) (PBT) on the properties of PBT/montmorillonite composites. The results of this study clearly showed that low levels (1.0-5.0 mol-%) of -SO_3Na groups resulted in the production of highly exfoliated nanocomposites by a simple extrusion process. Similar results were attained by Barber *et al*.[18] with the system poly(ethylene terephthalate) sulfonate ionomer/organically-modified montmorillonite clay nanocomposites prepared via melt extrusion. It was found that incorporation of the clay into the random ionomers leads to increased mechanical properties and slower crystallization rates.

Poly(hexamethylene tererephthalate) (PHT) is an aromatic polyester that has not achieved yet commercial realization but that is currently looked as an interesting thermoplastic with advantages on the other well-known polyterephthalates as PET and PBT for certain applications. No study on PHT-based nanocomposites has been reported to date. Results reported for PET/nanoclays mixtures have shown the difficulty of attaining extensive exfoliation due to the poor affinity of the polyester for the inorganic material, a problem that subsists even when partially ionized PET is used for building the composite. The objective of this work is to study the nanocomposites of PHT-sulfonated ionomers (PHT_xSI_y) with momtmorillonite by using different approaches for mixing and making use of compatibilizers. Octadecyltrimethylammonium and 1,12-dodecylenediammonium salts are used for compatibilization. The clay is used either unmodified or modified with alkylammonium soaps. The chemical formula of the organic compounds used in this work are drawn in Scheme I. Results obtained by the different procedures are compared and the effect of the compatibilizers on the mixing efficiency and composite properties are evaluated.



Scheme 1. Chemical structure of the organic components used for building nanocomposites

2.2. Experimental section

2.2.1. PHTSI·nanocomposites

Three types of nanocomposites have been prepared from PHTSI ionomer containing 5 mol-% of isophthalic sulfonate groups (prepared as described in previous work[19]) and Cloisites:

a) PHTSI·w%CL30B composites (w% indicates the percentage (w/w) content in clay) were prepared by mixing the PHTSI copolyester with Cloisite 30B (CL30B) in a twin screw mini-extruder (Haake, Minilab) at 150 ºC. The screws were used in counter-rotation with a screw speed of 75 rpm. To achieve a high degree of dispersion, the residence time was lengthened up to 20 minutes. GPC and NMR analysis were used to ensure that under the applied conditions the copolymer did not suffer perceivable degradation. PHTSI·w%CL30B composites with clay percentages of 1.5, 3 and 5% were thus prepared.

b) 18A·PHTSI·w%CL30B composites were prepared by applying the same procedure described above to obtain PHTSI·w%CL30B but using as polymer counterpart the previously prepared ionic complex 18A·PHTSI complex instead of the pristine copolyester ionomer. The ionic complex 18A·PHTSI was obtained by the method used by Pérez-Camero for the preparation of poly(γ-glutamic acid) complexes.[20] Briefly, a 0.02 M solution of the cationic surfactant 18ATMA·Br in $CHCl_3$ was slowly added to an equal volume of 0.02 M solution of PHTSI in the same solvent under magnetic stirring. Equimolar amounts of the two components were mixed in order to obtain a stoichiometric complex. The mixture was maintained under stirring for two hours and the complex was precipitated by adding to the solution methanol and then recovered by centrifugation. The complex was washed several times with water to remove the free surfactant and finally dried at 40 °C under vacuum for two days. 18A·PHTSI·w%CL30B composites with clay contents of 1.5, 3 and 5% were prepared from the 18A·PHTSI complex and Cloisite 30B.

c) $12A_2$·PHTSI·w%CLNa nanocomposites were prepared applying the following procedure: First Cloisite-Na was dispersed in THF at 60 ºC under stirring for 6 hours and then sonicated for 1 h in a Rosset cell at 0°C using a Bandelin HD 2200 Sonoplus ultrasonic homogenizer equipped with 2 mm diameter MS72 tip. A 0.02 M PHTSI solution in THF was added to the sonicated dispersion and the mixture was left under stirring for 2 hours. Then a 0.02 M solution of the $12A_2$·2HCl surfactant in THF was added drop-wise to the PHTSI/CLNa dispersion and the mixture was maintained under stirring for another 2 hours at 60 °C. The composite was precipitated with methanol and recovered by centrifugation. The precipitate was washed several times with water at 60 ºC to remove the unbound surfactant and then dried at 40°C under vacuum for two days. Composites containing 1.5, 3 and 5% of clay were thus prepared. To ascertain the composition in organics of the $12A_2$·PHTSI·w%CLNa composites, the clay had to be previously removed. Approximately 1 g of crude composite was stirred in chloroform (50 mL) for 3 h at room temperature and the suspension was then centrifuged at 6000 rpm for 15 min. This operation was repeated several times and the supernatants were then gathered, concentrated and precipitated into methanol. The ‘‘clay-free” polyester was filtered and dried under vacuum to constant weight and analyzed by ^{1}H RMN. The 1,12 dodecanediamine dihydrochloride ($12A_2$·2HCl) was obtained by dissolving 1,12-diaminododecane in hydrochloric acid 2.5M at 60 °C and stirring the solution at this temperature for 30 minutes. Upon slow cooling small crystals of the salt appeared which were filtered off, washed several times with water to remove the hydrochloride acid and finally washed with cool acetone.

2.3. Results and discussion

2.3.1. Preparation and composition of the nanocomposites

The route followed for the preparation of the three different types of nanocomposites studied in this work is depicted in Figure 1. All they are made of the PHTSI ionomer bearing 5% of isopthalic units and Cloisite nanoclays but composites 18PHT30B and 12PHTCL incorporate a third compound which is intended to improve the compatibility of the two basic components. In the first case, the cationic surfactant

18ATMA·Br was ionically coupled to the sulfonate ionomer to render a comb-like complex bearing octadecyl side groups which are expected to enter in close contact with the alkyl chains of CL30B and facilitate the entry of the polyester into the clay galleries. In the second case, the compatibility between the ionomer and the clay is intended to be favored by adding dodecilenediammonium ($12A_2·2HCl$), a doubly charged long alkylene segment able to interact ionically with the ionomer and with the unmodified montmorillonite (Cloisite-Na) at the same time. According to the function of the compatibilizer, the mixing method applied for the preparation of the composite was melt extrusion and precipitation, respectively. On the other hand, the composites PHT30B were prepared by simple melt extrusion of ionomer/CL30B mixtures, which is the method usually applied to obtain thermoplastic/clay composites.[21,22]

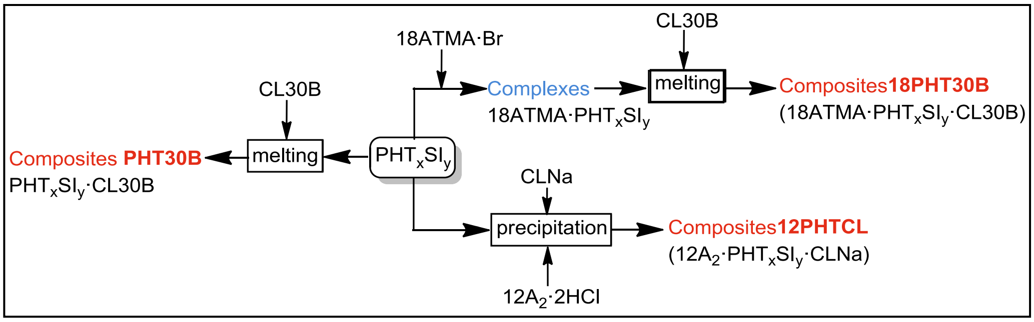


Figure 1. Routes of synthesis leading to the preparation of composites. PHTSI: copolyester ionomer with 5% of sulfonate units; 18ATMA: octadecyltetramethylammonium; $12A_2$: 1,12-dodecylenediammonium; CLNa: sodium Cloisite; CL30B: organoalkylammonium modified Cloisite.

In the preparation of 18PHT30B composites the ionic complex 18A·PHTSI was obtained in a first step by adding drop-wise the surfactant solution of the ammonium bromide or diammonium dichloride to the copolyester solution in chloroform or tetrahydrofuran. The precipitated complex was then recovered by filtration and their ^1H RMN spectra ascertained that it had the expected stoichiometric composition (spectra shown in Figure S1 of the SI file). After extrusion of the copolyester ionomer with Cloisite 30B, the composites were prepared and then analyzed by both viscosimetry and GPC to detect possible changes in the molecular weight of the copolyester ionomer after the treatment. The data obtained from these analyses proved that no perceivable degradation took place under the applied extrusion conditions (Table S1 of the SI file). At difference with the other two, $12A_2$·PHT·CLNa composites were prepared by simultaneous mixing of the THF solution of copolyester and surfactant with the Cloisite dispersion in the same solvent. The prevailing idea is to promote the simultaneous interaction of the diammonium salt with the negative charges of both the sulfonate ionomer and the unmodified montmorillonite. The content of ionomer and compatibilizer in the final composite was proven to be near unity by ^{1}H NMR of the extracted organic phase.

2.3.2. Thermal and mechanical behavior

The thermal stability of the nanocomposites under oxidative atmosphere was estimated by TGA. The weight loss *vs.* temperature traces for the ionomers and the different series of nanocomposites that have been prepared are compared in the plots shown in Figure 2. Thermal decomposition parameters measured on such traces for copolyesters, complexes and nanocomposites are gathered in Table 1. The decreasing in thermal stability of the polyester accompanied by an increasing complexity of the decomposition process with the content in sulfonate groups is a well-established fact that has been repeatedly reported for these and other closely related sulfonated copolyesters.[19] Nevertheless, PHTSI·CL30B nanocomposites displayed lower decomposition temperatures (Figure 2a) than the ionomer itself which is contrary to expectations and also to results recently reported for similar composites made from PET.[23] On the other hand TGA data indicated that the thermal stability of the 18A·PHTSI complex (Figure 2b) was up to nearly 20 ºC lower than those of the polyester ionomer. Addition of CL30B to the complex affords an enhancing effect on the decomposition temperature but it is not great enough as to recover the initial thermal stability of the copolyester and consequently the resistance to heat of 18A·PHTSI·CL30B nanocomposites is depressed. $12A_2$·PHTSI·CLNa nanocomposites (Figure 2c) exhibit a similar behavior with decays in decomposition temperatures of 40-50 ºC. Regarding the weight remaining after heating at 800 ºC, results are consistent with composition provided that both the clay and the sulfonate units are assumed to contribute to the residue left by these compounds. The conclusion that can be drawn from this study is that the thermal stability of PHT ionomers is impoverished by addition of the clay both in presence and in absence of compatibilizers. It should be noticed however that the weakening effect caused by mixing is not critical for the normal use of these compounds since onset decomposition temperatures remain well above 300 ºC in all cases.

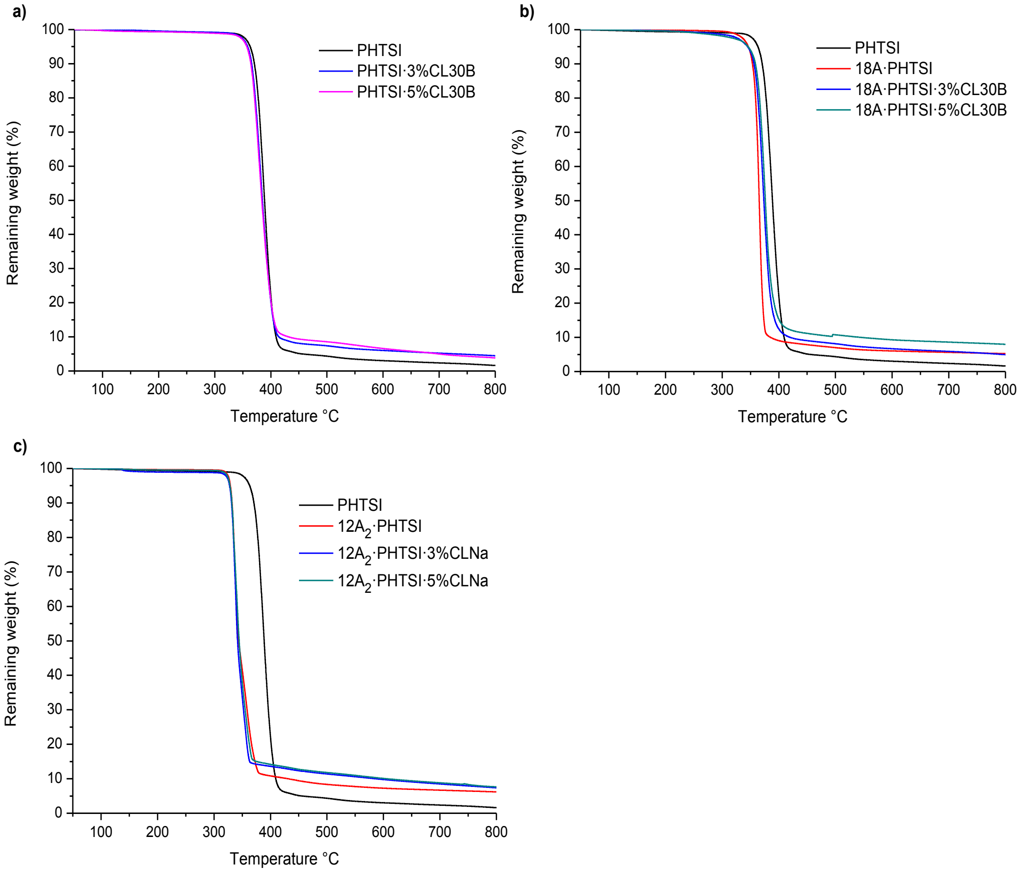


Figure 2. TGA traces of PHTSI nanocomposites with 3 and 5% (w/w) of clay recorded under oxidative atmosphere.

The copolyester ionomers, the complexes and the nanocomposites were also comparatively analyzed by DSC. Glass transition temperatures were measured on traces registered at heating from samples quenched from the melt and melting temperatures and enthalpies were recorded on heating traces recorded from pristine samples. Melting DSC traces grouped for types of nanocomposites and ionomer compositions are depicted in Figure 3 and thermal parameters measured in the DSC analysis are collected in Table 1.

Table 1. Thermal and mechanical properties of PHTSI copolyester, 18A·PHTSI complex and nanocomposites.

	TGA			DSC					Stress-strain[g]		
	${}^{o}T_{d}{}^{a}$	${}^{max}T_{d}{}^{b}$	RW^{c}	$T_{g}{}^{d}$	$T_{m}{}^{e}$	$\Delta H_{m}{}^{e}$	$T_{c}{}^{f}$	$\Delta H_{c}{}^{f}$	E	σ_{max}	ε_{max}
Copolyester	(ºC)	(ºC)	(%)	(ºC)	(ºC)	(Jg^{-1})	(ºC)	(Jg^{-1})	(Mpa)	(Mpa)	(%)
PHTSI	367	**387**/440	1	15	140 (142)	28 (27)	90	-27	643±15	33±1	569±20
PHTSI·1.5%CL30B	363	**381**/440	1.3	16	141 (136)	29 (28)	103	-29	726±20	38±2	452±10
PHTSI·3%CL30B	363	**381**/440	4	16	141 (136)	24 (27)	103	-30	837±10	42±1	450±10
PHTSI·5%CL30B	363	**379**	4.5	16	141 (137)	28 (27)	103	-30	906±10	44±2	334±15
18A·PHTSI	352	**366**	5	15	139 (145)	41 (31)	110	-37	681±10	32±1	464±20
18A·PHTSI·1.5%CL30B	360	**375**	3.4	NS	145 (145)	30 (33)	114	-34	697±20	34±0.5	106±10
18A·PHTSI·3%CL30B	359	**374**	5.4	NS	145 (146)	31 (30)	115	-35	747±20	35±1	33±15
18A·PHTSI·5%CL30B	359	**375**	8.3	NS	145 (145)	30 (33)	114	-35	919±40	37±2	14±1
12A$_2$·PHTSI·1.5%CLNa	330	**337**/357	7.5	18	143 (143)	38 (35)	100	-35	816±10	38±1	365±20
12A$_2$·PHTSI·3%CLNa	330	**337**/357	7.9	18	143 (143)	38 (28)	102	-34	1007±20	43±0.5	214±10
12A$_2$·PHTSI·5%CLNa	328	**338**/357	8.2	18	143 (143)	33 (27)	101	-31	1132±20	45±1	26±2

[a] Degradation temperature at which 10% weight loss was observed in TGA traces recorded at 10 ºC·min^{-1}. [b] Temperature of maximum degradation rate (in bold main degradation temperature). [c] Remaining weight at 800 ºC. [d] Glass transition temperature taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20 ºC·min^{-1}. [e] Melting temperatures and enthalpies were measured at the first heating at a rate of 10 ºC·min^{-1} In parenthesis, values recorded in the second heating. [f] Crystallization temperatures and enthalpies measured at cooling from 200 ºC at 10 ºC·min^{-1}. [g] Young modulus, maximum tensile stress and elongation at break measured at room temperature on a Zwick BZ2.5/TN1S.

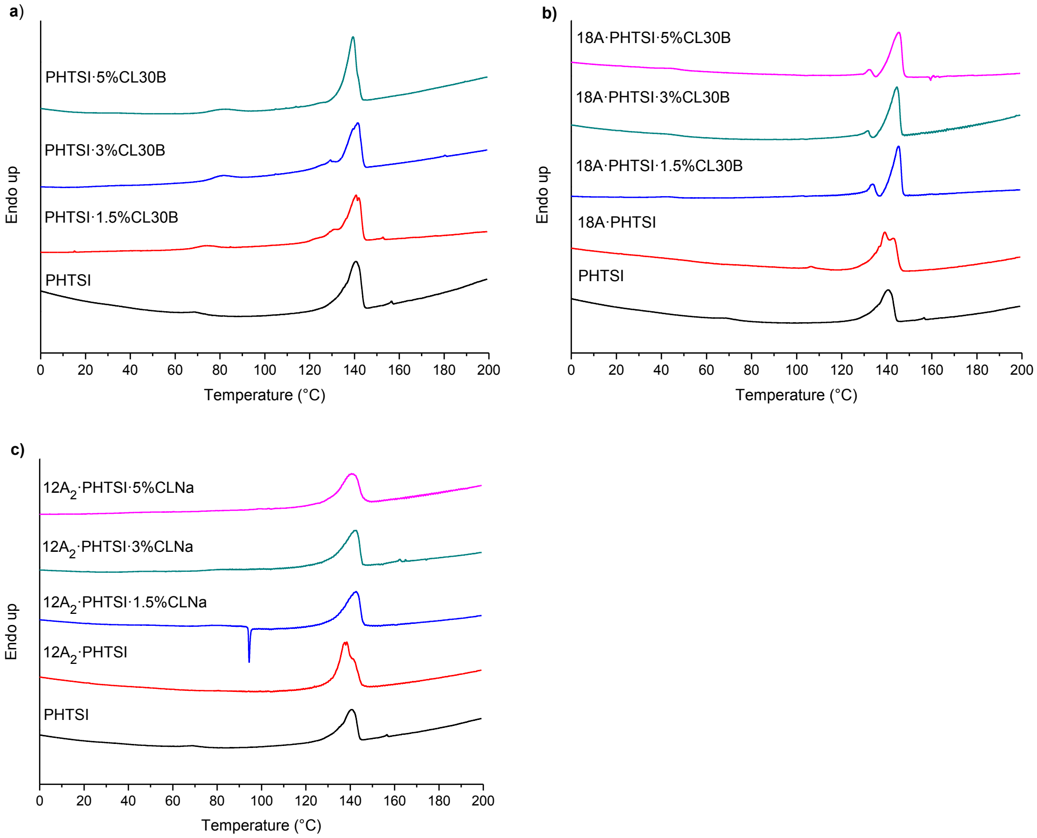


Figure 3. First heating DSC traces of PHTSI nanocomposites with 1.5, 3, and 5% (w/w) of clay.

It has been published that PHTSI ionomers show a T_g higher than PHT and that their crystallinity decreases rapidly with the content in sulfonate units. In this work it has been found that the addition of CL30B to 5% PHTSI copolyester does not exert significant influence either on T_m or on T_g. In fact, traces shown in Figure 3a display a similar melting endotherm around 140-141 ºC and T_g is maintained around 15-16 ºC for all the compositions. The 18A·PHTSI complex has the same T_g than the PHTSI copolyester and also displays the same melting behavior (Figure 3b) with a T_m around 140 ºC and without vestige of melting of the alkyl side chains. It is well known that comb-like ionic complexes made from polyacids and long alkylammonium surfactants show characteristic melting of the alkyl side chains at temperatures below 100 ºC.[24] The absence of melting of the paraffinic phase in 18A·PHTSI is fully consistent with the low concentration (5 mol-%) of alkyl groups present in this complex. The composites 18A·PHTSI·w%CL30B were found to melt 5 ºC above the T_m of PHTSI revealing a significant enhancing effect of the clay on the crystallization of the copolyester. Unfortunately, the glass transition of these composites could not be detected by DSC which prevented to appraise the influence of the clay on T_g. The analysis of the $12A_2$·PHTSI·w%CLNa nanocomposites series (Figure 3c) indicated a similar effect on melting when the alkylenediammonium was used as compatibilizer. As it is seen in Table 1, T_m increased about 4 ºC with the addition of CLNa regardless the concentration used. In this case the glass transition could be measured revealing a significant increase in T_g compared to the value displayed by the pristine copolyester. A worthwhile observation is that both 18A·PHTSI·w%CL30B and $12A_2$·PHTSI·CLNa composites were able to crystallize from the melt (Figure S2 of the SI). This fact becomes particularly interesting for the first family of composites because they were able in addition to recrystallize at lower supercooling with total recovery of the initial crystallinity. These results are a clear evidence of the nucleating effect exerted by the compatibilizer.

It has been previously reported that the incorporation of sulfonate groups in PHT gives rise to an enhancement of its mechanical properties. An increase in the Young's modulus and ultimate elongation with the magnitude of the effect increasing with the clay content along the 1.5 to 5.0 % (w/w) range was observed for PHTSI ionomers.[19] In this work it is shown how the mechanical properties of these ionomers are further affected by the presence of clay in the three types of nanocomposites that has been examined. The stress-strain curves registered from nanocomposites containing 3 % (w/w) of clay are shown in Figure 4 for illustration, and mechanical parameters measured for all nanocomposites in the tensile tests are given in Table 1. The addition of CL30B to PHTSI increased significantly both its elastic modulus and maximum stress but decreased its ductility up to near 25% (Figure 4a). The behavior of the 18A·PHTSI complex was not very different to that of the ionomer and composites 18A·PHTSI·wCL30B exhibited *E* and $\sigma_{\mathbf{max}}$ values were also comparable to those of composites PHTSI·CL30B but their extensibility was drastically diminished (Figure 4b). The case of 12A·PHTSI·wCL nanocomposites is noticeable since an increase in the *E* modulus of around 100% was attained for a content of 5% in CL although the elongation to break also largely decayed (Figure 4c). The conclusion that can be drawn from the tensile tests results carried out with these series of compounds is that the elastic modulus is in general increased in the nanocomposites and that the change is significantly more pronounced when compatibilizers are added. On the contrary, the ductility of the nanocomposites containing compatibilizers is very poor making these compounds too brittle for 5% of content in clay. It is unfortunate that the exceptional flowing exhibited by the PHTSI ionomers is disrupted in these compositions. Apparently the combined presence of compatibilizer and the nanoclay prevents either the formation of the ionic aggregates characteristic of the ionomer material or their mechanical function in the case that they exist.

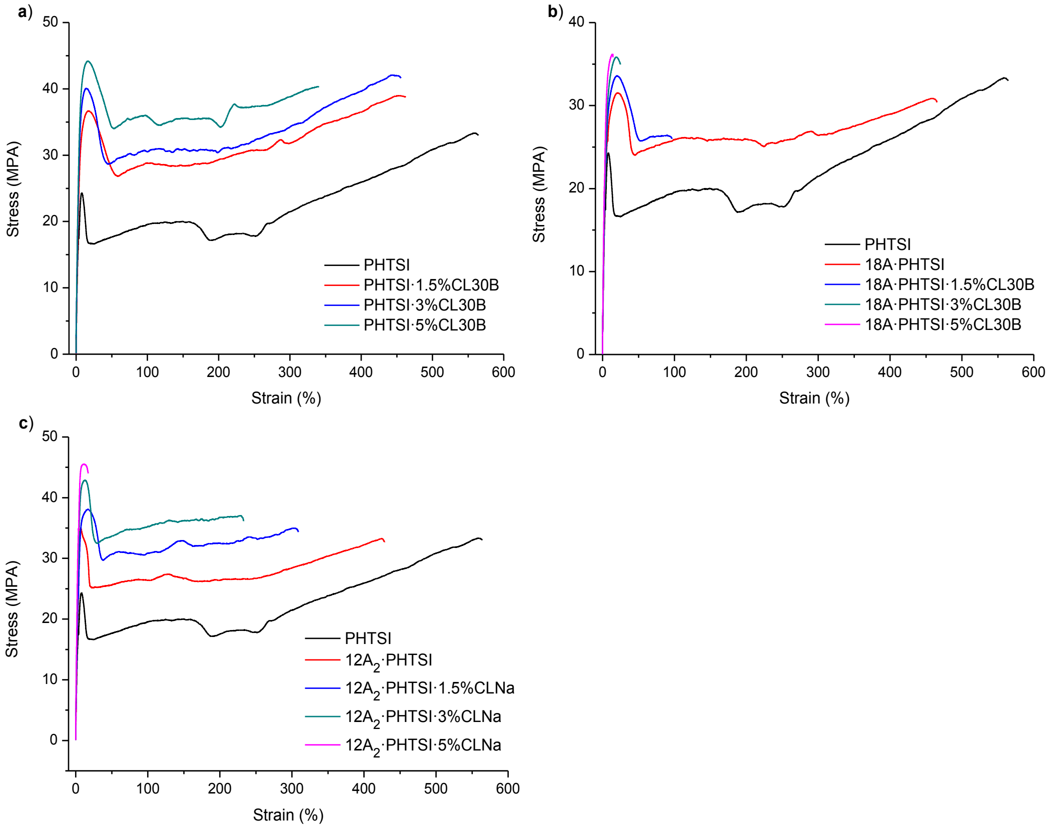


Figure 4. Stress-strain curves of PHTSI nanocomposites with 1.5, 3, and 5% (w/w) of clay

2.3.3. XRD analysis

Powder X-ray diffraction patterns (XRD) were recorded from the three types of nanocomposites and compared with the patterns of PHT, PHTSI copolyester, and cloisite. The profiles of the three groups are plotted in Figure 5 and the most prominent

Braggs spacings measured on such profiles are listed in Table S2 of the SI file. The X-ray diffraction pattern of pure PHT consists of five mean peaks arising from the triclinic crystal β-form usually adopted by this polyester.[25,26] These characteristic peaks are invariably present in the XRD patterns of copolyesters and nanocomposites indicating that, according to what was observed by DSC, the crystal structure of PHT is not substantially altered in such compounds. On the other hand, none of the the nanocomposite profiles show signs of the original Cloisite interlayer spacing indicating that a fully or almost fully distortion of the layered structure of the clay has taken place.

However a close inspection of the diffractograms revealed meaningful indications of structural relevance. The peak at 10-15 Å in the profile of PHTSI·5%CL30B nanocomposite appears doubled; whereas the lower spacing component of this peak should correspond to PHT, the another one with a spacing near to 15 Å could be interpreted as arising from a fraction Cloisite 30 B that has been compressed due to the ionic interaction with the ionomer (Figure 5a). On the other hand, the profile produced by 18A·PHTSI·5%CL30B (Figure 5b) displays a broad peak around 40-50 Å clearly indicative of a large separation between the silicate sheets with the formation of an extensively intercalate structure. Finally regarding $12A_2$·PHTSI·5%CLNa (Figure 5c), the peak at ∼10 Å that should be expected to arise from non-distorted Cloisite-Na is not present and no scattering at high spacings is detected. However a feeble shoulder around 13 Å is appreciated on the PHT peak which can be attributed to a small fraction of intercalate Cloisite-Na.

Another feature common to all the composite profiles is the absence of discrete scattering due to the paraffinic phase integrated by the alkyl chains associated to the organoammonium compounds used for compatibilization. In comb-like ionic complexes made from polyacids and long alkylammonium surfactants, a strong diffraction peak at 0.42 nm characteristic of the hexagonal crystal lattice of the alkyl side chains is invariably observed. In the present systems is obvious that the concentration of the alkyl groups is insufficient to allow the packing of the alkyl tails in crystallites of minimum size.

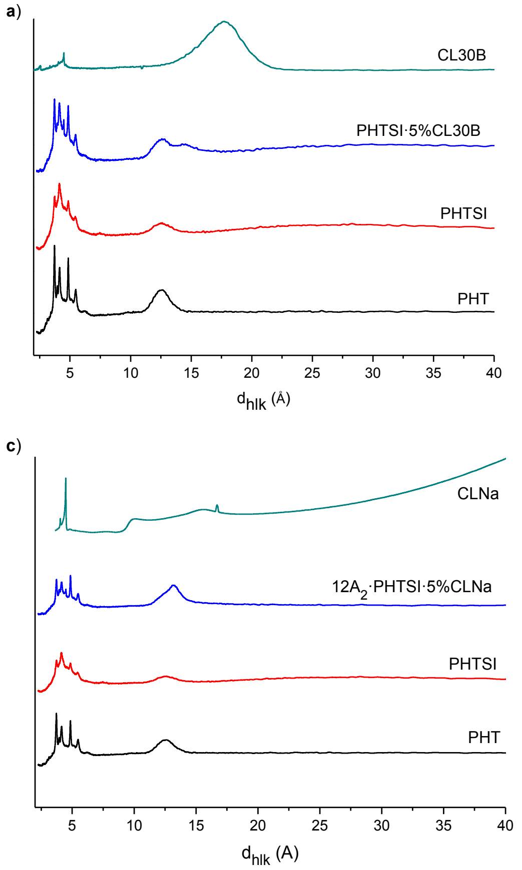


Figure 5. XRD profiles of composites and their components.

2.4. Conclusions

Three different sets of nanocomposites were prepared from the PHTSI copolyester ionomer containing 5 mol-% of sulfonated isophthalic units and Cloisite nanoclays, and either using compatibilizing additives or not. The structure and basic properties of the nanocomposites were found to be clearly affected by composition. In the absence of compatibilizers, the PHTSI/CL30B nanocomposites present an intercalate structure together with part of the Cloisite 30B layers slightly contracted. Nanocomposites prepared with the addition of compatibilizers (18A·PHTSI·wCL30B and $12A_2$·PHTSI·wCLNa) display extensive intercalation or even exfoliation. The thermal stability of all the nanocomposites was slightly diminished compared to that of the parent copolyester ionomer whereas melting and glass-transition temperatures were essentially unaffected by composition. Noticeably, the crystallization from the melt was particularly favored in 18A·PHTSI·wCL30B nanocomposites as a consequence of the outstanding nucleating effect exerted by the copolyester complex in this series. The elastic modulus of PHTSI was significantly increased in the three series of nanocomposites, the increment being larger for larger contents in nanoclays and attaining up to 100% of the original copolyester value for $12A_2$.PHTSI·5%CLNa. Conversely, the elongation to break of the nanocomposites was dramatically reduced in all cases. The negative effect of compatibilizers on ductility may be understood by assuming that the plasticizing role played by the ionic aggregates in PHTSI cannot be played in the nanocomposites

2.5. References

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2.6. Supporting information

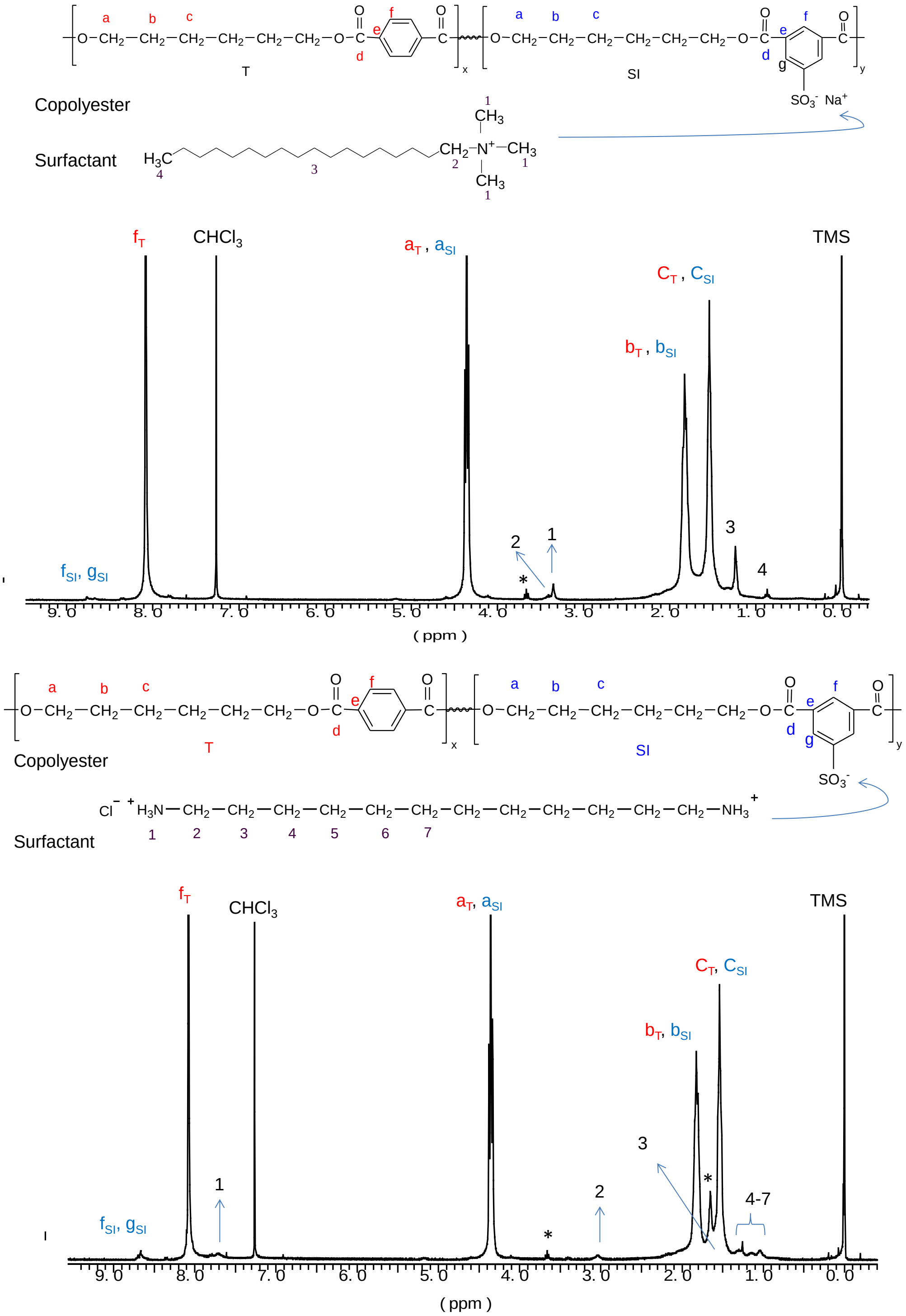

Figure S1. ^{1}H NMR of 18A·PHTSI (top) and 12A$_2$·PHTSI (bottom) complexes. * CH$_2$OH end groups.

Tabla S1. Intrinsic viscosity and molecular weight of PHTSI copolyester before and after extrusion.

Polyester	$[\eta]^a$	$M_v{}^b$	$M_w{}^c$	$Đ^c$
PHTSI	0.74	22,200	22,000	2.3
PHTSI·CL30B	0.74	22,200	22,000	2.3

[a]intrinsic viscosity measured in dichloroacetic acid at 25 ºC. [b] Viscosimetric molecular weight determined from the equation of Mark-howink using the constants a = 0.47 and K = 67 x 10^{-4} belonging to PET. [c] Weight average molecular weight (M_w) and polydispersity ($Đ^c$) determined by GPC.

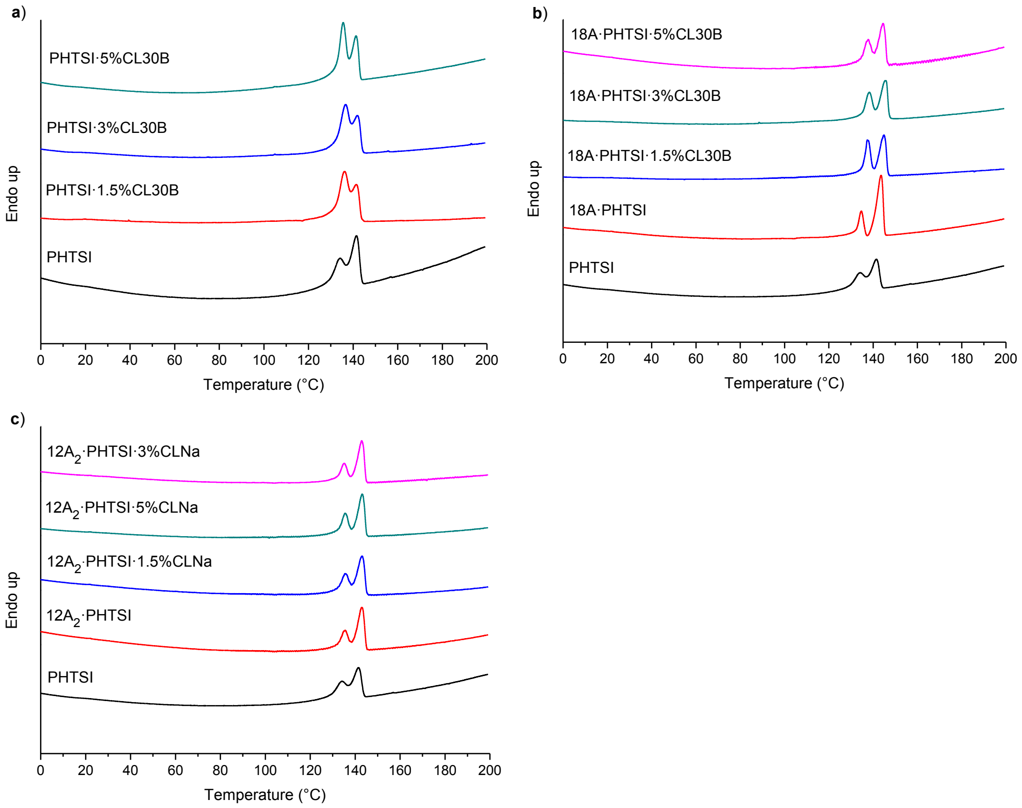

Figure S2. Second heating DSC traces of PHTSI nanocomposites with 1.5, 3, and 5% (w/w) of clay.

Table S2. Bragg spacings measured in powder diffraction patterns. Intensities visually estimated as follows: s, strong; m, medium; w, weak; vw, very weak.

	X-ray diffraction data																	
Polyester	d^{a} (Å)																	
PHT				12.5 (s)	6.24 (w)	5.47 (m)	4.86 (s)		4.14 (m)	3.94 (w)	3.72 (s)	3.42 (vw)	3.15 (vw)	3 (vw)	2.74 (vw)	2.62 (vw)		
PHTSI				12.5 (s)		5.45 (w)	4.86 (m)		4.13 (m)	3.95 (w)	3.73 (m)							
PHTSI·5%CL30B			14.5 (w)	12.5 (s)		5.45 (m)	4.86 (s)	4.49 (w)	4.13 (m)	3.95 (w)	3.73 (s)	3.44 (vw)	3.14 (vw)	3 (vw)	2.73 (vw)		2.57 (vw)	
18A·PHT$_9$SI				12.5 (m)		5.45 (m)	4.86 (s)		4.13 (m)	3.95 (w)	3.73 (s)	3.44 (vw)	3.14 (vw)	3 (vw)	2.73 (vw)	2.61 (vw)		
18A·PHTSI·5%CL30B	45.89 (w)			12.5 (m)		5.45 (m)	4.86 (s)	4.49 (w)	4.13 (m)	3.95 (w)	3.73 (s)	3.44 (vw)	3.14 (vw)	3 (vw)	2.73 (vw)	2.61 (vw)	2.57 (vw)	2.54 (vw)
12A$_2$·PHTSI				12.5 (s)		5.45 (m)	4.86 (s)		4.13 (m)	3.95 (w)	3.73 (s)	3.44 (vw)	3.14 (vw)	3 (vw)	2.73 (vw)	2.61 (vw)		
12A$_2$·PHTSI·5%CLNa		13.18 (s)		12.5 (s)		5.45 (m)	4.86 (s)	4.49 (w)	4.13 (m)	3.95 (w)	3.73 (s)	3.44 (vw)	3.14 (vw)	3 (vw)	2.73 (vw)	2.61 (vw)	2.57 (vw)	2.54 (vw)

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

Chapter IV.

General conclusions

I. PHT copolyesters containing different amounts of sulfoisophthalate units have been prepared by melt phase polycondensation. The new copolyesters were semicrystalline for contents in SI units below 20 mol-%. An increase in the T_g and a decrease in the melting temperature and enthalpy were observed for the copolyesters, which is attributed to both chain irregularity generated by the isophthalate units and the unfavorable ionic interactions created between the SI units. The mechanical properties of copolyesters were improved for low contents in sulfonated units as compared to PHT and they showed higher hydrodegradability than PHT with the degradation rate increasing with the content in sulfonated units.

II. High molecular weight PBS copolyesters containing ionic sulfonated groups up to ~15 mol-% were successfully synthesized by melt polycondensation following essentially the same procedure that is usually applied for the industrial preparation of PBS. The changes in thermal properties of PBS due to copolymerization were not significant and the copolyesters continued to be thermally stable and semicrystalline, and they even retained the ability to crystallize from the melt. Conversely, the mechanical behavior changed noticeably so that they became stiffer and stronger but also more brittle than PBS. The hydrodegradability was enhanced by copolymerization, an effect that was more pronounced when the copolyester was incubated in basic medium.

III. High molecular weight PBS was obtained by enzymatic polycondensation in the melt under mild conditions using CALB. The method was also successfully applied to the copolymerization of dimethyl succinate, L-glutamic acid dimethyl ester hydrochloride and 1,4-butanediol to produce ionic PBS bearing ammonium side groups. On the contrary the method systematically failed when the trimethylammonium L-glutamic derivative was used as comonomer. Enzymatic activity essays revealed that CALB was partially inactivated by the presence of glutamic acid and completely inhibited by the quaternized derivative. Thermal stability of the new PBS ionomers decreased respect to PBS but they continued to be heat resistant enough as to be able to be processed by melting. All they were semicrystalline and found to adopt the same crystal structure as PBS although their melting temperature and crystallinity decreased with the content in ionic groups. Melting viscosity and the T_g of the ionomers increased regularly with increasing contents in ionic groups. Antimicrobial activity results show that the PBS ionomers with contents equal o above 50 mol-% of ionic groups was found to significantly reduce the cell counts of both gram-positive and gram-negative bacterias.

IV. Poly(butylene succinate) ionomers containing phosphonium groups were synthesized for the first time by melt polycondensation at moderate temperatures from succinic acid, 2,2-(dihydroxymethyl)propyl-tributylphosphonium bromide and 1,4-butanediol. The molecular weight of these PBS ionomers decreased with the content in phosphonium units. They were semicrystalline with melting temperatures between that of the parent homopolyesters PBS and PPS, and their thermal stability decreased with the content in phosphonium units but the resistence to heat remained satisfactory high. Their T_g and in consequently their elastic modulus and tensile strength increased with the content in ionic groups giving greater stiffness to the copolyesters but also a shorter elongation to break. 15 mol-% cationic PBS ionomers containing phosphonium units are able to couple with 15 mol-% anionic sulfonated PBS ionomers to produce a semicrystalline complex. The microcrystallites resulting from the interactions between oppositely charged ions in the complex were still present after melting so that they act as efficient nuclei in the crystallization of the ionomers from the molten state.

V. Low molecular weight PBS terpolyesters containing 35 mol-% of ammonium glutarate and trimethylammonium glutarate units in total were synthesized by polycondensation using a scandium catalyst. All these terpolyesters were fairly stable to heat and were semicrystalline. They showed much poorer mechanical properties than PBS, a behavior that is consistent with their low molecular weights. The presence of these terpolyesters as compatibilizers in the preparation of nanocomposites of PBS with Cloisite gave rise to a significant increase in the Young modulus and the stress to yield, and in particular to a significant increment in the elongation to break. The capacity of these terpolyester ionomers to enhance the mechanical properties of PBS·CL nanocomposites was attributed to a binding effect based on a combination of their good compatibility with PBS and their strong ionic interaction with the anionically charged layer surfaces of Cloisite.

VI. Three different sets of nanocomposites were prepared from the copolyester ionomer containing 5 mol-% of sulfonated isophthalate units and Cloisite nanoclays either using compatibilizing additives or without them. In the absence of compatibilizers, the nanocomposites presented an intercalate structure together with a part of the Cloisite 30B layers slightly contracted due to the ionic interactions. Nanocomposites prepared with the addition of compatibilizers displayed extensive intercalation or even exfoliation. The thermal stability of all the nanocomposites was slightly diminished compared to that of the parent copolyester ionomer whereas melting and glass-transition temperatures were essentially unaffected by composition. The elastic modulus of the ionomer copolyester was significantly increased in the three series of nanocomposites. Conversely, the elongation to break of the nanocomposites was dramatically reduced.

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Mayka Irina Bautista Betancur was born on 22th of June 1984 in Sabana de Torres, Colombia. In 2007 the obtained his bachelor degree in chemical engineering by the Industrial University of Santander (UIS). After work two years in the oil industry, she decided to continue her studies focusing in plastics. In 2011 she obtained a master degree in Polymers and Biopolymers by the Polytechnic University of Catalonia (UPC) as beginning of his PhD. Research work under the superision of Dr. Sebastián Muñoz Guerra and Dr. Antxon Martínez de Ilarduya. The results generated in her research Ionic copolyesters and their nanocomposites: synthesis, characterization and properties are presented in this Thesis.

Publications

I. Sulfonated Poly(hexamethylene terephthalate) Copolyesters: Enhanced Thermal and Mechanical Properties. Bautista, M.; Martínez de Ilarduya, A.; Alla, A.; Muñoz-Guerra, S. *J. Appl. Polym. Sci*. **2013**, *129*, 9527-3535.

II. Poly(butylene succinate) Ionomers and Their Use as Compatibilizers in Nanocomposites. Bautista, M.; Martínez de Ilarduya, A.; Alla, A.; Muñoz-Guerra, S. *Polym. Compos.* **2015**, DOI: 10.1002/pc.23454.

III. Poly(butylene succinate) Ionomers with Enhanced Hydrodegradability. Bautista, M.; Martínez de Ilarduya, A.; Alla, A.; Muñoz-Guerra, S. *Polymers* **2015**, *7*, 1232-1247.

IV. Enzymatic Synthesis, Characterization and Biocide Properties of Poly(butylene succinate) Ionomers Containing Ammonium Groups. Bautista, M.; Martínez de Ilarduya, A.; Alla, A.; Muñoz-Guerra, S. To be submitted.

V. Poly(butylene succinate) Ionomers Containing Phosphonium Bromide Units. Bautista, M.; Martínez de Ilarduya, A.; Alla, A.; Muñoz-Guerra, S. To be submitted.

Communications

a) Sulfonated poly(hexamethylene terephthalate) copolyesters. Bautista, M.; Martínez de Ilarduya, A.; Alla, A.; Muñoz-Guerra, S. 1st International Conference in Polymers With Especial Focus In Early Stage Researchers (Polymar), 2013, Spain. Oral communication.

b) Poly(butylene succinate) Ionomers Containing Sulfonated Units. Bautista, M.; Martínez de Ilarduya, A.; Alla, A.; Muñoz-Guerra, S. XIII Reunión Del Grupo Especializado de Polímeros (GEP) de la RSEQ y RSEF, 2014, Spain. Oral communication.