

## Sulfonated Poly(hexamethylene terephthalate) Copolyesters: Enhanced Thermal and Mechanical Properties

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**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. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3527–3535, 2013

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### 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.<sup>1–5</sup> Several examples of random and telechelic copolyester ionomers derived from poly(ethylene terephthalate) (PET)<sup>6–10</sup> or poly(butylene terephthalate) (PBT)<sup>11–13</sup> 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 dyeing properties of polyester yarns<sup>6</sup> or their compatibility with other polymers<sup>14,15</sup> or nanoclays.<sup>16–21</sup> On the other hand poly(hexamethylene terephthalate) (PHT) is an aliphatic-aromatic polyester that present polymorphism with melting peaks between 110 and 140°C. Although it can be used for applications such as polymer for laminating processes,<sup>22</sup> 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 a 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.

### EXPERIMENTAL

#### Materials

Dimethyl terephthalate (DMT) (99+%), the sodium salt of dimethyl 5-sulfoisophthalate (DMSI) (98%) and hexanediol (HD) (97+%) were purchased from Sigma-Aldrich. These monomers were used without further purification. Tetra-butyl titanate catalyst (Merck-Schuchardt) (98%) was used as received. Solvents for purification and characterization, as trifluoroacetic acid, chloroform, diethyl ether, methanol, dichloroacetic acid, were all either technical grade or high-purity grade, and they were used as received.

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### Analytical Techniques

The intrinsic viscosities of the polymers dissolved in dichloroacetic acid were measured with an Ubbelohde viscometer thermostated at  $25^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ . Size exclusion chromatography (SEC) was performed on a Waters system equipped with a refractive index detector (RID-10A) using 1,1,1,3,3,3-hexafluoro-2-propanol as the mobile phase. The molecular weights and their distribution were calculated against poly(methyl methacrylate) standards using the Millennium 820 software. To prevent ionic aggregation, polymer samples were previously dissolved in a mixture of chloroform/trifluoroacetic acid (1/1) and precipitated with diethyl ether.

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

NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at 300.1 MHz for  $^1\text{H}$  and 75.5 MHz for  $^{13}\text{C}$ . About 10 mg for  $^1\text{H}$  or 50 mg for  $^{13}\text{C}$  of polymer samples were dissolved in 1 mL of a mixture of deuterated chloroform ( $\text{CDCl}_3$ ) and trifluoroacetic acid (TFA) (7/3 v/v). 64 and 5000–10,000 scans were acquired with 32- and 64-K data points and 1 and 2 sec of relaxation delays for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively.

The thermal behavior of the polyesters was examined by differential scanning calorimetry (DSC) with a PerkinElmer DSC Pyris 1 instrument calibrated with indium and zinc for the temperature and enthalpy. DSC data were obtained from 4 to 6 mg samples at heating and cooling rates of  $10^{\circ}\text{C min}^{-1}$  under nitrogen circulation ( $20\text{ mL min}^{-1}$ ). The  $T_g$  of the polyesters was measured from amorphous samples at heating rate of  $20^{\circ}\text{C min}^{-1}$ . Isothermal crystallization studies were carried out on polymer films heated up to  $200^{\circ}\text{C}$  at  $20^{\circ}\text{C min}^{-1}$  and cooled at the selected crystallization temperature. The samples were subjected to an isothermal process for 1 h and then heated up to  $200^{\circ}\text{C}$  at  $10^{\circ}\text{C min}^{-1}$ . TGA measurements were performed from 10 to 15 mg of sample under nitrogen flow of  $20\text{ mL min}^{-1}$  at a heating rate of  $10^{\circ}\text{C min}^{-1}$  and within a temperature range of  $30\text{--}600^{\circ}\text{C}$ , using a Perkin-Elmer TGA6 thermobalance.

Powder X-ray diffraction patterns were recorded from powdered samples coming directly from synthesis on an INEL CPS-120 diffractometer Debye-Scherrer configuration and using the  $\text{Cu K}\alpha$  radiation of wavelength 0.1542 nm.

Tensile testing was performed on bone shape specimens ( $2.7 \times 10\text{ mm}^2$ ) which were cut from isotropic films obtained by hot pressing with a thickness of about  $200\text{ }\mu\text{m}$ . Tensile tests were conducted at room temperature on a Zwick BZ2.5/TN1S universal tensile testing apparatus operating at a constant crosshead speed of  $10\text{ mm min}^{-1}$  with a 0.5 N preload and a grip-to-grip separation of 20 mm.

Hydrolytic degradation studies were made on amorphous films with a thickness of  $200\text{ }\mu\text{m}$  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 ( $\text{pH} = 5.2$ ) and left inside an oven at  $60^{\circ}\text{C}$  for several weeks. Samples were taken out every week and washed with distilled water previous to GPC and weight loss determinations.

### Synthesis of $\text{PHT}_x\text{SI}_y$ 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  $\text{PHT}_x\text{SI}_y$  copolyesters with SI unit contents above 10%, 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  $190^{\circ}\text{C}$ , and the mixture was stirred until all aromatic comonomers were dissolved in HD. The transesterification reaction was carried out at  $190^{\circ}\text{C}$  under a low nitrogen flow for a period of 2–3 h, along which methanol byproduct was distilled off. The polycondensation reaction was performed at  $250\text{--}280^{\circ}\text{C}$  under reduced pressure (0.5–1 mbar) for 1.5–2 h, 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.

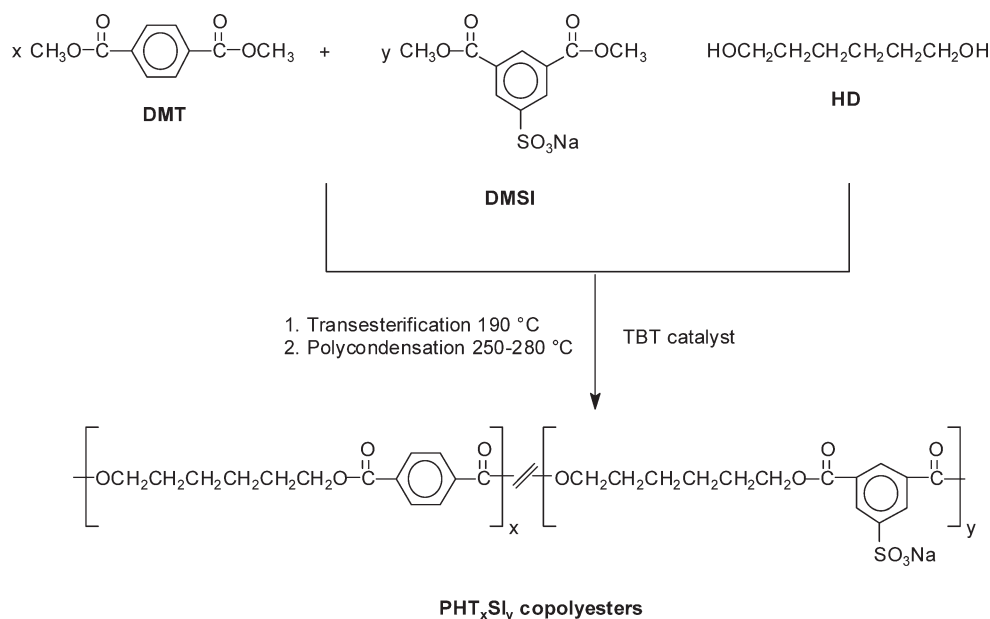
## RESULTS AND DISCUSSION

### Synthesis, Composition, and Microstructure of $\text{PHT}_x\text{SI}_y$ Copolyesters

The synthetic procedure followed in this work for the preparation of  $\text{PHT}_x\text{SI}_y$  copolyesters is depicted in Figure 1. The process consists of a two step melt polycondensation process. The first step was carried out at  $190^{\circ}\text{C}$  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%. It was observed that the final melt viscosity increased gradually with the content of SI units, to the point that copolymers containing 50% 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 crosslinks.<sup>7</sup>

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 I). The increase of the melt viscosity provoked by the interactions of ionic groups, which prevents 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  $3000\text{ cm}^{-1}$  that correspond to the CH's stretching vibrations. At around  $1710\text{ cm}^{-1}$  there is a



**Figure 1.** Outline of the synthesis route followed for the preparation of PHT<sub>x</sub>SI<sub>y</sub> copolyesters examined in this work.

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<sup>-1</sup> corresponding to the SO<sub>2</sub> asymmetric and symmetric stretching vibrations emerged. Additionally a new peak at 753 cm<sup>-1</sup> arising from the S-O<sup>-</sup> bond appear in the copolymers with intensity increasing with the content of SI units in the copolymer.

The chemical structure was further ascertained by NMR spectroscopy. Both <sup>1</sup>H and <sup>13</sup>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<sub>70</sub>SI<sub>30</sub> 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 I, there was a good correlation between feed and final copolyester compositions.

All copolyesters showed small signals in the <sup>1</sup>H 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% of SI units.<sup>10</sup> In the present case, the content of dihexyleneglycol units was within the range 1–3 mol % for all compositions except for the PHSI homopolymer where the content was about 5.4 mol %.

**Table I.** Composition and Molecular Weights of PHT, PHSI, and PHT<sub>x</sub>SI<sub>y</sub> Copolyesters

Polyester	Copolymer composition <sup>a</sup>		DHG <sup>c</sup>	Molecular weights		
	T/SI	Copolymer composition <sup>b</sup> T/SI		[η] <sup>d</sup>	M <sub>w</sub> <sup>e</sup>	D <sup>e</sup>
PHT	100/0	100/0	0.1	0.75	21,300	2.2
PHT <sub>95</sub> SI <sub>5</sub>	95/5	94.9/5.1	1.0	0.74	22,000	2.3
PHT <sub>90</sub> SI <sub>10</sub>	90/10	90.1/9.9	2.5	0.56	19,000	2.3
PHT <sub>80</sub> SI <sub>20</sub>	80/20	80.6/19.4	2.5	0.57	19,500	2.4
PHT <sub>70</sub> SI <sub>30</sub>	70/30	72.3/27.7	1.1	0.48	20,000	2.4
PHT <sub>60</sub> SI <sub>40</sub>	60/40	63.6/36.4	2.7	0.48	17,800	2.1
PHT <sub>50</sub> SI <sub>50</sub>	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

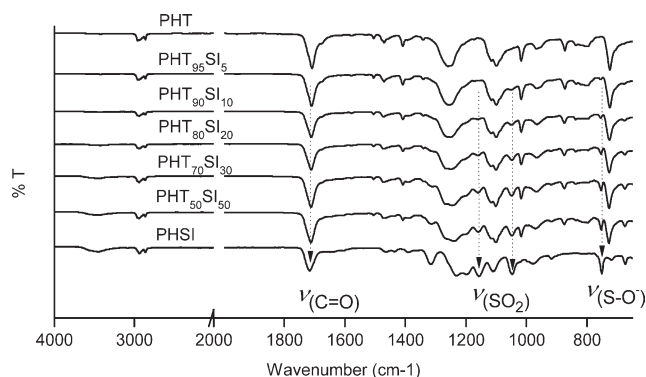
<sup>a</sup>Molar ratio in the initial feed.

<sup>b</sup>Determined from the aromatic proton resonances observed in the <sup>1</sup>H NMR spectra.

<sup>c</sup>Dihexylene glycol content (mol%) calculated from <sup>1</sup>H NMR spectra.

<sup>d</sup>Intrinsic viscosity (dL g<sup>-1</sup>) measured in dichloroacetic acid at 25 °C.

<sup>e</sup>Weight-average molecular weight (M<sub>w</sub>) and dispersity (D) determined by GPC.



**Figure 2.** FTIR spectra of PHT<sub>x</sub>SI<sub>y</sub> copolyesters and their parent homopolymers with indication of the main stretching vibrations.

According to our previous satisfactory experience in the analysis of this type of copolyesters,<sup>10</sup> <sup>13</sup>C NMR was used for the study of the microstructure of PHT<sub>x</sub>SI<sub>y</sub>. 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.<sup>10</sup> 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,<sup>23</sup> the number average sequence length and degree of randomness could be estimated (Table SI of Supporting

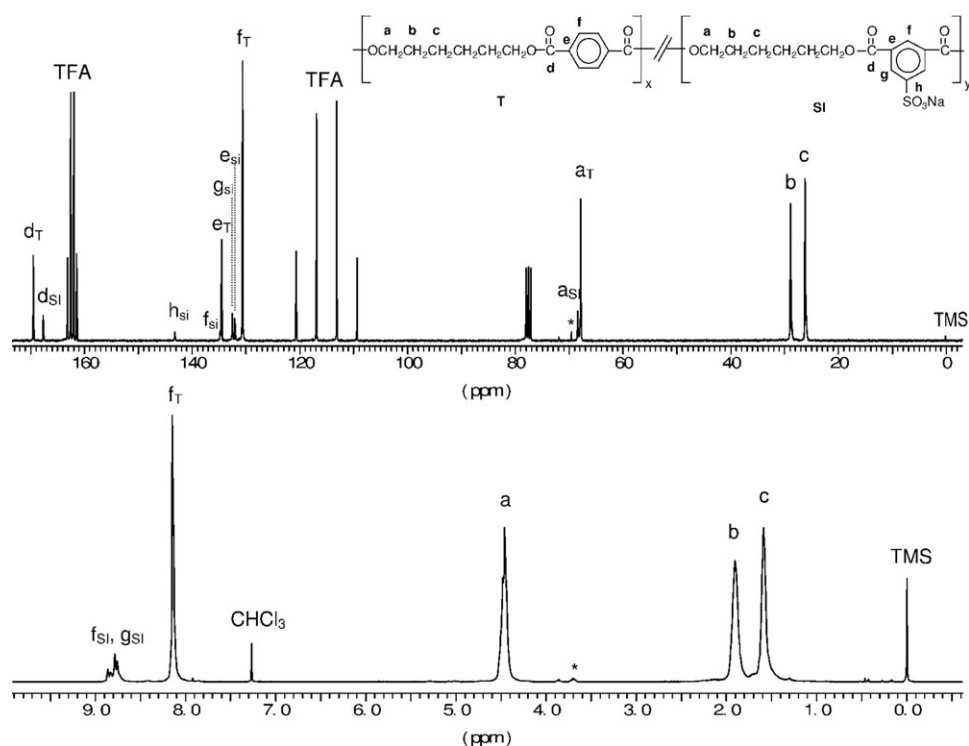
Information). The degree of randomness was close to 1 for all copolyesters, which indicates that they have a statistical distribution of terephthalate and sulfoisophthalate units along the polymer chain.

### Solubility of PHT<sub>x</sub>SI<sub>y</sub> Copolyesters

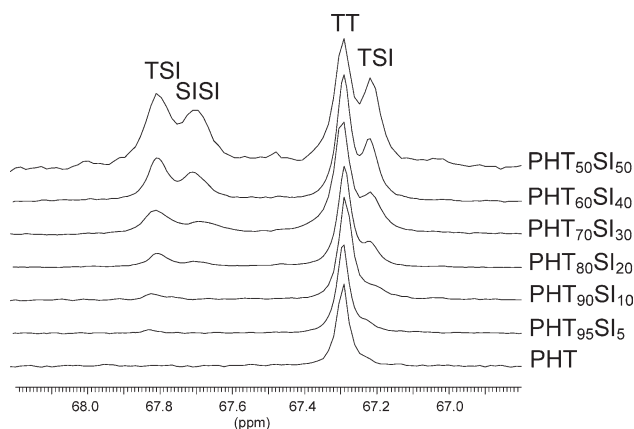
To evaluate the effect of the SI units on solubility, the behavior of the PHT<sub>60</sub>SI<sub>40</sub> copolyester in a variety of solvents with different polarity was compared with that observed for the PHT and PHSI homopolymers (Table II). A great difference in solubility was found according to 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<sub>60</sub>SI<sub>40</sub> were soluble in hot water, in DMSO and in DMF. The increasing content of sodium sulfonate groups in PHT<sub>x</sub>SI<sub>y</sub> copolyesters improved the solubility of them in both polar protic and 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.<sup>24</sup>

### Thermal Behavior of PHT<sub>x</sub>SI<sub>y</sub> Copolyesters

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°C



**Figure 3.** The 300.1 MHz <sup>1</sup>H NMR (bottom) and 75.5 MHz <sup>13</sup>C NMR (top) spectra of PHT<sub>70</sub>SI<sub>30</sub> recorded in a mixture of CDCl<sub>3</sub>/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  $^{13}\text{C}$  NMR spectra of  $\text{PHT}_x\text{SI}_y$  in the region corresponding to the oxymethylene carbons with dyad assignments.

**Table II.** Compared Solubilities<sup>a</sup> of PHT, PSI, and the  $\text{PHT}_{60}\text{SI}_{40}$  Copolyester

Solvent	Polyester		
	PHT	$\text{PHT}_{60}\text{SI}_{40}$	PHSI
Water	–	+	++
Ethanol	–	–	–
Diethyl ether	–	–	–
Acetone	–	–	–
THF	+	±	–
Chloroform	++	±	–
DMSO	–	++	++
DMF	–	++	+
NMP	+	++	++
TFA	++	++	++

<sup>a</sup>Estimated according to the method of Braun.<sup>25</sup> (–) 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.

**Table III.** Thermal Properties of PHT, PHSI, and  $\text{PHT}_x\text{SI}_y$  Copolyesters

Polyester	$T_g^a$ (°C)	$T_c^b$ (°C)	$T_m^c$ (°C)	$\Delta H_m^c$ (J g <sup>-1</sup> )	$^{\circ}T_d^d$ (°C)	$T_{d1}^e$ (°C)	$RW^f$ (%)
PHT	11	122	148	38	371	403	5
$\text{PHT}_{95}\text{SI}_5$	14	76	139	31	356	<b>374</b> /444	5
$\text{PHT}_{90}\text{SI}_{10}$	14	–	130	21	350	<b>369</b> /444	7
$\text{PHT}_{80}\text{SI}_{20}$	19	–	–	–	346	<b>364</b> /447/525	11
$\text{PHT}_{70}\text{SI}_{30}$	31	–	–	–	341	<b>352</b> /449/522	15
$\text{PHT}_{60}\text{SI}_{40}$	43	–	–	–	339	<b>347</b> /447/529	18
$\text{PHT}_{50}\text{SI}_{50}$	52	–	–	–	327	<b>340</b> /439/531	24
PHSI	78	–	–	–	316	<b>334</b> /443/528	34

<sup>a</sup>Glass transition temperature was taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 20°C min<sup>-1</sup>.

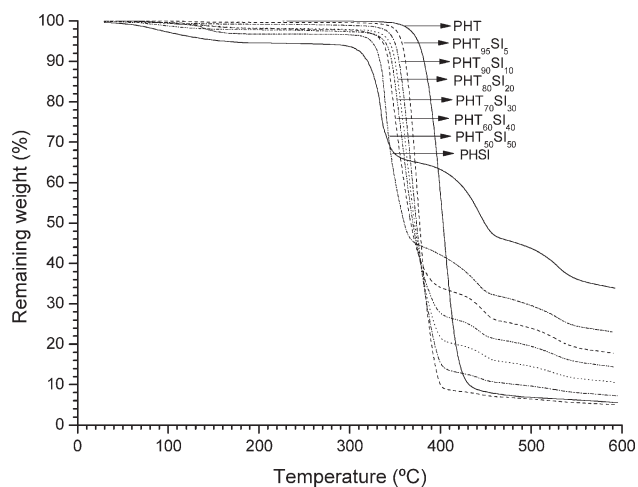
<sup>b</sup>Crystallization temperature was registered at cooling from 200°C at 10°C min<sup>-1</sup>.

<sup>c</sup>Melting temperature and enthalpy were registered at a heating rate of 10°C min<sup>-1</sup> from samples crystallized as indicated in b.

<sup>d</sup>Degradation temperature at which a 10% weight loss was observed in the TGA traces recorded at 10°C min<sup>-1</sup>.

<sup>e</sup>Temperatures of maximum degradation rates. In bold main degradation temperature.

<sup>f</sup>Remaining weight at 600°C.



**Figure 5.** TGA traces of  $\text{PHT}_x\text{SI}_y$  copolyesters and their parent homopolymers.

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 III, 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°C. On the other hand the remaining weight after the thermal degradation at 600°C increased continuously with the content of SI units (Table III).

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).

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°C, respectively) (Table III).

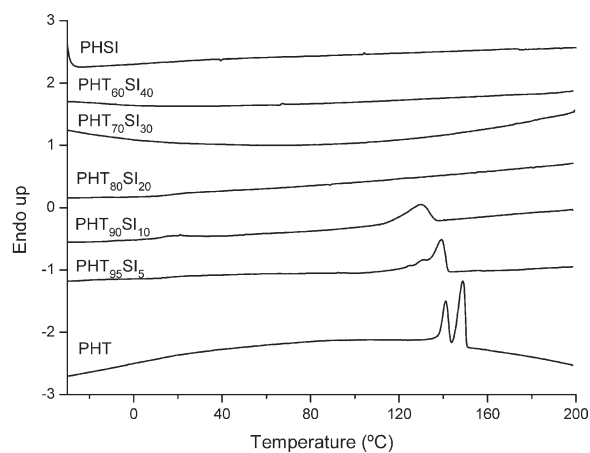


Figure 6. DSC thermograms (second heating) of  $\text{PHT}_x\text{SI}_y$  copolyesters.

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 crosslinks causing a reduction of the chain mobility. This behavior is in accordance with the results of Eisemberg et al.,<sup>26,27</sup> who reported that the  $T_g$  of ionomers increased linearly with the content of salt units.

#### Isothermal Crystallization of $\text{PHT}_x\text{SI}_y$ Copolyesters

To evaluate the crystallizability of  $\text{PHT}_x\text{SI}_y$  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  $\text{PHT}_{95}\text{SI}_5$  and  $\text{PHT}_{90}\text{SI}_{10}$  copolyesters at two different temperatures.

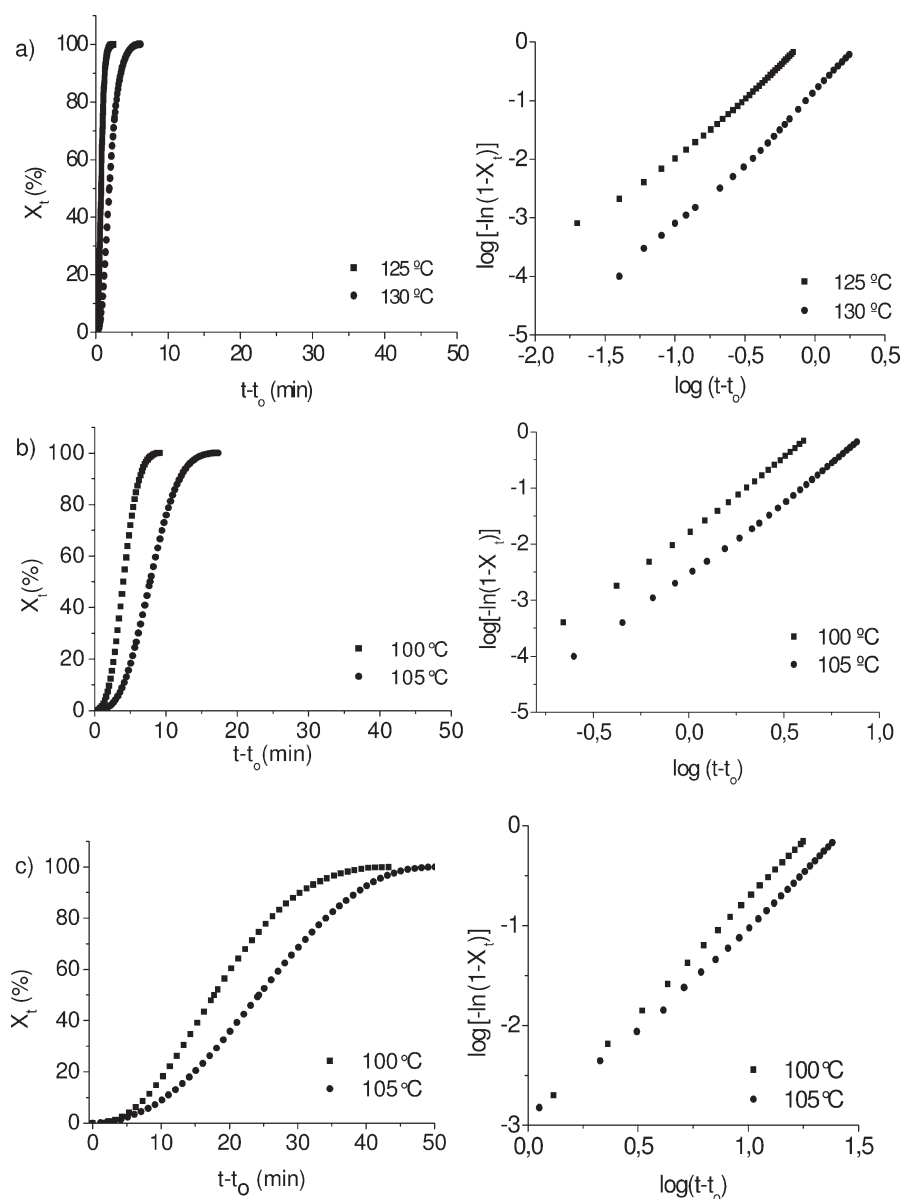


Figure 7. Relative crystallinity  $X_t$  versus crystallization time (left) and Avrami plots (right) for (a) PHT, (b)  $\text{PHT}_{95}\text{SI}_5$ , and (c)  $\text{PHT}_{90}\text{SI}_{10}$  at the indicated temperatures.

**Table IV.** Crystallization Parameters of Isothermally Crystallized PHT and PHT<sub>x</sub>SI<sub>y</sub> Copolyesters

Polyester	$T_c$ (°C)	$t_o^a$ (min)	Avrami parameters <sup>b</sup>		
			$n$	$\log K$	$t_{1/2}$ (min)
PHT	125	0.24	2.1	-0.1	0.95
	130	0.34	2.3	0.9	2.21
PHT <sub>95</sub> SI <sub>5</sub>	100	0.38	2.6	1.7	4.40
	105	0.75	2.6	2.5	8.53
PHT <sub>90</sub> SI <sub>10</sub>	100	1.69	2.3	3.0	19.49
	105	6.87	2.1	3.1	31.22

<sup>a</sup>Onset crystallization time.

<sup>b</sup>Avrami exponent  $n$ , constant of crystallization  $k$  ( $\text{min}^{-1}$ ), and crystallization half-time  $t_{1/2}$ .

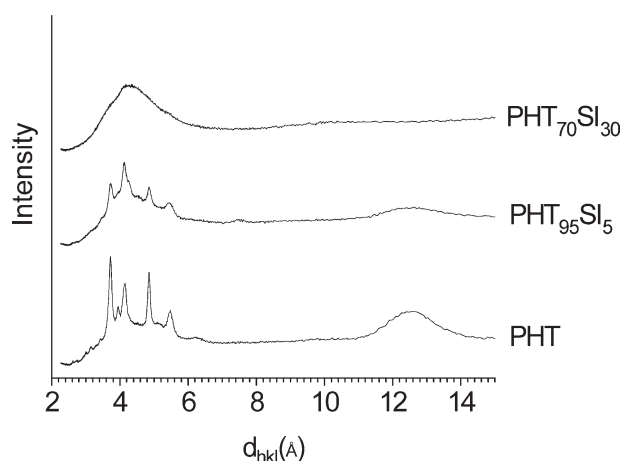
Unfortunately, it was not possible to register the crystallization enthalpy of PHT at these temperatures because the process is extremely fast in this case. Nevertheless, comparison of the registered data for the homopolymer and the copolyesters showed that the incorporation of SI units shifted the resulting 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 IV.

#### Crystalline Structure of PHT<sub>x</sub>SI<sub>y</sub> Copolyesters

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  $\alpha$ ,

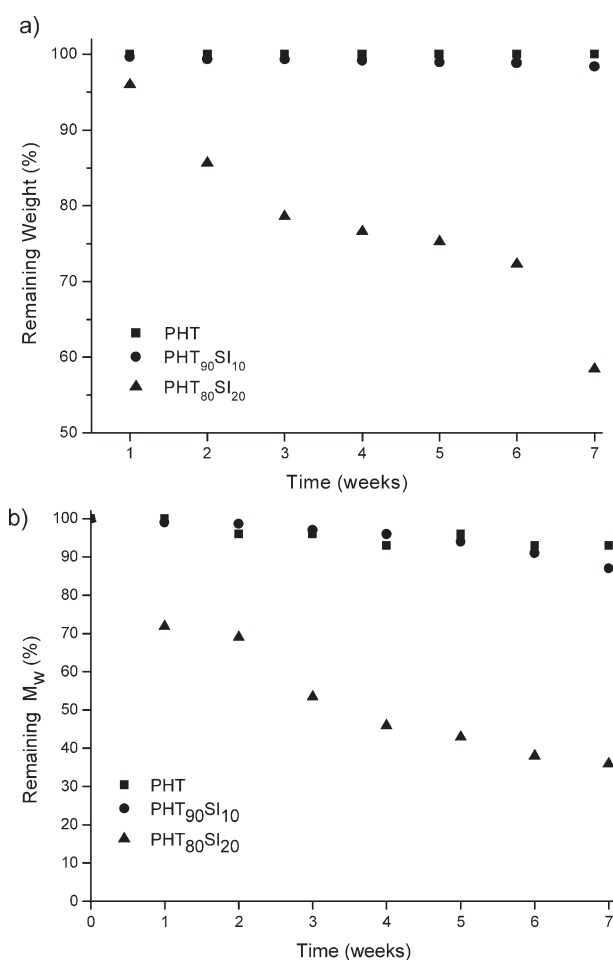


**Figure 8.** Powder WAXS diffraction patterns of PHT and the indicated PHT<sub>x</sub>SI<sub>y</sub> copolyesters.

**Table V.** Tensile Properties of PHT and PHT<sub>x</sub>SI<sub>y</sub> Copolyesters

Polyester	Young's modulus $E$ (MPa)	Maximum tensile stress $\sigma_{\max}$ (MPa)	Elongation at break $\epsilon_{\text{break}}$ (%)
PHT	539	26	16
PHT <sub>95</sub> SI <sub>5</sub>	550	29	569
PHT <sub>90</sub> SI <sub>10</sub>	700	30	200
PHT <sub>80</sub> SI <sub>20</sub>	759	31	170
PHT <sub>70</sub> SI <sub>30</sub>	814	32	125
PHT <sub>60</sub> SI <sub>40</sub>	908	37	24

$\beta$ , and  $\gamma$ , depending on the thermal or solvent treatment, in which the polyester is arranged in a nearly fully extended conformation.<sup>28–31</sup> The powder diffraction profiles recorded from PHT and two selected copolyesters of the PHT<sub>x</sub>SI<sub>y</sub> series are compared in Figure 8. The most prominent Bragg spacings measured on such profiles are listed in Table SII of Supporting Information. According to literature, the profile observed for PHT arises from a mixture of two  $\beta$ ,  $\beta'$  triclinic forms; these crystalline forms differ only in the local conformational disorder



**Figure 9.** The evolution of (a) the remaining weight and (b) weight average molecular weight for PHT and PHT<sub>x</sub>SI<sub>y</sub> copolyesters as a function of incubation time.

around the terephthaloyl groups.<sup>32</sup> As it could be expected from its lower crystallinity revealed by DSC broader diffraction peaks were observed for the PHT<sub>95</sub>SI<sub>5</sub> 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<sub>70</sub>SI<sub>30</sub> 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.

#### Mechanical Properties of PHT<sub>x</sub>SI<sub>y</sub> Copolyesters

The mechanical parameters, such as the Young's modulus, the maximum tensile stress and the elongation at break are compared in Table V. 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<sub>95</sub>SI<sub>5</sub> than observed for pure PHT (Table V). 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.

#### Hydrolytic Degradation of PHT<sub>x</sub>SI<sub>y</sub> Copolyesters

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°C and pH 5.2. The hydrolytic degradation was comparatively evaluated for PHT and the PHT<sub>x</sub>SI<sub>y</sub> copolyesters containing 10 and 20 mol % of SI units. 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<sub>90</sub>SI<sub>10</sub> whereas, a considerable reduction in both sample and molecular weights was observed for the PHT<sub>80</sub>SI<sub>20</sub> copolyester, with nearly 45% of its original weight being lost upon 7 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.<sup>10</sup> for PET copolyesters containing SI units, which revealed that the hydrodegradability of the copolyesters was very high as compared to PET.

#### 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<sup>-1</sup>. 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°C (PHT) to 78°C (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 unfavorable 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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