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Preparation and hydrolytic degradation of sulfonated poly(ethylene terephthalate) copolymers

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Abstract

A series of poly(ethylene terephthalate-*co*-ethylene 5-sodiosulfoisophthalate) copolyesters containing from 1 up to 50 mol% of sulfonated units was prepared by melt polycondensation from ethylene glycol and mixtures of dimethyl terephthalate and dimethyl 5-sodiosulfoisophthalate. The resulting copolymers had a random microstructure and contained oligo(ethylene glycol) units in amounts increasing with the content in sulfonated isophthalate units. Copolyesters with more than 20 mol% of 5-sodiosulfoisophthalic units were amorphous and easily soluble in water. The hydrodegradability of the copolyesters was very high as compared to poly(ethylene terephthalate), and increased with the content in sulfonated units. It was demonstrated that the susceptibility to acidic hydrolysis of these copolymers is mainly due to the presence of the sodium sulfonate groups, the influence of the oligo(ethylene glycol) units in this regard being noticeable but limited.

Keywords: Poly(ethylene terephthalate); PET copolymers; Sulfonated copolyesters

1. Introduction

Poly(ethylene terephthalate) (PET) modified with ionic groups constitutes a very effective approach to change significantly both chemical and physical properties of the parent polymer over a broad range [1]. Sodium sulfonate-containing PET ionomers, i.e. polymers containing small amounts (1–5 mol%) of sulfonated units, are known for long time and were originally commercialized by DuPont as textile fibers with improved dyeability to cationic dyes. The influence of sulfonation on viscosity, crystallinity, and mechanical properties has been investigated for these PET ionomers [2,3]. Most of the changes in the physical properties observed for these copolymers are interpreted in terms of the restricted mobility model made of aggregates of ion-pairs multiplets [4–6]. On the other hand, a literature survey on sulfonated PET copolymers revealed a number of reports addressing the influence of sulfonation on the hydrolytic stability of PET [7–10]. Although they all agree in pointing out the enhancing effect of the sulfonate group on the hydrodegradability of the polyester, no systematic study relating stability with composition of the sulfonated PET copolymers has been carried out so far.

In this paper we wish to report on poly(ethylene terephthalate-*co*-5-sodiosulfoisophthalate) copolymers, abbreviated PETSI, their preparation and detailed characterization, and their hydrodegradability under acidic conditions. The mild acidic hydrolysis of PETSI is examined as a function of the copolyester composition, including both the sulfonated units introduced under control and the oligo(ethylene glycol) units that eventually enter in the copolyester backbone, as a result of uncontrolled secondary side reactions occurring at polycondensation.

2. Experimental

2.1. Materials and measurements

Dimethyl terephthalate (DMT) (99 + %), dimethyl 5-sodiosulfoisophthalate (Na-DMSI) (99 + %), diethylene glycol (DEG) (99%), and ethylene glycol (EG) (99 + %) were all purchased from Sigma–Aldrich, and tetrabutyl

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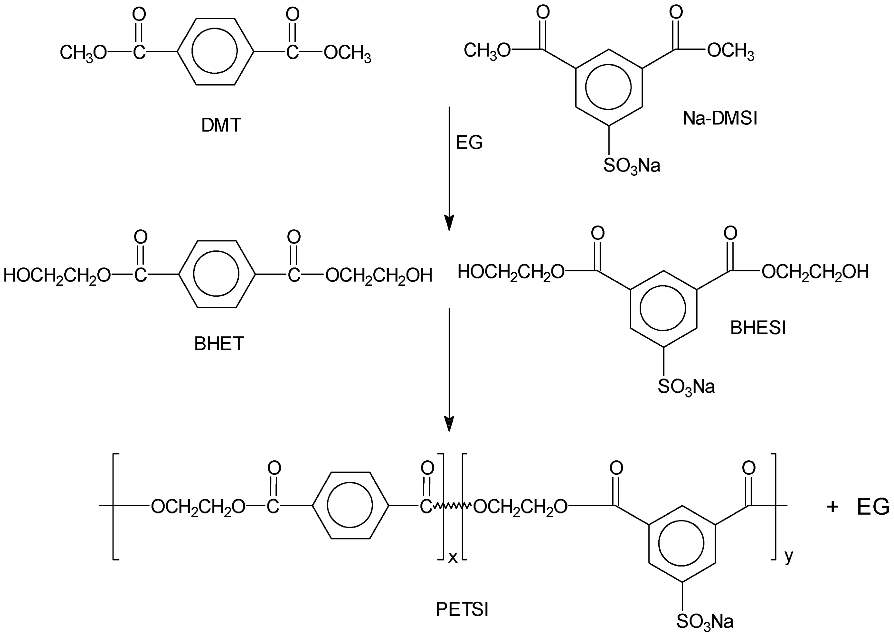


Scheme 1. Chemical synthesis of PETSI.

titanate (TBT) was supplied by Merck–Schuchardt. All of them were reagent grades and used as received. All solvents used for purification and characterization were of either technical or high purity grade and used as received.

^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer at 25.0 °C operating at 300.1 and 75.5 MHz, respectively. The spectra were internally referenced to tetramethylsilane. The polyesters were dissolved in a $CDCl_3$/trifluoroacetic acid (TFA) (1.5/1 v/v) mixture and 64 scans were acquired for ^1H and 1000 to 10,000 for ^{13}C NMR spectra, with 32 K data points and relaxation delays of 1 and 2 s, respectively. $^{13}C-^{1}H$ heteronuclear shift correlation spectra were recorded by means of the pulse sequences (*hxco*) implemented in the Bruker NMR instrument package. Gel permeation chromatography (GPC) analysis was performed on a Waters system equipped with a refractive index detector and using 1,1,1,3,3,3-hexafluoro-2-propanol as the mobile phase. The molecular weights and their distribution were calculated against monodisperse poly(methyl methacrylate) standards using the Millenium 820 software.

The thermal behavior of the polyesters was examined by differential scanning calorimetry (DSC) using a Perkin–Elmer DSC Pyris 1 instrument calibrated with indium. DSC data were obtained from 4 to 6 mg samples at a heating rate of 10 °C min^{-1} under a nitrogen circulation. Thermogravimetric analyses (TGA) were performed using a Perkin–Elmer TGA-6 thermobalance at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. Powder wide-angle X-ray diffraction patterns were obtained on flat photographic films with a modified Statton camera using nickel-filtered monochromatic Cu Kα radiation (wavelength = 1.5418 Å). The patterns were calibrated with molybdenum sulfide.

2.2. General procedure for the synthesis of the PETSI copolyesters

DMT, Na-DMSI, EG, and TBT catalyst were introduced into a three-necked 100-mL round-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum distillation outlet, using the selected comonomer ratios. A molar ratio 2.2:1 of glycol to the total amount of the DMT and Na-DMSI monomers was used in all copolymerizations. Transesterification reactions were carried out at 190 °C under a nitrogen flow, whereas the polycondensation reactions were performed in the range of 220–270 °C under a 0.5–1 mbar vacuum. The polymerization was allowed to proceed isothermally for the required period of time with simultaneous removal of the excess of the glycol by distillation. Finally, the reaction mixture was cooled down to room temperature and atmospheric pressure was recovered using nitrogen to prevent degradation. The resulting polymers were isolated by dissolving the reaction mixture in a $CHCl_3$/TFA (8/1 v/v) mixture, followed by the slow addition of cold diethyl ether under vigorous stirring. The precipitated polyesters were collected by filtration, washed with diethyl ether, and finally dried under reduced pressure.

The same procedure, with the corresponding changes in the composition of the feed, was used for the preparation of PET and the poly(ethylene-*co*-diethylene terephthalate) (PEDET) copolyester studied in this work.

Table 1
Characteristics of the PETSI copolyesters

Polyester	T/SI comonomer ratio[a]		Molecular weight[b]		Diol content[c]			
	Feed	Copolymer	M_w	M_n	EG	DEG	TEG	PEG
PET[d]	100/0	100/0	41,800	15,600	97.5	2.5	–	–
$PET_{99}SI_1$	99/1	99.0/1.0	29,700	9000	94.0	5.5	0.5	–
$PET_{98}SI_2$	98/2	98.1/1.9	22,500	7000	84.0	14.5	1.5	–
$PET_{95}SI_5$	95/5	95.6/4.4	21,900	6700	76.5	19.5	4.0	–
$PET_{90}SI_{10}$	90/10	91.7/8.3	48,000	17,200	64.5	28.5	7.0	–
$PET_{80}SI_{20}$	80/20	79.8/20.2	22,100	8500	68.0	25.5	6.5	–
$PET_{70}SI_{30}$	70/30	73.6/26.4	17,200	6500	45.5	28.5	18.5	7.5
$PET_{50}SI_{50}$	50/50	51.6/48.4	9500	2600	41.5	30.0	19.5	8.5
PEDET[e]	–	–	19,000	6000	96.5	3.5	–	–

[a] Terephthalate to 5-sodiosulfoisophthalate molar ratio in the initial reaction mixture and in the copolymer determined by ^{1}H NMR.

[b] Number- and weight-average molecular weights determined by GPC.

[c] Composition in glycols in mol% determined by ^{1}H NMR.

[d] Poly(ethylene terephthalate) prepared using the same procedure as used for the copolymers.

[e] PET copolymer containing 3.5 mol% of diethylene glycol units.

2.3. Hydrolytic degradation essays

Films of PET, and the PETSI and PEDET copolymers with a thickness of ~300 μm, were prepared by casting at room temperature from a 10% (w/v) solution in $CHCl_3$/TFA (8/1 v/v) on a silanized Petri dish. The films were cut into 14-mm diameter, 60 to 90-mg weight disks, which were dried in vacuo at 50 °C to constant weight. Samples were immersed in Elix-Millipore purified water (pH 4.35) in parallel experiments at 37 and 80 °C, respectively. After immersion for the fixed period of time, the samples were rinsed thoroughly in water and dried to constant weight. Sample weighting, GPC measurements, and NMR spectroscopy were used to follow the evolution of the hydrodegradation.

3. Results and discussion

3.1. Synthesis and characterization

The procedure applied in this work to produce the PETSI copolymers is outlined in Scheme 1. The process was conducted in two stages with the feed consisting of a dimethyl terephthalate and dimethyl 5-sodiosulfoisophthalate mixture with the selected molar composition, and an excess of ethylene glycol. A mixture of bis(2-hydroxyethyl) terephthalate (BHET) and the sodium salt of bis(2-hydroxyethyl) 5-sulfoisophthalate (BHESI), accompanied with additional amounts of higher oligoesters and oligo(ethylene glycol)s, was the product of the transesterification reactions happening in the first stage at 190 °C. The

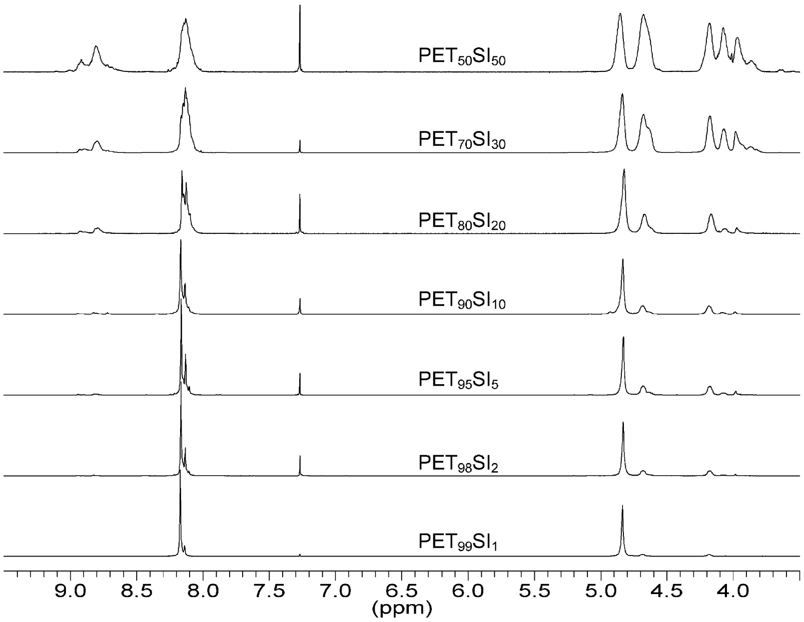


Fig. 1. Compared ^{1}H NMR spectra of PETSI.

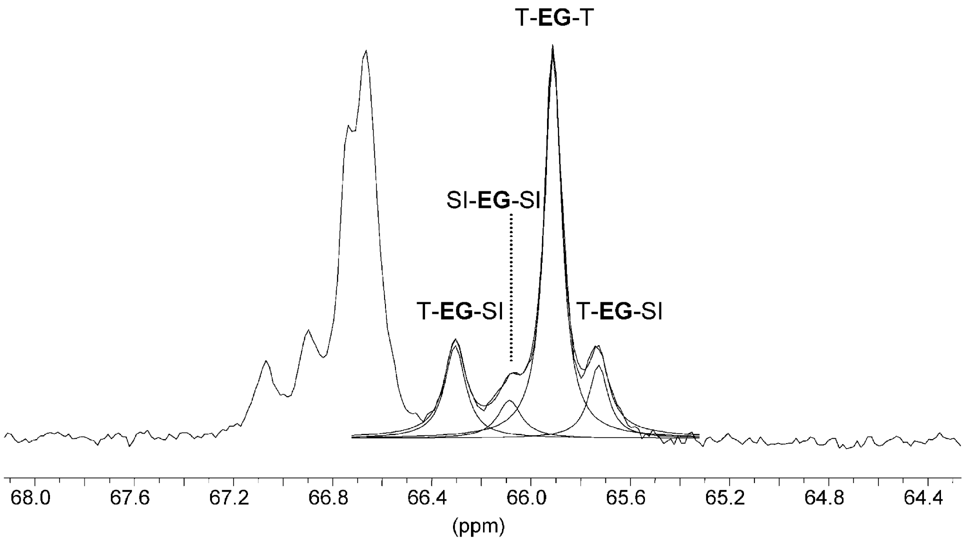


Fig. 2. ^{13}C NMR signal of the ethylene glycol units in $PET_{70}SI_{30}$, with indication of the dyad assignments and the deconvolution used for microstructure determination. The peaks on the left without labeling arise from diethylene glycol units.

copolymers were formed in the second stage conducted between 220 and 270 °C by cross transesterification reactions of the intermediate hydroxyethyl esters.

A series of PETSI copolyesters having a content in 5-sodiosulfoisophthalic units ranging from 1 to 50 mol% was prepared by this procedure. The most relevant characteristics of the resulting sulfonated copolyesters are collected in Table 1.

The chemical constitution and comonomer composition of PETSI was assessed by NMR spectroscopy. The ^{1}H NMR spectra of the series are compared in Fig. 1. The relative area of the aromatic proton signals appearing at 8.9 and 8.2 ppm for the 5-sodiosulfoisophthalic and terephthalic units, respectively, was measured to estimate the content of the two aromatic comonomers in the copolyesters, which was found to be essentially the same as that used in the reaction feed.

The complex signals observed in the 3.8–4.9 ppm region arise from the oxyethylene units contained in the diol counterpart of the copolymer. In the ^{13}C NMR spectra, the aliphatic carbon resonances appear as two complex groups of peaks situated in the 65–75 ppm range. In addition to the expected ethylene glycol units, diethylene glycol ($-CH_2CH_2OCH_2CH_2O-$), triethylene glycol ($-CH_2CH_2OCH_2CH_2OCH_2CH_2O-$), and even higher oligo(ethylene glycol) units are present in the PETSI copolyesters. An accurate assignment of the ^{1}H and ^{13}C peaks associated to the magnetically different ethylene protons and carbons present in the copolyesters was achieved by heteronuclear correlation (HETCOR) analysis. The relative content of the oligo(ethylene glycol) units increased with the degree of sulfonation of the copolymer, the amount of monoethylene glycol being reduced to less than 50 mol% in the $PET_{70}SI_{30}$ and $PET_{50}SI_{50}$ copolyesters. Signals arising from

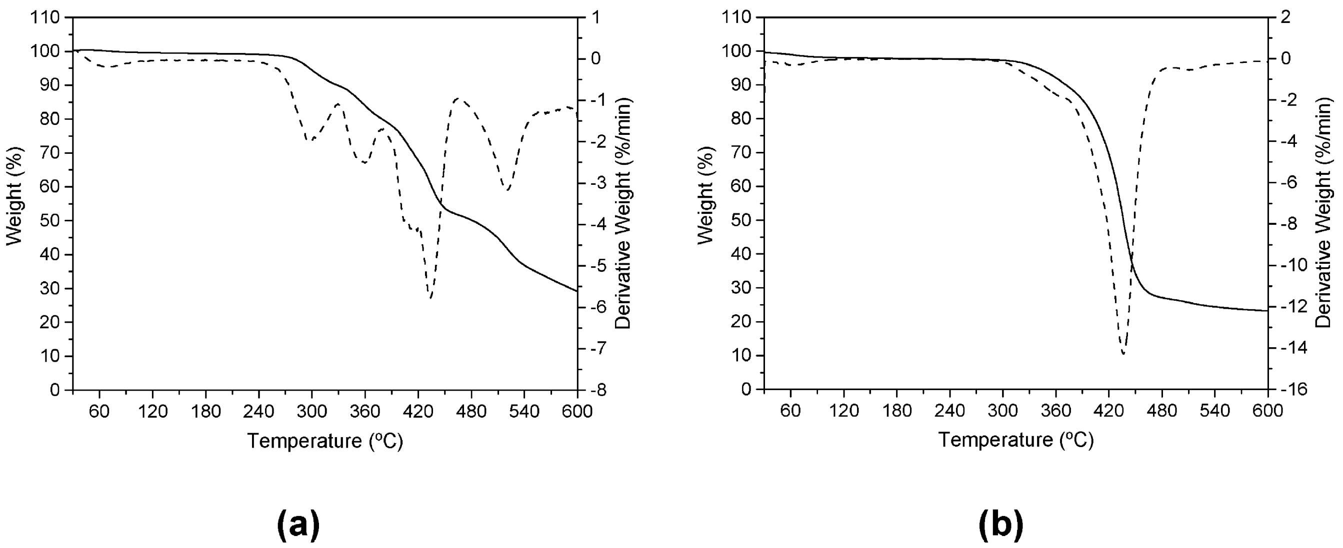


Fig. 3. TGA traces of (a) BHESI and (b) $PET_{80}SI_{20}$, and their corresponding derivative curves.

Table 2
Thermal and structural data of the PETSI copolyesters

Polymer	Thermal data^a										
	T_g (°C)	T_m (°C)	T_d (°C)	X-ray spacings (Å)^b							
PET	78	253 (46)	436	5.40	5.06	4.17	3.94	3.47	3.20	2.74	2.14
$PET_{99}SI_1$	74	240 (18)	438	5.48	*5.00*	4.17	*3.99*	3.47	*3.20*	2.78	*2.14*
$PET_{98}SI_2$	69	216 (7.4)	442	5.48		4.08		3.54		2.81	
$PET_{95}SI_5$	66	198 (7.6)	436	5.48		4.08		3.54		2.85	
$PET_{90}SI_{10}$	58	167 (3.5)	439	5.48		4.17		3.54		2.85	
$PET_{80}SI_{20}$	56	–	437					–			
$PET_{70}SI_{30}$	53	–	434					–			
$PET_{50}SI_{50}$	27	–	429					–			

[a] Glass-transition and melting temperatures (melting enthaply in J g^{-1} in parentheses) measured by DSC, and decomposition temperature measured by TGA as the peak of the derivative curve.

[b] Powder X-ray diffraction spacings recorded from the polymer coming directly from synthesis. Spacings of PET are consistent with a triclinic unit cell of parameters: $a_0 = 4.56$ Å, $b_0 = 5.94$ Å, $c_0 = 10.75$ Å, $\alpha = 98.5°$, $\beta = 118°$, $\gamma = 112°$, as reported by Daubeny et al. [11]. Additional spacings appearing upon annealing of $PET_{99}SI_1$ are given in italics.

hydroxyethyl end-groups were also identified and more noticeably detected as the molecular weight of the polymer decreased.

The aliphatic region of the ^{13}C NMR spectra contained adequate information for the evaluation of the comonomer distribution. In fact the signal arising from the ethylene glycol units at 65–67 ppm appeared to be resolved in four peaks, which could be assigned to the three different dyad sequences feasible in PETSI copolyesters, i.e. **T**-EG-**T**, **SI**-EG-**SI**, and **T**-EG-**SI** or **SI**-EG-**T** (Fig. 2). A quantitative analysis of these peaks in relation to the composition of the copolyester led to the conclusion that the microstructure of the polymer is almost at random.

The molecular weight of PETSI was estimated by GPC. With the exception of $PET_{90}SI_{10}$, the overall trend displayed by the series is that molecular weight decreased with the content of the copolyester in sulfonated units to a point that an oligomeric product consisting of about ten units in average was the result of the copolymerization of the equimolar mixture of DMT and Na-DMSI. In accordance with this trend, the homopolymer poly(ethylene 5-sodiosulfoisophthalate) could not be prepared by this method.

3.2. Thermal properties and structure

Thermogravimetric analysis of BHESI revealed that the thermal decomposition of this compound starts below 300 °C with the release of SO_2 gas in almost quantitative amounts. Nevertheless, the thermal stability of PETSI appeared to be not significantly affected by the presence of the sulfonated units, which is contrary to that reported previously by other authors [4c]. The TGA analysis of PETSI revealed decomposition temperatures (T_d) around 430 °C, such values being perfectly comparable with the decomposition temperature of PET. The TGA traces of the BHESI monomer and the 20 mol% sulfonated copolymer are shown in Fig. 3 and the T_d observed for the whole series of PETSI are compared in Table 2. Furthermore, in this table, it can be seen that both the glass-transition (T_g) and melting (T_m) temperatures of PETSI, determined by DSC, decreased as the content in sulfonated units increased. The enthalpy of fusion followed the same trend and no sign of crystallinity was detected for PETSI containing 20 mol% or higher of Na-SI units. The strong repressing effect of copolymerization on the crystallizability was also evidenced in the cooling DSC traces registered from molten

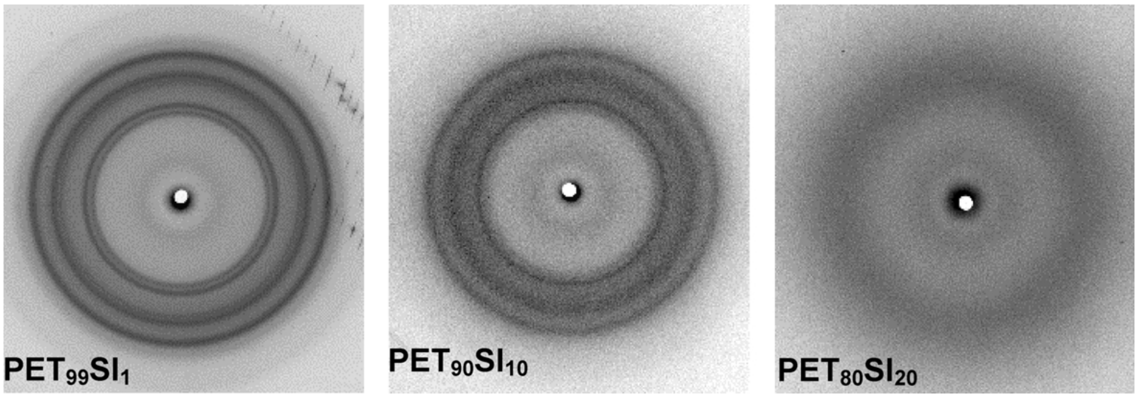


Fig. 4. Powder X-ray diffraction patterns of PETSI. The $PET_{99}SI_1$ sample was annealed as explained in the text.

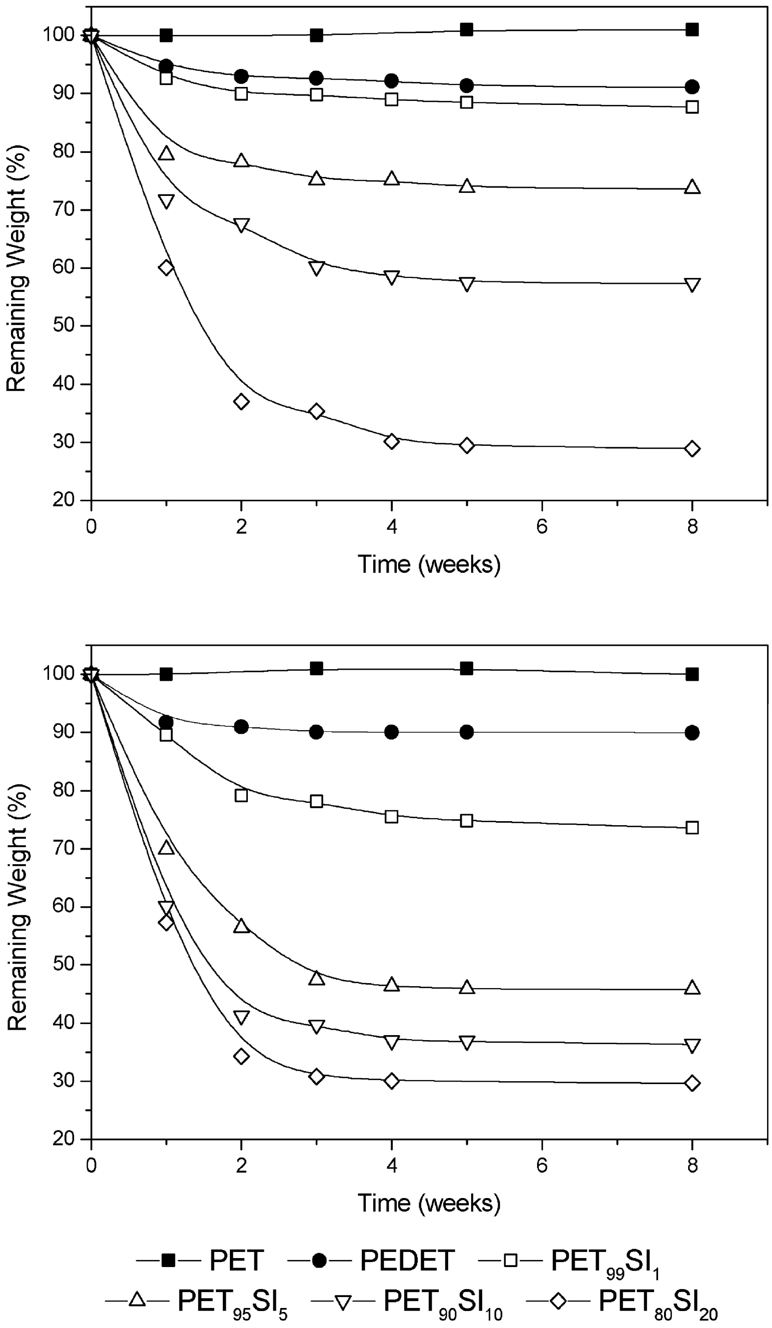


Fig. 5. The evolution of the remaining weight for PET, PETSI and PEDET samples immersed in water (pH 4.35) at 37 °C (top) and 80 °C (bottom) upon immersion time.

polymers at a cooling rate of 10 °C min^{-1}, which showed no crystallization exotherm as soon as the content in Na-SI reached 5 mol%. It should be noted that the content of this copolymer in DEG and TEG amounts around 20 mol%. The crystallinity of PETSI could be noticeably increased by annealing processes at a temperature 30–40 °C below the melting point.

Powder X-ray diffraction of PETSI corroborated the DSC results. As illustrated in Fig. 4, powder X-ray diffraction patterns consisting of sharp rings were obtained for PET$_{90}$SI$_{10}$, as well as for other less sulfonated members, whereas diffuse patterns characteristic of amorphous material were recorded from PET$_{80}$SI$_{20}$, PET$_{70}$SI$_{30}$, and PET$_{50}$SI$_{50}$. Comparison of the Bragg spacings observed for semi-crystalline PETSI to those observed for PET revealed that the same crystalline structure must be adopted in both cases. Additional spacings appearing upon annealing of PET$_{99}$SI$_1$ corroborated this similitude. According to what is known to happen in nitrated PET copolymers [12], the sulfonated units would remain confined in the amorphous phase of the material, since the bulkiness of the sulfonate group prevents them from entering the crystal lattice.

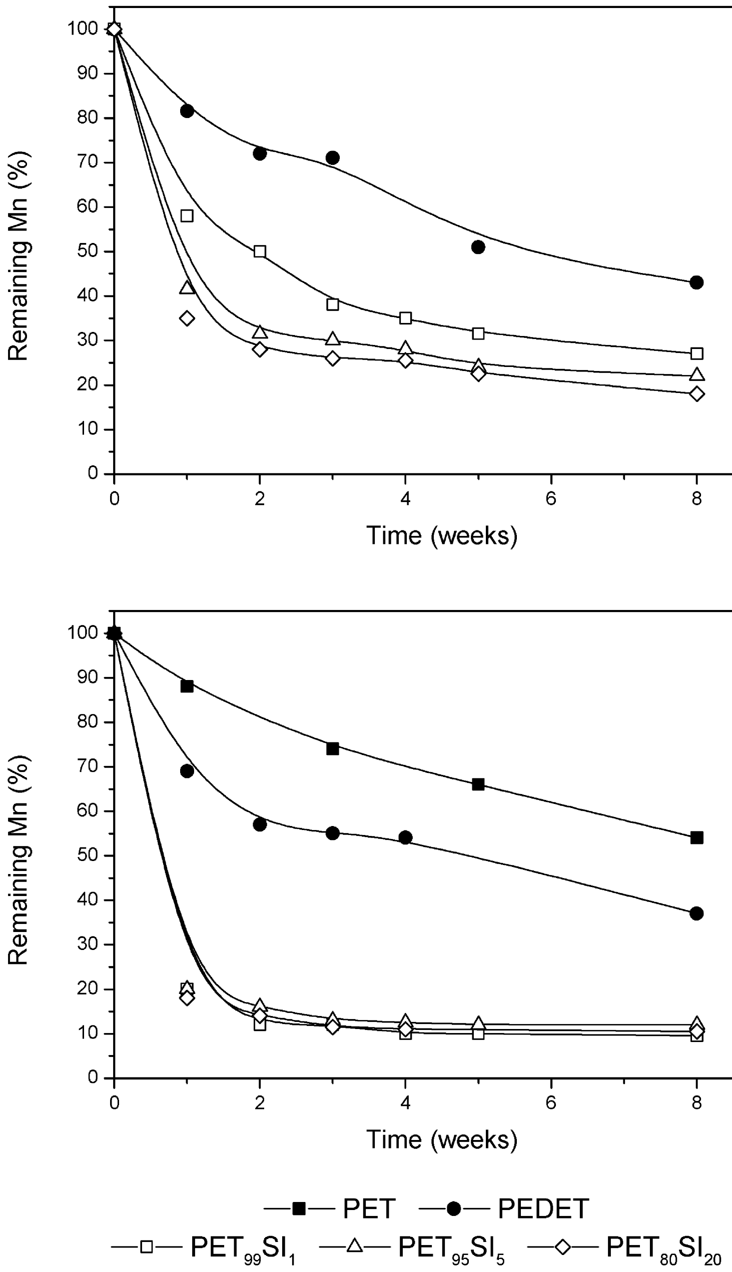


Fig. 6. Change in the number-average molecular weight of PETSI and PEDET samples immersed in water (pH 4.35) at 37 °C (top) and of PET, PETSI and PEDET samples at 80 °C (bottom) as a function of the immersion time.

3.3. Hydrolytic degradation

The hydrolytic degradation of the non-water soluble PETSI copolymers was explored at temperatures of 37 and 80 °C. Polymer disk samples were immersed in water at a pH of 4.35 for a total period of 8 weeks. Water-soluble $PET_{70}SI_{30}$ and $PET_{50}SI_{50}$ were not subjected to this study, since a different methodology would be required. The evolution of the remaining weight of the degraded disk samples upon degradation time is plotted in Fig. 5 for the essayed temperatures. In both cases, a significant loss of weight took place for all the polymers, the decay being more pronounced as the content in sulfonated units increased. As expected, degradation was accelerated by temperature, mainly as far as the polymers with low contents in Na-SI units are concerned. In all cases, the remaining sample weight displays an exponential decay with degradation time, to become stabilized after 3–4 weeks of immersion. The remaining final weight oscillated between 90% for $PET_{99}SI_{1}$ incubated at 37 °C and less than 30% for $PET_{80}SI_{20}$ incubated at 80 °C.

The molecular changes encompassing weight loss of PETSI were examined by GPC and NMR for two representative compositions, i.e. $PET_{95}SI_{5}$ and $PET_{80}SI_{20}$. As can be seen in Fig. 6, an abrupt fall in molecular weight took place within the first week of immersion for the two

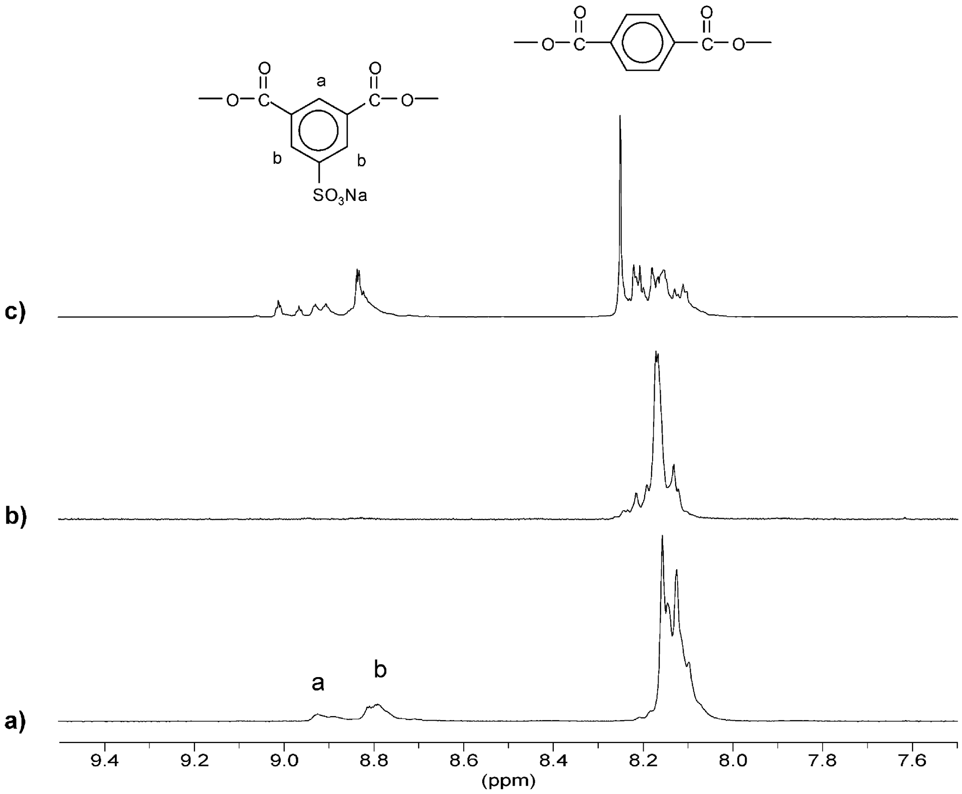
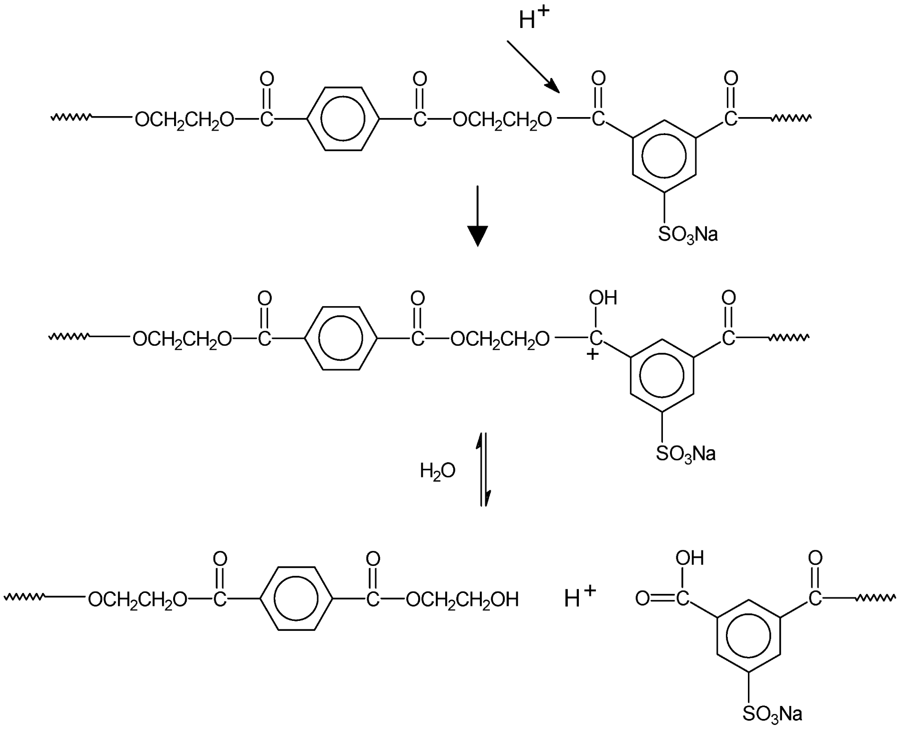


Fig. 7. Comparison of the signals in the aromatic region of ^{1}H NMR spectra of $PET_{80}SI_{20}$: (a) initial sample, (b) degraded disk and (c) residue left by the mother solution after evaporation to dryness.



Scheme 2. Mechanism of the hydrolytic degradation of PETSI under acidic conditions.

polymers. Apparently, ester hydrolysis happened very fast in the initial stage to almost cease for a certain chain length, which is shorter as the content in Na-SI of the copolyester increased.

The ^{1}H NMR analysis of the degraded disks and the residue left by the incubation water after evaporation, revealed an increasing presence of hydroxyethyl end-groups with degradation time, which is indicative of the occurrence of hydrolysis of the ester groups. As illustrated in Fig. 7, the changes observed in the aromatic signals of the ^{1}H NMR spectra evidenced that the degradation process involved mainly the sulfonated units.

Comparison of the spectra from the residual disks upon incubation revealed that the relative ratio of the terephthalate to 5-sodiosulfoisophthalate units increased in the residual polymer disk samples, whereas it largely decreased in the residue left by the mother solution, with the formation of 5-sodiosulfoisophthalic acid taking place in a certain extent. In view of these results, the hydrolytic degradation of PETSI under slightly acidic conditions is thought to proceed according to the reaction mechanism as depicted in Scheme 2.

The effect of sulfonation on the hydrodegradability could be in part accounted for by the presence in the copolymer of the oligo(ethylene glycol) units. In order to assess more accurately the role of the sulfonated units on the hydrodegradability of PET, the contribution of the oligo(ethylene glycol) units was evaluated separately. For this purpose, copolyester PEDET containing 3.5 mol% of diethylene glycol (DEG) units was prepared and its hydrolytic degradability behavior was evaluated and compared to that displayed by $PET_{99}SI_1$, which is the PETSI copolyester containing a similar amount of DEG units. The results of this study are plotted in both Figs. 5 and 6. Although an appreciable degradation is detected for PEDET, the decay is much more prominent in the case of $PET_{99}SI_1$, indicating that the Na-SI units are the main units responsible for the exceptionally high hydrodegradability displayed by the PETSI copolyesters.

Chisholm et al. [13] have recently carried out a detailed study on the hydrolytic degradation of sulfonated poly(butylene terephthalate) copolymers. In this work they discussed thoroughly the different reasons that can be invoked to explain the strong depressing influence of the 5-sodiosulfoisophthalate units on the hydrolytic stability. Two groups of factors, one of chemical nature and the other related to the accessibility of the polymer to water were considered: (a) the ester hydrolysis reaction rate is higher in the sulfonated polyester due to the inductive and/or catalytic effect exerted by the sodio sulfonate group, and (b) the hydrolytic stability of the sulfonated polyester is lower because of the greater hydrophilicity, the lower crystallinity, and the high polarity of the ionic aggregated microdomains of these copolymers, all facilitating the penetrability of water. Grobe et al. [14] reported that the inductive effect of the Na-SI group should be ignored since BHET and BHESI have the same hydrolysis rates under alkaline conditions. Chisholm et al. [13] reached to similar conclusions from hydrolysis experiments carried out on DMT and Na-DMSI. These results lead to favor the interpretation that hydrolysis enhancement is caused by the higher water absorption happening in the sulfonated poly(butylene terephthalate) copolymers. Such a hydrolysis mechanism can be readily postulated for the hydrolytic degradation of the PETSI copolymers.

Acknowledgements

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