Synthesis and Characterization of Sulfonated Copolyethersulfones

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ABSTRACT: The present article deals with the synthesis and characterization of some sulfonated copolyethersulfones. The synthetic approach differs from the post sulfonation approach traditionally reported in the literature. The synthetic procedure is based on the use of sulfonated monomers which are then reacted with previously synthesized telechelic hydoxy-ended poly (ether sulpnone)s. Combining the MALDI-TOF MS and ^{1}H NMR analyses, with SEC-Viscometry and TGA measurements, we demonstrate a powerful tool for characterizing the chemical composition, end chains, degree of sulfonation (DS) and molecular mass distribution (MMD) of disulfonated poly(arylene ether-sulfone) copolymers. The characterization techniques allowed to determine the exact nature of the copolymers synthesized and to reveal some interesting features about the reaction. DMA data show that the glass transition temperature of sulfonated copolymers with similar DS increase as raise their MMD. Copolymers with a DS of 10–11 mol % reach a T_g of 244–246 °C. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 3010–3023, 2010

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INTRODUCTION

Polyethersulfones are a class of polyaromatics of high importance for special applications which includes toughening modifiers for epoxy resins,[1,2] adhesives for metal to metal bonding,[3] membranes for separate gaseous and solid substances[4] and membranes for fuel cells.[5,6] The latter application is of increasing interest for the industrial exploitation of fuel cells with improved properties. Ioioiu and Sanchez[7] recently outlined in a review the key advances of polyethersulfones as membranes for proton exchange membrane fuel cells (PEMFC) and solid oxide fuel cells (SOFC).

In the field of PEMFC, perfluorosulfonic acid ionomers such as Nafion® and Flemion® have made a great breakthrough. These perfluorinated polymeric membranes provide high conductivities, up to 80 °C, thanks to their superacid perfluorosulfonic moieties and the high thermal and chemical stabilities related to their perfluorinated backbones.[8] Despite their advantages, existing drawbacks, namely high cost, high permeability to methanol, low conductivities and poor mechanical properties at temperatures exceeding 80 °C, make their use questionable in the context of PEMFC or direct methanol fuel cells (DMFC). Great efforts have been devoted toward the development of high-performance proton-conducting polymers for the mass market which can offset the limits of perfluorinated polymeric membranes.[5,9]

Sulfonated polyethersulfones constitute a promising class of materials as alternative to perfluorinated polymeric membranes because of their high mechanical strength and high chemical, thermal, and oxidative stabilities.[6,7] Several authors have dealt with the problem of introducing sulfonic moiety in the backbone of polyethersulfones. Among the different synthetic routes, the most diffused are as follows:

The chemical modification of commercial polyethersulfones either by aromatic electrophilic substitution[10–12] or nucleophilic substitutions[13];

The synthesis of sulfonated polymers starting from sulfonated monomers or oligomers reacted with standard monomers.[14–26]

The first approach is cheapest but can lead to chain breakings during industrial production.[27] Furthermore, the use of commercial polymers can encounter the additional problem that molecular mass distribution, and in general viscosity properties, are not optimized for thin film preparation required for membrane generation. The second approach based on the synthesis from monomers present the advantage of close control on the final structure of the backbone and of the properties (i.e., molar mass distribution, chemical structure, end groups etc.) of the polymers. An additional advantage of the synthesis from oligomers is the possibility to obtain controlled multiblock structures which lead to the

formation of well separated domains between the hydrophobic blocks (i.e., nonsulfonated) and the hydrophilic blocks (i.e., sulfonated). The creation of such morphologies has been outlined as a key advantage to control the water swelling properties of the membranes.[7]

The exact knowledge of the chemical structure of the backbone of polymers is of paramount importance when novel polymers are developed to evaluate their performances and potential application. Among the various techniques which can be used for this purpose NMR and MALDI-TOF MS (Matrix-Assisted Laser Desorption/Ionization–Time of Flight Mass Spectrometry) are among the most powerful tools. Recently, the combined use of NMR and MALDI-TOF MS has been reported for the fine characterization of some reactive copolyethersulfones.[28] The combined use of the two techniques has revealed high potentiality to shed more light on the structure and chemical composition of complex copolymers and to disclose the nature of side reactions.

In the present article, we present the synthesis of some sulfonated copolymers based on the use of sulfonated monomers reacted with some telechelic PES oligomers terminated with phenol groups at both ends (hereafter referred to as PES-OH) and having a number average molecular mass (M_n) of 4000 and 7000 g/mol, respectively. The nucleophilic aromatic polycondensation reactions were carried out for different times using different molar ratio of PES-OH samples and disulfonated dichlorodiphenyl sulfone monomer (referred as SDCDPS). The sulfonated PES copolymers synthesized are thoroughly characterized by NMR and MALDI-TOF MS to reveal their chemical structure, while thermogravimetric (TGA) and dynamic mechanical analysis (DMA) are used to determine the thermal properties of the polymer samples. Infrared spectroscopy (IR) was also used for the characterization of the sulfonic moiety in the main backbone of the polymers. Their molar mass distribution (MMD) was investigated by a multidetectors size exclusion chromatography (SEC) system.

The chemical composition of S-PESs were generally characterized by NMR and FTIR techniques.[16–18,20–23,29–35] However, these are averaging techniques and often some doubts may remain on the composition of the sulfonated PES samples, and on the nature of the end chains, which can influence the properties of the based polyelectrolyte membranes. In particular, often by these techniques is not easy to distinguish block copolymer from the corresponding homopolymers present in the polymeric material. When the M_n of the polymer sample is very high, the end groups could not be detected by NMR techniques.

MALDI-TOF MS is a powerful technique able to detect individual and intact polymer molecules even in a complex mixture, including species present in smaller amounts in a polymer sample.[36–40] It has permitted the identification of repeat units, chain ends, cyclic oligomers, and also of species present in a smaller amount in a lot of class of polymer samples. To the best of our knowledge, no data has ever been reported by literature on the characterization of sulfonated PES samples by MALDI-TOF MS technique.

Therefore, in this work we have focused our studies to demonstrating the enormous potentiality of combining MALDI and NMR techniques for a complete and unequivocal chemical characterization of sulfonated PES copolymers, to monitor their degree of sulfonation and also the progress and the kinetic of their polymerization reactions. Furthermore, in the present article the study of the copolymerization has been advanced by the use of SEC-viscometry which allows the careful determination of the molar mass distribution upon polymerization. Finally, the polymers obtained have been characterized in terms of their thermal properties by TGA and DMA. The control of the copolymerization conditions and the knowledge of: the nature of chain ends, the chemical composition and of the degree of sulfonation, may lead to samples with better properties than the sulfonated PES already synthesized and studied, which, therefore, could be used as polyelectrolyte proton exchange membranes in several fields, that is, as membranes for fuel cells.

EXPERIMENTAL

Materials
4,4′-Dichlorodiphenylsulfone (DCDPS) (98% of purity grade), dihydroxydiphenylsulfone (DHDPS) (98% of purity grade) hydroquinone (HQ) (99% of purity grade), potassium carbonate, and tetramethylenesulfone (sulfolane) were purchased from Aldrich Chemical (Italy). All reagents used in these experiments were obtained from commercial sources and utilized without any special purification. Potassium carbonate [K_2CO_3, anhydrous grade] was dried at 150 °C under reduced pressure. Tetramethylenesulfone was distilled under reduced pressure and stored under nitrogen until used.

Synthesis
Hydroxy-Ended PES Prepolymers
Two hydroxy-ended poly(arylene ether-sulfone)s with an average molar mass of 4000 and 7000 g/mol, respectively, were synthesized via nucleophilic condensation reaction of DCDPS with an excess of DHDPS as is outlined in Scheme 1. Typically, the polycondensation reaction was conducted in a 250-mL-three-neck flask equipped with an overhead stirrer and nitrogen inlet. To obtain the hydroxy-ended PES prepolymer having a theoretical average number molar mass (M_n) of 4 K [herein referred as PES-OH(4 K)], DCDPS (5.11 g, 1.78 × 10^{-2} mole) was added at DHDPS (4.89 g, 1.95 × 10^{-2} mole; 9.5 mol % excess) in 50 mL of tetramethylenesulfone solvent. K_2CO_3 (2.53 g, 1.83 × 10^{-2} mole; 2.8% mole excess with respect to the DCDPS) was then added to the mixture at 180 °C and the temperature was raised up to 190 °C. The mixture was allowed to react for 30 min at this temperature, then for 1 h at 205 °C and for 4 h at 225 °C, under a nitrogen flow. The reacted mixture was then added at a cooled ethanol (5- to 10-fold in excess), obtaining a precipitated white powder, which was filtered and then washed several times with water and with ethanol, and finally dried under vacuum at 120 °C overnight. The sample was then treated with THF at reflux for 12 h to solubilize the PES oligomers with a molar mass below 1500–2000 g/mol, as verified by MALDI-TOF analysis of the THF soluble fractions.
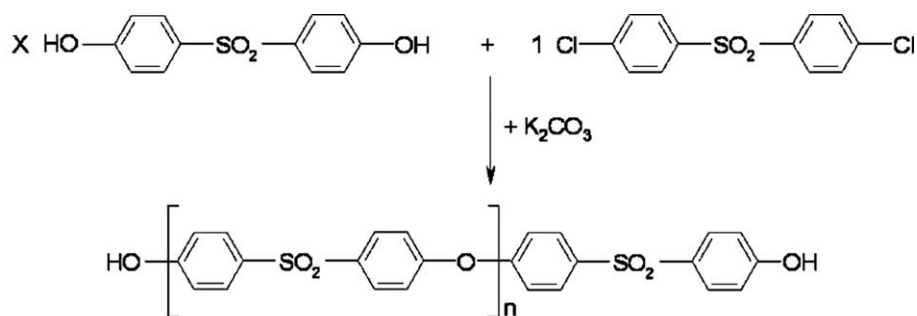
X=1.095 for PES-OH(4K)
X=1.05   for PES-OH(7K)

A PES-OH sample with a M_n of 7K g/mol [PES-OH(7 K)] has been synthesized using a DHDPS/DCDPS molar feed ratio of 1.05, following the same procedure.

3,3'-Synthesis of Disulfonated-4,4'-dichlorodiphenyl Sulfone (SDCPS)

Disodium of disulfonated dichlorodiphenyl sulfone momomer (DS-DSDCPS) was synthesized using 4,4'-dichlorodiphenyl sulfone (DCDPS) and fuming sulfuric acid, via electrophilic aromatic substitution, as reported in Scheme 2.[41] The polymerization was carried out into a 100-mL-three-necked flask equipped with a mechanical stirrer and a nitrogen inlet/outlet. DCDPS (28.7 g) was dissolved in 60 mL of fuming sulfuric acid, and the solution was heated to 110 °C for 6 h. The reaction mixture was allowed to cool to room temperature and added into 400 mL of ice water. Next, 180 g of NaCl was added and, subsequently, the disodium salt of disulfonated dichlorodiphenyl sulfone precipitated as a white powder. The latter was filtered and redissolved in 400 mL of cold deionized water, treated by 2 N NaOH aqueous solution to a pH of 6–7, and finally an excess amount of NaCl was added again to obtain the sodium form of the sulfonated monomer. The crude product was filtered and recrystallized from a mixture of alcohol (methanol) and deionized water (9/1, v/v), producing white needle-like crystals. The DS-SDCPS monomer was analyzed by MALDI-TOF MS using dithranol as a matrix), and by (^{1}H, ^{13}C) NMR tools. The results confirmed its structure and composition. MALDI-TOF mass spectra, besides peaks due to the matrix, shows a signal at m/z 490.3 ± 0.2 corresponding to the molecular mass of DS-SDCPS sample. ^{1}H NMR spectrum presents signals at δ (ppm): 7.6 (d, 1H); 7.8 (m; 1H); 8.3 (d, 1H), while ^{13}CNMR spectrum shows six expected signals, corresponding to the aromatic carbons, at δ (ppm): 128, 130, 133, 138, 139, and 147.

### Sulfonated Poly(arylene ether-sulfone) Copolymers

Di-sulfonated poly(arylene ether-sulfone)s (*S*-PES), having blocks of unsulfonated PES units were synthesized via nucleophilic condensation reaction of sodium salt disulfonated monomer with an telechelic PES-OH sample, using various PES-OH/SDCPS molar feed ratio at 180 °C for 12 h. The amount of DS-DSDCPS was calculated with respect to the concentration of hydroxyl end groups in the used PES-OH. In particular, four molar feed ratio (1.20, 1.05, 1.00, and 0.90) were used to prepare *S*-PES copolymers with different degrees of sulfonation (DS) and molar mass distributions (MMD), as described in Table 1. The synthesis is outlined in Scheme 3.

Typically, polycondensation was carried out in a 250-mL-three-neck flask equipped with an overhead stirrer and nitrogen inlet using tetramethylenesulfone as solvent and toluene as azeotropic agent. The reaction mixture was heated at 140 °C for 3 h, which stripped of most the toluene to dehydrate the system. The temperature was raised to 180 °C and the reaction was carried out for (12 h) hours under a nitrogen flow. The reacted mixture was then precipitated in 10-fold volume of a HCl aqueous solution 1 M; the precipitate white powder copolymer was washed several times with water and ethanol, and finally dried under vacuum at 120 °C overnight. As well as the PES-OH prepolymers, all copolymers were treated with THF at reflux to extract the low molar mass oligomers. After that were filtered and finally dried under vacuum at 120 °C overnight. The copolymer samples were referred as *S*-PES-mr(12 h) in Table 1, where with mr we indicate the PES-OH/SDCPS molar feed ratio.

Postpolymerization of S-PES-mr(12 h)

The postpolymerization reaction of sulfonated poly(arylene ether-sulfone) (*S*-PES) obtained after 12-h reaction, has been carried out at 180 °C under nitrogen flow in NMP for further 24 and 48 h, in presence of K_2CO_3 (0.01 g), under nitrogen flow. The product of reaction was precipitated in ethanol and washed several times in the same solvent. Finally, the product was dried at 150 °C overnight. The samples namely
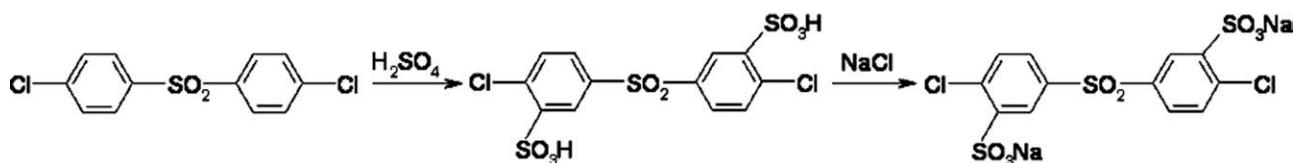
SCHEME 2 Synthesis of monomer sulfonated dichloro diphenil-sulfone sodium salt.

TABLE 1 Some Properties of Sulfonated and Unsulfonated PES Samples

Samples	$M_n{}^a$	T_g (°C)[b]	Char residue[c] (%)	$\eta_{inh.}$	DS[d] (%)
PES-OH (4 K)	4000	160	30	0.08	0
S-PES-0.90 (12 h)	8000	210	40.08	0.095	11
S-PES- 0.90(36 h)[e]	13,100	238	40.85	0.11	11
S-PES-0.90(60 h)[e]	16,800	244	41.44	0.13	11
S-PES-1.20(12 h)	7000	200	37.37	0.09	10
S-PES-1.20(36 h)[e]	13,800	241	40.65	0.12	10
S-PES-1.20(60 h)[e]	15,700	246	41.10	0.14	10
PES-OH (7 K)	7000	182	30	0.19	0
S-PES-1.00(12 h)	14,000	266	42.19	0.24	14
S-PES-1.05(12 h)	13,100	262	43.01	0.21	12

[a] Calculated by ^{1}H NMR analysis.
[b] Calculated by DMA measurement.
[c] Determined by TGA analysis at 800 °C.

[d] Degree of sulphonation.
[e] Synthesized by postcondensation reaction of S-PES-12 h samples.

as S-PES-mr(12 + x h)(with x = 24 or 48) are reported in Table 1.

Measurements

### NMR Spectroscopy

^{1}H NMR spectra were recorded using a Brucker 200 MHz. The samples were dissolved in d_6-DMSO at polymer concentration of about 30 mg/mL without any internal standard at 60 °C in temperature. The data were elaborated with 1D Win-NMR software applying the Lorentz-Gauss enhance function using appropriate Line broadening and Gaussian broadening parameters to improve the peaks resolution. The chemical shift resonances were accurately assigned to the specific proton and atoms, using the data reported in literature.[28,42]

MALDI-TOF Mass Spectrometry

The MALDI-TOF mass spectra were recorded in linear mode, using a Voyager-DE STR instrument (Perseptive Biosystem)
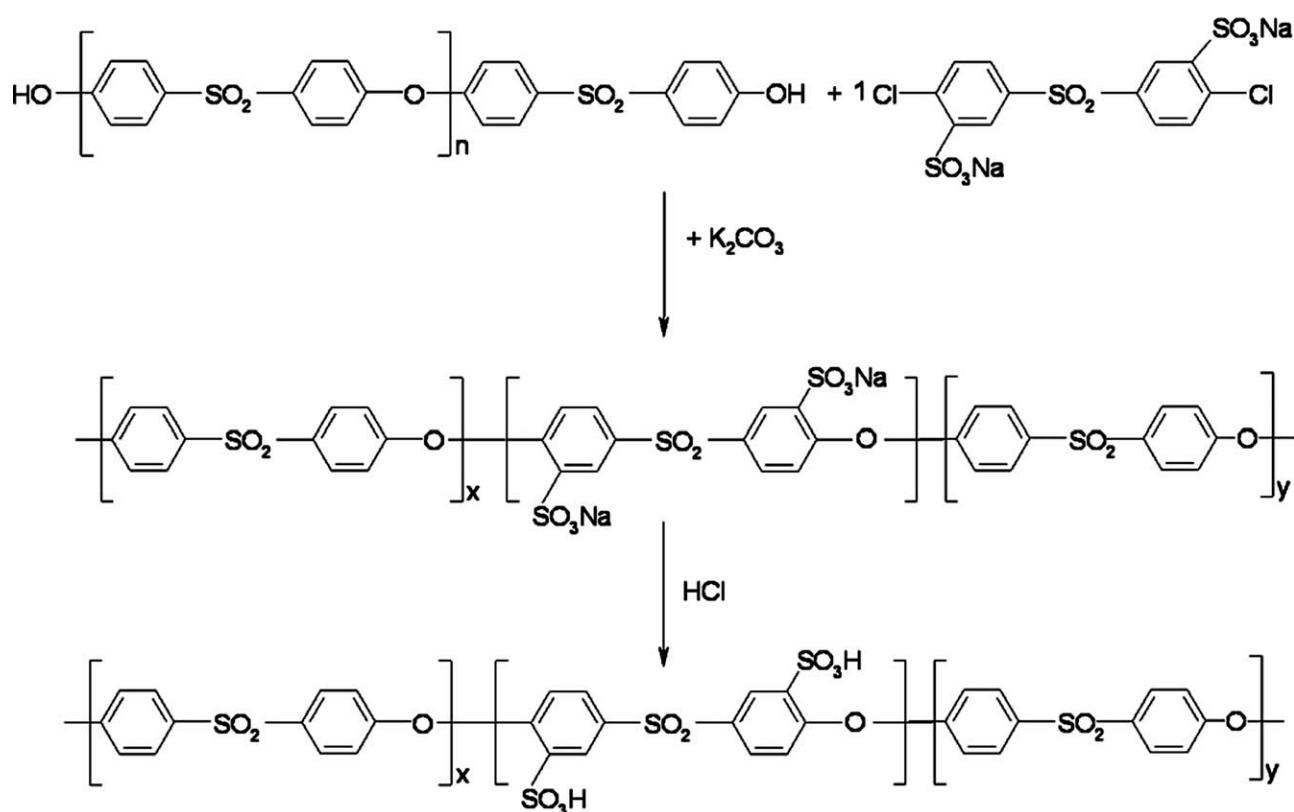
SCHEME 3 Typical synthesis of sulfonated poly(arylene ether-sulfone)s.

mass spectrometer, equipped with a nitrogen laser (λ = 337 nm, pulse width = 3 ns), working in a positive ion mode. The accelerating voltage was 25 kV, grid voltage and delay time (delayed extraction, time lag), were optimized for each sample to achieve the higher mass resolution (FWHM). Laser irradiance was maintained slightly above threshold. Samples used for the MALDI analyses were prepared as follows. Ten microliters of polymer solutions (3–4 mg/mL in CHCl$_3$/DMSO 90/10), were mixed with 30 μL of HABA solution (0.1 M in CHCl$_3$/THF 90/10 v/v). Then 1 μL of each analyte/matrix mixture prepared was spotted on the MALDI sample holder and slowly dried to allow analyte/matrix cocrystallization.

SEC-Viscometry

The molecular characterization (molar mass distribution MMD, intrinsic viscosity and conformation) of PES-OH prepolymers and of S-PES copolymers was performed by a multidetector size exclusion chromatography (SEC) system using N,N-dimethylacetamide (DMAc) as mobile phase. The chromatographic system consisted of an integrated GPCV2000 chromatographic system from Waters (Milford, MA) using two on-line detectors: (1) differential viscometer (DV); (2) differential refractometer (DRI model 2414) used as concentration detector. This multidetector SEC-DV system has been described in detail elsewhere.[43] The column set was composed of two Styragel mixed columns (HR5E and HR4E, 5 μm of particle size) from Waters. The experimental conditions consisted of: DMAc + 0.01 M LiBr as mobile phase, 80 °C of temperature, 0.8 mL/min of flow rate. It is well known that the on-line DV detector furnishes the relative viscosity η_r of each eluting polymeric fraction. By combining the instantaneous values of η_r and of the concentration, from the on-line DRI calibrated detector, the $[\eta] = f(V)$ experimental function, where $[\eta]$ denotes the intrinsic viscosity and V the elution volume, is directly obtained. From the SEC-DV system also some conformational properties of the polymers could be studied by means of the Mark-Houwink-Sakurada (MHS) equation $[\eta] = f(M)$ where M denotes the molar mass.

Thermogravimetric Analysis

Thermal stability of sulfonated poly(arylene ether-sulfone)s was studied using a TGA-500 V6.7 instrument (TA-INSTRUMENT) coupled with a TA-INSTRUMENT Explorer operating software. The analyses were performed under dynamic heating conditions, from 50 to 800 °C under nitrogen flow (60 mL/min), at a heating rate of 10 °C/min, using about 2 mg of sample. The weight and temperature of the thermobalance were calibrated using four high-purity magnetic standards (alumel, nickel, Ni$_{0.83}$Co$_{0.17}$ alloy, Ni$_{0.63}$Co$_{0.37}$ alloy) for the Curie temperature (152.6, 358.2, 554.4, and 746.4 °C, respectively) and some exact weight following both calibration procedures through the instrument control software.

Data recorded show the thermal behavior of poly(arylene ether-sulfone) samples in terms of weight loss percentage at the increasing of temperature. The slope of degradation curve depends on kind and amount of specific mechanism of degradation during temperature scanning.

FTIR Spectrometry

FTIR spectra of sulfonated poly(arylene ether-sulfone) in powder form, has been recorded on attenuated total reflectance spectroscopy (ATRIR) using a Perkin–Elmer FTIR spectrometer. Spectrometric analysis is useful to obtain further information regarding chemical structure and degree of sulfonation of PES samples studied because of the typical peaks of each functional group.

Dynamic Mechanical Analysis

Viscoelastic properties of each sample were determined by dynamic mechanical analysis (DMA). For the DMA analysis the specimens were prepared according to the following procedure: The polymers obtained from the syntheses were finely micronized in powder with an average dimension of 30 mm; and vacuum dried at 80 8 °C for 24 h. Then, 0.35 g of polymer powder was weighted in a standard material pocket purchased from Triton and pressed in a Carver press to obtain a uniform film within the pocket. The pocket was tested in single cantilever mode at 1 Hz with a free length of 15 mm. The samples were heated according to the following cycle: (1) heating at 5 °C/min from 0 to 280 °C; (2) quenching under nitrogen flow to 0 °C; (3) heating at 5 °C/min from 0 to 280 °C. The glass transition was calculated in the second heating scan.

Off-Line Viscosimetry

Inherent viscosity (η_{inh} = ln ηrel/C; C = 0.5 g/dL) was also determined by off-line viscosimetry using an Ubbelohde suspended-level viscometer in dimethylformamide (DMF) as solvent at 25 °C.

RESULTS AND DISCUSSION

Two series of sulfonated copolyether sulfones (S-PES) with controlled degree of sulfonation and having unsulfonated PES blocks were successfully synthesized through nucleophilic aromatic substitution polycondensation reaction of sodium salt of sulfonated dichloro difenilsulfone (S-DCDPS) with hydroxyl-ended PES telechelic polymers (PES-OH), as outlined in Scheme 3. The copolymer synthesis involves controlled amount of sulfonated activated halide (S-DCDPS) and a PES-OH sample with a note average molar mass (M_n) of 4000 or 7000 g/mol. Polycondensation reactions were carried at 180 °C for 12 h using various PES-OH/S-DCDPS molar ratios, calculated with respect to the hydroxyl amount of telechelic PES-OH prepolymers, taking into account its M_n values (see Table 1) and also that two OH groups are present in each chain. The synthesized copolymers are herein referred as S-PES-mr(x h), where mr represents the (PES-OH)/S-DCDPS molar feed ratio and x h the reaction time. The chemical compositions of all copolymers were evaluated by ^{1}H NMR, FTIR, and MALDI-TOF MS analyses, whereas their thermal properties and thermal stability were investigated by TGA and DMA analyses. By ^{1}H NMR analysis were also determined the degree of sulfonation (DS) and the M_n values of the sulfonated copolymers, while by viscosimetric measurements we have obtained some information about their molar masses (MM). Reliable values about their molar mass distribution were also calculated by SEC-DV tool.
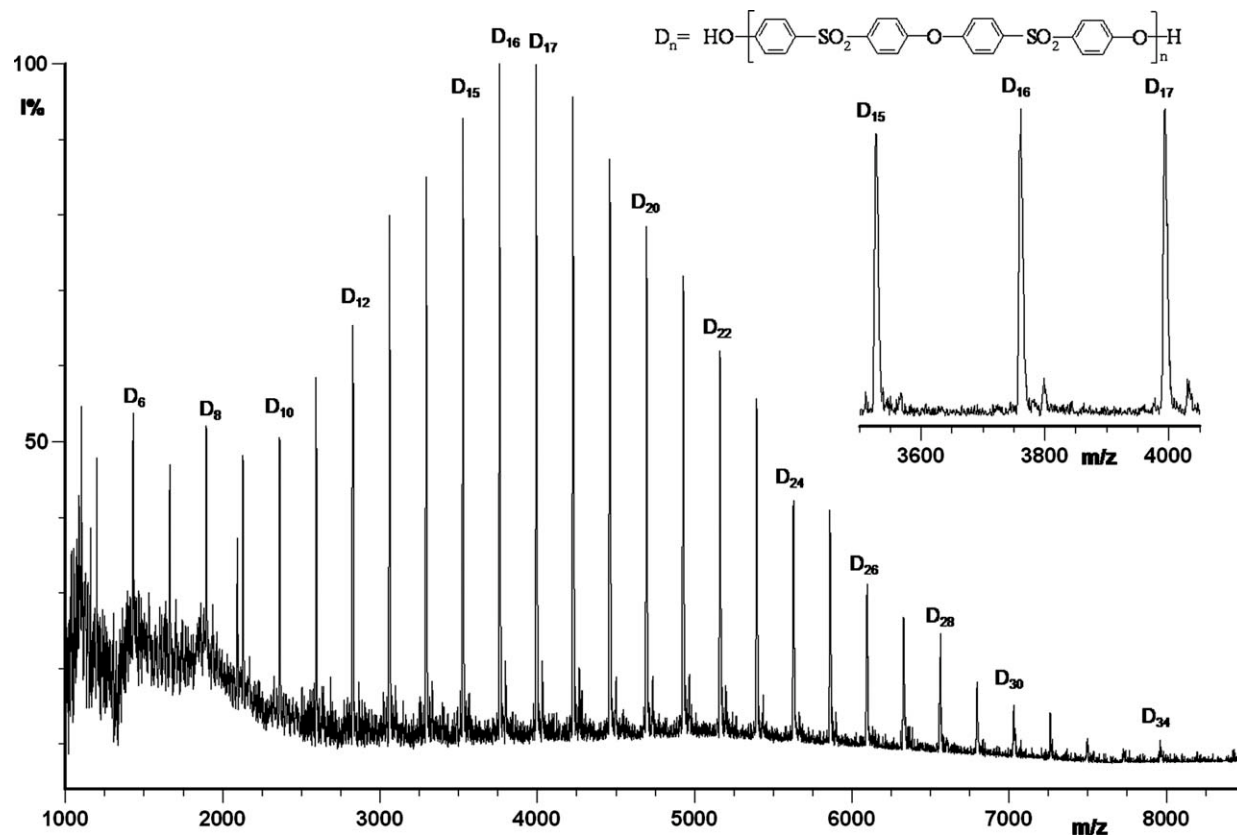
FIGURE 1 MALDI-TOF mass spectrum of PES-OH(4 K).

The *S*-PES copolymers were analyzed in detail by MALDI-TOF MS to identify how many disulfonated PES units are present for each chain and the various types of end groups, and also to afford a deeper insight in the reaction mechanism.

First, two PES-OH samples with an average number molar mass (M_n) of 4000 and 7000 g/mol, [herein referred as PES-OH(4 K) and PES-OH(7 K), respectively] were synthesized using a DHDPS/DCDPS molar ratio of 1.09/1 and 1.05/1, respectively, as outlined in Scheme 1. The nature of end groups of both PES-OH samples was confirmed by MALDI-TOF MS and ¹H NMR studies. MALDI-TOF mass spectrum of prepolymer PES-OH(4 K) is shown in Figure 1, it shows a single mass peak family, in the mass range 1000–8000 Da, corresponding to the sodiated ions of expected PES chains terminated with hydroxyl groups at both ends (species Dn in Fig. 1). The mass spectrum of PES-OH(7 K), as well as of PES-OH(4 K) in Figure 1, shows only single intense mass peak series corresponding to the sodiated ions of dihydroxy ended PES chains with n (repeating units) ranging from 9 (m/z = 2539) to 46 (m/z = 11,944); it shows the most intense peak at m/z 7469 corresponding to the oligomers with $n = 28$. ¹H NMR spectra of both PES-OH samples confirms this result, in fact they show two doublet centered at 6.82 ppm and at 7.67 ppm due to the resonance of the aromatic protons in ortho and in meta with respect to the hydroxyl end groups, as can be observe in Figure 2(a) that reports the spectrum of PES-OH(4 K). In Figure 2(a), the signals due to the resonances of these protons were labeled as a″

and b″, respectively. The aromatic protons in ortho to the sulfone groups of diphenyl sulfone moieties [protons b in Fig. 2(a) and in Table 3] and in ortho to the oxygen of diphenyl ether groups [protons a in Fig. 2(a) and in Table 3] in the backbone of PES-OH chains, give two doublets at 7.98 and 7.28 ppm, respectively. The M_n of both PES-OH polymers were calculated from the relative ¹H NMR integrals of the peaks due to the aromatic protons $H_{b″}$ belong to the end chains and the aromatic resonances due to the protons H_a in the backbone, using the eq 1. The calculated values are reported in Table 1.

$$X_n = (I_{b″}/I_a) + 1 \qquad (1)$$

Using both PES-OH samples we have synthesized four sulfonated PES copolymers, namely *S*-PES-0.5(12 h), *S*-PES-0.9 (12 h), *S*-PES-1.0(12 h) and *S*-PES-1.2(12 h).

These sulfonated PES copolymers were well characterized by MALDI-TOF MS and by ¹H NMR tools to obtain reliable information about their chemical composition and, especially on the nature of the end groups and also to know many sulfonated units are present along the chains.

MALDI-TOF MS
The MALDI-TOF mass spectrum of *S*-PES-0.9(12 h) sample is shown in Figure 3. It shows complex clusters of peaks from m/z 1300 up to m/z 9600, the mass difference between two homologous peaks belonging two contiguous clusters is
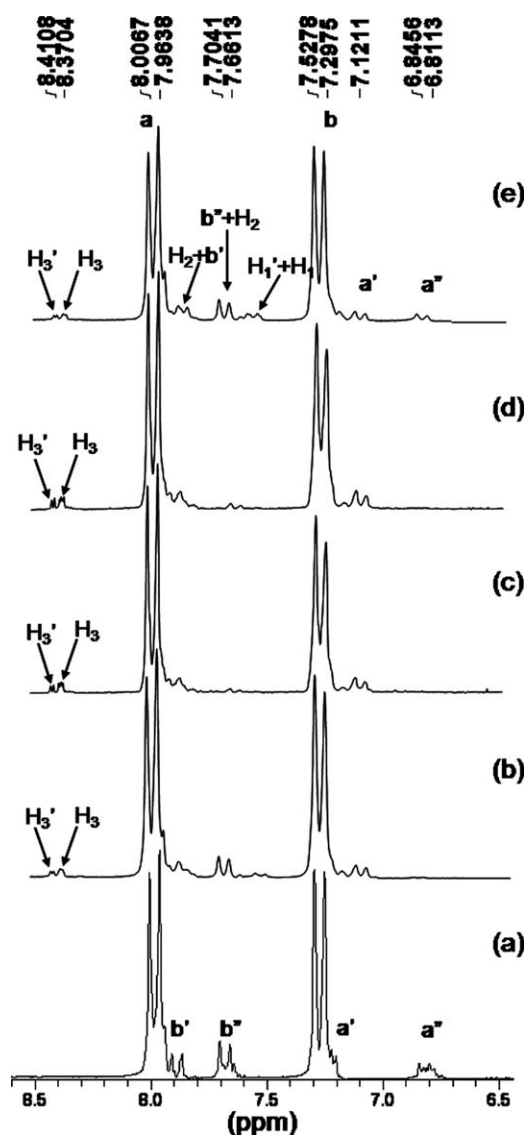
FIGURE 2 ^{1}H NMR spectra of PES-OH(4 K) (a); S-PES-1.2(12 h) (b); S-PES-1.05(12 h) (c); S-PES-1.0(12 h) (d); S-PES-0.9(12 h) (e).

232 Da (the mass of no-sulfonated PES repeating unit). The mass spectrum of S-PES-1.2(12 h) is very similar. Detailed information about the chemical composition and end chains of these copolymers can be argued from the expanded mass regions of their spectra, from m/z 2300 up to m/z 3000, reported in the inset in Figure 3 [Fig. 3(b,c)]. Both spectra show that each cluster present in the mass spectrum, is constituted of four families of peaks corresponding to the copolymer chains with different end groups (species $A_{n,\alpha}$, $B_{n,\alpha}$, $\Phi_{n,\alpha}$, and $X_{n,\alpha}$); their pertinent assignments are summarized in Table 2 where with n we indicate the unsulfonated PES units and α the disulfonated PES units. For SPES-0.9(12 h) sample the most intense mass peaks correspond to the co-oligomers with 2 disulfonated PES units (d-S-PES) along the chains and terminated with hydroxyl groups at both chains (Species $A_{n,\alpha=2}$), while the peaks corresponding to the families of co-oligomers with two d-S-PES units and terminated

with OH groups at one chains and chlorine at other end (species $B_{n,\alpha=2}$) dominate in the spectra of the S-PES-1.2(12 h) copolymer. On the basis of the nature of end chains, in the co-oligomer chains belong to the species $B_{n,\alpha=2}$ one disolfonated unit is present as end chain. Cycles co-oligomers (species $\Phi_{n,\alpha}$) having two d-S-PES units are also observed in the mass range m/z 1300/4000 of the mass spectra of both copolymers. According to the expanded spectra in Figure 2(b,c) we argue that the formation of cycles, if favored when the PES-OH/S-DCDPS molar feed ratio is more 1.0. In the spectra of both samples we observe also the presence of co-oligomers having three d-S-PES units ($X_{n,\alpha=3}$) along the chains, which one d-S-PES unit appear as mono sodium salt. The presence of these family of peaks indicates the incomplete conversion of sodium form synthesized S-PES copolymers in the corresponding acid form, by treatment with a solution of HCl 1 M (see Experimental section). Mass spectra of both copolymers, in the mass range higher than m/z 3400, show peaks corresponding to co-oligomers with three d-S-PES units belonging to the families $A_{n,\alpha}$ and $B_{n,\alpha}$. The same families of co-oligomers ($A_{n,\alpha}$, $B_{n,\alpha}$, $\Phi_{n,\alpha}$, and $X_{n,\alpha}$) were also observed in the MALDI-TOF mass spectra of disulfonated copolymers prepared from PES-OH(7 K) and referred as S-PES0.5(12 h) and S-PES0.5(12 h) in Table 1. MALDI-TOF mass spectrum of S-PES1.05(12 h), as well that of S-PES1.0 (12 h), shows homologous cluster of peaks from m/z 1500 up to m/z 10,000 and the most intense peaks are around m/z 5000 Da [Fig. 4(a)]. Comparing this mass spectrum with that of the S-PES0.9(12 h) in Figure 3(a), emerge that the copolymers obtained from PES-OH(7 K), by 12-h reaction, have an average molar masses (M_w and M_n) higher than of those synthesized from PES-OH(4 K), as confirm the viscosimetric and SEC-DV data in Tables 1 and 4, respectively. By inspection the enlarged sections of mass spectra of S-PES1.0(12 h) and S-PES0.5(12 h), in the mass range m/z 4150–4850, reported in Figure 4(b,c), respectively, we observe that these copolymers, beside the co-oligomer species discussed before, have also chains terminated with Chlorine at both ends (specie $C_{n,\alpha}$, in Fig. 4 and in Table 2).

NMR Characterization
^{1}H NMR spectra were also used to identify the molecular structure, the chemical composition, the end chains, and also to calculate the degree of sulfonation of the four S-PES copolymers discussed above. Complete assignments of the ^{1}H NMR spectra have been accomplished by comparison with literature data,[28,42] and with the spectra either of PES-OH(4 K) [see Fig. 2(a)] and of SDCPS monomer. The chemical shift resonances are summarized in Table 3. The ^{1}H NMR spectra of the disulfonated PES copolymers obtained after 12 h reactions and that of PES-OH(4 K) are overlaid in Figure 2.

The Figure 2 reports also the assignments of all peaks according to the chemical shifts assignments reported in Table 3. It permits to distinguish the disulfonated PES units from those unsulfonated PES blocks. These give two doublets centered at 7.98 ppm (protons Ha) and at 7.27 ppm (protons Hb), whereas the disulfonated PES units give signals in the regions: 8.35–8.41 ppm (protons H_3 and $H_{3'}$), 7.84–7.91 ppm (protons H_2 and $H_{2'}$), 7.50–7.62 ppm (protons H_1 and $H_{2'}$) and 7.12–7.20 ppm
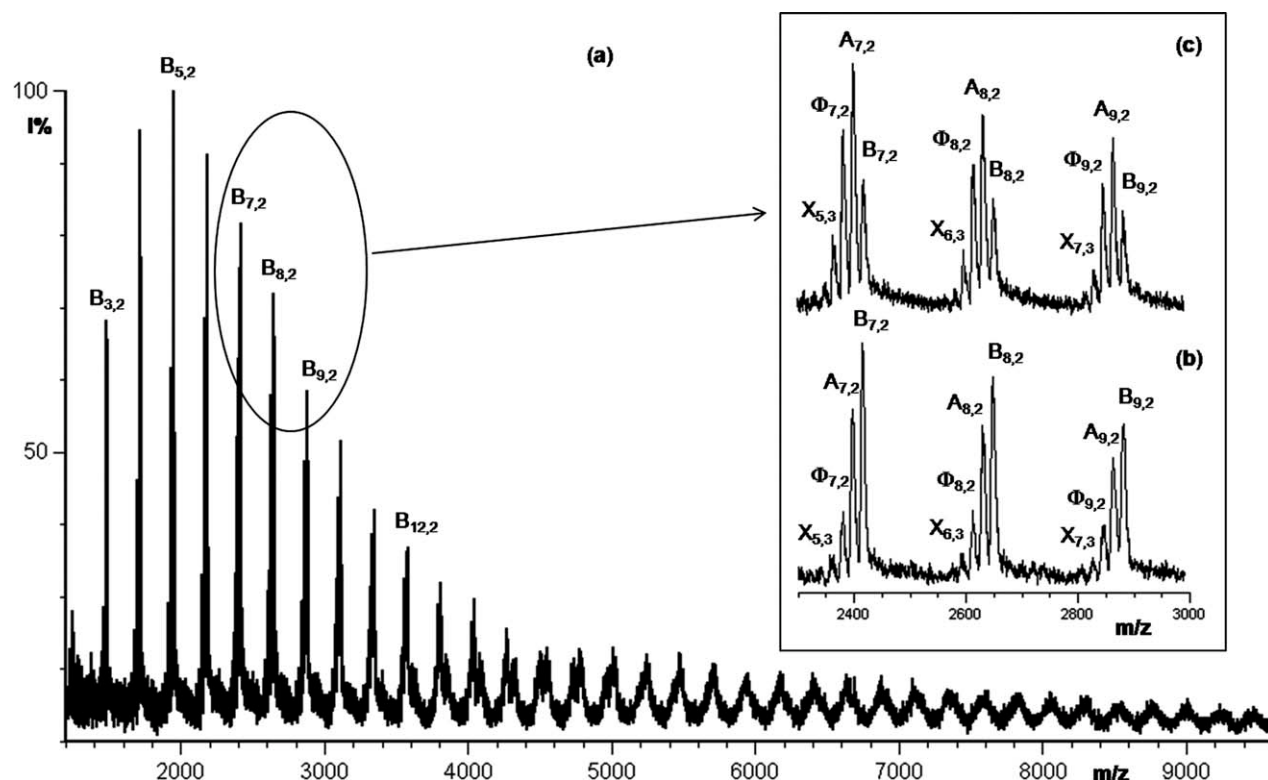
FIGURE 3 MALDI-TOF mass spectra of S-PES-0.9(12 h) (a) and enlarged section of the mass spectra of S-PES-0.9(12 h) (b) and S-PES-1.2(12 h) (c).

(protons H_1). The sufficient peak resolution permits to distinguish also the S-PES units in the backbone from those in the end chains; that is, the peaks H_3 belong the disulfonated units in the main chains that link two unsolfonated PES blocks, while the peaks $H_{3'}$ belong to same units in the end chains. From proton spectra in Figure 2(b–d) we can also characterize the phenol end groups (peaks $H_{a''}$ and $H_{b''}$). The intensities of the peaks due to the end groups decrease as increase the M_n of S-PES copolymers obtained after 12 h reactions. Since, using the integral area (I) of protons belonging to the unsolfonated PES blocks (protons H_a) and those due to the S-PES units (protons H_3 and $H_{3'}$), we have calculated the molar fractions of sulfonated (referred as C_{S-PES}) and unsolfonated PES units (C_{PES}), the degree of sulfonation (DS), the degree of polymerization (X_n) and the M_n of the S-PES(12 h) copolymers, using the eqs 2–6.

$$C_{PES} = (I_{H_a}/4)/(I_{H_a}/4 + I_{H_3} + I_{H_{3'}}) \qquad (2)$$

$$C_{S-PES} = 1 - C_{PES} \qquad (3)$$

$$DS = 2 \cdot C_{S-PES} \qquad (4)$$

$$X_n = (I_{H_a}/4 + I_{H_3}/2)/(C_{PES} \cdot I_{H_{a''}}/2 + C_{S-PES} \cdot I_{H_{3'}}) \qquad (5)$$

$$M_n = X_n \cdot (232.2 \cdot C_{PES} + 376.3 \cdot C_{S-PES}) \qquad (6)$$

where 232.2 and 376.3 correspond to the mass of unsolfonated as sulfonated repeating units, respectively.

The DS values, which define the average number of sulfonic acid groups (—SO_3H) in S-PES copolymer chains, correspond to the double of C_{S-PES} molar fractions (DS $= 2$ C_{S-PES}), as each sulfonated unit presents two SO_3H groups.

From ^1H NMR spectra we can also calculate the mol % of sulfonated units (S-PES) present as end chains ($C_{S-PES-ends}$) with respect to total amount of S-PES along the macromolecular chains, by eq 7

$$C_{S-PES-ends} = I_{H_{3'}}/(I_{H_3} + I_{H_{3'}}) \times 100 \qquad (7)$$

MALDI-TOF MS and ^1H NMR spectra revealed that all S-PES(12 h) copolymers are terminated with phenol and chlorine groups. This evidence suggest that nucleophilic substitution of both chlorine belonging to the sulfonated monomer used for synthesized them is not complete, and therefore it acts as coupling agent when both chlorine atoms are substituted and as terminal when only one chlorine atom is substituted during the polycondensation reaction between PES-OH and DS-DSDCPS. These data suggest also the kinetic of the substitution of chlorine atoms belong to the DS- DSDCPS is may be lower with respect to the corresponding unsolfonated DCDPS monomer. On the base of this result, we thought that the nucleophilic substitution condensation reaction between two copolymer chains terminated with these groups could be carried further giving a chain coupling, and thus an increase in molar masses distributions (MMD) of each copolymer. To confirm our hypothesis, we performed the postcondensation reaction of the S-PES0.9(12 h) and S-PES1.2(12 h) samples for other 24 and 48 h at 200 °C, as described in the experimental section. The progress of the postcondensation reaction has been followed by ^1H NMR and MALDI-TOF MS analyses. The MALDI-TOF MS results

TABLE 2 Structural Assignments of Peaks Displayed in the MALDI-TOF Mass Spectra of S-PES Samples Showed in Figures 3 and 4

Species	Structures[a]	$[M-H]^+ (n,\alpha)^{a,b}$
Φ	$M_{\Phi n,\alpha} = n \cdot 232.2 + \alpha \cdot 376.3$	1682.4 (4,2); 1914.6(5,2); 2146.8 (6,2); 2379.0 (7,2); 2611.2 (8,2); 2843.4 (9,2); 3075.6 (10,2); 3307.8 (11,2); 3540.0 (12,2); 3772.2 (13,2)
A	$M_{An,\alpha} = n \cdot 232.2 + \alpha \cdot 376.3 + 18$	1700.4 (4,2); 2076.7 (4,3); 1932.6 (5,2); 2308.9 (5,3); 2164.8 (6,2); 2541.1 (6,3); 2397.0 (7,2); 2773.3 (7,3); 2619.2 (8,2); 3005.5 (8,3); 2861.4 (9,2); 3237.7 (9,3); 3093.6 (10,2); 3469.9 (10,3); 3325.8 (11,2); 3702.1 (11,3); 3558.0 (12,2); 3934.3 (12,3); 3790.2 (13,2); 4166.5 (13,3)
B	$M_{Bn,\alpha} = n \cdot 232.2 + \alpha \cdot 376.3 + 412.3$	1718.4 (4,1); 2094.7 (4,2); 1950.6 (5,1); 2326.9 (5,2); 2182.8 (6,1); 2559.1 (6,2); 2415.0 (7,1); 2791.3 (7,2); 2637.2 (8,1); 3023.5 (8,2); 2879.4 (9,1); 3255.7 (9,2); 3111.6 (10,1); 3487.9 (10,2); 3343.8 (11,1); 3720.1 (11,2); 3576.0 (12,1); 3952.3 (12,2); 3808.2 (13,1); 4184.5 (13,2)
C	$M_{Cn,\alpha} = n \cdot 232.2 + \alpha \cdot 376.3 + 806.6$	1736.4 (4,0); 2112.7 (4,1); 1968.6 (5,0); 2344.9 (5,1); 2200.8 (6,0); 2577.1 (6,1); 2433.0 (7,0); 2809.3 (7,1); 2655.2 (8,0); 3041.5 (8,1); 2897.4 (9,0); 3273.7 (9,1); 3129.6 (10,0); 3505.9 (10,1); 3361.8 (11,0); 3738.1 (11,1); 3594.0 (12,0); 3970.3 (12,1); 3826.2 (13,0); 4202.5 (13,1)

[a] $n = x + y$; for each structure is also reported the respective pertinent equation to calculate the corresponding molecular mass (M), considering that the mass of PES and S-PES repeat units are 232.2 Da and 376.3 Da, respectively.
[b] The mass accuracy was better than $\Delta m = \pm 0.5$ Da.
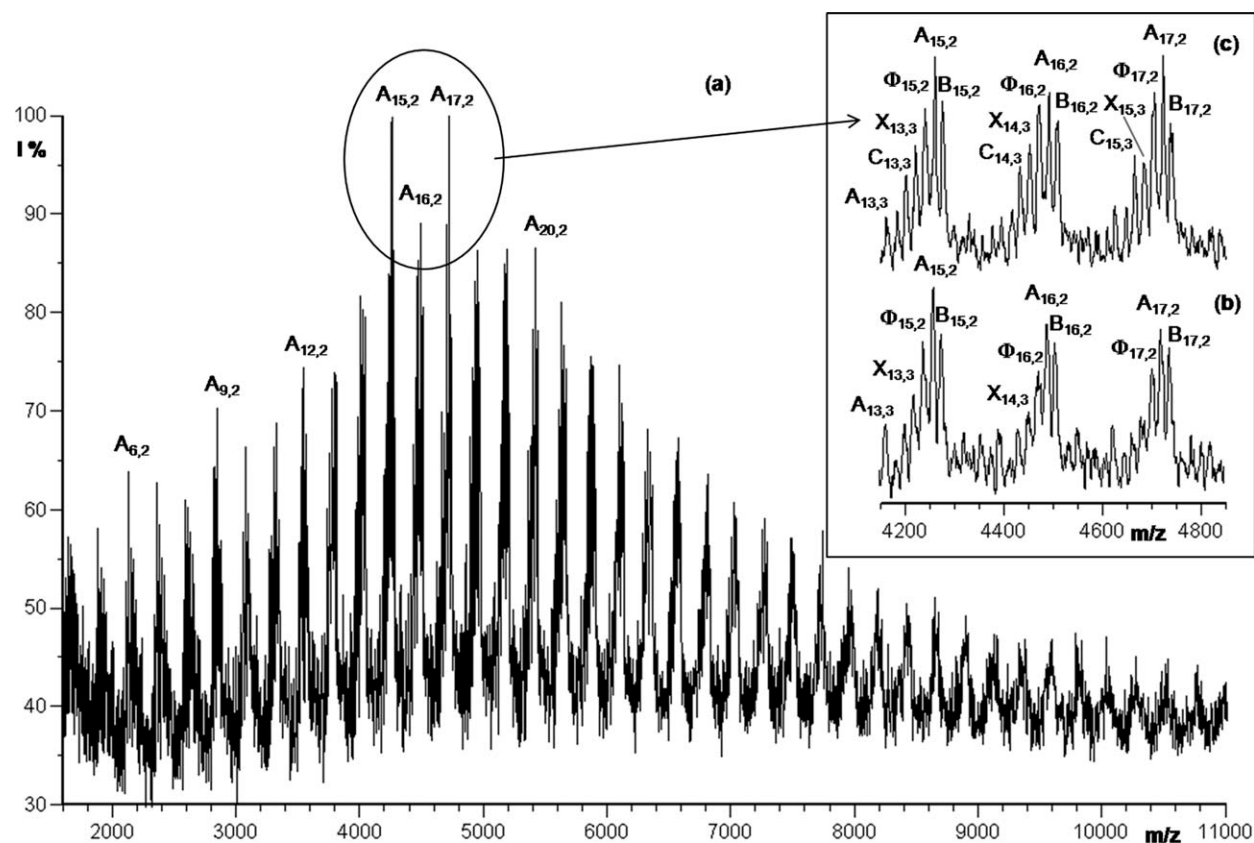
FIGURE 4 MALDI-TOF mass spectrum of *S*-PES-1.05(12 h) (a). The inset reports the enlarged sections of the spectra of samples *S*-PES-1.0(12 h) (b) and *S*-PES-1.05(12 h) (c).

indicate that the copolymers chains terminated with chlorine groups decrease with respect to those ended with phenol groups at both ends, confirming the progress of the condensation reaction. MALDI TOF mass spectra (not reported here for brevity) show homogeneous cluster of peaks ranging from m/z 2000 to m/z 26,000, indicating that the MMD of the copolymers increase, as expected. In these mass spectra the most intense peaks correspond to the families terminated with OH groups at both ends (species $A_{n,\alpha}$ with $\alpha = 2$ in Table 2), intense peaks corresponding to the same family of copolymer chains with $\alpha = 3$ and $a = 4$ were also observed in the mass range higher m/z 4000. The intensities of peak series $B_{n,\alpha}$ and $C_{n,\alpha}$ is very lower than of those observed in mass spectra of copolymer samples obtained after 12 h reactions (Fig. 3). Their intensity decrease compared to those of mass peak families $A_{n,\alpha}$ with increasing reaction time. Comparing the MALDI-TOF mass spectra of the copolymers obtained by postcondensation reaction with respect to those of the copolymers obtained at 12 h, in the mass range m/z 2000–5000 we have also observed un increment of the relative intensity of cycles co-oligomers (species $\Phi_{n,\alpha}$ in Table 2). These data suggest that cycles could be formed by postcondensation reactions involving the OH and Cl end groups belonging to the same macromolecular chain (species B in Table 2) or to two different chains (i.e., species $B_{n,\alpha}$ and $C_{n,\alpha}$ in Table 2). The kinetic of the postcondensation reaction was followed by means of ^{1}H NMR spectra of the

formed copolymers. As an example spectra of *S*-PES0.9(12 h), *S*-PES0.9(36 h) and *S*-PES0.9(60 h) are overlaid in Figure 5. With the other peaks normalized, it can be observed that as the postreaction time increase, the intensity of signals due to aromatic protons belonging to the end groups (protons: $H_{3'}$ at 8.38 ppm, $H_{b''}$ at 7.68 ppm, $H_{a''}$ at 7.69 ppm; see Table 3 for their assignments) gradually become smaller, indicating that the molar mass distributions increase, as confirm the M_n values calculated from the ^{1}H NMR spectra, which values are gathered in Table 1. These results were also confirmed by SEC-Viscometry and off-line viscometry measurements (see data in Table 1 and "Discussion" section). The degree of sulfonation of *S*-PES copolymers prepared by postcondensation reaction was calculated from their ^{1}H NMR spectra. For each copolymer the DS value does not change with respect to that of the corresponding *S*-PES(12 h) parent sample.

SEC-Viscometry
The summary of the molecular characterization of the PES-OH(4 K) and four *S*-PES samples by SEC-Viscometry is shown in Table 4. The table reports the molar mass of the chromatographic peak (Mp), the more important molar mass averages (M_n, M_w, M_z), the polydispersity indexes (M_w/M_n, M_z/M_w), the intrinsic viscosity [η] in DMAc + 0.05 M LiBr solvent at 80 °C of temperature and finally the coefficients of the MHS plot (intercept k and slope a). Wang et al.[44] have revealed that intrinsic viscosity data for sulfonated PES

TABLE 3 Assignments of the Signals due to the Aromatic Protons Belonging to the Sequences and of the End Groups Present in S-PES Copolymers

| Structures	H	Chemical shifts (ppm)
	a	7.29–7.32 (d)
	b	7.96–8.01 (d)
	a′	7.12–7.20 (d)
	b′	7.86–7.90 (d)
	H₁	7.08–7.18 (d)
	H₂	7.84–7.87 (d)
	H₃	8.36–8.38 (m)
	a″	6.80–6.84 (d)
	b″	7.65–7.70 (d)
	H′₁	7.63–7.67 (d)
	H′₂	7.78–7.85; 7.80–7.81(dd)
	H′₃	8.40–8.41 (d)

Sequences:

End groups:

The chemical shifts were measured with an accuracy of ±0.01 ppm.
Abbreviations used: d, doublet; dd, double doublet.

copolymers were not comparable to those of nonsulfonated polymers, since the polymer electrolyte chains interact via sulfonate groups. To suppress the polyelectrolyte effects, in accord with some authors[23] we have used NMP with 0.05 M LiBr, because the small amount of salt effectively suppressed the polyelectrolyte effect allowing improved characterization of the ion containing materials.

Data reported in Table 4 clearly confirm previous conclusions on the S-PES polymerization. By increasing the time of polymerization from PES-OH to S-PES 12 h and S-PES 60 h the average molar mass evidently increases. Specifically for the S-PES0.9 samples the weight average M_w increases from 8.1 kg/mol (PES-OH) to 21.4 kg/mol [S-PES 0.9(60 h)]. Quite interesting the polydispersity of the samples was narrow and almost constant ranging from 1.3 to 1.4. This polymerization tendency is evident also for the S-PES1.2 samples.

Figure 6 shows the comparison of the differential MMD of four samples: PES-OH(4 K), S-PES 0.9(12 h), S-PES 0.9(36 h) and S-PES 0.9(60 h). MMDs of samples clearly show the tendency in molar mass increasing. The molar mass increases from PES-OH to PES 0.9(12 h) and furthermore increases to PES 0.9(36 h) but there is not meaningful difference in molar mass between PES 0.9(36 h) and PES 0.9(60 h) samples.

Figure 7 shows the comparison of the MHS plot, $[\eta] = k\,M^a$, of four samples: PES-OH(4 K), S-PES 0.9(12 h), S-PES 0.9
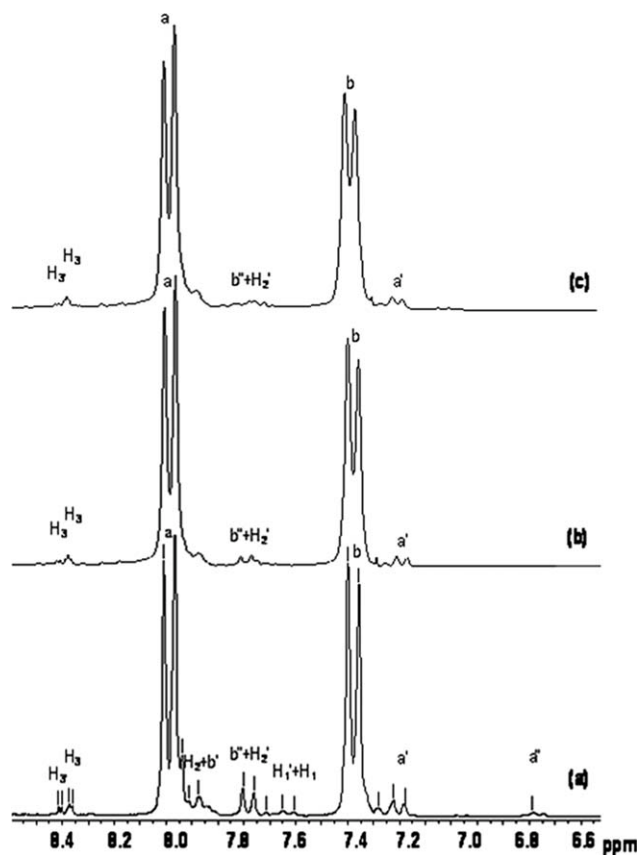
FIGURE 5 ¹H NMR spectra of S-PES-0.9 samples obtained at different reaction time: 12 h (a), 36 h (b), and 60 h (c).

TABLE 4 Summary of the Molecular Characterization of PES-OH and *S*-PES Samples by SEC-DV

Sample	M_p g/mol	M_n g/mol	M_w g/mol	M_z g/mol	M_w/M_n	M_z/M_w	$[\eta]$ dL/g	K	a
PES-OH(4 K)	7,300	6,300	8,100	10,700	1.29	1.31	0.063	1.91 E-04	0.65
S-PES 0.9(12 h)	13,850	9,150	12,850	17,300	1.40	1.35	0.077	1.88 E-04	0.64
S-PES 0.9(36 h)	22,700	16,050	20,900	25,700	1.30	1.23	0.108	2.31 E-05	0.85
S-PES 0.9(60 h)	23,600	15,100	21,400	27,800	1.41	1.30	0.108	2.47 E-05	0.84
S-PES 1.2(12 h)	9,850	8,100	10,950	14,700	1.36	1.34	0.068	1.77 E-04	0.65
S-PES 1.2(60 h)	23,300	15,950	21,450	26,800	1.35	1.25	0.122	1.68 E-05	0.89

(36 h) and *S*-PES 0.9(60 h). The slope *a* of the MHS plot for PES-OH and PES 0.9(12 h) samples is quite similar (*a* = 0.65). The slope *a* of the MHS plot for *S*-PES 0.9(36 h) and *S*-PES 0.9(60 h) samples is completely different (*a* = 0.85). In other words, the *S*-PES 0.9(36 h) and *S*-PES 0.9(60 h) samples were more extended (stiffer chain) in consequence of more sulfates functional groups in the polymeric chains. This conformation (polyelectrolytes) difference is evidently important because influence notably the final properties of the polymers.

Fourier Transform Infrared Spectroscopy

FTIR spectra were also used to confirm the presence of pendant —SO_3H groups on the sulfonated copolymer chains. Figure 8 shows the spectra of the parent telechelic PES-OH (4 K) and of the sulfonated copolymers *S*-PES0.9(12 h) and *S*-PES1.2(12 h) synthesized from it. The FTIR spectra of sulfonated *S*-PES samples show characteristic absorption bands at 1030 cm^{-1} due to the symmetric stretching vibrations of —SO_3H groups (indicated with the symbol ✦ in Fig. 8). The asymmetrical stretching vibrations of —SO_3H groups appear at about 1180 cm^{-1},[45] but we could not readily observe it due near overlapping absorbances. All *S*-SPE copolymers have gave FTIR spectra similar to those in Figure 8(b,c).

Thermal Properties

Thermal stabilities of the *S*-PES copolymers were investigated by TGA under nitrogen flow, and in Figure 9, we report the degradation curves of an unsolfonated PES and of

three disulfonated PES copolymers: *S*-PES1.2(12 h), *S*-PES 0.9(12 h) and *S*-PES1.05(12 h). Each sample was dried at 180 °C for 12 h before TGA analysis. The TGA curves in Figure 9 show that all *S*-PES copolymers present three thermal degradation steps ranging from 350 to 800 °C, leaving a char residue at 800 °C that increase as raise the DS of copolymers. The first decomposition step around 380–420 °C could be ascribed to the decomposition of the —SO_3H groups. Second and third thermal degradation steps occurring in temperature ranges 450–600 °C and 650–750 °C should be due to polymer main chain, in accord to the literature.[46] TGA curves of no predried sulfonated samples show also a weight loss between 100 and 200 °C due to the desorption of water bonded to the sulfonic groups.
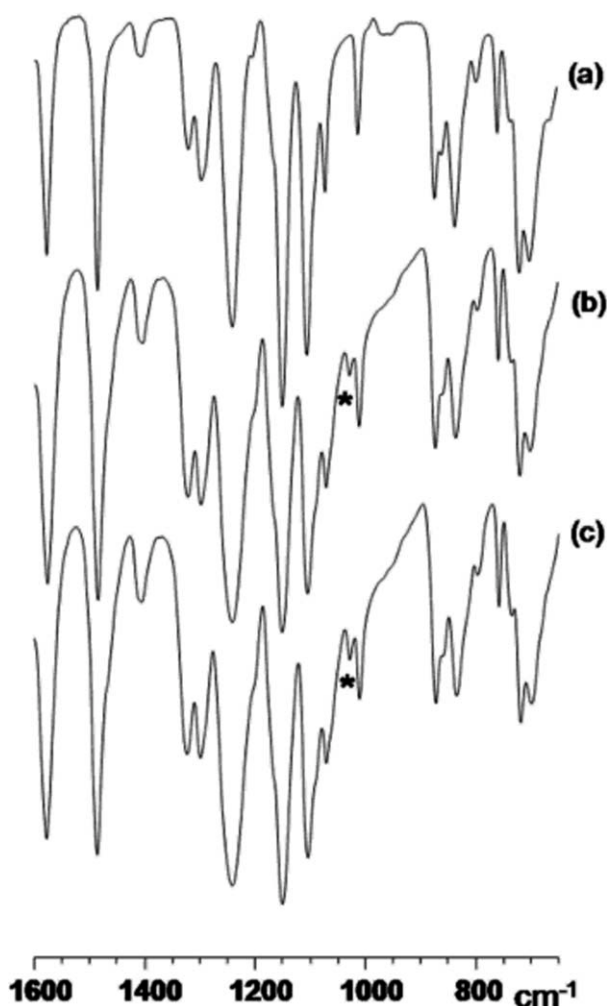
The glass transition temperatures (T_g) of all sulfonated copolymers were determined by DMA through heating and cooling cycles discussed in experimental section, and the results were listed in Table 1. For comparison, in Table 1 were also reported the T_g data of both telechelic PES-OH prepolymers. It may be noted that for the *S*-PES copolymers obtained at the same reaction time (12 h), the T_g values increase as increase either the DS and also the degree of polymerization (X_n) of the PES-OH parent, from which were synthesized. The T_g values of the copolymers prepared by postcondensation reaction starting from *S*-PES0.9(12 h) (Fig. 10) and *S*-PES1.2(12 h) (Fig. 11) increase compared to the initial copolymers, suggesting that post condensation influenced significantly the molar mass distribution. For both series of *S*-PES copolymers we observe that there is a clear
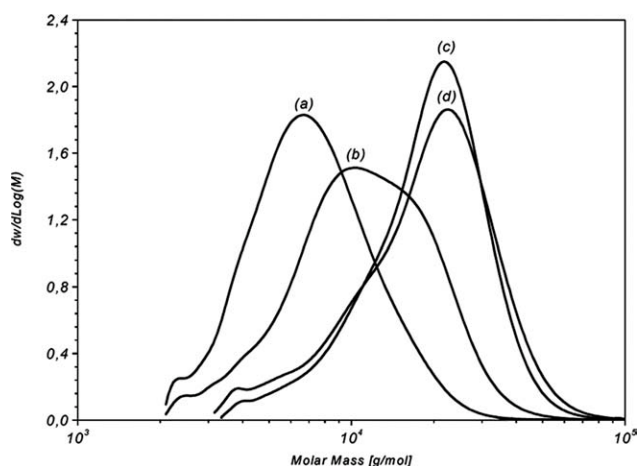
FIGURE 6 Comparison of the differential MWD of PES-OH(4 K) (a), *S*-PES-0.9(12 h) (b), *S*-PES-0.9(36 h) (c) and *S*-PES-0.9(60 h) (d).
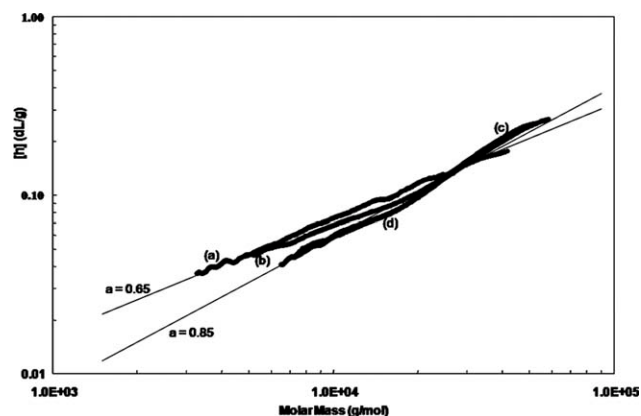

FIGURE 7 Comparison of MHS plot of PES-OH(4 K) (a), *S*-PES-0.9(12 h) (b), *S*-PES-0.9(36 h) (c), and *S*-PES-0.9(60 h) (d).

FIGURE 8 FTIR spectra of PES-OH(4 K) (a), S-PES-1.2(12 h) (b), S-PES-0.9(12 h) (c).

trend for the glass transition temperature which increase with the postcondensation time. The T_g increase is the results of the increase in molar mass which is shown in Table 1 and from SEC-viscometry data in Table 4. The data in Table 1 suggest that T_g between 244 and 246 °C is the
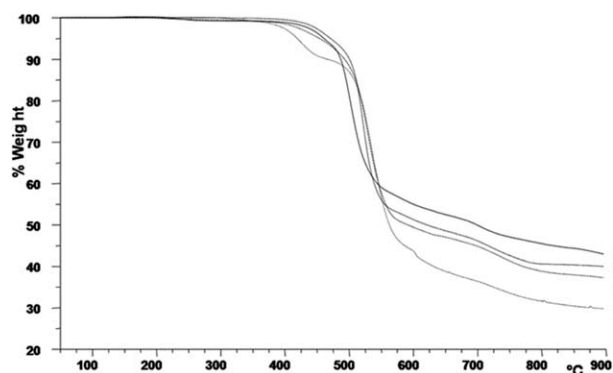
FIGURE 9 TGA curves of PES-OH(7 K) (a), S-PES-1.2(12 h) (b), S-PES-0.9(12 h) (c), and S-PES- 1.05(12 h) (d).
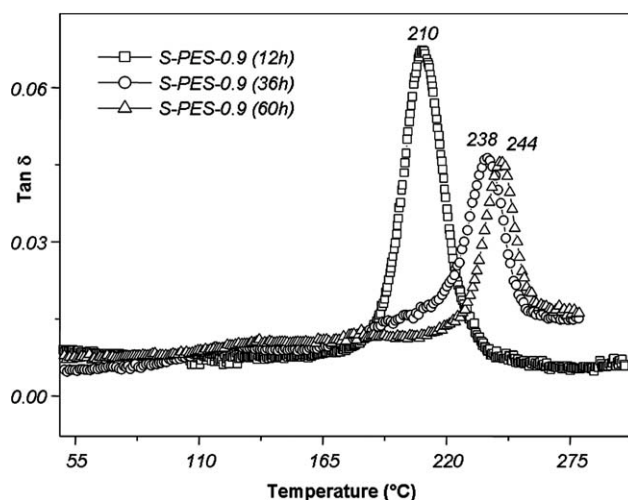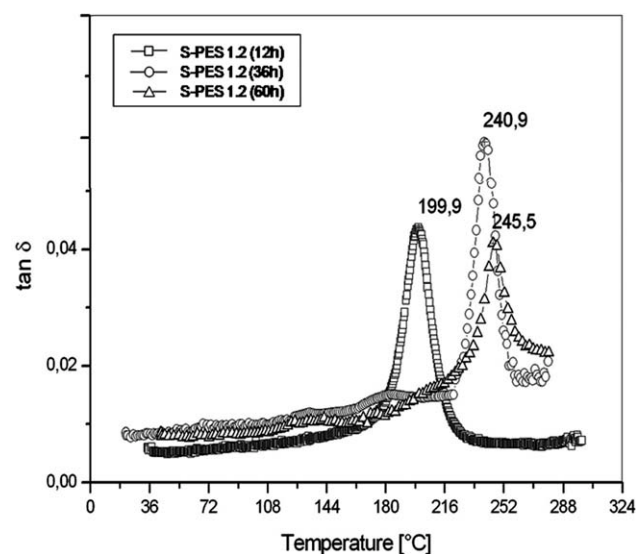

FIGURE 10 DMA curves of S-PES-0.9(12 h), S-PES-0.9(36 h), and S-PES-0.9(60 h).

threshold value which is commonly shown by this class of copolymers with a DS of 10–11 mol %.

CONCLUSIONS

Herein, we have highlight that the synthesis of sulfonated poly(arylene ether-sulfone) copolymers can be followed combining MALDI-TOF MS and ^{1}H NMR analyses, since detailed information about the end chains and of the average number of disulfonated units along the chains can be determined. SEC-Viscometry analyses allow to reliable data on the molar mass distribution of these copolymers and DMA data reveal that a T_g of 244–246 °C were reached for copolymer with a degree of sulfonation of 10–11 mol %, as increase their molar mass distribution. Therefore, as the chemical composition, the end chains, the degree of sulfonation and the molecular mass distribution affects the properties (i.e., water uptake, in-plane

FIGURE 11 DMA curves of S-PES-1.2(12 h), S-PES-1.2(36 h), and S-PES-1.2(60 h).

proton conductivity, mechanical) and morphology of the proton exchange membranes based on *S*-PES copolymers, in the next work we will investigate these correlations. So based on the results will be obtained we propose to synthesize and characterize *S*-SPES copolymers with higher MMD and DS.

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